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MINIREVIEW

Current Developments in the Chemical Upcycling of Waste Plastics Using Alternative Energy Sources

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Abstract: The management of plastics waste is one of the most urgent and significant global problems now. Historically, waste plastics have been predominantly discarded, mechanically recycled, or incinerated for energy production. However, these approaches typically relied on thermal processes like conventional pyrolysis, which are energy-intensive and unsustainable. In this Minireview, we discuss some of the latest advances and future trends in the chemical upcycling of waste plastics by photocatalytic, electrolytic, and microwave-assisted pyrolysis processes as more environmentally-friendly alternatives to conventional thermal reactions. We highlight how the transformation of different types of plastics waste by exploiting alternative energy sources can generate value-added products such as fuels (H_2 and other carbon-containing small molecules), chemical feedstocks, and newly functionalized polymers, which can contribute to a more sustainable and circular economy.

M. R. Karimi Estahbanati obtained his BSc and MSc degrees in chemical engineering from Shiraz University (Iran, 2010) and Sharif University of Technology (Iran, 2013). In 2019, he received a PhD degree from Université Laval (Quebec, Canada). After graduation, he joined the National Institute of Scientific Research (INRS) as a postdoctoral fellow. His current research focuses on the electrochemical treatment of microplastics and nanoplastics in water and the valorization of waste plastics.

Han Sen Soo is an Associate Professor at Nanyang Technological University (NTU), Singapore. He completed his undergraduate studies at MIT, after which he graduated with a Ph.D. degree from UC Berkeley. He then joined the Lawrence Berkeley National Laboratory as a postdoctoral fellow, before starting his independent career in the Division of Chemistry and Biological Chemistry at NTU in 2012. His research program is focused on artificial photosynthesis, especially the development of technologies to harvest solar and other forms of renewable energy to create fuels and chemical feedstocks from "waste" materials, such as plastics and non-food biomass.

1. Introduction

Since the 1950s, the production of plastics has increased twenty-fold, reaching 360 million tons (Mt) in 2018.[1] The vast use of plastics in recent years has caused a huge increase in plastics waste generation, resulting in a deteriorating environmental crisis. It is expected that around 12,000 Mt of plastics waste would be discharged into the environment by 2050 under the current trajectory.[2] Plastics waste in the environment is typically transformed into small debris called microplastics and nanoplastics, which have been discovered in some of the world's most remote ecosystems and can potentially inflict severe damage to the natural environment and human health.[3] At the same time, the global life-cycle greenhouse gas (GHG) emissions of waste plastics were 1.7 gigaton (Gt) of CO_2-equivalents in 2015 and is expected to increase around 4 times by 2050.[4] This means that GHG emissions from plastics waste would reach as high as

15% of the global carbon budget by 2050, according to the current plastics waste generation and management trends.[4]

To partly address these problems, some of the traditional approaches have been to develop ways to recycle or extract value from waste plastics. Two of the most common methods for plastics waste management are energy recovery through incineration[5] and mechanical recycling.[6] Mechanical recycling typically consists of processes such as grinding, extruding, compounding, and pelletizing, which result in physical transformations but do not change the chemical structure of the materials. Therefore, mechanical recycling techniques generally lead to the generation of a lower quality product, i.e. downcycling, owing to the poorer mechanical properties (e.g. strength), unreliable reproducibility of properties from batch to batch, and some residual color, smell, or odor in the recycled materials.[7] As a result, mechanical recycling methods have usually been adopted to prepare products like composites for construction, where a greater variance and tolerance in the product quality are common.[8] In contrast, a more sustainable and desirable approach is to upcycle waste plastics. Unlike recycling, upcycling must create products with higher quality from the waste plastics so that there will be additional practical and economic benefits.[9]

In this context, there are several different methods to upcycle waste plastics, including biological, mechanical, and chemical processes.[10] A few reviews have already been published on biological upcycling using microorganisms or enzymes to depolymerize and valorize plastics waste.[11] For example, Ru *et al*.[12] reviewed microbial valorization of plastics waste and reported that the enzymatic transformations suffer from low efficiency. Other problems associated with biological approaches for plastics upcycling are the costs of using or cultivating enzymes and microbes, the limited range of reaction conditions, and the limited scope to mainly condensation polymers.[11-13] During chemical upcycling processes, the plastics can be converted back to their monomers or some shorter-chain small molecules, which can be employed as fuels or feedstocks for repolymerization and the production of other value-added chemicals. Accordingly, plastics waste can be transformed into gaseous (like hydrogen and syngas),[14] liquid (including acids and fuels),[15] and solid (carbonaceous materials) products.[16] However, chemical upcycling processes are still plagued by practical challenges such as the separation of different types of plastics, the presence of contamination, the possible formation of corrosive gases, and the typical low selectivities of products.[9a, 10, 17] Although chemical upcycling is also more energy-intensive, it is a promising approach since a versatile range of accessible products may be achieved through the judicious development of catalysts and reaction conditions.

Although there has been intensive research on the chemical upcycling of waste plastics, only a very limited number of studies have focused on the use of alternative energy sources. The previous work on chemical plastics upcycling have predominantly relied on thermal processes like conventional pyrolysis, which are energy-intensive and unsustainable.[18] For instance, Das *et al*.[19] reviewed the previous attempts at generating value-added products from contaminated e-waste plastics using high-temperature extraction, incineration, hydrolysis, and pyrolysis, but concluded that the economic feasibility of all these techniques is one of the limiting factors that prevents future implementation. They also emphasized that other issues like contamination with high levels of heavy metals and challenges in bromine removal from the polymer matrix hinder more widespread adoption of e-waste upcycling. In another review, Zhuo and Levendis[6] examined the upcycling of waste plastics into carbonaceous nanomaterials with thermochemical methods and reported that there are obstacles such as the lack of consistent feedstocks, and the complexity, resource-intensity, and energy-intensity of the processes. Undoubtedly, although there are clear benefits for the chemical upcycling of plastics, current technologies are still not viable. Consequently, to partly overcome these difficulties, our team had previously reported on our efforts to chemically upcycle plastic wastes using solar energy.[17b, 17c, 20]

In this work, our intention is to critically assess the potential of exploiting alternative energy sources to chemically upcycle waste plastics more sustainably. Our literature review was directed towards photocatalytic,[17b, 17c, 20] electrolytic,[15b] and microwave-assisted pyrolysis (MAP)[8] processes as more environmentally-friendly alternatives to conventional thermal pyrolysis. These approaches can potentially be coupled with renewable energy sources such as solar, wind, ocean, geothermal, hydroelectric, and bioenergy, and may even be able to operate at ambient temperatures and pressures (Figure 1). Different plastics including polyvinyl chloride (PVC), polypropylene (PP), polyethylene (PE), polystyrene (PS), and polyethylene terephthalate (PET) can be converted through the application of alternative energy-driven processes into products such as H_2 and other fuels, chemical feedstocks, and newly functionalized polymers. The literature review covered the published papers from the Web of Science about the conversion natural and synthetic polymers, including plastics, to value-added solid, liquid, and gaseous products. We thoroughly screened the combination of the words plastic, polymer, photocatalytic, electrocatalytic, electrolytic, and microwave and their derivatives in the topic (title, abstract, keywords, and keywords plus) to find all the related publications from the early 1950s to 2021. Subsequently, we delved into individual papers, especially the reviews, to uncover more references. In this regard, there have been a small number of reviews that discussed the application of MAP on plastics together with biomass and other types of waste.[21] However, to the best of our knowledge, there have been no reviews dedicated to the application of the multiple alternative energy sources that we discussed here to upcycle waste plastics at the point of our search.

We will begin with a discussion on the state-of-the-art in photocatalytic processes that have been developed for upcycling plastics waste using light. Subsequently, we will evaluate the challenges and opportunities in synergizing electrolytic upcycling of plastics with sunlight and investigate how strategies like the solvent selection and operating temperature modifications can create practical technologies. Next, we will analyze how the latest developments in renewable energy-assisted MAP processes are being adopted to chemically upcycle plastics. We will then conclude by highlighting some of the possible research frontiers in this emerging field of plastics upcycling.

