



Energy, Materials and Telecommunication Centre

# MAGNETIC FIELD ENHANCED PHOTOELECTROCHEMICAL HYDROGEN GENERATION: AN EXPLORATION OF THE ROLE OF THE TiO<sub>2</sub>-BASED PHOTOANODE

by

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# PRODUCTION D'HYDROGÈNE PHOTOÉLECTROCHIMIQUE AMÉLIORÉE PAR LE CHAMP MAGNETIQUE : EXPLORATION DU RÔLE DE LA PHOTOANODE À BASE DE TIO<sub>2</sub>

# RÉSUMÉ

L'énergie solaire étant une source d'énergie intermittente, des stratégies de stockage de l'énergie sont nécessaires pour l'utiliser pendant les périodes où l'apport solaire est réduit. La conversion efficace de l'énergie solaire en hydrogène est un sujet de recherche essentiel, compte tenu de son importance dans l'écosystème de l'énergie solaire. Les dispositifs solaires excitoniques de troisième génération sont une technologie prometteuse en raison de leur capacité à surmonter la limite de Shockley-Queisser, ce qui promet des rendements plus élevés, des coûts de production plus faibles et la possibilité d'utiliser des matériaux non toxiques.

Parmi les stratégies à l'étude figurent les systèmes photoélectrochimiques (PEC) assistés par champ, dans lesquels des champs externes tels que des champs thermiques, mécaniques ou magnétiques sont appliqués à des configurations traditionnelles à trois électrodes PEC afin d'augmenter l'efficacité de la conversion du soleil en hydrogène (STH). Ici, nous considérons le champ magnétique comme une source de champ externe appliquée aux photoanodes à base de TiO<sub>2</sub> mésoporeux. Plus précisément, nous nous efforçons de déterminer les processus uniques au sein du système PEC où le champ magnétique a un effet en utilisant des techniques analytiques purement PEC. Des photoanodes sensibilisées par des points quantiques (QDs) à adsorption et réaction de couches ioniques successives (SILAR) sont également considérées comme des améliorations de l'absorption de la lumière afin de tester l'évolutivité du système.

Nous démontrons que le dispositif PEC à base de TiO<sub>2</sub> a montré une amélioration de 37% de la densité de photocourant même avec un petit champ magnétique de 11mT, tandis que les photoanodes sensibilisées par des QD ont montré une amélioration du photocourant de 25% sur CdS/TiO<sub>2</sub>, et de 17% sur CdSe/CdS/TiO<sub>2</sub> à une polarisation de 0,8V par rapport à la RHE. En outre, le dispositif a été testé contre un champ magnétique de 21 mT, et les résultats ont montré une amélioration de la densité de photocourant de 67 % pour le CdSe/CdS QD/TiO<sub>2</sub>.

En outre, l'étude de la source de l'effet a révélé que la modification de l'électrolyte par l'utilisation d'un électrolyte sulfite/sulfure basique avec l'anion sulfite piégeant les trous (pH 12,5), ou d'un électrolyte Na2SO4 neutre (0,5M, pH 7) a montré des niveaux similaires d'amélioration du photocourant, de même que l'utilisation de contre-électrodes multiples (Pt, Au, et graphite). Cette

observation révèle que l'amélioration du photocourant par le champ magnétique contient une contribution significative de l'électrode de travail. En outre, des tests de contrôle ont été réalisés avec des photoanodes en nano-poudre de TiO<sub>2</sub> en phase pure (Anatase et Rutile). La modification de la phase a montré un changement significatif dans les caractéristiques courantdensité-tension induites par le champ magnétique (vs RHE), ainsi que dans l'amélioration du photocourant enregistré, la photoanode à base de nanopoudre d'anatase montrant une réponse magnétique presque négligeable, ce qui révèle que la source du photocourant amélioré par le champ est contenue dans la couche de TiO<sub>2</sub>. Enfin, un test avec une photoanode FTO nue a été réalisé pour étudier l'effet de l'élimination progressive des couches du dispositif afin de s'assurer que tout effet observé était dû aux systèmes de matériaux dans la photoanode et qu'aucun artefact provenant des autres composants de la cellule PEC n'était observé. Le FTO nu n'a montré aucune réponse significative au champ magnétique, ce qui indique que l'amélioration de l'efficacité de la photoconversion due au champ magnétique est presque entièrement contenue dans la couche de TiO<sub>2</sub>, ce qui justifie une étude plus approfondie de la dynamique de l'électrode de travail en présence d'un champ magnétique.

Une analyse plus poussée des durées de vie des excitons et des porteurs de charge a été réalisée à l'aide d'expériences de décroissance du potentiel en circuit ouvert (OCPD), qui ont révélé que dans le cas des types de photoanodes TiO<sub>2</sub> nues et sensibilisées par des QD, le champ magnétique entraînait une réduction significative des recombinaisons globales, tandis que les recombinaisons de surface augmentaient. Dans le cas des photoanodes TiO<sub>2</sub> sensibilisées par des QD, le taux de recombinaison de surface n'a pas augmenté en raison de la passivation élevée des états de surface connue dans ces systèmes de QD, bien que les QDs CdSe/CdS soient connus pour avoir plus d'états de surface que le CdS, ce qui a également été observé comme une légère augmentation de la recombinaison de surface dans le cas de CdSe/CdS dans le profil de l'OCPD.

L'analyse de la spectroscopie d'impédance électrochimique (EIS) pour les trois systèmes a montré que les impédances des processus de surface et de masse diminuaient lors de l'application d'un champ magnétique, et que cette diminution augmentait avec l'intensité du champ magnétique, ce qui indique la possibilité d'une plus grande efficacité de séparation des charges dans la masse conduisant à une plus grande densité de charges à la surface, ce qui entraîne un plus grand nombre global de recombinaisons à la surface, comme on l'a vu dans l'OCPD. Cette idée est à nouveau rapidement corroborée par les diagrammes de Mott-Schottky du TiO<sub>2</sub> nu et du TiO<sub>2</sub> sensibilisé aux QD, des photo-anodes sensibilisées aux QD et des photo-

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anodes nues, où l'on observe une augmentation générale de la densité des porteurs de charges libres dans la masse et une réduction de la densité dans les sites de surface. Cela indique clairement que les sites de surface agissent comme des centres de capture et de recombinaison de charges plus efficacement en présence d'un champ magnétique, uniquement en raison de la densité accrue des charges présentes. Ces données pourraient également indiquer une injection de charge plus efficace dans les espèces d'oxydoréduction en tant que troisième accepteur de trous libres à la surface du système étudié.

**Mots-clés :** PEC assistée par champ magnétique ; génération d'hydrogène ; TiO<sub>2</sub> mésoporeux ; points quantiques SILAR ; recombinaison des porteurs de charge, transitions interdites de spin.

# ABSTRACT

Solar power, being an intermittent energy source, requires strategies to store energy to be used during times of reduced solar input. The efficient conversion of solar energy to hydrogen fuel is a pivotal research topic, given its importance in the solar energy ecosystem. Third-generation excitonic solar devices are a promising technology considering their ability to overcome the Shockley-Queisser limit, promising higher efficiencies, lower production costs and the possibility of utilizing non-toxic materials.

Of the strategies under investigation are field-assisted photoelectrochemical (PEC) systems, where external fields such as thermal, mechanical or magnetic fields are applied to traditional PEC three-electrode setups to boost the solar-to-hydrogen (STH) conversion efficiency. Here, we consider the magnetic field to be an external field source applied to mesoporous TiO<sub>2</sub>-based photoanodes. Specifically, an effort is made to determine the unique processes within the PEC system where the magnetic field has an effect using purely PEC analytical techniques. Successive ionic layer adsorption and reaction (SILAR) quantum dot (QDs)-sensitized photoanodes are also considered light absorber enhancements to test the system for scalability.

We demonstrate that the TiO<sub>2</sub> based PEC device showed a 37% improvement in photocurrent density even with a small magnetic field of 11mT, while the QD sensitized photoanodes showed improved photocurrent of 25% on CdS/TiO<sub>2</sub>, and 17% on CdSe/CdS/TiO<sub>2</sub> at 0.8V bias vs RHE. Further, the device was tested against 21mT magnetic field, the results showed an improvement in photocurrent density of 67% in the CdSe/CdS QD/TiO<sub>2</sub>.

Furthermore, the investigation into the source of the effect revealed that modifying the electrolyte by using a basic sulfite/sulfide electrolyte with the hole-scavenging sulfite anion (pH 12.5), or a neutral Na<sub>2</sub>SO<sub>4</sub> electrolyte (0.5M, pH 7) showed similar levels of photocurrent improvement, as did the use of multiple counter electrodes (Pt, Au, and graphite). This observation reveals that the magnetic field enhancement of the photocurrent contains a significant contribution from the working electrode. In addition, control tests were conducted with pure-phase TiO<sub>2</sub> (Anatase and Rutile) nano-powder photoanodes. The modification of phase showed a significant change in both magnetic field-induced current-density-voltage (vs RHE) characteristics, as well as the recorded photocurrent enhancement, with the anatase nano-powder based photoanode showing an almost negligible magnetic response revealing that the source of the field-enhanced photocurrent was contained within the TiO<sub>2</sub> layer. Finally, a test with a bare FTO photoanode was conducted to study the effect of progressively removing layers from the device to ensure that any

effect observed was because of the material systems within the photoanode and no artefacts from the other components of the PEC cell were being observed. The bare FTO showed no significant response to the magnetic field, indicating that the magnetic field enhancement of photoconversion efficiency is almost completely contained within the TiO<sub>2</sub> layer, justifying further investigation into the working electrode dynamics in the presence of a magnetic field.

Further analysis of exciton and charge carrier lifetimes were conducted using open circuit potential decay (OCPD) experiments, which revealed that in the case of both, bare TiO<sub>2</sub> and QD sensitized TiO<sub>2</sub> photoanode types, the magnetic field resulted in the significant reduction of bulk recombinations, while surface recombinations increased. While in the case of QD-sensitized TiO<sub>2</sub> photoanodes, the surface recombination rate did not increase owing to the high passivation of surface states known to happen in these QD systems, although CdSe/CdS QDs is known to have more surface states compared to CdS, which was also observed as a small increase in surface recombination in the case of CdSe/CdS in the OCPD profile.

Electrochemical impedance spectroscopy (EIS) analysis for all three systems showed that impedances across both surface and bulk processes reduced on the application of a magnetic field, and this reduction increased with the increase in the magnetic field strength, pointing towards the possibility of greater charge separation efficiency in the bulk leading to a higher density of charges at the surface resulting in a larger overall number of recombinations at the surface as seen in OCPD. This insight is again promptly corroborated with Mott-Schottky plots of bare TiO<sub>2</sub> and QD sensitized TiO<sub>2</sub>, the QD-sensitized and bare photoanodes, where a general increase in the free charge carrier density in bulk and reduced density in surface sites was observed. This clearly indicates that surface sites acts as charge capture and recombination centers more efficiently in the presence of the magnetic field owing purely to the increased density of charges present. This data could also indicate more efficient charge injection to the redox species as the third acceptor of free surface holes on the system under investigation.

**Keywords:** Magnetic field assisted PEC; Hydrogen generation; Mesoporous TiO<sub>2</sub>; SILAR quantum dots; Charge carrier recombination, Spin forbidden transitions.

# SOMMAIRE RÉCAPITULATIF

Face à l'escalade du changement climatique mondial, le monde se trouve à un carrefour critique. L'impératif d'une transition rapide des combustibles fossiles vers les sources d'énergie renouvelables est atténué par la nécessité de répondre aux besoins énergétiques mondiaux croissants. Il est reconnu depuis longtemps qu'il est nécessaire de passer à diverses approches en matière d'énergie propre et de s'adapter à des économies durables. Au premier plan de cette transition, l'hydrogène, en tant que moyen de stockage de l'énergie et carburant propre pour les secteurs difficiles à électrifier, apparaît comme une lueur d'espoir, prête à révolutionner le paysage des énergies renouvelables [6, 7]. La photoélectrocatalyse solaire (PEC), qui utilise la lumière naturelle du soleil et l'eau comme source, est une technologie prometteuse pour la production durable d'hydrogène, mais elle est confrontée à des défis majeurs [8-12]. Le besoin inhérent d'améliorer l'efficacité de la PEC, par le choix des matériaux de la photoanode et des architectures du système PEC, est lié à la compréhension actuelle de la communauté scientifique du processus photoélectrocatalytique lui-même [13, 14]. Dans ce travail, nous rapportons, à notre connaissance, la première observation d'une amélioration de l'efficacité de la PEC solaire pour le système de photoanode de TiO<sub>2</sub> mésoporeux (mTiO<sub>2</sub>) sensibilisé au CdS et au CdSe/CdS par des points quantiques (QD) en raison de la présence d'un champ magnétique passif, et nous cherchons à explorer les mécanismes photoélectrochimiques sous-jacents possibles.

Les technologies basées sur l'énergie solaire, y compris l'énergie solaire photovoltaïque (PV) et la conversion de l'énergie solaire en carburant pour le stockage de l'énergie, sont considérées comme des solutions essentielles pour la mise en place rapide et efficace d'un écosystème énergétique propre [15, 16]. Le grand défi que pose l'idée de déployer à grande échelle des actifs solaires pour remplacer les anciennes technologies de production d'électricité réside toutefois dans l'intermittence de la source d'énergie elle-même, à savoir le soleil. En tout point du globe, l'irradiation solaire est un phénomène diurne et pendant la nuit, les actifs photovoltaïques sont essentiellement inactifs [17]. Par conséquent, le rôle des combustibles solaires tels que l'hydrogène est un élément presque indispensable dans une économie propre, alimentée par le soleil 24 heures sur 24, en particulier compte tenu de la densité gravimétrique élevée de l'hydrogène en tant que source de combustible. En outre, la production d'hydrogène par fractionnement photoélectrochimique de l'eau représente une technique totalement verte et sans combustible fossile pour produire de l'hydrogène en tant que source de stockage d'énergie chimique, ce qui réduit encore le rôle des combustibles fossiles dans l'économie mondiale [18, 19].

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# Production d'hydrogène par voie photoélectrochimique (PEC)

## **Cellule PEC**

Une cellule PEC, comme son nom l'indique, est un type de cellule électrolytique alimentée par une source lumineuse, qui est généralement l'insolation solaire ou une simulation de celle-ci produite par un simulateur solaire.



Figure 1 Configuration d'une cellule PEC à trois électrodes à gauche et d'une cellule PEC à deux électrodes à droite [20].

En tant que telle, elle fonctionne sur la base de réactions d'oxydoréduction entraînées par une source d'énergie externe au niveau de deux électrodes distinctes. Par conséquent, un minimum de deux électrodes est nécessaire pour que les deux réactions individuelles de la demi-cellule aient lieu. Cependant, des configurations plus avancées comportant 3 électrodes ou un nombre encore plus élevé d'électrodes existent également en fonction de l'application ou de l'étude menée. La Figure 1 présente un exemple typique de cellule PEC sensibilisée par un semi-conducteur à deux ou trois électrodes.

La configuration à trois électrodes est souvent plus répandue dans les milieux de la recherche et c'est la principale configuration utilisée dans cette étude. Alors que la configuration à deux électrodes utilise uniquement une électrode de travail et une contre-électrode, la configuration à trois électrodes ajoute une électrode de référence au système. Comme son nom l'indique, une électrode de référence est un point de référence pour le potentiel appliqué à l'électrode de travail afin d'entraîner la réaction d'oxydoréduction sur ce site, tandis que la contre-électrode est configurée pour délivrer tout le courant provenant de l'électrode de travail, en veillant à ce qu'il ne passe pas par l'électrode de référence. La tâche consistant à s'assurer que les différentes électrodes remplissent leurs fonctions respectives est confiée à un potentiostat, qui maintient les électrodes aux potentiels appropriés. De cette manière, une configuration à trois électrodes « isole » essentiellement l'électrode de travail du reste du système et offre une méthode permettant d'étudier sélectivement la charge et la dynamique redox de l'électrode de travail séparément. Ainsi, l'efficacité d'une cellule PEC à trois électrodes est essentiellement l'efficacité de la photoélectrode, qui joue le rôle de l'électrode de travail [20].

Une configuration à deux électrodes, en revanche, est utilisée pour caractériser l'efficacité de l'ensemble du dispositif, y compris les électrodes de travail et les contre-électrodes, l'électrolyte et la manière dont ces éléments fonctionnent les uns par rapport aux autres pour entraîner des réactions d'oxydoréduction globales efficaces, et convient donc mieux à l'étude de dispositifs destinés à des applications pratiques à grande échelle.



Figure 2 Installation globale de séparation de l'eau utilisant une configuration à deux électrodes (gauche) [21] ; Configuration à deux électrodes utilisée pour étudier le volume réel de production d'hydrogène dans une chambre de réaction de chromatographie en phase gazeuse (droite) [22].

Une utilisation typique est l'étude du volume d'évolution des gaz produits tels que l'hydrogène et l'oxygène dans le cas de réactions de scission de l'eau à l'aide d'un chromatographe en phase gazeuse [23-25]. La Figure 2 illustre l'aspect pratique de cette configuration.

#### Séparation globale de l'eau et production d'hydrogène

L'effet Honda-Fujishima, découvert en 1972, a démontré le potentiel de production d'hydrogène par la division photoélectrochimique de l'eau sur des électrodes semi-conductrices utilisant l'énergie solaire. Cette percée a ouvert la voie à l'utilisation et au stockage à grande échelle de l'énergie solaire sous forme d'hydrogène, ce qui a permis de résoudre les problèmes d'intermittence associés à l'énergie solaire [26]. La réaction électrochimique de séparation de l'eau est endergonique, nécessitant une énergie libre de Gibbs de  $237 kJ mol^{-1}$ . Le processus nécessite donc un apport d'énergie, soit par irradiation solaire directe, soit par application d'un potentiel, soit les deux. Alors que l'utilisation de l'énergie solaire pure constitue un processus appelé photocatalyse, l'utilisation du seul potentiel électrique est appelée électrocatalyse. De même, lorsque les deux sources d'énergie sont utilisées, le processus est appelé

photoélectrocatalyse (PEC). Le type de processus à utiliser dépend des propriétés des matériaux utilisés pour construire la cellule en question, essentiellement leurs propriétés optiques et électroniques.

Pour piloter le processus à l'aide de la lumière, les semi-conducteurs constituent le choix idéal, étant donné que leur structure de bande contient un « écart » distinct entre la bande de valence et la bande de conduction, qui ne peut être franchi qu'en absorbant l'énergie d'une source externe égale à l'écart d'énergie. Cela leur donne la capacité d'absorber des photons lumineux d'une énergie suffisante et de promouvoir un électron de valence vers la bande de conduction, qui peut ensuite être extrait à l'aide d'un circuit électriquement polarisé ou d'une couche de charge de l'espace d'interface (comme dans le cas de la photocatalyse, où l'électron est directement transféré à l'espèce réactive en extrayant le potentiel chimique de l'électron de conduction plutôt que son potentiel électrique). La promotion ou l'excitation de l'électron vers la bande de conduction présente un autre avantage : l'espèce globale qui reste dans la molécule (si cet électron est désormais considéré comme une espèce liée de manière indépendante) est capable de se transférer d'une molécule à l'autre, c'est-à-dire que la molécule restante possède désormais une charge positive qui peut attirer un électron de la bande de conduction d'un atome ou d'une molécule voisin(e). Cela permet à une seule excitation de générer deux fois plus de charges, l'une provenant du transfert de l'électron de conduction et l'autre de l'acceptation d'un électron dans le centre de charge positif ainsi créé. Ceci est représenté en considérant l'espace laissé par l'excitation de l'électron comme un « trou », qui est une pseudo-particule équivalente à une charge positive qui contient l'équilibre de charge pour neutraliser les charges atomiques et représente également la mobilité de charge des électrons qui remplissent simplement l'espace disponible, généralement juste un ou deux ordres de grandeur inférieurs à la mobilité des électrons dans la plupart des semi-conducteurs [27, 28]. Dans la plupart des semi-conducteurs, l'électron excité est généralement lié à l'atome/molécule hôte, créant une paire électron-trou appelée « exciton ». L'électron peut alors être séparé du couplage de trous en polarisant le semi-conducteur avec un potentiel, ce qui génère un champ électrique interne à l'intérieur de la masse du semi-conducteur, poussant l'électron vers le circuit électrique extérieur.

Parallèlement, l'utilisation de semi-conducteurs photoactifs pour piloter des réactions d'oxydoréduction doit tenir compte d'autres considérations liées au choix approprié du matériau. Afin de piloter correctement la réaction, les positions des bandes de valence et de conduction doivent être correctement placées par rapport aux potentiels d'oxydoréduction des espèces individuelles subissant une réduction à la cathode et une oxydation à l'anode, ce que l'on appelle l'alignement des bandes. Si cet alignement des bandes ne se produit pas naturellement, ou si les différences de position des bandes sont très importantes, une polarisation du potentiel peut compenser la différence d'énergie requise pour transférer les électrons et les trous vers les espèces respectives ; cependant, cette forme d'apport d'énergie pour la même quantité de sortie réduit considérablement l'efficacité globale du dispositif et est souvent très indésirable. Dans le cas de la division de l'eau, le matériau choisi pour absorber la lumière et entraîner la réaction doit avoir une position de bande de valence plus positive que le potentiel redox  $O_2/H_2O$  de 1,23 V par rapport à l'électrode à hydrogène naturel (NHE, ou également RHE pour Regular Hydrogen Electrode) à pH = 0, pour entraîner la réaction d'oxydation, tandis que la bande de conduction doit être plus négative que le potentiel redox de  $H^+/H_2$  qui est de 0 V par rapport à la NHE. Bien sûr, ceci est le cas pour un système idéal où les autres composants tels que l'électrolyte ou le câblage électrique n'introduisent pas de résistances et de pertes supplémentaires, ce qui est presque toujours le cas.



Figure 3 Positions des bords des bandes de valence et de conduction par rapport à la NHE et par rapport au niveau du vide pour divers semi-conducteurs en contact avec un électrolyte aqueux à pH = 0. Les lignes en pointillé représentent les potentiels des réactions de dégagement d'hydrogène et de dégagement d'oxygène, respectivement [29].

Ces pertes nécessitent l'ajout de plus d'énergie que le potentiel d'oxydoréduction et sont connues sous le nom de surpotentiel. Pour les semi-conducteurs les plus courants étudiés aujourd'hui, les positions relatives des bords de bande avec les potentiels d'oxydoréduction de la séparation de l'eau, à savoir la réaction de dégagement de l'hydrogène (HER) et la réaction de dégagement de l'oxygène (OER), sont illustrées à la Figure 3. Dans notre cas, nous avons choisi TiO<sub>2</sub> (type n)

comme photoanode semi-conductrice en raison de son faible coût, de sa facilité d'accès, de sa faible toxicité et de sa bande interdite idéale.

#### Réaction de dégagement d'hydrogène (HER)

Le processus de division de l'eau en ses constitue processus de division de l'eau en ses constituants est une réaction simple, qu'elle soit réalisée par voie électrochimique, électrolytique ou chimique (ou thermochimique) [30], est représentée dans l'équation (1) ci-dessous [31-33].

$$2H_20 \rightleftharpoons 2H_2 + O_2, \ \Delta G^0 = 237.1 kJ$$
 (1)

Dans le cas du fractionnement de l'eau assisté par l'énergie solaire, l'énergie requise est fournie par les porteurs de charge générés par l'absorption de la lumière par la photoanode semiconductrice produisant un électron de la bande de conduction et un trou de la bande de valence. Ce processus peut être représenté comme suit [34] :

$$TiO_2 + h\nu \to e_{C.B.}^- + h_{V.B.}^+$$
 (2)

Cette réaction globale peut être séparée en deux réactions de demi-cellule à l'électrode de travail et à la contre-électrode, pour lesquelles deux mécanismes sont souvent proposés en fonction des conditions dans lesquelles la réaction a lieu. Généralement, en milieu acide avec un pH < 5, la réduction de l'hydrogène se fait par la voie de la réduction de l'ion hydronium, représentée dans l'équation (3) ci-dessous.

$$2H_30^+ + 2e^- \leftrightarrows H_2 + 2H_20 \tag{3}$$

L'évolution de l'oxygène à l'anode se fait par la voie de l'oxydation des molécules d'eau :

$$6H_20 \rightleftharpoons 0_2 + 4H_30^+ + 4e^- \tag{4}$$

Dans le cas des milieux alcalins, les demi-réactions respectives sont les suivantes :

$$2H_20 + 2e^- \leftrightarrows H_2 + 20H^- \tag{5}$$

$$40H^- \leftrightarrows O_2 + 2H_2O + 4e^- \tag{6}$$

Dans le cas des milieux neutres (pH = 5 à 7), la réaction de dégagement d'hydrogène se produit par la voie de l'ion hydronium décrite dans l'équation (3), tandis que le dégagement d'oxygène se produit par la voie de l'oxydation de l'hydroxyde décrite dans l'équation (6). Étant donné que nous nous intéressons dans cette étude aux HER réalisées principalement dans des milieux hautement basiques et neutres, nous nous limiterons ici à des discussions dans ce contexte.

Le mécanisme de réaction des HER à la photoanode en milieu alcalin ou neutre est un processus en deux étapes consistant en la réaction de Volmer, impliquant l'adsorption en surface d'un atome d'hydrogène sur le site actif de la surface, ce qui entraîne la libération d'un ion hydroxyde. Cette réaction est suivie soit par l'étape de Heyrovsky, où l'atome d'hydrogène adsorbé à l'étape précédente réagit avec une autre molécule d'eau à l'aide d'électrons à la surface de l'électrode, ce qui entraîne la libération d'une molécule d'hydrogène et d'un ion hydroxyde dans la solution, soit par l'étape de Tafel, où deux atomes d'hydrogène adsorbés à la surface de l'électrode se combinent pour former une molécule d'hydrogène sans nécessiter de transfert d'électrons à partir de la surface de l'électrode. Ces réactions sont détaillées ci-dessous.

$$H_2 0 + e^- \to M - H + 0H^- (Volmer) \tag{7}$$

$$H_2 O + e^- + M - H \to H_2 + OH^- (Heyrovsky)$$
(8)

$$2M - H \to 2M + H_2 (Tafel) \tag{9}$$

Où M-H représente l'atome d'hydrogène adsorbé sur un site actif de la surface d'un métal/semiconducteur (M). Une considération qui doit être faite ici est que, bien que l'étape de Tafel soit similaire dans le cas des milieux acides et alcalins/neutres, dans ce dernier cas, la source de l'hydrogène adsorbé provient de la dissociation des molécules d'eau dans la solution électrolytique alors que dans le cas des milieux acides, elle provient de l'abondance des protons libres dans la solution [33, 35, 36].

#### Transport de charges et efficacité du dispositive

Alors que les réactions d'électrode présentées dans la section précédente ont lieu à la surface, le processus d'absorption de la lumière, d'excitation et de génération de charges se produit principalement dans la masse du semi-conducteur. Bien que, avec l'augmentation de la profondeur dans la couche mince, la probabilité de pénétration de la lumière incidente diminue exponentiellement (ou presque), une relation connue sous le nom de loi de Beer-Lambert décrite par l'équation (10) ci-dessous [37-39].

$$I_d = I_0 e^{-\mu d} \tag{10}$$

Ainsi, les charges générées dans la masse, même si elles sont proches de la surface, doivent se déplacer vers la surface ou vers le circuit électrique extérieur pour pouvoir effectuer un travail utile et participer à la réaction d'oxydoréduction. Dans le cas des matériaux excitoniques, cela signifie que l'électron excité (et le trou) doivent être séparés de la liaison excitonique et transportés dans des directions opposées, puisque chaque type de charge entraînera une

réaction de réduction ou d'oxydation et vice-versa. À l'opposé, l'atome ou la molécule excité(e) a tendance à revenir de l'état excité de plus haute énergie à l'état fondamental de plus basse énergie en renvoyant l'électron de la bande de conduction à la bande de valence et en dissipant la différence d'énergie sous diverses formes, un processus connu sous le nom de recombinaison des porteurs de charge. Intuitivement, il est naturel de penser que la probabilité de cette recombinaison augmente plus l'électron ou le trou doit attendre longtemps pour atteindre la surface d'une électrode, une expression connue sous le nom de longueur de diffusion [40]. La période moyenne pendant laquelle l'électron reste dans la bande de conduction, capable de se déplacer librement dans le réseau cristallin avant d'être éventuellement capturé par un trou par recombinaison, est appelée durée de vie de l'électron.

Il est évident que pour qu'un dispositif de photoconversion soit très efficace, il doit présenter un très faible taux de recombinaison des porteurs de charge, étant donné que ce processus sert à libérer l'énergie absorbée par le rayonnement solaire incident vers l'environnement, ce qui représente une perte nette d'efficacité dans la collecte de la lumière pour le dispositif. En outre, le taux de recombinaison des porteurs est inversement proportionnel à la durée de vie de l'exciton ou de l'électron dans le matériau en vrac, ce qui permet au porteur de charge d'atteindre les sites catalytiques sur l'électrode avec une plus grande probabilité au lieu de se recombiner [41-44]. Pour que l'exciton survive suffisamment longtemps pour permettre à l'électron et au trou d'être découplés et de se déplacer indépendamment vers leurs électrodes respectives, il faut que s'établissent de fortes forces électrostatiques capables d'abaisser l'énergie de liaison de l'exciton, ce qui favorise la séparation des charges. En outre, un champ électrique convenablement dirigé dans la masse du matériau, en particulier une forte polarisation inverse, contribue à attirer les charges générées loin de leurs atomes hôtes et vers les extrémités de l'électrode, empêchant leur recombinaison [45, 46]. Si la séparation de l'exciton nouvellement formé en porteurs de charge individuels est le principal mécanisme de régulation de l'efficacité qui doit être optimisé, les charges séparées, tout en diffusant dans des directions opposées à l'intérieur du semiconducteur, peuvent également se rencontrer, cette fois en tant que charges libres, et compte tenu de l'attraction électrostatique entre des électrons et des trous de charge opposée, elles ont tendance à se recombiner. Il existe d'autres interfaces où une recombinaison similaire est possible, ainsi que de nombreux types de mécanismes de recombinaison impliquant un échange entre plusieurs particules, qui doivent tous être pris en compte.

#### Voies et mécanismes de recombinaison

La recombinaison des porteurs de charge libres peut se produire soit dans la masse du semiconducteur, soit sur les surfaces et les interfaces, en particulier à l'interface électrode/électrolyte [47]. En tant que tels, les dispositifs qui contiennent des interfaces multiples et des hétérojonctions offrent plus de sites de recombinaison. La recombinaison est un processus rapide et représente donc l'un des obstacles les plus importants à l'augmentation de l'efficacité des dispositifs photovoltaïques [48]. Dans un dispositif PEC basé sur une photoanode TiO<sub>2</sub> et destiné à la production d'hydrogène à partir de la division de l'eau, les voies de recombinaison suivantes ont été identifiées :

- **Recombinaison radiative:** La recombinaison directe des électrons de la bande de conduction avec les trous de la bande de valence entraîne généralement l'émission d'un photon d'énergie égale à la bande interdite. Cette catégorie de processus de recombinaison comprend l'annihilation directe des excitons sur l'atome hôte dont il a été question dans le paragraphe précédent, mais elle peut également se produire parmi les porteurs de charge libres qui se diffusent dans l'électrode. Étant donné que le processus produit un photon d'énergie presque égale (les défauts peu profonds peuvent également se recombiner radiativement mais éjectent un photon d'énergie légèrement inférieure), le processus est généralement capable de déclencher un événement d'excitation futur à partir du photon éjecté et n'est pas toujours une forme indésirable de recombinaison. Une présence anormalement élevée de centres de défauts radiatifs peut entraîner une perte d'énergie indésirable lors de la transition vers l'état de défaut, mais dans les couches de semi-conducteurs bien formées, les recombinaisons radiatives ne sont pas le processus d'optimisation le plus étudié de manière critique [49, 50]. Étant un processus médié par des photons, les recombinaisons radiatives sont plus courantes dans les transitions directes de bande interdite, et bien qu'elles soient également possibles dans les transitions indirectes de bande interdite, elles nécessitent l'émission simultanée d'un phonon, ce qui est un événement rare, ce qui rend ces transitions moins courantes [51-53]. Ce mécanisme est illustré à la Figure 4 (a).
- Recombinaison Shockley-Reid-Hall (SRH): Les recombinaisons SRH sont des événements de recombinaison impliquant la transition de l'électron de la bande de conduction vers un état de piège et sont donc également appelées recombinaisons assistées par piège. Les pièges sont essentiellement des états d'énergie intermédiaires localisés dans le réseau cristallin en raison de la présence de dopants, d'impuretés ou de

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lacunes et d'interstitiels. Le plus souvent, l'état de la bande intermédiaire est positionné indirectement par rapport à la bande de valence et/ou de conduction, ce qui implique que ces transitions nécessitent l'échange d'un phonon. Les phonons étant une forme d'énergie qui ne peut pas être facilement et immédiatement convertie en courant électrique, le transfert d'énergie vers ces quasiparticules représente essentiellement une perte nette d'énergie pour le système. Dans de nombreux semi-conducteurs, en particulier les semi-conducteurs oxydés tels que le TiO<sub>2</sub>, ces recombinaisons dominent, ce qui se traduit par une faible efficacité de conversion solaire-hydrogène (STH) pour l'ensemble du dispositif [54, 55]. C'est ce que montre la Figure 4 (b).

- Recombinaison Auger: Le processus de recombinaison auger implique la participation d'un troisième électron (dans la bande de conduction) ou trou (dans la bande de valence), qui absorbe l'énergie de l'événement de recombinaison et est excité à un niveau d'énergie plus élevé dans la même bande. Le porteur excité finit par se détendre jusqu'au niveau d'équilibre thermodynamique en transférant l'énergie excédentaire à la vibration du réseau sous forme de phonons. Comme ce processus ne libère pas de photons, l'énergie de la photoexcitation est complètement perdue pour les vibrations du réseau, ce qui rend cette voie de recombinaison indésirable dans le contexte d'un dispositif photovoltaïque. La Figure 4 (c) illustre le mécanisme de la recombinaison par effet tarière.
- Recombinaison de surface et d'interface: Enfin, la recombinaison des porteurs de charge peut avoir lieu aux interfaces entre deux matériaux ou entre la surface d'un semi-conducteur et l'électrolyte. Aux interfaces entre matériaux ou entre un solide et un liquide, il y a une transition abrupte entre les potentiels électroniques à l'intérieur de la masse d'un matériau et ceux de l'autre, étant donné que chacun peut exister dans sa configuration structurelle et cristalline individuelle. Ainsi, la présence de dislocations et de sites vacants est courante pour compenser la différence de paramètres de réseau, ce qui donne lieu à une forte concentration d'états de défaut et de piège. En outre, dans le cas d'interfaces entre deux phases telles qu'un solide et un liquide, comme une interface électrode/électrolyte, il y a un changement immédiat de l'ordre à la surface du solide, étant donné que les particules liquides sont plus mobiles et ne représentent pas un ordre à longue portée ou lié au temps. Ainsi, la présence de liaisons pendantes est courante et peut capturer des électrons ou des trous pour passivation des électrons non appariés dans ces états [56-59]. Ceci est illustré dans la Figure 4 (d).



Figure 4 Mécanisme des voies de recombinaison dans les semi-conducteurs : (a) radiatif, (b) Shockley-Reid-Hall (SRH), (c) auger et (d) interfaciale [60].

En outre, si une photoélectrode est structurée en une configuration en couches comme c'est le cas de nos photoanodes, la présence de multiples sites de recombinaison au sein de différentes couches donne lieu à la possibilité d'événements de transfert de rétro-électrons où l'électron de la bande de conduction d'une couche peut se recombiner avec un trou présent dans la bande de valence d'une couche voisine. Le transfert de charges libres dans le semi-conducteur en vrac ou le point quantique avec les ions oxydés dans l'électrolyte est également possible et est inclus



Figure 5 Voies de transfert d'électrons dans une photoanode à hétérostructure TiO<sub>2</sub>/QD. Les flèches vertes indiquent les voies de transfert d'électrons souhaitables conduisant à la séparation et à l'extraction des charges, tandis que les flèches rouges représentent les voies indésirables (recombinaison). La ligne en pointillé représente un état défectueux dans le QD.

dans ce mécanisme de recombinaison [61]. Ces effets deviennent encore plus importants lorsque la polarisation appliquée est faible, ce qui entraîne une mobilité plus faible des porteurs de charge et une plus grande densité de charge, en particulier au niveau des surfaces et des interfaces [42, 62, 63]. Par conséquent, les stratégies de passivation visant à minimiser ces recombinaisons de porteurs de charge sont également importantes et nécessitent d'autres complications de conception de la structure de l'électrode, en particulier dans le cas des structures sensibilisées par des points quantiques [64]. Ces différentes voies pour le cas de la photoanode TiO<sub>2</sub>/FTO sensibilisée par les QD sont illustrées à la Figure 5.

#### Interface Energétique

Lorsque les semi-conducteurs forment des interfaces avec d'autres matériaux ou liquides, la distribution distincte des bandes dans ces interfaces permet l'échange de porteurs de charge avec les niveaux d'énergie de la substance de contact à la recherche d'un état énergétique plus optimisé de l'ensemble du système, ce qui est réalisé en égalisant le niveau de fermi du semi-conducteur par rapport au matériau/substance de contact. Cet effet est localisé près de l'interface et entraîne donc une modification progressive des niveaux d'énergie en fonction de la distance par rapport à l'interface, jusqu'à saturation à une distance très éloignée de l'interface dans la masse du semi-conducteur, un phénomène connu sous le nom de « flexion de bande » en raison de la forme caractéristique des bandes du matériau semi-conducteur qui en résultent. [65, 66].

Ainsi, dans les cellules PEC, dès que la photoélectrode est plongée dans l'électrolyte, le flux de porteurs de charge à travers l'interface commence à se produire à partir de quelques nanosecondes à quelques microsecondes après le contact (en fonction des propriétés des deux substances en contact), et les niveaux de fermi commencent à s'égaliser. Une fois cette condition remplie, le système atteint un état stable. En fait, un réalignement similaire des bandes se produit lors de la sensibilisation avec des QDs dès que l'hétérojonction se forme. Dans le cas d'une photoanode de type n, le niveau de fermi du semi-conducteur se situe en dessous du potentiel d'oxydoréduction de l'électrolyte en raison de l'excès de porteurs chargés négativement à la surface du semi-conducteur (électrons), comme le montre la Figure 6. Cela entraîne un flux immédiat d'électrons de la surface de la couche semi-conductrice vers les espèces oxydées de l'électrolyte en raison de l'électrolyte entre les surfaces.



