Electrochromics for deformable display application

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NANYANG
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**ELECTROCHROMICS FOR DEFORMABLE DISPLAY
APPLICATION**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2016

ELECTROCHROMICS FOR DEFORMABLE DISPLAY APPLICATION

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Abstract

Deformable electronics with the ability to conform to non-planar and curvature surfaces while keeping the functionality is under vigorous development recently to cater for the ever-growing and demanding need of people for mechanically compliant consumer electronics that could achieve human-machine interactions in a deformable way. Prompted by such needs, deformable electronics like wearable bands to capture signals for monitoring human health; stretchable optical projector or camera to realize virtual reality display and foldable smartphones that allows the ultra-portability and durability are under development in the market place as the next generation electronics to realize unprecedented functionalities unreachable for the conventional rigid electronics.

As a very important component for the realization of human-machine interaction, a display system is greatly favored to feedback and transport information. Electrochromic display represents a non-emissive display genre with the advantage of high contrast, low power consumption and facile device assembly. The idea of adopting electrochromism for deformable display and information communication is still at its cradle and progressed in a limited fashion. In this study, the research is focused on feasible approaches and techniques for the realization of deformable electrochromic devices, in particular stretchable, wearable and foldable electrochromic devices.

To realize these, the research started from the design of deformable electrodes. In order to meet the requirements for low charge transfer resistance with rapid switching and large optical modulation, electrodes need to be endowed with high conductivity. The electrochromic devices subject to deformation are expected to suffer performance degradation as small as possible, which makes requisite the mechanical stability of the electrode against stretching or folding. Ag nanowires with the metallic low resistance and the reticulate network shape of high mechanical compliance are potential with an excellent preservation of the network resistance due to inter-sliding mechanism to accommodate strain. The network structure with open voids that obviates strong absorption could also lead to optical transparency of the percolating network. These beneficial properties well leveraged could be integrated with a stretchable or foldable substrate to function as the deformable electrode. An embedded Ag nanowires network

structure in PDMS was engineered to obtain the stretchable electrode. The electrode maintains an excellent conductivity at both the relaxed and 50% strained state. A nanopaper transfer technique was discovered and discussed in the thesis; the versatile transfer technique renders possible the transfer of various functional nanomaterials of different dimensions. Transparent conductive Ag nanowires percolating electrode was demonstrated with a high quality through this technique. The robust electrode was demonstrated as an excellent substrate to practice folding for the electrochromic devices. The display function is realized through the integration of electrochromes on the mentioned deformable electrodes. Unlike rigid conventional electrochromic devices, the morphology and thickness of the electrochrome need to be carefully designed in order to accommodate the deformation. Electrochemical deposition from the precursor offers an excellent solution to manually control the physical property of the electrochromic layer to fulfill the deformation function. Discrete WO_3 islands and thin WO_3 coatings were deposited for stretchable and foldable electrochromic applications respectively. The performance at relaxed and strained state as well as folded state was analyzed systematically to illuminate approaches for the buildup of durable deformable devices. A fully foldable solid state transparent electrochromic device based on small molecule slime and SWCNT protected Ag nanowire electrode was demonstrated as a potential technique for highly deformable electrochromics.

In conclusion, the thesis together with the herein encompassed techniques and approaches is believed to be able to provide some insightful ideas on the emerging topic of deformable electrochromics and meanwhile it serves as a good guidance for the realization of durable deformable electrochromic devices for display applications.

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Abbreviations

NW	Nanowires
Ag NW	Silver Nanowire
CNT	Carbon Nanotube
SWCNT	Single Wall Carbon Nanotube
ITO	Indium Tin oxide
FOM	Figure of Merit
IF	Improvement Factor
TCE	Transparent Conductive Electrode
AQS	Sodium Anthroquinone-2-Sulfonate
EV	Ethyl viologen
IPA	Isopropyl Alcohol
SEM	Scanning Electron Microscopy
FESEM	Field Effect Scanning Electron Microscopy
AFM	Atomic Force Microscopy
TEM	Transmission Electron Microscopy
XRD	X-ray Diffraction
EDS	Energy-dispersive X-ray spectroscopy
LED	Light Emitting Diode
LCD	Liquid Crystal Display
OD	Optical Density
PET	Polyethylene Terephthalate
PDMS	Polydimethylsiloxane
PC	Polycarbonate
PTFE	Polytetrafluorethylene
PVA	Polyvinyl Alcohol
PMMA	Poly(methyl methacrylate)
P3HT	Poly(3-hexylthiophene-2,5-diyl)
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDOT:PSS	Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
NC	Nanocellulose
CNF	Cellulose Nanofibril
PCNF	Physically liberated Cellulose Nanofibril
BCNF	Bacterial Cellulose Nanofibril
TEMPO	(2, 2, 6, 6-Tetramethylpiperidin-1-yl)oxyl
TCNF	TEMPO assisted oxidized Cellulose Nanofibril
QD	Quantum Dot
UV	Ultraviolet
DMF	Dimethylformamide

PU	Polyurethane
CVD	Chemical Vapor Deposition
SC	Sodium Cholate
SDBS	Sodium Dodecyl Benzene Sulfonate
CTE	Coefficient of Thermal Expansion

Chapter 1

Introduction

In this chapter, a brief introduction on the current progress of deformable electrochromic devices is presented. The issues that limit the performance of deformable electrochromic devices are identified and corresponding strategies to solve the problems are briefed. Finally, the organization of the dissertation was described with the major findings summarized in the end. This chapter serves as a guideline to delineate the objective of the current research and the proposed approaches to accomplish the goal.

1.1 Problem Statement

Electrochromism describes a phenomenon of a system that is able to change optical modulation under supplied voltage. This concept is introduced as early as 1973 by Deb.¹ Since then, electrochromism has been advanced tremendously with a broad range of electrochromes discovered spanning across inorganic semiconductor,²⁻⁵ conjugated polymer⁶⁻⁹ and small molecules etc.¹⁰⁻¹³ However, the majority of the applications were based on rigid indium tin oxide (ITO) on glass due to its excellent stability and good combination of transparency and conductivity.

With the growing demand for deformable electronics and consumable electronics, stretchable and foldable electronics has become a compelling concept for emerging electronic devices.¹⁴⁻¹⁶ Electrochromism for display application can be of low cost, minimal power consumption and has a flexible choice of functioning materials.¹⁷ Wearable and foldable electrochromics for futuristic display has become an appealing topic and irresistible trend for the next generation electronic devices.¹⁸ The concept was well received and has been spotted with great market value by tech giants like SAMSUNG and LG etc to develop such devices.

While a promising future was depicted, deformable electrochromism has been rarely successfully developed so far. The current progress has been majorly suspended at the flexible stage.^{5, 10, 19} Stretchable and foldable electrochromic devices that are functioning on curvature and other non-flat surfaces at rough deformation conditions are much more challenging to achieve. The development in this field is still in its cradle.

Though stretchable and foldable electronics are booming with some good demonstrations for applications like transistor,^{16, 20, 21} light-emitting diode (LED),^{16, 22, 23} sensor,²⁴⁻²⁶ heater etc.^{27, 28} The development of deformable electrochromics is rather limited. A good deformable electrochromic device requires necessary parameters like high conductivity of the deformable electrode, a stable electrode with little change in resistance under deformation, conformal contact between the electrochrome and the electrode, compatible choice of the electrolyte and electrochrome to avoid the decomposition of the electrolyte and failure of the electrode. Generally speaking, the currently reported performance for deformable electrochromic devices is poor with faint optical modulation.^{18, 29, 30} A major drawback lays in the electrode design with large charge transfer resistance which leads to

restricted redox reactions.^{19, 31} A delicate design of stretchable and foldable electrochromic devices with proper and perceptible performance is necessary for practical application and yet to be realized.

