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Metal Nanowire-Based Transparent Electrodes for Smart Window Applications

Par

Shengyun Huang

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Jury d'évaluation

Président du jury et examinateur interne

Examinateur externe

Examinateur externe

Directeur de recherche

Prof. Sergei Manzhos INRS-EMT

Prof. Tricia Breen Carmichael University of Windsor

Prof. Nianqiang (Nick) Wu University of Massachusetts Amherst

Prof. Dongling Ma INRS-EMT

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ABSTRACT

Nowadays, energy crisis has emerged as one of the serious issues that, if not addressed properly, can have dramatic consequences on our planet in the near future. Among the several factors that caused this crisis are rapid industrial and economic development, dramatic increase in the world's population, and heavy reliance on energy-based appliances. Consequently, research and development on new sustainable energy, energy conversion and storage technologies, and wise use of energy have attracted a great deal of interest. In particular, managing buildings' environment in a smart way emerged as one of the ways to address the energy issue as the construction sector uses as much as 30%-40% of the primary energy in the world. In a typical building, windows could be the major source of energy loss, or gain, depending on their design. Smart windows with tunable transmittance levels can reflect or block sunlight on scorching days and lower energy consumption by air conditioning appliances. Meanwhile, they can also be put in a transparent state to improve light harvesting in a low lighting condition, or enhance heat capture in cold weather. In addition, depending on personal preference, smart windows can control the transmission of solar radiation into buildings so as to tune visibility between indoors and outdoors for privacy and comfort. Although the efficiency depends on a variety of factors, their overall performance strongly relies on the transparent conductive electrodes used. Indium tin oxide (ITO) based transparent conductive electrodes have been the industrial standard for a long time. However, the use of ITO as a transparent electrode material has certain limitations, such as ever increasing cost due to indium scarcity, complicated processing requirements, sensitivity to acidic and basic environments, and high surface roughness. Moreover, ITO is brittle and can easily crack when used in applications where bending cannot be absolutely avoided. To overcome these issues, intense research efforts should be devoted to develop flexible, cheap, and solution-processable transparent conductive electrodes by exploring other materials for next generation smart windows. In this thesis, our work is mainly focused on developing nanowires (NWs) based network films and their practical applications as transparent conductive electrodes in high-performance suspended particle devices (SPDs) and electrochromic (EC) devices smart windows.

In the first part of the thesis, we developed a Cu-reduced graphene oxide core-shell NWs network film by vacuum filtration and subsequent thermal annealing. Moreover, a new SPD, holding a great potential for smart windows application, was built upon Cu-reduced graphene oxide coreshell NWs film as a transparent conductive electrode for the first time. As we know, Cu is 1000 times more abundant and 100 times cheaper than indium or silver. In addition, its electrical resistivity (16.8 n Ω m) is almost as low as that of silver, which is known to have the lowest resistivity (15.9 n Ω m) among all the materials. Based on these fundamental advantages, Cu NWbased transparent conductive electrodes have attracted growing interest as a potential alternative to ITO glass. However, several intrinsic drawbacks, such as low oxidation resistance, weak adhesion to substrates, and poor stability in harsh environments, have severely limited their widespread adaptation. With the wrapping of reduced graphene oxide, the Cu NW electrodes demonstrate both high optical transparency and electrical conductivity, as well as significantly improved stability under various testing conditions. The novel sandwich-structured SPDs, based on these electrodes, show large change in their optical transmittance (42 %) between "on" and "off" states, impressively fast switching time (20 s and 40 s for color bleaching and recovery, respectively) and superior stability. These high performances are comparable to those of the SPDs based on commercially available ITO electrodes. These promising results pave the way of our electrodes to be an integral part of a variety of optoelectronic devices, including energy-friendly and flexible electronics.

The Cu-reduced graphene oxide core-shell NWs network transparent conductive electrodes developed in Part I shows high optoelectronic performance and good stability. However, the area of such Cu-reduced graphene oxide core-shell NWs network film is too small due to the vacuum filtration method used during the film fabrication process, which is not suitable for large-area device application. Moreover, the high temperature thermal reduction process of the Cu-graphene oxide NWs, imperative during the electrode post-treatment, limits their application on flexible substrates. Ag, as another very promising candidate for transparent conductive electrodes, has the highest electrical conductivity among all the metals and better oxidation/corrosion resistance than Cu, which provides it with huge market opportunities. Therefore, in the Part II, we developed a free-standing, ultra-flexible and high-performance Ag NW transparent conductive electrodes with large size of 19 cm \times 9 cm using a facile and high-throughput automatic blade coating system for the first time, which is quite homogeneous and transparent over the entire area. Conventional solution-based electrode fabrication processes have several drawbacks for transparent conductive electrode electrode electrode applications, such as non-uniform morphology, difficulty of scale-up, high junction

resistance between NWs, poor adhesion to the substrate and low stability. The blade coating method exhibits more advantages in terms of higher film uniformity and easier operation as well as more convenient process scale-up. However, this automatic technique has so far rarely been applied in the fabrication of large-area NW transparent conductive electrode, highly likely due to the relatively rough surface of the NW film processed from this technique. In our case, with the smart use of a flexible and transparent polymer, the transparent conductive electrodes showed smoother surface, better conductivity, superior mechanical flexibility as well as strong structural integrity. The polymer played multiple roles: passivation (protection), and performance and structure strengthening. Our Ag NW transparent conductive electrodes showed excellent flexibility, which can be repeatedly bent for 10,000 cycles without any performance degradation, significantly better than commercial ITO-based transparent conductive electrodes. To explore the high potential of these transparent conductive electrodes, as a proof of concept demonstration we fabricated foldable SPDs for smart window applications, using Ag NW network-based film as transparent electrodes for the first time. Our devices showed large change in their optical transmittance (optical modulation 60.2 %) and fast switching time (21 s), as well as excellent stability. Significantly better than ITO-polyethylene terephthalate transparent conductive electrodebased electro-optic devices, the Ag NW electrode-based SPDs showed excellent mechanical flexibility, which can be folded by 180° for more than 200 cycles without obvious degradation of switching performance. The present method for fabricating large-area and ultra-flexible Ag NW transparent conductive electrode can be extended to fabricate a variety of NW-based nonplanar or curved electronic and optoelectronic devices in the future.

Although, the developed foldable Ag NW transparent conductive electrode-based SPDs in part II exhibited high optical modulation, fast switching time as well as excellent stability. The current SPDs technology requires a relatively high alternating current voltage of 110 V to control light transmission, which is not safe in use, especially in wearable devices. Moreover, nanoscale Ag NWs easily get oxidized and thus inevitably stop working in a long run as irreparable oxidation continues. Especially, when the Ag NW transparent conductive electrode was used as the anode in the EC device, the NWs lost their conductivity due to the oxidation during the charge carrier exchanging process with electrolyte. To address these issues, we developed a solid state, flexible EC device in the last part of the thesis. Such a device requires the delicate design of every component to meet the stringent requirements for transparency, flexibility and deformation

stability. However, the electrode technology in flexible EC devices remains stagnant, wherein inflexible ITO and fluorine-doped tin oxide are the main materials being used. Meanwhile, the brittle metal oxide usually used in an active layer and the leakage issue of liquid electrolyte during transformation further negatively affect device performance and lifetime. Therefore, we developed a novel and fully ITO-free flexible organic EC device by using Ag-Au core-shell NW (Ag-Au NW) network, EC polymer and LiBF₄/propylene carbonate/poly(methyl methacrylate) as electrodes, active layer, and solid electrolyte. The Ag-Au NW electrode integrated with a conjugated EC polymer together displayed excellent stability in harsh environments due to the tight encapsulation of the Ag NWs by the Au shell, and high area capacitance of 3.0 mF/cm² and specific capacitance of 23.2 F/g at current density of 0.5 mA/cm². The EC device showed high EC performance with reversible transmittance modulation in the visible region (40.2 % at wavelength of 550 nm) and near-infrared region (-68.2 % at wavelength of 1600 nm). Moreover, the device presented excellent flexibility and fast switching time. The strategies developed and demonstrated here for flexible EC devices may also serve as a platform technology for futuristic deformable electronics and optoelectronics.

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Figure 2.1 A schematic of the fabrication procedure for transparent Cu-GO NW films.

Figure 2.2 Photograph of the blade coating system used for preparing of Ag NW TCEs, and SPDs as well. It mainly includes three parts: (a) a vacuum chuck; (b) a micrometer adjustable film applicator; (c) a traverse pusher.

Figure 2.3 Four-point probe measurement on the top of the thin film.

LIST OF CHEMICAL COMPOUNDS, ABBREVIATIONS AND

SYMBOLS

Chemical Compounds

Cu	copper
Ag	silver
Au	gold
Pt	platinum
Та	tantalum
Si	silicon
In	indium
I_2	iodine
Ar	argon
H_2	hydrogen
N ₂	nitrogen gas
H_2O_2	hydrogen peroxide
CuCl2·2H2O	copper (II) chloride dihydrate
CaI ₂	calcium iodide
FeCl ₃	iron(III) chloride
CHCl ₃	chloroform
CH ₃ NO ₂	nitromethane

NaCl	sodium chloride
Fe(NO ₃) ₃ ·9H ₂ O	iron (III) nitrate nonahydrate
AgNO ₃	silver nitrate
LiBF ₄	lithium tetrafluoroborate
HAuCl ₄ ·3H ₂ O	gold(III) chloride trihydrate
NaOH	sodium hydroxide
Na ₂ SO ₃	sodium sulfite
$C_6H_8O_6$	L-ascorbic acid
WO ₃	tungsten trioxide
TiO ₂	titanium dioxide
MoO ₃	molybdenum trioxide
V ₂ O ₅	vanadium pentoxide
Nb ₂ O ₅	niobium(V) oxide

Abbreviations

TCE	transparent conductive electrode
NW	nanowire
GO	graphene oxide
rGO	reduced graphene oxide
CNT	carbon nanotube

ITO	indium tin oxide
R _s	sheet resistance
SPD	suspended particle device
AC	alternating current
DC	direct current
UV	ultraviolet
NIR	near-infrared
EC	electrochromic
PC	propylene carbonate
PMMA	poly(methyl methacrylate)
PVP	poly(vinylpyrrolidone)
PANI	polyaniline
PTFE	polytetrafluoroethylene
PVDF	polyvinylidene fluoride
PDMS	polydimethylsiloxane
DMF	N,N-dimethylformamide
L-AA	L-ascorbic acid
EG	ethylene glycol
HDA	hexadecylamine
IPA	isopropyl alcohol
2,5-PDA	pyrazine-2,5-dicarboxylic acid dehydrate

PET	polyethylene terephthalate	
STEM	bright field-scanning transmission electron microscopy	
CV	cyclic voltammetry	
HAADF	high angle annular dark field	
HRTEM	high-resolution transmission electron microscope	
NAA	neutron activation analysis	
SEM	scanning electron microscopy	
EDS	energy-dispersive X-ray spectroscopy	
TEM	transmission electron microscope	
XPS	X-ray photoelectron spectroscopy	
BE	binding energy	
XRD	X-ray diffraction	
Symbols		
Ω/sq	ohms per square	
cm	centimeter	
μm	micrometer	
nm	nanometer	
S	second	
min	minute	
h	hour	
°C	degree	

А	ampere
L	litre
g	gram
V	volt
θ	diffraction angle
λ	wavelength

LIST OF PUBLICATIONS AND CONFERENCE CONTRIBUTIONS

Journal Publications

- <u>Shengyun Huang</u>, Yannan Liu, Maziar Jafari, Mohamed Siaj, Haining Wang, Shuyong Zhao, Dongling Ma. Highly Stable Ag-Au Nanowire Networks for ITO-Free Flexible Organic Smart Window. Submitted to Advanced Functional Materials, minor revision.
- <u>Shengvun Huang</u>, Qingzhe Zhang, Fan Yang, Deepak Thrithamarassery Gangadharan, Pandeng Li, Fuqiang Ren, Baoquan Sun, Dongling Ma. A facile way for scalable fabrication of silver nanowire network electrodes for high-performance and foldable smart windows. Journal of Materials Chemistry A 2020, 8, 8620-8628.
- <u>Shengyun Huang</u>, Qingzhe Zhang, Pandeng Li, Fuqiang Ren, Aycan Yurtsever, Dongling Ma. High-Performance Suspended Particle Devices Based on Copper-Reduced Graphene Oxide Core-Shell Nanowires Electrodes. Advanced Energy Materials 2018, 1703658.
- Qingzhe Zhang, <u>Shengyun Huang</u>, Jiujun Deng, Zhenhe Xu, Giacomo Giorgi, Maurizia Palummo, Mohamed Chaker, and Dongling Ma. Ice-Assisted Synthesis of Black Phosphorus Nanosheets as a Metal-Free Photocatalyst: 2D/2D Heterostructure for Broadband H₂ Evolution. Advanced Functional Materials 2019, 29, 1902486.
- Fan Yang, Qingzhe Zhang, <u>Shengyun Huang</u>, Dongling Ma. Recent advances of near infrared inorganic fluorescent probes for biomedical applications. Journal of Materials Chemistry B, 2020, 8, 7856-7879.
- Fuqiang Ren, <u>Shengyun Huang</u>, Fan Yang, Aycan Yurtsever, Dongling Ma. Diameter Dependent Transparency Changes of Nanorod-based Large-are Flexible Smart Window Devices. Journal of Materials Chemistry A, 2018, 6, 24157-24165.

Conference Presentations

- <u>Shengyun Huang</u>, Fuqiang Ren, Dongling Ma. Copper-reduced graphene oxide core-shell nanowire films using as transparent conductive electrodes in high-performance suspended particle devices. Colloque annuel du CQMF, May 03-04, 2018, Montreal, Canada (*Poster presentation*).
- 2. <u>Shengyun Huang</u>, Fuqiang Ren, Dongling Ma. Study of transparent, conductive copper/reduced graphene oxide hybrid nanowire electrodes-based suspended particle

devices. International Conference on Energy, Materials and Photonics, July 08-11, 2018, Montreal, Canada (*Oral presentation*).

 Shengyun Huang, Fuqiang Ren, Dongling Ma. Exploration of copper-reduced graphene oxide core-shell nanowire films as transparent electrodes for high-performance suspended particle devices. ACS Fall National Meeting 2018, August 19-23, 2018, Boston, Massachusetts, USA (Oral presentation).

Patents

- 1. Shengyun Huang, Fuqiang Ren, Dongling Ma, et al. US Patent 15/586757, 2017. Granted
- 2. Shengyun Huang, Fuqiang Ren, Dongling Ma, et al. US Patent 16/125716, 2018.
- 3. Fuqiang Ren, <u>Shengyun Huang</u>, Dongling Ma, et al. US Patent 16/044863, 2018. *Granted*

CHAPTER 1 INTRODUCTION

In chapter 1, I give a brief introduction of transparent conductive electrode.

1.1 Transparent Conductive Electrode

Nowadays, electronic devices become an important part of our life, such as solar cells, smart phones, touch panels, flat display and smart windows, which are used not only for relaxation but also for communication and learning. Transparent conductive electrodes (TCEs) are an essential part in these electronic devices, which significantly affect the devices' performance and lifetime, as shown in Figure 1.1. TCEs rely on thin films of optically transparent and electrically conductive material. The global TCE market was about \$7.1 billion in 2018,¹ and is expected to grow with a compound annual growth rate of around 9% for period of 2018-2026 from the report of Touch Display Research in 2017.



Figure 1.1 Applications of transparent conductive electrodes in solar cells, smart phone, touch panel, flat display and smart window. The images are from the internet. https://www.digitalavmagazine.com/fr/2015/01/08/tcl-acude-a-las-vegas-con-el-tv-curvo-4k-mas-grande-del-mundo-con-110/tcl-4k-uhd-quantum-dot-tv-55-b/

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1.1.1 Development Process of TCE

The first report of a TCE was published in 1907, when Badeker reported that Cd thin films deposited in a glow discharge chamber could be oxidized to become transparent while remaining electrically conducting.² Since then, the commercial value of these thin films has been recognized, and the list of potential TCE materials has expanded to include, such as, GdInO_x, Al-doped ZnO, F-doped In2O3, and many others.

Since the 1960s, indium tin oxide (ITO) electrodes set the market standard for TCEs in most of electronics and optoelectronics.³ ITO has a ternary composition of indium, tin and oxygen in varying proportions, tuned depending on their application. For instance, to act as transparent electrodes, ITO typically has an oxygen-saturated composition with a formulation of 74% In, 18% O₂, and 8% Sn by weight. Indium oxide is a semiconductor and has bandgap between 3.5 to 3.7 eV. Therefore the large band gap leads to visible light transparent window. The conductivity of the ITO is due to the electrons donated to the conduction band. Because of the high carrier density, the conductivity approaches the level of metallic conduction. It has a high transparency (> 80%)and a low resistivity ($R_s < 100 \Omega/Sq$) and allows a precise control of its doping concentration and thickness. However, the use of ITO as a transparent electrode material has certain limitations, such as ever increasing cost due to indium scarcity, complicated processing requirements, sensitivity to acidic and basic environments, and high surface roughness. Moreover, ITO is brittle and can easily crack when used in applications where bending cannot be absolutely avoided. Therefore, intense research efforts have been devoted to develop flexible, cheap, and solution-processable TCEs by exploring other materials for next generation electronics and optoelectronics, such as flexible smart windows.

1.1.2 Performance Index of TCE

As TCEs in optoelectronic devices, electrical conductivity and optical transparency are obviously two key parameters that can significantly affect the device performance. Moreover, other properties, such as figure of merit, haze factor and surface roughness are also crucial factors evaluating a candidate material for use as the TCE, which will strongly influence device performance and lifetime.

1.1.2.1 Sheet Resistance

Electrical conductivity is a key parameter for the TCE materials. It is a fundamental property of materials that quantifies how strongly they conduct electric current. In the field of TCE, sheet resistance (R_s) is widely used instead of conductivity. It is a measure of the lateral resistance through a thin square of film. The key advantage of the R_s is that it allows an easy comparison between different samples, regardless of the size of the square

The resistance of a given object depends primarily on two factors: materials and its shape. The resistance (R) of the object can be defined according to the following formula:

$$R = \rho \frac{l}{A} \tag{1}$$

Where ρ *is* electrical resistivity, *l* is the length of the conductor, *A* is the cross-sectional area. The cross-sectional area can be split into the width *w* and the sheet thickness *t*, as shown in Figure 1.2.

The resistance can be then written as:

$$\mathbf{R} = \rho \frac{l}{wt} \tag{2}$$

As for R of one square piece, the *w* is equal to *l*, we can get:

$$R_{s} = \frac{\rho}{t}$$
(3)

From formula (3), we can see that value of R_s is related to ρ and *t* of the film, and independent of the size of the square. Therefore, R_s can be used to compare the electrical properties of TCE that are significantly different in size.



Figure 1.2 The schematic of sheet resistance for a thin film.

1.1.2.2 Transmittance

Transmittance (T) is another key parameter of TCE. It is the ratio of intensity of the transmitted light to that of the incident light and is always below 1. Transmission spectra is usually taken to evaluate the optical property of TCE at different wavelengths. In particular, the transmittance at 550 nm was most often selected for comparison because 550 nm is the most sensitive wavelength for human eyes.

As shown in Figure 1.3, when light goes through a thin film, reflection, absorption and scattering will occur simultaneously. The transmittance can be calculated using the following equation:

$$T = \frac{I}{I_0} = (1 - m)^2 e^{-(\alpha + S)x}$$
(4)

Where I_0 is the intensity of the incident light, x is the thickness of the thin film, m, α and S are reflection, absorption and scattering coefficient, respectively.

The absorption (Ia) is determined by the thickness of the materials and the absorption coefficient

$$I_a = I_0 e^{-\alpha x} \left(\alpha = 4\pi \kappa / \lambda \right) \tag{5}$$

Where κ *is* extinction coefficient.



Figure 1.3 The schematic illustration of transmitted light vs incident light.

1.1.2.3 Figure of Merit

In TCE research, it is important to rate the performance of new materials. In general, the figure of merit (FoM) is successfully used to evaluate the TCE. FoM is mainly determined by the transmittance and sheet resistance. It is defined as the ratio of direct current (DC) conductivity (σ_{DC}) to optical conductivity (σ_{Op}).

As we mentioned above in equation (3): $R_s = \frac{\rho}{t}$ and we know that $\sigma_{DC} = \frac{1}{\rho}$.

So we can get:

$$\mathbf{R}_{\mathbf{s}} = (\sigma_{DC}t)^{-1} \tag{6}$$

In the specific area of nanostructured films, the transmittance can be expressed using⁵⁻⁶

$$T = (1 + \frac{Z_0}{2}\sigma_{0p}t)^2$$
(7)

Combine equation (6) and (7), the relationship between transmittance (*T*) and sheet resistance (R_s) can be described as following equation⁶:

$$T = \left[1 + \frac{Z_0}{2R_s} \frac{\sigma_{OP}}{\sigma_{DC}}\right]^{-2}....(8)$$

Where Z_0 is the impedance of free space (377 Ω).⁶⁻⁸

Finally, we can get formula of FoM.

$$FoM = \frac{\sigma_{DC}}{\sigma_{Op}} = \frac{188.5}{R_s} \frac{\sqrt{T}}{1 - \sqrt{T}}$$
(9)

For industrial applications, the figure of merit value of TCEs should be larger than 35.9

1.1.2.4 Haze Factor

Another important parameter of TCEs is their light scattering, which is quantified in haze factor. The haze factor is defined as the percentage of light diffusely scattered compared to the total light transmitted.¹⁰ The needs of haze factor regarding TCE are different depending on applications.

For example, touch screens and display devices prefer TCE with low haze factor.^{3, 11} Because a high haze can lead to blurriness, which becomes an issue for touch screens and display devices. Haze is particularly important for smart window applications, in which light scattering will greatly reduce the sharpness of the window. However, solar cells performance would be enhanced by a large haze factor (>10 % is perferred) for the same transmittance and conductivity ¹²⁻¹³ Since scattering light enhances the optical path length of the photons in solar cells and futher increases their probability of being absorbed.

Previous studies indicate that the haze factor of NW TCE is sensive to NW diameters, the thicker the wires are, the larger the haze factor.¹¹ Niu *et al.* reported a modified polyol synthesis of Ag NWs with average diameters of ~13 nm, as shown in Figure 1.4a¹⁴. The optoelectronic performance of as-prepared 13 nm Ag NW TCE presents a low haze factor of ~1.2 % at a transmittance of 95%, better than that of commercial indium tin oxide (Figure 1.4b). The Ag NW etching can lead to diameter tailoring and roughness change, which can balance transmittance, conductivity and haze of TCE. Fang *et al.* developed high-performance hazy Ag NW TCE (Rs: 4 Ω sq-1, T: 88.4 % with haze of 13.3 %) through diameter tailoring for photovoltaics application, as shown in Figure 1.4a-b.⁷ The hazy Ag nanowire TCE based perovskite solar cells exhibit high power efficiencies up to 16.03% and 11.12% when illuminated from the bottom and top sides, respectively (Figure 1.4 c-d).⁷



Figure 1.4 (a) TEM image for thin Ag NWs. (b) Plots of haze factor versus transmittance of electrodes made with Ag NWs with different mean diameters. (c) Optical image of a hazy Ag NWs TCE (T: 88.4%, R_s: 4 Ω sq⁻¹, Haze: 13.3 %) and a commercial FTO TCE (T: 89.2%, R_s: 8 Ω sq⁻¹, Haze: 11.4 %). (d) Schematic structure of the hazy Ag NWs TCE based perovskite solar cell. (a-b) Reproduced with permission from Ref. 14. Copyright 2018 American Chemical Society. (c-d) Reproduced with permission from Ref. 7. Copyright 2018 Wiley-VCH.