Figure 6 Courbure de bande dans une photoanode de type n (réseaux de nanotubes de TiO₂ dans un électrolyte KOH 0,5M) (a) avant contact, (b) à l'état stable dans l'obscurité, et (c) à l'état stable avec une illumination supérieure à l'énergie de la bande interdite en circuit ouvert [67].

Ainsi, les porteurs de charge majoritaires sont lentement « vidés » de la surface du semiconducteur près de l'interface avec l'électrolyte, ce qui fait que le niveau de fermi à cette interface se déplace vers le haut avec l'appauvrissement des électrons dans cette région. En conséquence, cette « région d'appauvrissement » à la surface acquiert une charge positive nette et s'épaissit avec le temps jusqu'à ce que le niveau de fermi du semi-conducteur à l'interface devienne égal au potentiel d'oxydoréduction de l'électrolyte. Cette fine couche de semi-conducteur chargée positivement est appelée « couche de charge spatiale » et est souvent abrégée en SCL [68]. Dans l'obscurité, la charge positive de la SCL dirige les charges photogénérées de manière opposée vers les directions souhaitées en raison de la charge présente. Essentiellement, dans une configuration de photoanode, on souhaite que les électrons se déplacent plus profondément dans la masse pour être capturés par le contact arrière conducteur en vue d'être transportés vers la contre-électrode où la réaction de réduction a lieu, tandis que les trous devraient idéalement se diffuser vers la masse pour participer à l'oxydation de l'eau à la photoanode. Cependant, la charge positive du SCL empêche cette diffusion. Il faut donc appliquer des forces supplémentaires à l'électrode pour surmonter cette barrière générée par la SCL.

L'un de ces moteurs est généré par l'illumination, qui agit pour photogénérer des paires électrontrou qui peuvent ensuite être séparées en espèces de porteurs de charge individuels. Cependant, une autre fonction très importante est de remplir la masse de l'électrode avec une grande concentration de charges, essentiellement avec un gradient de concentration opposé à celui créé par le SCL. Cela s'explique à nouveau par la loi de Beer-Lambert présentée dans l'équation (10). La pénétration exponentielle de la lumière incidente entraîne la génération d'un nombre maximal

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de photoélectrons près de la surface, à proximité de la SCL, et au fur et à mesure que l'on s'enfonce dans la masse, l'intensité de la lumière est fortement atténuée en raison de l'absorption par les couches de matériau précédentes, ce qui entraîne la création d'un nombre beaucoup plus faible de charges. En conséquence, le gradient de concentration des électrons (porteurs majoritaires) est fortement orienté vers la masse du matériau, surmontant même la force de dérive de la SCL chargée positivement pour conduire les électrons vers la masse [69, 70]. En même temps, les photo-trous sont poussés vers la surface par le gradient de potentiel entraîné par la courbure de la bande vers le haut à la surface, considérant que les trous qui sont représentés comme l'absence d'électrons ont tendance à occuper des états d'énergie traditionnellement plus élevés [71, 72]. Ce gradient de potentiel, en plus de la force de diffusion, aide également les électrons à se déplacer vers l'intérieur, vers le bulk.

Deuxièmement, une polarisation potentielle peut être appliquée aux porteurs d'électrodes pour faciliter l'extraction des porteurs de charge et empêcher les événements de recombinaison, ce qui se traduit par une augmentation de l'efficacité globale du dispositif. Il convient toutefois de faire preuve de prudence, car l'application d'une polarisation potentielle représente en soi un apport d'énergie supplémentaire dans le système, ce qui réduit l'efficacité du processus. L'augmentation du photocourant qui en résulte doit compenser l'apport supplémentaire de charge si l'utilisation d'une polarisation d'entrée supplémentaire doit être justifiée. Un potentiel de polarisation inverse appliqué à la photoanode peut attirer les porteurs de charge majoritaires vers le contact arrière conducteur tout en augmentant l'épaisseur de la couche de charge d'espace empêchant les porteurs de charge majoritaires de passer au travers, améliorant ainsi ce que l'on appelle la « sélectivité des porteurs de charge » à l'interface de l'électrolyte. Cet effet réduit considérablement la recombinaison dans l'électrode, car les porteurs de charge se séparent efficacement et se déplacent plus rapidement dans des directions différentes, ce qui laisse très peu de temps aux événements de recombinaison pour se produire. En outre, une polarisation inverse (également connue sous le nom d'anodique) d'une photoanode de type n fait baisser le niveau de fermi du matériau de l'électrode, ce qui rend la courbure de la bande plus nette et augmente le gradient de potentiel dans le SCL [73-75]. Tous ces effets peuvent entraîner la séparation et le transport des charges, ce qui permet d'augmenter considérablement l'efficacité de la conversion solaire du dispositif.

# Efficacité de la récolte de la lumière

Un autre processus important qui définit l'efficacité d'une électrode solaire de production d'hydrogène est la proportion de lumière incidente absorbée par les matériaux de la photoélectrode qui sont convertis en excitons, un paramètre connu sous le nom d'efficacité de récolte de la lumière (LHE). Dans le cas des systèmes PEC, les matériaux des électrodes doivent présenter des bandes interdites pour produire des porteurs de charge suffisamment énergétiques capables d'entraîner des réactions chimiques.



Figure 7 Normes du spectre solaire. AM 0 représente le spectre dans l'espace où le rayonnement n'a traversé aucune atmosphère, tandis que AM 1,5 G représente le spectre standard moyen mondial reçu à la surface de la terre. La norme 1,5 D est le spectre de la lumière solaire directe, sans tenir compte des pertes dues à la diffusion diffuse [76].

Cependant, l'exigence d'une plus grande énergie des électrons (ou des trous) signifie généralement que le matériau ne peut absorber que le rayonnement de la région UV et plus loin du spectre solaire. Il en résulte une grande perte d'efficacité étant donné que ces parties du spectre solaire représentent généralement moins de 5 % du rayonnement incident, et que nous rejetons donc déjà près de 95 % de la précieuse ressource énergétique gratuite dont nous avons besoin avant même de prendre en compte des considérations telles que les efficacités internes liées à la séparation et au transport des charges [77].

La Figure 7 montre le spectre solaire standard AM 1,5 G utilisé pour caractériser les performances solaires photovoltaïques et permettre des comparaisons entre différentes configurations. Il est également plus proche du spectre solaire réel reçu à la surface de la terre, ce qui simplifie le passage du laboratoire au modèle pratique. Cette figure montre clairement que la majeure partie du rayonnement reçu se situe dans la gamme 400-1000 nm, avec une grande majorité se situant

entre 400 nm et 700 nm, ce qui représente la gamme visible du spectre électromagnétique, représentant 45-47% [78, 79]. Cependant, en termes d'activité catalytique, au moins pour la division de l'eau en hydrogène, la photostabilité dans les environnements aqueux acides et alcalins, ainsi que la facilité et l'abondance de l'approvisionnement en TiO<sub>2</sub> en font la perspective la plus lucrative, même aujourd'hui. Cependant, sa large bande interdite de ~3,2 eV signifie que son absorbance est limitée à la gamme des UV avec un bord de bande d'absorption commençant à environ 387 nm pour la phase anatase photocatalytiquement active [80].

Les stratégies visant à améliorer l'efficacité de la collecte de lumière des assemblages de photoélectrodes à base d'anatase-TiO<sub>2</sub> se concentrent principalement sur deux stratégies, les modifications chimiques et morphologiques de la structure [81-83], et la sensibilisation avec des matériaux absorbant la lumière visible tels que les points quantiques et la sensibilisation par colorant [84-86]. Parmi celles-ci, les méthodes de sensibilisation sont les plus prometteuses en raison de leur facilité de mise à l'échelle puisqu'elles utilisent des techniques bien connues de chimie humide et d'électrodéposition. Les points quantiques sont un système très étudié car leurs propriétés optiques et électroniques peuvent être finement ajustées et contrôlées [87, 88]. SILAR (Successive Ionic Layer Adsorption and Reaction) est une technique simple offrant une charge et une couverture élevées ainsi qu'un bon rapport coût-efficacité [89]. Les nanocristaux semiconducteurs à base de Cd ont été l'un des premiers systèmes de points quantiques à être déposés avec succès sur des photoanodes TiO<sub>2</sub> en tant que photosensibilisateurs de lumière visible et sont toujours utilisés en raison des rendements de conversion élevés qu'ils sont encore capables d'atteindre [90, 91]. Par conséquent, en tant que norme pour tester les performances de conversion de l'énergie solaire en hydrogène de différentes configurations de cellules PEC à base de TiO<sub>2</sub>, la sensibilisation au CdS et au CdSe/CdS à l'aide de la technique SILAR est une méthode simple et cohérente pour tester l'efficacité de l'amélioration des performances de récolte de la lumière de ces photosensibilisateurs.

## Transport de charges interfaciale

Un autre aspect important du fonctionnement efficace des dispositifs PEC est le transfert des charges photogénérées vers les espèces redox dans l'électrolyte où la réaction chimique réelle se produit. Ce processus se produit à l'interface entre l'électrode et l'électrolyte, à l'intérieur et à proximité de ce que l'on appelle la couche de Helmholtz de la double couche électrochimique (EDL). Avant d'étudier les aspects du système de matériaux ou de la solution électrolytique qui

optimisent cette double couche électrochimique pour un transfert de charge rapide et efficace, il convient de commencer par une brève introduction à la double couche électrochimique.

# Double couche électrochimique (EDL) / couche de Helmholtz

À l'interface de l'électrode semi-conductrice et de l'électrolyte, les interactions entre les ions en solution et l'électrode chargée électriquement donnent lieu à une structure potentielle à double couche qui agit comme un écran au champ électrique de l'électrode, ralentissant ainsi les réactions de transfert de charge à l'interface. La « double couche », comme on l'appelle, comprend deux régions distinctes très proches de la surface de l'électrode : la couche de Helmholtz, elle-même divisée en plans de Helmholtz interne (IHP) et externe (OHP), et la couche diffuse. La structure de ce système ainsi que l'ordre de ces couches sont illustrés dans la Figure 8.



Figure 8 Structure de l'EDL pour (a) la photocathode et (b) la photoanode montrant les plans de Helmholtz internes et externes et la couche diffuse [92].

L'accumulation de charges libres à la surface de l'électrode attire des ions non solvatés dans l'électrolyte qui sont chargés de manière opposée à la surface de l'électrode, connus sous le nom de « contre-ions », qui se fixent alors électrostatiquement à la surface de l'électrode en formant une fine région d'ions adsorbés d'une épaisseur de couche ionique presque unique connue sous le nom de plan de Helmholtz interne (IHP) [93]. Bien qu'il s'agisse de la définition habituelle de cette couche, souvent dans des cas tels que l'utilisation d'électrolytes aqueux ou de solvants polaires, les molécules de solvant polarisées, les ions partiellement solvatés ainsi que les chimisorbates liés aux espèces redox subissant des réactions sont également inclus dans cette couche tout en définissant le PHI comme l'ensemble des molécules/ions directement attachés chimiquement ou électrostatiquement à la surface de l'électrode [94, 95]. Au-delà de cette région, les ions qui interagissent faiblement avec le champ électrique de l'électrode, à savoir les ions entièrement solvatés et parfois les molécules de solvant polarisées, sont liés de manière purement électrostatique dans une région très proche de l'IHP. Les ions solvatés faiblement liés sont généralement plus mobiles que les ions adsorbés dans l'IHP et sont capables de répondre rapidement à tout changement dans le champ électrique de l'électrode [96, 97]. Au-delà de ces couches d'ions liés se trouve une région encore plus vaste d'espèces ioniques (ions entièrement et partiellement solvatés) qui, bien qu'elles ne soient pas liées par le champ électrique des électrodes, sont encore suffisamment influencées par la dérive générée pour que leur mouvement et leur distribution soient une combinaison de distributions électrostatiques et thermiques très faibles. Ici, la concentration d'ions diminue progressivement depuis les concentrations élevées au bord de l'OHP de manière exponentielle avec la distance jusqu'à ce qu'elle atteigne la concentration uniforme en vrac. Cette région est connue sous le nom de couche diffuse et représente essentiellement les bords extérieurs de l'influence du champ de l'électrode sur les espèces de l'électrolyte. Après cette région, nous entrons dans la masse de l'électrolyte où les concentrations ioniques sont constantes et où le mouvement est régulé par la diffusion et très légèrement par la migration électrostatique, étant donné que l'influence du champ électrique de l'électrode est maintenant considérablement écrêtée par la double couche. L'épaisseur de la couche diffuse est souvent caractérisée par la longueur de Debye qui délimite la frontière entre l'EDL et l'électrolyte en vrac [98, 99].

La variation du potentiel électrostatique en fonction de la distance par rapport à l'électrode est illustrée dans la Figure 9 (a) où nous pouvons observer une décroissance presque linéaire du potentiel en fonction de la distance à l'intérieur des plans de Helmholtz interne et externe, tandis que le potentiel décroît de façon exponentielle en fonction de la distance à l'intérieur de la couche diffuse jusqu'à ce que l'on atteigne la couche en vrac. Après ce point, nous pouvons observer sur la Figure 9 (b) que le potentiel reste presque constant jusqu'à ce que nous atteignions la couche diffuse sur la contre-électrode, où le potentiel suit à nouveau une décroissance exponentielle et ensuite une chute linéaire à l'intérieur des couches de Helmholtz.

Si l'EDL est un système physique important dans les dispositifs électrochimiques, sa présence peut être à la fois positive et négative en fonction de l'application. Dans le cas de la PEC, cependant, l'EDL présente à la fois des opportunités et des défis qui doivent souvent être équilibrés afin d'obtenir une efficacité optimale de la cellule PEC. Plus particulièrement, l'adsorption d'ions sur la surface de l'électrode bloque directement l'accès aux sites potentiels d'oxydoréduction actifs par les molécules qui subissent la réaction chimique à la surface de l'électrode, soit en occupant directement le site actif, soit par la constriction stérique des sites environnants, comme dans le cas de molécules adsorbées plus grandes telles que les ligands à longue chaîne [100-103]. En outre, ces ions de surface adsorbés peuvent être chimiquement passifs, en empêchant simplement les espèces redox d'accéder à la surface de l'électrode, ou chimiquement actifs, en participant au transfert de charge à la surface et en modifiant chimiquement la chimie de surface de l'électrode, ce qui entraîne sa dégradation, un processus connu sous le nom d'« empoisonnement de surface » [19].

De tels effets de dégradation sur l'électrode peuvent affecter à la fois les caractéristiques de performance et la stabilité à long terme [104-106]. En outre, même si la charge de contre-ion sur la couche de Helmholtz interne agit pour attirer les porteurs minoritaires vers la surface en favorisant une séparation de charge efficace, le même sens de polarisation peut piéger les charges électrostatiquement sur la surface, empêchant leur transfert vers des espèces réactives, ou même favorisant le piégeage sur des sites de surface, le tout conduisant à d'éventuelles pertes par recombinaison non radiative [70, 107, 108].

Ensuite, nous considérons la barrière potentielle générée par l'accumulation de charge dans la LDE qui agit en repoussant les charges et les espèces ioniques, en particulier les espèces actives d'oxydoréduction, pour qu'elles n'atteignent pas facilement la surface de l'électrode. Alors que le champ électrique qui crée la LDE est également responsable de la création d'un environnement ionique riche à proximité de l'électrode, qui comprend également les entités redox actives qui y sont mélangées, ce même environnement peut empêcher les espèces fraîches de réapprovisionner la couche de Helmholtz interne en raison de la barrière potentielle supplémentaire qu'elles doivent surmonter pour se rendre à l'électrode. Cela se voit dans les énergies d'activation supplémentaires apparentes dans les interfaces ayant une concentration élevée d'ions inactifs d'oxydoréduction comme les sels dans l'électrolyte qui réduisent la

concentration d'ions actifs d'oxydoréduction, à la fois dans la solution en vrac et dans la couche EDL [109].



Figure 9 Chute de potentiel à travers l'EDL montrant, (a) le profil près de l'électrode montrant clairement les différentes régions de l'EDL [1], et (b) le profil sur l'ensemble de la cellule de l'anode à la surface de la cathode montrant un gradient de potentiel presque constant dans la masse de l'électrolyte [110].

Les propriétés de la couche EDL constituent donc à la fois une opportunité et un obstacle, et une adaptation minutieuse des propriétés des matériaux ainsi que la conception des composants de la cellule sont nécessaires pour maximiser le gain et minimiser la perte dans cette région.

## Piégeur de trou

Pendant le fonctionnement de la cellule PEC utilisant une photoanode de type n, les électrons se déplacent vers la masse et sont consommés par le contact ohmique arrière, tandis que les trous se déplacent vers la surface de l'électrode. À la surface, les trous s'accumulent en attendant que les espèces réductrices soient adsorbées sur les sites actifs d'oxydoréduction, qui peuvent être caractérisés par des ions se déplaçant lentement dans un milieu liquide, en plus de surmonter les barrières imposées par la couche EDL, comme nous venons de le voir. Dans l'ensemble des dispositifs de séparation de l'eau et de production d'hydrogène PEC, la réaction d'oxydation de l'eau à la photoanode est particulièrement lente car elle implique le transfert de plusieurs électrons pour la production d'hydrogène. d'une seule molécule d'oxygène (équations (4) et (6)), ce qui

nécessiterait l'accumulation de plusieurs charges à proximité d'un seul site d'activation. Cependant, la concentration de charges s'accompagne souvent d'un taux de recombinaison plus élevé, et il est plus probable qu'à mesure que les trous s'accumulent, ils se recombinent avec les électrons libres avant de pouvoir participer aux réactions d'oxydoréduction. Toutefois, ces recombinaisons ont également un effet négatif sur la densité d'électrons libres, qui est directement liée à la capacité de production d'hydrogène et à l'efficacité du système. Par conséquent, lorsque l'on étudie uniquement la capacité du système à produire de l'hydrogène sans tenir compte de la réaction qui a lieu sur le site de la photo-anode, il est souvent avantageux d'inclure dans l'électrolyte des espèces plus aptes à accepter les charges de trous libres sur les sites de la surface de l'électrode. Bien entendu, cela présente également l'avantage d'empêcher l'empoisonnement de la surface par des réactions chimiques médiées par les trous sur les sites de surface [111, 112]. Lorsque ces agents « piègent » les trous qui s'accumulent à la surface de l'électrode, ils sont oxydés de manière irréversible, parfois en sous-produits utiles (comme le méthanol en formaldéhyde). Ils sont donc connus sous le nom de piégeurs de trous [113, 114]. Ces réactions sont particulièrement utiles dans le cas des dispositifs de génération d'hydrogène où la production d'oxygène à l'anode n'est pas nécessaire.



Figure 10 Effet du piégeur de trous de sulfite sur la performance PEC : (a) courbe courant-tension de l'hétérojonction CuWO<sub>4</sub> vs CuWO<sub>4</sub>/Sn<sub>2</sub>O(NCN) pour le piégeur de trous de sulfite (ligne pointillée dans l'encadré) et l'oxydation de l'eau (ligne continue) [5], et (b) stabilité à long terme à partir des caractéristiques courant-temps des photo-anodes BiVO<sub>4</sub> [115].

L'un des piégeurs de trous souvent utilisés, en particulier pour l'étude de la production d'hydrogène solaire, est l'anion sulfite  $(SO_3^{2-})$  qui sert efficacement à diminuer la barrière cinétique pour l'injection de trous de la surface de l'électrode à l'électrolyte, ce qui augmente considérablement le taux de transfert des trous vers les piégeurs de trous, empêchant l'accumulation de trous sur la surface de l'anode. L'anion sulfite associé à un électrolyte sulfuré est très efficace pour augmenter l'efficacité de la photoconversion et pour « nettoyer » l'électrode

des charges libres corrosives, ce qui prolonge la durée de vie de l'électrode [116, 117]. La Figure 10 montre ces deux effets sur la performance PEC pour l'anion sulfite piégeur de trous contre l'oxydation de l'eau pour certains systèmes de photo-anodes simples.

# PEC assistée par champ magnétique

L'utilisation d'un champ magnétique pour assister les processus photocatalytiques ne date pas d'hier, divers effets générés par un champ magnétique ayant été exploités pour améliorer l'efficacité des processus chimiques à transfert de charge, y compris l'électrochimie. Depuis la découverte de l'effet Honda-Fujishima en 1972, alors que la recherche sur l'électrolyse photocatalytique de l'eau a progressé rapidement, des efforts pour utiliser les propriétés magnétiques des matériaux concernés ont également été déployés périodiquement. La Figure 11 (b) l'illustre succinctement. L'effet d'un champ magnétique sur le processus d'évolution de l'hydrogène par PEC peut généralement passer par plusieurs voies. La littérature fait état d'effets magnétothermiques, d'effets magnétohydrodynamiques, d'effets de transfert de masse médiés par la force de Lorentz, ainsi que d'une influence sur les processus de régulation des porteurs de charge et de l'état de spin ionique (Figure 11).



Figure 11 Chronologie du développement des systèmes de photocatalyse assistée par champ magnétique [118].

Parmi les types de matériaux, les matériaux ferromagnétiques et paramagnétiques ou les matériaux fonctionnalisés avec des dopants ferro- et paramagnétiques sont des choix courants de photoélectrodes pour effectuer des études assistées par champ magnétique,

occasionnellement les effets magnétiques avec des matériaux diamagnétiques à cause des dopants et ou des magnétismes induits par des défauts de vacance peuvent apparaître dans ces matériaux sont également discutés [119]. Dans certaines études, le ferrimagnétisme, l'antiferromagnétisme et les matériaux superparamagnétiques sont également exploités [120]. Nous présentons un aperçu de l'état actuel de la recherche sur les systèmes PEC assistés par champ magnétique en détaillant les mécanismes proposés et les types de matériaux étudiés.

#### Force de Lorentz

Sous l'effet d'un champ magnétique, les particules chargées décrivent souvent des trajectoires circulaires, et dans le cas d'un mouvement sous un champ électrique préexistant, les trajectoires deviennent hélicoïdales. Dans le cas de particules de charge opposée, telles que les électrons et les trous, la force de Lorentz les pousse dans des directions circulaires opposées (dans le sens des aiguilles d'une montre ou dans le sens inverse), ce qui entraîne une séparation immédiate des charges qui, sous l'influence du champ électrique, seront également poussées dans des directions linéaires opposées. Par conséquent, la probabilité de recombinaison des porteurs est fortement réduite avec l'ajout d'un champ magnétique en conjonction avec un champ électrique provenant du potentiel de polarisation sur l'électrode [121, 122]. Ceci est clairement illustré dans la Figure 12.



Figure 12 Différence entre les caractéristiques de transfert des électrons et des trous dans une hétérojonction sans champ magnétique et avec champ magnétique, ainsi que l'influence de la force de Lorentz sur les électrons et les trous [123].

#### Effet magnétothermique

L'effet d'un champ magnétique variant dans le temps sur des nanoparticules fortement paramagnétiques ou ferromagnétiques est l'induction d'un mouvement oscillatoire dans ces dernières, ce qui entraîne une relaxation magnétique par laquelle les particules oscillantes transfèrent leurs oscillations aux particules environnantes en raison d'interactions mécaniques à leur interface, ce qui provoque un chauffage localisé appelé « hyperthermie magnétique ». Par ailleurs, les champs magnétiques variables dans le temps peuvent également induire des courants de Foucault dans la masse du matériau, ce qui peut également provoquer une thermalisation localisée. Par la suite, le champ thermique peut aider à catalyser les réactions d'oxydoréduction en influençant la recombinaison, le transport de masse et la cinétique de la barrière d'activation [124, 125].



Figure 13 (a) installation de chauffage magnétique utilisant un champ magnétique alternatif ainsi que le mécanisme d'amélioration de la réaction magnétothermique à la surface des nanoparticules [4], (b) chauffage localisé à la surface du catalyseur par rapport au chauffage global de la solution avec les méthodes de chauffage conventionnelles [126].

L'avantage de cette technique est que le chauffage est généré localement à la surface du catalyseur, ce qui signifie que l'énergie thermique n'est pas gaspillée pour chauffer les composants qui ne présentent pas de performances accrues dans un champ thermique, comme la masse de l'électrolyte, qui serait sinon également chauffée lors de l'utilisation d'une méthode de chauffage conventionnelle (Figure 13 (b)) [127].

## Effet magnétohydrodynamique

Les ions dans l'électrolyte d'une cellule PEC sont des particules fluides chargées dont le mouvement constitue un courant. De la même manière que le mécanisme de la force de Lorentz, ce mouvement, lorsqu'il est soumis à un champ magnétique, peut générer un « flux » à l'intérieur du fluide dont les interactions avec les particules de solvant voisines peuvent provoquer un

mouvement tourbillonnaire à l'intérieur de l'électrolyte, particulièrement important à proximité de la surface de l'électrode, où il peut aider à éliminer les bulles de gaz générées par les réactions d'oxydoréduction qui restent généralement adsorbées sur la surface pendant un certain temps, bloquant les sites actifs. En présence de ce flux qui est généralement perpendiculaire au mouvement ionique et qui balaie donc la surface de l'électrode, la force générée agit dans le sens d'un cisaillement sur la bulle attachée au site de la surface. L'augmentation de la convection et de la force de cisaillement qui en résulte permet aux bulles de se détacher de la surface à des tailles plus petites qui nécessiteraient autrement une augmentation de la flottabilité, de la tension superficielle et/ou de la force gravitationnelle pour séparer la bulle, qui s'échelonnent toutes avec la taille [121, 127-129]. Cet effet est clairement illustré dans les images de la surface des électrodes de la Figure 14.



Figure 14 Différence de taille des bulles d'hydrogène sans champ magnétique (a) et en présence d'un champ magnétique de 70 mT (b) montrant l'effet de la magnétohydrodynamique [130].

#### Magnétorésistance négative

Les matériaux ferromagnétiques spéciaux qui ont la propriété de générer un courant polarisé en spin en présence d'un champ magnétique présentent une diminution marquée de la résistance avec l'augmentation de l'intensité du champ magnétique. Cette propriété est due à la capacité des électrons polarisés en spin à traverser plus facilement les joints de grains, alors qu'auparavant ces interfaces provoquaient une diffusion des électrons entraînant une perte d'énergie, un événement représenté par la résistance électrique du matériau. Cette propriété, appelée magnétorésistance négative, permet aux électrons photogénérés de traverser rapidement la matrice du matériau en vrac et de s'y loger. atteindre la surface atteindre un plus grand pourcentage de séparation de charge aidant à augmenter la performance PEC [118, 122,

131, 132]. Le mécanisme détaillé pour le cas du  $Bi_2S_3$  riche en lacunes de Bi est illustré à la Figure 15. Ici, l'effet de la force de Lorentz est censé jouer un rôle synergique avec la diminution de la résistance au transfert de charge avec l'augmentation du champ magnétique (comme déjà décrit).



Figure 15 Mécanisme de séparation des charges assistée par champ magnétique dans une photoélectrode à magnétorésistance négative [133].

#### Effets de spin

Le mécanisme le plus simple et peut-être le plus anciennement proposé pour expliquer les effets d'amélioration de l'efficacité de l'électrolyse solaire de l'eau est le couplage des spins des porteurs de charge avec le champ magnétique externe. Le spin d'un électron (ou alternativement d'un trou) est un moment magnétique interne qui est un phénomène quantique. L'électron, un fermion, possède un nombre quantique de spin égal à la moitié, ce qui implique que son état de spin peut être soit +1/2, soit -1/2, appelés respectivement spin « haut » et « bas ». Comme il s'agit d'un moment magnétique, il suit les lois d'un dipôle magnétique placé dans un champ magnétique externe, dans lequel le dipôle se réoriente pour aligner son moment dipolaire parallèlement au champ magnétique externe. Dans un système quantique, si l'on considère que la particule quantique ne peut exister que dans l'un des deux états de spin décrits ci-dessus, cela implique que les spins peuvent s'aligner soit parallèlement, soit antiparallèlement au champ externe, ce qui représente respectivement les états de spin haut et bas. L'alignement des spins dans la direction parallèle au champ magnétique externe à l'intérieur des matériaux du photoélectrode donne lieu à un état connu sous le nom de polarisation de spin. Dans le cas de la polarisation des spins dans la masse, le degré de polarisation est défini comme la fraction de la population totale d'électrons dans l'un ou l'autre des deux états de spin possibles. Un pourcentage élevé

d'électrons dans un état de spin représente alors un degré élevé de polarisation pour cet état [134, 135]. Il est intéressant de noter que l'application d'un champ magnétique externe n'est pas toujours nécessaire, et que les interactions magnétiques générées en interne dans les matériaux, telles que le couplage spin-orbite et les interactions de champ d'échange photoinduites, peuvent également provoquer l'apparition de cet état [136]. La Figure 16 illustre ce phénomène dans un diagramme de bande d'énergie. La présence du degré de liberté du spin dans les systèmes de mécanique quantique entraîne l'existence de deux types de configurations électroniques lorsque des électrons non appariés sont impliqués, comme c'est le cas avec les espèces optiquement excitées, à savoir le singulet avec les deux électrons ayant des spins opposés (ou antiparallèles), et le triplet où les deux électrons non appariés ont des spins parallèles ou identiques.



Figure 16 Mécanisme de polarisation du spin dans le CsPbBr3 dopé au Mn [137].

Habituellement, dans les semi-conducteurs à configuration stable, l'état fondamental est une orbitale moléculaire entièrement remplie contenant deux électrons de spins opposés, comme l'exige le principe d'exclusion de Pauli. Ainsi, lors de la photoexcitation, les deux électrons, l'un dans la bande de valence et l'autre dans la bande de conduction, se trouvent dans la configuration singulet, étant donné que la photoexcitation est un processus de conservation du spin. La configuration singulet est également bien adaptée au processus de recombinaison en vertu des mêmes règles de mécanique quantique et des exigences de sélectivité de spin qui régissent la photoexcitation [138]. En revanche, la configuration triplet ne permet pas une recombinaison facile de l'électron excité, étant donné que la recombinaison radiative à partir de l'état triplet entraînerait l'occupation de l'état de valence par deux électrons de même spin. Par conséquent, les recombinaisons de l'état triplet à l'état singulet sont beaucoup moins fréquentes et médiées par des mécanismes très complexes impliquant le couplage spin-orbite, ce qui rend l'état triplet très durable [139, 140]. Ces transitions sont donc appelées « interdites au spin » [141-144].


Figure 17 Transitions photophysiques médiées par le spin et constantes de temps associées [145].

Cependant, le processus de polarisation du spin, en particulier dans un champ magnétique externe, peut favoriser les processus de transition interne d'un électron dans des états électroniques qui ne conservent pas la multiplicité de spin, les transitions dites intersystèmes (ISC) (Figure 17). Ces transitions s'opposent aux transitions de singulet à singulet qui conservent le spin (états désignés par S), appelées conversions internes (IC). Les transitions ISC amènent le porteur de charge excité à un état triplet, généralement désigné par un T, à partir duquel la relaxation vers l'état singulet fondamental (S0) nécessite à nouveau un changement de multiplicité de spin, ce qui ne peut être réalisé par voie radiative. La Figure 17 montre que ces transitions sont de l'ordre de la microseconde, contrairement aux transitions de fluorescence de l'ordre de la nanoseconde, ce qui laisse suffisamment de temps à l'électrode pour séparer et extraire le porteur de charge avec succès. Dans le cas de la PEC assistée par champ magnétique, ce phénomène est précisément largement exploité pour utiliser le champ magnétique externe afin d'influencer directement l'état de spin des porteurs de charge photoexcités et d'encourager les transitions ISC vers l'état triplet [146-148]. Il en résulte un taux de recombinaison fortement réduit à la fois au niveau de la masse et de la surface et, finalement, une efficacité de conversion solaire accrue [131, 132, 149, 150].

### Rapports sur la PEC améliorée par le champ magnétique

Plusieurs matériaux ont été rapportés dans la littérature qui ont montré les propriétés magnétiques détaillées dans les sections ci-dessus pour améliorer de manière synergique les

performances de la PEC dans la production de plusieurs combustibles solaires, y compris l'hydrogène à partir de l'eau. Nous présentons ici brièvement chacun de ces systèmes de matériaux. L'effet de la force de Lorentz a été observé dans les nanobelts de TiO<sub>2</sub>, Mn<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>@ZnO, Mn<sub>3</sub>O<sub>4</sub>/γ-MnOOH et le catalyseur hiérarchique Ni<sub>x</sub>Mn<sub>(0,5-x)</sub>O. Les matériaux à base de fer ont été largement testés pour montrer l'effet d'élimination magnétohydrodynamique des bulles, tandis que l'hétérojonction  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/oxyde de graphène réduit (rGO) montre une amélioration photocatalytique remarquable due à la magnétorésistance négative. Cependant, dans le cas de l'amélioration de la polarisation du spin, des articles sur les nanoplaquettes de Mn-CsPbBr<sub>3</sub>, les nanofils de ZnO dopés au Co, le BaTiO<sub>3</sub> riche en vides d'oxygène, le TiO<sub>2</sub> riche en vides de Ti ainsi que le ZnFe<sub>2</sub>O<sub>4</sub> enrichi ferromagnétiquement ont été rapportés [118, 121, 122, 124, 127, 129, 151-154].

### Objectifs de la recherche

L'objectif de cette recherche est d'analyser la performance des photoanodes à base de TiO<sub>2</sub> sur des substrats FTO utilisés pour le système PEC pour la production d'hydrogène à partir d'un électrolyte aqueux en présence d'un champ magnétique relativement faible. Bien que l'amélioration de l'efficacité de la conversion STH en présence d'un champ magnétique soit un phénomène connu, il n'y a pas eu beaucoup d'analyses détaillées sur l'origine de ce phénomène, en particulier en termes de dynamique des porteurs de charge à l'intérieur du système de matériaux et aux surfaces et interfaces. Dans le cadre de cette étude, nous tentons d'établir la quantité d'informations que l'on peut obtenir en utilisant uniquement des mesures basées sur la PEC.

L'étude de la littérature sur le sujet nous a permis de comprendre que peu d'efforts ont été faits pour déterminer quels composants de la cellule PEC sont influencés par le champ magnétique et contribuent à l'amélioration de l'efficacité de la production d'hydrogène à partir de l'énergie solaire. Étant donné que la PEC dans une configuration à trois électrodes est une technique utilisée principalement pour étudier l'électrode de travail (dans ce cas, la photoanode) de manière isolée, cet aspect de l'analyse expérimentale est souvent ignoré. L'objectif préliminaire était donc d'identifier, à partir de la photoanode, qui comprend ses différentes couches séparément, de l'électrolyte et de la contre-électrode, les composants qui ont participé à l'amélioration des performances sous l'effet du champ magnétique. Pour ce faire, la méthode suivante a été utilisée :

• La photoanode a été progressivement réduite couche par couche jusqu'à l'obtention d'un échantillon de FTO vierge. Lors du test de chaque couche, l'attention est portée sur l'observation ou non d'une magnéto-réponse lors de l'introduction d'un champ magnétique dans le système et, dans l'affirmative, sur l'ampleur de l'amélioration des performances. Le cas où le système cesse de répondre au champ magnétique lors de l'enlèvement d'une couche est particulièrement intéressant. À ce stade, nous pouvons conclure que la réponse magnétique peut être attribuée aux couches situées au-dessus de cette couche.

- L'électrolyte a été modifié à différents pH ainsi que les espèces ioniques. La réponse associée à différents niveaux de pH sera utile pour déterminer comment le champ magnétique interagit avec la concentration de protons dans l'électrolyte, tandis que la variation de l'espèce ionique nous permet de connaître l'interaction avec l'espèce particulière en solution. Bien entendu, ces interactions seront caractérisées par leur comportement à l'interface de l'électrode avec l'électrolyte. Enfin, les électrolytes choisis sont l'un avec un piégeur de trous (anion sulfite) et l'autre sans (Na2SO4 0,5M). Ainsi, la réponse magnétique avec le piégeur de trous nous permettra de commenter l'effet du champ magnétique sur les charges de surface de l'électrode. Toute variation de la réponse PEC qui suit le changement naturel d'activité entre les différents systèmes d'électrolytes nous permettra également de savoir que la masse de l'électrolyte n'est pas influencée par la présence d'un champ magnétique dans le système.
- Enfin, l'utilisation de plusieurs contre-électrodes nous permettra de vérifier si la réaction de la contre-électrode est influencée par le champ magnétique ou non. Trois contreélectrodes, le platine, qui est la norme, peuvent être utiles pour comparer les performances avec d'autres matériaux rapportés, à la fois avec et sans champ magnétique, tandis que l'utilisation d'une contre-électrode en or et en graphite nous donnera un contraste quant à l'effet de la variation du type de contre-électrode sur la réponse magnétique du système.

Avec les informations sur les systèmes affectés par le champ magnétique, nous pouvons nous concentrer sur la détermination des processus spécifiques qui sont influencés, en particulier dans la masse de l'électrode et à la surface, la cinétique de transfert de charge et la cinétique de réaction. Les processus les plus importants qui ont été identifiés dans la littérature sont la cinétique de séparation et de recombinaison des charges au niveau de l'électrode et de la surface. La voltampérométrie à balayage linéaire est utilisée pour caractériser les performances, tandis que la décroissance du potentiel en circuit ouvert est utilisée pour comprendre les durées de vie des porteurs de charge. Les spécificités de la dynamique des porteurs de charge peuvent être déduites de la spectroscopie d'impédance électrochimique.

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Enfin, les idées de conception du panneau solaire photovoltaïque qui serait intégré aux conducteurs de transmission et de distribution électrique pour permettre l'utilisation pratique de l'effet d'amélioration photovoltaïque assisté par champ magnétique, ainsi que les résultats d'un exercice de validation du marché mené pour déterminer si la technologie inventée représente une solution à un problème réel, sont présentés dans l'annexe.

## Organisation de la Thèse

Cette thèse a été divisée en six chapitres comme suit :

Le chapitre 1 est l'introduction qui présente une discussion détaillée sur le contexte du sujet, y compris les bases de la séparation photoélectrochimique de l'eau pour la production d'hydrogène, ainsi que les différentes techniques d'amélioration des performances assistées par un champ externe. Enfin, la motivation et les objectifs du projet de recherche sont présentés.

Le chapitre 2 détaille les méthodes de synthèse des matériaux et de fabrication des dispositifs, ainsi que la théorie de toutes les méthodes de caractérisation utilisées. Parallèlement à l'introduction de chaque méthode de caractérisation, les résultats des mesures de caractérisation ainsi que leur interprétation en termes de pureté, d'uniformité et de qualité du matériau synthétisé ou du dispositif fabriqué sont discutés.