1.2 Objectives and Scope

1.2.1 Develop strategies for deformable electrodes

To realize a deformable electrochromic device, the single most important issue to solve is the electrode design. As described earlier, the performance of current electrochromic devices are largely constrained by the brittle ITO based electrode that easily cracks under mild disturbance.^{32,33} Good mechanical compliance is necessary for deformable electrodes. The ability to take load and make conformation change in response to external force, while at the same time maintaining the high conductivity, is greatly desired.

Metallic nanowire based percolating network has the advantage of good conductivity, high transparency compared to carbon based materials that usually have a high resistance. The stretchability of the network as a result of the reticulate structure, which slides and realign under deformation,^{22, 34} allows it to be incorporated with elastomer matrix to form a conductive stretchable composite. Conductivity is expected to be well maintained without much change even under tensile stretching for this kind of composite electrode. Besides, the ductile and malleable nature of the metallic wire allows it to accommodate folding without breaking and cracking. This could promisingly satisfy its use for foldable electrode.

The first task is to realize a stretchable Ag nanowire based electrode. As mentioned before, the conductive network needs to be incorporated with a stretchable substrate to facilitate the stretching purpose since the conductive network itself is not freestanding.

Polydimethylsiloxane (PDMS) is the most common elastomer for stretching applications. A traditional method for the fabrication of composite involves a physical mixing between components as for commercial carbon black stretchable tape. While this is straightforward and easy to prepare, the resulted composite usually has a low conductivity due to ineffective contact between conducting elements.¹⁴ Techniques involving formation of the conductive layer first followed by combination of the layer within the elastomer to keep the integrity of the conductive network should be developed.

The second task relates to accomplishing a freely foldable transparent conductive electrode. Due to the intrinsic ductility of the Ag nanowire, we propose to realize this novel conductor with far superior flexibility and better electro-optical performance than ITO/ Polyethylene Terephthalate (PET). A delicate design of the conductive network as well as an efficient transfer technique to position the conductive network on the target substrate needs to be developed. Nanocellulose with extreme flexibility that allows folding, transparency, and high surface free energy is an excellent candidate and would be utilized as the substrate and to facilitate the transfer process.

1.2.2 Realization of stretchable and wearable electrochromics

Stretchable and wearable electrochromic display has great potential for camouflage, deformable display, anti-counterfeiting and even fashion applications. After the accomplishment of the stretchable electrode design, we have the basis for the design of stretchable and wearable electrochromics. The objective for this research is to realize a stretchable electrochromic display and later integrate it onto fabric textile.

After the stretchable function has been imparted to the electrode; we need to pair it with a compatible electrochrome that is able to stretch. Rogers, a pioneer in the development of stretchable electronics, has given a good suggestion for materials to achieve stretchability.¹⁴ That is synthesizing materials that stretch or creating structures that stretch. Electrochromic conjugated polymers usually possess some intrinsic stretchability,³⁵ but the performance and stability of the organic polymer usually causes great concerns. Inorganic semiconductor, on the other hand, has a generally better stability and optical modulation with particularly WO_3 receiving great attention even in the marketplace. Commercial WO_3 , however, is usually sputtered onto the target substrate, which is incapable of stretching. Thus a stretchable structure of the inorganic electrochromic layer needs to be designed.

Besides, WO_3 has a narrow operating window that does not exceed the oxidation potential of Ag, which allows reversible switching of the device. In contrast, if V_2O_5 was selected on the Ag based electrode, the oxidative bleaching of the electrochrome would lead to failure of the electrode and no response for the following switching.³⁶

1.2.3 Design for foldable electrochromic devices

The objective is to accomplish foldable electrochromic displays on nanopaper. Based on the nanopaper transfer technique that creates a conductive Ag nanowire network on nanopaper surface, the conductive network as well as the nanopaper is able to fold without obvious loss of conductivity. This transfer technique along with the foldable electrode serves as the foundation for the foldable display.

Unlike the inorganic electrochromic layer in stretchable electrochromics, it is less stringent for a special design of the electrochrome structure in foldable electrochromic devices due to the localized deformation at the folding crease only. A thin coating of WO_3 with the thickness controlled by deposition time should be able to form a functioning electrochromic layer as long as the coating remains a close contact with the underlying electrode that provides constant electrical current.

Although such a thin film configuration of the electrochrome could survive folding with reversible switching, the brittle inorganic layer would still undergo cracking. The effect of crack growth and therefore multi-crack formation would be detrimental for a high resolution display in the long run. The concept of small molecule electrochrome could be utilized. Such design obviates the physical constraints on the optical modulating layer so that it would be crack-free. Furthermore, the small molecule with the electrolyte can be incorporated into a solid state matrix and assembled into a transparent foldable solid state electrochromic device, which is one step closer to a practical futuristic electrochromic display which is fully foldable at the whole device level.

1.3 Dissertation Overview

Stretchable and foldable electrochromic display is an emerging field with great potential for futuristic electronics that needs urgent development. The thesis herein addresses the current issues that limit the performance of such deformable devices for feasible and practical applications. Efforts were made towards deformable electrode design and fabrication, electrochrome synthesis and device structure design for stretchable and foldable electrochromics.

Chapter 1 explains the importance of the current study with a brief description of the current progress in the field of deformable electrochromics. Problems that limit optical

modulation and challenges involved are identified. The objectives intended to achieve stretchable and foldable electrochromic devices and feasible approaches to realize the objectives are outlined.

Chapter 2 reviews the related techniques to achieve deformable electrochromics and the latest literature on stretchable and foldable electrochromic devices. The review starts from the state of art of the fabrication of stretchable electrodes and flexible transparent conductive electrodes. The comprehensive review provides instructive information for a proper design of deformable electrode suitable for electrochromic applications. Subsequently, flexible and bendable electrochromic devices are reviewed. The issues that prevent further bending to folding state are discussed and some of the research provides good suggestion on the electrochromes which might be possible for a good integration with deformable electrochromics. The reported works on stretchable and foldable electrochromics are reviewed in the end; problems that result in poor performance are analyzed. Approaches to improve the poor performance based on the analysis are suggested.

Chapter 3 explained in detail the optical switching mechanism for type I and type III electrochromic materials involved in the thesis. Switching kinetics with constructed models to simulate the dynamic process is summarized to help understand the real-time electrochemical redox reactions during color switching. The synthesis procedure as well as the mechanism is then described to gain understanding of the selected material and fabrication approaches. The working principles of characterization tools like Scanning Electron Microscopy (SEM), UV-vis (Ultraviolet-visible) spectrophotometer etc are also included in this chapter that serves as an instruction on how the data describing the electrochromic system is collected. Finally, the device fabrication procedures along with the schematics are presented for a good perception of the device configuration.

Chapter 4 presents our strategy for the realization of stretchable and wearable electrochromic displays. A highly conductive and stretchable elastomer by embedding Ag nanowires network into PDMS matrix is introduced. The stretchable conductor is able to

maintain a good conductivity up to 50%. Inorganic WO_3 islands from electrochemical deposition perfectly matched with the conductive network. The non-continuous functional layer was able to accommodate the strain and keep its functionality up to 50% tensile strain. The electrochromic performance of the stretchable device was studied at relaxed and strained conditions respectively to gain a good understanding of the device working process. Lastly, a fabricated stretchable electrochromic pixel display was integrated with fabric textile for wearable displays applications.

Chapter 5 described our strategy for the accomplishment of foldable electrochromic nanopaper display. A nanopaper transfer technique with the ability to transfer a versatile range of functional materials was established. Ag nanowires percolating network was successfully transferred to the nanopaper surface. An ultra-high figure of merit for this type of transparent conductor was observed. The nanopaper electrode was able to be folded till less than 10 μm radius with little loss of conductivity. When WO_3 thin coating was deposited, the electrochromic electrode was able to switch color and change its reflectance reversibly under voltage supply. When the electrochromic electrode was subject to folding, the display function can be well maintained. The performance at different folding cycles were recorded and analyzed to investigate the device foldability.