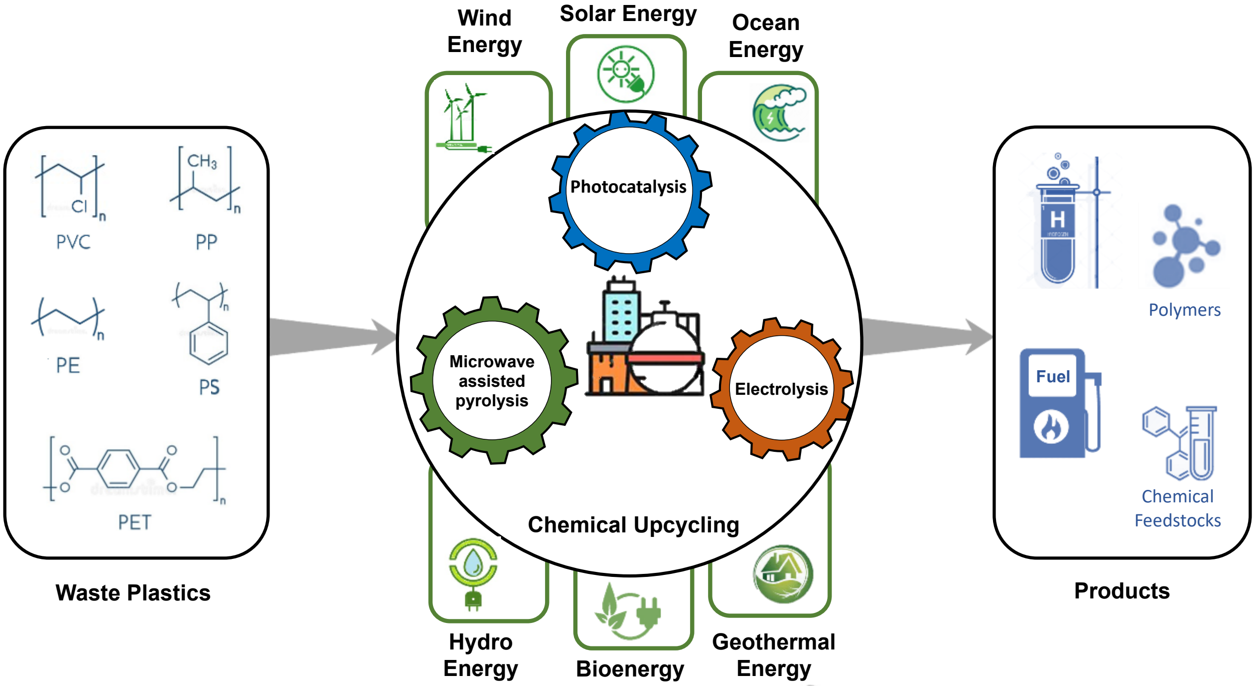

Figure 1. Chemical upcycling of different plastics waste by potentially renewable energy-driven photocatalytic, electrolytic, and MAP processes to generate value-added fuels, chemical feedstocks, and novel polymers.

2. Photocatalytic Upcycling

Photocatalysis is a promising and more sustainable approach to manage plastics waste since the process can be driven by the clean and inexhaustible solar energy, the reactions can take place under mild conditions – room temperature and atmospheric pressure, and the plastics can potentially be upcycled into value-added products. Unlike other alternative energy processes like electrolysis, sunlight is the only source of energy needed to drive photocatalytic reactions without any other external energy inputs. Therefore, the efficiencies of the photocatalytic processes and the product selectivities are highly dependent on the photocatalyst designs and the reaction conditions. Traditionally, carbon dioxide (CO_2) and water (H_2O) are the main products generated from the photodegradation of polymers. However, these products are undesirable since CO_2 is a greenhouse gas that will contribute to global climate change and the H_2O formed is typically contaminated. Consequently, researchers have been exploring alternative photocatalytic pathways with the aim of upcycling plastics waste into more cost-competitive products such as fuels and chemical feedstocks.[17b, 17c] Since several reviews on the conventional photodegradation of plastics to produce CO_2 and H_2O have already been published,[22] this Minireview will selectively center on papers that have reported the upcycling of plastics into value-added products. In this Minireview, we classify the photocatalytic plastics upcycling processes into three categories based on the main products formed, namely: (i) H_2 production by photoreforming plastics; (ii) photocatalytic conversion of plastics into carbon-neutral fuels; and (iii) post-synthetic modifications of polymers to repurpose plastics waste.

2.1. H_2 Production from the Photoreforming of Plastics

The efficiency of traditional photocatalytic water splitting is often low due to the intrinsic rapid recombination of photogenerated electron-hole pairs. Therefore, hole scavengers are normally added to consume the photogenerated holes, leaving only photoinduced electrons to reduce H_2O into H_2 fuel. However, this is not ideal since the introduction of sacrificial reagents will incur higher costs and also generate unnecessary waste. In this regard, the replacement of hole scavengers with plastics waste is an attractive approach, since the photogenerated holes can break down the polymers into small organic molecules at the oxidation sites, while H_2O is reduced to H_2 at the reduction sites of the photocatalysts. This plastics-to-H_2 idea can be traced back to 1981, when Kawai and Sakata first demonstrated the production of H_2 from H_2O by the decomposition of PVC using a platinized TiO_2 photocatalyst under 500 W Xe lamp irradiation.[23] Although the exact mechanisms were not fully understood then, this pioneering research opened up the possibilities for simultaneous plastics degradation and green fuel production through harnessing renewable sunlight.

In 2018, the Reisner group revived the concept of plastics-to-fuel transformation by reporting the production of H_2 by photoreforming plastics using the noble-metal-free CdS/CdO_x quantum dots.[24] The photoreactions were performed under visible light with the mild reaction conditions of ambient temperature and atmospheric pressure. A myriad of plastics including polylactic acid (PLA), polyurethane (PUR), and PET were shown to produce H_2 fuel over the CdS/CdO_x quantum dots in alkaline aqueous solutions under visible light illumination. This was credited to the moderate bandgap (2.4 eV) and suitable band positions of CdS (conduction band (CB): -0.5 V; valence band (VB): +1.9 V both *vs.* normal hydrogen electrode (NHE)), in which the photogenerated electrons were excited for H_2 production whereas the photogenerated holes oxidized plastics into organic molecules such as formate, acetate, lactate, and pyruvate. However, pretreatment of the plastics in strongly alkaline aqueous solutions (10 M NaOH) was needed to partially hydrolyze the polymers into monomers prior to the photoreactions. Besides, the presence of Cd in the photocatalyst limits its practical deployment owing to the highly toxic nature of Cd.

To overcome the toxicity issues, the same group reported an alternative Cd-free carbon nitride/nickel phosphide ($CN_x|Ni_2P$) catalyst for the photoreforming of plastics.[25] As widely accepted, carbon nitride (CN_x) is a metal-free, less toxic photocatalyst with promising activities for water dissociation and organic transformations.[26] In their study, cyanamide defects were artificially introduced into CN_x to improve its photocatalytic efficiency. This cyanimide-functionalized CN_x was then coupled with Ni_2P as a co-catalyst to inhibit the recombination of charge carriers. Upon visible light irradiation, the photogenerated electrons in CN_x were excited to the CB and transferred to the Ni_2P co-catalyst for H_2 formation, whereas the photogenerated holes transformed the plastics into CO_2 and organic molecules at the VB of CN_x (Figure 2a). The intimate contact between CN_x and Ni_2P facilitated the spatial separation of charge carriers and prolonged their lifetimes to participate in the photoredox reactions, thereby enhancing the catalytic activities. As shown in Figure 2b, after 50 h of simulated sunlight illumination over the $CN_x|Ni_2P$ photocatalyst, 82.5 ± 7.3 and 178 ± 12 $\mu mol/g_{sub}$ of H_2 with turnover numbers of 7.8 ± 0.7 and 16.8 ± 1.1 mol_{H2}/mol_{Ni} originated from PET and PLA, respectively. To approach real-world conditions, $CN_x|Ni_2P$ were tested for photoreforming polyester microfibers and food-contaminated PET bottles. After five days of photoirradiation, H_2 production yields of 104 ± 10, 22.0 ± 1.3, and 11.4 ± 1.2 $\mu mol/g_{sub}$ were attained from polyester microfibers, a clean PET bottle, and a contaminated PET bottle, respectively (Figure 2c). Notably, the photoreforming rate of microfibers increased as the reaction time proceeded owing to the enlarged surface area exposed to alkaline hydrolysis. In comparison to the clean PET bottle, a deterioration in the photoreforming rate was observed for the contaminated PET, possibly because the presence of oil limited access to the PET bottle.

In an effort to bring their plastics photoreforming process closer to commercialization, the $CN_x|Ni_2P$ photocatalyst was tested in an up-scaled, continuous system using seawater and lower-sunlight intensities to mimic real-world conditions. Their photoreforming system consists of a photoreactor, a reservoir, and a peristaltic pump (Figure 2d).[27] To ensure high chemical and mechanical resistance, the photoreactor was made from polyether ether ketone (PEEK) with a depth of 1.2 cm and equipped with two borosilicate windows of 25 cm^2 (0.2 cm thick). Prior to the photoreaction, the photocatalyst powders were dispersed in ethanol with the addition of Nafion. The suspensions were then drop-casted onto a clean frosted glass to form a photocatalyst panel (25 cm^2) with a photocatalyst loading of 1.92 mg/cm^2. The photocatalyst panel was held inside the photoreactor under simulated solar irradiation at a reduced power of 20 mW/cm^2. The substrate mixture (alkaline pre-treated PET in seawater) was directed from the reservoir to the reactor, where the photoreforming reactions took place. The substrate mixture was continuously circulated between the photoreactor and the reservoir at a flow rate of 2 mL/min. The gas product was analyzed and quantified by gas chromatography (GC). From their