Le chapitre 3 présente l'introduction théorique aux méthodes de caractérisation PEC et, immédiatement après, les résultats des mesures expérimentales PEC et l'analyse visant à déterminer l'effet du champ magnétique sur le système PEC. L'influence sur la séparation, le transfert et la recombinaison des charges est spécifiquement analysée, notamment en ce qui concerne la recombinaison globale et les recombinaisons de surface au sein de la photo-anode.

Le chapitre 4 résume les principaux résultats de ce travail de recherche et souligne les lacunes qui n'ont pas été prises en compte dans le cadre de ce travail et qui pourraient faire partie de futures recherches basées sur ce projet.

Une annexe est consacrée aux idées de conception d'un panneau solaire photovoltaïque commercial qui peut exploiter les performances améliorées de la collecte et de la conversion de l'énergie solaire en présence d'un champ magnétique. Le panneau conçu pour s'adapter à un fil conducteur électrique est présenté sous différentes variantes. En outre, les résultats d'une étude de validation du marché réalisée pour déterminer la viabilité de l'adoption commerciale à grande échelle de ce panneau solaire. Les problèmes spécifiques identifiés par les clients potentiels de

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# LIST OF ABBREVIATIONS

1D	One Dimension	OCP	Open Circuit Potential
3D	Three Dimensional	OER	Oxygen Evolution Reaction
AC	Alternating Current	OHP	Outer Helmholtz Plane
AM	Air Mass	PEC	Photoelectrochemical
Ag/AgCI	Silver/Silver Chloride	PCE	Photoconversion efficiency
ເັ	Capacitance	QD	Quantum Dot
CBM	Conduction Band Minimum	R	Resistance
CO2	Carbon Dioxide	RHE	Reversible Hydrogen Electrode
CdS	Cadmium Sulfide	SCL	Space Charge Laver
CdSe	Cadmium Selenide	SEM	Scanning Electron Microscopy
DC	Direct Current	SILAR	Successive Ionic Laver Adsorption
EDL	Electrochemical Double Laver	•	and Reaction
EDS	Energy-Dispersive X-ray	SRH	Shocklev-Reed-Hall
	Spectroscopy	STH	Solar to Hydrogen
Eα	Band Gap	SnO2	Tin Oxide
EIS	Electrochemical Impedance	U.S.	United States
	Spectroscopy	UV-Vis	Ultraviolet-Visible Spectroscopy
EJ	Exaioule	V	Voltage
ETL	Electron Transport Laver	VBM	Valency Band Maximum
FTO	Fluorine-doped Tin Oxide	Vol.%	Volume Percentage
GC	Gas Chromatography	W.m2	Watt per Meter Square
GDP	Gross Domestic Product	W	Watt
HDI	Human Development Index	Wt.%	Weight Percentage
HFR	Hydrogen Evolution Reaction	XPS	X-Ray Photoelectron Spectroscopy
IHP	Inner Helmholtz Plane	XRD	X-Ray Diffraction
IPCE	Incident Photon to Current	h	Hour
	Efficiency	kHz	Kilohertz
.1	Photocurrent Density	mHz	Millihertz
K.Imol <sup>-1</sup>	Kiloioule per Mole	mM	Millimolar
LCOE	Levelized Cost of Energy	mT	Millitesla
LSV	Linear Sweep Voltammetry	mV	Millivolt
M	Molar	min	Minute
MEG	Multiple Excitation Generation	ml	Milliliter
MS	Mott-Schottky	°C	Degree Celsius
MW	Megawatt	рН	Power of Hydrogen
Mt	Mega Tons	ul	Microliter
N2	Nitrogen	μι τ	Flectron Lifetime
NHE	Normal Hydrogen Electrode	v	
NIR	Near Infrared		
NWs	Nanowires		

## **1 INTRODUCTION**

In the face of escalating global climate change the world stands at a critical crossroads. The imperative for a rapid transition from fossil fuels to renewable energy sources is tapered by the need to meet increasing global energy needs. It has been long recognized that there is a need for a transition to diverse clean energy approaches coupled with adaptation towards sustainable economies. At the forefront of this transition, hydrogen, as an energy storage medium and a clean fuel for hard-to-electrify sectors, emerges as a beacon of hope, poised to revolutionize the renewable energy landscape [6, 7]. Solar-driven photoelectrocatalysis (PEC), using natural sunlight and water as the source, is a promising technology for sustainable hydrogen generation, but faces major challenges *[8-12]*. The inherent need to improve PEC efficiency, through the choice of photoanode materials and PEC system architectures, is entwined with the scientific community's present understanding of the photoelectrocatalytic process itself [13, 14]. In this work, we report, to our knowledge, the first observation of an enhanced solar PEC efficiency for the CdS and CdSe/CdS quantum dot (QD) sensitized mesoporous TiO<sub>2</sub> (mTiO<sub>2</sub>) photoanode system due to the presence of a passive magnetic field and seek to explore possible underlying photoelectrochemical mechanisms.

Solar-based technologies, including solar photovoltaics (PV) and solar to fuel conversion for energy storage, are seen as critical solutions for the establishment of a clean energy ecosystem quickly and efficiently [15, 16]. The great challenge in the idea of extensively deploying solar assets to replace legacy power generation technologies, however, lies in the intermittence of the energy source itself namely the availability of solar illumination on the earth's surface. At any place on the earth, solar irradiation is a daytime phenomenon and during the nighttime, photovoltaic assets are essentially inactive [17]. Therefore, the role of solar fuels such as hydrogen is an almost indispensable component in a clean, around-the-clock solar-driven economy, especially given the high gravimetric density of hydrogen as a fuel source. Furthermore, hydrogen generation through photoelectrochemical water splitting represents a completely green and fossil fuel-free technique to produce hydrogen as a chemical energy storage source, further reducing the role of fossil fuels in the global economy [18, 19].

## 1.1 Photoelectrochemical (PEC) hydrogen generation

## 1.1.1 PEC cell

A PEC cell, as the name implies, is a type of electrolytic cell powered by a light source, which is usually solar insolation or a simulation of such produced by a solar simulator. As such, it operates



Figure 1.1 Three-electrode PEC cell configuration on the left and two-electrode PEC cell configuration on the right [20].

on the basis of redox reactions driven by an external energy source at two separate electrodes. Hence, a minimum of two electrodes are required where the two individual half-cell reactions take place. However, more advanced configurations having 3 electrodes or an even higher number of electrodes also exist depending on the application or the study being conducted. A typical example of a two and three electrode semiconductor sensitized PEC cell is shown in Figure 1.1.

A three-electrode configuration is often more prevalent in research settings and is the main configuration used in this study. While the two-electrode configuration uses a working electrode and a counter electrode only, a three-electrode configuration adds a reference electrode to the system. As the name suggests, a reference electrode is a reference point for the potential applied on the working electrode to drive the redox reaction at this site, while the counter electrode is configured to deliver all of the current that is driven from the working electrode, making sure that none of it passes through the reference electrode. The job of ensuring the various electrodes perform their respective tasks is given to a potentiostat, which maintains the electrodes at the relevant potentials. In this way, a three-electrode configuration essentially 'isolates' the working electrode from the rest of the system and offers a method to selectively study the charge and redox dynamics at the working electrode separately. In this way, the efficiency of a three-electrode PEC cell is essentially the efficiency of the photoelectrode, which performs the role of the working electrode. [20].

A two-electrode configuration, on the other hand is used to characterize the efficiency of the complete setup including the working and counter electrodes, the electrolyte and how these perform in relation to each other to drive efficient overall redox reactions and are therefore more suited to study devices intended to be used for practical and large-scale applications.



Figure 1.2 Overall water splitting setup using a two-electrode configuration (left) [21]; Two-electrode configuration used to study actual hydrogen production volume in a gas chromatography reaction chamber (right) [22].

A typical use is to study the volume of evolution of produced gases such as hydrogen and oxygen in the case of water splitting reactions using a gas chromatograph [23-25]. Figure 1.2 illustrates how this configuration looks in practice.

## 1.1.2 Overall water splitting and hydrogen generation

The Honda-Fujishima effect, discovered in 1972, demonstrated the potential for hydrogen production through photoelectrochemical water splitting at semiconductor electrodes using solar energy. This breakthrough offered a pathway for large-scale solar energy utilization and storage in the form of hydrogen fuel, addressing the intermittency issues associated with solar power [26]. The electrochemical water splitting reaction is endergonic, requiring a Gibbs free energy of  $237 kJ mol^{-1}$ . Hence, the process requires an energy input either through direct solar irradiation, the application of a potential, or both. While the use of pure solar energy constitutes a process called photocatalysis, the use of only electrical potential is called electrocatalysis. In the same vein, when both energy inputs are used, the process is termed photo-electrocatalysis (PEC). The type of process to use depends on the properties of the materials used to construct the particular cell, essentially their optical and electronic properties.

To drive the process with light input, semiconductors are the ideal choice given that their band structure contains a distinct band 'gap' from the valence band to the conduction band that can

only be traversed by absorbing energy from an external source equal to (or greater than) the energy difference of the gap. This gives them the ability to absorb light photons of sufficient energy and promote a valence electron to the conduction band, which can then be extracted using an electrically biased circuit or an interface space charge layer (as in the case of photocatalysis where the electron is directly transferred to the reactive species extracting the chemical potential of the conduction electron rather than its electrical potential). The promotion or excitation of the electron to the conduction band has another advantage wherein the overall species that remains in the molecule, (if this electron is now considered as an independently bound species) is capable of transferring from one molecule to another, that is that the remaining molecule now has a positive charge which can attract an electron from the conduction band of a neighboring atom/molecule. This allows a single excitation to drive twice as much charge, one from the transfer of the conduction electron and a second from the acceptance of an electron to the positive charge center created as a result. This is represented by considering the space left from the excitation of the electron as a 'hole', which is a positively charge equivalent pseudo-particle which contains the charge balance to neutralize the atomic charges and also represents the charge mobility of the electrons that simply fill up the available space, usually just about one or two orders of magnitude lower than the electron mobility in most semiconductors [27, 28]. In most semiconductors, the excited electron is usually bound to the host atom/molecule creating an electron-hole pair known as an 'exciton'. The electron can then be separated from the hole coupling by biasing the semiconductor with a potential bias, which generates an internal electric field inside the semiconductor bulk, pushing the electron toward the outer electrical circuit.

At the same time, the use of photoactive semiconductors to drive redox reactions has some more considerations that need to be made in relation to the appropriate choice of material. In order to properly drive the reaction, the positions of the valence and the conduction bands must be appropriately placed with respect to the redox potentials of the individual species undergoing reduction at the cathode and oxidation at the anode, known as band alignment. If such band alignment does not happen naturally, or if the band position differences are very large, a potential bias can compensate for the difference in energy required to transfer electrons and holes to the respective species, however, this being a form of energy input for the same quantity of output, serves to reduce the overall efficiency of the device greatly and is often very undesirable. In the case of water splitting, the material chosen to absorb light and drive the reaction should have a valence band position which is more positive than the  $O_2/H_2O$  redox potential of 1.23V vs the natural hydrogen electrode (NHE, or also RHE for Regular Hydrogen Electrode) at pH = 0, to drive the oxidation reaction, whereas the conduction band needs to be more negative than the

redox potential of  $H^+/H_2$  which is 0V vs NHE. Of course, this is the case for an ideal system where the other components such as the electrolyte or the electrical wiring do not introduce additional resistances and losses, which is almost always the case.



Figure 1.3 Valence and conduction band edge positions relative to NHE and referenced from the vacuum level of various semiconductors in contact with an aqueous electrolyte at pH = 0. Dotted lines represented the potentials of hydrogen evolution and oxygen evolution reactions respectively [29].

These losses require the addition of more energy than the redox potential and is known as the overpotential. Of the most common semiconductors studied today, the relative band edge positions with the redox potentials of water splitting, namely the hydrogen evolution reaction (HER), and the oxygen evolution reaction (OER) are shown in Figure 1.3. In our case, we select  $TiO_2$  (n-type) as the semiconductor photoanode due to its low cost, ease of availability, low toxicity and ideally suited band gap, and further discussions in this thesis would be made in this context.

#### 1.1.3 Hydrogen evolution reaction (HER)

The process of splitting water into its constituents is a simple reaction whether achieved electrochemically, electrolytically or via chemical (or thermochemical) routes [30], is represented in equation (11) below [31-33].

$$2H_20 \rightleftharpoons 2H_2 + O_2, \ \Delta G^0 = 237.1 kJ \tag{11}$$

In the case of solar assisted water splitting, the energy required is given by the charge carriers generated from the absorption of light by the semiconductor photoanode producing a conduction band electron and a valence band hole. This process can be represented as follows [34]:

$$TiO_2 + h\nu \to e^-_{C,B_1} + h^+_{V,B_2}$$
 (12)

This overall reaction can be separated into two half-cell reactions at the working and counter electrodes, for which two mechanisms are often put forward depending on the conditions under

which the reaction is taking place. Typically, in acidic media with pH < 5, hydrogen reduction proceeds via hydronium ion reduction pathway, represented in equation (13) below.

$$2H_30^+ + 2e^- \leftrightarrows H_2 + 2H_20 \tag{13}$$

While oxygen evolution at the anode proceeds via water molecule oxidation pathway:

$$6H_20 \leftrightarrows 0_2 + 4H_30^+ + 4e^- \tag{14}$$

In the case of alkaline media, the respective half-reactions are as follows:

$$2H_2O + 2e^- \leftrightarrows H_2 + 2OH^- \tag{15}$$

$$40H^- \leftrightarrows O_2 + 2H_2O + 4e^- \tag{16}$$

In the case of neutral media (pH = 5 to 7) the hydrogen evolution reaction occurs via the hydronium ion pathway depicted in equation (13), while the oxygen evolution takes place via the hydroxide oxidation pathway depicted in equation (16). Given our interests in this study are the HER mainly performed in highly basic and neutral media; we shall restrict ourselves here forth to discussions in that context.

The reaction mechanism for HER at the photoanode in an alkaline or neutral medium is a twostep process consisting of the Volmer reaction, involving the surface adsorption of a hydrogen atom on the surface active site resulting in the release of a hydroxide ion. This is followed by either the Heyrovsky step, where the adsorbed hydrogen atom from the previous step reacts with another water molecule with the help of electrons at the electrode surface resulting in the release of a hydrogen molecule and a hydroxide ion into solution, or via the Tafel step where two adsorbed hydrogen atoms on the electrode surface combine to form a hydrogen molecule without the need for electron transfer from the electrode surface. These reactions are detailed below.

$$H_2 0 + e^- \to M - H + 0H^- (Volmer) \tag{17}$$

$$H_2O + e^- + M - H \to H_2 + OH^- (Heyrovsky)$$
<sup>(18)</sup>

$$2M - H \to 2M + H_2 (Tafel) \tag{19}$$

Where M - H represents the adsorbed hydrogen atom on a metal/semiconductor (M) surface active site. A consideration that needs to be made here is that while the Tafel step is similar in the case of both acidic and alkaline/neutral media, in the latter case, the source of the adsorbed hydrogen comes from the dissociation of water molecules in the electrolyte solution whereas in the case of acidic media, it comes from the abundance of free protons in the solution [33, 35, 36].

### 1.2 Charge Transport and Device efficiency

While the electrode reactions presented in the previous section take place at the surface, the process of light absorption, excitation and charge generation mostly happens in the semiconductor bulk. Although, with increasing depth into the thin film layer, the probability of penetration of the incident light decreases exponentially (or near exponentially), a relation known as the Beer-Lambert law described by equation (20) below [37-39].

$$I_d = I_0 e^{-\mu d} \tag{20}$$

As such, charges generated in the bulk, even if close to the surface need to travel to the surface or towards the outer electrical circuit to be able to perform useful work and participate in the redox reaction. In the case of excitonic materials, this means that the excited electron (and hole) need to be separated from the excitonic binding and transported in opposite directions since each charge type will drive either a reduction or oxidation reaction and vice-versa. Opposing this is the tendency for the excited atom or molecule to return from the higher energy excited state to the lower energy ground state by returning the electron from the conduction band to the valence band and dissipating the difference in energy in various forms, a process known as charge carrier recombination. Intuitively, it is natural to think that the probability of this recombination increases the longer the electron or hole has to wait to reach an electrode surface, an expression known as the diffusion length [40]. The average period of time the electron remains in the conduction band, able to freely move around the crystal lattice before eventually being captured by a hole through recombination, is called the electron lifetime.

It is evident that for any photoconversion device to be highly efficient, it must present with a very low rate of charge carrier recombination given that this process serves to release the energy absorbed from the incident solar radiation back to the ambient representing a net loss in light harvesting efficiency for the device. Also, the rate of carrier recombination is inversely proportional to the exciton or electron lifetime in the bulk material, allowing the charge carrier to reach the catalytic sites on the electrode surface with greater probability instead of recombining [41-44]. For the exciton to survive long enough to allow the electron and hole to be decoupled and travel independently towards their respective electrodes requires the establishment of strong electrostatic forces that can lower the binding energy of the exciton promoting charge separation. Additionally, a suitably directed electric field within the material bulk, particularly a strong reverse bias helps to attract the generated charges away from their host atoms and towards the electrode extremities preventing their recombination [45, 46]. While separation of the newly formed exciton into individual charge carriers is the primary efficiency regulating mechanism that requires

7

optimization, the separated charges while travelling in opposite directions within the semiconductor, can also encounter each other, this time as free charges, and given the electrostatic attraction between oppositely charged electrons and holes, tend to recombine. There are more interfaces where similar recombination is possible, as well as many types of recombination mechanisms involving an exchange between multiple particles, which all need to be considered.

#### **1.2.1 Recombination Pathways and Mechanisms**

Recombination of free charge carriers can occur either within the semiconductor bulk, or at surfaces and interfaces particularly at the electrode/electrolyte interface [47]. As such, with devices that contain multiple interfaces and heterojunctions, these offer more recombination sites. Recombination is a fast process and therefore represents one of the most significant barriers to scaling efficiencies of photovoltaic devices [48]. In a TiO<sub>2</sub> photoanode based PEC device intended for hydrogen generation from water splitting, the following recombination pathways have been identified:

- Radiative recombination: The direct recombination of conduction band electrons with valence band holes usually results in the emission of a photon of energy equal to the band gap. This class of recombination processes contain the direct exciton annihilation on the host atom discussed in the earlier paragraph but can also occur among free charge carriers diffusing/migrating within the electrode. Considering that the process outputs a photon of nearly equal energy (shallow defects can also recombine radiatively but eject a slightly lower energy photon), the process is usually capable of triggering a future excitation event from the ejected photon and is not always an undesirable form of recombination. An unusually high presence of radiative defect centers may cause an undesirable energy loss from transition to the defect state, but in well-formed semiconductor layers, radiative recombinations are not the most critically studied optimization process [49, 50]. Being a photon mediated process radiative recombinations are more common in direct bad gap transitions, and while these are also possible in indirect band gap transitions, they require the simultaneous emission of a phonon which is a rare event making these transitions less common [51-53]. This mechanism is shown in Figure 1.4 (a).
- Shockley-Reid-Hall (SRH) recombination: SRH recombinations are recombination events involving the transition of the conduction band electron to a trap state and are

therefore also called trap-assisted recombination. Traps are essentially localized intermediate energy states in the crystal lattice due to the presence of dopants, impurities or vacancies and interstitials. More often than not, the intermediate band state is positioned indirectly with respect to the valence and/or conduction band which implies that these transitions need the exchange of a phonon. Since phonons are a form of energy that cannot be easily and immediately converted to electrical current, the transfer of energy to these quasiparticles essentially represents a net energy loss for the system. In many semiconductors, especially oxide semiconductors such as TiO<sub>2</sub>, these recombinations dominate resulting in a poor solar-to-hydrogen (STH) conversion efficiency for the overall device [54, 55]. This is shown in Figure 1.4 (b).

- Auger Recombination: The auger recombination process involves the participation of a third electron (in the conduction band) or hole (in the valence band), which absorbs the energy of the recombination event and gets excited to a higher energy level within the same band. The excited carrier then eventually relaxes to the thermodynamic equilibrium level by transferring the excess energy to the lattice vibration as phonons. Since this process does not release photons, the energy from photoexcitation is completely lost to the lattice vibrations making this recombination pathway mostly undesirable in the context of a photovoltaic device. Figure 1.4 (c) shows the mechanism of auger recombination.
- Surface and Interface Recombination: Lastly charge carrier recombination can take place at interfaces between two materials or between the surface of a semiconductor and electrolyte. At the interfaces between materials or a solid and a liquid, there is an abrupt transition from the electronic potentials within the bulk of one material to the other given that each may exist in their individual structural and crystalline configurations. As such, the presence of dislocations and vacancy sites are common to make up for the difference in lattice parameters giving rise to a large concentration of defect and trap states. Additionally, in the case of interfaces between two phases such as a solid and a liquid, such as an electrode/electrolyte interface, there is an immediate change of order at the solid surface considering that the liquid particles are more mobile and do not represent either a long range or a time bound ordering. Thus, the presence of dangling bonds are common that can capture electrons or holes to passivate the unpaired electrons in these states [56-59]. This is shown in Figure 1.4 (d).



Figure 1.4 Mechanism of recombination pathways in semiconductors: (a) radiative, (b) Shockley-Reid-Hall (SRH), (c) auger, and (d) interfacial [60].

In addition, if a photoelectrode is structured in a layered configuration as is the case with our photoanodes, the presence of multiple recombination sites within different layers gives rise to the possibility of back-electron transfer events where the electron from the conduction band of one layer can recombine with a hole present in the valence band of a neighboring layer. Charge transfer of free charges in the semiconductor bulk or quantum dot with the oxidized ions in the electrolyte are also possible and are included in this recombination mechanism [61]. These effects become even more prominent at low applied bias resulting in a lower charge carrier mobility and also greater charge density especially at surfaces and interfaces [42, 62, 63]. As a result, passivation strategies to minimize these charge carrier recombinations are also important requiring further design complications to the electrode structure particularly for the case of quantum dot sensitized structures [64]. These different pathways for the case of QD sensitized TiO<sub>2</sub>/FTO photoanode is shown in Figure 1.5.



Figure 1.5 Back electron transfer pathways in TiO<sub>2</sub>/QD layered heterostructure photoanode. Green arrows indicate desirable electron transfer paths leading to charge separation and extraction while red arrows represent undesirable pathways (recombination). Dashed line is a defect state in the QD.

#### 1.2.2 Interface Energetics (Band Bending)

When semiconductors form interfaces with other materials or liquids, the distinct distribution of bands in them permits the exchange of charge carriers with the energy levels of the contact substance in search of a more optimized energy state of the whole system, which is achieved by equalizing the fermi level of the semiconductor to the contact material/substance. This effect is localized near the interface and therefore causes the energy levels to progressively change with distance from the interface until it saturates very far away from the interface into the semiconductor bulk, a phenomenon known as 'band-bending' due to the characteristic shape of the resulting bands of the semiconductor material. [65, 66].

As such, in PEC cells, as soon as the photoelectrode is dipped into the electrolyte, the flow of charge carriers across the interface begins to occur from anywhere between nanoseconds to microseconds after contact (depending on the properties of the two substances in contact), and the fermi levels begin to equalize. Once this condition is achieved, the system reaches a steady state. As a matter of fact, a similar realignment of bands happens during sensitization with QDs as soon as the heterojunction forms. In the case of an n-type photoanode, the fermi level of the semiconductor lies below the redox potential of the electrolyte owing to the excess of negatively charged carriers on the semiconductor surface (electrons), as shown in Figure 1.6. This causes an immediate flow of electrons from the surface of the semiconductor layer into the oxidized species in the electrolyte due to the difference in thermodynamic potential between the surfaces.



Figure 1.6 Band bending in an n-type photoanode (TiO<sub>2</sub> nanotube arrays in a 0.5M KOH electrolyte) (a) before contact, (b) steady-state in dark, and (c) steady-state with illumination above band-gap energy in open circuit condition [67].

As such, the majority charge carriers are slowly 'depleted' from the surface of the semiconductor close to the interface with the electrolyte causing the fermi level at this interface to move upwards with the depletion of electrons in this region. As a result, this 'depletion region' at the surface acquires a net positive charge and with time becomes thicker until the fermi level of the semiconductor at the interface becomes equal to the redox potential of the electrolyte. This thin layer of positively charged semiconductor is called the 'Space Charge Layer' and is often abbreviated as the SCL [68]. In dark conditions, the positive charge of the SCL directs the photogenerated charges oppositely to the desired directions due to the charge present. In essence, in a photoanode configuration, one desires the electrons to move deeper into the bulk to be captured by the conductive back contact for transport towards the counter electrode where the reduction reaction takes place, while the holes would ideally diffuse towards the bulk to participate in water oxidation at the photoanode. However, the SCL's positive charge prevents this from happening. One, therefore, needs additional drivers to be applied to the electrode to overcome this barrier generated by the SCL.

One such driver is generated through illumination, which acts to photogenerate electron-hole pairs that can then be separated into individual charge carrier species. However, another very important function this performs is to populate the electrode bulk with a large concentration of charges essentially with an opposite concentration gradient to the one created by the SCL. This is again because of the Beer-Lambert law shown in equation (20). The exponential penetration of the incident light causes the maximum number of photoelectrons to be generated close to the surface near the SCL and as we traverse deeper into the bulk, the light intensity is greatly attenuated owing to absorption from the preceding layers of material, therefore creating far fewer charges. As a result, the concentration gradient of electrons (majority carriers) is highly oriented towards the material bulk even overcoming the drift force from the positively charged SCL to drive the electrons toward the bulk [69, 70]. At the same time, the photoholes are driven towards the surface driven by the potential gradient driven by the upward band bending at the surface, considering holes which are represented as the absence of electrons tend to occupy traditionally higher energy states [71, 72]. This potential gradient, in addition to the diffusion force, also assists the electrons in moving inward towards the bulk.

Secondly, a potential bias can be applied to the electrode carriers to facilitate the extraction of charge carriers further and prevent recombination events, resulting in an increase in the overall efficiency of the device. However, care must be taken since the application of a potential bias itself represents an addition of energy input into the system, which in itself reduces the efficiency

of the process. The resulting increase in photocurrent must compensate for the additional input of charge if the use of additional input bias needs to be justified. A reverse bias potential applied to the photoanode can work to attract the majority charge carriers towards the conductive back contact while at the same time increasing the thickness of the space charge layer preventing majority charge carriers from tunnelling through, thereby enhancing what is known as 'charge carrier selectivity' at the electrolyte interface. This effect greatly reduces the recombination in the electrode since charge carriers separate efficiently and move in different directions more rapidly giving very little time for recombination events to take place. Additionally, a reverse (also known as anodic) bias to an n-type photoanode causes the fermi level of the electrode material to drop lower making the band bending sharper increasing the potential gradient in the SCL [73-75]. All of these effects can drive charge separation and transport which acts to greatly increase the solar conversion efficiency of the device.

## 1.3 Light Harvesting Efficiency

Another important process that defines the efficiency of a solar-based hydrogen generation electrode is the proportion of incident light absorbed by the materials on the photoelectrode that are converted into excitons, a parameter known as light-harvesting efficiency (LHE). In the case of PEC systems, electrode materials require to have band gaps to produce sufficiently energetic charge carriers capable of driving chemical reactions.



Figure 1.7 Solar Spectrum standards. AM 0 represents the spectrum in space where the radiation has not passed through any atmosphere, while AM 1.5 G represents the global average standard spectrum received on the earth's surface. The 1.5 D standard is the spectrum from direct sunlight neglecting the losses from diffuse scattering [76].

However, the requirement for greater electron (or hole) energies usually means the material can only absorb radiation from the UV region and farther, of the solar spectrum. This results in a great loss of efficiency given that these parts of the solar spectrum usually make up less than 5% of the incident radiation, and therefore we are already discarding nearly 95% of the precious free energy resource we require before even such considerations as internal efficiencies related to charge separation and transport [77].

Figure 1.7 shows the AM 1.5 G standard solar spectrum used to characterize solar photovoltaic performance and allow for comparisons between different configurations. It is also closer to the actual solar spectrum received on the earth's surface, making the transition from lab to practical model simpler. From this figure, it is clear that most of the radiation received is within the 400-1000 nm range, with a large majority lying between 400 nm to 700 nm, which represents the visible range of the electromagnetic spectrum, accounting for 45-47% [78, 79]. However, in terms of catalytic activity, at least for the splitting of water into hydrogen, the photostability in acidic and alkaline aqueous environments alike, as well as the ease and abundance of procurement of  $TiO_2$  makes it the most lucrative prospect even today. But, having a large band gap of ~3.2 eV means that it's absorbance is limited to the UV range with an absorption band edge beginning at about 387 nm for the photocatalytically active anatase phase [80].

Strategies to improve the light-harvesting efficiency of anatase-TiO<sub>2</sub>-based photoelectrode assemblies focus largely on two strategies, chemical and morphological structure modifications [81-83], and sensitization with visible light-absorbing materials such as quantum dots and dyesensitization [84-86]. Of these, the sensitization methods are most promising given their ease of scaling since they use well-known wet chemical and electrodeposition techniques. Quantum dots are a greatly studied system since their optical and electronic properties can be finely tuned and controlled [87, 88]. SILAR or Successive lonic Layer Adsorption and Reaction, is a simple technique offering high loading and coverage as well as cost effectiveness [89]. Cd-based semiconductor nanocrystals were one of the first reported quantum dot systems to be successfully deposited on TiO<sub>2</sub> photoanodes as visible light photosensitizers and are still in use owing to the high conversion efficiencies that they are still able to achieve [90, 91]. Therefore, as a standard to test the solar to hydrogen conversion performance of different TiO<sub>2</sub>-based PEC cell configurations, sensitization with CdS and CdSe/CdS using the SILAR technique is a simple and consistent method to test the effectiveness of the enhanced light harvesting performance of these photosensitizers.

## 1.4 Interfacial Charge Transport

Another important aspect of efficient PEC device function is the transfer of photogenerated charges to the redox species in the electrolyte where the actual chemical reaction occurs. This process happens at the interface between the electrode and the electrolyte within and close to what is known as the Helmholtz layer of the Electrochemical Double Layer (EDL). Before investigating the aspects of the material system or the electrolyte solution that optimize this EDL for fast and efficient charge transfer, we should start with a brief introduction to the EDL.

## 1.4.1 Electrochemical Double Layer (EDL) / Helmholtz Layer

At the interface of the semiconductor electrode and the electrolyte, interactions of the ions in solution with the electrically charged electrode gives rise to a double layered potential structure that acts to screen the electric field from the electrode effectively slowing down charge transfer reactions at the interface. The 'double layer' as it is known, comprises of two distinct regions very close to the electrode surface, the Helmholtz layer, which itself is divided into the inner (IHP) and the outer Helmholtz planes (OHP), and the diffuse layer. The structure of this system as well as the order of these layers are illustrated in Figure 1.8.



Figure 1.8 Structure of the EDL for (a) photocathode, and (b) photoanode showing the inner and outer Helmholtz planes and the diffuse layer [92].

The accumulation of free charges on the electrode surface attracts non-solvated ions in the electrolyte that are oppositely charged to the electrode surface, known as 'counterions', which then attach electrostatically to the electrode surface forming a thin region of adsorbed ions of almost single ionic layer thickness known as the inner Helmholtz plane (IHP) [93]. Whilst, this is the usual definition of this layer, often in cases such as with the use of aqueous or polar solvent electrolytes, polarized solvent molecules, partially solvated ions as well as chemisorbates related to the redox species undergoing reactions are also included within this layer while defining the IHP as the set of molecules/ions directly attached chemically or electrostatically to the electrode surface [94, 95]. Beyond this region, ions that interact weakly with the electric field of the electrode, namely fully solvated ions and sometimes polarized solvent molecules are found bound purely electrostatically in a region very close to the IHP. The loosely bound solvated ions are generally more mobile than the ions adsorbed within the IHP and are able to respond quickly to any changes in the electric field of the electrode [96, 97]. Beyond these layers of bound ions lies an even broader region of ionic species (fully and partially solvated ions), that though are not bound by the electrodes electric field, are still sufficiently influenced by the drift generated so that their motion and distribution are a combination of very weak electrostatic and thermal distributions. Here, the ion concentration gradually decreases from the high concentrations at the edge of the OHP exponentially with distance until it reaches the uniform bulk concentration. This region is known as the diffuse layer and essentially represents the outer edges of the electrode field influence over the species in the electrolyte. After this region, we enter the electrolyte bulk where ionic concentrations are constant, and motion is regulated by diffusion and very mildly through electrostatic migration considering the influence of the electrode's electric field is now considerably screened by the double layer. The thickness of the diffuse layer is often characterized by the Debye length which delineates the boundary between the EDL and the bulk electrolyte [98, 99].

The variation of electrostatic potential with distance from the electrode is shown in Figure 1.9 (a) where we can observe a nearly linear decay in potential with distance within the inner and outer Helmholtz planes whereas the potential decays exponentially with distance inside the diffuse layer up until the bulk layer is reached. After this point, we can observe from Figure 1.9 (b), that the potential remains almost constant till we reach the diffuse layer on the counter electrode, where the potential once again follows an exponential decay and then a linear drop inside the Helmholtz layers.

While the EDL is an important physical system in electrochemical devices, its presence can be both positive and negative depending on the application. In the case of PEC, however, the EDL presents both opportunities and challenges which must often be balanced with each other in order to derive optimum efficiency from the PEC cell. Most notably, the adsorption of ions on the electrode surface directly blocks potential active redox sites from being accessed by molecules that undergo the chemical reaction at the electrode surface either directly occupying the active site or through steric constriction of sites around as in the case of larger adsorbate molecules like long chain ligands [100-103]. Additionally, such adsorbed surface ions may be chemically passive, simply obstructing the redox species from accessing the electrode surface or chemically active, by participating in charge transfer at the surface and chemically modifying the surface chemistry of the electrode leading to degradation, a process known as 'surface poisoning' [19].



Figure 1.9 Potential drop across the EDL showing, (a) the profile close to the electrode clearly displaying the different regions of the EDL [1], and (b) the profile over the entire cell from the anode to the cathode surface displaying a near constant potential gradient in the electrolyte bulk [110].

Such degradation effects on the electrode can affect both the performance characteristics as well as the long-term stability [104-106]. Moreover, even though the counterion charge on the inner Helmholtz layer acts to attract minority carriers to the surface promoting efficient charge separation, the same polarization sense can trap charges electrostatically on the surface, preventing their transfer to reactive species, or even promoting trapping on surface sites all leading to eventual nonradiative recombination losses [70, 107, 108].

Next, we consider the potential barrier generated by the accumulation of charge in the EDL which acts to repel charges and ionic species, especially the redox active species from reaching the electrode surface easily. While the electric field which creates the EDL is also responsible for creating a rich ionic environment close to the electrode, which also includes the redox active entities mixed within it, the same environment can prevent fresh species from replenishing the inner Helmholtz layer due the additional potential barrier it needs to overcome to travel to the electrode. This is seen in the apparent additional activation energies in interfaces having a high concentration of redox inactive ions like salts in the electrolyte which lower the concentration of redox active ions, both in the bulk solution as well as in the EDL layer [109]. There is therefore both opportunity and obstacle with the properties of the EDL, and careful tailoring of material properties as well as design of the cell components are required to maximize gain and minimize loss from this region.

#### 1.4.2 Hole Scavenging

During the operation of the PEC cell using an n-type photoanode, electrons move towards the bulk and are consumed by the ohmic back contact, while holes move towards the electrode surface. At the surface, holes accumulate while waiting for the reductant species to be adsorbed on the redox active sites which can be characterized by slow moving ions in a liquid medium in addition to overcoming the barriers imposed by the EDL layer as just discussed. In overall water splitting and PEC hydrogen generation devices, the water oxidation reaction at the photoanode is especially sluggish since it involves the transfer of multiple electrons for the generation of just one oxygen molecule (equations (14) and (16)) which would need the accumulation of multiple charges close to a single activation site. However, the concentration of charges often comes with a higher rate of recombination, and it is more probable that as holes accumulate, they recombine with free electrons before they can participate in redox reactions. These recombinations, however, also adversely affect the free electron density which is directly related to the hydrogen generation capacity and efficiency of the system. Hence, when studying only the solar to hydrogen capacity of the system without regard to the reaction taking place at the photoanode site, it is often beneficial to include species within the electrolyte more suited to accepting free hole charges on the electrode surface sites. This of course, also has the added benefit of preventing surface poisoning through hole mediated chemical reactions at surface sites [111, 112]. As these agents 'scavenge' the holes accumulating in the electrode surface, they are irreversibly oxidized,

sometimes to useful by-products (such as methanol to formaldehyde). They are hence known as hole scavengers [113, 114]. Such reactions are particularly useful in the case of hydrogen generation devices where the production of oxygen at the anode is not required.



Figure 1.10 Effect of sulfite hole scavenger on PEC performance: (a) current-voltage curve of CuWO<sub>4</sub> vs CuWO<sub>4</sub>/Sn<sub>2</sub>O(NCN) heterojunction for sulfite hole scavenger (dashed line in inset) and water oxidation (solid line) [5], and (b) long-term stability from current-time characteristics of BiVO<sub>4</sub> photoanodes. [115].

One of the often-used hole scavengers particularly for studying solar driven hydrogen production is the sulfite anion  $(SO_3^{2-})$  which effectively serves to decrease the kinetic barrier for hole injection from electrode surface to electrolyte greatly increasing the rate of hole transfer to the hole scavengers preventing hole accumulation on the anode surface. The sulfite anion in conjunction with a sulfide electrolyte is very effective in increasing photoconversion efficiency as well as 'cleansing' the electrode off corrosive free charges prolonging electrode lifetime [116, 117]. Figure 1.10 shows both these effects on the PEC performance for the sulfite anion hole scavenger against water oxidation for some simple photoanode systems.

### 1.5 Field-assisted PEC hydrogen generation

A relatively new approach to enhancing the performance of photoelectrodes towards solar-driven PEC hydrogen generation is the application of external fields that aid in the efficient separation and transport of charge carriers towards their respective electrode surface post photoexcitation. Several external field inputs have been tested in recent years, including piezoelectric, ultrasonic, mechanical (stress and strain), plasmonic, thermal and magnetic. A very brief overview of each is presented along with their respective mechanism of operation.

#### 1.5.1 Piezoelectric field

The introduction of a piezoelectric material such as ZnO (wurtzite), Barium Titanate (BaTiO<sub>3</sub>), Bismuth Ferrite (BiFeO<sub>3</sub>), Lithium Niobate (LiNbO<sub>3</sub>) or PVDF (Poly-vinylidene Fluoride) as one of
the light-absorbing layers can allow the use of an external mechanical force, either constant or oscillating, to drive an additional piezoelectric potential to the electrode assembly. This added potential acts as an additional bias, which, if correctly oriented, can facilitate charge separation and reduce recombination.