Chapter 6 presents the approach to realize a fully foldable transparent solid state electrochromic device. Cracks were found on the brittle WO_3 foldable device. To further improve the foldability and assemble a fully foldable device, small molecule electrochrome methyl viologen was adopted as the new electrochrome, it can be readily incorporated with the electrolyte into a solid state matrix. The matrix was constructed into a solid state network through hydrogen bond. The soft nature of the slime suffers no mechanical failure from the folding. The nanopaper transfer technique was utilized to fabricate a double layered Single Wall Carbon Nanotube (SWCNT) @Ag electrode, in which the SWCNT anchors and bridges the nanowires for a better conductivity and adhesion to the nanopaper substrate. A lateral planar device structure to avoid the oxidation of Ag counter electrode was configured. The finally assembled device is transparent and fully foldable. The electrochromic performance of such device was

studied as a function of different folding cycles. A good retention of the performance was carried through repeated folding. The foldable device was in the end mounted onto human hands for camouflage demonstration.

Chapter 7 gives a summary of the established techniques for the realization of stretchable and foldable electrochromic devices. Despite demonstration of the concept, existing problems and suggested methods to improve the device performance were discussed. Feasible approaches and device configuration for enhanced performance was incorporated in the future work.

1.4 Findings and Outcomes

This research led to several novel outcomes by:

1. Realizing a functioning stretchable and wearable electrochromic display device with large reflective optical modulation by creating high performance discrete WO_3 islands. The device was based on our established method for a fully embedded stretchable Ag nanowire electrode with a high conductivity that allows for the reversible electrochemical redox reaction with large contrast.
2. Establishing the nanopaper transfer technique for a versatile range of functional materials. Example materials like graphene nanosheet, MoS_2 nanosheet, SWCNT, ZnO nanoparticles have been demonstrated. Ag nanowire percolating network when transferred demonstrates a high quality with a high figure of merit for promising transparent conductor applications. Multi-layer transfer was also possible with SWCNT@Ag demonstrated as a hybrid electrode with enhanced conductivity and adhesion property.
3. Developing the foldable electrochromic nanopaper based on the established nanopaper transfer method and the foldable nanopaper electrode. A quantitative study of the electrochromic performance dependence on the folding cycle was carried out. Factors leading to performance degradation were also identified. To further enhance the foldable performance, a fully foldable solid state electrochromic device was achieved on the improved nanopaper electrode. The electrochrome was switched to redox small molecule to improve the mechanical compliance of the electrochromic

layer.

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Chapter 2

Literature Review

Deformable display, especially non-emissive electrochromic display with its low power consumption from the memory effect, high contrast, ability of conformation changes responding to external forces, represents one of the most promising electronic systems for futuristic display applications such as foldable smart phone, stretchable e-book, camouflage wearables etc. Conventional electrochromism is based on rigid ITO/glass which greatly limits its potential application range. Strategies for deformable electrodes and the active electrochrome structure need to be carefully designed to achieve electrochromic devices with great mechanical compliance. In this chapter, techniques to realize stretchable and foldable electrochromics, starting from electrode design to the final electrochromic device assembly are reviewed to understand the current progress and problems to resolve in this field.

2.1 Deformable electrodes

To realize a deformable electrochromic device, great emphasis needs to be given to the electrode design first since its electrical conduction integrity under deformation is indispensable for a constant supply of electrical current to the device. This requires the choice of suitable soft conducting materials or creation of deformable structures.

A review on current strategies for stretchable electrodes as well as flexible transparent electrodes is presented.

2.1.1 Stretchable electrodes

Stretchability is greatly desired for the next generation electronics due to its excellent mechanical compliance that enables device functionality at arbitrary shape which greatly enlarges the application range of electronics devices for sensors,¹⁻⁵ displays,⁶⁻⁸ energy storage etc.⁹⁻¹⁴

The strategies for fabricating stretchable electrodes can be classified by materials that stretch or structures that stretch as suggested by Rogers.¹⁵ The former usually refers to composite materials of intrinsic stretchability such as SWCNT network composite, 3D foam composite or metal nanoparticle filled composite. The latter usually refers to brittle materials with limited stretchability like graphene but after bulking to form out of plane waves that accommodate strains, they can be stretched without sacrificing much of their electronic properties.

A pioneering work involving SWCNT elastomer composite was achieved by dispersing SWCNT in ionic liquid 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMITFSI) followed by jet-milling to form a uniform dispersion gel, which was then mixed with a commercial fluorinated copolymer matrix as shown below (figure 2.1).⁶ The viscous polymer matrix can even be printed and dried to form the conductive elastomer. The resulted elastomer can maintain a stable conductivity of 9.7 S cm^{-1} up to 118% strain. Other similar works involving CNT composite electrodes for stretchable electronics have also been reported.¹⁶⁻¹⁹

When Cu nanowire was dispersed in water/ Polyvinyl Alcohol (PVA) solution followed by freeze drying to form an aerogel foam (figure 2.2), the as formed composite possesses a 3D porous structure that allows for deformation.²⁰ PDMS was then infiltrated in the

pore to stabilize the conductor. The foam with ample internal space between pores to accommodate deformation allows for the stretchability. The composite with an initial conductivity of 0.83 S cm^{-1} increases by 19.5% at 60% strain after the first loading cycle and then remains a stable conductivity within 60% strain in 1000 cycles.

Figure 2.1 a) The fabrication process for the conductive SWCNT elastomer; b) a magnified SEM image of the SWCNT elastomer; c) stretchable SWCNT patterns printed on PDMS. (Reprinted with permission from Reference 6. © 2009 Nature Publishing Group.)

Figure 2.2 a) The synthesis schematic for the Cu nanowire aerogel; b) conductivity

change of the composite with strain; c) cycling stability test of the composite conductivity. (Reprinted with permission from Reference 20. © 2014 American Chemical Society.)

Ag nanoparticle has also been applied as good filler in stretchable matrix for stretchable conductors,²¹ in which Ag nanoflowers are mixed uniformly in dimethylformamide (DMF) with polyurethane (PU) pellets dissolved. The mixed suspension was then extruded into DI water tank from a syringe pump to form the stretchable fiber. The stretchable fiber was then cured at 115 to 155 °C for 10 mins to sinter and coalesce the Ag nanoflowers. The composite fiber with an initial conductivity as high as 41245 S cm⁻¹ was reported, but after the first stretching to 120% strain to overcome a small degree of irreversible plastic deformation, the conductivity dropped to 4056 S cm⁻¹. The fibers drops in conductivity with increased strain by one order of magnitude up to 70% stain but after releasing the strain, the conductivity can be recovered and the conductivity measured at 0% strain could be maintained through 500 stretching cycles to different strains.

Figure 2.3 a) The setup for wet spinning Ag-Pu stretchable fiber; SEM images for the fiber conductor at b) low and c) high magnifications; d) Conductivity of the fiber at different tensile stain; e) conductivity of the recovered fiber at 0% at different stretching cycles after stretching to various maximum strains. (Reprinted with permission from Reference 21. © 2015 American Chemical Society.)

For the method of creating structures that stretch for stretchable conductors, the general practice is to pre-strain the substrate first followed by transferring the functional material or conductor. After releasing, the transferred materials will buckle. The buckled structure either forms out of plane waves or in-plane lateral waves that become effective against

straining by aligning to the tensile direction under stretching.

A typical example work was done by growing super-aligned CNT ribbon forest which was drawn to a Teflon film substrate.²² After sputtering metal nanoparticle to enhance conductivity, the CNT ribbons are transferred to a pre-strained (100%) substrate. Upon releasing the substrate, out of plane sinusoidal waves were achieved for stretching. The conductor with an initial resistance of 610 Ω increased by only 4.1% after the first straining to 100% and became stabilized in following stretching cycles.