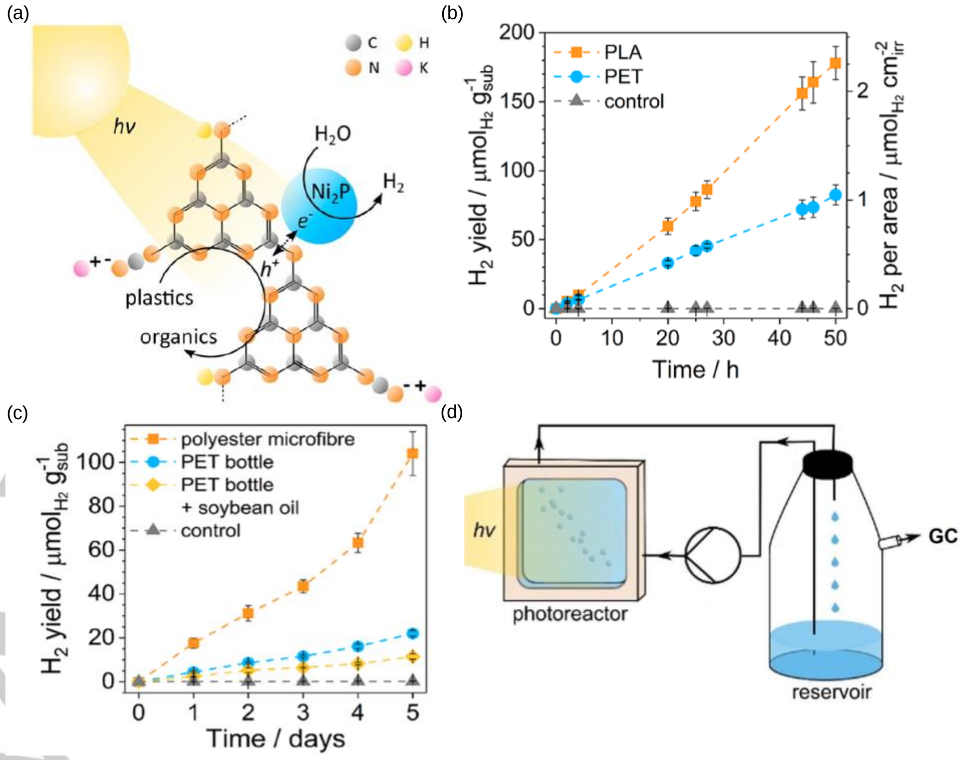

Figure 2. (a) An illustration of the redox processes that occur during the photoreforming of plastics over a $CN_x|Ni_2P$ photocatalyst. Time courses of H_2 evolution from the photoreforming of (b) PLA and PET, and (c) polyester microfibers, clean PET, and a PET bottle contaminated with soybean oil. Conditions: (i) $CN_x|Ni_2P$ (1.6 mg/mL); (ii) KOH aqueous solution (1 M, 2 mL); (iii) simulated sunlight illumination at 25 °C; (iv) pretreated PLA or PET (25 mg/mL), microfibers (5 mg/mL), or soybean oil (5 mg/mL). Reproduced with permission from Uekert *et al.*, copyright 2019 by the American Chemical Society.[25] (d) Simplified schematic of an up-scaled flow reactor for the photoreforming of plastics. Reproduced with permission from Uekert *et al.*, copyright 2020 by Wiley-VCH.[27]

experiments, the photoreforming of PET under simulated real-world conditions yielded 21 μmol/m^2·h of H_2. Remarkably, the photocatalyst panels maximized the incident light absorption and allowed facile reuse. To compare the efficiencies under different scales, both 1 cm^2 (0.5 x 2 cm) and 25 cm^2 (5 x 5 cm) photocatalyst panels were investigated. It was found that upscaling the photocatalyst panel from 1 to 25 cm^2 led to a three-fold deterioration in the production yields instead of the expected proportionate increment. This reduction in the H_2 yields was attributed to the mass transport discrepancies and deposition irregularities in the large panels. Besides, the strongly alkaline conditions used for the pre-treatment of the substrates unavoidably degraded the photocatalyst panel adhesion. Moreover, the conversions of plastics using the CdS/CdO_x quantum dots and $CN_x|Ni_2P$ photocatalysts never exceeded 50%, along with the formation of intractable organic mixtures, which are not favorable products.[24-25] Therefore, more research efforts are needed so that we can realize plastics photoreforming at larger scales.

2.2. Photocatalytic Conversion of Plastics into Carbon-Neutral Fuels

The photocatalytic conversion of plastics waste into short-chain hydrocarbon fuels not only helps to remediate the environment but also potentially reduces our heavy reliance on non-renewable fossil fuels and can create a carbon-neutral cycle with less secondary pollution. Since the photocatalytic transformation of plastics waste into hydrocarbon fuels involves only sunlight, photocatalyst, substrate, and a reaction medium, this process is highly desirable but very challenging. In particular, the non-polar C–C bonds in polymers are stable and kinetically inert, meaning that the selectivity for C–C bond activation is typically lower than the reactivity of other functional groups present in the polymers.[28]

To address this, our group developed a novel, visible-light-driven photocatalytic route using vanadium(V) photocatalysts to selectively cleave the C–C bonds of polyethylene, leading to full conversion of polyethylene into formic acid, alkyl formates, and CO_2.[20] Notably, formic acid is a form of liquid organic hydrogen carrier and a hydrocarbon fuel that reversibly releases CO_2 and can be directly fed into fuel cells,[29] whereas alkyl formates are widely used as refrigerants, solvents, and platform chemicals.[30] Remarkably, this photocatalytic plastics conversion was achieved using a low-power 48 W white light emitting diode (LED), in contrast to the high-power Xenon lamp that is conventionally used for photocatalytic reactions in the literature. More importantly, full substrate conversion was observed after only 6 days, which demonstrated a significant advance over the state-of-the-art photoreforming of plastics, where less than 50% of the substrate was converted after 18 days. However, in this study, modest heating of the reaction medium (a solution of acetonitrile and toluene) to 85 °C was required to fully solubilize the substrate, which may have inadvertently led to over-oxidation of the formic acid at the elevated temperature to CO_2. Besides, this study employed a homogeneous photocatalytic system, which is harder to be recycle for repeated usage.

Following our success on the photocatalytic C–C bond cleavage to repurpose plastics waste, the Xie group reported a heterogenous photocatalytic system to upcycle plastics into chemical products through two-step photocatalytic reactions that consist of a photooxidative C–C cleavage and a photoinduced C–C coupling.[31] Specifically, the first step involves a light driven C–C bond cleavage of the polymers and mineralization into CO_2, followed by a second step to reduce the CO_2 into acetic acid, an energy-rich C_2 fuel, by photoinduced C–C coupling of ·COOH radical intermediates (Figure 3a). Notably, both steps occurred over the same photocatalyst, single-unit-cell thick Nb_2O_5 layers, at ambient conditions under simulated solar irradiation without

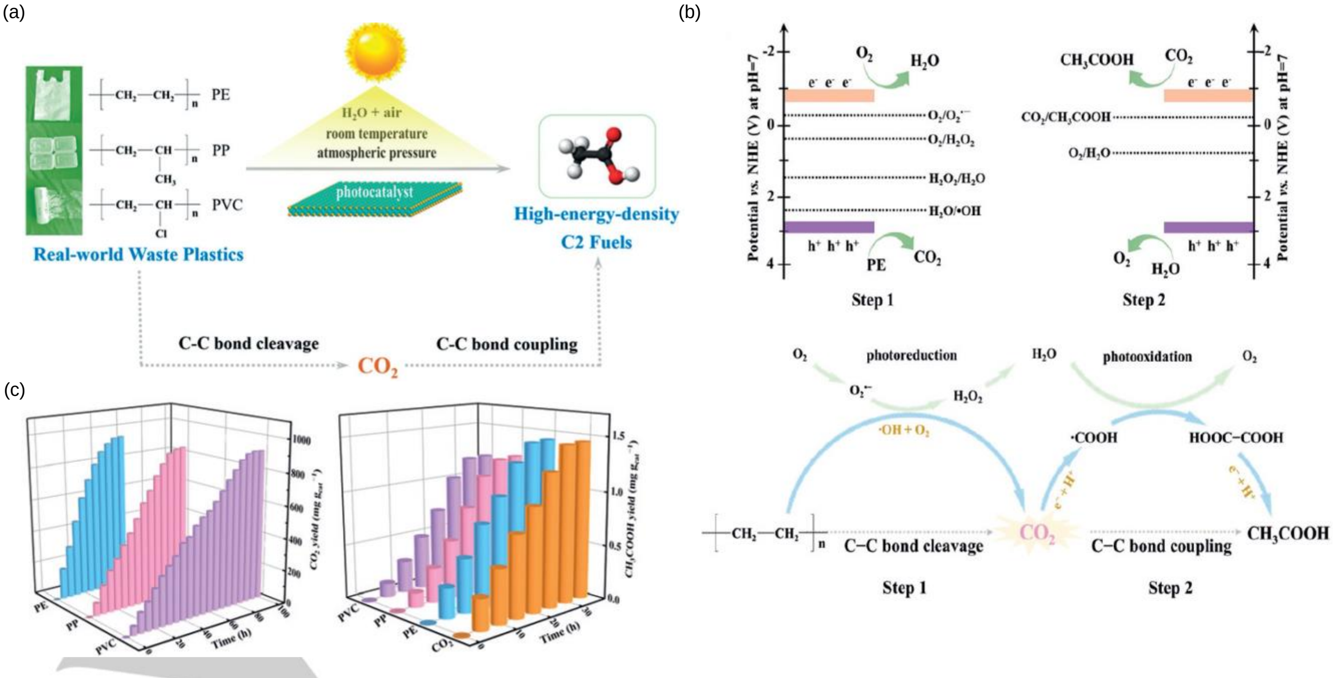

Figure 3. (a) Illustration of the photocatalytic plastic waste transformation into C_2 fuels *via* a designed two-step pathway under simulated natural environment conditions. (b) Top: Band-edge positions of single-unit-cell thick Nb_2O_5 layers together with the standard redox potentials of CO_2, O_2, H_2O, and H_2O_2. Bottom: Proposed mechanisms for the two-step C–C bond cleavage and subsequent C–C bond coupling to convert PE into CH_3COOH. (c) Left: Time courses of CO_2 generation from the photodegradation of PE, PP, and PVC. Right: Time courses for CH_3COOH production from the photodegradation of PE, PP, and PVC Reproduced with permission from Jiao *et. al*., Copyright 2020 by Wiley-VCH.[31]