Figure 1.11 Energy band modulation in a piezoelectric material: (a) and (c) are initial states, (b) under compressive stress, (d) under tensile stress ( $E_g$  is the band gap and  $\phi_P$  is the piezopotential); (e) and (f) show band bending at an n-type and p-type piezoelectric material respectively [155].

It can also modulate the band structure at the heterojunctions to improve light absorption efficiency. At surfaces, the additional potential can increase the surface charge density attracting more redox active species towards the electrode surface and thus increasing the rate of the reaction [156-158]. Figure 1.11 illustrates this mechanism in detail.

### 1.5.2 Thermal field

Thermal energy can accelerate the kinetics related to several processes within the photoelectrode to enhance the solar conversion efficiency of the device. Notably, the effect on increased mass transfer kinetics allows for the quick consumption of photogenerated charges allowing for the driving forces that help separate newly generated exciton pairs deep within the bulk. Additionally, the thermodynamics of the chemical reaction are also significantly altered given that the energy requirements can be offset from energy absorbed from thermalization with the established higher energy field from additional thermal energy input to the system, the so-called 'thermal field'. The energy distribution statistics of the particles is also skewed towards higher energies meaning that a greater probability of redox reactants can now cross the activation barrier towards conversion to products [159, 160]. Finally, charges trapped in defect and surface trap states can be released easily resulting in an overall higher incident light conversion efficiency [161, 162].



Figure 1.12 An illustrative outlook on how thermally assisted solar driven photoelectrochemical hydrogen production can enhance conversion efficiency [163].

In addition, thermally assisted PEC processes can also create unique opportunities in material selection, whereby thermally activated materials can be included in the photoelectrode structure to more effectively utilize the thermal fields. The coupling of thermoelectric or triboelectric generators with the ETL or light absorption layer can lower overpotentials via the generation of an additional bias voltage from the thermal input. Materials that show photothermal effect, such as Co<sub>3</sub>O<sub>4</sub>, MXenes as well as plasmonic nanoparticles can generate localized thermal fields of high intensity close to the photogeneration centers or reactive sites to magnify their performance augmenting characteristics to provide high energy conversion efficiencies [163].

However, at the same time, there are also drawbacks associated with the use of such thermal fields, most notably the increased degradation effects on the photoelectrodes given that effects such as surface poisoning are also boosted kinetically with the thermodynamic barrier being lowered. Increased costs associated with cooling systems designed to prevent overheating is another factor that needs careful consideration. Electrically, increased temperatures can lead to an increased resistance in circuit components, even in cell components and layers which can offset some of the beneficial effects of the thermally assisted enhancement. Therefore, while research in thermally assisted PEC systems is ongoing steadily, there are many factors to be optimized before commercial viability can be achieved.

### 1.5.3 Electric field

Considering that PEC operation already requires the application of an electric bias generating an internal electric field in the photoelectrode, the application of external electric fields to the light absorption and ETL layer through the use of polarization effects from the external bias field can offer promising opportunities in electric field assisted PEC hydrogen generation. The particular material family of interest here are ferroelectrics which are materials that can switch polarization according to the inducing electric bias. This essentially generates an additional electrical field from the polarization of the ferroelectric inside the photoelectrode essentially boosting the bias. As a result, charge separation is faster and more efficient resulting in smaller recombination losses within the bulk.



Figure 1.13 Mechanism of ferroelectricity in barium titanate on top showing the initial polarization state, polarization under an electric field and remnant polarization after the removal of polarizing field [3]. The bottom section shows polarization curves for ( $K_{0.5}Na_{0.5}$ )(Nb<sub>0.7</sub>Ta<sub>0.3</sub>)O<sub>3</sub> (KNNT) with 0 and 2 wt% ZnO [164].

At the same time, the surface adsorption presents with a domain-dependent pattern which results in selective adsorption of the reactant species over non-redox ions at active sites, and also with their timely desorption. Of course, the additional potential from the electric field can reduce the activation energy required to overcome the barrier potential of the reaction. There is also an increased surface charge density that can generate a greater concentration gradient of redox ions near the electrode surface for easy surface attachment allowing quick consumption of travelling charges before they can be captured by trap sites or recombination events [165, 166]. Figure 1.13 shows the alignment of polar domains in the crystal of a ferroelectric material as well as the hysteresis curve for such a material containing the saturation polarization and remnant polarization points.

#### 1.5.4 Electromagnetically Assisted

Materials that can absorb electromagnetic radiation and generate secondary physical phenomena (other than exciton generation) which can be used to restrict charge recombination, speed up mass and charge transfer rates or even influence reaction kinetics are very useful integrations for higher utilization of incident solar radiation. Here the input energy is more efficiently used and the output generated is greater due to the synergistic coupling of the secondary effect with the primary objective of generating charge carriers for redox reactions. Multiple effects can be exploited where light is the input source including photothermal, hot carrier generation, as well as plasmonic near and far field effects. This section primarily refers to electromagnetic fields that are setup by parts of the solar electromagnetic spectrum that are not directly absorbed by the active semiconductor layer to generate redox useful charge carriers, and as such are sometimes referred to as 'light-fields' to differentiate them from the radiation that is absorbed.

Photothermal materials can enhance PEC performance by absorbing radiation in the near infrared (NIR), and visible spectrum to generate localized thermal fields which, as from the previous section, can assist in charge separation, detrapping, lowering the activation barrier as well as improving charge transport of charges to the electrode contact and surface. If close to the surface-active sites, the so called 'nano heat source' from these photothermal centers can influence catalytic activity via reaction rate kinetics. Several materials, especially low band gap oxides like Ti<sub>2</sub>O<sub>3</sub>, rGO (reduced graphene oxide) as well as other carbon-based materials like nanotubes and transition metal dichalcogenides have been shown to contain this property. Another class of materials that can be used for this effect are plasmonic materials like metal nanoparticles (Au, Ag etc.) [167, 168].

IR (infrared) electromagnetic input can excite 'hot electrons' which are essentially conduction electrons that are excited to band states above the conduction band minimum in semiconductors or higher than the fermi level in metallic nanocrystals, which represent electron distributions above the expected thermal distribution [169, 170]. Hot electrons have higher energies than conduction electrons and are generally short-lived decaying into the thermal equilibrium state through phonon assisted intra-band relaxation. The equivalent hole carrier is known as hot holes and are generally found in band states below the valence band maximum. Together they are referred to as 'hot carriers'. Hot carriers having energies higher than the lattice thermal equilibrium, can either transfer this energy to the lattice as thermal energy resulting in thermally assisted enhancement effects taking place as already discussed, or in the case of heterojunctions with other semiconductor materials, inject into their conduction band if the materials are carefully chosen to

have the correct amount of energy. This 'auxiliary' light field excitation takes place in the case of low bandgap semiconductors which can absorb high energy photons to excite the electron above the conduction band minimum [171, 172]. These processes are shown in Figure 1.14.



Figure 1.14 Process of excitation and decay of hot carriers. (a) hot electron generation and injection into semiconductor conduction band [173], (b) decay pathways for hot electrons [174], (c) hot carrier population against thermal distribution of charge carriers at every stage of excitation to decay [175].

Another class of materials that can take advantage of light fields to enhance overall light absorption and generate secondary processes within a photoelectrode are plasmonic materials which can generate near and far field effects from surface plasmon resonance (SPR) phenomena. While the SPR property is quite widely known for the generation of hot electrons very effectively, other interesting and useful effects such as near field electric field enhancement and far field scattering can also enhance PEC charge collection efficiency. Firstly, plasmon resonance increases the light absorption at the resonance frequency. Further the generation and collection of hot carriers can induce thermal effects as described above, especially in the case of nanoparticles where the localized SPR effect, also known as LSPR, can generate an intense localized thermal field [176, 177]. The far-field scattering of light is another interesting property of

plasmonic materials. Essentially, incident light is strongly absorbed at the resonance wavelength which, if the material possesses a sufficiently high albedo can be scattered back into the active layer allowing the absorbers to absorb the scattered light resulting in a high light conversion efficiency [178].



Figure 1.15 Solar driven plasmon-assisted photocatalysis mechanisms [179].

Alternately, plasmonic materials can, by virtue of the strong polarization of their free electron cloud intensely concentrate incident electromagnetic energy into a nanoscale region resulting in a several orders of magnitude enhancement in the electromagnetic field locally. Such high intensity electric fields close to light absorption centers can greatly influence charge generation and recombination characteristics whereby they may greatly prolong exciton lifetimes long enough to efficiently separate them into individual charge carriers. Alternatively, the intense local electric fields may also provide the additional bias required to even separate the electrons and holes completely discouraging their recombination by modifying the local energetics [178, 180]. In case of strong dipole-dipole interactions with the semiconductor material, the plasmonic material can also directly generate electron-hole pairs in the semiconductor by directly transferring the plasmon energy to the semiconductor. This process is known as Plasmon-Induced Resonance Energy Transfer (PIRET) [181].

While the effects described above involve plasmonic oscillations in individual nanoparticles, the oscillations across the surface can couple resulting in collective oscillations of the surface charges

with the incident radiation, a phenomenon known as surface plasmon-polariton (SPP). The coupling with the incident radiation enhances the light absorption coefficient at this wavelength. The added advantage is that the interface can in fact be tuned to couple with light at a desired wavelength allowing high selectivity for the application. Additionally, the electric field across the interface is greatly intensified in a similar manner to the nanoparticle case, which provides both an additional bias to the photoelectrode as well as generate hot carriers throughout the interface [182].

## 1.5.5 Magnetic fields

With the fields we have seen till now, the inclusion of specific materials in the photoelectrode material matrix to convert the energy in the particular field in consideration into electrical or thermal energy, which can subsequently influence the electrochemical reaction kinetics or thermodynamics, is required to effectively convert the energy from the applied field into redox products. However, with the application of magnetic fields, the influence is directly over the charge carriers through coupling with their spin states which could take advantage of quantum processes such as spin forbidden transitions to reduce recombination rates, an observation also made by Mott as early as 1978 [183]. However, as this thesis is based mainly on the idea of magnetic field assisted PEC enhancement, the next section will consider this technique in fine detail and present the current state of the art in this emergent field.

# 1.6 Magnetic Field Assisted PEC

The use of a magnetic field to assist photocatalytic processes has a long history, with various magnetic field-generated effects being exploited for driving efficiency in charge transfer-mediated chemical processes, including electrochemistry. Since the discovery of the Honda-Fujishima effect in 1972, while the speed of research study in photocatalytic water electrolysis has progressed rapidly, efforts to use the magnetic properties of the materials involved have also been made periodically. Figure 1.16 (b) succinctly illustrates this. The effect of a magnetic field on the PEC hydrogen evolution process, usually can act through multiple process pathways. Reported in literature, are magnetothermal effects, magnetohydrodynamic effects, Lorentz force mediated mass transfer effects as well as influence on charge carrier and ionic spin state regulation processes (Figure 1.16).



Figure 1.16 Timeline of development of magnetic field assisted photocatalysis systems [118].

Among material types, ferromagnetic and paramagnetic materials or materials functionalized with ferro- and paramagnetic dopants are common photoelectrode choices for performing magnetic field assisted studies, occasionally magnetic effects with diamagnetic materials whence dopants and or vacancy defect induced magnetisms might arise in these materials are also discussed [119]. In some studies ferrimagnetism, antiferromagnetism and superparamagnetic materials are also exploited [120]. We present an overview of the current state of research in magnetic field assisted PEC systems detailing the mechanisms proposed and the types of materials studied.

## 1.6.1 Lorentz force

Under the application of a magnetic field, charged particles often describe circular trajectories, and in the case of motion under a pre-existing electric field, the trajectories become helical. In the case of oppositely charged particles, such as electrons and holes, the Lorentz force drives them in opposite circular directions (clockwise or counterclockwise) resulting in an immediate separation of the charges which under the influence of the electric field also will be pushed in opposite linear directions. As a result, the carrier recombination probability is greatly reduced with the addition of a magnetic field in conjunction with an electric field from the bias potential on the electrode [121, 122]. This is clearly illustrated in Figure 1.17.



Figure 1.17 Difference between electron and hole transfer characteristics in a heterojunction without a magnetic field and with a magnetic field, as well as the influence of Lorentz force on electron and hole [123].

### **1.6.2 Magnetothermal effect**

The effect of a time varying magnetic field on a strongly paramagnetic or ferromagnetic nanoparticles is the induction of oscillatory motion in them resulting in magnetic relaxation whereby the oscillating particles transfer their oscillations onto the surrounding particles due to mechanical interactions at their interface causing localized heating called 'magnetic hyperthermia'. Alternatively, time varying magnetic fields can also induce eddy currents in the material bulk which can also cause localized thermalization. Subsequently, the thermal field can help catalyze the redox reactions through influencing the recombination, mass transport and activation barrier kinetics [124, 125].



Figure 1.18 (a) magnetic heating setup using an alternating magnetic field along with the mechanism of magnetothermal reaction enhancement at nanoparticle surface [4], (b) localized heating at catalyst surface as against global solution heating with conventional heating methods [126].

The advantage of this technique is that the heating is generated locally at the catalyst surface which means thermal energy is not wasted in heating the components that do not present with enhanced performance in a thermal field such as the electrolyte bulk, which would otherwise also be heated when using a conventional heating method (Figure 1.18 (b)) [127].

# 1.6.3 Magnetohydrodynamic effect

The ions in the electrolyte of a PEC cell are charged fluid particles whose movement constitute a current. In the same manner as the Lorentz force mechanism, this motion when introduced to a magnetic field can generate a 'flow' within the fluid whose interactions with neighbouring solvent particles can cause a vortex motion inside the electrolyte which is especially significant close to the electrode surface, where it can help in removing bubbles of gas generated from the redox reactions which usually remain adsorbed on the surface for some time blocking active sites. In the presence of this flow which is usually perpendicular to the ionic motion and hence sweeps across the electrode surface, the force generated acts in a shearing direction to the attached bubble on the surface site. The resulting increase in convection and shear force allows bubbles to detach from the surface at smaller sizes which would otherwise require increased buoyancy, surface tension and/or gravitational force to separate the bubble, all of which scale with size [121, 127-129]. This effect is clearly shown in the electrode surface images in Figure 1.19.



Figure 1.19 Difference in hydrogen bubble size without a magnetic field (a), and in the presence of a 70mT magnetic field (b) showing the effect of magnetohydrodynamic effect [130].

## 1.6.4 Negative magnetoresistance

Special ferromagnetic materials that have the property of generating a spin polarized current in the presence of a magnetic field show a marked decrease in resistance with the increase in magnetic field intensity. This property is due to the ability of spin polarized electrons to tunnel

through grain boundaries more easily where earlier these interfaces would cause electron scattering resulting in energy loss, an event represented by electrical resistance of the material. This property is called negative magnetoresistance, and the presence of this property allows photogenerated electrons to quickly tunnel through the bulk material matrix and reach the surface



Figure 1.20 Mechanism of magnetic field assisted charge separation in negative magnetoresistance material mediated photoelectrode [133].

achieving a greater percentage of charge separation assisting in increased PEC performance [118, 122, 131, 132]. The detailed mechanism for the case of Bi vacancy rich  $Bi_2S_3$  is shown in Figure 1.20. Here, the Lorentz force effect is said to play a synergistic role along with the decrease in charge transfer resistance with the increase in magnetic field (as already described in section 1.6.1).

## 1.6.5 Spin mediated effects

The simplest of mechanisms and perhaps the earliest proposed for the enhancement effects in the efficiency of solar driven water electrolysis, is the coupling of charge carrier spins to the external magnetic field. The spin of an electron (or alternately, a hole) is an internal magnetic moment which is a quantum phenomenon. The electron, a fermion, possesses a spin quantum number value of one-half which implies that its spin state can be either +1/2, or -1/2 referred to as spin 'up' and 'down' respectively. This being a magnetic moment, it follows the laws of a magnetic dipole placed in an external magnetic field wherein the dipole reorients itself to align its dipole moment parallel to the external magnetic field. In a quantum system, considering that the quantum particle can exist only in one of the two spin states described above, implies that the

spins could align either parallel or antiparallel to the external field representing the spin up and down states respectively.

The alignment of spins in the direction parallel to the external magnetic field within the materials in the photoelectrode results in a state known as spin polarization. In case of spin polarization in the bulk, the degree of polarization is defined as the fraction of total electron population in either of the two possible spin states. A large percentage of electrons in any one spin state then represents a high degree of polarization for that state [134, 135]. Interestingly, the application of an external magnetic field isn't always required, and internally generated magnetic interactions within materials, such as spin-orbit coupling and photoinduced exchange field interactions, can also cause this state to come about [136]. An illustration of how this looks in an energy band diagram is shown in Figure 1.21. The presence of two types of electronic configurations when unpaired electrons are involved, as is the case with optically excited species, viz. the singlet with both electrons having opposite spins (or antiparallel), and the triplet where the two unpaired electrons have parallel or same spins.



Figure 1.21 Mechanism of spin polarization in Mn-doped CsPbBr<sub>3</sub> [137].

Usually, in semiconductors with stable configurations, the ground state is a fully filled molecular orbital containing two electrons of opposite spins as mandated by Pauli's exclusion principle. As such, on photoexcitation, the two electrons, one in the valence and the other in the conduction band, are in the singlet configuration, considering photoexcitation is a spin-conserving process. The singlet configuration is also well suited for the recombination process by virtue of the same quantum mechanical rules and spin selectivity requirements that govern photoexcitation [138]. On the other hand, the triplet configuration does not allow the easy recombination of the excited electron, given that radiative recombination from the triplet state would result in two electrons of the same spin occupying the valence state. As a result, triplet to singlet ground state

recombination are far less frequent and mediated by highly complex mechanisms involving spinorbit coupling, making the triplet state largely long-lived [139, 140]. These transitions are therefore referred to as 'spin-forbidden' [141-144].





However, the process of spin polarization, especially in an external magnetic field, can promote processes that internally transition an electron within electronic states that do not conserve spin-multiplicity, the so-called intersystem crossing (ISC) transitions (Figure 1.22). This is in contrast to the spin-conserving singlet to singlet transitions (states denoted by S), which are termed internal conversions (IC). ISC transitions take the excited charge carrier to a triplet state, usually designated with a T, from where relaxation back to the ground singlet state (S0) once again requires a change of spin multiplicity, which cannot be achieved radiatively. As such, from Figure 1.22, we can see that these transitions are on the order of microseconds as opposed to the nanosecond fluorescence transitions allowing sufficient time for the electrode to separate and extract the charge carrier successfully. In the case of magnetic field to directly influence the spin state of the photoexcited charge carriers and encourage ISC transitions to the triplet state [146-148]. The result is a greatly reduced rate of recombination at both the bulk and surface and, eventually an increased solar conversion efficiency [131, 132, 149, 150].

### 1.6.6 Reports of Magnetic field enhanced PEC

Several materials have been reported in literature that have shown the magnetic properties detailed in the sections above to synergistically enhance PEC performance in generating several

solar fuels including hydrogen from water. Here we briefly introduce each of these material systems. The Lorentz force effect has been seen in TiO<sub>2</sub> nanobelts,  $Mn_2O_3/g-C_3N_4$ , Fe<sub>2</sub>O<sub>3</sub>@ZnO,  $Mn_3O_4/\gamma$ -MnOOH and Ni<sub>x</sub>Mn<sub>(0.5-x)</sub>O hierarchical catalyst. Iron based materials have been extensively tested to show magnetohydrodynamic bubble removal effect, while  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/reduced graphene oxide (rGO) heterojunction shows a remarkable negative magnetoresistance driven photocatalytic enhancement. However, for the case of spin polarization enhancement, articles on Mn-CsPbBr<sub>3</sub> nanoplatelets, Co-doped ZnO nanowires, oxygen vacancy rich BaTiO<sub>3</sub>, Ti-vacancy rich TiO<sub>2</sub> as well as ferromagnetically enriched ZnFe<sub>2</sub>O<sub>4</sub> have been reported [118, 121, 122, 124, 127, 129, 151-154].

### 1.7 From lab to market

While the progress reported in magnetic field-assisted PEC fuel conversion of solar radiation is impressive, and worthy of praise, the worldwide problems that this research is expected to solve, especially those related to renewable energy and climate remediation, require that these technologies are effective and swiftly brought into a form by which they can be widely adopted across a large scale on the planet. In order to do this, the foremost requirement of a commercial-scale technology is cost-effectiveness and a lucrative return on investment, at the very least equal to those being offered by the prevalent technology of the time.

In the case of magnetic field-assisted solar technologies, while there might be a temptation to simply install permanent magnets within the solar panel's racking and mounting assembly, there are two probable problems that could arise with this solution: the first being the fact that good quality permanent magnets are an expensive component, especially at scale, and the second being the ability to interpret the increased power output from the solar cell as a true enhancement in efficiency particularly in monetary terms given that we are adding an additional input source of magnetic energy into the system. As such, a prudent alternative would be to utilize instead sources of magnetic energy which are present naturally by virtue of either the environment or any human-influenced economic activity, of which magnetism is an unused by-product. As a part of this study, solutions integrating with electrical power transmission and distribution infrastructure are developed. This section, therefore, briefly analyzes the merit behind selecting this industry to synergize with for a solution.

In addition, it is worthy of note that although this thesis is involved with investigating the phenomenon of magnetic field assisted PEC hydrogen generation, similar investigations in photovoltaics (PV) and solar to electrical conversion technologies have also been reported [184-

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187]. As such, it was considered important to develop designs which could take the 'idea' behind utilizing unused magnetic fields around electrical transmission and distribution lines to boost solar conversion efficiency, by designing solar PVs as a first step, and eventually integrating other solar technologies like PEC fuel generation as a future scope given the additional complexities associated with such systems.

While solar energy is one of the fastest growing renewable energy sources being adopted worldwide to accelerate the clean energy transition, there are still several challenges associated with the technologies currently available on the market today that act to considerably slow the speed of installation of more solar energy assets capable of replacing the carbon intensive fossil fuel-based power plants in operation today.



Figure 1.23 Projected contribution of different power generation sources to (a) power demand, (b) installed capacity [16].

Figure 1.23 shows the projected contributions of different energy sources towards energy demand in 2050, and from here it is clear that solar power is projected to make up a large portion of the renewable energy infrastructure. However, the problem which threatens to hinder this robust projection is the ability of the grid to incorporate the excess energy which these installations are expected to produce. At the same time, the prevalent solar technologies have problems related to cost vs efficiency, measured as the cost per kilowatt, the acquisition of land as well as policy considerations that make them harder to deploy on a large enough scale as compared to legacy

fossil-based technologies. Here we consider these problems briefly and elucidate why the integration of solar with electrical transmission and distribution infrastructure represents a synergistic combination of technologies to rapidly scale up the adoption of critical solar infrastructure.

### 1.7.1 Land

Utility scale solar projects require vast land assets over which the facility is installed including space not only for the panels themselves, but auxiliary generation infrastructure such as electrical equipment, maintenance and inspection infrastructure. Figure 1.24 clearly shows that solar PV is one of the most land intensive energy sources. In many countries around the world, the strain on limited land resources available causes encroachment and conflict with other types of land users especially agricultural in more rural areas where the activity is more prevalent [188, 189].





In addition, another challenge towards the fast scaling up of solar in the global energy economy is the extensions to the existing transmission grid network. With each utility scale solar plant that is brought online, the power generated needs to be directed towards the transmission grid, and this requires that transmission infrastructure connect to the solar plant at a point on the existing grid network. Considering the ambitious net zero energy goals set by the United States of America (US) for reducing almost 50% greenhouse gas emissions from the 2005 level set for 2030, the estimated increase to the transmission grid size from anywhere between 23% to 36% of its 2020 grid network and costing a minimum of USD ~1.5T in the most cost effective of models considered till now [191, 192].

Four possible options have been considered in the NREL's Interconnections Seams Study which have been shown below in Figure 1.25. What is apparent is that in even the case of design 3 which is reported to require the least expansion to the existing grid network, the extensive cross-country interconnections and dense additions to at least the US east coast is clearly visible. This presents a unique opportunity to address both these problems by placing the solar infrastructure within the bounds of the transmission and distribution corridor itself allowing a large, underutilized region of space to replace otherwise arable or mineable land while at the same time placing new solar infrastructure as close as possible to the existing grid network.

## 1.7.2 Profitability / Cost per kilowatt

The International Energy Agency (IEA) reports in their latest outlook report in 2023 that the levelized cost of solar PV has reduced by a remarkable 90% in the timeframe from 2010 to 2022 owing to robust policy decisions, innovation in technology and manufacturing methods as well as steadily growing funding sources for solar based projects from government as well as private participants. However, a recent phase of increase in levelized cost of energy (LCOE) is seen owing to global geopolitical events resulting in reduction in supply of key materials as well as bottlenecks in global supply chains [2].



Figure 1.25 Proposed macrogrid expansion models to enable the 2030 renewable energy transition in the US [193].

This trend is shown in Figure 1.26 (b) where the specific increase in cost can be attributed to the increase in the weighted average cost of capital (WACC) and commodities keeping the LCOE sustained over the period from 2020 to 2024 while technology improvements both in 2020 and

2022 helped reduce the cost of going solar breaking a trend of steady decline over the previous decade.



Figure 1.26 Development trends in solar PV: (a) year wise increase in installation capacity and projected to 2030 [2], (b) levelized cost of energy (LCOE) year wise trend in solar PV [194].

Clearly, there are volatilities in the market beyond the control of simply the market forces and the only consistent control variable that has seen unaffected growth positively impacting the financial viability of solar projects is the technology improvement, which essentially represents an improvement in the energy efficiency. As such, the continuous increase in efficiency and performance is still a very desired characteristic of progressively advanced PV technologies and configurations. Considering that solar PV and wind are currently projected to make up the majority share of renewables by 2050 at least, and the urgent need to rapidly scale the share of renewables over fossil fuels in order to achieve the below 1.5°C rise in global temperatures above pre-industrial levels target put forward by the Intergovernmental Panel on Climate Change (IPCC) [195]. However, technologies that deliver greater efficiencies are, today, extremely expensive, as NREL notes in its Solar Futures Study about the case of III-V solar cells [196, 197]. Thus, synergistic integrations of solar cells with freely available magnetic fields to assist in improving solar conversion efficiency is an ideal technique to viably increase the efficiency of the technology without making it too expensive for the market to adopt.

## 1.7.3 Capacity/Demand

Driven by the combination of population growth, progress and advancement of developing nations resulting in a higher per capita energy consumption as well as the transition to electrification of many fossil fuel industries such as transportation and logistics, home heating, electrical vehicle usage, and other so called 'end-user' activities, the need for more electrical power is an inevitable consequence, especially while chasing ambitious net zero targets. However, the current transmission infrastructure is neither adequately designed to handle decentralized, bi-directional transmission ecosystem nor do they have the carrying capacity to deliver the power loads required to satisfy the growing consumer demand expected in the coming years, even up to 2030 [2, 195].



Figure 1.27 Projected growth in electricity demand through to 2050 [198].

### 1.7.4 Policy considerations

The uncertainty related to policy and regulations is a major concern for the solar industry, which is capable of greatly delaying the great progress we are making towards a net zero future. Therefore, the ability to circumnavigate regulatory requirements through utilizing land whose regulatory approvals are already completed requiring minimal incremental approvals is an ideal solution to greatly reduce uncertainties in the power sector.

## 1.8 Research objectives

The objective of this research is to analyze the performance of TiO<sub>2</sub>-based photoanodes on FTO substrates used for the PEC system for hydrogen generation from an aqueous electrolyte in the presence of a relatively small magnetic field. While the enhancement of STH conversion efficiency in the presence of a magnetic field is a known phenomenon, there hasn't been much detailed analysis as to the origin of this phenomenon especially in terms of the dynamics of the charge carriers inside the material system and at the surfaces and interfaces. In the scope of this study, we attempt to establish how much information can be gained from using PEC based measurements alone.

From the survey of literature on the topic, the understanding we gained was that not much effort has been made to establish which of the components of the PEC cell are influenced by the magnetic field and contribute to the improved solar to hydrogen generation efficiency. Considering that PEC in a three-electrode configuration is a technique used primarily to study the working electrode (in this case the photoanode) in isolation, this aspect of the experimental analysis is often ignored. The preliminary objective therefore was to identify out of the photoanode, which include its different layers separately, the electrolyte and the counter electrode, which of the components participated in the magnetic field assisted enhancement in performance. To do this, the following method was used:

- The photoanode was progressively reduced layer-by layer until we obtained a blank FTO sample. While testing each layer, attention is given to whether or not a magneto-response is observed on introducing a magnetic field into the system, and if so, the magnitude of the improvement in performance. Of particular interest is the case when the system stops responding to the magnetic field on the removal of any layer. At this point, we can conclude that the magnetic response can be attributed to the layers above this layer.
- The electrolyte was varied at different pH as well as the ionic species. The associated response at various pH levels will be useful to determine how the magnetic field interacts with the proton concentration in the electrolyte, while varying the ionic species lets us know the interaction with the particular species in solution. Of course, these interactions will be characterized as their behaviour at the electrode interface with the electrolyte. Lastly, the electrolytes chosen include one with a hole scavenger (sulfite anion) and another without (0.5M Na<sub>2</sub>SO<sub>4</sub>). As such, the magnetic response with the hole scavenger will allow us to comment on the effect of the magnetic field with the surface charges on the electrode also. Any variation in PEC response which follows the natural change in

activity between the varying electrolyte systems will also let us know that the electrolyte bulk is not influenced by the presence of a magnetic field in the system.

• Finally, the use of multiple counter electrodes will let us test if the counter electrode reaction is influenced by the magnetic field or not. Three counter electrodes, platinum, which is the standard can be useful to compare performance against other reported materials, both with and without a magnetic field, while using a gold and graphite counter electrode will give us a contrast as to what varying the type of counter electrode has on the magnetic response of the system.

With the information about the systems affected by the magnetic field, we can focus on trying to determine the specific processes that are influenced, specifically in the electrode bulk and the surface, the charge transfer kinetics and the reaction kinetics. The most important processes that have been identified from literature are the charge separation and recombination kinetics at the electrode bulk and the surface. Linear sweep voltammetry is used to characterize the performance, while open circuit potential decay is used to understand the charge carrier lifetimes. Specifics about the charge carrier dynamics can be inferred from electrochemical impedance spectroscopy.

Finally, the design ideas of the solar PV panel that would be integrated with electrical transmission and distribution conductors to initially allow the practical usage of the magnetic field assisted photovoltaic enhancement effect, as well as the results of a market validation exercise conducted to determine if the technology invented represents a solution to a real world problem, are presented in the appendix.

# 1.9 Thesis organization

This thesis has been segregated into six chapters as follows:

Chapter 1 is the introduction which presents the detailed discussion about the background of the topic including the basics of photoelectrochemical water splitting for hydrogen generation as well as the various external field assisted performance enhancement techniques. Lastly the motivation and the objectives for the research project are provided.

Chapter 2 details the material synthesis and device fabrication methods as well as the theory on all the characterization methods used. Along with the introduction of each characterization method, the results of the characterization measurements as well as their interpretation in terms of purity, uniformity and quality of the material synthesized or the device fabricated are discussed.

Chapter 3 presents the theoretical introduction to the PEC characterization methods and immediately following, the results of the PEC experimental measurements and analysis to determine the effect of the magnetic field on the PEC system. The influence on charge separation, transfer and recombination are specifically analyzed especially with respect to bulk recombination and surface recombinations within the photoanode.

Chapter 4 summarizes the main findings of this research work and points out gaps which were not considered as part of the current work, and which could form part of future research based on this project.

An appendix is dedicated to ideas to design a commercial solar photovoltaic panel that can exploit the improved performance of solar energy harvesting and conversion in the presence of a magnetic field. The panel designed to fit around an electrical conducting wire is presented in different variations. Additionally, the results of a market validation survey performed to determine the viability of large-scale commercial adoption of this solar panel. Specific problem areas identified by potential customers in the solar as well as electrical transmission and distribution industry are presented, and a potential problem-solution fit is proposed.

# 2 MATERIALS SYNTHESIS AND CHARACTERIZATION

In order to achieve the research objectives stated in the preceding chapter, photoanode devices were fabricated and characterized structurally, morphologically and compositionally. These characterization measurements allowed us to verify the material purity of the sample with respect to the intended electrode that was being targetted, as well as the consistency of the layer dimensions and surface characteristics, and also the homogeneity of spread (in the case of titanium dioxide) or the uniformity and homogeneity of penetration (in the case of quantum dot sensitization).

This chapter discusses the techniques used for the fabrication of the various different devices, including those based on commercial mesoporous titania paste (mTiO<sub>2</sub>), which are the primary devices used to characterize the mechanics of magnetic field-assisted PEC. At the same time, fabrication of control devices prepared from commercial anatase and rutile nanopowders is also detailed, along with the SILAR method for QDs sensitization of the mTiO<sub>2</sub> devices. Next, the chapter introduces the material characterization methods used after which the result of each technique is presented and analyzed.

# 2.1 Device structure

## 2.1.1 Photoactive Layer / Electron Transport Layer (ETL)

The photoactive layer contains the light-harvesting material whose function is to absorb the incoming radiation and generate photoelectrons and photoholes, together referred to as photocarriers. The efficiency of the solar device is then determined by the portion of the incident solar spectrum that the photoactive layer can absorb and convert into photocarriers [27, 199]. The photogenerated charge carriers are then injected into the electron transport layer, which again needs to be efficiently done [27]. The electron transport layer, on the other hand, serves to quickly extract the photogenerated electrons, a process known as 'charge separation', and prevent the recombination of electron and holes, a major source of efficiency loss in solar devices (both solar cells and PEC fuel cells) [27, 200, 201].

Figure 2.1 below shows the basic structure of a PEC water splitting cell with the position of the ETL layer and the photoactive layer in the photoanode structure and the direction of electron and hole current, as well as the mechanism of redox reactions at each electrode.



Figure 2.1 Mechanism of Photoelectrochemical Water Splitting Cell showing the position and action of ETL layer on the Photoanode.

Mesoporous titanium dioxide (mTiO<sub>2</sub>) designated as 18NR-AO (active opaque) from GreatCell Solar containing a blend of ~20nm sized active anatase nanoparticles along with larger anatase scattering particles up to 450nm is used both as the photoactive layer and the electron transport layer. Additionally, for the case of control experiments, pure phase anatase (aTiO<sub>2</sub>) (<25nm, 99.7% trace metal basis) and rutile (rTiO<sub>2</sub>) (<100nm, 99.5% trace metals basis) nanopowders, ethyl cellulose and alpha-terpineol were obtained from Millipore Sigma. The paste and nanopowders were used as obtained from the supplier (GreatCell Solar) for device preparation without any further purification.

### 2.1.2 Conductive Layer

Fluorine doped Tin Oxide (FTO) coated glass with a sheet resistance of ~15 ohms/cm<sup>2</sup> were used as the conductive substrates over which the photoanode ETL was deposited. The conductive substrate provides a pathway for charge carriers from the ETL to the external circuit. FTO is a commonly used substrate material owing to its high conductivity and stability in a large range of electrolytic media from acidic to highly basic [202]. Figure 2.2 shows a cross-sectional SEM image of such a FTO coated glass sample. The FTO substrates used in this study were purchased from Pilkington Glasses.



Figure 2.2 Cross sectional SEM image of FTO glass [203].

# 2.2 Device fabrication

# 2.2.1 Substrate preparation

FTO substrates as received from the supplier are cleaned in preparation for loading the ETL and active layers on top. Impurities on the substrate can increase the ohmic resistance of the photoanode, as well as provide additional sites for electron-hole recombination resulting in loss of efficiency [204]. A typical cleaning cycle involves first cleaning with soap and water to remove organic contaminants and residues from manufacturing and environmental exposure. Next, the substrates were kept in acetone and deionized water respectively and immersed in an ultrasonic bath for 20 minutes. After each sonication step, the substrates were removed and dried in a nitrogen gas flow. Finally, to completely remove organic contamination, the substrates were treated in an ozone chamber for 15 minutes. The substrates were then labelled and stored for future usage. All FTO substrates including those used for control and blank tests were prepared using the same methodology to keep substrate layers consistent across samples indicating any effects observed differently across samples to the variation in thin film ETL and active layer components.

## 2.2.2 Nanopowder paste (control devices)

A standard recipe to create a paste from nanopowders from previous reported literature was used [205]. 1g of nanopowder (anatase or rutile) is mixed with 0.5g of ethyl cellulose, 1mL of alphaterpineol, 1mL of deionized water and 5mL of ethanol in a beaker and kept under magnetic stirring for 12h. The solvent is then evaporated using a rotary evaporator until the volume of the mixture is reduced to half of the initial volume.

# 2.2.3 Deposition of Photoactive Layer / Electron Transport Layer

Thin films of 18NR-AO anatase active layer, or anatase or rutile nanopowder paste, were deposited using the doctor blade method as shown in Figure 2.3 The FTO is secured in place as well as its active area marked off using three pieces of scotch tape which also demarcates the thickness of the thin film as being at most the thickness of the tape.



Figure 2.3 Details of Doctor Blade method for the deposition of thin film of anatase active opaque paste on FTO glass substrate.

A small quantity of paste is then placed on a clean glass tube. The glass tube with the paste is then slid across the surface of the FTO sample while maintaining a light pressure on the tape to prevent material from flowing out from the sides. This results in a homogenous film of uniform thickness on the FTO surface.

Subsequently the sample is left to dry for 10 minutes at room temperature to allow the film to relax and allow readily volatile solvents to slowly evaporate as well as help the film to self-organize. This transitions the film from a wet state to a semi-solid state and helps it to adhere more firmly to the FTO substrate underneath. The sample is then heated at 120°C for 6 minutes to further evaporate solvents and binders in the paste and to further bind the paste to the FTO as well as for strong adhesion of the layers in the sample, since heating at a moderate temperature can promote bonding between individual  $TiO_2$  nanoparticles as well as between the nanoparticles and the underlying substrate layer. It also prepares the film for subsequent annealing by preheating the  $TiO_2$  layer and reducing thermal shock [206].

Finally, the sample is sintered at a temperature of 500°C for 30 minutes to completely remove all organic materials such as binders and thickening agents from the paste while at the same time initiating recrystallization of the TiO<sub>2</sub> nanoparticles resulting in a smooth crystalline layer which has better charge transport properties, lesser defects and improved catalytic activity compared to the poorly crystalline paste [207, 208].