Figure 2.4 a) The formed sinusoidal out of plane waves after buckling; b) resistance change of the conductor upon stretching. (Reprinted with permission from Reference 22. © 2012 John Wiley and Sons.)

For graphene, the stretchability can also be achieved through the pre-straining method. When chemical vapor deposition (CVD) grown few layer graphene was transferred to an isotropically pre-stretched (12%) PDMS substrate (figure 2.5 a), it gains stretchability after release. The conductor maintains a stable resistance up to 11% stretching. In comparison, for the graphene transferred to PDMS without pre-straining (inset on the left), the prepared conductor shows one magnitude of increase in resistance at 6% strain.²³

Similarly, few layer graphene has also been shown to be transferred to a VHB tape with unequal pre-stretching of 10% and 500% at the two planar axes. The as-formed bulked graphene shows a crumpled structure after the release (figure 2.5 b).²⁴ The crumpled graphene conductor can be stretched to 450% at the longer pre-stretched axis while maintaining the resistance without much change.

Figure 2.5 a) Resistance test of graphene on pre-stretched PDMS (inset on the left is for graphene transferred on flat PDMS, inset on the right shows the change in shape for graphene under stretching); (Reprinted with permission from Reference 23. © 2009 Nature Publishing Group.) b) Crumpled graphene on pre-stretched VHB tape; d) resistance test of the stretchable graphene conductor at different tensile strain. (Reprinted with permission from Reference 24. © 2013 Nature Publishing Group.)

As a short summary, the electrical properties (σ or R) at relaxed and strained state as well as the respective techniques to achieve the stretchability are tabulated below.

Table 2.1 summary of the reviewed stretchable electrodes and their properties

Material	Method	Initial electrical property	On-strain electrical property	Comparative Features
SWCNT ⁶	Polymer-composite	9.7 S cm^{-1}	Stable up to 118%	The conductive composite is intrinsically stretchable; Fabrication process is simple and straightforward; Good bonding between the elastomer and the conductive elements.
SWCNT ²⁵	Polymer-composite	57 S cm^{-1}	Stable up to 35%	
Cu aerogel ²⁰	Porous foam-PDMS	0.83 S cm^{-1}	19.5% increase in the first 60%; stabilized in the following cycles within 60% strain	
Ag nanoparticle ²¹	Filler blending	41245 S cm^{-1}	Reduced to 4056 after the first 120% pretraining and relax; In the following cycles, conductivity gradually reduce with strain with ~20 times reduction at 50%	
Cu nanowire ²⁶	PDMS composite	$8.6 \text{ } \Omega/\text{sq}$	$\sim 33 \text{ } \Omega/\text{sq}$ at 50% strain	

Super-aligned CNT ²²	Prestretched to 100% - release	610 Ω	4.1% increase in the first 100% strain; stabilized in the following 100% strain	Prestrain process is required to obtain stretchability; Able to maintain a stable electrical property up to the prestrained level; Limited adhesion between the conductive element and the elastomer.
MWCNT ²⁷	Stretch-release-buckle to form sinusoidal waves	211 Ω /sq	50% increase in the buckle forming first stretch at 40% strain; stabilized later within 40%	
Graphene ²³	Biaxial prestretch to 12% - release	200-300 Ω	Stable within 11% strain in either direction	
Graphene ²⁴	Biaxial prestretch to 10% and 500% respectively	~ 10 K Ω	< 2 times increase at 450% strain; relatively stable within 200% strain.	

2.1.2 Flexible transparent electrodes

Apart from the high mechanical compliance like stretchability, optical transparency is another important parameter required for numerous electronic applications. The reviewed strategies above are all related to stretchable conductors with low transparency. In this section, we are going to focus on techniques for the fabrication of high quality transparent conductors with good deforming ability like bending, folding and even stretching abilities.

Transparent conductive electrode represents one of the most demanding electronic components in various optoelectronic applications like touch panel,²⁸⁻³⁰ solar cell,³¹⁻³⁴ LED,³⁵⁻³⁷ and of course the focus of our study, electrochromic devices.³⁸⁻⁴⁰ High transparency and at the same time high conductivity are greatly appreciated but the two factors are always contradictory. Thus the choice of conductive materials and techniques adopted to reach their best possible performance are of great importance.

The conductivity of materials is determined by free carrier concentration multiplied by free carrier mobility while the absorption is also closely affected by the carrier concentration.⁴¹ A large carrier concentration is beneficial for a good conductivity but it may also absorb more of incident light.⁴² A good conductor bears a nice balance of the carrier concentration and mobility. Currently, transparent conducting oxide, carbon based materials like CNT and graphene, metallic wires and grids shows great potential and a good transparent conductor performance. With the ever growing stringent requirements

for futuristic consumer electronics, deformation ability such as bending, folding and even stretchability becomes necessary to cater for the needs for large conformation change.¹⁵ The current TCE market is dominated by ITO for its high transparency and good conductivity. However, the intrinsic brittleness of inorganic materials makes it susceptible to deformation and incurs the loss of conductivity easily.^{43,44} The development for high performance ITO alternatives with high mechanical compliance is thus necessary and becoming an irresistible trend for the next generation electronics.

The use of carbon based materials like CNT and graphene for TCE has long been attracting immense attention due to their abundant source, stability and appealing intrinsic electrical properties like low carrier concentration and high mobility.⁴⁵

Wu⁴⁶ demonstrated SWCNT films with good performance of 30 Ω/sq , 83%. SWCNT was dispersed by Triton X-100 surfactant followed by filtration on the filter membrane. After washing away the surfactant and dissolving the membrane away, SWCNT can be collected on the desired substrate. The SWCNT can be flexible on a Mylar sheet (figure 2.6). Similarly, SWCNT dispersed by SDS surfactant followed by spray coating on PET could also produce TCE with good performance of 70 Ω/sq , 80% after acid treatment.⁴⁷

Figure 2.6 a) digital photos of collected SWCNT films of 50 nm and 150 nm thickness respectively; b) SWCNT TCE of diameter of 10 cm; c) the TCE can be flexed on a Mylar sheet; d) the Atomic Force Microscopy (AFM) surface image of a 150 nm thick SWCNT film; (Reprinted with permission from Reference 46. © 2004 The American Association for the Advancement of Science.) e) The opto-electrical performance of spray coated SWCNT film before and after acid treatment. (Reprinted with permission from Reference 47. © 2007 American Chemical Society.)

Apart from the wet solution process for SWCNT TCE fabrication, techniques like floating catalyst chemical vapor deposition or fixed catalyst chemical vapor deposition have been developed.⁴⁵ SWCNT from the floating method can be collected on a sacrificial/intermediate substrate placed at the terminal of the reactor. The SWCNT film can then be transferred to the desired substrate like glass or PET. Performance of 50 Ω/sq , 70%⁴⁸ and 84 Ω/sq , 90%⁴⁹ have been reported through this method. On the other hand, the fixed catalyst method usually produces superaligned CNT in the reactor, which can be drawn to the target substrate through roll-to-roll method (figure 2.7).⁵⁰ Performance for such TCE is reported to be 1 k Ω/sq , 80%. The large resistance comes from the relatively large gap between the aligned CNT bundles, which through post treatment like laser trimming and metal deposition can be greatly reduced. The drawn film is flexible due to the softness of thin nanotubes and the interstitial gap between the CNT bundles can make them even stretchable along the direction perpendicular to the drawn direction.

Figure 2.7 a) Superaligned CNT drawn to form a TCE film; b) SEM top view image of the film; c) schematic for the roll to roll process for continuous fabrication of TCE films; d) flexible TCE as the top electrode for touch panel application. (Reprinted with permission from Reference 50. © 2010 John Wiley and Sons.)