involving any sacrificial agents. The VB maximum and CB minimum of the Nb_2O_5 atomic layers were measured to be +2.5 V *vs.* NHE and –0.9 V *vs*. NHE at pH 7, respectively (Figure 3b). Gratifyingly, the band positions of the Nb_2O_5 atomic layers strategically straddle the redox potentials of $H_2O/\cdot OH$ (+2.32 V *vs.* NHE) to facilitate the plastic photooxidation in Step 1, and the corresponding CO_2 conversion into acetic acid (–0.6 V *vs*. NHE) by photoreduction reaction in Step 2. Remarkably, PE, PP, and PVC converted into CO_2 (100% conversion) within 40, 60, and 90 h of reaction, respectively, since the total number of moles of carbon in the produced CO_2 is equal to the amount of CO_2 dissolved in solution (Figure 3c). The CO_2 stemming from the plastics degradation then served as the reactants for acetic acid formation. As shown in Figure 3c, the amounts of acetic acid generated increased as the reaction proceeded with average production rates of 47.4, 40.6, and 39.5 $\mu g/g_{cat}\cdot h$ for PE, PP, and PVC, respectively. This photoactivity was attributed to the single-layered properties of Nb_2O_5, in which the exposed surface sites could be maximized and promoted the photocatalytic conversion efficiencies. Although this work delivered a proof-of-concept for a two-step photocatalytic conversion of plastics into a valuable chemical feedstock, there are still some shortcomings that need to be addressed before this technology can be industrially viable. Firstly, the Nb_2O_5 photocatalysts are atomically thin layers, which presents a major challenge for mass production, since yields are low per batch of synthesis.[32] Moreover, the atomically thin photocatalysts tend to agglomerate because of the high surface energy, which will passivate the active surface sites and compromise their catalytic properties. Furthermore, Nb_2O_5 materials are wide band gap semiconductors, so only a small portion of the UV region of sunlight is used. And finally, the acetic acid yields are currently on the order of 0.2%, which means that the plastics are mostly mineralized rather than upcycled.

2.3. Post-Synthetic Modifications to Repurpose Plastics Waste

Other than depolymerizing the plastics waste into fuels, post-synthetic functionalization of plastics waste has also attracted growing research attention. PS is often discarded without recycling now owing to its chemical inertness and high thermal stability.[33] Recently, the Leibfarth group developed a photocatalytic C–H fluoroalkylation method to impart additional chemical functionalities to PS to diversify its physical and interfacial properties, thereby upcycling it to a value-added form.[34] This C–H functionalization was performed using a ruthenium (Ru) based catalyst, $Ru(bpy)_3Cl_2$, to photocatalytically generate electrophilic fluoroalkyl radicals that will react with the aromatic rings, while preserving the beneficial thermomechanical properties of the parent PS. From Figure 4a, 32 ± 2 mol% trifluoromethylation of PS was realized when combining pyridine-*N*-oxide with trifluoroacetic anhydride (TFAA) in a stoichiometric ratio of 1:1.1 relative to the repeat unit in the presence of $Ru(bpy)_3Cl_2$ (1 mol% loading in dichloromethane) under 420 nm blue light illumination at room temperature. Of note, the level of polymer C–H trifluoromethylation could be easily tuned by varying the stoichiometric ratio of pyridine-*N*-oxide and TFAA compared to the repeat unit, as summarized in Figure 4b. Remarkably, this photocatalytic C–H fluoroalkylation method is applicable to a variety of PS samples ranging from pristine PS to post-consumer or post-industrial expanded PS with a tunable degree of fluoroalkylation without making changes to the molecular weight distribution (MWD) of the polymers. Moreover, this functionalization could be extended to polyesters, polycarbonates, and PET containing aromatic rings. In addition, the hydrophilicity of PS-based polymers was also improved by the incorporation of bromodifluoromethyl and chlorodifluoromethyl groups, which highlighted how C–H functionalization to upcycle

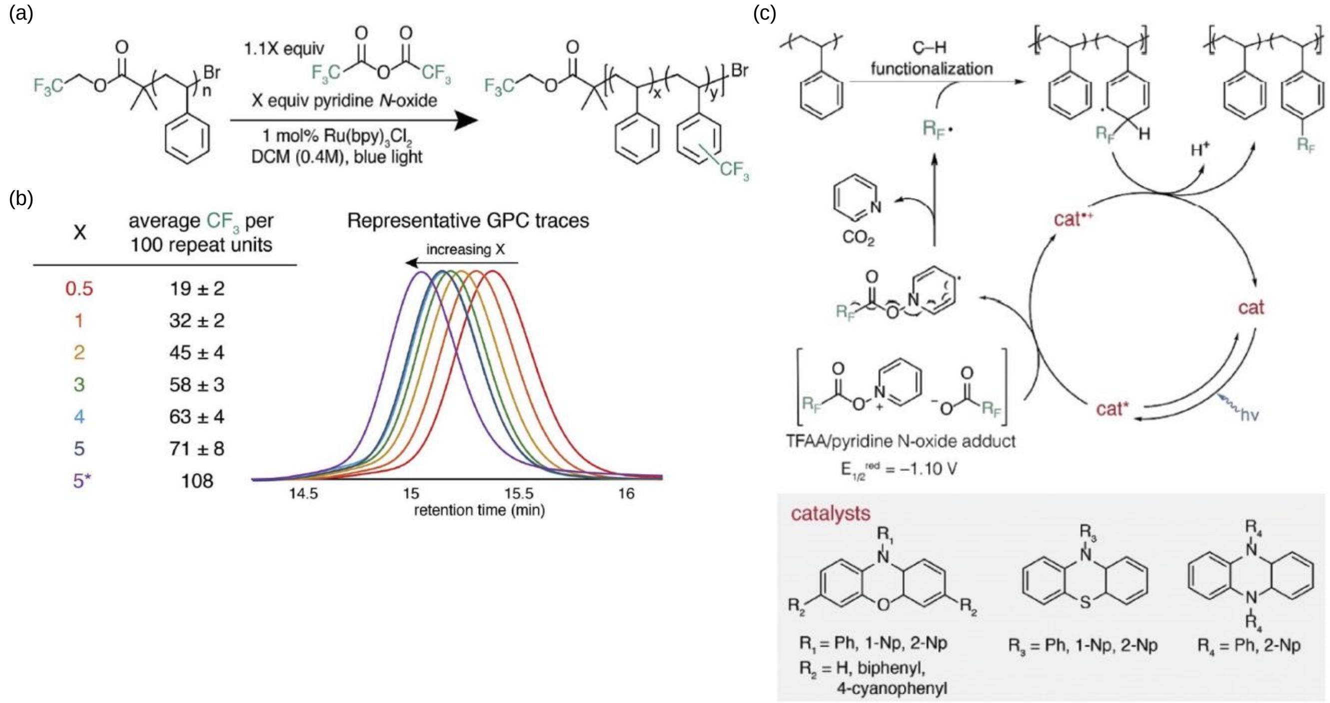

Figure 4. (a) Reaction conditions for the photoredox catalytic trifluoromethylation of PS. (b) Degree of trifluoromethylation and GPC chromatograms corresponding to various equivalents of pyridine-*N*-oxide and TFAA relative to the number of repeat units using $Ru(bpy)_3Cl_2$ as the photocatalyst. Reproduced with permission from Lewis *et al.*, copyright 2019 by the Royal Society of Chemistry. (c) Proposed mechanism for the perfluoroalkylation of PS and the organic photoredox catalysts (left: phenoxazines; middle: phenothiazines; right: dihydrophenazines) that were used. Reproduced with permission from Lewis *et al.*, copyright 2020 by the Royal Society of Chemistry.

plastic waste could be achieved by diversifying their properties.

However, Ru is an expensive, heavy, carcinogenic, and toxic transition metal. In this regard, the Leibfarth group improved the C–H fluoroalkylation protocol by replacing $Ru(bpy)_3Cl_2$ with organic photoredox catalysts, namely phenoxazines, phenothiazines, and dihydrophenazines (Figure 4c).[35] Among these candidates, the dihydrophenazine organocatalyst demonstrated the highest reactivity and selectivity for the fluoroalkylation of PS. Similarly, the use of dihydrophenazine also facilitated easy tuning of the extent of C–H fluoroalkylation, while maintaining the MWD and molar mass (M_n) of the parent PS. In addition, perfluoroalkyl and chlorodifluoromethyl groups could be installed on PS using the organic photoredox catalysts. This method is not only extendable to high molecular weight post-consumer and post-industrial PS waste, but could also be utilized for the trifluoromethylation of poly(bisphenol A carbonate), which demonstrated the versality of their C–H functionalization method for chemically repurposing plastics waste. Nonetheless, although the organocatalysts are improvements relative to $Ru(bpy)_3Cl_2$, phenothiazines are very toxic to aquatic life with persistent effects. Furthermore, each alkylation step will generate stoichiometric equivalents of a carboxylate salt and pyridine, the latter of which is a possible carcinogen with genotoxic and neurotoxic effects. Hence, the organocatalysts, reaction media, and by-products formed from the C–H fluoroalkylation process must be confined and suitably disposed, which creates a secondary source of waste.