# 2.2.4 Quantum Dots Sensitization

To showcase the scalability of enhanced PEC hydrogen generation using a magnetic field, the underlying photoanode device architecture is gradually improved to demonstrate that with better light harvesting capability, the efficiency of an already more efficient photoanode by applying a magnetic field, can be improved even further. QDs are used to boost the light harvesting efficiency of the photoanode allowing absorption of the visible spectrum as opposed to the mainly UV light absorption capability of TiO<sub>2</sub>, and as such also forms part of the active layer whenever employed. We use quantum dots as a showcase for future advanced experimental work for utilizing the improved performance of TiO<sub>2</sub> photoanodes in magnetic fields to drive higher light collection devices.

For this reason, a very well-known system of quantum dots, cadmium sulfide (CdS) and cadmium selenide (CdSe/CdS), were chosen whose light absorption efficiency in the visible range of the electromagnetic spectrum is known to be high, and at the same time, can be synthesized using relatively low-cost precursors as well as facile synthesis methods given that the QDs are not the actual focus of the discussion. An additional shell layer of ZnS is also deposited on each QD system which offers better surface passivation. The QDs are deposited on the mTiO<sub>2</sub> photoanode systems exclusively.

An extremely easy synthesis technique for the deposition of CdS and CdSe QDs onto anatase layers is Successive Ionic Layer Adsorption and Reaction also known as SILAR. This technique involves immersing the FTO sample with the mTiO<sub>2</sub> anatase layer deposited as per section 2.2.3, into successive solutions of cationic and anionic species one after the other resulting in the sequential adsorption of ionic species onto the sample.

## 2.2.5 SILAR for QDs

Here we have deposited quantum dots of CdS, and cadmium selenide CdSe/CdS using cadmium acetate dihydrate (Cd(CH<sub>2</sub>COO)·2H<sub>2</sub>O, 98%), disodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O  $\geq$  98%), sodium borohydride (NaBH<sub>4</sub>), selenium powder (Se, 99.5+%), zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)2·2H<sub>2</sub>O,  $\geq$  98%) which were purchased from Millipore Sigma, while methanol and ethanol were obtained from VWR Avantor.

For the case of CdS, the mTiO<sub>2</sub> layered sample is immersed into a solution of Cd<sup>+2</sup> ions for a sufficient period, which in our case happens to be 1 min, allowing the film to adsorb the cationic species forming a layer. The sample is then removed from the solution and quickly rinsed to remove all traces of the cationic precursor solution and effectively 'stop' the adsorption reaction. Next, the sample is immersed into a solution of anionic species (S<sup>2-</sup>) for 1 min and rinsed resulting in the adsorption of sulfide ions onto the sample surface which then react with the already adsorbed cadmium ions to form a thin layer or quantum dot of CdS. This process can be repeated for multiple cycles to vary the thickness of the eventual QD film.

An additional layer of surface passivation of ZnS was deposited in order to passivate the surface states and introduce a protective layer against oxidation given that both CdS and CdSe/CdS are prone to. This can lead to an improved performance over the long term in addition to an increase in lifetime of the photoanode due to prevention of degradation of the CdS or CdSe layers.

To do this, a cationic solution of  $Zn^{+2}$  is used in alternation with a solution of  $S^{2-}$  anions. A 0.1 M  $Zn(CH_2COO)\cdot 2H_2O$  in 20 ml of methanol is used as the cationic agent after which the samples are rinsed in 20ml methanol. A 0.1 M solution of  $Na_2S\cdot 9H_2O$  in 20 ml of 1:1 mixture of DI water and methanol forms the anionic agent, and the samples are washed in 20 ml of 1:1 mixture of DI water and methanol which forms one complete cycle for depositing a ZnS passivation layer.



Figure 2.4 Detailed method for the synthesis of CdS quantum dots using SILAR.

For the case of CdS, we use a solution of 0.05 M Cd(CH<sub>2</sub>COO)·2H<sub>2</sub>O in 20 ml of methanol as the cationic agent, while the rinse solution was 20ml methanol. The anionic agent used is 0.05 M of Na<sub>2</sub>S·9H<sub>2</sub>O in 20 ml of 1:1 mixture of DI water and methanol. A 1:1 mixture of DI water and methanol was also used as the rinsing solution. CdS QDs were deposited using 5 cycles of CdS and 2 cycles of ZnS passivation layer.



Figure 2.6 Detailed method for the synthesis of CdSe quantum dots using SILAR.

In the case of CdSe/CdS QDs, we initially deposit layers of CdS as a buffer which helps in minimizing lattice mismatch of the CdSe layer grown on the top reducing strain as also reducing the defects in the CdSe layer which can act as recombination sites. The CdS layer also helps charge separation and transport to the conductive FTO layer because it has a bandgap intermediate between the CdSe and the mTiO<sub>2</sub> ETL which offers a stepwise increase in the conduction energy allowing an efficient charge transport across the QD-ETL interface. The slightly larger bandgap of CdS also allows greater light harvesting efficiency given that photons in the bandgap of CdS, CdSe and TiO<sub>2</sub> can all be harvested.



Figure 2.5 Images of prepared photoanode samples: (a) bare-TiO<sub>2</sub> based, (b) CdSsensitized, and (c) CdSe/CdS-sensitized.

Thus, after 5 cycles of CdS (as before), a solution of 0.03 M Cd(CH<sub>2</sub>COO)·2H<sub>2</sub>O in 20 ml of methanol as the cationic agent followed by a solution of 0.06 M of NaBH<sub>4</sub> and 0.03 M of Se powder

in 40 ml of ethanol as the Se<sup>2-</sup> agent is used in 3 cycles to form a CdSe layer. These precursors are stirred under an inert N<sub>2</sub> atmosphere until the Se completely dissolves in the ethanol and presents a clear solution. The rinse solutions are 20ml methanol and 20ml of ethanol respectively. Finally, 2 cycles of ZnS passivation as before completes the CdSe/CdS QD-sensitized sample. The final QD sensitized samples as well as bare mTiO<sub>2</sub> photoanodes are shown in Figure 2.5 for comparison.

# 2.3 Structural and Optical Characterization

Several characterization techniques were employed to study the quality, structure, morphology, crystallinity, homogeneity of the TiO<sub>2</sub> films as well as the uniformity of the QDs deposited using chemical composition studies. Additionally, studies on the band structure of the layers as well as interfaces allowed us to characterize the optical properties of the photoanode in order to model probable mechanisms. These techniques are briefly detailed, and the results of the measurements are presented in the sections that follow.

# 2.3.1 X-Ray Diffraction (XRD)

# 2.3.1.1 Method

XRD is a very well-known technique to analyze the crystal structure of powder as well as thin film samples. An XRD scan can give useful information on the degree of crystallinity of a sample along with the phases, such as anatase of rutile in the case of  $TiO_2$ , in which the sample is present. One can also comment on the purity of the sample considering if peaks in the scan other than the ones belonging to the material under investigation is seen.

XRD uses the Bragg's Law which gives a relation between the wavelength of incident light on a diffracting surface, such as a crystal lattice, and scattering angles where superposition of the waves will result in constructive interference causing peaks in the pattern. Essentially:



$$n\lambda = 2dsin\theta \tag{21}$$

Figure 2.7 Principle of XRD (inset) and XRD pattern of TiO₂ in the anatase phase for commercial active opaque paste (post annealing) and commercial nanopowder identifying the various crystal planes.

where:

 $\lambda$  is the wavelength of the incident monochromatic X-Ray source

d is the distance between the adjacent crystal planes arranged parallelly

 $\theta$  is the scattering angle

In this way, the interatomic spacing and the orientation of the crystal plane can be easily determined. Figure 2.7 shows, as an example, how such a scan will appear for the case of  $mTiO_2$  18NR-AO paste as well as the anatase nanopowder identifying the relevant peaks along with the miller indices of the corresponding crystal planes. Here we also see that the annealing of the mTiO<sub>2</sub> recrystallizes the paste in the anatase phase. All XRD patterns were captured using a

Bruker D8 Advance x-ray diffractometer equipped with a Cu K $\alpha$  source ( $\lambda = 1.542\dot{A}$ ) and a Lynxeye XE-T 500 µm compound silicon strip detector with 192 channels and <380 eV energy resolution at 8keV. All diffraction measurements were performed in Bragg Brentano ( $\theta$ -2 $\theta$ ) geometry.



Figure 2.8 Bruker D8 Advance XRD diffractometer (a), and sample holder with anatase nanopowder for measurement (b).

Figure 2.8 shows an image of the diffractometer system used for the measurements of all samples reported in this study as well as the loaded sample holder for the XRD diffractogram acquisition for the anatase nanopowder reported in Figure 2.7. The XRD measurements were taken for a 20 range from 5° to 80°, where most major peaks for titania are found. The measurements were taken with a step size of  $0.02^{\circ}$  and a time per step of 1s.

### 2.3.1.2 Results

Here, we use XRD to analyze the thin films on the photoanode devices to determine if a uniform or mixed phase of the TiO<sub>2</sub> ETL layer is present, as well as establish the degree of crystallinity of the thin film. Firstly, a blank FTO sample is measured to establish the substrate peaks and subsequently disregard them from the analysis of photoanode devices. Subsequently, sample devices of each type used are measured from mTiO<sub>2</sub> designated as mTiO<sub>2</sub>, anatase nanopowder and rutile nanopowder. Lastly, mTiO<sub>2</sub> samples sensitized with CdS and CdSe/CdS SILAR quantum dots are also measured.



Figure 2.9 X-Ray Diffraction analysis of prepared photoanode devices (a). Peak splitting in QD sensitized photoanodes (b) and (c).

Figure 2.9 shows the observed XRD patterns for various photoanode samples tested. It can be clearly seen that the TiO<sub>2</sub> thin film in the case of photoanodes fabricated with the anatase and rutile single phase nanopowders retain their phase characteristics and display the characteristic peaks associated with the anatase (JCPDS No.: 21-1272) and rutile (JCPDS No.: 21-1276) respectively. In addition, the mTiO<sub>2</sub> based photoanode devices can also be seen to clearly crystallize in the anatase phase with the FTO peaks clearly identified separately. For the case of QD sensitized photoanodes, the major crystal peaks are visible in the form of changes in the relative peak intensity since the weak diffraction peaks of the QD crystals are overshadowed by the much stronger diffraction peaks from the thicker TiO<sub>2</sub> and FTO layers as similarly reported in literature [209-211].

However, some varying features are indicative of the presence of the CdS and CdSe peaks as in the relative broadening and splitting of the (101) peak vs the anatase nanopowder due to CdS as well as the FTO (110) peak at 26.59° (JCPDS No.: 041-1445) due to CdSe visible in Figure 2.9 (b) and (c) indicative of contributions from the CdS and CdSe crystals. Also visible is the relative intensities between these two peaks on going from the CdS to the CdSe/CdS sensitized photoanode. While in CdS, the contribution to the intensity is only from the CdS crystal, it acts to

increase the intensity of the anatase (101) peak relative to the FTO (110) peak, whereas in the case of CdSe/CdS, both peaks are given an extra push from the respective layers (CdS and CdSe), making the (110) FTO peak appear relatively larger than the anatase (101).

# 2.3.2 Scanning Electron Microscopy (SEM)

SEM is an imaging tool to analyze the surface morphology and microstructure of the sample either in the form of a device where cross-sectional imaging can provide information regarding the size of different layers, uniformity in thickness as well as the quality of interfaces and often the visualizations of defects especially line and planar defects. Additionally, analyzing SEM images of surfaces can provide details on surface composition particularly through the visualization of different grains and features which can help infer the presence of impurities, degradation of surface through processes such as corrosion as well as ascertain important surface parameters of devices such as roughness, porosity, grain size and grain boundaries etc. which may influence material properties eventually impacting device performance.



Figure 2.10 Components and Process of SEM imaging setup.

The complete setup of an SEM imaging process is detailed in Figure 2.10. An SEM microscope generates a high energy beam of electrons from either a thermionic source heated to temperatures of 2700-2900 K, or a field emission source using a high work function material held at strong electric fields allowing electrons to eject from the material surface through quantum tunneling. The emitted electrons are further accelerated to higher energies using an anode held at voltage differences between 200V-30kV with the electron gun. The high energy beam is

collimated and focused using condenser lenses to a small spot size allowing for high resolution imaging. The highly focused beam interacts with the sample surface and ejects secondary electrons from the atoms in the surface which directly contacts the electron beam. These secondary electrons are scattered randomly and are collected in a secondary electron detector where the intensity of the electron beam is analyzed using the Rutherford scattering cross section relation (eq. 22) to determine the morphology of the scattering surface [212, 213].

$$\frac{d\sigma}{d\Omega} = \left(\frac{Ze^2}{16\pi\epsilon_0 E}\right)^2 \frac{1}{\sin^4\left(\frac{\theta}{2}\right)}$$
(22)

In our analysis SEM imaging is performed using a Tescan Vega 3 LMH scanning electron microscope equipped with a thermionic tungsten filament as the electron source and an Everhart-Thornley secondary electron scintillator-detector for imaging. The system is shown in Figure 2.11.



Figure 2.11 Tescan Vega 3 LMH SEM/EDX system.
# 2.3.3 Energy Dispersive X-Ray Spectroscopy (EDX)

EDX is an elemental mapping spectroscopy used along with SEM imaging which allows spatial determination of the elemental composition of a sample. Figure 2.10 shows an x-ray detector as part of the SEM system which is the main component used in EDX mapping of the sample. As the electron beam raster scans the sample, it releases secondary electrons, backscattered electrons as well as characteristic x-rays from the elements present in the sample. The principle of emission of characteristic x-ray is shown in Figure 2.12.



Figure 2.12 Mechanism of Characteristic X-Ray production in an EDX process.

An incident electron from the electron beam can strike and eject a core-level electron, whereby a vacancy is created in the inner shell of the atom. This prompts one of the outer electrons to drop down to the available vacancy in the lower energy level and emit an x-ray photon whose energy is characteristic of the energy difference between the orbital from where the electron drops down and the energy level of the inner shell orbital where the vacancy is present.

The x-ray detector in the SEM column placed next to the sample stage can receive the x-ray emissions from these characteristic transitions and determine the energy of the photon and as a result characterize the element corresponding to the photon emission. As the detector scans the incoming x-ray photons in combination with the raster scanning position of the SEM electron beam, a spatial map of elements contained in the sample can be gradually built up revealing the elemental quality of the sample material. It can also provide a semi-quantitative measurement of

elemental composition, which can be used to compare similar samples for relative stoichiometric composition. A Quantax xFlash x-ray detector coupled with the Tescan Vega 3 SEM system as described earlier was used to collect and analyze EDX data at a working distance of 15mm. This unit is identified in Figure 2.11 towards the left side of the SEM tower.

# 2.3.4 SEM and EDX Results

The cross-sectional SEM image of the CdS an CdSe/CdS sensitized devices are shown in Figure 2.13. We can see that the doctor blade method used results in a uniform film of ~15  $\mu$ m thickness. This is consistent with the film thickness expected using the doctor blade method and also allows for consistency in comparing device performance across multiple experiments throughout literature also [214, 215]. Also, the device fabrication process can be seen to give a homogenous



Figure 2.13 SEM images of mTiO<sub>2</sub> thin films on FTO substrates sensitized with (a) CdS, and (b) CdSe/CdS quantum dots.

layer strongly bound to the FTO layer underneath. The film interface with the FTO layer underneath appears uniform across the length of the film and suggests good adhesion.

Additionally, EDX elemental mapping and spectroscopy were performed to analyze the quality of the SILAR quantum dots deposited as well as confirm the purity of the sample with respect to the chemical composition of the quantum dot sensitized mTiO<sub>2</sub> layer. Figure 2.14 shows the EDX spectrum and elemental map of the CdS sensitized photoanode. While the elemental analysis shows uniform and homogenous spread of Ti, O, Cd, Zn and S across the mTiO<sub>2</sub> film layer, with traces of oxygen within the FTO and the silica from the glass substrate, the EDX spectrum shows

presence of no impurities within the film layer confirming the uniform, homogenous penetration of the quantum dot sensitization across the entire thickness of the mTiO<sub>2</sub> ETL layer.



Figure 2.14 EDX spectrum and map of CdS sensitized mTiO<sub>2</sub> photoanode.

Secondly, EDX analysis is presented for the CdSe/CdS sensitized photoanode in Figure 2.15. Similar to the case of CdS, here again we observe uniform spread of the elements Ti, O, Cd, Se, Zn and S across the ETL layer confirming the homogenous penetration of the photosensitizer quantum dots into the ETL layer thickness, and the spectrum presents no impurities which cannot be accounted for in either the photoactive, ETL or the FTO glass substrate. The presence of Na in the spectrum is from the precursor used as the cationic sulfide agent in the synthesis of the SILAR quantum dots.



Figure 2.15 EDX spectrum and map of CdSe/CdS sensitized mTiO<sub>2</sub> photoanode.

# 2.3.5 X-Ray Photoemission Spectroscopy (XPS)

## 2.3.5.1 Method

XPS is a powerful surface analysis technique which can offer information about the chemical and elemental composition of the material sample as a function of depth which h is useful in trying to understand the mechanisms occurring at the electrode-electrolyte interface where surface states are involved.



# Figure 2.16 Principle of operation of XPS analysis showing the origin of the O1s signal of Oxygen: (a) shows the sample surface irradiated by X-ray photons eventually causing the emission of a core electron from the 1s orbital in (b) [216].

XPS is fundamentally based on the photoelectric effect, wherein a high energy x-ray can release an electron from a material. The kinetic energy of the released electron is dependent on the amount of energy from the incident x-ray which is used to free the electron from the atom it was bound to, essentially giving its binding energy. Thus:

$$E_k = h\nu - E_b - \phi \tag{23}$$

where:

 $E_k$  is the kinetic energy of the ejected electron

hv is the energy of the incident x-ray photon

 $E_b$  is the binding energy of the electron under investigation in the atom

 $\phi$  is the work function of the material, which is the energy required to remove an electron from the surface of the material to a point just outside the surface calculated as the difference in energy between the fermi level of the material and the vacuum level.

If a detector is able to scan across different values of kinetic energies of electrons, a spectrum across electron energies against the intensity/count of electrons of each energy received at the



Figure 2.17 PHI Quantes XPS system used to measure XPS data.

detector can be generated which is the resulting XPS spectrum. At energies corresponding to energy levels on the material, peaks are identified which can allow us to identify the electronic structure of the sample under investigation. PHI Quantes using an Al K $\alpha$  ( $h\nu = 1486.6eV$ ) monochromatic x-ray source with an energy resolution of 0.8eV was used to capture XPS data. Figure 2.17 shows an image of the system used to gather XPS data of the photoanodes used in this study.

## 2.3.5.2 Results

XPS spectroscopy provides information on the presence and the bonding state of the elements in the material sample. As such, XPS can identify crystal compositions of molecules in low concentrations where analysis like XRD usually results in the crystal peaks being absorbed into the signal noise resulting in an inability to resolve peak features clearly. However, it must be stated that XPS is a surface sensitive technique and provides information from the first few nanometers to a few micrometers depending on instrument capabilities.



Figure 2.18 XPS spectrum of CdS sensitized mTiO<sub>2</sub> photoanode. (a) survey scan, (b) Ti 2p, (c) O 1s, (d) S 2p, (e) Cd 3d, and (f) Zn 2p.

Figure 2.18 shows the XPS spectrum for the CdS sensitized photoanode sample. Here, we can clearly identify the Cd 3d peaks as well as the S 2p peaks showing the Cd atoms bonded to the S as CdS, while the presence of the Zn 2p peaks also confirms the presence of ZnS passivation layer. The survey scan shows the peaks from various molecules in the photoanode sample. We observe contributions from the CdS sensitized mTiO<sub>2</sub> ETL layer, while minor presence of synthesis precursors are observed. Of particular note is that the sample is free of any contaminants that could be considered ferromagnetic in nature. As such, the experiment confirms the proper deposition of quantum dots while at the same time demonstrates that any magnetic field effect is directly related to electronic interactions between the different components of the photoanode system.

Similarly, the XPS measurement of the CdSe/CdS sensitized mTiO<sub>2</sub> photoanode system is presented in Figure 2.19. Again, we observe the presence of the Cd 3d, S 2p and Zn 2p peaks along with the Se 3d peaks confirming the existence of CdSe and CdS bonded species in the ETL

layer. Once again, the survey scan reveals peaks corresponding to the synthesized materials and no presence of impurities either ferromagnetic or otherwise is found showing successful deposition of CdSe/CdS SILAR QDs on the mTiO<sub>2</sub> ETL layer. Therefore, in relation to the SEM/EDX data, we can confirm the uniform and homogeneous deposition of quantum dots in the material sample.



Figure 2.19 XPS spectrum of CdSe/CdS sensitized mTiO<sub>2</sub> photoanode. (a) survey scan, (b) Ti 2p, (c) O 1s, (d) S 2p, (e) Cd 3d, (f) Se 3d, and (g) Zn 2p.

Finally, UV-Vis absorption spectroscopy is presented for all the device configurations used in this study to optically characterize the devices for the purpose of comparison to existing literature as further evidence of material and device quality, as well as to understand the photoelectrochemical behaviour which is tested in the section that follows.

#### 2.3.6 Ultraviolet-Visible Spectrophotometry (UV-Vis)

## 2.3.6.1 Method

UV-Vis spectrophotometry is used to determine the specific wavelengths a material can absorb in the ultraviolet and visible range of the electromagnetic spectrum. Typically, a sample is irradiated with a light source which can emit across the UV and Visible range (200-800 nm), such as a Xe lamp. The emitted light from the source passes through the sample and the transmitted light is collected at a detector which scans across the source range and measures the intensity of light received at each wavelength, which is essentially the transmittance of the sample at the corresponding wavelength when divided by the intensity of incident light at the same wavelength.

The Beer-Lambert Law is used to correlate the absorbance, A of the sample to the transmittance, T as follows:

$$A = -\log_{10}T\tag{24}$$

This gives us the absorption spectra of the sample under investigation which can be used to identify electronic transitions in the material layers as spectral features. Thus, we can investigate the specific wavelengths the sample can absorb which helps us to characterize the optical properties of the sample. Typical UV-Vis spectra of all types of samples used in this study are



Figure 2.20 UV-Vis spectra of devices used in the current study.

shown in Figure 2.20 as an example of how such spectra look. Here we observe a typical pattern of gradual rise in absorption at higher energies and as soon as the illuminating wavelength becomes lower in energy than the band gap of the material, the absorbance immediately drops to the baseline value for the material under investigation. Additionally, the UV-Vis spectrum of the sample can be used to determine the band gap between the valence and conduction bands of the material using Tauc analysis. The UV-Vis absorbance is used to construct a Tauc plot. It uses the absorption coefficient,  $\alpha$  of the material which can be determined from the UV-Vis absorption spectrum at a given wavelength, which can then be substituted into the Tauc equation given below:

$$(\alpha h\nu)^{1/n} = B(h\nu - E_g)$$
<sup>(25)</sup>

here:

v is the frequency of the light which can be related to the wavelength  $\lambda$ , as  $v = \frac{hc}{\lambda}$ 

*n* is a factor that depends on the type of electronic transition (= 2) for  $mTiO_2$ ,

and (= 1/2) for CdS and CdSe/CdS SILAR sensitized mTiO<sub>2</sub> photoanodes.

B is a constant

 $E_q$  is the energy of the band gap

The linear segment of the Tauc plot can be extrapolated to give the x-intercept which represents the band gap energy of the material [217].

UV-Vis spectra were obtained using Perkin Elmer Lambda 750 UV-Vis-NIR spectrophotometer with a double beam deuterium and tungsten halogen light source and high sensitivity photomultiplier and peltier-cooled PBS detectors. The UV-Vis measurements were performed at the Université du Québec à Montréal (UQAM) Nanogam centre.

# 2.3.6.2 Results

Figure 2.22 shows the UV-Vis spectrum as well as the calculated Tauc plots of the quantum dot sensitized samples. Using this, we can conclude that the bandgap of the CdS sensitized photoanode samples comes out to 2.5 eV, and that of the CdSe/CdS sensitized photoanode samples is around 1.94 eV which agrees with reported literature [218-223]. The absorption spectrum is also seen to display the presence of Mie scattering effects which shifts the baseline to a rising line rather than a horizontal baseline, and thus the bandgap intercept considers this feature while determining the point of rise.



Figure 2.22 UV-Vis absorption spectroscopy, and (inset) Tauc plot of (a) CdS sensitized and (b) CdSe/CdS sensitized photoanode samples.

Next, we look at the UV-Vis spectra of the bare  $TiO_2$  photoanodes which includes the mTiO<sub>2</sub>, as well as the control anatase,  $aTiO_2$  and rutile,  $rTiO_2$  samples. This is shown along with the UV-Vis



Figure 2.21 Tauc plots for anatase (aTiO<sub>2</sub>), rutile (rTiO<sub>2</sub>) and mesoporous titania (mTiO<sub>2</sub>) photoanode samples with UV-Vis absorbance spectrum (inset).

absorbance spectrum in Figure 2.21. As expected, the absorbance edges for all bare-TiO<sub>2</sub> samples lie in the UV range between 3-3.2 eV. The mTiO<sub>2</sub> shows absorption between the pure

anatase and rutile based sample spectra possibly due to the large size distribution of the particles and varying crystallinity.

As a result, we have completely characterized the devices used in the context of this thesis. We conclude the uniform and homogenous application of anatase titania ETL layer using the commercial 18NR-AO paste, as also the deposition of quantum dots uniformly along the entire thickness of the ETL layer. Most importantly, no traces of impurities, especially ferro

magnetic were found allowing us to attribute any magnetic field dependent effects in PEC to electron dynamics in the system.

# 2.4 Summary

The characterization measurements, in conclusion, reveal that the synthesis and fabrication methods used resulted in successful photoanode devices as per requirement. The measurement results are summarized in Table 1 below.

Sample	XRD Phase	XPS Chemical Analysis	SEM Morphology	EDX Composition	UV-Vis Bandgap
mTiO₂	Anatase (JCPDS No.: 21- 1272)		Uniform thin film (~15-20 µm)		3.0 eV
aTiO₂	Anatase (JCPDS No.: 21- 1272)				3.1 eV
rTiO <sub>2</sub>	Rutile (JCPDS No.: 21-1276)				3.2 eV
FTO	Cassiterite (JCPDS No.: 14- 1445)				
ZnS/CdS@mTiO₂	Anatase (JCPDS No.: 21- 1272) with CdS major peaks	Ti 2p O 1s Cd 3d Zn 2p S 2p	Uniform thin film (~15-20 µm)	Ti, O, Cd, S, Zn Si, Mg, Al, Ca (from glass) F, Sn (from FTO)	2.5 eV

Table 1 Results of material and device characterization measurements.

				Na (precursor)	
ZnS/CdSe/	Anatase	Ti 2p O 1s Cd 3d	Nanoparticles (20nm to 450nm)	Ti, O, Cd, Se,	1.94 eV
CdS@mTiO₂	(JCPDS No.: 21-			S, Zn	
	with CdS	Se 3d		Si, Mg, Al, Ca	
		Zn 2p S 2p		(from glass)	
				F, Sn (from FTO)	
	major peaks			Na (precursor)	

Hence, the following conclusions can be drawn from this analysis:

- Anatase and rutile single-phase commercial nanopowder photoanodes presented their phase characteristics and correctly displayed peaks corresponding to anatase (JCPDS No.: 21-1272) and rutile (JCPDS No.: 21-1276) respectively.
- Mesoporous TiO<sub>2</sub> (mTiO<sub>2</sub>) based photoanodes crystallized in the anatase phase, while also presenting clear and sharp FTO peaks separately identified.
- QD sensitized mTiO<sub>2</sub> photoanodes displayed relative changes in peak intensity ratios indicating the presence of the weak diffraction peaks of smaller QD crystals which were overshadowed by the stronger peaks from the thicker mTiO<sub>2</sub> and FTO layers, confirming the deposition and penetration of QD crystals in the mTiO<sub>2</sub> layer.
- CdS and CdSe peaks were indicated by:
  - Broadening and splitting of the anatase (101) peak due to the closely located CdS peaks.
  - Changes in peak intensity of the FTO (110) peak at 26.59° (JCPDS No.: 041-1445) due to the presence of the CdSe peak.
- Cross-sectional SEM analysis revealed:
  - $\circ$  The morphology and quality of mTiO<sub>2</sub> thin films deposited on FTO substrate.
  - $\circ$  The doctor blade method resulted in a uniform film of ~15 µm thickness.
  - Strongly bound ETL layer of mTiO<sub>2</sub> to underlying FTO substrate and uniform adhesion across the interface layer.
  - EDX showed uniform and homogenous presence of QD crystal elements throughout the mTiO<sub>2</sub> layer.
  - No presence of impurities especially ferromagnetic in nature were observed in the elemental mapping.

- XPS clearly identified the presence of Cd 3d, S 2p and Zn 2p peaks in the CdS QD sensitized sample and an additional Se 3d peak in the CdSe/CdS sensitized sample indicating the correct intended bonding states of the QDs in the sample.
- XPS survey scans detected no presence of any impurities or spurious contaminants which are intrinsically magnetic (for example magnetic transition metals or rare earth metals) indicating that the magnetic response of the photoanode is due to a magnetically active material within the photoanode.
- UV-Vis absorption spectroscopy and subsequent Tauc plot analysis confirmed the bandgaps of mTiO<sub>2</sub>, aTiO<sub>2</sub>, rTiO<sub>2</sub>, ZnS/CdS@mTiO<sub>2</sub> as well as ZnS/CdSe/ CdS@mTiO<sub>2</sub> as consistent with literature.

# **3 PEC CHARACTERIZATION AND CARRIER DYNAMICS**

The materials and devices constructed in the previous section are designed with the purpose of using them in a three-electrode PEC cell in order to test the performance of the device in solar driven electrochemical hydrogen generation in an aqueous electrolyte. The measurements are taken both in the presence of, as well as without a magnetic field in order to comment on whether or not the application of the magnetic field has a positive or negative impact on the solar to hydrogen conversion efficiency of the device, and also to understand the different ways in which a magnetic field affects the processes taking place within the chosen electrochemical system.

This chapter provides a detailed overview of the electrochemical measurement techniques used to perform these evaluations, and then presents the results of the measurements performed on the devices prepared, immediately after introducing each technique. Finally, each section analyzes the results and offers probable interpretations considering both the mechanism of the measurement as well as any previous information from other measurements in order to pinpoint how the magnetic field influences the solar conversion efficiency of the device. We begin, however, with a detailed description of the PEC setup used and experimental procedure in the first section.

# 3.1 PEC setup

A standard three electrode electrolytic cell configuration is used for all PEC measurements. A borosilicate glass chamber with a quartz window for UV transmission from Adams and Chittenden Scientific Glass Coop with three electrode ports serves as the photoelectrochemical cell (show in Figure 3.1 (a) and (b)). The photoanode as prepared previously is used as the working electrode



Figure 3.1 PEC cell (a) and (b), and electrodes used (c) in the study.

(WE). The active area of the photoanode was marked off by covering the remaining area with epoxy. An area of ~0.2 cm<sup>2</sup> is targeted to form the active area. The counter electrode (CE) is either graphite, gold or platinum while Ag/AgCl is used as the reference electrode cell (show in Figure 3.1 (c)). A 2M solution of Na<sub>2</sub>SO<sub>4</sub> in DI water serves as the pH neutral electrolyte, while a 0.25M solution of Na<sub>2</sub>S.9H<sub>2</sub>O and 0.35M Na<sub>2</sub>SO<sub>3</sub> (pH = 12.5) acts as a basic electrolyte with hole scavenger (SO<sub>3</sub><sup>2-</sup>). The electrolyte in each case is purged with N<sub>2</sub> for 30 minutes to remove any dissolved oxygen that may interfere with measurements prior to use in experiments.



Potentiostat

Operating Setup (under illumination)

Figure 3.2 Components of measurement apparatus, and setup under illumination.

Illumination of the WE is done with the help of a Class AAA Solar Simulator from Sciencetech Inc equipped with a 300 W Xe Arc Lamp followed by an ASTM G-173-03 standard Air Mass (AM) 1.5G filter to produce a standardized solar spectrum which can be used to compare photoanode performance across experiments performed in literature. The incident power of the light source is set to an intensity of 100 mW/cm2 using a silicon pyranometer, a standard known as 1 sun. The electrochemical measurements were taken using a Gamry Interface 1010E single channel Potentiostat. This setup, along with the individual components of the measurement system is shown in Figure 3.2.

The measurements under the influence of a magnetic field are taken by placing a cylindrical N35 neodymium permanent magnet (75mm x 28mm) directly behind the PEC cell as shown in Figure 3.3, either one such magnet producing an 11 millitesla field at the sample site (designated as

11mT), or two such magnets joined together giving a 21mT magnetic field at the sample site (designated as 21mT).



Figure 3.3 (a), (b) Cylindrical permanent magnet used to measure PEC performance in the presence of a magnetic field.

This configuration is illustrated below in Figure 3.4 (a) showing the complete setup, as well as the layered structure of a PEC cell under bias along with images of the setup during measurement.



Figure 3.4 (a) PEC configuration for magnetic field measurement (on the left, structure of photoanode and components of PEC cell layered and under bias) (b) and (c) images of PEC cell with magnet behind illuminated photoelectrode from two angles.

We now describe in detail the process of performing a series of magnetic and non-magnetic measurements to define one complete experiment in this context.

# 3.2 Experimental procedure

A standard sequence of steps used in the case of each electrochemical measurement is detailed below. Additional steps unique to particular measurements are separately described in the section which describes the specific electrochemical measurement technique in detail.

- 1. The PEC setup is prepared on the electrochemical workstation and all connections are verified, and the potentiometer is turned on.
- 2. For the particular measurement under focus, all measurements are taken without the magnetic field applied to establish the baseline values.
- 3. The neodymium magnet is carefully and slowly placed behind the PEC cell as shown in Figure 3.4 (b) and (c).
- 4. The same measurements as performed in step 2 are repeated to obtain data for the device while in the presence of a magnetic field.

PEC performance of several prepared devices (mTiO<sub>2</sub>+CdS, mTiO<sub>2</sub>+CdS/CdSe and bare-mTiO<sub>2</sub> and also control samples with anatase (aTiO<sub>2</sub>), rutile (rTiO<sub>2</sub>) and bare-FTO was measured using linear sweep voltammetry (LSV) under the dark as well as with continuous and chopped illumination to determine the device's J-V characteristics. A one sun illumination power corresponding to 100 mW cm<sup>-2</sup> was employed in all cases.

Additionally, LSV measurements were taken both in the absence of an external magnetic field (designated as 0mT) and the presence of a magnetic field. Open circuit voltage (OCP) decay measurement and analysis was used to analyze the exciton generation and recombination dynamics and offered insights into the role of the application of a magnetic field on the recombination characteristics of the photoanode. Electrochemical impedance spectroscopy (EIS) provided information on carrier dynamics and participation of the different layers of the photoelectrode and the components of the PEC cell itself.

All measurements reported here were taken with the south pole of the magnet towards the sample since the polarity of the magnet did not seem to affect the performance characteristics. The polarity, as well as the magnetic field strength due to the magnet(s) at the sample position inside the PEC chamber was measured using a Lakeshore 425 gaussmeter. The gaussmeter probe was calibrated using a zero-gauss chamber before each measurement.

## 3.2.1 Linear Sweep Voltammetry (LSV)

### 3.2.1.1 Method

LSV is an electrochemical technique used to characterize the photocurrent response and the photoelectrochemical activity of a given photoanode. Features of the LSV curve such as the onset potential give information about the photoconversion efficiency. In the case of photoanodes where oxidation reaction occurs, the experiment is performed from a small forward bias potential with respect to the reference electrode, and the bias voltage is swept uniformly towards a reverse bias value.

The rate of sweeping is known as the scan rate and is also an important parameter that tells us about the PEC system under study. The most important of these is determining if a process or feature in an LSV experiment is due to a faradaic process (occurring at the photoanode involving charge transfer processes), or at the electrochemical double layer involving capacitive or charge storage processes. In the case of faradaic processes, the value of the peak current, or the current at a point of interest on the LSV curve (containing a feature like a peak, say) should vary linearly as the square root of the scan rate  $\nu$ , i.e.  $i \propto v^{\frac{1}{2}}$ . On the other hand, if the process is capacitive, it varies linearly with the scan rate, i.e.  $i \propto \nu$ .

The scan range, which is the initial and final voltage, is determined from the light onset potential determined from the open circuit voltage (OCP) decay measurement. The initial voltage is taken to be slightly higher than the light onset potential from OCP, while the final potential is taken as the dark onset potential which indicates the initiation of electrochemical processes even without illumination. This can therefore help to clearly distinguish between dark currents and photoinduced current. The experiment is then performed in the dark and illumination conditions to reveal the photoresponse properties of the system.

LSV measurements were taken from an initial voltage of -1.2V vs the Ag/AgCl reference electrode to a final voltage of 0.2V vs Ag/AgCl with a scan rate of 20mV/s and a step size of 1mV for all samples under investigation, in both the non-magnetized experiments as well as the measurements taken in the presence of a magnetic field at the photoanode site. These results were then converted into the standard voltages vs RHE using the relation [224]:

$$V_{RHE} = V_{Ag \setminus AgCl} + 0.197 + pH \times (0.059)$$
(26)

where:

 $V_{RHE}$  is the voltage vs RHE

 $V_{Aq \setminus AqCl}$  is the voltage vs Ag/AgCl electrode

pH is the pH of the electrolyte

In the case of the two electrolyte systems we are using, becomes:

$$Sulfite \setminus Sulfide: V_{RHE} = V_{Ag \setminus AgCl} + (0.9351)$$
(27)

$$0.5M Na_2 SO_4: V_{RHE} = V_{Ag \setminus AgCl} + (0.6106)$$
(28)

## 3.2.1.2 LSV characteristics for CdS and CdSe/CdS QDs on mTiO<sub>2</sub> ETL layer

The PEC configuration used was with the as-fabricated photoanodes as the working electrode, Ag/AgCl (saturated with KCl) as the reference electrode, and a Pt counter electrode. Figure 3.5 (a) shows the photocurrent density (J) vs potential (V vs RHE) curves in the presence of a magnetic field showing the progressive increase in efficiency of solar to hydrogen conversion efficiency from the bare mTiO<sub>2</sub> based device to the CdS sensitized device, the CdS/CdSe sensitized device, and finally the effect of a varying magnetic field strength on the performance of the CdSe/CdS based device from 11mT to 21mT. The CdSe/CdS sensitized device is already known to perform better in comparison to the CdS sensitized device from literature, as they have a larger spectral absorption bandwidth compared to only CdS quantum dots as well as better charge separation and transfer to the ETL layer owing to the stepwise energy level created by the CdSe and CdS layers [225] [226]. Additionally, it appears that even in the presence of a magnetic field (of 11mT), they have a better performance compared to the CdS sensitized devices.