1.1.2.5 Surface Roughness

Surface roughness is quantified by the deviations in the direction of the normal vector of a real surface from its ideal form. If these deviations are large, the surface is rough; if they are small, the surface is smooth. Roughness plays an important role in determining how a real object will interact with its environment. As for TCE field, the rough morphology of surfaces can alter the operational conditions of microelectronic devices.

1.2 Alternative Materials of ITO TCEs

To overcome drawbacks of ITO electrode, many alternative transparent conductive materials such as carbon nanotubes (CNTs), graphene, conducting polymer, metal mesh and metal NWs, have been studied in the past few years. The optoelectronic of various families of TCEs indicated that Cu/Ag NWS network and graphene films have comparable properties to the ITO (Figure 1.5a).¹⁵ However, the material and process cost for Cu/Ag NWs network is significantly lower than ITO, as show in Figure 1.5b.¹⁵



Figure 1.5 (a) Optoelectronic properties of various TCE. (b) Material versus process cost of various TCE. Reproduced with permission from Ref. 15. Copyright 2015 Elsevier.

1.2.1 Carbon Nanotubes

In 1993, first experimental observations of CNTs were made by Iijima *et al.*¹⁶ Since then, CNTs have attracted a great deal of interest due to their excellent properties, such as super mobility (>10⁵ cm²/Vs),¹⁷ large current carrying capacity (10⁹ A/cm²)¹⁸ and high electrical conductivity (2×10⁷ S/cm)¹⁹. CNTs thin film has good electrical conductivity, high structural stability, excellent flexibility, and desirable optical properties (low refractive index and low haze).²⁰ The theoretical analysis shows that CNTs thin film can possibly obtain a high electrical conductivity of 9×10^4 S/cm,²¹ which is 10 times higher than that of ITO film.

In 2004, Wu *et al.* first described continuous films of pure single-walled CNTs (SWCNTs) as new TCEs with R_s of 30 Ω /sq, T of 83 % (at 550 nm) and conductivity of 6600 S/cm using a vacuum filtration method (Figure 1.6 a-c).²² In the same year, Hu *et al.* reported ultrathin and uniform SWCNTs networks of varying CNT densities for TCEs prepared by a vacuum filtration method (Figure 1.6d-e).²³ In the following decade, significant effort has been dedicated to developing high optical and electrical performance SWCNT-based TCEs by a number of groups.²⁴⁻²⁸



Figure 1.6 (a) Transparent SWCNT films with thickness of 50 nm and 150 nm on quartz substrates. (b) A large, 80-nm-thick SWCNT film on a sapphire substrate 10 cm in diameter. (c) AFM image of a 150-nm-thick transparent SWCNT film surface (color scale: black to bright yellow, 30 nm). The text in (a) and (b) lies behind the films. SEM images of CNT network of varying densities resulting from filtering (c) 7 mL and (d) 400 mL of CNT suspensions. (a-c) Reproduced with permission from Ref. 22. Copyright 2004 AAAS. (d-e) Reproduced with permission from Ref. 23. Copyright 2004 American Chemical Society.

Recently, significant progress for SWCNTs-based TCEs was obtained by Cheng's group.^{20, 29-30} Jiang *et al.* reported a film of isolated SWCNTs synthesized by an injection floating catalyst chemical vapor deposition (CVD) method, in which crossed SWCNTs were welded together by graphitic carbon (Figure 1.7a).²⁰ The SWCNTs-based films showed a record performance with average sheet resistance of 41 Ω /sq at transmittance of 90 % (Figure 1.7b).²⁰ Wang *et al.* proposed a continuous synthesis, deposition and transfer technique for the fabrication of high-quality and meter-scale dimension SWCNT thin films with excellent optoelectrical performance (Figure 1.7c-f). The as-prepared SWCNT films have a low sheet resistance of 65 Ω /sq and a high transmittance of 90 % at wavelength of 550 nm. However, several problems remain: i) high production costs. The CNTs can be synthesized by various methods, such as laser ablation, electric arc discharge, catalytic CVD, laser-assisted CVD and plasma-enhanced CVD.^{26, 31-35} Most of these methods are highly energy-consuming and expensive; ii) high junction resistance between CNTs, which is

much higher than the intrinsic CNT resistance. Therefore, the overall electrical property of CNTbased TCE is largely dominated by the resistance at intertube junctions.³⁶ iii) severe aggregation of CNTs into bundles due to their ultra-high length-diameter ratio, which significantly lowers the light transmission;³⁷ and iv) lacking of simple and scalable fabrication technique for producing large-area, uniform and robust CNT-based TCE.



Figure 1.7 (a) Typical TEM image of isolate SWCNTs with the carbon-welded joints. Scale bar, 10 nm. (b) Transmittance at wavelength of 550 nm versus sheet resistance of treated SWCNT TCE together with the previously reported results for untreated CNT TCEs in the literatures and a superior ITO TCE on a polymer substrate. The inset is optical image of an 80 mm × 80 mm SWCNT TCE. (c) Schematic showing the apparatus designed for the synthesis, deposition, and transfer of meter-scale SWCNT films. SWCNTs were grown continuously by a floating catalyst CVD technique in the reactor and then collected by a gas-filtration and transfer system. When the membrane filter is able to move around the filtration chamber, a large-area SWCNT thin film can be continuously deposited on it, and roll-to-roll transferred onto a flexible PET substrate. (d) A photograph of the home-made apparatus (scale bar, 0.5 m). (e) A SWCNT thin film transferred on a flexible PET substrate with a length of more than 2 m. (f) A roll of uniform SWCNT thin film on the PET substrate (scale bar, 0.1 m). (a-b) Reproduced with permission from Ref. 20. Copyright 2018 AAAS. (c-f) Reproduced with permission from Ref. 29. Copyright 2018 Wiley-VCH.

1.2.2 Graphene

Graphene, an atomically thin layer (0.34 nm) of sp²-bonded carbon atoms with the honeycomb lattice structure, has emerged as an attractive candidate for various application due to its unique structure and exceptional physical properties, such as high electron mobility (>15000 cm²/s) electrical conductivity and optical transparency, good mechanical flexibility, and excellent chemical stability. It is a basic two-dimensional (2D) building unit for many carbon materials of all other dimensionalities, such as zero-dimensional (0D) fullerenes, one-dimensional (1D) nanotubes and three-dimensional (3D) graphite, as shown in Figure 1.8b.³⁸ Graphene was first observed by Geim *et al.* using mechanical exfoliation (Figure 1.8a),³⁹ which led to an explosion of interest. Graphene now can be prepared using different kinds of methods, such as mechanical exfoliation,³⁹ chemical vapor deposition,⁴⁰⁻⁴² epitaxial growth on SiC,⁴³ and chemical exfoliation.⁴⁴ Theoretical estimates indicate that the sheet resistance of graphene is 62.4/N Ω /sq, where N is the number of monolayer of graphene.⁴⁵ Nair *et al.* found that graphene absorbed 2.3 % of incident white light due to its unique electronic structure.⁴⁶ De *et al.* calculated that four randomly stacked graphene layers can display transmittance of 90% with sheet resistance of 10 Ω /sq.⁴⁷



Figure 1.8 (a) Photograph of a large graphene on an oxidized Si wafer. (b) Graphene is a basic building material block for graphitic materials of all other dimensionalities. It can be wrapped up in to 0D fullerenes, rolled into 1D nanotubes and stacked into 3D graphite. (a) Reproduced with permission from Ref. 39. Copyright 2004 AAAS. (b) Reproduced with permission from Ref. 38. Copyright 2010 Nature Publishing Group.

Over the past few years, plenty of work has been attempted on the design and preparation of high-performance graphene-based TCE.^{42, 48-52} Kim *et al.* reported large-scale graphene films

using CVD on thin nickel layer (Figure 1.9a).⁴² The graphene was then transferred to PDMS substrate with sheet resistance of ~280 Ω /sq at transmittance of 80 % (Figure 1.9b). However, the electrical and optical properties of graphene/PDMS TCE remains unsatisfactory. Bae *et al.* developed the roll-to-roll production of 30-inch monolayer graphene on copper substrate and further used layer-by-layer stacking to fabricate a doped four-layer graphene/PET TCE (Figure 1.9c).⁴⁸ The graphene/PET TCE shows high-performance with sheet resistance ~30 Ω /sq at ~90 % transparency and was further used to fabricate four-wire touch panel (Figure 1.9e-f).



Figure 1.9 (a) SEM images of graphene films on nickel film by CVD method. (b) Flexible graphene films on the PDMS substrate TCE. (c) Schematic of roll-to-roll production of graphene TCE. (d) Roll-to-roll transfer of graphene films from a thermal release tape to a PET film at 120 °C. (e) A graphene TCE-based touch panel connected to a computer with a control software. (a-b) Reproduced with permission from Ref. 42. Copyright 2009 Nature Publishing Group. (c-e) Reproduced with permission from Ref. 48. Copyright 2010 Nature Publishing Group.

However, the high process temperature (1000 °C) of CVD inhibits the utilization of graphene for various device application, and the complex doping procedure makes it incompatibly with high-throughput production required for practical application. Chemical reduction of graphene oxide

(GO) has been considered and now accepted as a cost-effective approach for scaling-up the production of graphene, the controllable assembly of which or with other materials towards functional structures is highly concerned at present.⁵³⁻⁵⁸

1.2.3 Conducting Polymer

Conducting polymers are organic polymers that conduct electricity. In 1977, H. Shirakawa, A. J. Heeger and A. MacDiarmid discovered similar high conductivity in doped polyacetylene.⁵⁹⁻⁶⁰ For the discovery and development of conductive polymer, they were awarded the Nobel Prize in Chemistry in 2000. However, polyacetylene was not applied to practical applications due to its instability under ambient conditions. Conductive polymers drew the attention of scientists and encouraged the rapid growth of the field in the 1980s. A broad range of commonly available polymers, such as polyaniline (PANI),⁶¹ polypyrrole (PPY)⁶² and polythiophene⁶³, were found to exhibit high electrical conductivities by simple chemical doping. Figure 1.10 shows Structure of PANI, PPY and poly(3,4-ethylenedioxythiophene) (PEDOT) in their neutral forms. Among these polymers, PEDOT was first discovered in 1988⁶⁴ and brought to the forefront in the research and industrial laboratories.



Figure 1.10 Structure of PANI, PPY and PEDOT in their neutral forms.

PEDOT, a positively doped conducting polymer, with fairly high conductivity and transparency, is regarded as a promising candidate for ITO TCE replacement due to its cost-effective and flexible properties. However, the insolubility of PEDOT in most solvents inhibits its practical application. In the 1990s, Starck *et al.* first doped PEDOT with negatively charged poly (styrenesulfonate) (PSS), which added aqueous solubility to the PEDOT as well as served as counterion for stabilizing

the positive charges of PEDOT.⁶⁵ The doping of PSS in PEDOT addresses two big issues between the application and research, leading to the largest technical application success. Aqueous suspensions of PEDOT:PSS can be commercially obtained with different conductivity. However, the conductivity of PEDOT:PSS is usually remarkably lower than that of ITO and secondary dopant is required.⁶⁶⁻⁶⁹ Kim *et al.* studied the effect of the solvent treatment on PEDOT:PSS and obtained the highest conductivity of 1418 S/cm.⁷⁰ The AFM phase images show that pristine films consist of disconnected, conducting PEDOT-rich grains with weak phase separation, whereas the doped films reveal better connection and fairly well defined phase separation (Figure 1.11 a-d). Xia *et al.* reported a facile method to significantly enhance the conductivity of PEDOT:PSS films from ~0.3 to ~3000 S/cm after being doped with H₂SO₄.⁶⁹ Figure 1.11e shows the conductivities of PEDOT:PSS films through treatment with different concentrations of H₂SO₄ solutions. The H₂SO₄-doped PEDOT:PSS TCE based solar cells showed comparable photovoltaic performance to that of ITO TCE, as shown in Figure 1.10f.



Figure 1.11 AFM phase images of PEDOT:PSS films with various solvent treatments: (a) Pristine PEDOT:PSS; (b) Doped with DMSO 5 vol% (389 S/cm); (c) Doped with EG 6 vol% (634 S/cm); (d) Solvent post-treated and doped with EG 6 vol% (1330 S/cm). (e) Conductivities of PEDOT:PSS films after treated with different concentrations of H₂SO₄ solutions at 160 °C. (f) The current density-voltage curves of ITO and a H₂SO₄-treated PEDOT:PSS film TCE based solar cells under AM 1.5G illumination. (a-d)
Reproduced with permission from Ref. 70. Copyright 2011 Wiley-VCH. (e-f) Reproduced with permission from Ref. 69. Copyright 2012 Royal Society of Chemistry.

Despite the great gains in PEDOT:PSS, one of the remaining key issues is its poor electrical stability. PEDOT:PSS can decrease conductivity upon exposure to UV light, high temperature or high humidity.⁷¹⁻⁷² Another issue is that the optical and electrical properties of PEDOT:PSS are still lower than that of ITO, which inhibits its widespread adoption.

1.2.4 Metal Mesh

It is well known that most of metals exhibit outstanding electrical conductivity due to their high free-electron density. Meanwhile, the metal films have poor transmittance because of large reflection. These properties severely limit their application in TCE. Therefore, ultrathin film or metal mesh is required to meet the optical transmission of TCE. For continuous ultrathin film, the transmittance is generally lower than 56 % when their sheet resistance is comparable to that of commercial ITO TCE.⁷³⁻⁷⁴ Metal mesh, allowing 100 % optical transmission through the holes, can meet the requirement of TCE.

For traditional metal mesh, the line width is normally larger than 100 µm, which leads to high surface roughness and big shadowing loss.⁷⁵ To address this issue, many novel printing techniques were involved.⁷⁶⁻⁷⁷ Jiang et al. reported a reverse-offset printing method to print a uniform and ultrathin Ag mesh TCE with low sheet resistance of 17 Ω /sq at high transmittance of 93.2 %, as shown in Figure 1.12a.⁷⁸ One merit of the reverse-offset printing process is its high resolution. The printed lines can be downscaled to as small as 5 µm with good line thickness uniformity and edge straightness (Figure 1.12a). Owing to the above features, organic solar cells using the Ag meshes achieved a high power conversion efficiency (PCE) of 8.3 %, which is comparable to that obtained on ITO TCE (8.5%). Recently, Schneider et al. combined the 3D capabilities and the nanoscale resolution of electrohydrodynamic NanoDrip printing to pattern high aspect ratio Ag and Au mesh TCEs (Figure 1.12b).⁷⁹ The patterned Ag and Au meshes showed very small line widths from 80 to 500 nm (Figure 1.12c). The as-prepared metal mesh TCE can be tailored on demand for various applications, such as low sheet resistance (8 Ω /sq at transmittance of 94%) as well as high transmittance (97 % with sheet resistance of 20 Ω /sq). Although the metal mesh showed superior optical and electrical properties, the electrohydrodynamic printing is expensive and not suitable for large-scale production.



Figure 1.12 (a) Ultrathin Ag mesh TCE by reverse-offset printing. Top: schematic for fabrication process; Bottom: SEM images and surface profile measurement. (b) Illustration of high-aspect ratio pattering using electrohydrodynamic NanoDrip printing. (c) Printed square silver (left) and truncated hexagonal gold (right) grids. (a) Reproduced with permission from Ref. 78. Copyright 2018 Wiley-VCH. (b-c) Reproduced with permission from Ref. 79. Copyright 2016 Wiley-VCH.

Besides conventional highly-ordered patterned metal meshes as mentioned in above, several novel methods, such as crack template,⁸⁰⁻⁸¹ grain boundary template,⁸² bioinspired template⁸³ and electrospinning polymer fiber template,⁸⁴ have been developed during these years. In 2014, Han *et al.* fabricated a cheap, highly transparent, conductive and flexible metal mesh TCE via a self-formed crack template.⁸⁵ The fabrication process mainly includes four steps: preparation of TiO₂ template film, self-cracking, Ag film deposition, and template film lift-off (Figure 1.13a). The resulting Ag meshes TCE showed better optoelectronic performance than ITO as well as good adhesion to flexible substrates. In the same year, they developed two different metal meshes for specific application, inspired by leaf venation and spider web networks (Figure 1.13b-c).⁸⁶ Nonetheless, achieving large-area and high-performance TCE with these bio-inspired networks remain a great challenge. Wu *et al.* presented a facile fabrication process incorporating electrostatic spinning PVA template and vacuum Au film deposition to develop a new kind of metal nanotrough network TCE.⁸⁴ The metal nanotrough TCE exhibited both superior optoelectronic performances

(sheet resistance of 2 Ω /sq at transmittance of 90 %) and remarkable mechanical flexibility. Recently, they combined the electrostatic spinning and electroless deposition to prepare highperformance metal mesh TCEs.⁸⁷ The process is scalable and occurs at ambient temperature.



Figure 1.13 (a) Schematic of metal mesh fabrication by using crack template. The structures of gel film, cracks and network are shown on the right column. (b) Schematic of the leaf venation network fabrication method. (c) Schematic of the spider web network fabrication process and SEM images of spider web network-Ag based TCE. (a) Reproduced with permission from Ref. 85. Copyright 2014 Wiley-VCH. (b-c) Reproduced with permission from Ref. 86. Copyright 2014 Nature Publishing Group.

1.2.5 Metal Nanowires

The networks of metal NWs hold great promise for low-cost transparent electrode application because of their high electrical and optical properties, as well as their solution-processability.³ The key to metal NW TCE is the growth of thin diameter, long, smooth and highly pure metal NWs. Up to now, great efforts on metal NW network TCEs have been mainly made on Cu NWs and Ag NWs due to their high conductivity and simple wet-chemical synthesis.

1.2.5.1 Cu NW TCE

Copper is 1000 times more abundant and 100 times cheaper than indium or silver. Moreover, its electrical resistivity (16.8 n Ω ·m) is almost as low as that of silver, which is known to have the

lowest resistivity (15.9 n Ω ·m) among all the materials. Based on these fundamental advantages, Cu NW-based TCEs have attracted growing interest as a potential alternative to ITO glass.



Figure 1.14 (a) SEM image of Cu NWs. Inset is as-prepared Cu NWs in mother liquor. (b-c) Highresolution SEM and TEM images of Cu NWs. (d) Photograph of large-scale reaction flask after growth of Cu NWs. (e) Optical image of Cu NW network film. (f) SEM of Cu NWs with Cu nanoparticles attached to one end. (a-c) Reproduced with permission from Ref. 88. Copyright 2005 American Chemical Society. (d-f) Reproduced with permission from Ref. 89. Copyright 2010 Wiley-VCH.

In general, Cu NWs can be synthesized via a wet chemical method by reducing Cu ions in the presence of capping ligands in solution. In 2005, Zeng *et al.* reported that high-quality and ultralong Cu NWs (diameter: 90-120nm, length: 40-50 μ m) can be synthesized in large scale under mild conditions for the first time (Figure 1.14a-c).⁸⁸ In the synthesis, Cu(NO₃)₂ was reduced by N₂H₄ in the presence of ethylenediamine (EDA) as capping ligand in basic solution. Rathmell *et al.* scaled up the reaction 200 times (from 6 mg to 1.2 g) through modifying the experimental parameters to demonstrate the high potential of this synthesis method for large-scale production (Figure 1.14 d).⁸⁹ Then, they fabricated Cu NW TCE via vacuum filtration, as shown in Figure 1.14e. However, the Cu NW TCE showed a low transmittance of 65 % at sheet resistance of 15 Ω /sq due to aggregation and low aspect ratio (diameters: 90±10 nm; lengths: 10V±3 μ m) of Cu

NWs (Figure 1.14f). To address this issue, many efforts have been attempted during the following years.⁹⁰⁻⁹¹ Xia *et al.* developed ultra-long and thin Cu NWs with diameters of 24 ± 4 nm and lengths of several tens to hundreds of micrometers (Figure 1.15 a-c).⁹² The Cu ions were reduced by glucose using hexadecylamine (HDA) as capping agent. Wiley *et al.* increased the aspect ratio of Cu NWs as high as 5700 (200 µm in length and 35 nm in diameter) by modifying the EDA-based synthesis (Figure 1.15 d-e).⁹³ These nanowires were used to prepare Cu NW TCE via rod coating with a transmittance > 95 % at a sheet resistance < 100 Ω /sq (Figure 1.15f). Recently, Yang *et al.* reported a new approach to synthesize ultrathin Cu NWs using tris(trimethylsilyl)silane as a mild reducing reagent, with an average diameter of 17.5 nm and a mean length of 17 µm (Figure 1.15g).⁹⁴ The uniform Cu NW TCE was fabricated by vacuum filtration high optoelectronic performance (Figure 1.15h).



Figure 1.15 SEM (a) and TEM (b) images of Cu NWs prepared using HDA as capping agent. (c) XRD pattern of the Cu NWs. (d-e) SEM images of ultra-long Cu NWs prepared by N₂H₄. (f) Optoelectronic performance of various TCES. (g) SEM image of ultrathin Cu NWs. (h) Plot of transmittance versus sheet resistance for ultrathin Cu NW TCEs. (a-c) Reproduced with permission from Ref. 92. Copyright 2011 Wiley-VCH. (d-f) Reproduced with permission from Ref. 93. Copyright 2014 Royal Society of Chemistry. (g-h) Reproduced with permission from Ref. 94. Copyright 2015 American Chemical Society.

Although great efforts have been achieved for high optoelectronic Cu NW TCEs by a number of groups,⁹⁵⁻⁹⁹ their low oxidation resistance and poor stability in harsh environments prohibit their widespread adaptation. To address these issues, it is necessary to protect the Cu NWs with an antioxidative layer, which can significantly improve their stability. These materials should be able to completely eliminate the exposed Cu surface. Various materials, including graphene oxide,¹⁰⁰ graphene,¹⁰¹ metal oxide¹⁰² and metal,¹⁰³ have been attempted. Ruoff et al prepared hybrid films composed of reduced graphene oxide (RGO) and Cu NWs (Figure 1.16a).¹⁰⁰ Thanks to tight encapsulation of the reduced graphene oxide, the hybrid films show improved electrical conductivity, higher oxidation resistance and better adhesion to substrate than Cu NW films. Furthermore, the Prussian blue-based electrochromic devices on RGO/Cu NW films performed significantly better than that on pure Cu NW films. Lee et al. first successfully synthesized a Cu NW-graphene core-shell (Cu NW-G) nanostructure via a plasma-enhanced CVD process at temperatures as low as 400 °C.¹⁰⁴ The Cu NW-G TCE showed excellent optoelectronic properties compared to the traditional ITO TCE. In addition, Cu NW-G TCE exhibited remarkable chemical stability and thermal oxidation due to the tight encapsulation of the graphene (Figure 1.16b). The potential suitability of Cu NW-G TCE was demonstrated by fabricating polymer solar cells, which showed higher PCE than those with pure Cu NW TCEs. However, as we mentioned in above, CVD method is not compatible with low-cost and high-throughput production required for practical applications. Recently, Yang et al. reported a solution-based method to wrap RGO nanosheets on the surface of thin Cu NWs.¹⁰⁵ The Cu-RGO core-shell NW network TCE showed excellent stability in air and comparable performance to ITO thin film (sheet resistance ~28 Ω/sq , haze ~2 % at transmittance of ~90 %). Besides carbon materials, Wiley et al. utilized metals, such as Ni, Ag, Au, Pt to protect Cu NWs from oxidation.^{103, 106} However, due to the galvanic replacement, encapsulation is complete and the core-shell NWs are rough. Recently, Yang et al. developed thin Cu-Au core-shell NWs using trioctylphosphine as strong binding ligand to prevent galvanic replacement reactions.¹⁰⁷ The epitaxial overgrowth of a thin Au layer on Cu NW can greatly increase their resistance to heat (80 °C), humidity (80 %) and air for at least 700 h, while keep their optoelectronic performance (sheet resistance of 35 Ω /sq at transmittance of ~89 % with a haze < 3%) (see Figure 1.16c). More recently, Le *et al.* developed a facile adsorption and decomposition process for galvanic replacement free and large-scale synthesis of highly stable Cu-Ag core-shell NWs (Figure 1.16d).¹⁰⁸ The Cu-Ag core-shell NW TCEs showed excellent stability

at high temperature of 140 °C and standard harsh environment (85 °C, 85 % RH) for at least 500 h.