Going forward, there are several general criteria that should be met before this photocatalytic plastics upcycling approach can be practically deployed:

i. The photocatalysts used should consist of affordable, less toxic, and abundantly available materials.
ii. The synthetic procedures for preparing the photocatalysts should be simple and easy to scale up.
iii. The design of existing photocatalysts and reaction media should be fine-tuned to improve the activities and selectivities.
iv. For operational convenience, the reactions should be conducted in heterogenous systems and/or continuous flow for large-scale production with easy recycling of the photocatalysts.

3. Electrolytic Upcycling

Electrolysis is a promising and sustainable alternative approach to thermal processes because it can be conducted in aqueous solvents with electricity that can, in theory, be generated from solar energy, and also generally operates at ambient temperatures and pressures. Most previous work on the electrocatalytic upcycling of polymers have focused on lignin conversion,[36] although there are a few instances of synthetic plastics transformations. There are a number of reports for the valorization of waste plastics for electrolytic applications that can be categorized as the production of (i) solid carbonaceous materials, (ii) value-added chemicals, and (iii) electricity. The first category aimed at upcycling waste plastics into carbonaceous materials that can be embedded in electrodes, like carbon nanotubes in Fe-N-CNT[16] and carbon in $Mo_2C@C/N$.[37] Although the waste plastics upcycling methods in these examples did not directly use renewable energy (mainly pyrolysis[16] or hydrothermal[37] processes), nonetheless, the carbon materials that were produced were employed in the generation of H_2 from water by electrolysis. In this Minireview, we will focus this section to cover only the studies in the second and third categories that describe the electrocatalytic upcycling of waste plastics to generate value-added products in electrolyzers or the production of electricity in a fuel cell, respectively.

Table 1 summarizes all the previous instances on the direct electrocatalytic upcycling of waste plastics to small molecule products. These studies mainly aimed to adapt existing electrocatalytic processes for small molecule substrates into procedures for plastics upcycling. To ensure compatibility with the transformation of plastics, the anode materials should be optimized to allow the polymers with high molecular weights to diffuse into the anode pores. In this context, the anodes that had been previously developed for the electrocatalytic conversion of lignin may be suitable to be adapted for plastics conversion because of their relatively similar molecular sizes. However, cleavage of the chemically inert bonds in many of the common plastics requires strong oxidants such as Ag^{2+} ($E^0 = 1.98$ V), Co^{3+} ($E^0 = 1.9$ V), and Ce^{4+} ($E^0 = 1.7$ V).[38] Thus, controlling the selectivity to generate specific products is not trivial. As seen in Table 1, precious metals such as Pt[39] and Ag,[15a] as well as earth-abundant metals including Ni[15b] and Fe[40] were employed as the electrode. As expected, a lower applied voltage was required for the operation at higher temperatures (Table 1). For instance, Myrene *et al.*[15a] applied a potential of 2.2 V for the oxidation of PET at ambient temperature, whereas Hori *et al*.[39] could conduct this oxidation at 800 °C with an applied potential of only 0.92 V. Table 1 further highlights that PET is the most commonly examined plastic for upcycling by electrocatalysis, likely because it is also the most frequently recovered synthetic plastic.[15a] On the other hand, analysis of the products in Table 1 suggests that most of the previous research resulted in the generation of gaseous products such as H_2, CH_4, C_2H_6, C_3H_4, C_5H_{12}, and syngas,[14, 15b, 39-40] whereas only one work reported the generation of terephthalic acid,[15a] which is a solid under ambient conditions. Notably, the terephthalic acid was produced

Table 1. Reaction conditions and outcomes from existing electrocatalytic processes for upcycling waste plastics.

Plastic type	Solvent	Temperature (°C)	Products	Maximum conversion (%)	Applied voltage (V)	Anode/Cathode	Ref.
PET	methanol: water mixture (1:1)	21	Terephthalic acid, CO_2	17	2.2	Ag/AgCl	[15a]
PET	-	800	H_2, CO, CH_4	~100	0.92	Fe_2O_3/ $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	[40]
PET	H_3PO_4 (85%)	200	H_2, CO_2	-	0.55	Pt/Pt	[39]
HDPE	Sn	1000	H_2, syngas	-	0.195	Sn/Ni-yttria stabilized zirconia	[14]
PP	KOH : NaOH (1 : 1.4 (w : w))	350-400	H_2, CH_4, C_2H_6, C_3H_4, C_5H_{12}	68.5	1.5	Ni/Ni	[15b]

at the lowest reported operating temperature (21 °C), which likely enhanced the selectivity because of the milder reaction conditions.

On the contrary, electrocatalytic processes at high temperatures appear to lead to more extensive oxidative degradation to generate gaseous products. For example, Jiang *et al*.[15b] converted PP to H_2, CH_4, C_2H_6, C_3H_4, and C_5H_{12} in a solar thermal electrochemical process (STEP) at 400 °C. As seen in Figure 5a, STEP takes advantage of a solar thermal collector and a photovoltaic panel to combine thermal energy to increase the reaction temperature with electrical energy for electrocatalysis, respectively. They showed that the main difference between the generated gases by STEP and pyrolysis is the amount of H_2 produced, whereas no significant differences were observed for CH_4, C_2H_6, C_5H_{12}, and C_3H_4 (Figure 5b). Around 10 times more H_2 could be generated with the hybrid electrocatalytic STEP than pyrolysis. A part of this remarkable difference is attributed to the production of about one-third of the H_2 at the cathode through electrolysis, as seen in Figure 5b. Notably, unlike pyrolysis, plastics upcycling by STEP is feasible at lower temperatures (i.e., below 300 °C). From a thermodynamic perspective, providing more thermal energy compensates for and thus reduces the required electrical energy for STEP and vice versa (Figure 5c). Therefore, the operating temperature of STEP should be optimized to identify the ideal surface area for thermal and photovoltaic solar collectors (Figure 5a). However, since their supporting electrolyte (KOH/NaOH) would not be a conductive fluid phase at lower temperatures, Jiang *et al*.[15b] were unable to explore and improve their system at lower temperatures. Related to this, besides temperature, solvents also play critical roles in the success of electrocatalytic strategies to upcycle plastics. Table 1 illustrates how different solvents, including methanol/water solutions, concentrated H_3PO_4, molten Sn, and molten KOH/NaOH eutectics were employed for the electrocatalytic conversion of plastics. Although electrocatalytic processes are promising and may be more sustainable, major challenges are undeniably the low solubility of plastics in conductive electrolyte solutions and the slow rates of the electrocatalytic oxidations at ambient temperature.

One technical problem for the electrocatalytic upcycling of waste plastics is the low solubility of most plastics in aqueous solutions, which leads to a low rate of oxidation. For instance, the electrocatalytic conversion of PET to terephthalic acid in a 0.1 M aqueous NaCl solution was only 0.51%, whereas the use of a 1:1 water/methanol solvent increased the yield to 17%.[15a] To avoid the issue of poor plastics solubility in conductive media, most