Graphene has also been actively studied for TCE application. With wet chemical processing method, graphite was exfoliated with surfactant sodium cholate (SC) in

water.⁵¹ After density gradient ultracentrifugation treatment, graphene solution with an average thickness of around 1.1 nm is obtained. The solution was filtered through mixed ester cellulose membrane which was later dissolved to collect the graphene TCE layer. (figure 2.8) The obtained TCE demonstrates a performance of 2000 Ω/sq , 75%. The density gradient ultracentrifugation method is beneficial for a uniform distribution of the graphene thickness which is favorable for a good TCE performance. Without this, a degraded performance of 4000 Ω/sq , 78% transparency is demonstrated.⁵² Besides, the choice of the surfactant would also phenomenally affect the electro-optical property. When graphene was exfoliated in sodium dodecyl benzene sulfonate (SDBS), the thus obtained TCE film gives a performance of only 22.5 k Ω/sq , 62%.⁵³

Figure 2.8 a) The schematic for the exfoliation of graphite with surfactant SC; b) obtained graphene suspension; c) graphene TCE film; d) the TCE performance of graphene TCE film fabricated using exfoliated graphene with different thickness. (Reprinted with permission from Reference 51. © 2009 American Chemical Society.)

Different from the solution processing method, graphene grown from CVD method has a good structural integrity with monolayer or few layers on a relatively large scale. The less structural defect is more beneficial for improved TCE performance. Monolayer graphene grown on Cu foil from CVD method was transferred to glass substrate assisted by poly(methyl methacrylate) (PMMA). Multiple layers can be achieved through layer by layer transferring of the monolayer graphene. TCE performance for 4 layer graphene and 8 layer graphene has been reported to be 200 Ω/sq , 90%⁵⁴ and 300 Ω/sq , 80%⁵⁵ by different researchers. Growth of few layers graphene followed by PMMA transferring

produces TCE of 100 Ω/sq , 90%.⁵⁶ The use of PMMA for graphene transfer is advantageous for keeping the integrity of graphene during transferring as the supporting layer; however PMMA is difficult to be fully dissolved. The residue is not only detrimental for the electrical property but also increases the surface roughness with undissolved PMMA particles which generates cracks and defects when new graphene layer is introduced above.⁴⁵

To resolve this problem and avoid the dissolving of organic polymer supporting layer, Bae³⁰ developed a roll to roll transfer method involving a commercial thermal release tape. The copper foil with CVD monolayer graphene was first attached to the tape and rolled through the etching tank, after which the graphene would be transferred to the tape. Then the tape passed through another roller and was pressed against the target substrate. The transfer was facilitated at an elevated temperature to release the adhesive on the tape. Graphene was then transferred to the target substrate for use as the TCE. (Figure 2.9) The TCE for a 4 layered graphene film shows 50 Ω/sq , 90.1%, the performance was further improved through Nitric acid doping with the final product showing 30 Ω/sq , 90%, which is the best reported data so far for transferred graphene TCE. The TCE on PET shows good flexibility and maintenance of the conductivity and was applied for touch panel application.

Figure 2.9 a) The schematic for the roll to roll transfer of CVD monolayer graphene; b) TCE performance of the 4 layered graphene film; c) photograph of the graphene TCE applied for touch panel; d) flexibility test of the TCE under bending. (Reprinted with

permission from Reference 30. © 2010 Nature Publishing Group.)

CNT and graphene based materials with their relatively low carrier concentration and high mobility are ideal for high performance TCE.⁴¹ However, the high mobility for graphene and CNT is only anisotropic along the graphene plane or CNT axis.⁴⁵ The interlayer conductivity can be 3000 times lower than the in-plane conductivity in graphite.⁵⁷ When made into a film, the effective mobility and thus conductivity would be much smaller due to the existence of defects and interconnection between the conducting carbon materials. That's why for solution processed graphene where the connection between graphene flakes determines the electrical pathway, the electro-optical performance is way worse than that of the CVD graphene TCE although it is also difficult for CVD graphene to reach their intrinsic electrical performance in large scale without defects.

As a conclusion, besides their attractive electrical property, it is currently still very difficult to produce high quality carbon based TCEs ($< 10 \text{ } \Omega/\text{sq}$, $> 90\%$) due to the defects and anisotropic property. CVD graphene represents the most promising TCE with the best reported electro-optical performance getting close to the high quality standard. Although it is not the first choice for some applications where conductivity is greatly preferred like large area displays, it can be quite competent for touch panel applications where a lower threshold for conductivity is required ($\sim 500 \text{ } \Omega/\text{sq}$, $\sim 85\%$).⁵⁰

Metal based TCEs on the other hand are receiving great popularity for their excellent performance and facile fabrication process. The most successful candidates are metal nanowires, and metal grids. Metal like Ag has a very high carrier concentration, about 2 orders magnitude of graphene and 1 order magnitude of semiconductor TCEs.^{41, 45} This intrinsic electrical property largely determines the good conductivity of Ag. At the same time, percolating mesh or network of Ag with void space in between helps maintain a high level of transparency.

Ag grid has been demonstrated to be a good candidate for TCE. Solution processible method involving the replication of stainless steel mesh with Ag nanoparticles produced a transparent grid. The conductivity of the grid is imparted by chemical sintering of the nanoparticle to induce coalescence. (Figure 2.10 a-c) The Ag grid can be directly formed on the target substrate like PET, which makes the a flexible TCE of $9 \text{ } \Omega/\text{sq}$, 75% .⁵⁸

The quality of the grid can be enhanced without the interference from polymer stabilizer by combining lithography and thermal evaporation. Ag grids network of different pitch and line width were developed and studied as the parameters that affect the TCE performance (figure 2.10 d-f). A good TCE performance of $18 \Omega/\text{sq}$, 90% was achieved.⁵⁹ Currently, the best commercial Ag grid comes from NanoWebTM of ROLITH with around $3 \Omega/\text{sq}$, 95% for submicron Ag lines. This represents a very competent substitute for ITO.

Figure 2.10 a) Self-assembled grid that replicates the stainless steel template; b) SEM morphology of the Ag nanoparticles after chemical sintering; c) flexible Ag grids on PET; (Reprinted with permission from Reference 58. © 2011 Royal Society of Chemistry.) d) Ag grids fabricated from lithography; e) sheet resistance as a function of pitch and wire width; f) TCE performance of the Ag grids of different pitches. (Reprinted with permission from Reference 59. © 2012 American Chemical Society.)

Metallic wire based percolating networks represents another promising type of high performance TCE. Ag nanowires have been widely adopted for TCE application. The TCE film can just easily be fabricated through roll coating. Hu⁶⁰ studied Ag NW TCE by roll coating Ag nanowires on PET with a performance of $8 \Omega/\text{sq}$, 80%. The TCE has a good flexibility against bending while in comparison brittle ITO/PET sharply increased its resistance. The resistance of single nanowire resistance as well as nanowire junction resistance is studied by thermal evaporating contacting pad on crossed Ag nanowires. The resistance of a single nanowire is only a few hundred ohms while the junction resistance can be more than $1 \text{ G}\Omega$. This is direct evidence that inter-wire junction resistance is the limiting factor for a good conductivity. A galvanic displacement method by immersing

Ag nanowires into HAuCl_4 to obtain a thin Au layer that connects adjacent nanowires is proposed to reduce junction resistance. Through this treatment, a TCE film can go down in sheet resistance from thousands ohms/sq range to tens ohms/sq range.

Figure 2.11 a) Ag nanowire ink; b) the roll coating set-up; c) bending test for Ag nanowires and ITO TCE; d) testing of single wire resistance and junction resistance; e) galvanic displacement of Au to reduce junction resistance. (Reprinted with permission from Reference 60. © 2010 American Chemical Society.)