Furthermore, the effect can be easily seen to scale with the strength of the magnetic field also seeing how a 21mT field is able to generate a larger photocurrent compared to the 11mT magnetic field for the case of the CdSe/CdS devices. The result, as can be seen in Figure 3.5 (b) is a remarkable increase in photocurrent density from 7.8 mA/cm<sup>2</sup> to 13.01 mA/cm<sup>2</sup> at 0.8V vs RHE, representing an increase in solar to hydrogen conversion efficiency of 67% for the CdSe/CdS sensitized photoaode.



Figure 3.5 Comparison of LSV performance characteristics of (a) different device configurations to an 11mT magnetic field and CdSe device to a 21mT field, (b) CdSe device (performance improvement) on application of a 21mT field vs without a magnetic field.

Even at lower magnetic field intensities of 11mT, the effect is quite pronounced in the case of both quantum dots employed, a feature critical to future real-world applicability of the phenomenon given strong magnetic fields are not often found in nature. As is visible from Figure 3.5, the photocurrent density at 0.8V vs RHE in the CdS sensitized device (Figure 3.5 (b)) goes from 4.87 mA/cm<sup>2</sup> at 0mT or without a magnetic field, to 6.09 mA/cm<sup>2</sup> in the presence of an 11mT magnetic field, an increase of 25% in solar to hydrogen conversion efficiency. Similarly, we see in the case of CdSe/CdS (Figure 3.5 (a)) that the percentage increase in performance at 0.8V vs RHE is 17%, from 7.31 mA/cm<sup>2</sup> at 0mT to 8.57 mA/cm<sup>2</sup> in the presence of an 11mT magnetic field.

Such an increase in performance of the photoanode with the simple application of a very low magnetic field is significant, considering that neither of the light harvesting materials, either CdS or CdSe are considered magnetic in their pure state, and at room temperature [227-230].

We now proceed to investigate a simpler photoanode, one without the light harvesting layer of quantum dots to see if the positive influence of a small magnetic field is still present, and the differences in the photocurrent response characteristics, if any, which could provide more insights into the exciton dynamics or charge transfer mechanisms playing a role in the enhanced performance of the photoanode in the presence of a magnetic field.

#### 3.2.1.3 JV characteristics of a bare mTiO<sub>2</sub> based photoanode

The interesting phenomenon observed with quantum dot sensitized mTiO<sub>2</sub> photoanodes in the previous section raises the question as to where within the photoanode (or even the PEC cell),

does the effect originate and what layers are being influenced (perhaps even more than one) by the presence of a magnetic field. As such, LSV measurements were performed to obtain the JV photocurrent characteristics for a bare mTiO<sub>2</sub> photoanode, to determine the response of the photoelectrochemical hydrogen generation performance to a small magnetic field. Figure 3.6 shows the JV photocurrent characteristics, particularly the light response without a magnetic field



Figure 3.6 LSV photocurrent characteristics for bare mesoporous TiO<sub>2</sub> photoanode without (0mT), and in the presence of an 11mT magnetic field; inset: photocurrent at 0.8V vs RHE showing increase in photoresponse in the presence of an 11mT magnetic field.

(0mT curve) as well as the light response in the presence of an 11mT magnetic field. From here we see that even in the case of the basic photoanode consisting of a thin film of mTiO<sub>2</sub> applied on an FTO substrate, we are able to see a marked response to a magnetic field towards the photoelectrocatalytic production of hydrogen. The increase in performance of the photoanode at 0.8V vs RHE is 37% which is considerably higher than the performance boost seen even in the quantum dot sensitized devices.

This is indeed an interesting observation and posits the question as to how the exciton dynamics are changing (if at all) in the presence of a magnetic field, considering that PEC water splitting for hydrogen generation is highly focused on the efficient generation and harvesting of excitons. Thus, it is important to take a look at the recombination dynamics of the photoanode using open circuit voltage (OCP) decay analysis which could provide insights into the regions in the photoanode (material bulk or surface/interface) where recombination is being affected, either positively or negatively to give rise to the JV characteristics observed.

#### 3.2.2 Time dependent performance enhancement

Another interesting feature of the magnetic response is the time dependence of the photocurrent improvement. In another experiment, the LSV measurements were taken for an mTiO<sub>2</sub> photoanode in a sulfite/sulfide electrolyte and a platinum counter electrode, after placing the magnet against the cell, every two minutes to see if the increase in photocurrent observed was immediate, or if it gradually increased over time towards a maximum saturation value. The results of this experiment are presented in Figure 3.7 for the case of a TiO<sub>2</sub> photoanode in a sulfite/sulfide electrolyte solution using a platinum counter electrode. The magnetic field strength used is 21mT corresponding to the best efficiency improvement seen till now. Figure 3.7 (a) shows the total increase in photocurrent before magnetization and after saturation of the magnetization effect, while Figure 3.7 (b) shows the time variation of the increase in photocurrent clearly showing that the magnetic field influence lasts for more than 30 minutes post application of the field. It is useful to note that we do not report the current density in this case, as the objective is to compare the same sample over an extended period of time, and as such, normalization to unit area is not required.



Figure 3.7 LSV time-dependent characteristics for mTiO<sub>2</sub> photoanodes in sulfite/sulfide electrolyte and a platinum counter electrode (a) light comparison before magnetization and at maximum magnetic current saturation, (b) time varying photocurrent improvement with initial pre-magnetization dark and light current in dashed line (Inset shows photocurrent saturation region zoomed).

This could be indicative of effects beyond spin dependent transitions, and a combination of processes within the electrode system and their interaction with the bulk could be affected, both by the magnetic field directly, and also due to the change in conditions brought about by the spin dependent effects. While a few candidates are discussed in the sections that follow, a deeper understanding is not within the scope of this investigation and is reserved for future projects.

#### 3.2.3 Control and blank tests

An important point to establish before any further investigation into the mechanics of the effect observed is the source of the magnetic field enhanced photocurrent. Related literature appears to consider the effect a property of the working electrode materials and a comprehensive and conclusive demonstration of the argument that the effect indeed originates from no other source in the system such as the counter electrode or ions within the electrolyte bulk does not exist to our best knowledge. Hence, it is important to consider experiments that unequivocally confirm that the photocurrent enhancement from the application of a magnetic field is attributed to the photoanode, or preferably a material layer within, after which further investigation can reveal deeper insights.

#### 3.2.3.1 Counter electrode control

First, we consider varying the counter electrode. Most importantly, the platinum counter electrode currently used is metallic in nature, and although not considered to be magnetic in the form it is used in the counter electrode, it is useful to eliminate it as a candidate. In that pursuit, therefore, LSV measurements under a magnetic field were performed using a gold electrode, as well as a graphite electrode without changing other components of the system, that is the electrolyte or the working electrode, where a bare mTiO<sub>2</sub> photoanode was used. This is shown below in Figure 3.8 (a) where the time varying nature is once again visible clearly. The total increment in photocurrent



Figure 3.8 LSV light characteristics of mTiO<sub>2</sub> photoanode with a (a) gold counter electrode, and (b) graphite counter electrode, under the application of a 21mT magnetic field. Pre-magnetization light and dark curves are presented as dashed lines as a baseline reference. Inset provides magnified view of photocurrent saturation region from 0V onwards.

at 0.8 V vs RHE is approximately 69% from 0.246 mA/cm<sup>2</sup> before magnetic field application to 0.414 mA/cm<sup>2</sup> almost 80 mins post magnetic field application.

Another set of measurements using a graphite electrode is shown in Figure 3.8 (b) where once again a smooth increment in the photocurrent is observed up to almost 40 mins post application of the magnetic field. From these results, it is clear that changing the counter electrode does not remove the magnetic field effect although it is regulated to a certain degree which can easily be attributed to the reactivity of the counter electrode and its effectiveness to catalyze the counter reaction. However, since the magnetic effect remains more or less consistent, we can say that there isn't a noticeable contribution from the counter electrode to the enhanced photocurrent from the application of the magnetic field.

#### 3.2.3.2 Electrolyte control

The second most important element of the PEC system whose contribution to the magnetic field assisted enhancement effect needs to be determined is the electrolyte solution, particularly the electrolyte bulk. The possibility of both the solvent ions as well as the dissolved ionic species interacting with the magnetic field and working 'usefully' to promote the reaction kinetics is indeed a possibility that requires investigation. In order to do so, we decided to investigate the mTiO<sub>2</sub> photoanode in a 0.2M aqueous Na<sub>2</sub>SO<sub>4</sub> solution (pH = 7) with a graphite counter electrode which is known to be both non-magnetic as well as does not leach ions into the electrolyte solution as is a risk with the standard platinum electrodes [231-233]. The advantage of this electrolyte solution



Figure 3.9 LSV light characteristics of mTiO<sub>2</sub> photoanode with a graphite counter electrode in a 0.2M aqueous Na<sub>2</sub>SO<sub>4</sub> solution, under the application of a 21mT magnetic field. (a) Comparison of light and dark premagnetization with maximum magnetized light photocurrent, (b) time evolution of magnetically assisted photocurrent enhancement with pre-magnetization light and dark curves presented as dashed lines as a baseline reference is that it does not contain a hole scavenger species. As a result, we can investigate to see if any special effects of hole scavenging while in the presence of a magnetic field are also responsible for the results obtained in the previous sections.

Figure 3.9 shows the results of the measurement showing both, the span of the photocurrent enhancement under a magnetic field influence in part (a) while also showing the time evolution of the photocurrent from minimum at zero magnetic field, to maximum at 40 minutes after the application of the 21mT magnetic field in part (b). The results are similar compared to the case of the sulfide/sulfite electrolyte presented earlier where the activity of the hole scavenger helps saturate surface state effects and a smoother curve is observed. However, there is still a distinct time variation with respect to the magnetic field, and the percentage increase in photocurrent is almost similar indicating that the effect of the electrolyte and the hole scavenger species towards the photocurrent improvement is minimal if any.

#### 3.2.3.3 Pure phase nanoparticles

While the mTiO<sub>2</sub> crystallizes in the anatase phase, it is a commercially manufactured paste with variation in particle size as well as sample purity. As such traces of rutile may be present, as also the presence of binders and additives. The surface morphology of the resulting thin film is also different, as well as the presence of defect states such as oxygen vacancy sites is known to exist in this system. It is thus important to understand if the pure phase nanopowders offer differing reactions to the presence of a magnetic field, and if so, the mere variation of the type of material in a layer of the photoanode presenting with varying results points towards the particular layer



Figure 3.10 LSV pre-magnetization light and dark, as well as maximum light photocurrent in the presence of a 21mT magnetic field for (a) anatase, and (b) rutile pure phase nanopowder based photoanodes.

being strongly influenced and contributing greatly to the photocurrent enhancement effects seen in the presence of a magnetic field. We present here, the LSV measurements obtained for the case of high purity anatase and rutile nanopowders with controlled particle sizes below 25 nm, and 100 nm respectively as prepared using the synthesis and device fabrication methodology given in chapter 2. The PEC cell configuration is the aqueous 0.2M Na<sub>2</sub>SO<sub>4</sub> and the graphite counter electrode, once again, offering the best combination of minimally magnetic components to be able to distinguish any features on the curve. The results shown in Figure 3.10, not only offer an extremely insightful picture towards the mechanics behind the magnetic field assisted PEC hydrogen generation process, but also indicate the sources of the effect quite clearly.

We can very clearly see that the anatase nanoparticle based photoanode has very minimal performance enhancement due to the application of a magnetic field. On the other hand, the rutile nanoparticles based photoanode has a very strong reaction, in the region before the photocurrent saturation, and partially within the photoactive region between -0.1V and 0.1V. Now, as stated before, of the two phases of TiO<sub>2</sub> considered here, the rutile phase has been demonstrated to be ferromagnetic especially due to the oxygen vacancy centres. Such defect centres usually appear as humps, or peak features in the LSV outside the photoactive region representing charge trapping and detrapping which lowers or raises the photocurrent from the baseline dark value. This is clearly what is seen in the case of the pure phase rutile based photoanode as well.

At the same time, it must be said that the manufacturer specifications indicate that these nanopowders are high purity and hence the presence of vacancy defects is minimal compared to commercially mass produced paste for economies of scale applications. As a result, the anatase nanopowder shows almost no response to the magnetic field retaining its original photocurrent profile, nevertheless offering a very small perturbation just outside the photoactive region pointing to the fact that some oxygen vacancies are inherent in TiO<sub>2</sub>, and defect free samples are of course, nearly impossible to produce. At the same time, device fabrication processes could also have equally introduced small quantities of defects which are inevitable.

We thus, now, have a sample set where the modification of one single layer, from the anatase to the rutile to the mTiO<sub>2</sub> takes the magnetic response from disappearance of the magnetic effect to strong enhancement of the photocurrent signal in the presence of a magnetic field. We have also established that the presence of defect states in the bulk and surface, most likely from oxygen vacancy centres strongly regulate the magnetic field effect observed in previous samples as well. The source of the magnetic field assisted PEC enhancement effect can be very strongly attributed to the properties of the TiO<sub>2</sub> layer alone, and its interaction with the various layers that it comes into contact with. Although this seems now well established, we will present a further modification

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of the photoanode setup to even more strongly demonstrate the importance as well as the contribution of the  $TiO_2$  layer to the magnetic field effect.

#### 3.2.3.4 Blank FTO

Finally, to confirm the extent of the contribution of the TiO<sub>2</sub> layer also to the magnetic field assisted photocurrent enhancement, a test was performed using a blank FTO sample as the working electrode, without either a photoactive semiconductor layer or an electron transport layer. This test is purely to test the LSV characteristics of the configuration with and without the application of an external magnetic field, and so greater analysis in this context will not be undertaken. As such, the result is presented, not in terms of current density, but rather in terms of absolute current values as measured by the potentiostat, considering the device could not be marked off with epoxy to determine a calculable active area since this exercise does not make sense in this context.

Secondly, the FTO sample was prepared using the same FTO cleaning procedures as for other samples, before application of the  $TiO_2$  layer using the doctor blade method (detailed in section 2.2.1). Post cleaning, the FTO sample was simply annealed in air at a temperature of 500°C for 30 minutes, as is the device fabrication procedure for the other photoanode samples also. Thus, the device received follows the same preparation conditions as the others to maintain



Figure 3.11 LSV pre-magnetization light and dark characteristics and maximum photocurrent characteristics in the presence of a 21mT magnetic field for a bare FTO working electrode sample.

consistency. The PEC analysis was then conducted using a cell containing aqueous  $0.2M Na_2SO_4$  as the electrolyte, and a graphite counter electrode similar to the pure phase nanopowders. The results of the LSV sweep are presented in Figure 3.11.

From here, is very clear that the FTO sample is not photoactive as is the expectation from literature. However, the effect of a magnetic field on the photocurrent also completely disappears. The photocurrent after the application of the magnetic field was tracked for about 22 minutes to keep the procedure consistent with the minimum time for saturation of magnetic field effect from previous samples. However, even after a long exposure to the magnetic field, no visible enhancement effect from the magnetic field is noticeable. Considering that merely the addition of the mTiO<sub>2</sub> layer to the same configuration of the PEC setup returns the strong magnetic field enhancement effect to the system, it is appropriate to conclude with the dataset acquired in this section, that the mTiO<sub>2</sub> ETL and photoactive layer is responsible for the influence of the magnetic field on the photoelectrochemical water splitting and hydrogen production.

## 3.2.4 Open circuit potential (OCP) decay

#### 3.2.4.1 Method

OCP decay measurements provide an invaluable tool to study the charge carrier dynamics inside the working electrode and the electrode-electrolyte interface including recombination kinetics, whether it is happening at the surface or bulk of the photoanode. It also provides insight on the efficiency of charge separation, charge carrier lifetimes as well as characteristics about the space charge layer, and the electrochemical double layer.

A standard experiment is performed by illuminating the photoanode to generate excitons in the bulk material while restricting the flow of current in the external circuit of the cell between the WE and CE. This is called the open circuit condition. As more and more excitons are generated over time, the electrons accumulate in the photoanode bulk, while the holes migrate towards the electrode-electrolyte interface and are consumed by the electrolyte. This creates an intrinsic electric field in the semiconductor bulk of the photoanode which is opposite to the electric field in the space charge region. As a result, the potential required to maintain an open circuit condition, OCP, becomes more cathodic with time.

As the photoanode is kept under illumination, the OCP value slowly becomes stable over time. The voltage value at which stabilization occurs is known as the photocurrent onset potential and is the minimum value of bias required at the photoanode to produce a noticeable photocurrent above the dark baseline. As this point is reached, the light source is switched off stopping the generation of new electron-hole pairs creating a cascade of photoelectron recombinations with the oxidized species in the electrolyte resulting in the OCP voltage following an exponential anodic decay. The decay of OCP towards its dark equilibrium value follows first order kinetics and is directly proportional to the number of carriers generated. The resulting curve can be described by the following equation:

$$V(t) = V_0 \exp\left(-\frac{t}{\tau}\right) \tag{29}$$

where:

V(t) is the OCP at time t

 $V_0$  is the initial value of the OCP which corresponds to the photocurrent onset potential

 $\tau$  is the time constant of the decay and is related to the recombination lifetime of the exciton

The characteristics of this decay can offer a lot of information about the nature of processes taking place within the bulk as well as the surface of the electrode. When the decay starts, the charge carriers trapped on surface states which include defects and vacancies are readily accessible to the oxidized species in the electrolyte. This results in a very short carrier lifetime on the surface and hence a greater time constant. While excess carriers in the bulk of the semiconductor have lesser density of recombination centers and have to diffuse towards the surface before they can recombine. As a result, the initial decay profile represents the rate of surface recombinations and on greater timescales, bulk recombination begins to dominate and therefore OCP decay profile on these time scales represents the bulk charge transport properties of the system.

OCP decay profiles were taken for a total time of 200 seconds, beginning with the sample illuminated at the start and allowing 25 seconds of illumination from the start of the experiment after which the light onset potential was found to be reached, and illumination was turned off. The sample period of the OCP measurement was set to 0.5 seconds.

#### 3.2.4.2 OCP decay characteristics and exciton lifetime analysis

The variation in JV photocurrent enhancement in the presence of a magnetic field suggests exciton generation and recombination dynamics at the photoanode and anode/electrolyte interface could be affected by the application of magnetic fields. Typically, TiO<sub>2</sub> on its own is known to have poor charge separation and transfer efficiency due to the large number of surface

states and defects sites which acts as nonradiative recombination centres for photogenerated excitons [234].

Additionally, the sensitization of TiO<sub>2</sub> with QDs such as CdS or CdSe/CdS can act to passivate the surface states, as well as reduce recombination probability through fast charge transfer, that even without the presence of a magnetic field can result in a very low level of recombination loss [226, 235]. As a result, the capacity for improvement in performance by reducing the recombination losses is highest in a bare mTiO<sub>2</sub> photoanode and lesser in CdS sensitized mTiO<sub>2</sub>, and the least in CdSe/CdS sensitized mTiO<sub>2</sub>. This behaviour is similar to what was observed in the JV analysis. Therefore, it makes sense to suspect that the recombination dynamics are being influenced by the application of a magnetic field. To further analyze if this is indeed the case, OCP decay characteristics were studied for each of the device configurations.

Figure 3.12 shows the OCP decay characteristics both without and in the presence of a 11mT magnetic field. Figure 3.12 (b) shows the two cases post light shutoff and with the curve normalized to the same starting point so that decay rates are directly comparable. From here is it



Figure 3.12 Open circuit voltage decay curves for bare mesoporous TiO₂ photoanode with and without the application of a magnetic field. (a) Complete sweep in light and dark, (b) decay characteristics after light shutoff normalised to the same starting point (inset: Exciton Lifetime vs OCP).

is quite clear that although in the presence of a magnetic field, the rate of exciton recombination is faster at the beginning, in the later part however, the magnetic field curve quickly catches up and eventually overtakes the decay curve without a magnetic field, after which the rate of OCP decay progresses much more slowly in the presence of a magnetic field vs without. This is a very important observation since the initial phase of OCP decay immediately after light shutoff is dominated by surface recombinations which follow first order kinetics according to the Shockley-Read-Hall (SRH) mechanism [236]. As such, these recombinations are dependent on the concentration of traps close to the surface, of which there are many, being made up of step edges, oxygen vacancies, line defects and Ti interstitials. In contrast, bulk excitons recombine via band-to-band mechanisms via the bulk defects which are significantly smaller in number, following second order kinetics which results in a comparably slower decay profile [237]. Additionally, in anatase, the photogenerated charge carriers can diffuse within ~1 ns from the bulk towards the depletion layer, while the application of a more positive potential can significantly increase the lifetime of photoholes to ~30 ms allowing a significant buildup of charge at the electrode surface [238, 239]. The surface recombinations are also very quick to die down, and once they do, the OCP decay curve is dominated in the later stages, by bulk recombinations [239-242].

This implies that the application of a magnetic field, in the case of a bare mTiO<sub>2</sub> photoanode, significantly reduces bulk recombinations, but increases surface recombinations due to the enhanced charge separation efficiency resulting in fast diffusion of the minority carriers to the electrode surface, resulting in a significant increase in the charge density at the surface. However, since both bulk and surface recombinations affect the photoresponse characteristics and performance of the photoanode in the JV measurement, which was observed to significantly increase, a possible reasoning keeping both the JV and OCP decay observations together could indicate that a significant reduction in bulk recombination could arise from an elongation of the lifetime of the bulk exciton, which makes it more probable to be separated into individual charges. The holes then migrate to the surface of the electrode, in much greater numbers resulting in an increase in surface charge density at the electrode/electrolyte interface [243].

Moreover, of the photogenerated electrons, a fraction are also driven towards the surface during irradiation and are trapped in surface traps [244-247]. This is owing to localized fields created by defect states near the surface, thermal excitations or even owing to high electron concentration in the bulk generating a concentration gradient which can overcome the internal electric field of the space charge region. When the holes migrate towards the surface, there exists a probability that some holes would recombine with the trapped electrons in the surface states giving rise to



Figure 3.13 Open circuit voltage decay curves for CdS quantum dot sensitized mesoporous TiO<sub>2</sub> photoanode with and without the application of a magnetic field. (a) Complete sweep in light and dark, (b) decay characteristics after light shutoff normalized to the same starting point (inset: Exciton Lifetime vs OCP).

the surface recombinations. The increased surface charge, as seen before, would therefore cause the rate of recombinations to also increase given that the surface recombination reaction follows first order kinetics which means that the rate of recombination is directly proportional to the number of free charges available.

In order to see if recombination kinetics are affected in the same way within the quantum dot sensitized devices, we present the OCP decay curves for CdS sensitized device in Figure 3.13. Over here we see that the decay characteristics represent a different story with the decay in the OCP due to a magnetic field being slower than the decay without a magnetic field for the complete period after light cut-off representing a significant reduction in both bulk and surface recombinations.

This can be attributed to the enhanced surface state passivation of SILAR quantum dots which generally reduce the active recombination centers on the TiO<sub>2</sub> surface resulting in a large reduction in the surface recombinations [240]. As a result, the contribution of surface states to the OCP decay, even in the initial phase after light cut-off, is very low in the case of surface passivated

photoanodes. In both cases, however, it is clear that bulk recombinations are reducing with the application of a magnetic field (from the analysis of OCP decay after ~80s). However, it is to be noted that the QD sensitization comes with the introduction of new surface defects from the QD crystal, in this case from sulfur vacancies in the CdS, however with the help of the wide band-gap ZnS passivation, these surface states are quenched significantly [248].

Next, we consider the OCP decay profiles of CdSe/CdS QDs sensitized mTiO<sub>2</sub> devices, presented in Figure 3.14. Here we can see that surface recombination phase in the initial decay region of the curve is nearly similar in the magnetic and non-magnetic measurements with the non-magnetic case even briefly outperforming the case with magnetic field. Here, it is relevant to mention that in the case of CdSe/CdS QDs, the surface defects owing to the heterojunction formation leading to lattice mismatch resulting in uncoordinated Cd atoms on the surface [249]. Even though, the introduction of a surface passivation layer can again quench these surface



Figure 3.14 Open circuit voltage decay curves for CdSe/CdS quantum dot sensitized mesoporous TiO<sub>2</sub> photoanode with and without the application of a magnetic field. (a) Complete sweep in light and dark, (b) decay characteristics after light shutoff normalized to the same starting point (inset: Exciton Lifetime vs OCP).

states significantly, there will remain a significant difference in the concentration of these states compared to CdS QDs, especially those which are also surface passivated. As a result, we see a brief increase in the surface recombination rate with a magnetic field, most likely arising from the increased surface charge as in the case of the bare mTiO<sub>2</sub> photoanode. The decay characteristics after the ~80s, where the magnetic curve decay is significantly slower than non-magnetic decay, supports the hypothesis that bulk recombinations, even in the case of the CdSe/CdS QD sensitized photoanodes, are reduced by the application of a magnetic field.

Another aspect of this decay that is interesting to note is the relationship between the exciton lifetime and the OCP (also referred to as  $V_{oc}$ ). These profiles are shown in the inset of Figure 3.12 (b), Figure 3.13 (b) and Figure 3.14 (b) for the case of bare mTiO<sub>2</sub>, CdS sensitized and CdSe/CdS sensitized mTiO<sub>2</sub> samples respectively. The relationship between the OCP and exciton lifetime can be described by the relationship [250]:

$$\tau = -\frac{k_B}{e} \left(\frac{dV_{OC}}{dt}\right)^{-1} \tag{30}$$

where:

au is the exciton lifetime

 $k_B$  is the Boltzmann constant

e is the electronic charge

At low photopotentials, which correspond to lower values of  $V_{oc}$  surface traps dominate the electron transfer kinetics and consequently influence the lifetime of the charge carrier while at higher photopotentials it is the bulk recombination that influence the charge transfer efficiency [251]. This happens mainly because of the low occupancy of the conduction band states owing to a lower Fermi level value at low potentials [252]. This again shows that in the case of the bare mTiO<sub>2</sub> device the lifetime of the charge carriers at the surface is significantly lesser in the presence of a magnetic field as compared to when there is no magnetic field, whereas at higher values of photopotential above ~0.4V vs RHE, the bulk recombinations are dominant at which point, the curve in the presence of an 11mT magnetic field is above the 0mT signifying an increased lifetime of bulk carriers in the photoanode.

Similarly, we see a marked improvement in the lifetime in the case of CdS and the CdSe/CdS sensitized devices as well. In addition, the trends observed with the OCP decay profile also fit well into the lifetime analysis. While the CdS devices clearly have a significantly higher lifetime across all photopotentials indicating a very low participation rate from surface trapping mechanisms, the trend with respect to CdSe/CdS although clearly showing a higher electron lifetime in the presence of a magnetic field, shows the curves almost touching each other in the intermediate region around ~1.1V vs RHE where the rate of surface recombination for the case of the curve in the presence of the magnetic field seems to reduce possibly indicating a faster saturation of surface states and slower takeover from bulk recombinations.

In fact, if seen clearly, this trend can be seen across all three types of samples in this region. Herein, the conclusion from Bisquert et al., 2014 could proffer an interesting possibility. They identify three distinct regions in the electron lifetime vs OCP profile where the intermediate region represents a Marcus Inverted Region causing the recombinations to increase with increasing photovoltage, which eventually reaches a peak rate and starts to again reverse. What is interesting here is that the marcus inversion region while clearly visible in the nonmagnetic curves, is almost non-apparent in the magnetic field curve. This could potentially point to the influence of the magnetic field on the surface state recombinations as well. Since the marcus inversion region occurs due to a competition between a driving force encouraging recombinations and an opposing driver from the lattice reorganization energy, it is possible that due to the magnetic field, an additional opposing force is acting on the charge carriers and the surface states. Since this is brought on by the introduction of a magnetic field, it is reasonable to consider that the opposition from the spin forbidden Pauli repulsion could act to reduce the Gibbs free energy change of the recombination reaction potentially bringing it to a peak earlier than in the nonmagnetic case. We now look to other electrochemical measurements particularly Electrochemical Impedance Spectroscopy (EIS) to further investigate the details of how a magnetic field influences a PEC system, especially one using a TiO<sub>2</sub>-derived photoanode for hydrogen generation.

## 3.2.5 Electrochemical impedance spectroscopy (EIS)

#### 3.2.5.1 Method

EIS is a technique to investigate charge carrier dynamics in electrochemical cells due its ability to distinguish between charge recombination, transport and diffusion processes unlike other electrochemical techniques where contributions due to these often overlap. EIS can separate these contributions in the form of equivalent resistances, capacitances and inductances, eventually describing the system in the form of an equivalent circuit model.

High frequency impedance response in the Nyquist plot is usually associated with Intrinsic charge carrier dynamics (inside the photoanode) while low frequency response is dominated by surface and interface charges.

Here we measure EIS in dark conditions while applying a small AC bias with an amplitude of 10 mV over a frequency range from 100 kHz to 10 MHz. In addition, a constant potential DC bias of 0.2V corresponding to the LSV voltage where the photocurrent is maximum and saturated is also applied and summed with the AC bias. A sampling rate of 10 points per decade is used.

The flat band potential can be determined from the Mott-Schottky (MS) curve that can offer insights into the surface charge of the electrical double layer which in conjunction with other
results could tell us about the bulk and surface recombination kinetics. MS analysis can also show the density of free charge carriers inside the space charge layer via the slope of the linear segment of the MS plot and is often an indicator of the reduction or increase in bulk recombinations depending on whether the space charge layer contains more or less free charges respectively [253].

MS measurements are performed under dark conditions from an initial voltage of -1V to a final voltage of 1V with a voltage step of 0.1V. An AC voltage of 10mV rms is applied at a frequency of 1kHz. A 30 second delay before measurement is used to condition the working electrode and stabilize the electrode before data acquisition.

The insights from OCP decay analysis can be investigated in greater detail as well as supported with more evidence from impedance spectroscopy which can further isolate the photoelectrochemical activity from the electrode into individual regions which react differently to a sinusoidal bias input. As such, we can separately observe the contributions from the bulk, surface and interface charge transfer dynamics. Herein, we present the results from EIS measurements using the Nyquist and Mott-Schottky (MS) plots for the bare mTiO<sub>2</sub> as well as the QD sensitized devices. All EIS spectra presented here are taken in the dark so as to not include interference from light induced effects.

#### 3.2.5.2 Nyquist analysis

We begin once again with the case of the bare-TiO<sub>2</sub> photoanode. Figure 3.15 shows the nyquist plot comparison for the measurement with as well as without the influence of a magnetic field. The Constant Phase Elements (CPE) are considered to account for any contributions from the experimental apparatus other than those that are electrochemically active (photoelectrode, counter electrode, reference electrode and the electrolyte). As such, the residuals from such sources can be included within these CPE elements. In both cases, two semicircles can be clearly observed, one representing the high frequency regime starting from the origin till ~10k $\Omega$ , and the second representing the low frequency regime at higher impedance values. It is known that the high frequency regime represents the charge transfer resistance in the bulk and space charge layer while the lower frequency semicircle represents the charge transfer dynamics at the electrode/electrolyte interface and alludes to the surface reaction kinetics representing the surface recombinations [254-257]. Thus, we can clearly observe the result of a magnetic field as reducing the impedances associated with both the bulk and surface processes. Reconciling this with the OCP decay observations as well as with LSV indicates clearly that the increased rate of surface

charge recombinations seen in OCP decay would need to come from an increase in the concentration of charge carriers at the surface since a decrease in charge transfer resistance across the electrode/electrolyte layer acts to quickly inject holes into the adsorbed species on the photoanode surface preventing the probability of their recombination with surface trapped electrons.

Therefore, in terms of representing the first order kinetics of the surface recombinations which is shown in Eq. (31) where  $k_{SR}$  is the rate constant of the surface recombination reaction and  $[h^+]$  is the concentration of charges (holes) on the surface. The observed reduction in the radius for the low frequency semicircle, acts to actually reduce the rate constant of the reaction,  $k_{SR}$ .

$$Rate_{SR} = k_{SR}[h^+] \tag{31}$$

Hence an observed increase in the rate can only be justified by a much larger increase in the hole concentration  $[h^+]$ . Consequently, this can result from an improved charge separation resulting in a greater number of charges diffusing to the surface layer. As a result, the number of electrons reaching the conductive substrate would also proportionately increase representing the observed increased in the photocurrent in the LSV measurements. This hypothesis is further supported by



Figure 3.15 Nyquist plot of bare-TiO<sub>2</sub> photoanodes take at bias voltage of 0.2V vs RHE in dark without a magnetic field (0mT) as well as in the presence of an 11mT magnetic field (inset is equivalent circuit) [224].

the reduced radius of the high frequency semicircle in the nyquist plot as well, which represents a reduced diffusion resistance in the bulk in the presence of a magnetic field which directly implies a reduced bulk recombination rate. We now consider the case of quantum dot sensitized mesoporous TiO<sub>2</sub>-based FTO photoanodes. The corresponding nyquist plots for the case of CdS and CdS/CdSe are shown in Figure 3.16 (a) and (b) respectively. From here, again we see that there are two semicircular regions (inset in Figure 3.16 (b) shows the semicircles in the case of CdSe/CdSe) in each case representing the high and low frequency regimes which correspond to bulk diffusion resistance and surface/interface charge transfer resistances respectively. Here also we can observe that the magnetic field significantly reduces both the bulk and surface recombination resistances and the resulting increase in charge separation and transport efficiency relates the observations made for these devices in their OCP decay profiles.



Figure 3.16 Nyquist plots for (a) CdS sensitized, and (b) CdSe/CdS sensitized mesoporous TiO<sub>2</sub> on FTO, comparing the impedance characteristics without (0mT) as well as in presence of a magnetic field (11mT). Inset in figure (b) is magnified region marked in the primary plot showing the semicircle region. Dashed lines correspond to extrapolation of arcs in low frequency regime showing nearly semicircular behaviour.

Another observation from the CdSe/CdS nyquist plots is the presence of multiple off-curve data points which essentially cause the semicircle to look extremely jagged. It is well known that the presence of surface irregularities in SILAR grown quantum dot films are major recombination centers for surface charges [258, 259]. The presence of these recombination sites especially in the CdSe/CdS quantum dots grown using the SILAR method is known to introduce inhomogeneities in the structure as well as distribution of the QDs on the TiO<sub>2</sub> films results in the generation of back electron and surface trap recombination sites on the device [260]. The presence of such irregularities work towards deviating the impedance characteristics of the electrode away from ideal semicircularity. Especially, for the case of uncontrolled defects that may arise during the SILAR growth process, these can show up in impedance spectroscopy plots in the form of extreme jagged features as can also be seen in the case of CdSe/CdS from Figure

3.16 (b) [261, 262]. This is clear from the initial section of the curve, where an association with smoothness and circularity can be seen and with the extrapolation of these sections (dashed lines in Figure 3.16 (b)), we see significant deviations within the points lying towards the low frequency region in the arc associated with the surface processes indicative of surface irregularities. Specifically, in the case of heterojunctions, the possibility of additional trap sites introduced by the lattice mismatch between the CdS and CdSe layers can also distort the smoothness of impedance curves by providing additional recombination and charge transfer pathways [263, 264].

We further investigate this relationship with the application of a stronger magnetic field of 21mT on the CdSe/CdS system considering it is the best performing system as per the J-V characteristic curves. We again observe a significant decrease in the impedance characteristics of the



Figure 3.17 Comparison of nyquist plot for CdSe/CdS sensitized TiO<sub>2</sub> photoanodes without a magnetic field and in the presence of a 21mT magnetic field. Inset shows high frequency characteristics in greater detail.

photoanode when magnetized, and when comparing with Figure 3.16 (b), the magnitude of reduction of impedance between the photoanode in the presence of a magnetic field is clearly greater with a 21mT magnetic field as compared to an 11mT magnetic field, showing a direct relationship between the strength of the magnetic field, a feature also clearly seen in the J-V characteristics for the CdSe/CdS sensitized samples. This further lends credence to the proposed magnetic field driven mechanisms on the mitigation of recombinations due to spin forbidden transitions.

#### 3.2.5.3 Mott-Schottky (MS) analysis

Analysis of the MS curve of a PEC photoanode can offer insights into the bulk charge dynamics of the system. As such, the analysis shifts focus to what insights can be gained through Mott-Schottky analysis. We begin with the analysis of the MS plot for the bare mTiO<sub>2</sub> electrode. This is shown in Figure 3.18. While the MS plot, based on the Mott-Schottky equation given below in Eq. (32), which predicts the curve to be linear especially in the region close to the flat-band potential where the capacitance is dominated by the depletion region, which is of course the case in an ideal semiconductor/electrolyte interface [265, 266].

$$\frac{1}{C^2} = \frac{2}{\epsilon \epsilon_0 A^2 e N_D} \left( V - V_{fb} - \frac{k_B T}{e} \right)$$
(32)

However, in the case of bulk semiconductors and mesoporous anatase, the presence of defect states and surface traps can cause charges to accumulate and distort the capacitance values, particularly as the voltages become higher towards the high anodic bias region of the plot. In addition, the porosity of the semiconductor materials can allow the penetration of electrolyte deeper into the semiconductor film modifying the dielectric properties of the film layer, hence impacting the capacitance behaviour [267-270]. These processes can cause the Helmholtz capacitance ( $C_H$ ) to nearly equal the space charge capacitance ( $C_{SC}$ ), resulting in deviations from linearity which manifests as multiple linear slopes on the curves as well as curvatures on the MS plot. These features are also clearly visible in Figure 3.18 (from approximately between 0.4V to 0.8V and again between 1V to 1.6V for the 0mT curve, and from 1.6V to 1.8V in the case of the 11mT curve).

While the slope closer to the flat band represented by the low anodic bias regime which is close to the flat band allows us to gauge the majority carrier density in the space charge region while at high reverse bias, the slope at higher reverse bias is determined by an additional contribution from the Helmholtz capacitance which is driven by the trap state density and minority carrier concentration given that as reverse bias increases, the space charge layer or depletion layer becomes smaller and smaller [267, 271, 272]. As such, we can comment using these features on the MS plot, the influence of the magnetic field on these charge transfer layers in the device. In Figure 3.18, we have considered the slope of the low anodic regime representing the majority carrier density in the space charge region. We can calculate the carrier density from the slope of the MS plot using the following relation:

$$N_d = \frac{2}{e\epsilon\epsilon_0 slope} \tag{33}$$

where:

 $N_d$  is the donor density of the carrier under investigation,

*e* is the elementary charge =  $1.602 \times 10^{-19}$  C,

 $\epsilon_0$  is the permittivity of free space =  $8.854 \times 10^{-14}$  F/cm,

 $\epsilon$  is the relative permittivity of the semiconductor material, in this case, TiO<sub>2</sub>, ~76 [273, 274],

*slope* is the slope of the linear fit of the MS plot in the region of interest.