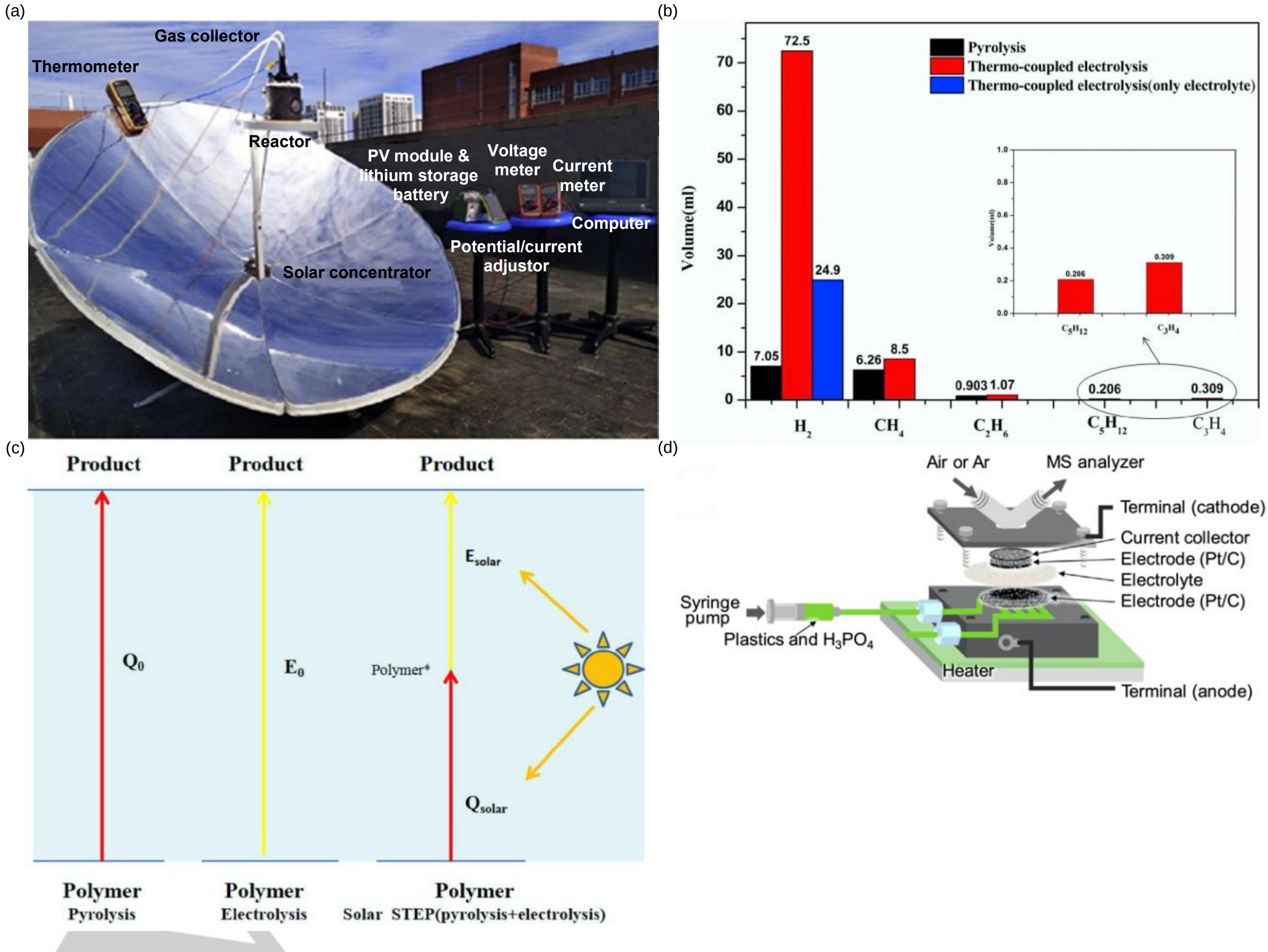

Figure 5. (a) An illustration of how thermal and electrical energy from the sun are combined for solar thermal-coupled electrolysis (STEP).[15b] (b) Comparison of the generated fuels from STEP with those from the pyrolysis of PP.[15b] (c) An illustration of how STEP can combine thermal energy with electrolysis, in contrast to pyrolysis that only provides heat.[15b] Parts (a), (b), and (c) have been adapted with permission from Jiang *et al*., copyright 2020 by Elsevier Inc. (d) Schematic of a flow cell to generate either chemicals or electricity through the upcycling of plastics.[39] This image is reproduced with permission from Hori *et al*., copyright 2020 by Elsevier Inc.

previous studies focused on the electrocatalytic conversion of the primary depolymerization products from condensation plastics (e.g. 6-acetamidohexanoic acid, the primary acetylation product of Nylon-6)[41] or model molecules such as methyl pivalate, which possesses similar functional groups to poly(methyl methacrylate)[42]. However, the direct production of value-added chemicals from waste plastics is still not overcome since there are no obvious pathways for converting the plastics to these depolymerization products or model molecules. To partly address the low solubility of plastics, one approach was to dissolve them in acids at high temperatures, which could be applied mainly for polyurethane, Nylon, and Vinylon.[39] For example, Hori *et al*.[39] successfully dissolved rope, sponge, cable ties, stockings, and PET in 85% phosphoric acid at 200 °C and valorized them into H_2 in an electrolyzer.[39] Other methods (Table 1) were to use (i) a mixture of plastic and catalyst powders at high temperatures (800 °C) without using a solvent,[40] (ii) low-temperature molten salts like KOH/NaOH at 350-400 °C,[15b] and (iii) molten metals like Sn at 1000 °C.[14] These approaches simultaneously addressed the issue of the low plastics solubility and low rates of reaction by operation at medium to high temperatures. Although these high temperature processes facilitated the plastic dissolution, new problems arose, such as the identification of suitable ion exchange membranes with high conductivity and durability at such elevated temperatures.

Besides solubility, another challenge in the electrocatalytic upcycling of plastics is their slow oxidation rates at ambient temperatures. For example, the maximum terephthalic acid yield (as the sole product) was only 16.9% in the electrolysis of a low concentration of PET (0.1% (w/w)) at ambient temperature.[40] Based on the current technologies, the electrocatalytic upcycling of plastics may be feasible only at elevated temperatures. Operating at high temperatures can still be sustainable if the thermal energy is derived from renewable energy sources like sunlight for STEP, as shown in Figure 5a. While flat plate solar collectors can efficiently generate temperatures up to only 120 °C, concentrated solar collectors can produce temperatures exceeding 300 °C. However, even higher temperatures above 500 °C will usually require centralized solar receivers that will be prohibitively expensive.

In their recent work, Jiang *et al*.[15b] used a parabolic solar concentrator to generate temperatures up to 400 °C for STEP (Figure 5a). Although the pyrolysis of PP does not usually exceed 28.4% conversion at 350 °C, they discovered that STEP led to a 68.5% conversion, leading to a product composition of 31.5%, 7.85%, and 60.6% (w/w) solids, liquids, and gases, respectively. This example illustrates the viability of electrocatalytic upcycling of waste plastics at moderately high temperatures using only renewable solar energy. STEP is kinetically more favorable and can be driven by less combined electrical and thermal energies (Figure 5c) compared to electrolysis at ambient temperature alone or pyrolysis at even high temperatures. Further research is still required to evaluate the capital costs of the solar thermal capturing facilities, including the components like the solar thermal collectors, solar tracking systems, and photovoltaic panels. Moreover, in addition to the carbon-containing products, H_2 or electricity generation can also be valuable.

Another approach for the electrocatalytic upcycling of waste plastics is the generation of electricity in a fuel cell with plastics as the fuel. An interesting capability of an electrolytic cell is the possibility of operating either in an electrocatalytic or in a fuel cell mode. In an electrocatalytic mode, the upcycling of waste plastics is usually accomplished by producing hydroxyl radicals from water at the anode, which will oxidize the plastics. Simultaneously, the water is reduced at the cathode to evolve H_2 molecules by consuming the electrons derived from water oxidation. In a fuel cell mode, hydroxyl radicals are still produced at the anode, but O_2 is reduced instead at the cathode to produce water and generate electricity. While the cathode is held under O_2-free conditions in the electrocatalytic mode, it is fed with air during the fuel cell mode.

In an example of this dual function fuel cell-electrolyzer, Hori *et al*.[39] produced H_2 at a low cell voltage of only +0.55 V (in electrocatalytic mode), and could also generate electricity on the order of mW.cm^{-2} (in fuel cell mode) from PUR (Figure 5d). During operation, PUR was dissolved in H_3PO_4 and either air or argon were injected to generate electricity or H_2, respectively. In another study, Hibino *et al*.[40] developed a solid oxide fuel cell with an anode consisting of Fe_2O_3, which could oxidize PET at 800 °C at the open-circuit voltage while being reduced to FeO, after which it could be re-oxidized back to Fe_2O_3 by anodic polarization. Complete consumption of PET was observed in this fuel cell, leading to a higher power density (0.57 W cm^{-2}) than other experiments with cellulose, lignin, PUR, or protein as the fuel. The flexibility of electrolytic cells to work as either an electrolyzer or a fuel cell is noteworthy since it offers the possibility to periodically generate value-added chemicals or fuels when excess electricity is available or just electricity at peak demand on an electrical grid.

To realistically deploy electrocatalytic processes to upcycle waste plastics, further research is necessary to address the practical challenges, especially the low solubilities of plastics in conductive electrolyte solutions and the slow rates of polymer electrocatalytic oxidations at ambient temperature. In addition, more work is needed to optimize the operating parameters for electrocatalytic processes to improve the conversions of plastics and the selectivities toward desired products like solar fuels.

4. Microwave-Assisted Pyrolysis

Pyrolysis is a thermochemical recycling process in which polymeric materials are heated without air so that the macromolecular structures will be broken down into smaller units, either in the form of monomers or partial degradation products. Pyrolysis is versatile and can produce multiple products, such as oils, gases, monomers, or other valuable chemicals. The reaction conditions can be easily altered to optimize the desired product yields based on adjusting the following parameters:[43]

i. Reaction temperature
ii. Heating rate
iii. Reaction/residence time
iv. Reaction phase
v. Reactant’s viscosity
vi. Operating pressure
vii. Reactor type
viii. Catalysts
ix. Solvent or reaction media
x. Plastic structure and composition

Among these parameters, the reaction temperature and heating rate (low/fast/flash heating) are especially crucial, since pyrolysis is an endothermic process that requires large inputs of energy for the cracking of the polymeric chain. Consequently, the polymer-monomer equilibrium during depolymerization and the extent of monomer production is strongly influenced by temperature.[44] Below a critical temperature known as the ceiling temperature, the rate of depolymerization is lower than that of polymerization, resulting in low efficiency for the degradation of polymeric materials.[45] It is interesting to note that when there is a large disparity in polarity between the monomer and the solvent, there is an increase in enthalpy and consequently a decrease in the ceiling temperature.[45] Particularly, during PS pyrolysis, it has been shown that the conversion and selectivities of reactions significantly depend on the solvents used and the polymer concentrations.[46]

Traditionally, fossil fuels or the polymers themselves are combusted to provide the activation energy for pyrolysis. In this manuscript, we focus on the use of more sustainable, process-intensified alternative energy sources such as microwaves for the recovery of chemicals from plastics waste through pyrolysis. The application of microwave technology for the thermal valorization of polymers has received much attention over the last two decades since it has been found to reduce energy consumption and processing time for chemical reactions, and also provides a unique, more uniform, internal heating process compared to conventional heating systems (Figure 6a).[47] In conventional thermal processes, heat is usually supplied externally and transferred from the material’s surface towards the interior by conduction, convection, and radiation. Hence, the heating efficiency significantly depends on the inherent thermal conductivity of the material. In contrast, microwave heating has an inverted temperature profile since electromagnetic radiation transmits throughout the sample, which absorbs some of the energy for vibrational and rotational motion and is hence converted into thermal energy. Microwaves, like other electromagnetic radiation, consist of two perpendicular components: a magnetic field and an electric field. The latter contributes predominantly to the microwave heating of materials by dipolar polarization and conduction.[21e, 43a, 47]