Based on this observation that junction resistance determines the overall conductivity, some efforts have been taken for improved TCE performance. A novel and facile graphene oxide (GO) soldering method was suggested.³⁶ Ag nanowires were bar-coated on glass, followed by immersing the electrode in GO solution. (Figure 2.12) Notably, due to electrostatic interaction, GO was observed to wrap around the junction between Ag nanowires. Sheet resistance of the resulting TCE continues to decrease with prolonged immersion time in GO solution. The quality of GO soldered TCE can be comparable to high temperature annealed Ag nanowire TCE with a reported performance of 14 ohms/sq, 88%. The soldered Ag nanowire on PET shows a great flexibility with constant resistance under repeated bending radius of 4 mm for 12000 cycles. By embedding the soldered Ag nanowires into polyurethane acrylate (PUA) elastomers, the advanced structure stability even allows it to be repeatedly stretched while keeping a good retention of the original conductivity after the release.

Figure 2.12 a) The fabrication scheme for GO soldered Ag NW. b) SEM image of the GO wrapping around Ag nanowire junctions; c) bending test of the TCE at a radius of 4mm; d) Resistance of the stretchable electrode as a function of tensile strain. (Reprinted with permission from Reference 36. © 2014 American Chemical Society.)

Another method to alleviate the effect of junction resistance on the TCE conductivity is to increase the length of metallic wires since the total number of metallic wires needed to maintain the same conductivity could be smaller based on the percolation theory.^{61, 62} Fewer numbers of wires equals to fewer junctions, which would in turn lead to a higher conductivity. A novel method involving electrospun fiber network as the template was discovered.⁴⁴ The template was then subject to metal deposition through evaporation. After transferring the polymer scaffold together with the deposited metal, solvent was used to dissolve the template leaving the metallic wire on the target substrate. (Figure 2.13) Since evaporation is a directional depositing method, nanotroughs instead of wires were obtained. The nanotrough has an average dimension of 400 nm width, 1 mm length. The resulted large dimension of the metallic nanotrough is also reported with good single wire conductivity close to its bulk form. The resulted TCE performance especially for Cu nanotrough TCE delivers a state of art electro-optical performance of 2 Ω/sq , 90%. The TCE film can be transferred to a variety of surfaces like paper, textile and curved bottle by dissolving away the supporting template. The conductive paper can keep the conductivity through crumpling. After transferring the nanotrough to PDMS, the conductor can even be stretchable with 40% increase in resistance at 50% tensile strain.

Figure 2.13 a) the schematic for nanotrough fabrication; b) performance of the nanotrough TCE composed of different metals; c) the nanotrough network can be transferred to various substrates like glass, plastic, paper, textile and bottle; d) foldability of the nanotrough network electrode on newspaper. (Reprinted with permission from Reference 44. © 2013 Nature Publishing Group.)

To summarize, the electro-optical properties of the reviewed TCEs are listed in table 2.2.

Table 2.2 Summary for the discussed TCEs obtained from different techniques

Material	Technique	Performance	Deformation ability	Figure of Merit*
ITO ^{36, 63}	Sputtering	12 Ω /sq, 88%	Poor flexibility, break at mild bending	237.9
SWCNT ⁴⁶	Dispersed by Triton X-100 surfactant followed by filtration	70 Ω /sq, 80%	Flexible on Mylar sheet	22.8
SWCNT ⁴⁹	Floating catalyst chemical vapor deposition	84 Ω /sq, 90%	Flexible on PET	41.5
Super-aligned CNT ⁵⁰	Fixed catalyst chemical vapor deposition	1 K Ω /sq, 80%	Rolled onto PET for flexible touch panel	1.6

			application; stretchable in the direction vertical to the drawing direction	
Graphene ⁵¹	Exfoliated to monolayer in sodium cholate surfactant	7 K Ω /sq, 75%	Collected on quartz	0.17
Graphene ⁵⁴	CVD growth followed by layer- by- layer transfer	200 Ω /sq, 90%	Transferred on quartz	17.4
Graphene ²³	Few layered graphene transferred by PDMS contacting	280 Ω /sq, ~85%	Flexible on PET, stretchable on PDMS	7.9
Graphene ³⁰	Thermal release tape transfer followed by acid treatment	30 Ω /sq, 90%	Flexible touch panel demonstrated	116.1
Ag ⁵⁸	Ag nanoparticles fused into grids	9 Ω /sq, 75%	Flexible on PET	135.4
Ag ⁵⁹	Thermal evaporated Ag film patterned into grids by lithography	18 Ω /sq, 90%	Fabricate on glass	193.6
Ag ⁶⁰	Ag nanowires rolled coated	8 Ω /sq, 80%	Flexible on PET	199.6
Ag ³⁶	Ag nanowires with reduced junction resistance by GO wrapping	14 Ω /sq, 88%	Flexible on PET, stretchable on PUA elastomer	204.0
Cu ⁴⁴	Cu nanotrough templated by electrospun polymer scaffold	2 Ω /sq, 90%	Flexible on PET, foldable on newspaper, stretchable on PDMS	1742.4

*Figure of Merit is based on the ratio of DC conductivity to optical conductivity σ_{dc}/σ_{op} , which could be obtained from $T = (1 + \frac{188.5}{Rs} \frac{\sigma_{op}}{\sigma_{dc}})^{-2}$.

2.1.3 Nanopaper for novel transparent electronics

Nanocellulose along with the derived nanopaper is recently emerging as a new type of transparent substrates with excellent optical transparency, outstanding mechanical strength and stable thermal properties. These combined advantages make it a competent substrate for foldable electronics that is difficult for conventional plastics.

Nanocellulose as a ubiquitous natural resource could be obtained from natural cotton, Kraft pulps and many other cellulose-containing biomasses.^{64, 65} Taking wood from trees as an example, the wood is composed of a hierarchical structure that breaks down from wood bulk to large cellulose fibers, to microfibrils and the elementary fibril as shown in figure 2.14.⁶⁶ For conventional cellulose fibers, the composing cellulose is in the range of tens of microns^{40, 67} which could be further liberated into cellulose nanofibrils with the diameter of a few tens nanometer and length in micrometers through methods like physical liberation,⁶⁸ acid hydrolysis,⁶⁹ enzyme disintegration⁷⁰ or surface charge induced separation etc.⁶⁴

Figure 2.14 the schematic showing the hierarchical structure of cellulose composed trees. (Reprinted with permission from Reference 66. © 2013 American Chemical Society.)

The downsizing to nanoscale of the cellulose fibrils brings advantages in manifold aspects. To start with, a smaller diameter compared to the incident light wavelength is beneficial for reduced light scattering which makes the cellulose nanofibrils “invisible” to the incident light and leads to the high transparency of its assembled film. Yano⁷¹ studies this size effect through impregnation of nanocellulose matrix with various transparent resins. It shows that the cured composite only suffers little transparency compared to the

pristine resin even under a high nanocellulose content of 60-70 wt% (figure 2.15 a, b). The suppressed scattering with the reduced size could be expected from the radiative-transfer equation of Chandrasekhar⁷² in the absence of considering light absorption, which is expressed by $T = 1 / (1 + 0.75\rho\sigma_{\text{set}}h)$ where ρ is the density, σ_{set} is the scattering cross section of the unit scattering object and h is the thickness of a randomly stacked slab. It is obvious that the small dimensional contributes to the reduced scattering, especially the backward scattering that leads to the enhanced transparency.⁷³

The reduced size of the nanofibrils also leads to densely packed structure of the nanopaper accompanying the strong interfibrillar cohesion due to the large amount of hydrogen bond formed between fibers during drying. Due to the mismatch in refractive index between cellulose (around 1.5) and air (1),⁶⁷ the travelling light at the interface between them would severely scatter and cause the opaque texture of paper. The densely packed nanopaper structure eliminates the air cavities as the internal scattering center and the further suppressed light scattering leads to a high transmittance.⁷⁴

However, the haze might exist for the nanopaper and it is found that surface scattering plays an important role determining the clarity of nanopaper.⁷⁴ If the surface could be polished smooth, nanopaper could turn from translucent to transparent as shown in figure 2.15 c, d.