Figure 1.16 Four different antioxidative layer for Cu NWs. (a) Hybrid films composed of reduced graphene oxide and Cu NWs. (b) Synthesis of the Cu NW-G core-shell nanostructure by the low-temperature plasmaenhanced CVD. (c) Ultrathin Cu-Au core-shell NWs with excellent stability. (d) Schematic diagram of galvanic replacement free formation of Cu-Ag core-shell NWs. (a) Reproduced with permission from Ref. 100. Copyright 2013 American Chemical Society. (b) Reproduced with permission from Ref. 104. Copyright 2015 American Chemical Society. (c) Reproduced with permission from Ref. 107. Copyright 2017 American Chemical Society. (d) Reproduced with permission from Ref. 108. Copyright 2019 American Chemical Society.

1.2.5.2 Ag NW TCE

Ag, as another very promising candidate for TCEs, has the highest electrical conductivity $(6.3 \times 10^7 \text{ S/m})$ among all the metals and good oxidation/corrosion resistance, which renders it huge market opportunities.¹⁰⁹ In 2000, Yang *et al.* first synthesized Ag NWs through mesoporous silica template, which are too short to be used in TCE application.¹¹⁰ In 2002, Xia *et al.* reported soft solution-processed Ag NWs with small diameters of 30-60 nm and long lengths up to ~50 µm.¹¹¹⁻¹¹² In 2008, Peumans *et al.* first developed solution-processed Ag NW continuous networks as TCEs, which exhibited optical and electrical properties equivalent to or better than that of ITO TCE.¹¹³ The organic solar cells based on these Ag NW TCEs showed a comparable PCE to that of ITO TCE.

During subsequent decades, high-performance Ag NW-based TCEs were obtained by many groups.^{109, 114-115} However, these TCEs suffer from inherent limitations that severely restrict their widespread practical application. For instance, poly(vinylpyrrolidone) (PVP) has been widely used as a ligand in the synthesis of Ag NWs, which however introduces an insulating barrier around each NW and thus dramatically increases the contact resistance between NWs and decreases the overall electrical conductivity of TCEs. To address this issue, many efforts have been made, involving heating, plasmonic and pressing treatments, to get rid of the ligand layer. For example, Peumans et al. utilized thermal annealing at a temperature of 200 °C to reduce the sheet resistance of Ag NWs TCE from >1 k Ω /sq to ~100 Ω /sq.¹¹³ The reduction in sheet resistance is because thermal annealing can remove PVP surfactant layer and fuse Ag NWs together. However, continued annealing at 200 °C for more than 40 min led to an increase in sheet resistance as the Ag NWs broke into disconnected droplets (see Figure 1.17a). Brongersma et al explored a lightinduced plasmonic nanowelding technique to assemble Ag NWs into large interconnected networks with lower sheet resistance(Figure 1.17b).¹¹⁶ The small gaps between Ag NW junctions enable effective light concentration and heating only at the point where the NWs need to be fused together, preventing damage to plastic substrates. Lee et al. developed the flash-induced plasmonic interactions of Ag NWs for exceptionally low sheet resistance of ~5 Ω /sq, high transparency of 90 % as well as strong adhesion on substrates.¹¹⁷ Recently, Choy et al. demonstrated a low-cost, robust and room atmosphere process to fabricate Ag NWs network comprising Ag NWs and Ag nanoparticles.¹¹⁸ The Ag nanoparticles was selectively grown in situ at Ag NWs junctions via plasmon-induced chemical reaction technique at room temperature (see Figure 1.17c). Besides plasmonic treatments, they also proposed a simple alcohol-based solution approach to weld crossed Ag NWs by chemically growing Ag solder at the junctions, forming Ag NWs network TCE with improved electrical conductivity and operational stability (Figure 1.17d).¹¹⁹ Suganuma et al. demonstrated that the electrical conductivity of Ag NW TCE can be improved by mechanical pressing at 25 MPa for 5 s at room temperature.¹²⁰ This simple process significantly decreased the sheet resistance of Ag NW TCEs from 6.9×10^6 to 8.6 Ω /sq, while kept their transparency of 80 % (Figure 1.17e). Interestingly, Ren et al. found that capillary force could be a powerful driving force to cause self-limited cold welding of the Ag NWs junctions.¹²¹ They can simply applied moisture on Ag NW TCE to weld Ag NWs junctions without any other support techniques (Figure 1.17f).

The moisture-treated Ag NW TCEs showed a dramatic decrease in sheet resistance, while kept their transparency.



Figure 1.17 (a) Sheet resistance vs thermal annealing time for Ag NW TCE at 200 °C. Inset is SEM image of Ag NW TCE after 40 min of annealing. (b) Schematic of plasmonic welding Ag NWs junctions and TEM image of Ag NWs junction after welding. (c) Schematic of selective growth Ag nanoparticles on Ag NWs junctions via plasmon-induced chemical reaction. (d) The resistance variation of different Ag NW TCE with and without alcohol-based chemical treatment. (e) SEM image of the Ag NW TCE pressed at 25 MPa for 5 s and sheet resistance of Ag NW TCE after pressing at various applied pressures. (f) SEM images of Ag NWs junctions before and after moisture treatment. Scale bar: 200 nm. (a) Reproduced with permission from Ref. 113. Copyright 2008 American Chemical Society. (b) Reproduced with permission from Ref. 116. Copyright 2012 Nature Publishing Group. (c) Reproduced with permission from Ref. 119. Copyright 2014 American Chemical Society. (d) Reproduced with permission from Ref. 119. Copyright 2015 Wiley-VCH. (e) Reproduced with permission from Ref. 120. Copyright 2011 Tsinghua University

and Press Springer-Verlag Berlin Heidelberg. (f) Reproduced with permission from Ref. 121. Copyright 2017 American Chemical Society.

In addition, regarding electrode fabrication various solution-based processes, such as spin coating,¹²² spray coating,¹²³ vacuum filtration,¹²⁴ brush coating¹²⁵ and rod coating,¹²⁶ have been developed to prepare flexible Ag NW TCEs. For example, Johansson et al. used spin coating method to prepare flexible Ag NW-polyethylenenaphthalate (PEN) TCE and applied them for solar cells application.¹²⁷ The Ag NW-PEN TCE showed comparable transparency and conductivity to the traditional ITO-based electrode. Suganuma et al. developed a facile, fast and one-step methodology to fabricate highly conductive and stretchable Ag NW TCE via combining spray coating with a high-intensity pulsed light (HIPL) technique.¹²⁸ As shown in Figure 1.18a, Ag NWs ethanol dispersion was first deposited on cleaned polyurethane (PU) substrate by spray coating method. After drying for a few seconds in air, the Ag NW films were treated with HIPL at room temperature in air. The resulting Ag NW TCEs retained a low sheet resistance of $< 10 \Omega/sq$ under 100 % strain or after 1000 continuous stretching-relaxation cycles. Ko et al. reported highly stretchable and highly conductive Ag NW electrodes via vacuum filtration and film transfer technique (see Figure 1.18b).¹²⁹ A very recent study by Won et al. reported a vacuum filtration method that achieved ultra-thin/flexible Ag NW-polyimide (PI) TCE for electronic skin application.¹³⁰ The Ag NW-PI TCE showed excellent flexibility and stretchability, compared electrical and optical properties to that of ITO electrode. Dong et al. demonstrated flexible and high-performance Ag NW-PI TCEs by a spin coating and patterning method used in nonfullerene organic solar cells.¹³¹ The fabricated flexible solar cells displayed a power conversion efficiency of 11.6%. In order to obtain large-area flexible Ag NW TCE, Cui et al. developed a Meyer rod coating method for scalable roll-to-roll deposition of Ag NW TCEs (Figure 1.18c).¹³² The asprepared Ag NW TCE showed high optoelectronic performance (sheet resistance of 20 Ω /sq at transmittance of 80 %) and excellent robustness. More recently, Jiang et al. reported a flexible Ag NW TCE with anisotropic conductivity by a facile conical fibers array-guided liquid transfer approach, which gave significantly different conductivity through directions of parallel with and vertical to the brushing direction.¹²⁵ However, these conventional film deposition processes generate several drawbacks for TCE applications, such as non-uniform morphology, difficulty of scale-up, high junction resistance between NWs, poor adhesion to the substrate and low stability in harsh environments. To address these issues, alternative approaches, such as LangmuirBlodgett,¹³³ capillary printing,¹³⁴ and modified Meyer rod coating,¹³⁵ have also been attempted. Ko *et al.* adopted and modified a conventional Meyer rod coating technique to fabricate large-area (> 20 × 20 cm²) and flexible TCEs based on cross-aligned Ag NW networks with high optoelectronic performance (sheet resistance of 21.0 Ω /sq at transmittance of 90.4 %).¹³⁵ The alignment of Ag NW TCE by modified rod-coating assembly was carried out by dragging a Meyer rod at a constant velocity and predefined rod-substrate gap distance over a Ag NW solution on the substrate (see Figure 1.18d). They also demonstrated large-scale, flexible, and transparent touch screens using these cross-aligned Ag NW TCEs, which showed highly uniform and precise touch sensing performance across the entire region. Despite the remarkable process, however, the development of simple, scalable and cost-effective fabrication technique for producing large-area, uniform, robust and flexible Ag NW TCEs still remains a great challenge.



Figure 1.18 (a) Schematic of flexible Ag NW TCEs via spray coating method. (b) Schematic diagram of highly stretchable and foldable Ag NW electrode fabrication process by vacuum filtration and transfer technique. (c) Meyer rod coating setup for scalable Ag NWs coating on PET substrate. (d) Photograph and schematic of solution-processed rod-coating alignment of the Ag NWs on substrate. (a) Reproduced with permission from Ref. 128. Copyright 2016 Tsinghua University Press and Springer-Verlag Berlin

Heidelberg. (b) Reproduced with permission from Ref. 129. Copyright 2012 Wiley-VCH. (c) Reproduced with permission from Ref. 132. Copyright 2010 American Chemical Society. (d) Reproduced with permission from Ref. 135. Copyright 2017 American Chemical Society.

1.3 Smart Window

Smart windows provide dynamic control of photon flow that minimizes the energy loss, as well as improves human comfort. At present, electrically controllable smart window technologies mainly include electrochromic devices, suspended particle devices and liquid crystal devices, *etc.* Here, we focus on two of the major types of smart windows, electrochromic devices and suspended particle devices.

1.3.1 Electrochromic Device

Electrochromism refers to the special functionality of materials, who can change their color via reduction or oxidation by the application of a small external voltage. Glazing employing these electrochromic materials can thus change their optical characteristics of transparency and adsorption of solar radiation according to needs, by simultaneously reducing visible light and NIR transmission through the window. Usually, typical electrochromic devices have a multilayer structure consisting of two transparent conducting layers, an active electrochromic layer, a counter electrode layer and an electrolyte layer, as show in Figure 1.19.¹³⁶ This device structure is referred to as the battery type and is the most common geometry for electrochromic devices. In the off or bleached state, cations, such as Li⁺, reside in the electrolyte and the counter electrode. When the device is switched on, a voltage applied between the opposing conducting layers drives cations to migrate from the counter electrode, through the electrolyte and into the electrochromic electrode through a Faradaic process, changing its oxidation state and its optical properties. The origin of electrochromism studies is usually traced to the pioneering work by Deb, whose investigations at the American Cyanamid Corporation in the U.S.A. during the 1960s were first published in seminal papers on electrophotography using tungsten oxide films in 1969 and on basic properties of such films in 1973.¹³⁷⁻¹³⁸ Since then, electrochromic materials were gradually attracting interest both in academia and industry.¹³⁹



Figure 1.19 Electrochromic device stack schematic, depicted in a darkened state. Electrons flow through an external circuit into the EC material, while ions flow through the electrolyte to compensate the electronic charge. Reproduced with permission from Ref. 136. Copyright 2014 Royal Society of Chemistry.

Many transition-metal oxides, such as WOx,¹⁴⁰⁻¹⁴¹ Ta-doped TiO₂,¹⁴²⁻¹⁴³ MoO₃,¹⁴⁴ V₂O₅¹⁴⁵ and Nb₂O₅.¹⁴⁶⁻¹⁴⁷, exhibit the capability of electrochromism and have been extensively explored in electrochromic devices. For example, Yu et al. presented a facile route to fabricate flexible $Ag/W_{18}O_{49}$ films as both transparent electrodes and electrochromic devices with tunable sheet resistance (7-40 Ω/sq) and transmittance (58-86% at 550 nm).¹³³ In addition, the coloration efficiency of these films with different thickness of W₁₈O₄₉ NWs were between 32.67 to 35.7 cm²/C. They also demonstrated the solid electrochromic devices using Ag/W₁₈O₄₉ NW films and ITO-PET films as the work and counter electrodes, respectively (Figure 1.20a). The solid electrochromic devices were further applied in portable electrochromic glasses and smart window (see Figure 1.20 a-c). Lee et al. developed an electrochromic energy storage window with a high internal charge storage capacity (466.5 mA hr m⁻² at current density of 150 mA m⁻²) via using Tadoped nano-TiO₂ nanocrystals as active material (Figure 1.20 d-e).¹⁴² The electrochromic devices also show capability of independent control of visible light and near-infrared transmittance with high dynamic range modulation (89.1 % at 550 nm and 81.4 % at 1600 nm) (see Figure 1.20f). Milliron *et al.* reported synthetic protocols for incorporating NbO_x nanocrystals, and they achieved it by introducing ITO nanocrystals into NbO_x glass, realizing a new amorphous structure (Figure 1.20g-i).¹⁴⁷ The resulting material demonstrated a previously unrealized optical switching behaviour that enabled the dynamic control of solar radiation transmittance through windows.



Figure 1.20 (a) Structural schematic diagram of $W_{18}O_{49}$ -based electrochromic device. (b-c) Optical images of $W_{18}O_{49}$ -based electrochromic glasses and window model. (d-e) Absorption spectra and TEM image of Ta-doped TiO₂ nanocrystals. The inset shows an optical image of the dispersion. (f) Transmittance spectra and the corresponding optical images of a Ta-doped TiO₂ film at three different applied potential. (g) ITO nanocrystals covalently linked to amorphous NbO_x. (h-i) High-resolution STEM image and transmittance spectra of a typical ITO-in NbO_x film. (a-c) Reproduced with permission from Ref. 133. Copyright 2017 American Chemical Society. (d-f) Reproduced with permission from Ref. 142. Copyright 2019 Elsevier. (g-i) Reproduced with permission from Ref. 147. Copyright 2013 Nature Publishing Group.

However, the most widely used method for processing the metal oxide film is sputter coating, which requires high vacuum processing condition.^{140, 146, 148} Spray or printing coating is an attractive option for lowering fabrication and processing costs, which can also be further integrated with the roll to roll technology for industrial scale production.¹⁴⁹ Moreover, metal oxides often show inherent brittleness and long switching time, which is incompatible with flexible electronics. Recently, conducting polymers have attracted interest as a promising class of materials for flexible and solid-state electrochromic devices due to the potential of simultaneously manipulating photophysical and redox properties through synthetic design, their flexibility and solution

processability.¹⁵⁰ Apart from these advantages, fast switching and reversible Vis/NIR modulation also make the polymers suitable for next generation electrochromic devices. For example, Wei *et al.* developed a new integrated multifunctional flexible electrochromic device using ordered polyaniline (PANI) nanowire arrays as electrodes. (Figure 1.21a-d).¹⁵¹ The electrochromic device showed high areal capacitance (0.017 F/cm² at 5 mV/s) and high stability as a supercapacitor. This proposed electrochromic device can potentially be applied as a smart window or curtain for cars, roofs and rooms. Recently, Meng *et al.* reported a new donor-acceptor conducting polymer, poly[4,7-bis(3,6-dihexyloxy-thieno[3,2-b]thiophen-2-yl)]-benzo[c][1,2,5]thiadiazole (PBOTT-BTD) as an active layer to build electrochromic supercapacitor devices of considerable capacitance and stability (Figure 1.21e-f).¹⁵² The PBOTT-BTD based electrochromic supercapacitor devices showed a maximum area capacitance of 2.5 mF/cm² at a current density of 0.1 mA/cm².



Figure 1.21 Polymer active layer based-electrochromic devices. (a-d) Electrochromic devices based on polyaniline. (e-f) Electrochromic devices based on PBOTT-BTD. (a-d) Reproduced with permission from Ref. 151. Copyright 2012 Royal Society of Chemistry. (e-f) Reproduced with permission from Ref. 152. Copyright 2017 Wiley-VCH.

1.3.2 Suspended Particle Device

A competing technology with electrochromic smart window is suspended particle device (SPD)

smart window. SPDs, also called dipole particle suspension devices, have received less attention in the scientific community so far. SPDs composed of elongated rod-like or needle-shaped particles suspended in a medium that is sandwiched in between two TCEs represent one of the most promising systems for smart window applications due to their unique properties, such as precise and instant light control, long lifetime and excellent stability.



Figure 1.22 Schematic illustration of the SPD without (a) and with (b) AC voltage.

The development of SPDs spans many years. The first SPD was discovered by Edwin Land in 1930s, also called light valve.¹⁵³ Their operation is based on the variation of the orientation of elongated particles with an applied electric field, which can result in changes to optical absorption, reflection, and scattering of composites, and thereby the transmission of the photon flux. SPDs have two distinctly different states: on and off. When there is no external voltage, the nanorods are randomly distributed in the droplets due to the Brownian movement. As a result, a significant number of photons are blocked, which is termed as the "off" (dark) state, as shown in Figure 1.22a. With an external electric field is "on", the nanorods are polarized in the spherical droplets and rotate to align themselves, which increases the transmittance of the device, known as the "on" (transparent) state (Figure 1.22b).

Recently, many efforts have been attempted on the design and preparation of NWs or spherical nanoparticles based SPDs. For example, Timusk *et al.* used electrospun TiO₂ anatase NWs suspended in a polydimethylsiloxane matrix and found that the device based on such a system can selectively control light transmittance depending on the diameters of TiO₂ NW (Figure 1.23a-c).¹⁵⁴ However, the transmittance modulation of these devices is very low due to high aspect ratios of

NWs. Han *et al.* reported a SPD with tunable transparency under relatively small (1-5 V) external electrical voltage in the visible region via colloidal assemblies of ZnS/SiO_2 and Fe_2O_3/SiO_2 core/shell nanoparticles (Figure 1.23d). ¹⁵⁵ These spherical nanoparticles based SPD can work under small (1-5 V) external electrical voltage.



Figure 1.23 Optical microscopy images of (a) chaotic and (b) aligned TiO₂ NWs. (c) Specular reflectance for PDMS free standing films containing chaotically distributed and aligned TiO₂ NWs. (d) SPDs prepared using ZnS/SiO₂ and Fe₂O₃/SiO₂ core/shell nanoparticles. (a-c) Reproduced with permission from Ref. 154. Copyright 2014 IOP Publishing Ltd. (d) Reproduced with permission from Ref. 155. Copyright 2018 American Chemical Society.

1.4 Research Objectives and Organization

1.4.1 Objectives

This thesis is divided into three parts with three highly related objectives. Specifically, three different types of TCEs are developed based on metal NWs and further used in SPDs and electrochromic devices for their practical applications, respectively.

Part I: Preparation of copper-reduced graphene oxide core-shell NWs network films and their great potential as TCEs in SPDs.

Cu NWs-based TCEs have attracted growing interest as a potential alternative to ITO TCEs due to their low cost and high electrical conductivity. Up to now, great improvements have been made in the performance of Cu NW TCEs. Unfortunately, there are still factors limiting their widespread use, such as low oxidation resistance, poor adhesion to the substrate, and low stability in harsh environments. Graphene, an atomically thin layer of sp²-bonded carbon atoms, has unique structure and exceptional physical properties, such as high electrical conductivity, mechanical flexibility, good chemical stability, and optical transparency, which make it an ideal material for various optoelectronic devices. Chemical reduction of graphene oxide (GO) has been considered and now accepted as a cost-effective approach for scaling-up the production of graphene, the controllable assembly of which with other materials towards functional structures is highly concerned at present. Combining Cu NWs and rGO into single nanoarchitecture, a yet challenging task, will undoubtedly lead to a new range of potential applications for TCEs. Basically, the graphene could improve not only oxidation resistance and the stability of Cu NW due to the tight encapsulation, but also their adhesion to substrates. Similarly importantly, the graphene on the Cu NW surface can bridge individual Cu NWs, which will further enhance the electric and thermal conductivity of the Cu NW films.

The objective for this section is:

1. Synthesizing and characterizing small diameter and high aspect ratio of Cu-GO core-shell NWs

2. Preparing Cu-rGO core-shell NW films.

3. Investigating the optical and electrical properties, surface roughness as well as long-term stability of Cu-rGO core-shell NW films.

4. Fabricating SPDs using Cu-rGO core-shell NW films as TCEs and investigating SPD performance.

Part II: Scalable fabrication of Ag NW electrodes and their practical application as flexible TCEs in foldable SPDs

Although, the Cu-rGO core-shell NWs TCE developed in Part I shows high optoelectronic performance and good stability. The high temperature thermal reduction process of the Cu-GO NWs, imperative during the electrode post-treatment, limits their application on flexible substrates. Moreover, the area of such Cu-rGO core-shell NWs TCE is too small due to the vacuum filtration method used during the film fabrication process, which is not suitable for large-area device application. Ag, as another very promising candidate for TCEs, has the highest electrical conductivity among all the metals and better oxidation/corrosion resistance than Cu, which provides it with huge market opportunities. Ag NWs networks have been explored for the preparation of flexible electrodes for next-generation optoelectronics by many groups. However, the development of simple, scalable and cost-effective fabrication of large-area, uniform, robust and flexible Ag NW TCEs still remains a great challenge.

The objectives for this section are:

1. Scaling up the synthesis of thin diameter and high aspect ratio of Ag NWs.

2. Preparing large-area and flexible Ag NW network films.

3. Investigating the optical and electrical properties, surface roughness, adhesion, long-term stability as well as flexibility of Ag NW network films.