Moreover, contrary to traditional pyrolysis, microwave-assisted pyrolysis (MAP) possesses several benefits for industry applications, including precise, fast, selective, and controlled heating with low production costs. MAP has also been identified as an energy-efficient alternative to the conventional heating technologies employed for the treatment of waste plastics since they have high calorific values. A small fraction of the energy-rich products from the MAP of waste plastics can be used to sustain the temperatures or combusted to produce electricity for the microwaves, thus circumventing the need for any extra energy source. However, microwave heating in poorly absorbing materials can be less effective than conventional thermal heating. Microwave heating may cause variations in the temperature distribution in the sample, which can create challenges in measuring and controlling the uniformity of temperature profile in the sample during MAP. For this issue, Sturm *et al.*[48] experimentally and numerically showed that non-uniform heating patterns form during microwave heating, which are fundamentally distinct from the distributions during conventional thermal heating. As shown by the numerical modeling results in Figure 6b, since the temperature patterns in the outermost regions of the microwave reactor are different from the inner regions, inhomogeneity of heating and consequently inefficient heat transfer can decrease the presence of high boiling point liquids and the product selectivity of MAP.[48]

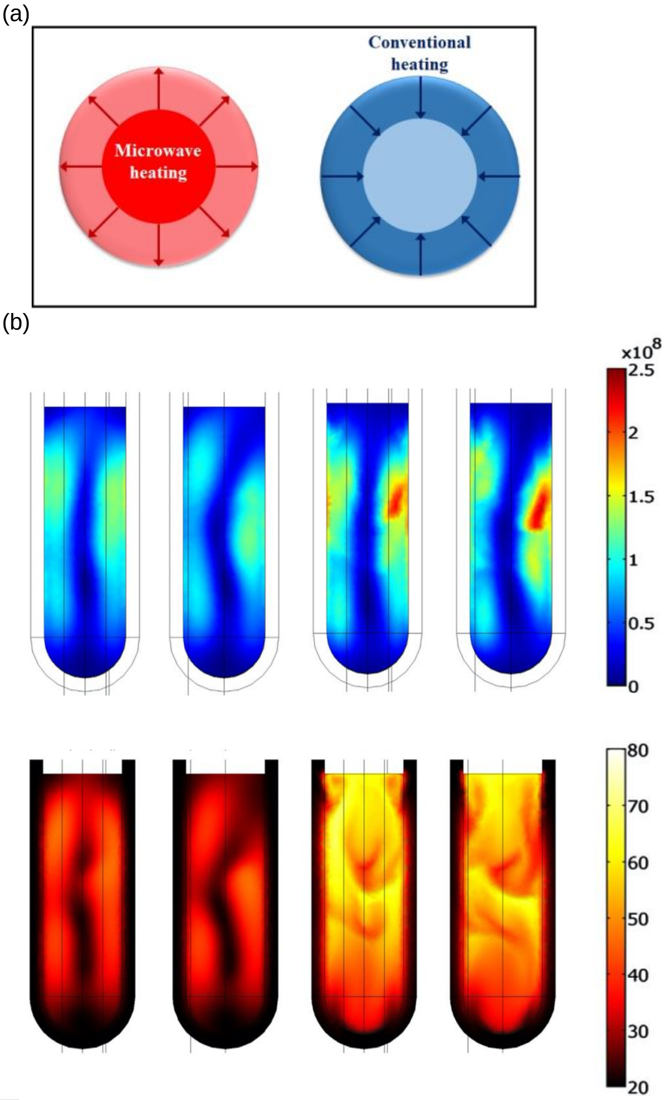

Figure 6. (a) Differences in the temperature profiles for heat transfer in microwave (left) and conventional heating processes (right). (b) Numerical simulations for different views of the heat generation (W/m^3, top panel) and temperature (ºC, bottom panel) during microwave heating processes.[48] For each row, the simulation results correspond to the front and left side views for 1 second and also the front and left side views for 2 seconds after exposure to microwave field, from left to right. Reproduced with permission from Sturm *et al.*, copyright 2013 by Elsevier Inc.

Similar to conventional heating, MAP reactions have several parameters processes that need to be optimized, as listed below:[43a, 47]

i. Microwave frequency and wavelength
ii. Microwave mode (multimode or single mode)
iii. Dielectric properties of the material
iv. Reaction temperature
v. Surrounding medium properties
vi. Reactor design/type
vii. Other inherent material properties (e.g., type, size of sample, moisture, and water content)

By varying the parameters above, the yield and quality of products from MAP will be different. However, polymers are usually transparent to microwaves and are poor absorbers since they possess small dielectric constants. Therefore, the cracking of the polymeric chain by MAP will need to be enhanced when the materials are mechanically blended with other effective microwave absorbers prior to pyrolysis so that a high temperature can be achieved in a short time. Undri *et al.*[49] studied the impact of varying the ratio between the polymer substrate and carbon as a microwave absorber during the MAP of waste PS (see Table 2 for the reaction conditions). They observed that decreasing the ratio of carbon to PS resulted in a high yield of liquids containing moderate amounts of styrene and small amounts of solids and gases, although the viscosity and density of the liquid products appeared to be independent of the carbon/PS ratio. In another study by this group, they examined the impact of using different microwave absorbers on the reaction time and the amount and composition of the liquid fractions that formed. They showed that although replacing carbon with silicon carbide as the microwave absorber generally resulted in similar yields of products, the reaction times (i.e., residence times of the feeds in the reactors) were remarkably increased.[50] Furthermore, they found that the microwave power is inversely proportional to the liquid yield.[49] Table 2 summarizes some other examples of the MAP of styrene, although there are still no clear trends in the operating conditions or obviously outstanding candidates as microwave absorbers to maximize the yields of the products.

Besides PS, pyrolysis of PE has also been investigated by both conventional thermal [51] and microwave heating (Table 2). It was shown that MAP could be applied to the depolymerization of high-density PE and aluminum-coated polymer laminates (e.g., a toothpaste tube), which led to a high yield of oils and waxes while producing aluminum as a co-product.[52] The degradation of PE was carried out at different temperatures in a semi-batch scale microwave reactor, but interestingly, the yields of liquid and gas products did not appear to depend on the temperature. In addition, the results showed that the yields of products and consequently the hydrocarbon fractions generated from the MAP of PE waste were generally similar to the conventional degradation of pure PE.[47, 52b] These studies suggest that MAP is not only valuable for processing single stream plastics, but can be utilized as an integrated method to simultaneously separate and upcycle aluminium-coated packaging waste as well as de-pulped drink-cartons (e.g. Tetra Pak containers), which are often metal-coated composites that cannot be readily recycled mechanically.[52a, 52b]

Microwave heating has also been successfully applied for the pyrolysis of PVC and acrylonitrile butadiene styrene (ABS). Goodman[43a] investigated the impact of microwave power, exposure time, and microwave absorber choice on the yields of the liquids, gases, and residue materials, as well as the product distribution during the MAP of both PVC and ABS. Complete depolymerization of both PVC and ABS were observed when MAP was employed in the presence of carbon char as the microwave absorber.[43a] Their research also highlighted that higher quantities of monomers could be recovered through MAP than traditional thermal pyrolysis.[53]

In addition to pure polymers, MAP has also been applied to recover chemical feedstocks from complex polymeric material composites such as tires. These materials usually consist of a

Table 2. MAP of PS and PE with different absorbers and reaction conditions.

Feed	Absorber	Operation conditions	Special apparatus/method	Yield of products (wt%)	Ref.
PS	Silicon carbide	Power: 220 W Temperature: 300 ºC Reaction time: 60 min	Using N_2 gas to carry the vapor from the reactor to the collection flask.	Solid: - Liquid: - Gas: -	[59]
PS	Iron coil	Power: 700 W Temperature: 1200 ºC Reaction time: -	Using a cylindrical reactor made of baked clay to improve the microwave-metal interactions during pyrolysis in the oven.	Solid: 5 Liquid: 80 Gas:15	[60]
PS	Copper coil	Power:- Temperature: - Reaction time: 16 min	Reactor connected with cold traps.	Solid: ~18 Liquid: ~80 Gas: ~6	[61]
PS	Aluminum coil	Power:- Temperature: - Reaction time: 12-14 min	Similar to reference [60].	Solid: - Liquid: 88 Gas: 9-10	[62]
PS	Graphite	Power:2000 W Temperature: 775 ºC Reaction time: 10 min*	Oven connected with a cooled water condensation system.	Solid: 19 Liquid: 71 Gas: 9	[63]
PS	Carbon black	Power:3000 W Temperature: 364-578 ºC Reaction time: 22-46 min	1. Oven connected to a condensing system. 2. Placing a fractionating column between the oven and the condensing system.	Solid: 9.8-16.7 Liquid: 73.5-86.5 Gas: 3.7-9.8	[49]
PS	Silicon carbide	Power: 3000 W Temperature: 574 ºC Reaction time: 91 min	1. Oven connected to a condensing system. 2. Placing a fractionating column between the oven and the condensing system. 3. Oven connected with a N_2 gas stream.	Solid: 8 Liquid: 85 Gas: 7	[50]
PS	-	Power: 3000-6000 W Temperature: - Reaction time: 59 min	-	Solid: 6.83 Liquid: 89.25 Gas: 8.92	[64]
PE	Activated carbon	Power: - Temperature: 400-600 ºC Reaction time: -	Using a reactor equipped with a stirrer where the blades are slanted at 30º to the vertical.	Solid: 6-11.3 Liquid: 27.3-54.9 Gas: 34.8-62	[65]
PE	Carbon	Power: 3000-6000 W Temperature: 578-599 ºC Reaction time: 75-100 min	Similar to reference [49].	Solid: 0.4-0.6 Liquid: 80.2-83.9 Gas: 15.7-19.2	[66]
PE	Carbon	Power: 1250-5000 W Temperature: 450-700 ºC Reaction time: 0.5-6 min	Using a reactor equipped with an agitation system that consists of an impeller with two 45º pitched blades.	Solid: - Liquid: ~ 81-93 Gas: -	[52b]