Figure 3.18 Mott-Schottky plots for bare-TiO<sub>2</sub> without the application of a magnetic field and with the application of an 11mT magnetic field. Dashed lines are linear fit approximations for near flat band region used to determine the free charge carrier density in the space charge layer.

On calculating the slopes from the linear approximation from the dashed lines in Figure 3.18, we find that the values are:

$$slope_{0mT}^{maj} = -2.05 \times 10^{10}$$
  
 $slope_{11mT}^{maj} = -1.84 \times 10^{10}$ 

Where *slope<sup>maj</sup>* represents the MS slope for the majority carrier close to the flat band. From here as well as from Eq. (33), as the slope is inversely proportional to the free charge carrier density in the space charge region, it indicates that in the presence of an 11mT magnetic field, there is a greater density of free charge carriers in the bulk indicative of the reduction in bulk charge recombinations leaving a greater density of free charges available to permeate through the semiconductor material.

On the other hand, an analysis of the high reverse bias regime contains contributions from charges trapped in surface and defect states whose response to the applied bias at these voltages are greater than at low voltages where the bias is unable to provide enough energy to overcome the trap state potential barrier. As such, they do not contribute to the capacitance at lower voltages. The additional contributions from the surface state trapping and de-trapping dynamics essentially manifest in the form of a 'pseudo' flat band which, although does not physically represent the space charge characteristics of the device, still depends on the surface state



Figure 3.19 Slope characteristics for bare-TiO<sub>2</sub> photoanode based on high voltage linear section of the MS plot indicative of influence on Helmholtz layer capacitance and surface charge dynamics. Dashed lines are linear fit approximations.

dynamics, and therefore as a purely comparative tool can provide valuable clues to the behaviour of the minority charge carriers in this region [271, 275-277].

Figure 3.19 presents an approximate linearization of the slope at high reverse bias representing the contribution of the minority carrier to the MS plot. The immediate observation from here is the difference in relative slopes which can be once again calculated using Eq. (33) as follows:

$$slope_{0mT}^{min} = -1.28 \times 10^{10}$$
$$slope_{0mT}^{min} = -1.42 \times 10^{10}$$

with the superscript *min* representing that the slope is with respect to the high voltage regime. Immediately apparent is the nature of the slope as compared to the near flat band where the slope for the MS plot in the presence of a magnetic field was greater than the MS plot without the magnetic field. In this region, however, the plot without the magnetic field is greater than the one in the presence of a magnetic field. Along the same lines as before, this represents that the region under investigation essentially contains relatively fewer free charge carriers when a magnetic field is applied compared to when it is not. This could mean that free charges travelling from within the bulk of the semiconductor are eventually passivated before they have the time to reach the Helmholtz layer, either through greater and faster charge trapping or rapid recombination near the surface. Additionally, it could also represent a greater injection of charges to the redox active species or the hole scavenger species in the electrolyte as seen from the reduction in the nyquist semicircles for the same PEC system. Comparison with both OCP and nyquist indicate that all these process are enhanced from the application of a magnetic field, given the significantly higher charge density coming from the bulk.

Another useful insight that can be gained from the MS plot is the flat band potential at the semiconductor/electrolyte interface. In an n-type semiconductor, charge recombination typically delays the onset of photocurrent to more positive potentials which can efficiently promote charge separation [278]. As such a relative positive shift in the flat band potential of the device could indicate an increase in the rate of recombination of free charge carriers, however this observation is not uniquely associated with this cause and so the flat band potential shift needs to be correlated with other experimental data, such as JV analysis, OCP decay as well as impedance spectroscopy.

Magnetic Field (10 <sup>-3</sup> T)	V <sup>maj</sup> (V)	N <sub>d</sub> <sup>maj</sup> cm <sup>-3</sup>	V <sup>min</sup> (V)	$N_d^{min}$ $cm^{-3}$
0	0.428	$9.07 \times 10^{19}$	0.216	$1.51 \times 10^{20}$
11	0.441	$1.01 \times 10^{20}$	0.533	$1.37 \times 10^{20}$

Table 2 Mott-Schottky parameters for bare-TiO<sub>2</sub> photoanode without as well as in the presence of an 11mT magnetic field.

Table 2 contains the relevant parameters from Mott-Schottky analysis on a bare  $mTiO_2$ photoanode. From here we can observe the change in the flat band potential from the low anodic bias region close to the flat band to be ~ (+)13mV, while for the high reverse bias region, the relative shift observed is ~ (+)317mV. In the case of n-type mTiO<sub>2</sub>, surface states are deep hole traps formed at surface hydroxyl and surface oxygen vacancies, which at large anodic bias, usually release an excess of holes into the conduction band [279-284]. This sudden release of minority carriers near the surface, causes fast recombinations with majority carriers travelling from deeper in the bulk essentially quenching the free charge carrier density in the space charge layer causing the relative decrease in slope, but also causing the flat band potential to shift towards more positive values as can be seen from the flat band potentials for the minority carriers in Table 2 [285, 286]. As such, it is therefore evident from the Mott-Schottky curves of the bare mTiO<sub>2</sub> photoanodes without a magnetic field and in the presence of an 11mT magnetic field, that bulk recombinations are suppressed leading to an increase in majority charge carrier density in the bulk, whereas diffusion of the minority charge carriers towards the surface generates a large surface recombination rate decreasing the carrier density when potentials large enough to free surface trapped charges are released into the conduction band.

Of course, the comparative charge carrier density between the non-magnetic and magnetic case is important here. Consider that the slope (and hence free charge carrier density) of the MS plot when surface effects were not significant was greater in the non-magnetic case, while in the presence of the magnetic field, the situation is reversed with the magnetic slope becoming larger. This points towards another subtle process that could be taking place especially within trap sites both in the bulk and the surface. As already mentioned before, the density of trap sites is greater on the surface than in the bulk, particularly in the case of n-type TiO<sub>2</sub> systems. As such, trapping (as well as de-trapping) dynamics can also be regulated by magnetic fields using spin forbidden transition statistics as also mentioned earlier. If such a process were to happen in parallel, it would

cause the trap states to empty faster and also reduce trapping rates leading to a large increase in free charges in the conduction band, both electron and holes. This, given the higher order statistics of electron-hole recombination rate kinetics, would result in a greater rate of recombination, hence depletion of free charges. A model of this nature could then easily explain the reversal of free majority charge carriers being seen in the space charge layer when surface trap activation is present vs when it is not significant.

The analysis shifts towards the quantum dot sensitized photoanodes. Figure 3.20 shows the MS plots for the magnetic as well as non-magnetic measurements with the linearization performed in both the near flat band region as well as at the high reverse bias anodic region. As in the case of previous measurements such as the OCP decay, we again see here a minimal effect from surface states which is attributable to the surface passivation properties of SILAR grown CdS quantum dots.



Figure 3.20 Mott-Schottky plots for CdS sensitized TiO<sub>2</sub> without the application of a magnetic field and with the application of an 11mT magnetic field. Dashed lines represent the linear fit approximations of (a) low anodic bias region near the flat band, (b) high anodic bias with contributions from Helmholtz capacitance.

However, the differences in free charge carrier concentration are clearly visible with both the near flat band and high anodic regions as discussed previously in the case of bare mTiO<sub>2</sub> samples showing a considerable reduction in slope on the application of an 11mT magnetic field. The critical parameters for the MS plot of the CdS sensitized quantum dots have been tabulated in Table 3.

 Table 3 Mott-Schottky parameters for CdS sensitized TiO2 photoanode without as well as in the presence of an 11mT magnetic field.

Magnetic Field	$V_{fb}^{maj}$	N <sub>d</sub> <sup>maj</sup>	$V_{fb}^{min}$	$N_d^{min}$
(10 <sup>-3</sup> T)	(V)	<i>cm</i> <sup>-3</sup>	(V)	<i>cm</i> <sup>-3</sup>
0	0.531	$1.45 \times 10^{20}$	0.181	$2.36 \times 10^{20}$
11	0.532	$1.84 \times 10^{20}$	0.204	$2.61 \times 10^{20}$

Here again, we see a considerable rise in majority free carrier density on the application of a magnetic field, which carrier density can be seen to remain high even with the surface effects and Helmholtz capacitance coming in to play at higher reverse bias conditions. However, a very small surface recombination effect is still visible on comparing the change between  $N_d^{maj}$  vs  $N_d^{min}$ . While in the case of the non-magnetic measurement, the value changes by 63% of the value of  $N_d^{maj}$ , this change is just 42% of  $N_d^{maj}$  in the presence of an 11mT magnetic field, showing that the few remaining surface traps, when emptied, are still causing an increase in surface recombinations, while at the same time generating a much lower trapping rate given the high positive shift in flat



Figure 3.21 Mott-Schottky plots for CdSe/CdS sensitized TiO<sub>2</sub> without the application of a magnetic field and with the application of an 11mT magnetic field. Dashed lines represent the linear fit approximations of (a) low anodic bias region near the flat band, (b) high anodic bias with contributions from Helmholtz capacitance.

band potential visible from the extrapolation of the reverse bias region. Thus, we can conclude that for the case of CdS sensitized  $mTiO_2$  photoanode sample also, the results are consistent as with the bare  $mTiO_2$  and the previously observed measurements.

Lastly, we consider Mott-Schottky analysis for the CdSe/CdS sensitized mTiO<sub>2</sub> photoanode samples. The two regimes under investigation are presented in Figure 3.21. Here, as in the case of bare mTiO<sub>2</sub>, we see a significant reduction in slope with the application of a magnetic field, while at the same time observing quite a large change in slope in the high reverse bias region showing the re-introduction of some surface state activity from the CdS sensitized sample due to the reasons elucidated earlier. Additionally, the parameters calculated from the MS plot for CdSe/CdS are also presented below. The regular features are once again visible in the case of CdSe/CdS also reaffirming the observations made in the other measurements, viz. LSV, OCP and Nyquist. While at the same time, an increase of 109% in free charge carrier density is seen in the high reverse bias region indicating a significantly larger defect concentration compared to the CdS quantum dots. At the same time, this increase is limited to only 43% on the application of an 11mT magnetic field, indicating an influence of the magnetic field on the trapping/de-trapping dynamics of the photoanode material. What this is indicative of, is that even surface recombinations and trap state recombinations are being reduced by the application of a magnetic field due to spin forbidden transitions. However, charges at the surface are being depleted at a faster rate possibly owing to a much higher charge injection rate into the redox species in the electrolyte which is evident from the reduced interfacial charge transfer resistance in the nyquist plot for all three samples.

Magnetic Field (10 <sup>-3</sup> T)	V <sup>maj</sup> fb	N <sub>d</sub> <sup>maj</sup> cm <sup>-3</sup>	V <sup>min</sup> (V)	N <sub>d</sub> <sup>min</sup> cm <sup>-3</sup>
0	0.513	6.03 × 10 <sup>19</sup>	0.145	$1.26 \times 10^{20}$
11	0.522	9.16 × 10 <sup>19</sup>	0.197	$1.31 \times 10^{20}$

Table 4 Mott-Schottky parameters for CdSe sensitized TiO<sub>2</sub> photoanode without as well as in the presence of an 11mT magnetic field.

### 3.3 Chronoamperometry

#### 3.3.1.1 Method

Chronoamperometry, as the name suggests, is the analysis of the variation of the photocurrent with time. It is performed under a constant bias over the measurement period; however, the bias potential is initially applied as a step potential wherein the potential of the photoanode is near instantaneously ramped up from zero to the bias value and subsequently held constant. The current response to such a sudden stimulation offers many insights into the charge transfer kinetics of the system.

This measurement is often used to study the stability of the working electrode over an extended operating period, as has also been done here, but it can also be very useful to determine many aspects of processes taking place within the photoanode material. As an example, the variation of the bias potential can help identify if a given phenomenon is triggered due to defect or trap states since a stronger electric field within the material can help release trapped charges more easily resulting in a faster decay rate in the case of defect mediated processes.

In terms of device stability, the accumulation of charges (holes in the case of mTiO<sub>2</sub>), results in the corrosion of the electrode surface through side reactions with reactive species in the electrolyte, which can non-reversibly alter the electrode surface causing performance loss. High accumulation of charges at the interface due to slow transfer to the redox species can alternatively cause electrostatic and mechanical stress and can alter the local energy band structure such as the band bending causing the charge transfer rates to further reduce and recombinations to increase [287-290].

Chronoamperometry is used to investigate the long-term stability of the photoanode under continuous illumination without and in the presence of a magnetic field. The experiment is performed with a pre-step voltage as well as a constant bias of 0.9V vs RHE at which point the LSV photoresponse is saturated representing the maximum photo-potential of the system. A sample period of 0.1s is used and the measurement is conducted for 10800 seconds or four hours. The magnetic field applied is 21mT.

#### 3.3.1.2 Results

Figure 3.22 shows the results of the chronoamperometry measurements performed on a CdSe/CdS sensitized mTiO<sub>2</sub> photoanode both without and in the presence of a 21mT magnetic



Figure 3.22 Chronoamperometry measurements on an mTiO<sub>2</sub> photoanode in sulfite/sulfide electrolyte with a platinum counter electrode.

field. The measurements are performed in a sulfite/sulfide electrolyte system with a platinum counter electrode. In terms of absolute values of photocurrent, the magnetic field retains about 58% of the initial photocurrent value, while in the case of the photoanode measured without the application of a magnetic field, only 52% of the original photocurrent density remains after a period of four hours of operation.

The results of the long-term stability tests clearly show that the magnetic field prevents the accumulation of holes at the electrode surface promoting fast transfer of charges to the redox species possibly by preventing the chemical combination with corrosive species. This could happen because of spin alignment with the ionic adsorbate due to the magnetic field making chemical bonding unfavorable, and possibly favoring the charge transfer pathway which is mediated via energy and band alignment considerations. Additionally, the prevention of surface recombinations through spin forbidden mechanisms can also keep the photocurrent density higher, favorably impacting solar conversion efficiency. We can therefore confirm the effect of the magnetic field on the surface charges as well as the recombination at surface sites using the results from the stability study to further strengthen our arguments in conjunction with the results obtained in previous sections.

## 3.4 Summary

In summary, we conducted a variety of photoelectrochemical characterizations on photoanode devices in order to determine their response to a static magnetic field applied from directly behind the PEC cell, and in case any difference in PEC performance characteristics different from when no magnetic field is applied, investigate the underlying causes and determine the processes and components within the PEC system contributing to the observed difference.

The observed results and conclusions derived from them are summarized below.

- **PEC setup:** Three electrode glass cell with quartz window
  - Photoanode (working electrode): mTiO<sub>2</sub> as ETL layer and photoabsorption layer, mTiO<sub>2</sub> + (CdS or CdSe/CdS sensitization), pure phase anatase or rutile paste (from nanopowders) as ETL and photoabsorption layer used as a control, blank FTO as a blank control.
  - **Reference electrode:** Ag/AgCl.
  - **Counter electrode:** Platinum, gold or graphite.
  - **Electrolyte:** Sulfite/sulfide (SO<sup>3-</sup>/S<sup>2-</sup>) (pH = 12.5) and 0.5M Na<sub>2</sub>SO<sub>4</sub> (pH = 7).
- Illumination: Class AAA solar simulator with AM 1.5G filter.
- **Magnetic field:** Cylindrical neodymium permanent magnet generating field strength at sample site:
  - **11mT:** Single magnet
  - **21mT:** Two magnets attached
- Linear Sweep Voltammetry:
  - mTiO<sub>2</sub> bare photoanode showed a 37% increase in photocurrent density at 0.8V
     vs RHE in the presence of an 11mT magnetic field.
  - QD sensitized photoanodes showed photocurrent enhancements of 25% and 17% for the CdS and CdSe/CdS sensitized samples respectively.
  - Application of a 21mT magnetic field increased the photocurrent in a CdSe/CdS sensitized sample by a factor of 67% at 0.8V vs RHE.
  - This implies that magnetic fields enhance the PEC hydrogen generation performance across all devices.
  - Control and blank tests:
    - Magnetic field enhancement is observed when using different electrolytes across pH range and presence or absence of hole scavenger species.

- Enhancement effect is also observed when using different counter electrodes.
- This implies that the electrolyte and the counter electrode are minimally affected by the application of a magnetic field.
- Using pure phase nanopowders of anatase and rutile samples displays different degrees of photocurrent enhancement indicating that the working electrode and specifically the TiO<sub>2</sub> ETL layer is the major contributor towards the observed effect.
- The anatase nanopowder based sample showed almost no response to the application of a magnetic field offering a blank control test confirming the ETL layer in the working electrode as the source of the magnetic field effect.
- An additional blank control test with a bare FTO photoelectrode also displayed no visible effect on photocurrent density on the application of a magnetic field.
- Hence these control experiments indicate that the working electrode needs to be further investigated in order to better understand the processes and layers/interfaces that are influenced by the presence of a magnetic field.
- Time dependent photocurrent response is seen in all photoanodes that show an enhancement in photocurrent on the application of a magnetic field, where a gradual increase in the photocurrent density with time is observed for a period of up to 40 minutes after the application of the field.

## • Open circuit potential decay:

- Photoanode is held at the open circuit potential while being illuminated for a period of 25 seconds until the OCP stabilizes under illumination.
- Decay of the open circuit potential after shutting off illumination provides insight into the charge carrier lifetime and recombination dynamics.
- In the case of the mTiO<sub>2</sub> and CdSe/CdS sensitized samples, the OCP decay profile in the initial stages after light shut-off showed a faster decay in the presence of a magnetic field as compared to without a magnetic field.
- The faster decay rate eventually slows down and at longer time scales (>80s), becomes slower in the presence of the magnetic field.
- For the CdS sensitized photoanodes, the OCP decay when in the presence of a magnetic field always remains slower than when no magnetic field is applied.

- This implies that the magnetic field reduces recombinations in the bulk of the photoanode where majority of the charge carriers are generated, represented by the longer timescale decay of the OCP.
- The initial OCP decay regime is governed by surface recombinations which appear to be greatly increased due to the application of a magnetic field but could also be due to the increased surface charge density resulting from a greater migration of free charges from the bulk arising from the reduction in bulk recombination.
- Surface recombination rate is governed by first order kinetics and are directly proportional to the free charge density, and also the density of surface defect and trap sites.
- CdS quantum dots have a surface passivation quality and therefore does not present the free charges with the greater trap site density restricting the rate of surface recombinations.
- OCP decay measurements therefore support the hypothesis that the application of a magnetic field greatly reduces bulk recombination through highly efficient charge separation but may increase the surface recombination rate due to an increase in surface charge density.
- Nyquist analysis:
  - Nyquist plots were recorded for the mTiO<sub>2</sub> and the CdS and CdSe/CdS sensitized mTiO<sub>2</sub> samples were recorded between a frequency range of 100 kHz to 10 mHz.
  - Both low and high frequency semicircles in the nyquist plots of all samples tested reveal a reduction in the radii.
  - This indicates that bulk charge transfer resistance reduces as does the interface charge transfer resistance
  - This also indicates an increase in the double layer capacitance indicating an increase in surface charge density.
  - On correlating these observations with those made in the OCP decay experiment, it demonstrates that the magnetic field is able to prevent charge carrier recombinations overall through efficient charge separation at the generation site by a combination of spin forbidden transitions, and opposing Lorentz forces on oppositely charged carriers, as well as at defect and trap states at the surface through spin forbidden effects.

- Additionally, a higher accumulation of charges on the surface drives an overall greater surface recombination as well as charge injection into the electrolyte redox active species.
- Mott-Schottky analysis:
  - MS analysis showed a greater free charge carrier density in the bulk in the presence of a magnetic field indicating a lower rate of recombination.
  - At the same time the free charge carrier density for minority carriers at the surface was found to be slightly lower when a magnetic field is applied pointing towards a higher rate of recombination from a greater concentration of trapped charges as well as more efficient charge injection into the redox species in the electrolyte.
  - Shifts in flat band potential also indicated an increased efficiency of charge separation and migration within material bulk and a larger concentration of surface charges driving a high positive shift in flat band potential in the high reverse bias region for all samples.

Correlating with other PEC measurements, these observations explicitly state that the application of a magnetic field reduces bulk recombinations by inducing spin forbidden transitions and opposing Lorentz forces on oppositely charged carriers as a result of which a large accumulation of minority carriers takes place at the surface resulting in a higher absolute rate of surface recombinations. However, the higher concentration of charges on the surface also acts to efficiently discharge the accumulated carriers into the electrolyte redox species driving a greater number of electrode reactions which also manifests in the form of increased photoelectrocatalytic activity as observed in LSV photocurrent density.

## **4** CONCLUSIONS AND FUTURE OUTLOOK

In conclusion, this thesis analyses the results of the magnetic field enhanced photoelectrochemical performance of commercial mesoporous titania based photoanodes. The objective of the investigations performed is to understand the specific mechanisms that could be influenced by the presence of a magnetic field, using photoelectrochemical analytical techniques. Special attention is considered on surface and non-radiative recombination processes which are known to be a major contributor towards the inefficiency of third generation excitonic photovoltaic materials. At the same time, control and blank photoanode samples, as well as variation in electrolyte and counter electrodes are employed to understand the specific aspects of the PEC cell system that are affected by the application of a magnetic field.

We have successfully fabricated photoanode devices of thin film mesoporous TiO<sub>2</sub> on FTO glass substrate, as well as anatase and rutile pure phase photoanode as control samples, using the doctor blade method. The resulting devices contained a uniform and homogenous thin film ETL layer of TiO<sub>2</sub>, with thickness around 15-17µm as seen from cross sectional SEM analysis of the devices. Additionally, quantum dot sensitized devices were also successfully synthesized using the SILAR method to deposit QD systems of CdS and CdSe/CdS on already fabricated mTiO<sub>2</sub> device samples. The homogenous, uniform deposition of high quality and purity quantum dots were confirmed using EDX elemental analysis on cross sectional sample, bonding state of identified chemical species using XPS, and crystal phase using XRD. Optoelectronic properties of device systems were identified using UV-Vis absorption spectroscopy, and results were compared to literature to confirm the correct fabrication of device systems.

Photoelectrochemical analytical techniques were used to characterize the device performance in the absence and in presence of a magnetic field of varying strengths of either 11mT or 21mT. Linear sweep voltammetry measurements showed an increase in photocurrent density of up to 67% at 0.8V vs RHE for the CdSe/CdS sensitized photoanode in the presence of the 21mT magnetic field, also producing the highest recorded photocurrent among all the devices at 13.01 mA/cm<sup>2</sup>. The percentage increase in photocurrent density was seen to scale with the strength of the magnetic field, while QD sensitization even though presented with reduced percentage enhancement but showed greatly increased photocurrent density in absolute terms representing the most efficient of the devices tested in the presence of a magnetic field. This observation hinted towards the contribution of the large number of defect states particularly oxygen vacancies as a contributor towards the observed effect.

Furthermore, the increase in photocurrent density in linear sweep voltammetry was also observed to increase over time for 30 minutes before a saturation in the LSV curve was reached. This pointed to complex carrier dynamics being affected by the magnetic field. In addition, the magnetic field effect was seen with different electrolytes (sulfite/sulfide at pH 12.5 and Na<sub>2</sub>SO<sub>4</sub> at pH 7), and with different counter electrodes (platinum, gold and graphite), indicating that these components contributed minimally, if at all to the photocurrent enhancement in the presence of a magnetic field. The focus with this shifted to the working electrode, where control tests were conducted with pure phase nanopowders of anatase and rutile as the ETL layers. Here, we observed a difference in magnetic field response. While rutile which is known to be ferromagnetic owing to oxygen vacancies in the crystal structure displayed a larger enhancement in photocurrent density, anatase which is known to be more catalytically active to the PEC hydrogen generation process in comparison to rutile displayed almost no response to the presence of a magnetic field. Since the pure phase nanopowders were known to contain fewer defect centers compared to the commercial mesoporous titania which also crystallized in the anatase phase, this result indicated that the ETL layer in the photoanode contributed significantly, or perhaps even wholly to the photocurrent increase in the presence of a magnetic field. Finally, a blank FTO with no ETL or photoabsorbent layer was tested. This sample also displayed no noticeable change in photocurrent in the presence of a magnetic field compared to the absence of the field. Hence with this, we were able to conclude that the photocurrent enhancement phenomenon is completely contained within processes that involve the TiO<sub>2</sub> ETL layer.

Next, open circuit potential decay experiments were conducted to gain insight into the carrier lifetime and recombination dynamics within the mTiO<sub>2</sub> photoanode systems. In all cases, a significant reduction in exciton recombination was observed in the presence of a magnetic field during the later phase of the open circuit decay after shutting off the illumination source indicating that bulk recombinations were being significantly decreased by the magnetic field and charge separation efficiency in the bulk was enhanced. In the case of the mTiO<sub>2</sub> photoanode sample as well as the CdSe/CdS sensitized mTiO<sub>2</sub> sample, the initial phase of the open circuit decay was faster in the presence of the magnetic field than without. This feature, however, was not seen in the CdS sensitized mTiO<sub>2</sub> sample, where even the surface recombinations were seen to reduce with the application of a magnetic field. This observation was corroborated once again with the relationship between the exciton lifetime and the open circuit potential, which showed surface recombinations corresponding to low open circuit potential values showing lower lifetimes in the presence of a magnetic field values showing lower lifetimes at higher open circuit

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potential values were higher in the case of all samples tested. These observations offered clues to consider spin forbidden transitions as a probable cause as well as the Lorentz force from the magnetic field and applied electric field contributing towards fast charge carrier separation in the bulk, while at the surface, the greater accumulation of charges was thought to drive a faster rate of reaction despite opposition from spin forbidden forces resulting in increased recombinations owing to their first order kinetics.

In order to further investigate this proposition, electrochemical impedance spectroscopy was used. Nyquist analysis of all samples showed two distinct semicircles classified as low frequency corresponding to bulk diffusion and surface state dynamics, and high frequency corresponding to charge transfer resistance. With the application of a magnetic field, both semicircles were seen to reduce in diameter implying a lower resistance to charge transfer in the bulk which indicates an improvement in charge separation as well as charge transfer efficiency, and at the same time an increase in the double layer capacitance indicating a greater charge density at the electrode surface reconciling with the observations made from open circuit potential decay studies. The reduced low frequency semicircle in all cases also indicated a reduction in the charge transfer resistance at the electrode/electrolyte interface which can also be indicative of high surface potential displaying high levels of charge injection into the redox species in the electrolyte. In addition, a stronger magnetic field of 21mT further reduced the radii of the two semicircles in agreement with the magnetic field strength scaling observed in LSV experiments also.

Lastly, Mott-Schottky analysis was performed to determine the free charge carrier density and the flat band potential. In all samples, a considerable increase in free charge carrier density was observed in the low anodic bias region corresponding to the majority carrier density in the bulk indicating a high charge separation efficiency. The highest change in free charge carrier density from the surface to the bulk was observed, once again, with the CdSe/CdS sensitized sample which showed a 109% change without the application of a magnetic field, when comparing the low anodic and the high reverse bias carrier densities, which changed to 43% with the application of a magnetic field. At the same time, in the high reverse bias region, contributions from Helmholtz capacitance offered insights into surface and interface dynamics. The free charge carrier density in this region displayed a reversal of trend indicating greater charge capture at surface defect sites and higher recombinations at the surface and interface. Moreover, for the mTiO<sub>2</sub> sample, the flat band potential shifted by +13mV in the low anodic bias region and +317mV in the high reverse bias region under the influence of the magnetic field indicative of the contribution of surface traps in the overall performance of the system. In the CdS sensitized sample, the flat band

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potential shifted by a smaller value in both regions: +1mV in low anodic and +23mV in the high reverse bias showing the influence of the surface passivation property of these QD systems. The corresponding values in the case of the CdSe/CdS sensitized samples were +9mV and +52mV respectively. These flat band potential shifts support strongly the increased surface charge hypothesis stemming from a greater hole accumulation in the case of an n-type TiO<sub>2</sub> photoanode. While the reduced percentage increase in free charge carrier density from the bulk to the surface shows that even the surface recombinations are reducing in comparison due to spin forbidden transition effects, and possibly higher rates of charge injection into the electrolyte which reconciles with the reduced interfacial charge transfer resistance observed in nyquist plots.

Stability test of the CdSe/CdS sensitized photoanode were performed using chronoamperometry studies where a relative 52% reduction in photocurrent density was observed over four hours of operation in the presence of a magnetic field, while without the magnetic field applied the decay over four hours was 58% showing a better photostability under the influence of a magnetic field, due to fast capture of charges at the electrode interface preventing hole accumulation and side reactions with ionic species which results in reduced electrode poisoning and degradation.

Consequently, this thesis represents a simple method to enhance the efficiency of third generation photovoltaic devices for the conversion of solar energy into storable hydrogen fuel. The application small magnetic fields which are commonly found can be leveraged to achieve theoretical increments in efficiency of nearly 67% as demonstrated here. In fact, as a probable application of this research, we have also developed a solar panel that can be designed to fit around electrical transmission and distribution wires. This type of solution offers multiple advantages over conventional solar technologies if they can be properly realized. A preliminary market survey of 48 industry experts as well as electrical and transmission industry executives reveals that this solution could resolve problems with land acquisition, cost per kilowatt of energy production over the panel's lifetime, realize increase in demand projected over the next few years more rapidly and also reduce some regulatory requirements offering an exciting opportunity to produce a commercializeable product. This however represents only the beginning of the possible investigations that can be conducted into this system. More investigations into the effect of defect and surface states can help to further optimize the system. Also, investigations with eco-friendly QD systems also need to be conducted to further improve the environmental impact profile of the system.

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# **6** LIST OF PUBLICATIONS

# 6.1 Patents and Intellectual Property

V. Venkataraman, G.S. Selopal, F. Rosei, A method and system for photocurrent generation, in: W.I.P. Organization (Ed.), 2024.

# 7 APPENDIX

## 7.1 CONDUCTING WIRE ENCAPSULATED PHOTOVOLTAICS

The ultimate objective of any research undertaking should be to achieve real world applicability, either as a stand-alone new product, or as a part of existing systems where it is able to offer better performance and efficiency in comparison to the component currently being used. This would allow the knowledge gained from experimental work in the laboratory to be made useful to humanity and create value for the research effort. In a similar pursuit, a design for the application of magnetic field enhanced photocurrent phenomenon was conducted so that a practical way to bring this effect to commercial use where it could positively impact the energy generation ecosystem could be developed.

It is important to note here that even though the experimental analysis in the preceding chapters of this thesis relates to PEC hydrogen generation, the application of magnetic fields to simpler systems such as photovoltaic panels has also been reported in literature, as previously discussed. However, the practical application of magnetic field enhancement, even in the field of solar PVs does not exist to the best of our knowledge. In addition, PVs are the simplest form of solar energy harvesting devices, with PEC and other green hydrogen systems, often considered as PV systems with additional components. As such, the introduction of commercializeable designs for magnetic field enhanced solar PVs is a good starting point before more complex systems are considered. With that in mind, despite the consideration of PEC systems enhanced with magnetic fields in the previous sections of this report, the practical application and designs presented within the sections of this appendix will deal with PVs, which also represents a significant milestone.

In order to expose the photovoltaic materials to a magnetic field, one can simply add a layer of permanent magnets to a solar PV panel. The only problem with this solution is that it represents a large increase in cost through the addition of expensive, possibly rare-earth magnets to the system, but also a very heavy component considering the weight of neodymium magnets being high which could require a complete redesign of the structural elements of the panel's racking setup. An easier method is to look for places where the magnetism is already present, either naturally or through the human activity that is taking place there and the magnetic field is a by-product of this activity (essentially representing a net loss of energy). One such place, that immediately came to mind when considering this approach around electrical transmission and distribution wires. The idea of the present section is to introduce the proposed designs and their various embodiments that were conceived of in this direction.

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It is important to note that these designs are a preliminary idea based on the materials science aspect of the photovoltaic materials tested in the lab, with the intention of patenting towards further research and development. It is not a final product which has been extensively tested in the field, and as such questions of electrical and structural integrity which may arise are problems beyond the scope of this thesis which will be dealt with in future projects for further refinement of the concept. Items relating to electrically connecting the system or harvesting the generated photocurrent and injecting the electrical energy back into the transmission grid are also not considered at this point. While this chapter offers some idea to the desired properties of the materials, it does not provide a comprehensive justification or a very specific list of materials that have been tested and confirmed to function as desired.

## 7.1.1 The principal design

The simplest design one can imagine is that of a hollow cylindrical panel containing the solar photovoltaic around the outer surface of the cylinder, with the hollow being sufficiently large to tightly fit the conducting wire that it is intended to fit around. This can be seen in Figure 7.1, where



Figure 7.1 Principal embodiment with only a cylindrical shell.

the conducting wire has been shown in brown, the cylindrical panel body is in white while the solar cells are represented in red. This embodiment is the simplest representation of this idea. However, in terms of practicality, it may not be the best design considering it has a very small surface area and therefore will not represent a significant increase in power generation.

The properties of the material layers can be considered. The conductor is intended to carry high voltages, and as such, the material layers should be designed with these planned applications into account. Therefore, the most important material is the one in direct contact with the conductor.



Figure 7.2 Glass insulator used on a high voltage transmission line [291].

Of course, the material should be so chosen that it does not attenuate the magnetic field at the solar cell site so as to reduce the performance of the magnetically assisted photovoltaic effect of the panel. Secondly, the material in direct contact with the conductor should also be able to resist the high temperatures the conductors can reach while carrying high currents, especially in the case of ultra high voltage transmission wires. There may even be a requirement for the material to have the ability to regulate the temperature of the conducting wire, wherein the heat would be needed to be dissipated out through the contact layer through an as yet uncertain mechanism.

A simple modification can be considered to the principal design in Figure 7.1, which can help it increase its surface area to collect more sunlight. This new design with the modification is illustrated in Figure 7.3. The addition of 'fins' to the principal embodiment represents a slight increase in active area resulting in a significant increase in solar power output.



Figure 7.3 Principal embodiment with fins.

The challenge here is to maintain the weight of the fins in such a manner that it does not cause any additional loading stresses on the wire beyond the operating safety limits specified by the manufacturers. The design may also need to be tested for wind and snow loading, especially in colder regions. As such, the fins are not restricted at any angle with the main cylindrical part and can be adjusted to allow at least the snow to fall away more easily. As with the wind loading aspect, the fins may be designed to have more aerodynamic cross sections so as to minimally stress the wire.

### 7.1.2 Panels with multiple wires

The problems identified with the principal designs can be accounted for if the panel forms a structure along with the load bearing components of the transmission network, such as the towers. If so, then it would be judicious to design the panels to have a greater surface area to encompass all the wiring being contained inside a single transmission or distribution corridor. Such a design might even help increase the total wiring that can be installed for a given width of corridor giving it a greater power density that can help increase capacity in a relatively short period of time. Of course, this is speculative at present, but an interesting opportunity for future research.

The simplest design to create such a panel is shown in Figure 7.4. Not only does this embodiment allow for the greatest solar collection area of all the designs seen until now, but it also presents the greatest structural stability for the conducting wires given that it is able to integrate easily with the structural components of the transmission infrastructure, namely the towers. Again, this



Figure 7.4 Embodiment of solar panel with multiple wires.

design may not necessarily integrate with transmission towers as they are designed today, and one might need to either redesign these structures to synergistically fit the panels or complementary structures which are already designed with carrying large solar panels above them in mind can be leveraged. One such example is the solar carport shown in Figure 7.5.



Figure 7.5 Solar carport [292].

A slightly off-centre embodiment can be realized if the panel isn't required to be flat as in the case with Figure 7.5, but rather may gain several additional functions such as optimal tilt angle for maximum collection efficiency, one can be flexible with the angle between the panel segments between adjacent wires. Such an embodiment is demonstrated in Figure 7.6.



Figure 7.6 Panel with multiple wires and tilt between adjacent panel segments.

One can consider such variations if, for example, snow loading is a factor, or if more aerodynamic shapes are needed to effectively counter wind resistance as well as circulate air to cool the panels as well as the wiring structures. The option of which of the embodiments to use between Figure 7.5 and Figure 7.6 could also depend on the location, cost and structural considerations and as such the patent contained both possible configurations to include intellectual property rights for both inventions.

### 7.1.3 Internal variations

While the discussion up until now contain ideas for variation in the overall structure of the panel especially focussing on optimizing external parameters (surface collection area, weight etc.), one may also include variations to the design to optimize internal parameters such as heat from the wiring. A cross-section of the embodiment of two such variations is illustrated in Figure 7.7.



Figure 7.7 Internal variation in contact method.

An important aspect of the design is the need to cool the conducting wires. While this may also be accomplished with thermal cooling materials, the ability to cool the wires using a natural flow of air should also be considered. As such, the designs in Figure 7.8 contact the wires with the minimum contact area so that a large space is left for mechanisms that may allow for the free flow of air in this area from the outside allowing a natural cooling effect. The figure on top has the substrate material directly contacting the wire assuming that it has both electrical and thermal insulation properties. However, in the case this is not possible, the variation in the bottom picture can be employed where a special thermally insulating pad can contact the wire between the substrate and the wire.

The advantage of this method is that it can be used in conjunction with any of the previous designs showing variation in the external structure. Another advantage of this method is that the minimization in contact area also works to reduce the weight of the panel overall and lends to reduced structural strength requirements for all components involved. This could act to be another cost saving measure also for the system. At the same time, the ability to cool using natural air flow can also reduce the requirements of the materials used particularly the substrate which may not need to be as thermally insulating given that it would now be contacting the wire at a much lower temperature than if the heat had not been taken away by the air. Also, considering that air is magnetically neutral with a permeability of 1, it will not attenuate the magnetic field from the wire further reducing the need for special properties from the substrate. Such flexibility in material properties would result in lower cost materials being used further decreasing system costs.

#### 7.1.4 Multiple absorption centers

An important consideration for efficiency of a solar panel is the fraction of incident light absorption. The greater the value, the more efficient the solar panel is expected to be. The same is true for the embodiments considered here. With the principal cylindrical design, it is possible to construct or embed additional features into the panel that could absorb the reflected light from the primary panels exposed directly to the solar radiation. Most solar photovoltaic materials have an albedo that represents a loss of energy via reflectance [293, 294]. In order to recollect this reflected energy, the design of the panels can be modified to capture the reflected energy as shown in Figure 7.9.



Figure 7.9 Principal embodiment with multiple surfaces to collect reflected radiation.

The choice of materials would be done on the basis of the spectral reflectance of each previous layer to ensure that the most optimized materials are being used. While this might be an expensive and highly complex variation to design compared to the principal designs, it could prove useful in regions with low solar luminosity or less sunshine hours annually where extracting the maximum

energy from available sunshine is a path towards viable solar power generation. Weight of the solar panel might be an issue that will need special attention in this case.