4. Fabricating large-area and foldable SPDs using Ag NW network films as TCEs and investigating the performance of these SPDs.

Part III: Fabrication of highly stable Ag-Au NW network for ITO-free flexible organic electrochromic device

The Ag NW TCEs-based foldable SPDs in part II exhibited high optical modulation, fast switching time as well as excellent stability. However, the current SPDs technology requires a relatively high alternating current voltage of 110 V to control light transmission, which is not safe in use, especially in wearable devices. In contrast, EC devices can tune their optical properties by applying

a small DC voltage. However, it is hard to develop a fully ITO-free flexible EC device which completely relies on Ag NW TCEs, because of the poor chemical stability and electrochemical stability of Ag NWs in the EC environment. Nanoscale Ag NWs easily get oxidized and thus inevitably stop working in a long run as irreparable oxidation continues. Especially, when the Ag NW TCE was used as the anode in the EC device, the NWs lost their conductivity due to the oxidation during the charge carrier exchanging process with electrolyte.

The objectives for this section are:

1. Synthesizing and characterizing highly stable Ag-Au core-shell NWs.

2. Preparing flexible Ag-Au core-shell NW network films.

3. Investigating the optical and electrical properties, surface roughness, long-term stability as well as flexibility of Ag-Au core-shell NW network films.

4. Preparing and characterizing solid electrolyte.

5. Characterizing active, conjugated polymer material.

6. Fabricating solid and flexible EC devices using Ag-Au core-shell NW network films as TCEs and investigating the performance of these EC devices.

1.4.2 Thesis organization

This thesis is divided into four chapters and organized as follows:

Chapter 1 Introduction: This chapter briefly introduces the background and development of TCE, focusing on their application in EC devices and SPDs. It also presents the objectives of this thesis.

Chapter 2 Experimental and Characterization: This chapter presents the experimental details of the synthesis of Cu NWs, Cu-GO core-shell NWs, Ag NWs and Ag-Au core-shell NWs as well as the fabrication of related TCEs. The fabrication and characterization techniques for the SPDs and EC devices are also described.

Chapter 3 Results and discussion: This chapter is divided into three parts.

Part I: Preparation of copper-reduced graphene oxide core-shell NWs network films and their great potential as TCEs in SPDs, and the publication related to this part is

Shengyun Huang, Qingzhe Zhang, Pandeng Li, Fuqiang Ren, Aycan Yurtsever, and Dongling Ma, High-Performance Suspended Particle Devices Based on Copper-Reduced Graphene Oxide Core– Shell Nanowire Electrodes. *Adv. Energy Mater.* 2018, 8, 1703658.

Part II: Scalable fabrication of Ag NW electrodes and their practical application as flexible TCEs for foldable SPDs, and the publication related to this part is

Shengyun Huang, Qingzhe Zhang, Fan Yang, Deepak Thrithamarassery Gangadharan, Pandeng Li, Fuqiang Ren, Baoquan Sun and Dongling Ma, A Facile Way for Scalable Fabrication of Silver Nanowire Network Electrodes for High-Performance and Foldable Smart Windows. *J. Mater. Chem. A*, 2020, 8, 8620-8628

Part III: Fabrication of highly stable Ag-Au NW network for ITO-free flexible organic electrochromic device, and the publication related to this part is

Shengyun Huang, Yannan Liu, Maziar Jafari, Mohamed Siaj, Haining Wang, Shuyong Xiao and Dongling Ma, Highly Stable Ag-Au Nanowire Network for ITO-Free Organic Electrochromic Device. Submitted to Advanced Functional Materials, minor revision.

Chapter 4 Conclusions and Perspectives: The chapter presents the main conclusions based on the results and analysis as well as some potential work in this research direction in the future.

CHAPTER 2 EXPERIMENTAL AND CHARACHERIZATION

In this chapter, experiment details for the synthesis and characterization of Cu NWs, GO, Cu-GO core-shell NWs, Ag NWs, Ag-Au core-shell NWs and related TCEs are described. The first section mainly introduces the synthesis of Cu-GO core-shell NW with small diameter and high aspect ratios, and preparation and characterization Cu-rGO core-shell NW TCEs and related SPDs. Then, we scaled up synthesis of Ag NWs and prepared large-area and high-performance flexible Ag NW TCEs by scalable, automatic blade coating. Moreover, as a proof of concept, we developed large-area and foldable Ag NW-based SPD smart window. The last section focuses on the synthesis of highly stable Ag-Au core-shell, and related TCEs. We further fabricated ITO-free organic electrochromic device using Ag-Au core-shell NW network film as TCE.

2.1 Chemicals and Materials

Copper (II) chloride dihydrate (CuCl₂·2H₂O, 99.0%), glucose, hexadecylamine (HDA, 98%), iodine (I₂, 99.999%), 3-glydidoxypropylmethyl dimethoxy silane (97%), laury methacrylate (96%), 2,2'-azobis(2-methylpropionitrile) (98%), calcium iodide (CaI₂, 99.95%), ethylene glycol (EG, anhydrous, 99.8%), poly(methyl methacrylate) (PMMA, average Mw=350000), iron(III) chloride (FeCl₃), chloroform (CHCl₃), nitromethane (MeNO₂), propylene carbonate (PC, anhydrous, 99.5%) and acetonitrile were obtained from Sigma-Aldrich Inc. Isoamyl acetate (>99%), isopropyl alcohol (IPA, >99.5%), 2-hydroxyethyl methacrylate (97%), 2-ethylhexanoate (≥99%), toluene (≥99.5%), heptane (99.8%), acetic acid (≥99.7%), phenylbis(2, 4, 6-trimethylbenzoyl)phosphine oxide, pyrazine-2,5-dicarboxylic acid dehydrate (2, 5-PDA, 95%), lithium tetrafluoroborate (LiBF4, 98%, anhydrous), ethanol, methanol (99.9%) and sodium chloride (NaCl, lab grade) were purchased from Fisher Scientific Co. Graphite powder (99.999%, 200 mesh), iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, >98%) and silver nitrate (AgNO₃, >99.9%) were purchased from Alfa Aesar Co. 3-acryloxypropylmethyl dimethoxy silane (95%) and trimethylmethoxy silane were purchased from Gelest Company. IT3935 (CAS#1150123-93-5, 4,7-bis[3,4-dihydro-3,3bis[(octyloxy)methyl]-2H-thieno[3,4-b][1,4]dioxepin-6-yl]-2,1,3-Benzothiadiazole) is commercially available from 1-Material Inc. The support polymer matrix chemical was supplied by Aleene. Poly(dimethylsiloxane) (PDMS) was prepared by mixing the base and curing agent (SYLGARD® 184, Dow Corning) at a ratio of 10:1, and the liquid mixture was degassed. The

ITO-polyethylene terephthalate (PET) was purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. All of the chemicals were used as received without further purification.

2.2 Synthesis of Cu, Cu-GO, Ag and Ag-Au NWs

2.2.1 Synthesis of Cu NWs

Cu NWs were synthesized following the modified approach developed by Xia *et al.*⁹² Typically, CuCl₂·2H₂O (210 mg), glucose (500 mg), HDA (1500 mg), and water (35 mL) were added to a reactor and magnetically stirred at room temperature overnight. The solution was then transferred into an oven and heated at 100 °C for 6 h. After the reaction, the Cu NWs were washed with 60 °C water and IPA several times by repeated centrifugation-redispersion processes in order to remove excess HDA and glucose. Subsequently, the Cu NWs were rinsed using IPA. Finally, the purified Cu NWs were dispersed in IPA.

2.2.2 Synthesis of GO

Graphite oxide was synthesized from natural graphite (Alfa Aesar, 200 mesh) by using a modified Hummers method.¹⁵⁶ The colloidal dispersion of GO was then obtained by ultrasonic exfoliation of graphite oxide in deionized water, followed by mild centrifugation to remove non-exfoliated sheets.

2.2.3 Preparation of Cu-GO core-shell NWs

The core-shell structure was achieved by mixing GO aqueous solution with Cu NW-in-IPA suspension. The weight ratio of Cu NWs to GO was tuned at 1:1, 5:1 and 10:1. The mixture dispersion was stirred for 30 min, followed by ultrasonication for 1 min to form the core-shell structure. The mixture was then separated by centrifugation to remove excess GO. Finally the resulting products were dispersed in IPA for storage. The ratio of Cu NW diameter to GO thickness was adjusted and optimized for balancing the optical and electrical properties of core-shell hybrid NW films.

2.2.4 Large-scale synthesis of Ag NWs

Ag NWs were synthesized by adding AgNO₃ in EG with small amounts of NaCl and Fe(NO₃)₃. Typically, 1260 mL of EG was firstly hosted in a 5 L three-necked, round-bottomed flask at room temperature and heated to 110 °C for 1 h. Then, 30 mL of Fe(NO₃)₃ (40 mM) solution in EG and

6 mL of NaCl (30 mM) solution in EG were rapidly added to the above preheated EG solution. After 20 min, 300 mL of EG solution containing 5.2 g of AgNO₃ was slowly injected to the mixture solution. Finally, the mixture was kept at 110 °C for 15 h without magnetic stirring, and then quickly quenched to room temperature. Ag NWs were collected by centrifugation, followed by two cycles of washing with IPA. The obtained suspension containing Ag NWs was diluted by IPA to certain concentrations for further use.

2.2.5 Synthesis of Ag-Au core-shell NWs

In 23.6 mL of H₂O were added in sequence 200 μ L of HAuCl₄ (0.25 M), 1.2 mL of NaOH (0.2 M), and 15 mL of Na₂SO₃ (0.01 M). The solution was left undisturbed overnight before use. Another solution was prepared by mixing 46 mL of H₂O, 10 mL of polyvinyl pyrrolidone (PVP, M_w=40 000, 5 wt%), 2 mL of L-ascorbic acid (L-AA, 0.5 M), 2 mL of NaOH (0.5 M), 500 μ L of Na₂SO₃ (0.1 M) and 60 mg Ag NWs in a glass vial, which was then merged with the Au precursor solution. The reaction was then allowed to proceed undisturbed at room temperature for 6 h. Finally, Ag-Au NWs were collected by centrifugation and washed with H₂O and isopropanol. Such obtained NWs had an average Au shell thickness of ~3.5 nm, which could be changed by varying the quantity of the Ag NWs involved in the synthesis. For instance, the average Au shell thickness could be changed to ~7 and ~12 nm by altering the mass of the Ag NWs to 40 and 20 mg, respectively.

2.3 Preparation of Cu-rGO, Ag and Ag-Au NW TCEs

2.3.1 Preparation of Cu-rGO core-shell NW TCEs

Prior to the deposition of NW films, the glass substrate was firstly thoroughly cleaned by ultrasonic treatment in acetone, deionized water and IPA sequentially and dried by using nitrogen gas. The Cu-GO NWs were subsequently diluted in IPA and deposited by vacuum filtration (see Figure 2.1) on a filter membrane (SartoriusTM PTFE, pore size 0.45 μ m), followed by pressure-aided NW film transfer to the glass substrate. Briefly, the Cu-rGO NW film/membrane was placed on the glass substrate with the NWs in contact with the glass. A 3kg weight was then placed on the top for 5 h. The PTFE filter membrane was then peeled off. By varying either the volume or concentration of Cu-GO NWs in solution, the films with varied thicknesses and thus different transparencies can be obtained. To obtain higher conductivity, the films were reduced by thermal annealing under

mixed atmosphere (Ar 95% & H_2 5%) at different temperatures from 200 to 360 °C for 2 h. The thermal treatment step enhances the degree of reduction of the films, and also importantly, it sinters the NWs together to create intimate contact junctions.



Figure 2.1 A schematic of the fabrication procedure for transparent Cu-GO NW films.

2.3.2 Preparation of large-area and ultra-flexible Ag NW TCEs

Prior to preparing a transparent Ag NW electrode using an automatic doctor blade film coater, the glass or PET substrates were first cleaned by ultrasonic treatment in soap water, acetone, deionized water and IPA sequentially, and dried by using nitrogen gas. The Ag NW ink was prepared by dispersing Ag NW in IPA solvent with concentration of 5-10 mg/ml. The glass or PET substrates were then fixed onto a flat vacuum chuck of the doctor blade film coater (as shown in Figure 2.2) by a vacuum pump while the Ag NW ink was pipetted in a line on top of the substrate. A film applicator was then quickly pulled over the Ag NW ink by a traverse pusher, spreading it across the surface of the glass into a thin, uniform film. The speed of the traverse pusher is very important and we found for our case, >50 mm/s was suitable. If the speed was below 50 mm/s, we can't get a uniform NW film. The Ag NW films with different transmittance can be obtained simply by varying the concentration of Ag NWs in the ink and the height of the film applicator. After that, a layer of transparent polymer was coated onto the surface of Ag NW film in the same way and dried in a vacuum oven at 80 °C for several minutes. Finally, the flexible, thin, free-standing Ag NW TCE was peeled off from the glass substrate.



Figure 2.2 Photograph of the blade coating system used for preparing of Ag NW TCEs, and SPDs as well. It mainly includes three parts: (a) a vacuum chuck; (b) a micrometer adjustable film applicator; (c) a traverse pusher.

2.3.3 Preparation of Ag-Au NW core-shell TCE

Prior to preparing a transparent Ag-Au NW electrode, the glass slide was first cleaned by ultrasonic treatment in soap water, acetone, deionized water and isopropanol sequentially, and dried by using nitrogen gas. The Ag-Au NWs were subsequently diluted in isopropanol and deposited by vacuum filtration on a filter membrane (Sartorius polytetrafluoroethylene (PTFE), pore size 0.45 μ m), followed by pressure-aided NW film transfer to the glass substrate. Briefly, the Ag-Au NW film/membrane was placed on the glass substrate with the NWs in contact with the glass under the stress of 10 kPa for 5 h. The PTFE filter membrane was then peeled off. By varying either the volume of or concentration of Ag-Au NWs in the suspension, the films with varied thicknesses and thus different transparencies can be obtained. To obtain a higher conductivity, the films were reduced by thermal annealing under mixed atmosphere (Ar 95% and H₂ 5%) at 250°C for 30 min to remove the residual PVP and form intimate contact among the NWs. After that, a layer of PDMS was coated onto the surface of Ag-Au NW films by spin coating and dried in a vacuum oven at 120 °C for 1 h. Finally, the flexible NW-based TCE was peeled off from the glass substrate. For comparison, the Ag NW TCE was prepared following the same procedure, with the only exception being the use of as prepared Ag NWs.

2.4 Preparation of Active Layer in SPDs and EC Devices

2.4.1 Synthesis of polyiodide nanorods

Typically, 4.5 g of I₂, 3 g of CaI₂ and 13 g of nitrocellulose were dissolved in 137 mL of isoamyl acetate at room temperature, heated to 65 °C and kept at this temperature for 40 min under vigorous stirring. After the mixture was cooled down to 45 °C, 3.5 g of pyrazine-2,5-dicarboxylic acid (2,5-PDA), 7.6 mL of methanol and 0.6 mL of deionized water were slowly added. The reaction mixture was maintained at 45 °C for 3 h with magnetic stirring, and then quenched to room temperature. After that, the mixture was ultrasonicated for 2 h to form a uniform dispersion. Finally, the product was washed 3 times with isoamyl acetate by going through centrifugation-redispersion cycles to remove excess chemical, and redispersed in isoamyl acetate for the next step of SPD preparation or all kinds of material characterizations.

2.4.2 Preparation of the suspension medium

The suspension medium was polyalkylmethacrylate polymer and prepared following the steps described below.¹⁵⁷ First, 1.13 g of 2-hydroxyethyl methacrylate, 4.09 g of 1-hexanethiol, 48.88 g of laury methacrylate and 40 mL of toluene were mixed under vigorous stirring and heated to 60 °C under the protection of Ar. Then, 0.4 g of 2,2'-Azobis(2-methylpropionitrile) dissolved in 20 mL of toluene was added to the preheated mixture. The reaction mixture was maintained at 60 °C for 21 h and refluxed for 3 h. Finally, the polymer was purified by short path distillation method at 90 °C.

2.4.3 Preparation of the polymer matrix

The siloxane polymer matrix was synthesized by the polymerization of 3-acryloxypropylmethyl dimethoxy silane and 3-glydidoxypropylmethyl dimethoxy silane as follows:¹⁵⁸ 45 g of dimethyl diphenyl siloxane copolymer was dissolved into 380 mL of heptane and refluxed for 1 h. Then, 0.04 g of tin 2-ethylhexanoate was introduced. After 12 min, 1.5 g of 3-glydidoxypropylmethyl dimethoxy was further added. The mixture was allowed to react at 100 °C for 1 h. Subsequently, 2.5 g of 3-acryloxypropylmethyl dimethoxy silane was slowly dropped into the mixture within 5 min for the first end-capping step. The capping reaction was allowed to proceed for 1 h. Then 15 g of trimethylmethoxy silane was added into the mixture for the final end-capping reaction which lasted for 2 h. The resultant mixture was cooled down to room temperature and filtered using a

filter paper. The polymer was collected by layer separation. Finally, the purification procedure was carried out by using the short path distillation method at 90 °C.

2.4.4 Synthesis of EC polymer

A three-necked 250 mL flask was equipped with a mechanic stirrer, an argon inlet, a pressureequalizing dropping funnel capped with an argon outlet, was thoroughly dried by a torch and cooled to room temperature under the continuous flow of argon. Into this reaction flask, compound IT3935 (1.30 g, 1.28 mmol) was dissolved in chloroform (100 mL). A solution of anhydrous FeCl₃ (1.04 g, 6.4 mmol) in nitromethane was added dropwise over a period of 30 min to the stirred monomer at room temperature. The mixture was stirred 72 h at room temperature. It was then precipitated into methanol (200 mL). The precipitate was filtered, re-dissolved in chloroform (250 mL) and stirred for 8 h with hydrazine monohydrate (10 mL). After evaporation, the concentrate was precipitated into methanol (300 mL), the precipitate was filtered through a Soxhlet thimble and subsequently extracted via a Soxhlet extractor by methanol for 24 h, followed by a mixed solvent (chloroform : methanol = 80:20) for 24 h and finally by chloroform for 24 h. The mixed solvent extracted fraction was concentrated by evaporation, and precipitated in methanol (300 mL), filtered, dried and collected as a dark green solid, referred as the EC polymer.

2.4.5 Preparation of gel-like electrolyte

0.66 g of LiBF₄ was first dissolved in 2 g of PC. After the LiBF4 was fully dissolved, 7.86 g of acetonitrile was mixed with the solution. 1.5 g of PMMA was slowly added into the blended solution and stirred at 1000 rpm overnight. Viscous and clear gel-like solution was obtained after the PMMA was fully dissolved.

2.5 Fabrication of SPDs and EC Devices

2.5.1 Fabrication of SPDs based on Cu-rGO core-shell NW TCEs

The Cu-rGO TCE based SPD was prepared as follows. Firstly, the polyiodide nanorods dispersed in isoamyl acetate were mixed with the suspension medium of polyalkylmethacrylate polymer. The solvent was then distilled by a rotary evaporator. After that, the suspension was mixed with the UV curable siloxane polymer and photoinitiator of phenylbis(2, 4. 6trimethylbenzoyl)phosphine oxide to form the complicated structure, numerous droplets (composed of polyiodide nanorods dispersed in suspension medium) embedded in the polymer.

Then the as-prepared Cu-rGO core-shell NW based TCEs were cleaned by ultrasonic treatment in IPA and dried by using nitrogen gas flow. Adhesive spacers were used to define the thickness and device geometry on the cleaned TCE. The viscous polymer encapsulated droplets were then filled into the space defined by the spacers, and subsequently covered by another cleaned TCE. Finally, the device was achieved by exposing it to UV lights in a UV-ozone chamber for 2 min to cure the polymer matrix.

2.5.2 Fabrication of large-area and flexible Ag NW TCEs-based SPDs

The Ag NW TCE-based flexible SPD was prepared by a blade coating method. To prepare the flexible SPD, first, the photoactive layer was prepared as follows: a mixed suspension was obtained by mixing the polyiodide nanorods dispersed in isoamyl acetate with the polyalkylmethacrylate polymer. Subsequently, the solvent was distilled by a rotary evaporator. The above suspension was then mixed with UV curable siloxane polymer matrix and phenylbis(2, 4, 6-trimethylbenzoyl)phosphine oxide to form the polymer composite, composed of numerous droplets embedded inside the polymer matrix. After degassing, the viscous polymer matrix encapsulated droplets was deposited onto the as-prepared Ag NW TCE by blade coating and cured through UV light exposure in a UV-ozone chamber for 30 seconds. Finally, the device was achieved by laminating another Ag NW TCE on the cured polymer matrix using a laminator.

2.5.3 Fabrication of EC devices based on Ag-Au NW TCEs

The EC device was prepared as follows. First, the as-prepared Ag-Au NW TCEs were cleaned by isopropanol and dried by using N₂ gas flow. Then, the EC polymer was deposited onto the Ag-Au NW TCE by spray coating. After that, the gel electrolyte described above was deposited onto the EC polymer film using tape as spacer. The as-prepared samples were then dried in an oven for 5 h at 60 °C to allow the acetonitrile to be evaporated, leading to a solid electrolyte film. Finally, the device was completed by placing another Ag-Au NW TCE on the top.

2.6 Characterizations

2.6.1 Scanning electron microscopy and energy dispersive X-ray spectroscopy

Scanning electron microscopy (SEM) is used to observe the morphology and size of the nanomaterials.¹⁵⁹ When an incident stream of electrons interact with atoms in the sample, various signals containing surface topography and composition of the samples could be produced for

detection. These types of signals are secondary electrons, back-scattered electrons, X-ray and *etc*. Secondary electrons have very low energy and originate from within a few nanometers below the sample surface. Due to this, secondary electrons can give great topographical contrast and be used to observe surface morphology of sample. Characteristic X-rays can be detected in SEM equipped with energy-dispersive X-ray spectroscopy (EDS) mode and be used to determine elemental composition in the material. In my experiment, Ag and Ag-Au NWs were purified first after synthesis and re-dispersed in IPA. After that, a drop of IPA suspension containing samples was deposited on clean silicon substrate and dried in air. For the TCEs and SPDs, samples were just fixed on the holder. Low and High-resolution SEM images were obtained by using TESCAN LYRA3 microscope at 10 kV. Meanwhile, EDS was used to determine the elemental composition of SPD at different areas on the sample during SEM measurements.

2.6.2 Transmission electron microscopy and energy dispersive X-ray spectroscopy

Transmission electron microscopy (TEM) is another type of electron microscope that can directly observe morphology, size and structure of materials by using a beam of electrons to transmit through an ultra-thin specimen and an image can be formed from the interaction of the electrons with the specimen. The TEM has almost same operation principles with light microscope but uses electrons instead of light. TEM can get a significantly higher resolution image (as small as individual atoms) than light microscopes due to the smaller de Broglie wavelength of electrons. In my experiment, NWs dispersed in IPA solvent were deposited onto nickel or copper TEM grids coat with a thin carbon film. After that, the grids were dried in the air before measurements. Low and high-resolution TEM images were obtained at different locations for the samples using a JEOL 2100F microscope at 200 kV equipped a charge-coupled device camera. Meanwhile, EDS was used to test the elemental composition of NWs during TEM measurements.