* The short reaction times may have resulted in incomplete pyrolyses of the PS in this study.

complicated mixture of multiple components including rubbers (both natural and synthetic), fillers (e.g., various grades of carbon black, silica), reinforcing materials (textiles and metals), and chemicals additives (e.g., zinc oxide, stearic acid, and sulfur).[54] Unlike many polymers that do not strongly absorb microwaves, tires are excellent microwave absorbing materials since they contain carbon black and metal wires.[55] During the MAP of tires, the ratio between the microwave power and tire mass was found to play a significant role in the yields and compositions of the products and could be optimized to increase the quantities of gas and aromatic liquid products.[55] Lowering the microwave power led to a decrease in the viscosity, density, and calorific values of the liquid products obtained during the MAP of various tire brands.[56]

The experimental results of Wang et al. showed that the amounts of H_2, CH_4, and high quality liquid products including limonene, xylene, toluene, and benzene have increased when MAP was applied to waste tires compared to those of conventional thermal pyrolysis.[57] Moreover, they indicated that the quality of the MAP-derived carbon black ash also had improved pore structure and more oxygen-containing functional groups. Separately, Athanassiades reported that the application of MAP on tires produced chars and oils that exhibited similar properties as conventional thermal pyrolysis (e.g., surface area, pH, and ash-content for the chars; the carbon, hydrogen, nitrogen, and sulfur contents of the oils).[54a] However, microwave heating has the additional benefit of a higher energy efficiency and more uniform heating, which minimized hot-spot formation.[54a]

The product yields obtained from the MAP of tires varied depending on the microwave power and pyrolysis time, as presented in Figure 7a and Figure 7b, respectively. Notably, at a given pyrolysis time, the oil yields remained constant within experimental error when the microwave power increased from 400 W to 560 W,[57] before decreasing modestly on further increase to 800 W. On the other hand, the yields of gaseous products rose steadily together with the microwave power, while the yields of solid products remained fairly constant. In addition, Figure 7b illustrates that longer pyrolysis times led to lower solid yields, which translated to an improved degree of tire pyrolysis as well as enhanced yields of gas and liquid products.[58]

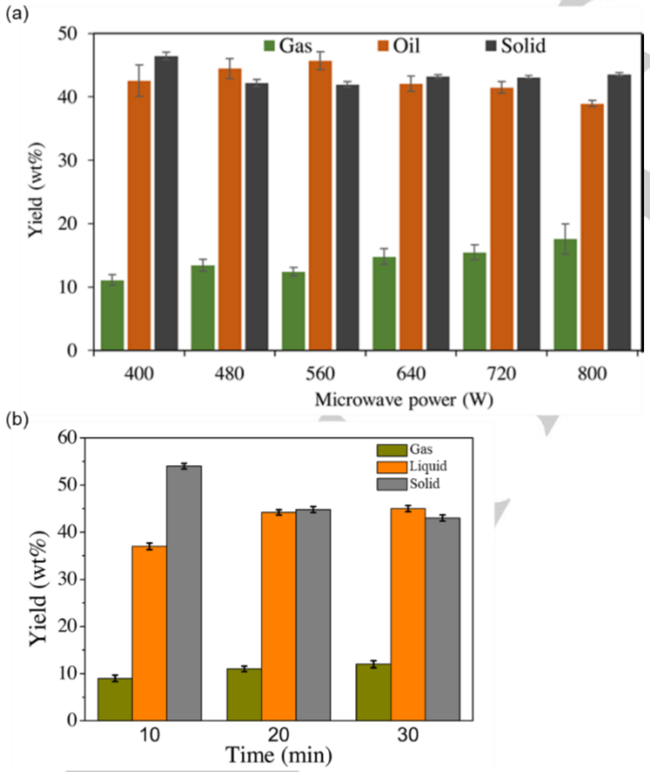

Figure 7. Yields of the products in the three phases as a function of (a) microwave power[57] and (b) pyrolysis time,[58] obtained from the MAP of waste tire rubber powder derived from truck tires without steel cords. Reproduced with permission from Bing *et al.*, copyright 2021, and Song *et al.,* copyright 2017 by Elsevier Inc.

Based on the research to date, MAP has enormous potential for energy and cost reductions in industrial scales for the recovery of chemicals from plastics waste and the conversion of used tires into value-added products. The physics of microwave heating are different from conventional thermal heating, which has been found to result in complete pyrolysis with reductions in the pyrolysis time and energy as well. Despite the issues arising from the inhomogeneity of the heating profile during MAP, microwave heating technique is still one of the more sustainable and process-intensified alternative energy sources that have been successfully implemented to enhance and accelerate chemical reactions, and is promising for deployment to upcycle plastics waste in the future.

5. Summary and Outlook

In this review, we have evaluated the potential of exploiting alternative energy sources to chemically upcycle waste plastics. In particular, we focused on photocatalytic, electrolytic, and MAP processes as more sustainable alternatives than conventional thermal pyrolysis, since they can be coupled with renewable energy sources. We assessed the challenges and opportunities in converting different types of plastic waste feedstocks to create fuels (e.g., H_2 and other small molecules), value-added chemicals, and novel polymers. In addition to incorporating renewable energy sources, other green and sustainable factors for these new processes include the possibility of working at ambient temperatures and pressures, as well as the use of more eco-friendly solvents.

Nonetheless, a series of challenges remain before these technologies can be realistically deployed. Although it can be directly integrated with solar energy harvesting, a major obstacle for photocatalytic plastics upcycling is the need for more inexpensive and less toxic photocatalysts with high efficiencies and selectivities. Besides, most existing studies necessitate the pretreatment of plastics in corrosive or caustic solutions or organic solvents, which will add costs. The electrolytic conversion of plastics waste suffers from a dearth of research, meaning that there is still no technology to electrocatalytically recycle plastics waste at ambient temperatures and pressures at acceptable rates. Among the different alternative energy sources for plastics waste upcycling, MAP is probably the closest to industrial implementation. Based on the latest developments, MAP of plastics is more advantageous than conventional thermal pyrolysis in terms of product yields, processing times, and energy efficiencies. However, despite a few investigations on the basic mechanisms involved during microwave heating, the product formation pathways and the effects of the polymer chain lengths, polymer structures, and the presence of multiple components in composites are still not well understood.

To overcome the difficulties in the chemical upcycling of plastics waste, a key enabler is to separate different types of plastics to enhance the reproducibility of feedstocks from batch to batch, although more research will be necessary to ensure the cost-effectiveness of these technologies. Further strategies are also needed to ensure a sufficiently high level of tolerance to contamination on the waste plastics. These approaches can significantly improve the product selectivity. In addition, given the wide range of operating parameters for chemical recycling processes, we may be able to systematically compile the data and take advantage of machine learning to optimize the process performances, rates of reactions, and operating parameters. For photocatalytic plastics upcycling technologies, more active and stable candidates are needed to harvest a broader range of the solar spectrum. Moreover, photocatalysts that can be more readily reused and scalable will be critical. Regarding the electrolytic approaches, further research is necessary to investigate the solvent selection and reaction temperature to tackle the low solubilities of plastics and the slow rates of reaction. For example, greener solvents including deep eutectic solvents, ionic liquids, supercritical/subcritical fluids, and bio-based/renewable solvents should be evaluated for their efficacies in facilitating electrolytic degradation of plastics. Finally, for the MAP of plastics, additional attention can be directed towards increasing microwave absorption and ensuring uniform temperature distribution in the reactor through different tactics such as changing the particle sizes of the absorbers, varying the sample loads, and examining the effects of different pressures (e.g., high pressure or vacuum) in combination with microwave heating.

We anticipate that further investments and research would help to overcome the challenges and gaps in chemical upcycling using alternative energy sources, which should aid in the creation of more sustainable, greener, and circular methods to manage the global waste plastics crisis.

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Keywords: photocatalysis • electrolysis • microwave-assisted pyrolysis • plastics upcycling • polymer

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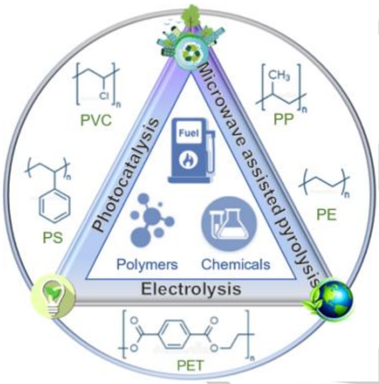

This Minireview highlights the state-of-the-art in exploiting alternative energies via photocatalysis, electrolysis, and microwave-assisted pyrolysis to chemically upcycle plastics waste into value-added products such as H_2, carbon-neutral fuels, chemical feedstocks, and functionalized polymers. The advances and challenges for each technology are reviewed to give insights into future trends for more sustainable plastics waste management.