Figure 2.15 a) and b) Transparency obtained by resin impregnation of bacterial cellulose matrix; (Reprinted with permission from Reference 71. © 2005 John Wiley and Sons.)

c) and d) transparency achieved by surface polishing of the nanopaper. (Reprinted with permission from Reference 74. © 2009 John Wiley and Sons.)

Cellulose nanofibrils have a potentially extremely high mechanical strength for a single fiber with Young's modulus of 138 GPa and tensile strength of 2 GPa,^{75, 76} which could even compete with Kevlar, a bullet-proof high strength fiber material. For randomly distributed nanopaper, the strength is lower than the theoretical value but a much higher mechanical strength is observed compared to the regular paper due to the small dimension of the nanofibril with intense packing and correspondingly a higher interfibrillar bonding strength.⁶⁷ The fibrous structure of the assembled nanopaper also shows an excellent ability for the alleviation of stress and thus foldability is possible for this novel substrate.^{77, 78} Furthermore, an outstanding stability that tolerates processability at 200°C and a low coefficient of thermal expansion (CTE) of 5-10 ppm K⁻¹ was found on the nanopaper substrate,⁷⁹ which is much lower than conventional plastics of 20-100 ppmK⁻¹.⁷⁷ The generally low tolerance for elevated temperature and the high CTE greatly limits the process techniques and might cause functional material failure during processing under heat due to the large mismatch of the expansion coefficient. For example, the acrylic resin sheet expands by 3.1% when temperature rises from 20 °C to 150 °C whereas for bacterial cellulose the expansion is only 0.05%.⁷⁸ Besides, the affinity to water and large surface energy ensures a good wetting condition on nanopaper and it is also advantageous for printing applications.⁷⁷ Nanocellulose is thus seen amenable to a broad range of processing conditions that could be well exploited for large scale printing or roll-to-roll purpose in place of the traditional inconvenient and slow large batch processing as seen in glass based display industry.

As a short summary, the transparency as well as the good mechanical strength with the thermal stability makes nanopaper a great potential candidate for transparent flexible and even foldable electronics. To develop it into electrodes, some tentative exploration has been seen in approaches like sputtering ITO or Meyer Rod coating Ag nanowires or CNT onto the nanopaper surface to induce conductivity. Electro-optical performance of 12 Ω/sq, 65% for ITO, 200 Ω/sq, 60% for CNT and 25 Ω/sq 78% has been reported (figure

2.16 a,b).⁷³ Depending on the nanopaper substrate and the ink formulation used for the rod coating, SWCNT on nanopaper with $200 \Omega/\text{sq}$, 82% was reported elsewhere.³⁵ Composites of nanocellulose and SWCNT with a low transparency and conductivity of 3.23 S/cm was reported for a 10 wt% SWCNT-Nanopaper (figure 2.17 c,d).⁸⁰ The current approaches for realization of nanopaper based TCE is not very satisfactory with poor electro-optical performance reported. The methods need to be renovated for enhanced TCE quality to be suitable for electronic applications with acceptable performance. Furthermore, the currently reported exploring work on the flexibility of nanopaper based electronics like nanopaper LED,³⁵ nanopaper solar cell⁷³ and nanopaper transistor^{77, 79} etc. are still based on flat state or mild bending to a radius of a few millimeters which is far below the folding capability of the fibrous nanopaper with great mechanical compliance. The foldability of the nanopaper as well as the electrode needs to be fully leveraged and systematically studied for electronic devices to achieve low ultra-low folding radius for deformable applications.

Figure 2.16 the digital photo of a) an ITO sputtered nanopaper TCE and b) the spectra of nanopaper TCEs coated by Ag nanowire and CNT; (Reprinted with permission from Reference 73. © 2013 Royal Society of Chemistry.) c) The digital photograph of a

SWCNT-nanopaper composite of 10 wt% SWCNT; function of the composite conductivity on SWCNT content. (Reprinted with permission from Reference 80. © 2014 American Chemical Society.)

2.2 Deformable electrochromic displays

Electrochromic materials can be switched reversibly in its optical absorption property through applied current or voltage that induces band structure change.⁸¹ Usually a redox active element is necessary to facilitate the non-emissive change of optical modulation. Electrochromics has currently been widely adopted in applications like smart window,⁸²⁻⁸⁴ paper-like display,⁸⁵⁻⁸⁷ anti-reflection coating etc.⁸⁸⁻⁹⁰

With the booming growth of deformable consumer electronics and increasing demand for flexibility of the next generation electronics, electrochromics is now being actively developed to cater for such needs. Electrochromic display device, with low cost and low power consumption⁹¹ is believed to be quite promising for futuristic display applications. Conventional EC device is based on rigid ITO/glass, which is not compatible with deformable applications. For a deformable EC device, both the conductive substrate and the active electrochrome need to be designed for a proper performance. Some research has shown results that realized flexible or bendable electrochromic devices based on electrode like ITO/PET, graphene/PET, Ag/PET. These electrodes offer a certain degree of flexibility, or more specifically bendability. However, further bending to high bending angle (or equally small bending radius) to reach folding state is not possible with the current electrode configuration, either due to the flexibility limit for the conducting element or the plastic substrate itself, not to mention stretchability that requires even more mechanical compliance.

We first take a look at the progress of flexible or bendable EC device before moving on to more deformable EC systems.

2.2.1 Flexible and bendable electrochromics

As mentioned earlier, the major demonstrations of bendable electrochromics are based on conducting electrodes on PET. The choice of the electrochrome on the other hand can be quite versatile as long as it is thin with small internal stress during bending, ranging from nanoparticle thin film, 2D thin sheet layer, polymer thin film or small molecules etc.

Ultrathin 2D $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ nanosheet with an average thickness of around 1.4 nm was synthesized from exfoliation of tungstic acid in dodecylamine.⁹² After deposition of the nanosheet onto ITO/PET as the working electrode with another ITO/PET as the counter, liquid electrolyte was injected in between to close the circuit. The assembled device demonstrates a good contrast of 48% at 798 nm wavelength driven between -3 volt to 3 volt. The device can be colored in 5.1 s and bleached in 13.4 s. When slightly bent and cycled for 400 times, the EC performance is non-degrading and almost the same as the device tested flat. (Figure 2.14)

Figure 2.17 a) Transmission Electron Microscopy (TEM) image of the thin $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ sheet; b) the assembled electrochromic device structure; c) contrast testing; d) flexibility demonstration of the device testing in flat and bent form. (Reprinted with permission from Reference 92. © 2013 Nature Publishing Group.)

PproDOT-Me₂ was reported to be polymerized and grown onto ITO/PET substrate.⁹³ A polymer gel electrolyte consisting of PEGDMA and PEGMA with LiTRIF as the intercalating salt and PC as the plasticizer was mixed with photo-initiator and cured to gain some mechanical strength. Through adjusting the ratio between PEGDMA and PEGMA, the optimized gel electrolyte has a good flexibility to 3 mm bending curvature

that exceed the bending limit of the commercial ITO/PET substrate. The counter electrode, ITO/PET sandwiched the electrolyte and working electrode. The assembled device delivers a high contrast of 53% and was shown to keep a working function under bending.