2.6.3 X-ray diffraction

X-ray diffraction (XRD) is one of most common non-destructive techniques used for identifying the crystalline structure of materials. It can give information on phases, structures, preferred crystal orientations and other parameters, such as average grain size, crystallinity and crystal defects. It is very simple to prepare XRD samples via depositing NWs suspensions on glass substrate and dried in a fume hood to form a thin film. Herein the XRD study for NWs was performed with XRD diffractometer (Bruker D8 Advance) using Cu *Ka* radiation source (λ =0.15418 nm) at a 40 kV tube

voltage and 40 mA tube current. Diffraction patterns were collected in the 2θ from 20 to 80° with the step of 0.1° and counting time of 15 s per step.

2.6.4 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive spectroscopic technique that can identify elements on the surface of material (usually from top 0 to 10 nm), including the elemental composition, chemical state, empirical formula as well as electronic state. XPS can detect all elements except for hydrogen and helium. In my experiment, XPS was used to measure the NWs elements composition and the oxidation state. For the sample preparation, NWs dispersed in IPA solvent were deposited onto silicon substrates and dried in the air before measurements. XPS study for NWs was carried out using a VG Escalab 220i-XL equipped with a hemispherical analyzer for a Twin Anode X-ray Source. The C1s peak at binding energy of 284.6 eV was used as the reference line to accurately determine the positions of other spectral lines. The Casa XPS software was used to handle the fine structure of the photoelectron lines.

2.6.5 Neutron activation analysis

Neutron activation analysis (NAA) is the nuclear process used to determine the concentrations of elements in various materials. It allows the precise identification and quantification of the elements, especially the trace elements in the sample. When neutrons activate the nucleus of the atom, it allows the total elemental content to be observed regardless of the oxidation state, physical location, or chemical form of the desired element. NAA is very sensitive and is therefore used to measure for minor elements, which are present in very low concentrations. In my experiment, NAA measurements were acquired using a SLOWPOKE nuclear reactor to determine the weight content of Au and Ag in the Ag-Au core-shell NWs. For samples preparation, Ag-Au core-shell NWs were dispersed in deionized water for measurements.

2.6.6 Atomic force microscopy

Atomic force microscopy (AFM) is a high resolution kind of scanning probe microscopy, with demonstrated resolution on the order of fractions of several nanometers. It offers both qualitative and quantitative information on many physical properties including size, surface texture, morphology and roughness of the samples. AFM has three major abilities, force measurement, topographic imaging and manipulation. It can be operated in three basic modes, such as contact

mode, tapping mode and non-contact mode in ambient air or liquid surrounding. In my experiment, the AFM was used to characterize the surface morphology and roughness of the ITO and NWsbased TCEs. AFM images of TCEs were obtained using a Bruker MultiMode 8-HR microscopy with the ScanAsyst mode.

2.6.7 Photo-induced force microscopy

Photo-induced force microscopy (PiFM) is a recently developed technique, which couples scanning probe microscope with infrared irradiation light source. In my experiment, I used PiFM to determine the uniformity of EC polymer on the TCEs. The VistaScope (MolecularVista, San-José, USA) scanning probe microscope is an atomic force microscope coupled with an incident mid-IR ranged electromagnetic source (770 to 1910 cm⁻¹) assembled by overlapping 4 quantum cascade laser sources having a wavelength dependent maximal intensity. The topography and PiFM images'] resolution was 512 x 512 pixels and the scan rate was 1 line per second. The PiFM spectra were each recorded in 30 seconds and locally resolved by the probe tip apex in the sideband mode (default mode for thin-film observations). The PiFM images were captured by irradiating the samples at the specified wavenumbers with their respective maximum intensity during the scans.

2.6.8 Four point probe

The four-probe method is the primary technique to measure the R_s of TCE. As shown in Figure 2.3, a four-point probe consists of four electrical probes in a line, with equal spacing between each of the probes. It allows elimination of contact and wire resistance from measurements. The theory of the four-point probe method was developed by Smits:¹⁶⁰

$$R_S = 4.532 \frac{V}{I} \tag{10}$$

Where V is voltage and I is current. For this measurement the current I is fixed and the voltage can be measured. It should be noted that the equation is only valid if $l \gg s \gg t$, otherwise the correction factor has to be used. (*l* is the length of the conductor, *s* is the distance between two points, and *t* is the thickness of conductor)



Figure 2.3 Four-point probe measurement on the top of the thin film.

In my experiment, the sheet resistance of TCE was obtained using S-302 Four-point probe.

2.6.9 Absorption and transmittance spectroscopy

The absorption and transmittance spectra of all samples were measured by a UV-visible-NIR spectrophotometer (Cary 5000) at scan speed of 600 nm/min. All experiments were done in two modes: absorption mode and transmittance mode. For absorption spectra, NWs suspensions were filled in a quartz cuvette for measurement. For transmittance spectra, NWs-based TCE cut into a small piece for measurement. A reference was used to obtain a baseline before each experiment.

2.6.10 Cyclic voltammetry

Cyclic voltammetry (CV) is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. CV is performed by cycling the potential of a working electrode, and measuring the resulting current. Herein, electrochemical measurements were carried out using three electrode system on electrochemical workstation (CHI 660E, CH Instruments), where Ag NW or Ag-Au NW films were used as the working electrode, Ag/Ag^+ as the reference electrode and Pt as the counter electrode in the 0.5M LiBF₄ anhydrous PC electrolyte.

2.6.11 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a powerful technique used to determine materials' thermal stability and their fraction of volatile components by monitoring the weight change that occurs as samples are heated at a constant rate. Herein, we used TGA (TA Instruments Q500) to analyze the thermal stability of the EC polymer. The experiment was carried out from room temperature to 1000 °C at the heating rate of 5 °C/min in N₂ atmosphere.

2.6.12 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is one of most frequently used techniques in the field of thermal characterization, which measures temperatures and heat flows associated with thermal transitions in materials. In this technique, the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. In my experiment, I used DSC (Mettler Toledo) to measure the thermochemistry of EC polymer. The maximum temperature for DSC measurements was set at 300 °C, using the heating/cooling rate of 5 °C/min in N₂ atmosphere.

2.6.13 Proton nuclear magnetic resonance

Proton nuclear magnetic resonance (¹H-NMR) is the application of nuclear magnetic resonance in NMR spectroscopy with respect to hydrogen-1 nuclei within the molecules of a substance, in order to determine the structure of its molecules. In my experiment, I used ¹H-NMR spectra to determine the molecule of oligomers IT3935. The data was collected on Bruker Advance 500 MHz in solvent of CDCl₃.

CHAPTER 3 RESULTS

This chapter is divided into three different parts, each corresponding to an article. The first part is about preparation of high-performance Cu-rGO core-shell NW TCEs and their practical application on new SPDs. The novel Cu-rGO core-shell NW TCEs-based SPDs show large change in their optical modulation, impressively fast switching time and superior stability. However, the high temperature thermal reduction process of the Cu-GO NWs, imperative during the electrode fabrication, limits their application on flexible substrates. In the second part, we develop another large-area, free-standing Ag NW network-based TCE, which exhibits high transparency, excellent conductivity, superior flexibility and strong structural integrity under mechanical stresses. In particular, regarding the flexibility, TCEs can be bent 10,000 times without any performance degradation, significantly better than commercial ITO-based TCEs. To explore the high potential of these TCEs, as a proof of concept demonstration we fabricated foldable SPDs for smart window applications, using Ag NW network-based film as transparent electrodes. However, nanoscale Ag NWs easily get oxidized and thus inevitably stop working in a long run as irreparable oxidation continues. The situation is even worse if they have to be used in a harsh environment. Especially, when the Ag NW TCE was used as the anode in the EC device, the NWs lost their conductivity due to the oxidation during the charge carrier exchanging process with electrolyte. Therefore, we developed a highly stable Ag-Au NW network TCEs and applied them in ITO-free flexible organic EC devices in the last part. The EC device showed high EC performance with reversible transmittance modulation, excellent flexibility and fast switching time

3.1 High-Performance Suspended Particle Devices Based on Copper-Reduced Graphene Oxide Core–Shell Nanowire Electrodes

Shengyun Huang, Qingzhe Zhang, Pandeng Li, Fuqiang Ren, Aycan Yurtsever, and Dongling Ma

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As introduced in Chapter 1, energy crisis has become as one of the serious issues facing humanity over the past decades. Research and development on sustainable energy, energy conversion and energy storage technologies have attracted a great deal of interest. In particular, managing buildings' environment in a smart way emerged as one of the promising ways to address the energy issue as the construction sector uses as much as 30 to 40 % of the primary energy in the world. In a typical building, windows could be the major source of energy loss, or gain, depending on their design. Smart windows provide dynamic control of photon flow that can minimize the energy loss, as well as improve human comfort. These windows are based on an actively switchable electro-optical material that is sandwiched between two transparent electrodes. Although great progress has been made in identifying the optimal materials for such active windows, there is still a great need to improve their key elements, especially the performance of the transparent electrodes.

In this paper, we report a new SPD, holding a great potential for smart window applications, which we built upon Cu-rGO core-shell nanowire NW films as a TCE for the first time. With the wrapping of rGO, the Cu NW electrodes demonstrate both high optical transparency and electrical conductivity, as well as significantly improved stability under various testing conditions. The novel sandwich-structured SPDs, based on these electrodes, show large change in their optical transmittance (42 %) between "on" and "off" states, impressively fast switching time (20 s and 40 s for color bleaching and recovery, respectively) and superior stability. These high performances are comparable to those of the SPDs based on commercially available ITO electrodes. These promising results pave the way of our electrodes to be an integral part of a variety of optoelectronic devices, including energy-friendly and flexible electronics.

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Vous pouvez le consulter à l'adresse suivante : DOI : 10.1002/aenm.201703658
3.2 A Facile Way for Scalable Fabrication of Silver Nanowire Network Electrodes for High-Performance and Foldable Smart Windows

Shengyun Huang, Qingzhe Zhang, Fan Yang, Deepak Thrithamarassery Gangadharan, Pandeng Li, Fuqiang Ren, Baoquan Sun and Dongling Ma

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Although above mentioned Cu-rGO core-shell NW TCEs can be potentially used for highperformance SPDs, the high temperature thermal reduction process of the Cu-GO NWs, imperative during the electrode fabrication, limits their application on flexible substrates. Herein, we report a facile and high-throughput automatic blade-coating assembly technique for developing large-area, free-standing Ag NW networks-based films, which exhibit high transparency, excellent conductivity, superior flexibility and strong structural integrity under mechanical stresses. In particular, regarding the flexibility, TCEs can be bent 10,000 times without any performance degradation, significantly better than commercial ITO-based TCEs. The excellent TCE performance and super-flexibility are attributed to the smart use of a flexible polymer, which not only partially embedded Ag NWs to protect Ag NWs from oxidation, but also promoted their intimate contact to enhance conductivity and formed a strong supportive matrix to endow flexibility. To explore the high potential of these TCEs, as a proof of concept demonstration we fabricated foldable SPDs for smart window applications, using Ag NW network-based film as transparent electrodes for the first time. Our devices showed large change in their optical transmittance (optical modulation 60.2 %) and fast switching time (21 s), as well as excellent stability. Significantly better than ITO-PET TCE-based electro-optic devices, the Ag NW electrode-based SPDs showed excellent mechanical flexibility, which can be folded by 180° for more than 200 cycles without obvious degradation of switching performance. The present method for fabricating large-area and ultra-flexible Ag NW TCEs can be extended to fabricate a variety of NW-based nonplanar or curved electronic and optoelectronic devices in the future.

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3.3 Highly Stable Ag-Au Nanowire Network for ITO-Free Flexible Organic Electrochromic Device

Shengyun Huang, Yannan Liu, Maziar Jafari, Mohamed Siaj, Haining Wang, Shuyong Xiao and Dongling Ma

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As mentioned in part two, we developed large-area, free-standing Ag NW network-based TCE with high optoelectronic performance and excellent flexibility. However, nanoscale Ag NWs easily get oxidized and thus inevitably stop working in a long run as irreparable oxidation continues. Especially, when the Ag NW TCE was used as the anode in the EC device, the NWs lost their conductivity due to the oxidation during the charge carrier exchanging process with electrolyte.

In this paper, we have demonstrated a robust epitaxial deposition method for the synthesis of Ag-Au core-shell NWs, which showed excellent thermal and chemical stability. A flexible TCE was prepared using these ultrastable core-shell NWs with outstanding optoelectnic performance. In addition, it showed remarkable thermal oxidation and electrochemical stabilities because of tight encapsulation of the Ag NWs by the impermeable Au shell. A flexible EC device was then successfully assembled using the stable Ag-Au NW film, green EC polymer, LiBF₄/PC/PMMA and Ag-Au NW film as the working electrode, active layer, solid electrolyte and counter electrode, respectively. The Ag-Au NW TCE and deposited EC polymer together showed high area capacitance and specific capacitance. The EC device showed high EC performance with reversible transmittance modulation, excellent flexibility and fast switching time. The strategies developed and demonstrated here for flexible EC devices may also serve as a platform technology for futuristic deformable electronics and optoelectronics

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Shengyun Huang, Yannan Liu, Maziar Jafari, Mohamed Siaj, Haining Wang, Shuyong Xiao and Dongling Ma*

S. Huang, Dr. Y. Liu, Prof. D. Ma

Énergie, Matériaux et Télécommunications, Institut National de la Recherche Scientifique (INRS), 1650 Boul. Lionel-Boulet, Varennes, Quebec J3X 1S2, Canada

Email: ma@emt.inrs.ca

M. Jafari, Prof. M. Siaj,

Department of Chemistry, Université du Québec à Montréal, NanoQAM/QCAM, Montreal, QC H3C 3P8, Canada

Dr. H. Wang, Dr. S. Xiao

1-Materials Company, 2290 Chemin St-Francois, Dorval, Quebec H9P 1K2, Canada

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Abstract

Solid and flexible electrochromic (EC) devices require a delicate design of every component to meet the stringent requirements for transparency, flexibility and deformation stability. However, the electrode technology in flexible EC devices stagnates, wherein brittle indium tin oxide (ITO) is the primary material being used. Meanwhile, the inflexibility of metal oxide usually used in an active layer and the leakage issue of liquid electrolyte further negatively affect EC device performance and lifetime. Herein, a novel and fully ITO-free flexible organic EC device was developed by using Ag-Au core-shell nanowire (Ag-Au NW) networks, EC polymer and LiBF₄/propylene carbonate/poly(methyl methacrylate) as electrodes, active layer, and solid electrolyte, respectively. The Ag-Au NW electrode integrated with a conjugated EC polymer together displayed excellent stability in harsh environments due to the tight encapsulation of the Ag NWs by the Au shell, and high area capacitance of 3.0 mF/cm² and specific capacitance of 23.2 F/g at current density of 0.5 mA/cm². The device showed high EC performance with reversible transmittance modulation in the visible region (40.2 % at 550 nm) and near-infrared region (-68.2 % at 1600 nm). Moreover, the device presented excellent flexibility (up to 1000 bending cycles) and fast switching time (5.9 s).

1. Introduction

Development of flexible electronics and optoelectronics will lead to the great innovation in portable and wearable electronics and communication devices, such as flexible pressure sensors, foldable displays and smartphones.^[1] Electrochromic (EC) devices capable of achieving dynamic modulation of transmittance over the visible (Vis) and near-infrared (NIR) regions are widely used in smart windows, antiglare mirrors, and electronic displays.^[2] They have become an area of considerable research focus due to their unique properties, such as low working voltage, fast switching speed and low cost. Traditionally, the EC device is based on brittle indium tin oxide (ITO) transparent conductive electrodes (TCEs), which however substantially limits its application range. For example, Yu et al. developed a new route for fabricating flexible transparent smart windows by using Ag nanowires (NWs) in one electrode, however, the ITO TCEs were used as the counter electrodes in their EC devices.^[3] A very recent study by Schott and co-workers reported poly(3,4-ethylene dioxythiophene)-based flexible EC device that still achieved on ITO TCEs.^[4] It is hard to develop a fully-ITO-free EC device, which completely relies on Ag NW TCEs, because of the poor chemical and electrochemical stability of Ag NWs in the EC environment.^[5] In addition, the other components of the devices, such as active layer and electrolyte, must also meet the stringent requirements of flexibility and stability.

To realize a well-functioning flexible EC device, three crucial components have to be carefully designed, of which the first is the TCEs. TCEs are an indispensable component in various optoelectronic devices, including liquid crystal displays, touch panels, solar cells, and EC device.^[6] Although ITO thin films have accounted for the great majority of the current TCE market due to their good optical and electrical properties, their future applications are limited by the high cost of the sputtering process, the scarcity of the indium resource and the low mechanical flexibility of

ITO.^[7] To overcome all these drawbacks, many alternative materials have been studied including carbon nanotubes,^[8] graphene,^[9] conducting polymer^[10] and metal NWs.^[11] Among these candidates, Ag NW network films show bright prospects due to the high electrical conductivity of Ag $(6.3 \times 10^7 \text{ S/m}, \text{ the highest among all the metals})$ and a facile solution-based fabrication process of the NWs, as well as the strong endurance against deformations like stretching and bending.^[12] However, nanoscale Ag NWs easily get oxidized and thus inevitably stop working in a short time period as the irreversible oxidation continues. The situation is even worse if they have to be used in a harsh environment. For example, Jiang et al. reported that the Ag NW electrodes were severely oxidized after exposure to air for 60 days and Ag NWs gradually broke into separated nanoparticles, thus leading to very high sheet resistance eventually.^[13] In addition, the poor electrochemical stability of the Ag NW electrodes represents another big issue. Especially, when the Ag NW TCE was used as the anode in the EC device, the NWs lost their conductivity due to the oxidation during the charge carrier exchanging process with electrolyte.^[14] To address this issue, it is necessary to protect the Ag NWs with a robust, antioxidative layer, which can significantly improve their stability. These materials should be able to form a compact layer and completely eliminate the exposed Ag surface; otherwise oxidation will be inevitable in a long run. Various materials, including ion-gel film,^[13] TiO₂^[15] and graphene,^[16] have been attempted. In most of the reported work, the coated Ag NWs showed enhanced stability against oxidation, but not at the level of withstanding a harsh environment, quite likely due to the incomplete coverage of the coating material. Here, we developed a successful case of robust deposition of conformal Au shell on the surface of the Ag NWs to provide sufficient protection, which showed excellent chemical and thermal stability.

Another major component for a flexible EC device is the active layer whose optical properties

change *via* electrochemical redox reactions under an applied voltage. Materials that are known to reveal this capability and have been extensively explored in EC devices are transition-metal oxides, such as WO₃,^[17] Ta-doped TiO₂,^[18] MoO₃,^[19] V₂O₅^[20] and Nb₂O₅.^[21] However, the most widely used method for fabricating the metal oxide film is sputter coating, which requires high vacuum processing condition.^[17a, 21a, 22] In this regard, spraying or printing coating is an attractive alternative for lowering fabrication and processing costs, which can also be further integrated with the roll-to-roll technology for industrial-scale production.^[23] Moreover, metal oxides often show inherent brittleness and long switching time, which is incompatible with flexible electronics. Recently, conjugated polymers have attracted interest as a promising class of materials for flexible and solid-state EC devices because of the potentiality of simultaneously manipulating their redox and photophysical properties *via* synthetic design as well as their flexibility and solution processability.^[24] Apart from these advantages, fast switching and reversible Vis/NIR modulation also make the polymers suitable for the next generation of EC devices.

The last key component for a flexible EC device is an electrolyte. As we know, lithium salt dissolved in water, propylene carbonate (PC) or N,N-dimethylformamide, has been widely used as an electrolyte in EC devices, because of their high conductivity and good stability.^[25] However, liquid electrolyte is prone to evaporation and leakage, which will significantly affect the device performance and lifetime.^[26] Gel electrolytes have been developed to avoid these problems, which not only can avoid the leakage of electrolyte, but also offer the electrolyte of flexibility. For example, Lee *et al.* developed an ultra-flexible and high-performance supercapacitor device based a gel-like polymer electrolyte. ^[27]

In this paper, we carefully designed all three essential components. Firstly, we synthesized robust Ag-Au core-shell NWs (denoted as Ag-Au NWs) by an epitaxial deposition method, which

showed outstanding chemical and thermal stability in harsh environments. Ag-Au NWs have been reported by some groups. For example, Kim et al. prepared highly conductive, stretchable and biocompatible Ag-Au NW composite for wearable bioelectronics.^[28] Liu et al. used Ag-Au NW films as the surface-enhanced Raman scattering substrate for biological molecular analysis and detection.^[29] However, Ag-Au NWs were rarely used in EC devices, especially in polymer-based EC devices. The Ag-Au NW TCEs were then prepared by vacuum filtration, followed by polydimethylsiloxane (PDMS) layer deposition. The developed Ag-Au NW TCEs exhibited high optical transmittance with low sheet resistance, which are comparable to those of commercial ITO TCEs. Moreover, they showed excellent stability in harsh environments (work at bias voltage of 2 V) and superior flexibility. As for the active layer, we synthesized a printable cyan-color EC polymer, which showed excellent long-term stability and outstanding air processability. The spraycoated EC polymer film on the Ag-Au NW electrode together showed high area capacitance of 3.0 mF/cm² and specific capacitance of 23.2 F/g at current density of 0.5 mA/cm². A solid electrolyte with high transmittance of almost 98% and sufficient flexibility was successfully prepared by additive engineering with acetonitrile, which is one of the most volatile organic solvents, and also can easily dissolve electrolyte salts of LiBF₄, PC and poly(methyl methacrylate) (PMMA). Finally, we assembled a flexible EC device composed of an ultra-stable Ag-Au NW electrode, the EC polymer active layer, LiBF₄/PC/PMMA electrolyte and another Ag-Au NW electrode. The device showed an interesting feature in transmittance modulation in the Vis region (40.2 % at wavelength of 550 nm) and NIR region (-68.2 % at wavelength of 1600 nm), which is very different from that of metal oxide-based devices. In addition, the device showed fast switching response of ~5.9 s and outstanding mechanical flexibility. The high-performing flexible EC device holds great promise

for the next-generation smart window, which combines energy storage and electrochromism and has a significant impact on our future life.