Figure 7.10 Working principle of bifacial solar panel (p-type and n-type) [295].

A similar logic is exploited in the case of bifacial solar panels, where a transparent substrate allows radiation reflected by the surroundings such as the ground can be absorbed via incidence from underneath the panel (Figure 7.10). Theoretical increases in efficiency of bifacial solar panels are at anywhere between 10-20% from monofacial, but an operating efficiency increase of commercial bifacial solar panels is at least around 5-10% [296-299].

## 7.1.5 Electrically insulated embodiments

While it may be possible to get very close to the conducting wire for lower voltage applications such as distribution lines, the idea that for very high voltage and ultra high voltage transmission conductors, even with the best of insulation materials, it may not always be possible to get very close to the conducting wire without risking secondary failures such as arcing or overheating of



Figure 7.11 Embodiment with the photovoltaic surface far from conducting wire.

the contact layer. In such cases, designs that can structurally hold a solar panel with a large diameter, supported with insulating contacts to the conductor would prove useful.

This embodiment is illustrated in Figure 7.11 where a transmission line insulation stage, similar to the one depicted in Figure 7.2 is used to hold the panel far from the conductor. This embodiment ensures electrical safety and represents the ability to scale the concept toward higher voltage applications if the need arises to design the panel in this way. An added benefit of this variation is that the large diameter of the panel ensures a very large surface area over which solar radiation can be collected. Additionally, air flow cooling of the wire can be more easily achieved given the large space available within the panel's interior.

#### 7.1.6 Abstract and Claims

Resulting from the design ideas developed from the sections above, a PCT patent application with international publication number: WO 2024/073854 A1, was submitted with the following abstract and claims that represent the innovations done in the invention from the existing prior art [300].

#### 7.1.6.1 Abstract

A system and a method for photocurrent generation, the system comprising sheathed electrical wires supporting at least one photovoltaic cell, wherein the at least one photovoltaic cell is supported by an outer surface of an electrical sheath of the sheathed electrical wires, wherein the at least one photovoltaic cell on the electrical sheath produce photocurrent when exposed to light. The method comprises electrically insulated connection of sheathed electrical wires supporting photovoltaic materials to transmission wires of an operating grid, whereby the photovoltaic materials produce photocurrent when exposed to light. The method may comprise locating solar panels in electrically insulated connection with grid wires of a transmission network to both generate power from solar irradiation of the solar panels and transmit the power generated to end users on the transmission network.

### 7.1.6.2 Claims

List of claims filed in the patent application are as follows:

1. A system for photocurrent generation, comprising sheathed electrical wires supporting at least one photovoltaic cell, wherein the at least one photovoltaic cell is supported by an outer

surface of an electrical sheath of the sheathed electrical wires, wherein the at least one photovoltaic cell on the electrical sheath produce photocurrent when exposed to light.

- 2. A system as claimed in claim 1, wherein the electrical sheath is made in a material having a heat resistance in a range between 70°C and 150°C, and a magnetic permeability selected so that a magnetic field at a surface of the wires is at most a magnetic field at a surface of the at least one photovoltaic cell.
- 3. A system as claimed in claim 1, wherein the electrical sheath is made in a transparent material having a heat resistance in a range between 70°C and 150°C, and a magnetic permeability selected so that a magnetic field at a surface of the wires is at most a magnetic field at a surface of the at least one photovoltaic cell.
- 4. A system as claimed in claim 1, wherein the electrical sheath comprises at least a first layer of a material having a heat resistance in a range between 70°C and 150°C in direct contact with the electrical wires and a second layer of a material having a magnetic permeability selected so that a magnetic field at a surface of the wires is at most a magnetic field at a surface of the at least one photovoltaic cell, the second layer of a material supporting the at least one photovoltaic cell.
- 5. A system as claimed in claim 1, wherein the electrical sheath comprise a first layer of heatresistant ceramic in direct contact with the electrical wires and a second layer over the first layer supporting the at least one photovoltaic cell on selected surface areas of the outer surface of the electrical sheath, the second layer being made in one of fiberglass, carbon steel, a composite thereof, an alloy and a combination of alloys.
- 6. A system as claimed in claim 1, wherein the electrical sheath comprises a material having a magnetic permeability selected so that a magnetic field at a surface of the wires is at most a magnetic field at a surface of the at least one photovoltaic cell, and, selectively at contact positions of an inner surface of the electrical sheath with the electrical wires, a heat resistance in a range between 70°C and 150°C.
- 7. A system as claimed in claim 1, wherein the at least one photovoltaic cell comprises photovoltaic materials that display an increase in photocurrent in presence of a magnetic field of at least 0.5 mT.
- 8. A system as claimed in claim 1, wherein the at least one photovoltaic cell comprises at least one of: perovskite solar cells, dye sensitized solar cells, quantum dot sensitized solar cells and third generation solar photovoltaic cells.

- 9. A system as claimed in claim 1, wherein the electrical sheath is one of: a tubular sheath, a tubular sheath comprising radially extending wings, a panel sheath and a multi- surface sheath.
- 10. A system as claimed in claim 1, wherein the electrical sheath is made in a first material having a permeability selected so that a magnetic field at the surface of the wires is at most a magnetic field at the surface of the at least one photovoltaic cell, the first material being selectively coated an inner surface thereof with a second material having a heat resistance in a range between 70°C and 150°C at contact positions of the inner surface thereof with the electrical wires.
- 11. A system as claimed in claim 1, wherein the electrical sheath is made in a first material having a magnetic permeability selected so that a magnetic field at the surface of the wires is at most a magnetic field at the surface of the at least one photovoltaic cell, the first material being at least selectively coated at contact positions of an inner surface thereof with the electrical wires with a second material having a heat resistance in a range between 70°C and 150°C.
- 12. A system as claimed in claim 1, wherein the electrical sheath is made in a first material having a magnetic permeability selected so that a magnetic field at the surface of the wires is at most a magnetic field at the surface of the at least one photovoltaic cell, the first material being at least selectively coated at contact positions of an inner surface thereof with the electrical wires with a second material having a heat resistance in a range between 70°C and 150°C, the first material being further selectively coated on the inner surface thereof between the contact positions with the electrical wires with at least one third material selected as a photovoltaic material absorbing light in a selected electromagnetic spectrum range.
- 13. A system as claimed in claim 1, wherein the sheathed electrical wires are in electrically insulated connection with transmission wires of an operating grid, and magnetic fields generated by the transmission wires optimize photocurrent generation by the at least one photovoltaic cell on the electrical sheaths.
- 14. A method for current generation, comprising electrically insulated connection of sheathed electrical wires supporting photovoltaic materials to transmission wires of an operating grid, whereby the photovoltaic materials produce photocurrent when exposed to light.
- 15. The method of claim 14, comprising positioning at least one photovoltaic cell on an outer surface of an electrical sheath of the sheathed electrical wires, and electrically insulated connecting the sheathed electrical wires to the transmission wires of the operating grid, whereby the at least one photovoltaic cell on the electrical sheaths produces photocurrent when exposed to light.

- 16. The method of claim 14, comprising positioning at least one photovoltaic cell on an outer surface of an electrical sheath of the sheathed electrical wires, and electrically insulated connecting the sheathed electrical wires to the transmission wires of the operating grid, the method comprising selecting the electrical sheath in a material having a heat resistance in a range between 70°C and 150°C, and a magnetic permeability selected so that a magnetic field at a surface of the electrical wires is at most a magnetic field at a surface of the at least one photovoltaic cell, whereby the at least one photovoltaic cell on the electrical sheaths produces photocurrent when exposed to light.
- 17. The method of claim 14, comprising selecting a photovoltaic material that displays an increase in photocurrent in presence of a magnetic field of at least 0.5 mT, selecting an electrical sheath in a material having a heat resistance in a range between 70°C and 150°C, sheathing electrical wires in the electrical sheath into sheathed electrical wires, the electrical sheath comprising at least one photovoltaic cell in the photovoltaic material on an outer surface thereof, and electrically insulated connecting the sheathed electrical wires to the transmission wires of the operating grid, the method comprising selecting the material of the electrical sheath with a magnetic permeability selected so that a magnetic field at a surface of the electrical wires is at most a magnetic field at a surface of the photovoltaic material.
- 18. A method for current generation, comprising locating solar panels in electrically insulated connection with grid wires of a transmission network to both generate power from solar irradiation of the solar panels and transmit the power generated to end users on the transmission network.
- 19. The method of claim 17, comprising selecting a photovoltaic material that displays an increase in photocurrent in presence of a magnetic field of at least 0.5m for the solar panels.
- 20. The method of claim 17, comprising forming the solar panels by photovoltaic cells supported on an outer surface of the sheathed electrical wires, for magnetic field enhanced photocurrent generation from the transmission wires of the operating grid using a magnetic field generated by the transmission wires of the operating grid as solar power produced by the photovoltaic cells is converted to electrical energy.

We have therefore successfully developed a first application of our research observations detailed in the previous chapters, realizing a solar panel design to fit around electrical transmission and distribution conductors, and various embodiments that can offer avenues to issues that may arise during further product development.

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### 7.2 MARKET VALIDATION

The first step towards successful commercialization of a novel product designed from physics developed in a laboratory, often referred to by the category 'deep tech', is to present to any potential funding sources, the presence of a sufficiently large and viable market for the technology idea. The best method to determine the existence of such a market is to conduct a survey on the most severe problems present in the industry selected as a potential market segment and to demonstrate a direct ability by the product to solve the problems, known as a problem-solution fit.

The survey activity for the proposed solar photovoltaic panel described in the previous section, known as a market 'validation', was performed under the Lab2Market program, a joint initiative of the Natural Sciences and Engineering Research Council (NSERC) of Canada, which was a 16-week long program. Under the program, interviews with potential customers identified through secondary market research were conducted to try to establish a problem-solution fit. The results of the exercise are given in the sections below.

### 7.2.1 Background and secondary market research

As previously described in section 1.7, the major problems concerning the solar power generation industry as well as the electrical transmission and distribution industry were identified using secondary market sources such as market research reports, studies, and peer-reviewed articles. Information from these sources were used to determine hypotheses around possible stakeholders to approach for primary market research as well as the possible problem statements to compare against to form a problem-solution fit. From this exercise, land acquisition, land location (close to transmission grid), efficiency and cost per kilowatt, carrying capacity of the current transmission infrastructure, and delays and hinderances from policy requirements were the most severe issues the two industries were considering immediate solutions for.

### 7.2.2 Primary market research

As part of the NSERC's Lab2Market program, primary stakeholders from the industries identified as potential future customers for the technology were engaged through online platforms such as LinkedIn, email, trade shows and conferences. A significant number of the interviewees were connected with at the site of three major conferences: the IPPSA 2023 conference at Banff, Alberta; the GES 2023 at Calgary, Alberta; and the Re+ 2023 conference at Las Vegas, Nevada. A total of forty-two face-to-face interviews were recorded over online platforms such as zoom meetings and google hangouts while a few interactions were conducted in-person. About five

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interviews were recorded indirectly as part of panel discussions at the conferences. The data was then codified to identify parameters such as pain area and problem severity (high pain severity to happy) so that the data could be analyzed for patterns. From the data collected, we can now analyze the results as follows below.

## 7.2.3 Results

## 7.2.3.1 Market

Our secondary market research indicated that the most promising market segments to target as potential customers for our solution are T&D (Transmission and Distribution) and Solar EPC (Engineering, Procurement and Construction) companies. Since T&D would eventually need to be involved as they own the infrastructure over which our panels would be installed, we decided to consider engaging with them directly in order to determine if a problem-solution fit existed with our solar panel design. At the same time, we also realized the prospects of EPCs considering their close working relationship with T&D entities, which would allow us an alternate pathway to engage with T&D operators in the case where they were not immediately receptive or enthusiastic about the idea.

## 7.2.3.2 Transmission and Distribution

The landscape of T&D operators can be divided into the TSOs, or Transmission System Operators, as well as the DSOs, or Distribution System Operators. Entities like Hydro-QC or BC-Hydro who operate across both spectrums can be labelled TSO-DSO. We were successful in talking to several TSOs, DSOs, TSO-DSOs, as well as representative organizations such as Electricity Canada, ENTSO-E (Europe) and SEPA (US).

We observed that organizations in this space can be of multiple types. Crown corporations (in Canada), or public sector utilities whose majority stakeholdership lies with a government entity, designated as public entities, privately operated entities where the stakeholdership lies with a board and private investors, ISOs or Independent System Operators, who are regional entities and RTOs or Regional Transmission Operators who handle larger geographies with interstate interconnects under their management. The latter two are mostly regulated and controlled by the government. DSOs are generally smaller and can be either public or private.

Considering the novelty of our solution, and the maturity of the technology for readiness being low, we found that most private operators, either TSOs or DSOs, were reluctant to take on the

risk of engaging with a new and untested technology. Our meeting at FortisAlberta, a DSO operating in the state of Alberta (AB) raised concerns regarding the structural safety of the solution and pointed out that if we proposed to install the panels on existing towers, it would not pass wind and snow loading requirements. They also pointed out that almost 80% distribution poles in AB were wooden and did not have a large load bearing capacity.

Hydro One, a TSO-DSO rejected the idea stating that the consequences of failure are very high, and they do not allow any third-party systems even on their right of way. The current policy is to restrict farming as far as possible. In very extreme cases, parking spaces are permitted since they consist of minimal structures and in very rare cases community gardens and railway lines are permitted to pass across their right of way.

Others such as Equs, a DSO and AESO a TSO-DSO were more receptive towards innovations but imposed strict conditions on safety including electrical and structural as well as the need for a strong business case to be proven beyond doubt before being able to engage actively in installing the solar panels along their infrastructure. These responses convinced us that privately owned TSOs/DSOs would not be able to commit to installing our solar panels even on a test case basis unless preliminary data and performance statistics had been collected from elsewhere and showed the technology to perform as claimed while being both safe and reliable. We therefore do not consider them to be our early adopters.

Next, we consider the case of publicly owned TSO-DSOs which can vary in scale from the small municipal operators to large provincial and state level or regional ISOs and RTOs such as Hydro-QC. We were able to secure interviews at Hydro-QC (including Hilo) and Tampa Electric (including TECO Energy) who were both very excited at the prospect and realized the value the technology would provide if developed successfully. Additionally, these organizations have funds dedicated to innovation projects, and also have dedicated facilities for testing and experimenting with new electrical technologies including high voltage systems.

In addition, these entities are well recognized in the industry and trusted for their evaluation of new technologies and certification of compliance for new technologies. Their participation and assent to our solar panel would provide the confidence in smaller and privately owned players to invest in the solution. We would therefore consider public TSO-DSOs/ISO/RTOs to be our early adopters.

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#### 7.2.3.3 Solar EPC

Solar EPCs are almost exclusively privately owned companies and work on contracts from TSO/DSOs as well as generators (operators of power generation facilities) in constructing new solar projects, and sometimes these companies also have the expertise to construction transmission and distribution infrastructure giving them a connection to the TSO/DSOs.

The advantage we have with these entities is that they are regularly competing with each other in the market and need to constantly innovate in order to outpace the competition. As such, they have a broad portfolio of products that can be leveraged for compatible designs that could integrate well with our concept and solution, and at the same time they are also looking for new solutions to present to their customers to appear unique from their competitors.

In the first case, opportunities such as the solar carport and Heliostation from VCT group offers us a structure ideally suited to support our solar panels on top. On talking to three executives from VCT, they were all confident that these structures could as easily be placed one in front of the other for many kilometers on end with our solar panels on the top. This is advantageous to us since VCT have already structurally qualified their design and have also approved its structural safety from the relevant government authorities, leaving us with only the task of assuring the electrical safety of our panels.

Similarly, other EPC companies working particularly in the solar racking space were found to have such parking canopies in their product portfolio at the Re+ conference, and almost every one of them were keen on developing further products based on their designs. Many were also keen, as VCT, on sharing technology development costs since they are able to receive tax credits, or SRED credits for such activities. We, therefore, consider these EPCs also as our early adopters.

We now analyze the responses of interviewees against our identified pain areas. In the following section, we consider each hypothesis separately and consider its validation/invalidation on the basis of data collected from our conversations.

### 7.2.3.4 Land

Table 5 presents the responses from all interviews conducted which reference problems with land. What is interesting to note here is that since land is such an important component of the solar energy generation ecosystem, as well as the T&D ecosystem, issues with land are always high priority wherever they are referenced. We have observed a similar case in our conversations as well.

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From our analysis, we see that land is a major problem for nearly 68% of all respondents interviewed. The ways in which land problems arise are different for different entities though. While TSOs mostly consider that generation facilities should be located closer to the transmission network, solar generators contend that connecting to the grid is difficult because ideal solar sites are located far away from consumption centers where the grid is prevalent.

Worries from environmental agencies over the utility of the land and the ecology of the surroundings is also often cited as issues complicating the acquisition of land for solar projects. Lastly conflicts with agriculture, sometimes mining, and often also the local population is a very real problem that delays or at times even terminates a solar project.

Considering that we are able to successfully avoid the problem of interconnect closer to load and existing grid, as well as remove the requirement of acquiring new land for constructing solar projects, and in the case of environmental impact reduce considerably the assessments considering the T&D land already has several of these assessments conducted, we are ideally suited to offer a solution to this problem. We therefore conclude that our hypothesis that our solar panel offers solutions to the problems of land acquisition stand validated.

Organization/Affiliation	Remarks
Electricity Canada	<ul> <li>Idea is non-intrusive (big plus)</li> <li>No shadow impact</li> <li>Right of way is 10m on each side at least can be used for maintenance</li> </ul>
Aquatera Utilities	<ul> <li>Dealing with the utility can be difficult</li> <li>Lots of bureaucracy to connect to grid</li> <li>Hence generation is preferred close to load</li> </ul>
Alberta Electric System Operator	<ul> <li>Very poor interconnects to existing network</li> <li>Cost of expansion is not borne by developers</li> <li> Close to load is preferred</li> <li>Utility of land is lost</li> <li>Prime farmland being taken</li> </ul>

#### Table 5 Interviews referencing issues with Land

	•	Scalability needs huge amount of land
FortisAlberta	•	Backlash against solar Takes away fertile land Oil and gas contaminated land (fear of repetition)
Renewable Ene Services	rgy •	Good sites aren't abundant Large land area required (2 sq. Mi. For 150 mw) Conflict between surface and mineral rights holders Decommissioning security to the landowner Wetlands> wetlands assessment report> time, money and delays Auc rejected foothills solar facility because it was near a lake affecting migratory pathways of birds Can affect economics
Renewable Ene Services	rgy •	Grid interconnects create land issues
ENTSO-E	•	Location very distant from load no space for storage < complicates project
Burns & McDonnell	•	Foundation and soil requirements limits areas where projects can be developed Acquiring land is a concern> conflicts with farmland
Korea Hydro and Nuck Power	ear •	South Korea is not favorable for renewables Hilly terrain and uneven topography limits where solar can be installed
Greengate Energy	•	Level of literacy on energy is low in the population < causes conflicts Greater collaboration with community is required

• Microsoft	Partnerships with indigenous are crucial < special case for Canada/north America where land ownership is disputed by first nations Adoption is a big challenge
• Cenovus Energy	Development with indigenous communities is critical for successful renewables implementation
• Energera Inc.	Land use is a critical issue with renewables, particularly solar
• Innergex •	Land acquisition is a major issue Solutions like solar on landfills have been tried however these are not large enough to scale
• VCT Group	Depending on project type, cost of land and availability of right of way are major barriers to renewable energy
• VCT Group	Compared to rooftops, land is a major problem for utility scale projects Customers who have large land cannot connect to grid
• Énergie Solaire Québec	In qc, more power lines are needed which are not popular with the local population Projects next to grid network takes years to get govt. Approval Solar farms can't be constructed next to client (TSO)
• ENTSO-E	Solar farms are trickier due to competition with agriculture Public acceptance is also not favorable
CanMet Energie ●	300 remote communities are not connected to north American grid

•	Zoning and permitting is complicated due to land use issues for project developers
• The Nevar Company •	Nimby-ism is a serious problem Rural land with grid capacity is hard to acquire> people need to be educated Can't build on core forest Agri-voltaics need to be integrated with bee farming, goat farming, maple trees
Tampa Electric •	Land is very expensive close to load
• Tempa Electric	Most facilities are very far away Battery/storage next to load is also difficult
• Hydro-Quebec •	Long-term capacity planning does not take into consideration ecology, local population and the environment First nations need to be consulted> layer of complexity Markets like India and Japan are ideally suited for this type of solution
• BrightNight	Land is a major problem Competition with wetlands and agriculture
BBA Consultants	Ideal solar sites are far away from transmission network Expanding transmission is a very expensive and time consuming proposition involving bureaucracy
• Skyfire Energy Inc.	Ideal solar sites are in rural, far flung areas Network interconnect is very complex in these cases
Charge Solar	Big talk about redeveloping the Toronto transmission system

- Project will require reworking the land use planned 80 years
   ago
  - Ideal test case for implementation

## 7.2.3.5 Cost per kilowatt / Efficiency

Table 6 collects remarks from all interviews conducted which consider low rate of Rol, or break even, as well as high capex since it includes the risk and the uncertainty of quick recovery, increase in efficiency/performance of panels given that would increase hourly revenues and therefore recover costs faster. Of special note is the case for TSOs/DSOs who are concerned about having to expand the grid network to connect new far flung renewable projects given that the costs for these expansions are often borne by the TSO. References to this issue has also been highlighted as a validating data point in Table 6.

Here again it is interesting to note that the idea of efficiency or its financial implications, as well as cost recovery, is a very high severity issue wherever it is referenced. This is due to the fact that solar (and most renewable energy sources), are capital intensive, requiring a large upfront investment before even a single watt of energy is generated from the project. Therefore, long investment recovery cycles make the project unviable as it introduces risks and uncertainties.

We are able to see here that close to 78% of respondents referenced this issue in some form or the other as described in previous sections, revealing that this pain area is a topic of major concern and effective solutions are being explored very seriously. We see that while solar generation companies consider the capex investment as a major hurdle, TSO/DSOs who are majorly tasked with interconnecting new projects to their existing infrastructure are interested in reducing the upfront costs associated with the expansion. Both references have been identified as giving a positive fit to our hypotheses and are included in the analysis for cost and profitability related validations. Another interesting aspect of cost that came to light were the costs associated with regulatory approvals. While uncertainties related to policy and regulation are considered as a separate pain area, the associated cost for approvals and paperwork are also discovered to add to the returns equation. Given that our solution works to reduce costs (from land, approvals, permitting etc.), while also delivering enhanced power, it manages to resolve two variations of this problem. We can thus also consider the hypothesis related to efficiency or Rol successfully validated.

Organization/Affiliation	Remarks/statements/notes
Hilo/Hydro-Quebec (Formerly)	<ul> <li>Main issue in qc is the lack of investment in the network</li> <li>They didn't invest (on expansion) at the right time spikes causes equipment damage and loss of energy&gt; inefficiency</li> <li>Increasing capacity is very expensive</li> <li>Technologies such as bricks which heat up during low demand and heat the house during spikes disconnecting the house from grid and demand have been tried</li> <li>Building one more dam will take millions of dollars and at least 15 years to come online</li> </ul>
Electricity Canada	<ul> <li>Cost effectiveness is a valuable prospect only if it does not complicate the system</li> <li>Line loss calculations are built into the system during planning</li> </ul>
Aquatera Utilities	<ul> <li>Board is pushing for green, waste to energy solutions connecting renewables to grid is very expensive</li> <li>Shortage in physical assets&gt; projects are delayed!</li> <li>Break even for large investment project is currently 30 years, whereas 10-15 years would have been reasonable</li> </ul>
Equs	<ul> <li>Equs is a policy driven board</li> <li>Focus is on efficiency, cost effectiveness and quick turnaround</li> <li>Conversation on solar is around efficiency and independence</li> <li>Members currently pay a premium for line losses</li> </ul>
Alberta Electric System Operator	<ul> <li>Energy density is an issue with renewables</li> <li>Cost of connecting to grid is often borne by utility/TSO</li> <li>Royalty for TSOs on renewable energy is needed to incentivize</li> </ul>
FortisAlberta	<ul> <li>Project should make economic sense</li> <li>Transmission generated project makes economic sense due to economies of scale</li> <li>Tif - municipalities create a fund and it is added to tax</li> </ul>

#### Table 6 Interviews referencing Cost and Profit issues.

• Renewable Energy Services •	Interconnecting capacity is a cost burden, and nobody wants to pay for it BC hydro projects are overbudget cost> hesitancy to engage in renewables New technology should offer better cost per mw can your tech track the sun? If so, efficiency might improve
• Renewable Energy Services	Bifacial panels are new upcoming technology which claim 15-25% increase in performance, but only deliver 10% realistically Tracker systems would add to efficiency and revenue reactive power is an issue> causes losses
• Burns & McDonnell	Important considerations are recovery mechanism, financial goals and rate of return Storage technologies is a concern for cost recovery if it is not treated as load (i.e. Customer pays> cost amortized)
• VCT Group	Virtual net metering incentivizes to build more solar making it more efficient Residential solar: returns are not great because size is limited Utility solar: needs a lot of upfront capital Increase in performance would interest the market
Southern Alberta Institute of Technology	Return on investment is a critical factor Spurred interest in bidirectional/bifacial solar panels
• Quanta Canada Renewables	Cost competitiveness and pricing models have made renewables more lucrative over the years More innovation is required in battery chemistries and more efficient power delivery
Energera Inc.	Critical problems with renewables today are storage, economics and land use
Canada-ASEAN • Business Council	Capex (capital expenditure) is an important issue with renewables particularly solar
Criterium Energy •	Growth depends on whether or not you can add value
Petronas Canada	Carbon offsets and carbon credits (ITMOS) can improve Rol
Schneider Electric	Interconnection of grid is expensive Increasing grid capacity for lesser cost is crucial

• Energir •	Drivers of qc grid is economics and security solar cost is still a bit higher than grid Net metering is capped to 50 kw> disincentivizes residential Major cost factors: installation and engineering (soft costs) Rooftop solar as no utility cost
Quebec Solar	Connection studies and permits come at a hefty price for utility solar Some components are very costly Net metering is limited to 50kw
VCT Group	Cost is a barrier to solar Prohibitive entry and capital expenditure means we have to pay for whole system to produce energy upfront Going to grid is very expensive Major cost items: panels, system balancers, labor Work on cashflow and rate of return is crucial
• VCT Group •	Challenges to renewables is return on investment how many years to pay off? Capital intensive: pre planning capex, cost to connect to grid Monofacial to bifacial improves efficiency (even 10% increase itself is enough to interest industry)
Canada-ASEAN Business Council	Asean mainly dependent on coal, oil and gas G7 grant of \$15 billion will help eliminate coal and incentivize renewables
• Charge Solar •	Availability and pricing of solar products are out of control Interconnection with utility is expensive and time consuming Convincing customer to take risks on LCOE is hard since cost to upgrade utility is eventually transferred to customer
Énergie Solaire Québec	Solar cost is getting lower but still higher than hydro More investment in power lines needed
ENTSO-E •	Increased efficiency in solar is what people are looking for

• CanMet Energie •	Wind is more cost effective than solar now Economic viability crucial for project developers Installed costs, performance and efficiency (e.g. Bifacial) government funds help
• Studio X •	Optimized performance very important Power processing capability is poor and needs to be increased
Arizona Public Services	Buy back is getting smaller Supply chain is a problem which makes the system cost more
Wolfe Research	How quickly can you recover investment (5-10 years ideal) Utility scale challenges: pricing and locking in a fixed rate
• Skyfire Energy Inc. •	Utility scale projects are delayed costing cad 30k per day in damage Reduced losses is a big win Carbon tax is challenging
• Ontario Energy Board	Challenges: investment, cost recovery and managing of risk Losses in transmission network are huge

## 7.2.3.6 Capacity vs Demand

Table 7 encapsulates the interactions which reference Grid Capacity, Grid Reliability, or Increasing Power Demand. Around 45% of all respondents touched upon this subject. Secondary research data also shows this issue to be a serious matter of concern within the industry. It is interesting to note that almost all T&D entities interviewed flagged this subject as a major concern of high severity. Given that this market is one of our early adopters identified, we would like to state that solving this problem would give us a great advantage in pitching our product more successfully to future T&D customers. We therefore see immense value in adding the proposed feature to make our panel wiring suitable to carry transmission/distribution current to offer additional pathways to route power.

### Table 7 Interviews referencing grid Capacity as an issue.

<b>Organization/Affiliation</b>	Remarks/statements/notes
Hilo/Hydro-Quebec (Formerly)	<ul> <li>In qc, power is the issue</li> <li>Demand higher than supply</li> <li>5% dam capacity kept on standby to account for this&gt; lost opportunity cost</li> <li>Coming of EVs will further kill the network</li> </ul>
FortisAlberta	<ul> <li>Challenge is that capacity is too less, in fact, it is completely exhausted</li> <li>Interconnect problems require bigger wire, which is a big expense</li> </ul>
Direxyon Technologies	<ul> <li>Congestion is a major challenge to the expansion of renewables</li> <li>Bad quality of batteries restrict the capability of expansion</li> </ul>
Renewable Energy Services	<ul> <li>Interconnecting capacity - major problem - nobody wants to pay for it</li> </ul>
Renewable Energy Services	<ul> <li>Challenges: grid interconnect to T&amp;D is straining capacity</li> </ul>
ENTSO-E	<ul> <li>Southern Germany has a gap in generating capacity compared to central Germany</li> <li>Europe needs deep electrification for high efficiency gain (EV, heat pump)</li> <li>Implied more electricity</li> </ul>
Schneider Electric	<ul> <li>Challenges to renewables: interconnection of grids and grid capacity</li> </ul>
Energir	<ul> <li>Hydro-qc needs more winter capacity</li> <li>Qc needs: 25 TWh by 2030 and 100 TWh by 2050 additional</li> <li>Dams take 10-15 years to commission</li> <li>Wind installations to be 1200 mw by 2030&gt; only 10 TWh</li> </ul>
VCT Group	<ul> <li>In the case of utility scale solar, we have customers with large land, but grid is not able to handle the additional generation</li> </ul>

Charge Solar	<ul> <li>Application timelines to connect to utility are very large</li> <li>Fill out a form to request to see if the capacity exists</li> <li>Project above 10 kw need connection impact assessment</li> <li>Above two items itself cost cad 10k just to apply</li> </ul>
Énergie Solaire Québec	<ul> <li>Challenges: sources other than hydro face issues in hookup to grid network</li> <li>Hydro-qc transmission capacity is pretty full</li> </ul>
CanMet Energie	<ul> <li>Challenges: how do we integrate renewable energy sources in Canada's grid</li> </ul>
Ontario Energy Board	<ul> <li>Capacity is a pain area with solar energy</li> <li>Certainty is a problem which needs to be solved with renewables</li> </ul>
Southern Alberta Institute of Technology	<ul> <li>Grid reliability and availability are the biggest challenges to renewables</li> </ul>
Canada-ASEAN Business Council	<ul> <li>Grid balancing is a major issue restricting renewables</li> </ul>
Tampa Electric	<ul> <li>Capacity/demand is increasing faster than construction can keep up</li> </ul>
Tempa Electric	<ul> <li>Capacity is not sufficient given demand projections</li> </ul>
Hydro-Quebec	<ul> <li>Long term capacity planning is not well integrated</li> <li>Balancing supply and demand is a challenge</li> </ul>

## 7.2.3.7 Policy / Regulatory

Table 8 lists the interviews where issues with policy or regulation particularly related to its frequent volatility as well as uncertainty in the long term is brought up. We observe that our solution, although does offer some level of insulation from these risks, cannot entirely protect from them.

We observe that especially in the case of EPCs, who do most of the paperwork related to permitting and clearances, the problem always comes up. Considering our technology to be a

multi-use solution, we feel we are offering this market segment, one of our early adopters, a useful value addition. We consider the hypothesis validated for the specific case of the Solar EPC market segment.

Organization/Affiliation	Remarks/Statements/Notes
Faure	Oil Royalties are still dominant
Equs	Restrict growth of renewables
Alberta Electric System Operator	<ul> <li>They should create a royalty on renewable energy use for example for TSOs/ISOs</li> <li>Subsidies disrupt the market causing reliability issues</li> </ul>
	Climate neutral by 2050
ENTSO-E	<ul> <li>Upgrading AC to DC line&gt; permitting procedure is as if it is new line</li> </ul>
	• Supply chains are subject to regulations, sanctions
Burns & McDonnell	<ul> <li>Permit logistics influence project lucratively</li> </ul>
VCT Group	<ul> <li>Virtual net metering in the US incentivizes to build more, whereas in Canada Feed in Tariff encourages old projects to be upgraded.</li> <li>In Canada, you are not incentivized to build more than you require</li> </ul>
Enserva	<ul> <li>Policy towards Biofuels has forced \$10 Billion worth of Biofuel investments to leave Canada for the US</li> </ul>
Greengate Energy	<ul> <li>Lack of commitment to and end goal in renewables</li> <li>2050 net zero is too far away and policy may change in the interim&gt; industry cannot plan on this long a timeline</li> </ul>

 Table 8 Interviews referencing Regulatory and Policy issues.
Energir	<ul> <li>Hydro-QC has imposed regulatory barriers in QC for Solar</li> <li>Net metering is capped at 50KW per year consumption</li> </ul>
Quebec Solar	<ul> <li>Lots of overseas manufacturing due to policy&gt; Supply delays</li> <li>Approvals by Utility is very slow</li> <li>Utility scale: Grid connection studies come at a hefty price</li> <li>Net metering limited to 50 KW</li> </ul>
VCT Group	Barriers to renewable: Prohibitive entry
VCT Group	• Paperwork for regulatory connection, space on the grid a major challenge
Charge Solar	<ul> <li>US putting sanctions on China&gt; good for Canada</li> <li>Chip shortage problem caused up to 20 month delay for some projects</li> <li>Application timelines to connect to utility still very high</li> <li>Incentives change frequently as in the case of residential solar for example where energy auditor has to do testing&gt; can take months in rural areas</li> </ul>
The Nevar Company	<ul><li>Regulations change frequently</li><li>Typical permitting cycle is 2-3 years</li></ul>
Wolfe Research	<ul> <li>Government incentives are a challenge to navigate State level net metering&gt; California changed rules recently</li> <li>IRA is uncertain&gt; prevents long term commitment</li> </ul>
Skyfire Energy Inc.	<ul> <li>Policy uncertainty is a major challenge</li> <li>Carbon Tax is challenging</li> <li>Canada green grants is very good.</li> </ul>

## 7.2.4 Threats and Risks

The largest threat to the development of the product at this stage is from electrical safety concerns. Handling high voltages safely is a difficult engineering problem even in normal cases and specialized materials may need to be employed. The effort will of course, always be to minimize the use of exotic materials which may be rare and expensive, and to that effect, we have even proposed a few design variations on the technology that naturally take care of this issue, however these have not yet been tested and proven.

The next biggest risk comes from our conversations with T&D operators such as Hydro One and DSOs such as FortisAlberta who expressed a certain inertia with major changes to their infrastructure. In each case, they stated that the current T&D poles are structurally insufficient to handle the loads, and generally they would not allow any third parties to install/erect untested and unverified equipment on their property. This requires rigorous testing of the technology and the generation of long-term usage data to be able to convince these players that the technology is ready for use.

Finally, given that the system we are proposing would completely disrupt the mechanics of construction and installation of new transmission lines, we would need to develop and train the human resources to be able to handle this change. This would also introduce a new threat in the form of resistance from traditional contractors and construction workers who may not be open to spending the time and effort related to learning the new techniques for installation of our panels. The ideal scenario would be to try and prefabricate as well as use on-site automation for installation as much as possible, something that would need to be considered at the design stage as well as when manufacturing techniques are being explored.

## 7.2.5 Status of validation

From Secondary Data analysis, we were able to identify a suitable set of Market Segments consisting of:

- 1. Electric T&D Utilities (including TSO/DSO)
- 2. Solar EPC, especially those with products in Racking

Extensive Secondary Data Analysis revealed the following set of problem areas which we were ideally suited to tackle with our Solar Panel solution:

- 1. Land
  - 1.1. Acquisition of land close to consumption/load.

- 1.2. Conflicts with connecting to the grid.
- 1.3. Conflicts with alternate land use (agriculture).
- 1.4. Conflicts with local population.
- 1.5. Environmental concerns.
- 2. Cost per kilowatt / Profitability / Efficiency
  - 2.1. Low efficiency of panels compared to other renewable sources.
  - 2.2. Large initial capex resulting in longer recovery times.
- 3. Capacity/Demand
  - 3.1. Grid not having the ability to add more generation output.
  - 3.2. Grid interconnectivity due to lack of network expansion.
  - 3.3. Growing demand for energy due to population/economic activity
- 4. Policy Uncertainty
  - 4.1. Incentive Payout
  - 4.2. Frequent policy change
  - 4.3. Permitting process and regulations

We then proceeded to validate each hypothesis through multiple interactions with decision makers at organizations in our market segments and industry experts to understand the current most important pain areas, attempts at solutions and reasons for failure. From their feedback, we were able to successfully validate the presence of high severity concerns in the following hypotheses:

- 1. All issues with land, for all market segments under consideration.
- 2. All issues with Efficiency/revenue/Rol for all segments.
- 3. All concerns related to Capacity and Demand for the Solar EPC segment.

The pain areas for Policy and Regulation are certainly present, however we conclude that we are at best able to offer a partial resolution to the problem which may not be reliable and repeatable to every case. We are therefore not considering it a verified value add for our technology.

We also identified challenges and concerns related to the current state of our technology, which gives us the ideal path forward. In short, it is now critical to develop the technology to a state where it is capable of demonstrating repeatably, reliably and accurately the value propositions and problem solutions claimed. In addition, concerns related to the safety of operation, particularly for electrical and structural safety were raised as immediate concerns which need to be tested and demonstrated in operating conditions and for long periods of time.

We have therefore arrived at the conclusion, that we would be looking to secure grants related to Technology development (TD), which can include direct funding from capable partners such as IREQ/Hydro-QC, as well as grants from agencies such as NSERC's Alliance grant which require collaboration and contribution from private or public partners, or the Phase I grant offered by NSERC under their Idea2Innovation program, which is a grant requiring the technology to be developed a little further on the TRL scale (TRL 4 or higher), but can become viable once the TD at low voltage and high current proves successful. Other Innovation Sandbox and Incubation program suggested by the industry experts during our conversations are also an option being considered. An example would be the Technoclimat program offered by Hydro-QC. Engaging in these programs would also keep the industry segment updated on our progress and it would make it easier to transition when the technology is sufficiently mature.