2. Results and Discussion

To construct a flexible composite EC device, we first individually optimized each component of the NWs-polymer-electrolyte device. The flexible and stable Ag-Au NW-embedded-PDMS TCE (denoted as Ag-Au NW TCE hereafter) was developed to address the problems of conventional Ag NW coated polyethylene terephthalate (PET) or PDMS TCEs, such as poor adhesion^[30] and easy oxidation in a relatively short time period.^[13] To protect Ag from oxidation, we adopted the core-shell strategy to coat each Ag NW with a thin outer layer of Au. We first synthesized Ag NWs by a modified polyol synthesis method.^[31] The morphology of these pure Ag NWs were characterized by the scanning electron microscope (SEM) and transmission electron microscope (TEM). As shown in Figure 1 a-b and Figure S1a, the average diameter of the as-prepared Ag NWs is around 49.4 ± 8.4 nm, which have a very smooth surface. The Ag-Au NWs were prepared via the conformal deposition of Au shell on the Ag NWs using L-ascorbic acid (L-AA) as a reducing agent and sodium sulfite as a ligand. The sodium sulfite can selectively bound Au³⁺ and lowered the Au reduction potential, so that both the ligand-assisted oxidative etching and galvanic replacement did not dominate.^[32] The galvanic replacement reaction between Au³⁺ and Ag was also suppressed by creating an alkaline condition with the addition of NaOH.^[33] Under these conditions, it was not necessary to control the injection rate nor the concentration of Au³⁺ solution to avoid the formation of voids in the Ag templates^[33b, 34] or homogeneous nucleation of Au nanoparticles in solution in our synthesis; this is quite different from the previously reported work. The Ag-Au NW core-shell structure was confirmed by using various electron microscopy and spectroscopy methods. After coating with a Au layer, the diameter of the resulting core-shell NWs

increased by about 7.1 nm (Figure 1c and Figure S1b). From the TEM images in Figure 1, it can be observed that after the Au coating, the NW surface became less smooth. Figure 1e shows a brighter contrast on the edge of the core-shell NW, suggesting the enrichment of heavier Au atoms. Energy dispersive X-ray (EDX) mapping further verified the core-shell nanostructure of the Ag-Au NWs (Figure 1f-h). It was found that Ag atoms (denoted by red color) located in the central region of the NWs, while Au atoms (green color) were mainly distributed in the outer edge. The line scan of Au and Ag across the NW diameter (Figure S2) further resolves the distribution of Au and Ag in a single NW yielding the Au shell thickness of ~3.5 nm. The shell thickness could be regulated from 3.5 nm to 7 and 12 nm by varying the number of Ag NWs added into the reaction solution. As shown in Table S1, the atomic percent of Au in the core-shell NWs was determined to be 12.1 %, 18.5 % and 26.7 % *via* neutron activation analysis (NAA), which corresponded to the average Au shell thicknesses of ~3.5 nm, ~7 nm and 12 nm, respectively.

Figure 2a shows the UV/Vis absorption spectra of isopropanol dispersion of Ag NWs and Ag-Au NWs. As synthesized Ag NWs showed two absorption peaks, at 356 and 389 nm, which were ascribed to the transverse localized surface plasmon resonance mode of bulk Ag and one-dimensional Ag nanostructures, respectively.^[35] The optical response of the Ag NWs was observed to be markedly affected by the Au coating. Upon the deposition of a Au shell, only one broad band was observed. Figure 2b shows the X-ray diffraction (XRD) pattern of Ag and Au-Ag NWs. The Ag NWs showed four diffraction peaks at the angle of 2θ of 38.1° , 44.3° , 64.4° and 77.6° , corresponding to the (111), (200), (220), (311) crystalline planes, respectively. The diffraction pattern matched well with that of the face-centered-cubic (FCC) crystal structure of Ag (JCPDS Card No. 04-0783).^[36] The Au coating basically did not affect the XRD pattern, except for slight peak broadening, since Ag and Au have similar lattice constants (JCPDS: 4-0783 and 4-0784) with

the latter being slightly smaller.^[37] X-ray photoelectron spectroscopy (XPS) was further used to study the surface chemical composition of Ag and Ag-Au NWs. The high-resolution Ag 3d scan for Ag NWs (Figure S3) shows a doublet from the spin-orbital splitting of Ag 3d_{3/2} (374.1 eV) and 3d_{5/2} (368.1 eV), with an intensity ratio of 2:3.^[38] The result shows that only zerovalent Ag was detected, indicative of the successful reduction of the Ag precursor, which is in agreement with the previous reports.^[39] For comparison, no obvious Ag 3d binding energy shift was observed for Ag-Au NWs (Ag 3d_{3/2} at 374.2 eV, Ag 3d_{5/2} at 368.2 eV), as shown in Figure S3 and Figure 2c, indicating the absence of Ag-Au alloy in the Au coated Ag NWs.^[40] The peaks at 87.6 eV and 83.9 eV in the high-resolution Au 4f spectrum (Figure 2d) are ascribed to Au 4f_{5/2} and Au 4f_{7/2}, respectively, with an intensity ratio of 3:4, confirming the presence of metallic Au.^[39b] The result further confirms the Au deposition on Ag NW.

To evaluate the stability of core-shell NWs against oxidation, H_2O_2 was introduced into the suspensions of Ag and Ag-Au NWs. As shown in Figure S4a-b, the absorption of Ag NWs significantly dropped after 1 hour, suggesting the transformation of Ag NWs to Ag⁺. In clear contrast, the absorption spectrum of the Ag-Au NWs remained essentially unchanged, implying the high chemical inertness of the Ag-Au NWs against highly oxidizing H_2O_2 . We further immersed the fabricated Ag and Ag-Au NW TCEs (their fabrication and characterizaitions to be described in the later text) into H_2O_2 solution and monitored the change of their sheet resistance (Figure S4c-d). Figure S4d shows that the Ag-Au NW TCE maintained the good conductivity after being immersed into 0.85 M H_2O_2 for 120 min, while the Ag NW TCE became nonconductive after the exposure to H_2O_2 as short as 20 min. To make clear the possible reasons for their different durability in H_2O_2 , we checked the morphology of the Ag and Ag-Au NWs TCEs after immersion in H_2O_2 for 30 min. The Ag NWs were severely etched away and left behind some traces of Ag

nanoparticles, while the morphology of Ag-Au NW TCE remained unchanged after the immersion in H_2O_2 for 30 min (Figure S4e-f). All these results strongly support that a robust and compact Au shell was formed around the Ag NWs, with a complete surface coverage. The benefits of the Au shell to the Ag NWs and TCE are obvious.

The flexible Ag-Au NW TCEs were prepared using solution deposition technique. Firstly, a uniform core-shell NW network was deposited on a glass slide substrate by vacuum filtration, followed by annealing at 250 °C for 30 min to remove the polyvinyl pyrrolidone (PVP) ligand and to sinter the junctions among the NWs. Then the PDMS viscous liquid was spin-coated onto the core-shell NW networks and cured in an oven. Such prepared composite films can be readily peeled off the glass substrate to obtain the flexible Ag-Au NW TCE. Figure S5 shows typical SEM images of Ag-Au NW TCEs, demonstrating that the NWs were well connected. Figure 3a summarizes the optical and electrical performance of different NW network films: bare Ag, Ag-Au (~3.5 nm thick Au), Ag-Au (~7 nm thick Au) and Ag-Au (~12 nm thick Au). The results show that Ag and Ag-Au (~3.5 nm thick Au) NW TCEs had similar properties, both exhibiting excellent figures of merit. The figure of merit of TCEs is defined as the ratio of direct current (DC) conductivity (σ_{DC}) to optical conductivity (σ_{Op}). An approximate relationship between sheet resistance (R_s), transmittance (T), σ_{DC} and σ_{Op} is given by the following equation for the NW TCEs: $T = \left[1 + \frac{Z_0}{2R_s} \frac{\sigma_{OP}}{\sigma_{DC}}\right]^{-2}$, where Z_0 is the impedance of free space (377 Ω).^[41] For industrial applications, the figure of merit value of TCEs should be larger than 35.^[14] As shown in Figure S6, the figure of merit values of the Ag-Au (~3.5 nm thick Au) NW TCEs could be tuned up to 120.1, which is superior to that of most high-performing TCEs, such as graphene (114),^[42] Cu NWs (87)^[43] and Ag NWs (96).^[14] However, with the increase of Au shell thickness, we noticed an obvious decrease in the electrical conductivity and figure of merit values (as shown in Figure 3a

and Figure S6). This is because the electrical conductivity of Au (4.5×10^7 S/m) is 40% lower than that of Ag (6.3×10^7 S/m). In addition, the Au shell deposition decreases the aspect ratio of the NWs, which will also lead to reduced figure of merit values. Another important parameter of TCEs is their haze factor, which is defined as the percentage of diffusely scattered light to the total transmitted light.^[44] Haze is extremely important for smart window applications, in which high light scattering will significantly reduce the sharpness of the window. Figure 3b shows the haze values of the three types (Ag NW, Ag-Au NW of different Au thickness and ITO-PET) of TCEs as a function of their total transmittance at 550 nm. The fabrication procedure of all the NW TCEs was kept the same in order to eliminate process-induced inhomogeneity. Generally, the haze values of all these TCEs decreased linearly with total transmittance, which is consistent with the previous reports.^[35b, 45] Interestingly, the Ag-Au (~3.5 nm thick Au) NW TCE exhibited the same level of haze as the Ag NW TCE, which is comparable to or even slightly lower than that of ITO-PET TCE (total transmittance 88%, haze value 4.9 %). As the Au shell got thicker, the haze values significantly increased. To evaluate the oxidation resistance of the developed TCE in a harsh environment, in addition to the above mentioned H₂O₂ tests, the Ag NW and Ag-Au NW TCEs were also placed in a high humidity (85% RH) and high temperature (85 °C) environment for 5 days. Figure 3c shows the change in the sheet resistance of Ag NW and Ag-Au NW TCEs during the thermal oxidation stability test. After 5 days of exposure to the harsh environment, the sheet resistance of the pure Ag NW TCE increased by about 2.5 times due to the Ag oxidation. It is known that when the Ag NWs are oxidized, the formation of silver oxides on NWs' surface causes the increase of both the junction resistance and electrical resistivity of the Ag NWs. In contrast, all the Ag-Au NW TCEs, including those with a thin Au shell of 3.5 nm, remained almost their initial sheet resistance values after the exposure test of 5 days. In other words, the oxidation resistance of

the core-shell NW TCEs was similar, regardless of the Au shell thickness, indicating the excellent encapsulation of the Ag NWs by the Au shell in all three cases. It further suggests that even as thin as 3.5 nm Au shell can provide strong protection to the Ag core NWs. It can be deduced that the Au layer is compact and has complete surface coverage; otherwise, Ag oxidation is inevitable. We further studied the long-term stability of the NW-based TCEs in air under ambient conditions (Figure S7). The sheet resistance of the Ag-Au (3.5 nm thick Au) NW TCEs, without any additional encapsulation, remained nearly constant after the exposure for 90 days. However, the sheet resistance of the Ag NW TCEs became 2.3 times higher than its initial value after 90 days' exposure. The structure of these NWs was invesitgated with XRD pattern to evaluate the enhanced stability observed above against oxidation in the presence of the Au shell. As shown in Figure S8, for the Ag NWs films after long-term stability test, two additional XRD peaks at 32.2° and 46.2° emerged, which is in line with formation of Ag₂O^[46].

The Ag-Au NW TCE also possessed outstanding flexibility, which is indispensable for emerging optoelectric devices, such as flexible EC devices and photovoltaic devices. The flexibility of Ag-Au NW and ITO-PET TCEs was further evaluated by recording the variation of sheet resistance after repeated bending tests (Figure 3d). Impressively, the sheet resistance of the Ag-Ag NW TCEs remained almost unchanged after 5000 bending cycles. In contrast, the ITO-PET TCEs showed a sharp increase in its sheet resistance within the first few cycles of the bending test. Since ITO is a brittle inorganic material, it can easily crack under even a small strain. While the superior mechanical flexibility of Ag-Au NW TCE can be attributed to the flexibility of both PDMS and NWs themselves as well as the strong interface between them.

Electrochemical property is a key parameter that must be studied first before the metal-based NW films can be used as electrodes in the EC device, because they (such as Cu NWs and Ag NWs) can

be easily oxidized under the applied voltage when used as anodes.^[14] To investigate the electrochemical stability of our developed Ag-Au NW electrodes, cyclic voltammetry (CV) tests were performed using a three electrodes configuration with Ag NW or Ag-Au NW films as the working electrode, Pt as the counter electrode and Ag/Ag⁺ as the reference electrode in the 0.5M LiBF₄ anhydrous PC electrolyte. The typical CV diagram for the pure Ag NW electrode is depicted in Figure 4a. The Ag NW TCE exhibited an oxidation peak (~0.7 V) followed by flattened curve without corresponding reduction peak in the reverse voltage scan at the first CV cycle, indicating that the TCE could not be successively "recovered" after the Ag NWs oxidation. The oxidized Ag NW electrode lost its conductivity at the second cycle of the measurement, and the CV diagram did not show any redox peaks (Figure 4a, red line). In contrast, the Ag-Au NW TCEs displayed a stable CV in the scan range of 0 to 1.5 V, and even worked in 0 to 2.0 V (Figure 4b). They had the same oxidation peaks at ~ 0.7 V, which was the similar to the oxidation peak of Ag NW TCE. Whereas, corresponding reduction peaks could be found in the reverse voltage scan in every CV cycle (Figure S9). To understand better the different electrochemical stability between the Ag NW and Ag-Au NW TCEs, we checked the morphology of both types of the electrodes after the electrochemical tests. As shown in Figure 4c, the network structure of the Ag NW TCEs was damaged in certain regions due to NW breakage, thus leading to the loss of conductivity. In comparison, the morphology of the Ag-Au NW TCEs remained almost unchanged, and the NW network was still well connected everywhere after the electrochemical tests (Figure 4d). The results imply that the Au shell successfully protected the Ag NWs against the oxidative dissolution and break down under the oxidizing condition.

To evaluate the potential of our NW TCEs in practical application, we used a spray-coating method to deposit a uniform EC polymer film on the Ag-Au NW TCE, as schematically illustrated in

Figure 5a. The EC polymer was synthesized by polymerizing oligomers labeled as IT3935, as presented in Figure S10. The proton nuclear magnetic resonance (¹H-NMR) spectrum of oligomers is shown in Figure S11. The synthesized EC polymer was characterized by thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC). As shown in Figure S12a, the EC polymer started to exhibit obvious weight loss at around 300 °C and the major weight loss occurred in the range of 350-450 °C due to decomposition of the EC polymer. The total weight loss was about 81% up to 1000 °C. Based on the thermal property obtained from TGA measurements, the maximum temperature for DSC measurements was set at 300 °C. Basically, the DSC result revealed no prominent cystalline/amorphous phase transitions for the EC polymer (Figure S12b), suggesting that it was not crystalline. The UV/Vis absorption spectrum of the polymer in toluene is shown in Figure 5b, in which two absorption peaks were observed at 403 nm and 665 nm, corresponding to the electron-rich portion of polymer backbone and to the intramolecular donoracceptor interaction arising from the covalent bonding of 3,4-propylenedioxythiophene (ProDOT, electron-rich) and 2,1,3-benzothiadiazole (BTD, electron-deficient) building units, respectively.^[47] More details for synthesis can be found in the Experimental Section.

Figure S13 displays atomic force microscope (AFM) topography image and the photo-induced force microscope (PiFM) spectrum at the four labeled positions of EC polymer film on the Ag-Au NW TCE. The EC polymer film was very smooth with the root mean square roughness (R_{ms}) of ~0.34 nm (Figure S13a), showing the same PiFM spectrum at randomly selected measuring positions (Figure S13b). The Nano-Infrared PiFM spectrum shows strong peaks at ~1559 cm⁻¹ and ~1639 cm⁻¹, which correspond to the C=N and C=C stretching vibrations in BTD, respectively.^[48] The bands appearing at ~815 cm⁻¹ and ~865 cm⁻¹ are associated with the vibrations of C-S-C bond in thiophene ring, while those at ~1031 cm⁻¹ and ~1092 cm⁻¹ are the characteristic bending

vibration of the C-O-C in ProDOT.^[49] The results suggest the uniform chemical composition throughout the polymer film. This finding was also in line with the DSC results, *i.e.*, the polymer film was amorphous, because otherwise the vibration modes will vary depending on the specific crystallization status at various positions.

The electrochemical property of the EC polymer was studied after it was spray coated onto the Ag-Au NW TCE (denoted as EC polymer/Ag-Au NW TCE hereafter) using a standard threeelectrode configuration in 0.5 M LiBF₄/PC solution. The CV experiments were conducted between -0.2 and 1.5 V at different scan rates from 25 to 125 mV/s (Figure 5c). The EC polymer/Ag-Au NW TCE exhibited an oxidation onset around 0.36 V and a pair of redox peaks at all the scan rates. These CV curves revealed the typical behavior of a Faradaic-type electrode, suggesting the synthesized cyan-color polymer can act as a suitable material for electrochemical supercapacitors. The EC polymer/Ag-Au NW TCE was found to be electrochemically stable; it could maintain most of the capacitance after 200 cycles of scanning between -0.2 to 1.5 V at the rate of 25 mV/s in ambient air (Figure S14). Figure 5d shows the corresponding galvanostatic charge/discharge curves of the EC polymer/Ag-Au NW TCE at current densities from 0.05 to 0.5 mA/cm². The slope of the galvanostatic charge/discharge curves are consistent with the observations from the CV curves. Moreover, each curve showed a non-linear profile, which further confirms the Faradic behavior of the EC polymer/Ag-Au NW TCE. On the basis of the discharge curves, the area and specific capacitance of EC polymer/Ag-Au NW TCE was calculated (Figure 5e). The area and specific capacitance reached 3.0 mF/cm² and 23.2 F/g, respectively, at a current density of 0.5 mA/cm², which are comparable with those of reported conjugated polymers, such as 2.0 mF/cm² and 25.0 F/g for poly[4,7-bis(3,6-dihexyloxy-thieno[3,2-b]thiophen-2yl)]benzo[c][1,2,5]thiadiazole,^[50] 1.7 mF/cm² for poly(6,6'-BEDOT-iI-But₂)^[51] and 2.5 mF/cm² for poly(6,6' -BEDOT-iI-Hex2) derivative.^[51]

After confirming the excellent performance of the EC polymer and the NW TCE, we further construct a novel ITO-free EC device with both electrodes being the Ag-Au NW TCEs. As schematically illustrated in Figure S15, the solid state flexible EC device was fabricated using the Ag-Au NW network/EC polymer as the working electrode/active layer, the Ag-Au NW TCE as a counter electrode and LiBF₄/PC/PMMA as the solid electrolyte. The EC device lifetime is known to be significantly affected by liquid electrolyte evaporation and leakage. Although the situation has been improved by incorporating liquid electrolyte with a polymer matrix to get a gel electrolyte, the electrolyte still suffers from low ionic conductivity and has evaporation and leakage issues. In this context, we developed a new solid state electrolyte by applying acetonitrile as a solvent to dissolve LiBF₄, PMMA and PC followed by acetonitrile evaporation. As illustrated in the inset in Figure S16, the prepared gel electrolyte in the glass vial showed excellent transparency. After drying in an oven at 60 °C for 6 h, the acetonitrile completely evaporated, leading to a solid electrolyte film with good flexibility for device assembly. The transparency of the electrolyte film was measured using a glass as reference. As shown in Figure S16, transmittance of the electrolyte film reached ~98% at most wavelengths in the range of 350-2000 nm.

We further studied the EC performance of devices, as presented in **Figure 6**. Figure 6a shows the Vis/NIR transmission spectra of the fabricated EC devices, in their colored/bleached states, and corresponding photographs. Interestingly, it was observed that which the device showed the opposite transmittance modulation in the Vis and NIR regions. When the device was in its original state (Figure 6a, black line), it showed a low optical transmittance of 9.3 % at 550 nm, to which human eyes have the highest sensitivity, while a high optical transmittance of 82.7 % at 1600 nm.

Upon the application of an external bias of 1.2 V for 30 s, the optical transmittance of device at 550 nm increased to 49.5 %, while at 1600 nm it decreased to 14.5 %. This interesting feature provides an opportunity to tune Vis and NIR lights oppositely. The speed of EC devices' response between the colored and bleached states was measured from the transmittance spectra in real time. The switching time is defined as the time for bleaching $(t_{b,90\%})$ and coloring $(t_{c,90\%})$ to reach 90% of a full transmittance change between the fully bleached and colored states.^[52] Here, an external bias of 1.2 V and -1.0 V was alternately applied for 30 s. The bleached-colored tests were carried out for more than 200 cycles and only 4 cycles were revealed in Figure 6. It can be seen that at 550 nm, the $t_{b,90\%}$ and $t_{c,90\%}$ were ~3.2 s and ~2.7 s, respectively (Figure 6b), similar to those observed at 1600 nm (Figure 6c). The switching time for our devices is faster than those reported previously, for instance, Ta-doped TiO₂ (9.5 s, 52.6 s),^[18a] a-WO₃ amorphous film (5 s, 12 s),^[17a] c-WO₃ crystalline film (166 s, 68 s),^[17a] P₈W₄₈/W₁₈O₄₉ hybrid NW (26 s, 52 s),^[53] polycyclic aromatic hydrocarbon (65 s, 5 s),^[54] and tetraphenylethene-diphenylamine derivatives (4.2 s, 7.9 s).^[55] The fast switching time should be attributed to the intimate contact between the Ag-Au NWs and EC polymer.

Finally, the mechanical flexibility of the EC devices was investigated by repeated bending at a small radius of 5 mm. As shown in Figure 6d, the transmittance modulation of the Ag-Au NW TCEs-based EC devices decreased to about 88.1 % of the initial value after 400 cycles and maintained at the same level for the next 600 bending cycles. For comparison, the EC devices were also fabricated on ITO-PET TCEs under the same conditions. However, the ITO-PET TCEs based EC devices completely lost their function after 200 bending cycles. The lack of stability of the ITO-PET TCEs is related to the formation of micrometer sized cracks after several cycles of bending, resulting in larger sheet resistance (Figure S17a-b). In contrast, there were no cracks in

the NW TCEs, which was in line with the super-flexible NW TCEs-based EC devices (Figure S17c-d).

3. Conclusion

In conclusion, we developed a robust conformal deposition method to synthesize Ag-Au core-shell NWs, which exhibited excellent chemical and thermal stability. Flexible and high performance TCE was prepared using these ultrastable core-shell NWs with outstanding optical and electric properties. In addition, the developed NW TCEs revealed remarkable thermal oxidation and electrochemical stabilities because of tight encapsulation of the Ag NW by the impermeable Au shell. A flexible EC device was then successfully assembled using the stable Ag-Au NW film, cyan-color EC polymer, LiBF4/PC/PMMA and Ag-Au NW film as the working electrode, active layer, solid electrolyte and counter electrode, respectively. The Ag-Au NW TCE and deposited EC polymer together showed high area capacitance (3.0 mF/cm²) and specific capacitance (23.2 F/g) at current density of 0.5 mA/cm². The experimental results demonstrated the interesting feature in transmittance modulation at Vis (40.2 % at wavelength of 550 nm, to which humans have the maximum visual sensitivity) and NIR lights (-68.2 % at wavelength of 1600 nm). Moreover, the device showed fast switching response of ~5.9 s and excellent mechanical flexibility. The high-performance and flexible EC device holds great promise for the next-generation smart window, which has a significant impact on our future life.

4. Experimental Section

Materials: Silver nitrate (AgNO₃, >99.9%,) and iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, >98%) were purchased from Alfa Aesar Co. Sodium chloride (NaCl, lab grade), IPA (>99.5%), ethanol (99.9%), methanol (99.9%) and lithium tetrafluoroborate (LiBF₄, 98%, anhydrous) were purchased from Fisher Scientic Co. Gold(III) chloride trihydrate (HAuCl₄·3H₂O,

ACS reagent), sodium sulfite (Na₂SO₃, >98.0%) iron trichloride (FeCl₃, anhydrous), ethylene glycol (EG, 99.8%, anhydrous), L-Ascorbic acid (L-AA, >99.0%), PMMA (average M_w =350 000), PVP (average M_w =40 000), trichloromethane (CHCl₃, >99.5%), nitromethane (CH₃NO₂, >99.0%), acetonitrile (CH₃CN, anhydrous, 99.8%) and PC (99.5%, anhydrous) were purchased from Sigma-Aldrich. IT3935 (CAS#1150123-93-5, 4,7-bis[3,4-dihydro-3,3-bis[(octyloxy)methyl]-2*H*-thieno[3,4-*b*][1,4]dioxepin-6-yl]- 2,1,3-Benzothiadiazole) is commercially available from 1-Material Inc. The ITO-PET film was purchased from Zhuhai Kaivo Optoelectronic Technology Inc. All chemicals were used without further purification.

Synthesis of Ag NWs: In a typical synthesis, EG (1260 mL) was firstly hosted in a three-necked flask and heated to 110 °C. After 60 min, 6 mL of 30 mM NaCl solution in EG and 30 mL of 40 mM Fe(NO₃)₃ solution in EG were added to the above flask and kept for 20 min. Then, 5.2 g AgNO₃ in 300 mL EG solution was slowly injected to the above reaction mixture. Finally, the mixture was allowed to react at 110 °C for 15 h and then quenched to room temperature.

Synthesis of Ag-Au NWs: The Au precursor solution was prepared by adding H₂O (23.6 mL), HAuCl₄ (200 μ L, 0.25 M), NaOH (1.2 mL, 0.2 M) and Na₂SO₃ (15 mL, 0.01 M) in sequence to a 50 mL round bottom flask. The mixture solution was left undisturbed for 12 h before use. Another solution was obtained by mixing H₂O (46 mL), PVP (10 mL, 5 wt%), L-AA (2 mL, 0.5 M), NaOH (2 mL, 0.5 M), Na₂SO₃ (500 μ L, 0.1 M) and Ag NWs (60 mg) in a flask. The mixture was then merged with the Au precursor solution and allowed to proceed undisturbed at room temperature for 6 h. Finally, Ag-Au NWs were washed with H₂O and IPA and collected by centrifugation. Such obtained NWs had an average Au shell thickness of ~3.5 nm, which could be changed by varying the quantity of the Ag NWs involved in the synthesis. For instance, the average Au shell

thickness could be changed to ~7 and ~12 nm by altering the mass of the Ag NWs to 40 and 20 mg, respectively, during the synthesis.

Preparation of Ag-Au NW TCEs: The glass slide was first cleaned in soap water, deionized water, acetone and IPA, and dried by using N₂ gas. Then, the Ag-Au NWs were diluted in IPA and deposited on a Sartorius polytetrafluoroethylene filter membrane (pore size 450 nm) by vacuum filtration. Afterwards, the NW film was transferred to the glass slide *via* pressure-aided method. In brief, the Ag-Au NW film/membrane was placed on the glass slide with the NWs in contact with the glass for 5 h under the stress of 10 kPa. After that, the filter membrane was peeled off. The NW film/glass with different transparencies can be obtained by varying either the concentration or volume of Ag-Au NWs suspension. The Ag-Au NW film/glass was then annealed under Ar 95%/H₂ 5% mixed atmosphere at 250°C for 30 min to obtain a higher conductivity. After that, a PDMS layer was coated onto the surface of Ag-Au NW film by spin coating and dried in a vacuum oven at 120 °C for 1 h. Finally, the flexible Ag-Au NW TCE was obtained by peeling off the film from the glass slide. For comparison, the Ag NW TCE was prepared following the same procedure, with the only exception being the use of as prepared Ag NWs.

Synthesis of EC polymer: A three-necked 250 mL flask equipped with a mechanic stirrer, an argon inlet and a pressure-equalizing dropping funnel capped with an argon outlet was thoroughly dried by a torch and cooled to room temperature under the continuous flow of argon. Into this reaction flask, 1.30 g compound IT3935 was first dissolved in 100 mL chloroform. Then, 1.04 g anhydrous FeCl₃ in nitromethane was added dropwise over a period of 30 min to the above solution. The reaction mixture was stirred at room temperature for 72 h, and then precipitated into 200 mL methanol. The precipitate was collected by filtration and re-dissolved in 250 mL chloroform. Then, 10 mL hydrazine monohydrate was added, and the mixture was stirred for 8 h. After evaporation,

the concentrate was further precipitated into 300 mL methanol. After that, the precipitate was filtered by a Soxhlet thimble and subsequently extracted *via* a Soxhlet extractor by methanol for 24 h, followed by a mixed solvent (chloroform : methanol = 80:20) for 24 h and finally by chloroform for 24 h. The mixed solvent extracted fraction was concentrated by evaporation, and precipitated in 300 mL methanol, filtered, dried and collected as a cyan solid, referred as the EC polymer.

Preparation of gel-like electrolyte: To make an electrolyte, LiBF₄ (0.66 g) was first dissolved in PC (2 g) solution. After that, acetonitrile (7.86 g) was introduced to the above solution. Then, PMMA (1.5 g) was slowly added into the mixture solution with magnetic stirring for 12 h. After PMMA was fully dissolved, viscous and transparent gel-like electrolyte was obtained.

Fabrication of EC device based on Ag-Au NW TCEs: The EC device was prepared as follows. First, the Ag-Au NW TCEs were cleaned by IPA and dried by using N₂ gas flow. Then, the EC polymer was deposited onto the Ag-Au NW TCE by spray coating. After that, the gel electrolyte described above was deposited onto the EC polymer film using tape as spacer. The as-prepared samples were then kept in an oven at 60 °C for 5 h to make the acetonitrile evaporate, leading to a solid electrolyte film. Finally, the EC device was completed *via* placing another Ag-Au NW TCE on the top.

Characterization: The morphology of the Ag and Ag-Au NWs was measured by a TEM (JEOL 2100F), equipping with an EDX spectrometer operated at 200 kV. The structure of the Ag-Au NW TCE was characterized using a SEM (LYRA3, Tescan), operated at 10 kV. The crystal structures of Ag and Ag-Au NWs were further examined by an XRD (D8 Advance, Bruker), using a Cu K α radiation source (λ =0.15406 nm) operated at 40 kV and 40 mA. The chemical compositions of Ag and Ag-Au NWs were further studied by an XPS (VG Esclab220i XL), operated with an Al K α

source. NAA measurements were acquired by a SLOWPOKE nuclear reactor to determine the weight content of Au and Ag in the Ag-Au NWs. UV-Vis absorption and transmission spectra of the samples were performed with an UV-Vis-NIR spectrophotometer (Varian, Cary 5000). Haze measurement was carried out on an UV-Vis-NIR spectrophotometer (Perkin Elmer, Lambda 750) with an integrating sphere. The surface topography of the TCEs was investigated by an AFM (MultiMode 8-HR, Bruker). The topography and PiFM spectra of EC polymer film on the Ag-Au NW electrode were acquired using VistaScope (MolecularVista, San-José, USA) scanning probe microscope. The sheet resistance of ITO-PET TCEs and NW TCEs was studied by a four-point probe (S-302). ¹H NMR spectra of oligomers IT3935 was collected on Bruker Advance 500 MHz. The thermochemistry of the EC polymer was analyzed by TGA (TA Instruments Q500) and DSC (Mettler Toledo) under N₂ atmosphere. Electrochemical measurements were carried out using three electrodes on electrochemical workstation (CH Instruments, CHI 660E).

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Conflict of Interest

The authors declare no conflict of interest.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at.

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Figure 1 (a-b) SEM and TEM images of Ag NWs; (c-d) SEM and TEM images of Ag-Au NWs; HAADF-STEM image (e), and the corresponding EDX mapping images (f-h) of Ag-Au NWs. In the EDX maps, red color represents Ag and green color represents Au. The scale bar in (h) is 50 nm.



Figure 2 (a) UV-VIS absorption spectra of pristine Ag NWs and Ag-Au NWs. (b) XRD spectra of pristine Ag NWs and Ag-Au NWs. Slight broadening of the XRD peaks was observed for the Ag-Au NWs due to Au layer coating. (c) Ag 3d and (d) Au 4f XPS spectra of Ag-Au NWs. The black dotted lines indicate the raw spectral data, and the color lines are fitted deconvolutions.



Figure 3 (a) Plot of transmittance at 550 nm versus sheet resistance for the Ag NW TCE and Ag-Au NW TCEs with different thickness (~3.5 nm, ~7 nm, ~12 nm) of Au shell. (b) Haze factor versus transmittance measured at 550 nm for Ag NW, Ag-Au NW and ITO-PET TCEs. (c) Plots of sheet resistance variation versus time for Ag NW and Ag-Au NW TCEs at 85 °C/85% RH. (d) Variation in sheet resistance of the ITO-PET, Ag NW and Ag-Au NW (~3.5 nm thick Au) TCEs as a function of the number of bending cycles (bending radius: 5 mm).



Figure 4. CV test results of (a) Ag and (b) Ag-Au NW TCEs in the standard three-electrode setup. Measurements were done in 0.5 M LiBF₄/PC at a scan rate of 25 mV/s. SEM images of (c) Ag and (d) Ag-Au NW TCEs after electrochemical stability tests. The core-shell NWs were very stable, however, Ag NWs were partially damaged. Arrows and ellipses highlight broken Ag NWs.



Figure 5. (a) Schematic illustration of a cyan EC polymer coated on Ag-Au NW TCE. (b) UV-Vis absorption of cyan EC polymer. The inset is an optical image of cyan polymer in toluene solution. Electrochemical behaviors of EC polymer/Ag-Au NW TCE in a three-electrode configuration. (c) CV curves at different scan rates. (d) Galvanostatic charge/discharge curves at different current densities. (e) Area capacitance and specific capacitance of EC polymer coated on the Ag-Au NW TCE calculated from galvanostatic charge/discharge at different current densities.



Figure 6. EC performance of Ag-Au NW TCE based device. (a) Transmittance measurements and the corresponding photographs. Real-time transmittance changes measured at (b) 550 nm and (c) 1600 nm during 200 consecutive cycles. (d) Cycling behavior of the ITO-PET and Ag-Au NW TCE-based EC devices bent to a bending radius of 5 mm.
The completely ITO-free flexible organic EC device showed high performance with reversible transmittance modulation in the visible region (40.2 % at wavelength of 550 nm) and near-infrared region (-68.2 % at wavelength of 1600 nm). Moreover, the device presented excellent flexibility (up to 1000 bending cycles) and impressively fast switching time (5.9 s).

Ag-Au Core-Shell Nanowires, ITO-Free Electrodes, Flexible Electrochromic Devices

S. Huang, Dr. Y. Liu, M. Jafari, Prof. M. Siaj, Dr. H. Wang, Dr. S. Xiao and Prof. D. Ma*

Highly Stable Ag-Au Core-Shell Nanowire Network for ITO-Free Flexible Organic Electrochromic Device



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Supporting information

Highly Stable Ag-Au Core-Shell Nanowire Network for ITO-Free Flexible Organic Electrochromic Device

Shengyun Huang¹, Yannan Liu¹, Maziar Jafari², Mohamed Siaj², Haining Wang³, Shuyong Xiao³ and Dongling Ma¹,*



Figure S1. Average diameter change after the Au deposition process. It was measured from multiple SEM images (a) before and (b) after the deposition process. The average diameter change (increase) of the NW was around 7 nm, suggesting an average shell thickness of 3.5 nm.



Figure S2. (a) HAADF-STEM image of a single Ag-Au NW. (b) EDX cross-sectional line scan of the Ag (red) and Au (green) along the yellow line marked in (a).



Figure S3. Ag 3d XPS spectra of Ag NWs and Ag-Au NWs.



Figure S4. UV-Vis spectra of (a) Ag NWs and (b) Ag-Au NWs dispersed in IPA before and after the exposure to H_2O_2 . (c) Schematic illustration of Ag or Ag-Au NW TCE immersed into H_2O_2 solution. (d) Variation in sheet resistance of the Ag NW and Ag-Au NW TCEs immersed into 0.85 M H_2O_2 solution. SEM images of (e) Ag and (f) Ag-Au NW TCEs 30 min after immersion into 0.85 M H_2O_2 solution 30 min. Red arrows in (e) highlight some traces of Ag nanoparticles.



Figure S5. SEM images of flexible Ag-Au NW TCEs: (a) top-view and (b) tilted-view with an angle of 55°.



Figure S6. Figure of merit values of the Ag, Ag-Au (~3.5 nm thick Au), Ag-Au (~7.0 nm thick Au), Ag-Au (~12.0 nm thick Au) NW TCEs as a function of NWs' concentration in dispersion used for the TCE fabrication.



Figure S7. Variation in the sheet resistance of pure Ag NW and the Ag-Au NW (~3.5 nm thick Au) TCEs exposed to air at room temperature for 90 days.



Figure S8. XRD spectra of Ag NWs and Ag-Au NW after long-term stability test.



Figure S9. CV curves of the Ag-Au NW TCE up to 50 cycles.



Figure S10. Synthetic pathway to cyan EC polymer.



Figure S11. ¹H-NMR (500 MHz, CDCl₃) spectra of IT3935: *δ* 8.279 (s, 2H), 6.664 (s, 2H), 4.207 (s, 4H), 4.108 (s, 4H), 3.559 (s, 8H), 3.416-3.442 (d, 8H), 1.276-1.327 (m, 48 H), 0.861-0.889 (m, 12H).



Figure S12. (a) TGA of EC polymer measured at a heating rate of 5 °C/min in N_2 atmosphere. (b) DSC performed on EC polymer, using the heating/cooling rate of 5 °C/min in N_2 atmosphere. The data correspond to the second heating and cooling cycle.



Figure S13. (a) AFM topography image and (b) PiFM spectra of EC polymer/Ag-Au NW TCE.



Figure S14. Stability of EC polymer/Ag-Au NW TCE measured in 0.5 M LiBF₄/PC solution in ambient air through CV at a scan rate of 25 mV/s.



Figure S15. Schematic illustration of a Ag-Au core-shell NW TCE based EC device.



Figure S16. Transmittance spectrum of the solid ionic electrolyte on a glass slide. Plain glass slide was used as reference. The inset is the photograph of the as-prepared ionic conductor in a glass vial.



Figure S17 AFM images of the ITO-PET TCE after the bending test (a) 2D image and (b) 3D image with R_{ms} of 124.1 nm. AFM images of the Ag-Au NW TCE after the bending test (a) 2D image and (b) 3D image with R_{ms} of 7.1 nm. The arrow in (a) points to the crack.

Table S1 Au contents measured by NAA for Ag-Au NWs of different Au shell thickness prepared by adding different quantities of Ag NWs during the shell formation process.

Different thickness	mol% Au in Ag-Au NWs
measured by SEM	from NAA report
~3.5 nm	12.1
~7 nm	18.5
~12 nm	26.7

CHAPTER 4 CONCLUSIONS AND PERSPECTIVES

4.1 Conclusions

TCEs are an essential part in not only smart windows, but also solar cells, touch panels and flat displays. Commercially, ITO electrodes set the market standard for TCEs in most of these applications. However, the use of ITO as a transparent electrode material has certain limitations, such as ever increasing cost due to indium scarcity, complicated processing requirements, sensitivity to acid and basic environments, and high surface roughness. Moreover, ITO is brittle and can easily crack when used in applications where bending cannot be absolutely avoided. Therefore, intense research efforts have been devoted to develop flexible, cheap, and solution-processable TCEs by exploring other materials for next generation electronics and optoelectronics, such as flexible solar cells and smart windows. Among these candidate replacements, metal nanowire (NW) films hold great promise for low-cost transparent electrode application because of their excellent electrical and optical properties, as well as their solution-processability. In this thesis, we focus on the designing and preparation of Cu or Ag related NW network films and their practical applications for TCEs in SPDs and EC devices. So, the results of this thesis project are divide into three parts based on the structures of the TCEs and their potential optoelectronic applications.

Part I is mainly focused on the combination of Cu NW and rGO to obtain Cu-rGO core-shell NWs and their potential application as TCEs. Basically, the graphene could improve not only oxidation resistance and the stability of Cu NWs due to the tight encapsulation, but also their adhesion to substrates. Similarly importantly, the graphene on the Cu NW surface can bridge individual Cu NWs, which will further enhance the electric and thermal conductivity of the Cu NW films. The highly transparent, conductive and stable Cu-rGO core-shell NW films were then used as electrodes to fabricate SPDs for the first time. The Cu-rGO NW film based devices exhibit excellent optical modulation of 42%, which is comparable with, and even better than, that of commercially available ITO electrodes. In addition, the device shows good stability and reversibility during all the switching processes. The response time for bleaching and coloration processes can be as short as 20 and 40 s, respectively. Therefore, it can be readily anticipated that the Cu-rGO NW TCE has great commercial potential for SPDs and further for other optoelectronic devices.

In part II, we presented a simple and low-cost method to prepare large-area, ultra-flexible, stable, free-standing Ag NW based high performance TCEs. The success relies on the intelligent use of a flexible polymer and automatic blade coating. The electrode showed a high transparency with superior electrical conductivity, excellent stability against oxidation, remarkable flexibility and robust structural integrity. Their high potential in flexible optoelectronics was well demonstrated in SPDs, which showed large optical modulation >60% and fast switching response about 20 s. Compared with ITO-PET TCEbased SPDs, our Ag NW TCE-based devices showed significantly better flexibility, which could maintain their functionalities after being folded up to 180° for 200 times (the maximum cycle number under the current investigation), without forming any micro cracks as occurred to the commercial ITO-PET TCE. Regarding the continuous operation on curved surfaces, we used a beaker as an example, demonstrating high contrast in the onand-off states. Such high performance, flexible SPDs hold great promise in smart window/glass application, which will have a profound impact on our daily life in the future. The simple route for fabricating large area Ag NW TCEs is also expected to pave the way for manufacturing next-generation flexible optoelectronic devices.

Part III is mainly focused on development of highly stable Ag-Au NW network for ITOfree flexible organic EC device. We successfully demonstrated a robust epitaxial deposition method for the synthesis of Ag-Au core-shell NWs, which showed excellent thermal and chemical stability. Flexible and high performance TCE was prepared using these ultrastable core-shell NWs with outstanding optical and electric properties. In addition, it showed remarkable thermal oxidation and electrochemical stabilities because of tight encapsulation of the Ag NW by the impermeable Au shell. A flexible EC device was then successfully assembled using the stable Ag-Au NW film, green EC polymer, LiBF4/PC/PMMA and Ag-Au NW film as the working electrode, active layer, solid electrolyte and counter electrode, respectively. The Ag-Au NW TCE and deposited EC polymer together showed high area capacitance (3.0 mF/cm²) and specific capacitance (23.2 F/g) at current density of 0.5 mA/cm². The experimental results demonstrated its interesting feature in transmittance modulation at Vis (40.2 % at wavelength of 550 nm) and NIR lights (-68.2 % at wavelength of 1600 nm). Moreover, the device showed fast switching response of ~5.9 s and excellent mechanical flexibility. The high-performance and flexible EC device hold great promise in smart window applications, which will combine energy storage and building's energy saving and have a profound impact on our daily life in the future.

4.2 Perspectives

We have developed three types of metal NW network films and studied their pratical application as TCEs in SPDs and EC devices. However, despite of certain progress we made, the research area of TCEs is still in its infant stage and significant efforts are still needed for further development of these kinds of next-generation TCEs and their utilization for electronic and optoelectronic applications. There are several interesting research directions in this highly promising field.

4.2.1 Synthetic procedures optimization

As we mentioned in part I, high performance and stable Cu-rGO NW TCEs were obtained using vacuum filtration and followed by thermal annealing, however, they are still far from sufficient for large-scale production. To this end, the rapid microwave-assisted synthesis of Cu NWs in aqueous solution should be explored with the goal of large quantity and high yields. Compared to traditional convective heating approaches, microwave irradiation is believed to be able to accelerate the reaction rate and precisely control the reaction temperature throughout a reaction system. Meanwhile, thermal annealing treatment process of Cu and GO nanomaterials, is still an obstacle for many applications, especially for flexible electronics. Therefore, in future, a facile efficient reduction method as well as a fast technological process for fabricating high-quality large-area Cu-rGO core-shell NW film should be developed, which should well match the mass roll-to-roll production of TCEs.

4.2.2 Cu-Au core-shell NWs

As mentioned, we successfully synthesized ultra-stable Ag-Au core-shell NWs and related TCEs, and the resulting EC devices showed high performance and excellent stablily (part III). The Ag-Au NWs TCEs based. However, Ag is 1000 times scarcer and 100 times more expensive than Cu. In addition, the electrical resistivity of Cu (16.8 n Ω ·m) is as low as that of silver (15.9 n Ω ·m). In Ag-Au cores-shell NW nanostructures, Ag was protected from oxidation by Au layer and offer the nanostructure good electricity. Therefore, the Cu should be good candidate for replacing Ag in the core-shell NW nanostructures. Moreover, to evaluate the potential of Cu-Au core-shell NW for

practical application, the TCEs and related electronics and optoelectronics should be further studied.

4.2.3 Solar cells application

As we know, an energy crisis is one of the most serious issues facing the world because of the rapid economic expansion, large increase in world population and human reliance on energy. Therefore, it is very important to develop sustainable energy conservation and conversion technologies. Smart windows and solar cells have been considered as two of the most promising solutions to energy issues. Smart windows, such as those based on SPDs and EC devices, provide dynamic control of photon flow that minimizes the energy loss, as well as improves human comfort. Solar cells, or photovoltaic cells, can convert sunlight directly into electrical energy, and thus have been considered as one of the state-of-the-art solutions to energy issues. Although the efficiency depends on a variety of factors, their overall performance strongly relies on the TCEs used. In this thesis, we have developed three types of metal NW network films and applied them as TCEs in smart windows application (SPDs and EC devices). Despite of certain progress we made in energy conservation, but next, more work needs to be done in energy conversion (solar cells). In addition, we should study and establish the relationships between solar cells performance and the sheet resistance and transparency of electrodes developed herein, which will provide the feedback and help with further material and electrode optimization.

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RÉSUMÉ

Électrode transparente à base de nanofils métalliques pour l'application aux fenêtres intelligentes

L'introduction

Actuellement, les appareils électroniques et optoélectroniques occupent de l'importance dans nos vies. On les retrouve dans les cellules solaires, les téléphones intelligents, les écrans tactiles/plats et les fenêtres intelligentes. Ces dispositifs ne servent pas uniquement à la relaxation mais font d'usage dans la communication et l'apprentissage. Les électrodes conductrices transparentes (ECTs) sont des composantes essentielles dans ces dispositifs électroniques. Elles agissent significativement sur leur performance et leur espérance de vie. Les ECTs sont des matériaux de films minces optiquement transparents et électriquement conducteurs. La valeur du marché mondial des ECTs était d'environ 7.1 billion de dollars en 2018, [1] et son taux de croissance annuelle composée est prévue autour de 9 % pour la période entre 2018-2026, d'après le rapport de Touch and Display Research en 2017.

En 1907, la première publication d'un ECT a paru. Badeker a écrit que les films minces de Cd déposés dans une chambre à décharge éclairée pourrait s'oxyder et devenir transparents tout en maintenant leur conductivité électrique. [2] Depuis ce moment, l'importance commerciale de ces films minces est reconnue. De plus, la liste des matériaux pouvant constituer des ECTs s'est étendue pour aujourd'hui inclure GdInO_x, ZnO dopé avec Al, In₂O₃ dopé avec F et nombreux autres. À partir des années 1960, les électrodes d'oxyde d'indium et d'étain (ITO) plafonnent le standard du marché des ECTs, en grande partie, dans les secteurs électroniques et optoélectroniques. [3] ITO a une composition tertiaire d'indium, d'étain et d'oxygène en proportions adverses, ajustable selon ses applications. À titre d'exemple, la composition d'ITO est saturée en oxygène en proportions massiques de 74 % In, 18 % O₂ et 8 % Sn lorsqu'employé comme une électrode transparente. [4] Cette combine lui dote une transparence élevée (>80 %), une faible résistivité ($R_s < 100 \Omega/Sq$) et admet un contrôle précis sur la concentration et l'épaisseur de dopage. Toutefois, l'usage d'ITO s'accompagne de quelques limitations. Parmi, un coût continuellement croissant lié à la rareté de l'indium, des procédés essentiels de fabrication

compliqués, une sensibilité en milieu acide et basique et une rugosité surfacique élevée. Plus encore, ITO est vitré faisant de lui susceptible aux bris face à des torsions mécaniques et inadmissible aux applications flexibles. En réponse à ces limitations, des efforts de recherche intenses explorant les matériaux électronique et optoélectronique de prochaine génération, tels que ceux des fenêtres intelligentes flexibles, ont été consacrés au développement d'ECTs flexibles, abordables et fabricable en solution.

Depuis les cinq dernières années, plusieurs matériaux transparents conducteurs alternatifs ont été étudiées, soient les nanotubes de carbone (NTCs), le graphene, les polymères conducteurs, les mailles métalliques et les nanofils (NFs) de métaux. Les études des propriétés optoélectroniques des diverses ECTs suggèrent que le réseau des Cu/Ag NFs agencés au graphene est comparable à ITO (Figure R1a). [15] Pourtant, le réseau des Cu/Ag NFs est nettement moins dispendieux que ITO en matière de coût de matériaux et de fabrication, tel qu'illustré à la Figure R1b. [15]





Objectif de la thèse

La thèse est divisée en trois parties ayant des objectifs fortement interreliés. Spécifiquement, trois principales types d'ECTs différentes ont été développées à base de NFs de métaux, avec but de constituer des dispositifs à particules suspendues (DPSs) et des dispositifs électrochromes (EC) pour leurs applications pratiques respectivement.

Partie I : Préparation de réseau pelliculaire de NFs de noyau cuivrique revêtus de graphène réduit et leur grand potentiel comme ECTs dans les DPSs.

Pour substituer les ECTs à base d'ITO, les NFs de Cu ont attiré une attention croissante vu leur faible coût de production et leur conductivité électrique élevée. Jusqu'à présent, des améliorations notables ont été faites dans la performance des ECTs à base des NFs de Cu. Malheureusement, des facteurs contraignantes empêchent toujours leur usage répandu, tels qu'une susceptibilité accrue à l'oxydation, une adhésion défavorable au substrat et une instabilité dans des environnement arides. Le graphène est une fine couche atomique de carbone hybridé sp². Ce matériau a des propriétés structurales uniques et des propriétés physiques exceptionnelles. On retrouve notamment une haute conductivité électrique, une flexibilité mécanique, une bonne stabilité chimique et une transparence optique. Ces derniers font du graphène un matériau idéal pour de nombreux dispositifs optoélectroniques. Le choix de préférence, en termes d'efficacité de coût et de production à grande-échelle, est la réduction chimique de l'oxyde de graphène. L'agencement contrôlé du graphène avec d'autres matériaux pour but de générer des structures fonctionnelles occupe actuellement un intérêt scientifique considérable dans la communauté scientifique. La combinaison des NFs de cuivre et d'oxyde de graphène réduit en un seul produit est un défi, quoique sa réussite mène certainement à une gamme de nouvelles applications des ECTs. En principe, l'ajout du graphène bénéficierait la résistance et la stabilité des NFs de Cu par le biais d'un revêtement serré. En plus, l'adhésion des NFs de Cu au substrat seraient favorisée. Également, la présence de graphène à la surface des NFs de Cu agirait tel un pont pour unir les NFs de Cu individuels. L'effet de ce pontage accroîtrait la conductivité électrique et thermique des films de NFs de cuivre.

Les objectifs de cette section sont :

- Synthétiser et caractériser le diamètre fin et l'aspect-ratio élevé des NFs de Cu-GO noyaurevêtement.
- 2. Préparer et caractériser les films des NFs de Cu-rGO noyau-revêtement.
- Investiguer les propriétés optiques et électriques, la rugosité surfacique et la stabilité à long-terme des films de NFs de Cu-rGO noyau-revêtement.
- Fabrication et investigation des DPSs en utilisant des ECTs à base des films de NFs de CurGO noyau-revêtement.

Partie II : Fabrication de réseau de films de NFs d'Ag indépendant de substrat, à grande surface et leur application pratique comme ECTs flexible dans des DPSs pliables.

Les ECTs pouvant subvenir à des déformations mécaniques significatives tout en maintenant leur intégrité structurale et en demeurant hautement électriquement conducteurs sont fortement recherchées et de besoin urgemment dans les dispositifs optoélectroniques flexibles et pliables. Cependant, la technologie en matière d'électroniques flexibles stagne où l'ITO rigide occupe principalement l'abondance. Plusieurs groupes ont exploré les réseaux de NFs d'Ag pour la préparation d'électrodes flexibles de prochaine génération optoélectronique. Quoique le développement de simple, de grande quantité, à large recouvrement, uniforme, robuste et flexible d'ETCs à base de NFs d'Ag reste un défi à surmonter.

Les objectifs de cette section sont :

- 1. Accroître la synthèse de NFs d'Ag de diamètre fin et d'aspect-ratio élevé.
- 2. Préparer et caractériser le réseau de film de NFs d'Ag flexibles à recouvrement élevé.
- Investiguer les propriétés optiques et électriques, la rugosité surfacique, l'adhésion, la stabilité à long-terme et la flexibilité des réseaux de film de NFs d'Ag.
- 4. Fabriquer des DPSs pliables à recouvrement élevé utilisant un réseau de film de NFs d'Ag comme matériau ECT, et investiguer la performance de ces DPSs.

Partie III: Fabrication de réseau de films de NFs d'Ag-Au hautement stable pour constituer des dispositifs organiques électrochomes dépourvus d'ITO.

Les dispositifs EC solides et flexibles doivent impérativement conformiser le design de chacun de leurs composants afin de respecter les exigences de transparence, flexibilité et stabilité mécanique. Cependant, la technologie en matière d'électroniques flexibles stagne où l'ITO rigide occupe principalement l'abondance. Jusqu'à maintenant, plusieurs groupes de chercheur ont mesuré une performance optique et électrique élevée pour les ECTs à base de NFs de Cu ou d'Ag. Tandis que, le développement de dispositif EC uniquement dépendant des NFs de Cu ou d'Ag dans un environnement EC, entièrement sans ITO, est incommode. Cette difficulté s'explique par la faible stabilité chimique et électrochimique des NFs de Cu ou d'Ag dans des environnement EC.

Entretemps, la couche d'oxyde de métal fragile souvent utilisée dans la couche active et les problèmes de fuite de l'électrode liquide durant la transformation affecte davantage négativement la performance et la durée de vie des dispositifs EC.

Les objectifs de cette section sont :

- 1) Synthétiser et caractériser le réseau des films de NFs d'Ag-Au noyau-revêtement.
- 2) Préparer et caractériser le réseau de films de NFs d'Ag-Au noyau-revêtement.
- Investiguer les propriétés optiques et électriques, de rugosité surfacique, stabilité à long terme et flexibilité du réseau de film de NFs d'Ag-Au noyau-revêtement.
- 4) Préparation et caractérisation de l'électrode solide et du matériau active polymère conjugué.
- Fabriquer des dispositifs EC solides et flexibles utilisant les ECTs à base du réseau de films Ag-Au noyau-revêtement et investiguer la performance de ces dispositifs EC.

Résultats

Dans la première partie de la thèse, nous avions rapporté un nouveau DPS renfermant un fort potentiel pour les applications de fenêtres intelligentes. Le DPS était construit avec les films de NFs de Cu-rGO noyau-revêtement comme ECT, pour la première fois. Un schéma du processus de préparation des films de NFs de Cu-Go est illustré dans la Figure R2a. Premièrement, les NFs de Cu-GO noyau-revêtement étaient synthétisés en mélangeant la solution aqueuse contenant GO avec une dispersion des NFs de Cu dans IPA. Les NFs de Cu-GO noyau-revêtement étaient subséquemment dilués dans IPA et déposés par filtration sous vide à l'aide de membranes filtres, suivi d'un transfert du film de NFs sur un substrat de verre assisté par pression. Les NFs de Cu-GO noyau-revêtement forment une suspension colloïdale très stable dans IPA. En revanche, les NFs de Cu avaient complètement précipités en 24 h, tel que montré dans les inserts du haut de la Figure R2b, c. La longueur et le diamètre moyens des NFs de Cu synthétisés étaient de 40 ± 10 et 30 ± 10 nm respectivement (Figure R2b). Pour les NFs de Cu-GO noyau-revêtement, une couche duveteuse, représentative de GO, épaisse de quelques nanomètres est observable à la surface des NFs de Cu dans la Figure R2c. On a trouvé qu'avec l'enrobage de rGO, les électrodes de NFs de Cu démontrent simultanément une transparence optique et une conductivité électrique élevée. En addition, une stabilité substantiellement améliorée dans une variété de condition était percevable.



Figure R2. (a) Un schéma de la procédure de fabrication des films de NFs de Cu-GO transparents. Les images MET des NFs de Cu (b) à agrandissement élevé et faible (en insert). Les inserts du haut en (b) et (c) sont des photos de la dispersion des NFs de Cu (b) et des NFs de Cu-GO (c). dans IPA après 24 h d'entreposage. Bien que les NFs de Cu précipitaient presque totalement (b), la dispersion de nos NFs de Cu-GO préservait son uniformité après un jour de temps (c).

Pour évaluer le potentiel des applications pratiques, nous avions construit un nouveau DPS basé sur les ECTs de NFs de Cu-rGO. Les Figures R3a et b montrent l'image optique des DPSs préparés dans les états <<allumé>> et <<éteint>> respectivement. La Figure R3c montre le spectre de transmittance correspondant entre 300 et 900 nm. Par comparaison, les DPSs ont aussi été fabriqués sur des substrats d'ITO ECTs commercialement disponibles, en utilisant exactement les mêmes conditions pour la couche électro-optique. La réponse électro-optique en termes de différence de transmission entre les états <<allumé>> et <<éteint>> est comparable, et même meilleure, pour les DPSs à base de Cu-rGO par rappot à celles à base d'ITO. La nouvelle structure sandwich des DPSs, basée sur les ECTs de NFs Cu-rGO, démontre un changement large dans sa transmittance optique (42 %) entre les états <<allumé>> et <<éteint>>, commutant dans un délais temporel impressionnant (20 s et 40 s pour la perte de l'opacité et le retour de la couleur, respectivement) et une stabilité supérieure, illustrée à la figure R3d, e. Ces hautes performances sont comparables à celles des DPSs à base d'électrodes ITO commercialement disponibles. Ces

résultats prometteurs pavent le chemin de nos électrodes à prendre une place intégrale dans une variété de dispositifs optoélectroniques, autant dans ceux énergiquement efficaces et flexibles.



Figure R3. (a) Performance comparative entre notre film et celui de ITO ECT : Les images optiques de nos DPSs quand un voltage externe est <<éteint>> (a) et <<allumé>> (b). (c) Spectres de transmission des deux DPSs dans les états <<allumé>> et <<éteint>>. La performance de notre électrode est semblable à celle de ITO ECT. (d) La transmission de lumière en fonction du temps du DPS durant les périodes l'allumage (premières 20 s) et l'éteignement (prochaines 40 s). La transmittance totale des points 1 et 2 sont 4.3 % et 46.5 % respectivement. (e) Répétition de 250 cycles d'allumage et d'éteignement consécutives et mesurage de la transmittance du DPS.

Les résultats correspondants dans cette section sont publiés dans l'article suivant :

Shengyun Huang, Qingzhe Zhang, Pandeng Li, Fuqiang Ren, Aycan Yurtsever, and Dongling Ma, High-Performance Suspended Particle Devices Based on Copper-Reduced Graphene Oxide Core– Shell Nanowire Electrodes. Adv. Energy Mater. 2018, 8, 1703658.

L'ECT à base du réseau de NFs de Cu-rGO noyau-revêtement développée dans la Partie I démontre une haute performance optoélectronique et une bonne stabilité. Toutefois, l'aire d'un tel film de réseau de NFs de Cu-rGO noyau-revêtement est trop minime à cause de l'étape de la

filtration sous-vide lors de la fabrication. Ce qui n'est pas propice pour les applications de dispositifs à large surface de recouvrement. Plus encore, la température élevée exigée pour le processus de réduction des NFs de Cu-GO, lors du post-traitement, limite leur application sur des substrats flexibles. En conséquence, dans la Partie II, nous développions un produit indépendant de substrat, de 19 cm x 9 cm hautement performant et ultra-flexible d'ECTs à base de NFs d'Ag utilisant un système à revêtement automatique facile et à haute vitesse, pour la première fois. Le résultat était un film assez homogène et transparent sur toute sa surface, telle que montrée à la Figure R4. Les procédures de synthèse d'électrodes conventionnelles en solution ont quelques désavantages pour les applications des ECTs. Parmi on retrouve une morphologie non-uniforme, une production à grand-échelle difficle, des résistances aux jonctions entre des NFs élevées, une faible adhésion au substrat et une basse stabilité. La méthode de revêtement à la lame présente plus d'avantages en termes d'uniformité du film et aisance opérationnelle, tout de même qu'une procédure de production à l'échelle plus convenable. Cependant, cette technique automatique a, jusqu'à présent, été rarement appliquée dans la fabrication d'ECT NF de large surface, possiblement à cause de la surface relativement rugueuse du film de NFs produit par cette technique. Dans notre cas, avec l'utilisation intelligente d'un polymère transparent et flexible, l'ECT avait une surface plus lisse, une meilleure conductivité, une flexibilité mécanique supérieure et une forte intégrité structurale. Le polymère a rempli plusieurs rôles : la passivation (protection) et le renforcement de la performance et de la structure. Notre ECT de NFs d'Ag a fait preuve d'excellente flexibilité, observée par une reproductibilité après avoir été plié pendant 10 000 cycles sans dégradation dans la performance. Cette observation valide que notre ECT est significativement meilleure que les ECTs basés sur ITO commercial.



Figure R4. (a) Illustration schématique de la fabrication du ECT de NFs d'Ag flexible. Les inserts sont des photos de NFs d'Ag dispersés dans une solution IPA (en haut) et un applicateur de film ajustable avec un micromètre (milieu). (b) Faible agrandissement image TEM de NFs d'Ag. L'insert montre un agrandissement de l'image TEM d'un NF d'Ag individuel. Les images SEM du ECT flexible de NFs d'Ag : vue de haut (c) et pivotée à un angle de 55° (d). (e) Photographie d'une ECT flexible de NFs d'Ag repliée à 180°. Les photos de larges surface (18 cm x 9 cm) d'une ECT de NFs d'Ag avant (f) et après (g) un repliement de 180°. Les lignes pointillées rouge démarquent les rebords du film flexible des ECTs de NFs d'Ag.

Pour explorer le potentiel élevé de ces ECTs, comme preuve de concept démonstrative, nous fabriquions des DPSs pliables pour des applications de fenêtres intelligentes. Le réseau de film de NFs d'Ag était utilisé à titre d'électrode transparente pour la première fois (Figure R5a). Figure R5b et c montrent des photos du DPS préparé avec une aire d'environ 9 cm x 9 cm dans les états opaque <<éteint>> et transparent <<allumé>> respectivement. Nos dispositifs ont montré un grand changement dans leur transmittance optique (modulation optique de 60.2 %) et dans leur vitesse

de délai de commutation (21 s), tout en manifestant une excellente stabilité, telle que montrée dans la Figure R5d et e.



Figure R5. (a) Schémas structuraux du DPS flexible utilisant le film de NFs d'Ag comme ECT. Les photos de notre DPS flexible à large recouvrement (9 x 9 cm²) lorsqu'un voltage externe de 110 V est (b) <<éteint>> et (c) <<allumé>>. (d) Spectre de transmission de trois DPSs dans les états <<allumé>> et <<éteint>>. Les performances de nos électrodes sont comparables à celles des ECTs ITO-PET commercialement disponibles. (e) Répétition de 250 cycles d'allumage et d'éteignement consécutives et mesurage de la transmittance du DPS.

Pour investiguer la flexibilité mécanique du dispositif, d'où leur usage diverse sur des surfaces courbées, les DPSs d'ECT de NFs d'Ag étaient pliés jusqu'à même 180° et testés. Figure R6a montre un DPS attaché à la surface courbée d'un bécher, soit un bécher intelligent, qui a une couleur bleu foncé dans l'état opaque. Après l'application d'un voltage AC, le dispositif devenait transparent rapidement et uniformément, révélant deux stylos marqueurs placés à l'intérieur du bécher (Figure R6b). Significativement meilleurs que les dispositifs électro-optiques ECT basé sur ITO-PET, les DPSs basés sur les électrodes de NFs d'Ag ont montré une flexibilité mécanique excellente, pouvant plier de 180° pour plus de 200 cycles sans dégradations obvies dans la performance de commutation (Figure R6c, d et f). La présente méthode de fabrication d'ECTs de NFs d'Ag de large surface et ultra-flexible peut étendre jusqu'à la fabrication d'une variété de dispositifs électronique et optoélectronique courbés ou non-planaires dans un future proche.



Figure R6. Photos des états <<éteint>> et <<allumé>> d'un DPS couvrant la surface d'un bécher, i.e., un bécher <<intelligent>>. La courbure du bécher est d'environ 32 mm. (c, d) Les photos des états <<éteint>> et <<allumé>> d'un DPS replié à 180°. (f) Le comportement cyclique des DPSs d'ECTs à base de NFs d'Ag et de ITO-PET sur le bécher et repliés à 180° pendant 200 cycles.

Les résultats correspondants dans cette section sont publiés dans l'article suivant:

Shengyun Huang, Qingzhe Zhang, Fan Yang, Deepak Thrithamarassery Gangadharan, Pandeng Li, Fuqiang Ren, Baoquan Sun and Dongling Ma, A Facile Way for Scalable Fabrication of Silver Nanowire Network Electrodes for High-Performance and Foldable Smart Windows. J. Mater. Chem. A, 2020, 8, 8620-8628

Bien que les DPSs basés sur l'ECT de NFs d'Ag développés dans la Partie II ont montré une modulation optique élevée, un court délai de commutation et une excellente stabilité. La technologie actuelle des DPSs requiert un courant alternative (AC) d'une tension relativement élevée de 110 V pour contrôler la transmission de lumière, ce qui n'est pas sécuritaire. Surtout dans les applications de dispositifs vestimentaires. Plus encore, les NFs d'Ag à l'échelle nanométrique sont facilement oxydés. À long terme, l'oxydation continuelle inévitable et irréparable les prévient de fonctionner tels que prévus. Spécialement, lorsque les ECTs de NFs

d'Ag étaient utilisés comme l'anode dans le dispositif EC, les NFs ont perdu leur conductivité due à l'oxydation pendant le processus d'échange des transporteurs de charges avec l'électrolyte. Alors, dans la dernière partie de la thèse, nous avions développé un nouvel dispositif EC flexible et organique, totalement dépourvu de ITO, en utilisant un réseau de NFs Ag-Au noyau-revêtement (Ag-Au NFs), un polymère EC et LiBF4/propylene carbonate/poly(methyl méthacrylate) comme électrode, couche active et électrolyte solide.



Figure R7. (a-b) Images MEB et MET des NFs d'Ag; (c-d) Images MEB et MET des NFs d'Ag-Au; image HAADF-STEM (e), et les images cartographiques EDS correspondantes (f-h) des NFs d'Ag-Au. Dans les plans EDS, la couleur rouge représente l'Ag et la couleur verte représente l'Au. L'échelle est de 50 nm.

D'abord, nous avions synthétisé les NFs d'Ag en utilisant une méthode précédemment rapportée avec des petites modifications.⁴² Les images MEB et MET des NFs d'Ag purs sont montrées dans les Figure R7a et b. Les NFs d'Ag-Au ont été préparés ensuite par la méthode de dépôt conforme des atomes d'Au sur les NFs d'Ag utilisant l'acide ascorbique (AA) comme agent réducteur et le sulfite de sodium comme ligand. La structure des NFs d'Ag-Au noyau-revêtement était confirmée en utilisant plusieurs techniques de microscopie électronique et des méthodes spectroscopiques (Figure R7c et d). La Figure R7e montre un contraste plus prononcé sur les bordures des NFs noyau-revêtement, suggérant un enrichissement local des atomes lourds d'Au. La cartographie EDS a davantage confirmé la structure noyau-revêtement des NFs d'Ag-Au (Figure R7f et h).


Visiblement, les atomes d'Ag (couleur rouge) étaient distribués dans la zone centrale des NFs, tandis que les atomes d'Au (couleur verte) étaient principalement localisés dans la région externe.

Figure R8. (a) Illustration schématique d'un polymère vert EC revêtu sur l'ECT de NFs d'Ag-Au. (b) Absorption UV-Vis du polymère EC vert. L'insert est une image du polymère vert dans une solution de toluène. Les comportements électrochimiques du ECT/polymère EC de NFs d'Ag-Au dans une configuration à trois-électrodes. (c) les courbes CVs à des vitesses de balayages différentes. (d) Courbes de charge-décharge galvanostatiques à des densités de courant différentes. (e) Aire capacitive et capacitance spécifique d'un polymère revêtu sur l'ECT de NFs d'Ag-Au calculées des courbes de charge-décharge galvanostatiques à des densités de courant différentes.

Les ECTs flexibles de NFs d'Ag-Au étaient ensuite préparées par la technique de déposition de solution. Les électrodes de NFs d'Ag-Au intégrées avec un polymère EC conjugué ont ensemble démontré une excellente stabilité dans des environnements arides due à l'encapsulation ferme des NFs d'Ag par le revêtement d'Au. De plus, une aire capacitive élevée de 3.0 mF/cm² et une capacitance spécifique de 23.2 F/g à une densité de courant de 0.5 mA/cm² (Figure R8). Les dispositifs EC ont montré une performance EC élevée avec une modulation de transmittance réversible dans la région du visible (40.2 % à une longueur d'onde de 550 nm) et dans la région du proche infrarouge (-68.2 % à une longueur d'onde de 1600 nm) (Figure R9a). Plus encore, le dispositif a présenté une excellente flexibilité et un temps de commutation rapide (Figure R9b- d). Les stratégies développées et démontrées ici pour les dispositifs EC flexibles pourraient aussi servir de plateforme technologique futuriste pour l'électronique et l'optoélectronique déformables.



Figure R9. Performance EC du dispositif ECT de NFs d'Ag-Au. (a) Mesures de transmittance et les graphiques correspondants. Mesures des changements de transmittance en temps-réel à (b) 550 nm et (c) 1600 nm pendant 200 cycles consécutives. (d) Comportement cyclique des dispositifs EC d'ECT de ITO-PET et de NFs d'Ag-Au lorsque pliés à un rayon de 5 nm.

Les résultats correspondants dans cette section ont été soumis pour publication:

Shengyun Huang, Yannan Liu, Maziar Jafari, Mohamed Siaj, Haining Wang, Shuyong Xiao and Dongling Ma, Highly Stable Ag-Au Nanowire Network for ITO-Free Flexible Organic Electrochromic Device.