A very interesting method involves the use of small molecule as the electrochrome.⁹⁴ The uniqueness of this method lies in that no specific thin film has to be deposited and thus there is no concern for mechanical failure. One representative work dissolved methyl viologen as the electrochrome in water and graphene quantum dot as the electrolyte. PVA was dissolved to increase the viscosity of the solution and the electrochromic gel was sandwiched between two ITO/PET substrates. The work reports a special combination of viologen and graphene quantum dot in which the quantum dot act as the electrolyte like KCl (figure 2.15) during viologen oxidation and reduction. The assembled device shows a working condition on-bend. However, the contrast drops from around 50% in flat condition to 15% when bent and the device suffers from performance degradation after running for 3000 s.

Figure 2.18 a) Schematic showing the device structure; b) CV comparison for viologen-KCl system and viologen-graphene quantum dot system; c) the device maintains function when it is bent; d) the transmittance switching of the bent device when driven between -2.8 V and 0 V. (Reprinted with permission from Reference 94. © 2014 John Wiley and

Sons.)

Since the flexibility of the ITO is very poor, some demonstrations of flexible EC devices have been centered on substitutes like Ag⁹⁵⁻⁹⁷ and graphene^{98, 99}. Both substitutes are flexible and good candidates to replace ITO. However, Ag is vulnerable to oxidation which would result in loss of conductivity and subsequently failure of the device, thus compatible electrochrome with low driving potential (some conducting polymer and WO₃) as well as a choice of stable counter electrode like ITO or noble metal needs to be carefully considered.^{95, 96} Cai³⁹ demonstrated WO₃ nanoparticle electrochemically deposited onto Ag grid/ poly(3,4-ethylenedioxythiophene) (PEDOT) electrode on PET. A large contrast of 81.9% at 633 nm is achieved. The electrochromic electrode sustains more than 90% performance through 1200 bending cycles to a radius of 20 mm.

Graphene, although more stable, suffers from low conductivity and thus very poor modulation performance. CVD graphene transferred to PET with a sheet resistance of 2-5 kΩ/sq was adopted as an electrode to drive the coloration of polynorbornene.¹⁰⁰ Compared to ITO/PET in the electrochromic performance, the operating voltage to drive the graphene electrode is almost doubled than ITO electrode with the redox current much smaller than on the ITO electrode. The switching time is not mentioned but could be expected to be very long. Similarly, 3 layered CVD graphene transferred to PET with a sheet resistance around 300 Ω/sq was reported as the electrode.⁹⁸ WO₃ nanoparticle film with a thickness of 500 nm was sputtered onto the working electrode as the electrochromic layer with an optical modulation of 31.2%. In comparison, when only 1 layer of graphene with sheet resistance of around 500 Ω/sq was used as a control sample, the resulted contrast was only 5.7%. A full device was assembled with the counter electrode as 3 layered graphene covered by sputtered NiO, the device was shown to be functioning under mild bending. Switching time test and long term cycling were not performed.

Instead of using graphene as the electrode to conduct current, graphene itself has also been exploited as an electrochromic material.⁹⁹ It is found that during charging of graphene, the injected electron alters the Fermi level and due to Pauli blocking that suppresses inter-band optical transition, the transparency of graphene could be enhanced through this band structure engineering.¹⁰¹ Multiple layer graphene grown on nickel and

subsequently transferred to PVC substrate was used symmetrically as both the working and counter electrode. Ionic liquid [DEME][TFSI] was chosen as the electrolyte. Parameters such as operating voltage and graphene layer numbers were studied that affected the device optical modulation. It was found that a high modulation of 55% at 850 nm for 80 layered graphene could be achieved when driven at 5 V. The charging process takes 3.5s while the discharging takes around 0.25s to complete. The device can be patterned into pixel display and bent to a radius of 1cm whiling keeping its functionality.

Figure 2.19 a) Digital photos for multiple layered graphene that changes optical modulation at a driven voltage of 5 V; b) Dependence of transmittance of the EC device on graphene layer number and the driven voltage; c) the switching rate of the device; d) pixel display of the graphene based EC device. (Reprinted with permission from Reference 99. © 2014 Nature Publishing Group.)

2.2.2 Stretchable and foldable electrochromics

Deformable electrochromic devices with the ability to be stretched or folded are expected to be highly demanded for the next generation display electronics for wearable display,

camouflage, anti-counterfeiting and fashion applications. The realization of deformable electrochromic devices requires deformable electrodes and compatible electrochromes. Compared to flexible EC devices, stretchable and foldable electrochromics has been rarely developed with acceptable performance.

As for stretchable e-textile, Sotzing et al.¹⁰² early reported a facile strategy for the fabrication of electrochromic spandex. The stretchable substrate was immersed in poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) solution to form the conductive electrode. The as prepared electrode has a conductivity of only 0.1 S/cm. A thin electrochromic film was spray coated onto the electrode. The device structure was illustrated in figure 2.17 with PEDOT:PSS as both the working and counter electrode. The fabric electrode shows a change in color from brown to green under supplied voltage and when the fabric electrode instead of the whole device was stretched to 20%, it is still able to function. A control sample was fabricated on stainless steel with a conductivity of 9800 S/cm. The device shows a fast switching in 318 ms while the fabric device was much slower with a switching time 14.53 s. Since the conductivity is very poor for the fabric electrode, the optical modulation was very faint and not quantitatively measured. Besides, the loss of stretchability and correspondingly increase of fabric electrode resistance was found only after a few stretching cycles,¹⁰³ a gradual degradation of performance was expected. Furthermore, since PEDOT:PSS is also electrochemically active, when used as the electrode its resistance might not be stable and experience a large increase when reduced/de-doped. This imposes a serious concern on the stability of the fabric device.

Figure 2.20 a) The schematics for the electrochromic fabric device structure; b) digital

photographs for the PEDOT:PSS fabric electrode and the color change of the assembled device; c) the fabric EC electrode stretched for 20% showing a working condition. (Reprinted with permission from Reference 103. © 2010 American Chemical Society.)

Last year, Bao and coworkers¹⁰⁴ developed a chameleon inspired e-skin that is able to change color by applying pressure to the device. The e-skin is actually composed of an electrochromic device and a pressure sensor coupled with an external circuit to regulate the applied voltage. The electrochrome is a stretchable conjugated polymer, P3HT spin-coated onto SWCNT/PDMS electrode. The SWCNT coated electrode was adopted for both working and counter electrode with a sheet resistance of around 2 k Ω /sq. The commercial poly(3-hexylthiophene-2,5-diyl) (P3HT) switches from a neutral red color to an oxidized blue color. The device was able to work at 20% strain with a small sacrifice of the contrast and increase of the switching time. When the device was connected with the tactile sensor, it is able to switch color gradually with increased input pressure. The work done represents the state of art development for electrochromic wearables. There are still some problems involved in this work though. Low conductivity of the electrode often results in enlarged operating window to drive optical modulation and observed small redox current due to the small driving over-potential.^{98, 100} SWCNT electrode of sheet resistance of 2 k Ω /sq is too high and not quite suitable for electrochromic switching. As can be seen from figure 2.18 a and b, the device modulation (+1V/-1V) in absorption is much inferior to the electrode performance which indicates only a small fraction of electrochemical redox reaction has occurred. Besides, when a small pressure was applied (which means a small oxidative over-potential), the color switching was very faint. Only when a large pressure of over 200 kPa was applied can we observe the color change more phenomenally. But this point refers to a much larger potential than the indicated 1 V to drive the oxidative reaction. Such a large requisite potential for perceptible modulation is also due to the low electrode conductivity and the large working window might lead to electrolyte degradation and poor device stability which was not studied.

Figure 2.21 a) Absorption spectra of P3HT film at oxidation and reduction state; b) the switching of the electrochromic device at 0% between +1 V/-1 V; c) the switching of the device at 20% strain; d) demonstration of the color switching of the electrochromic device controlled by applied pressure. (Reprinted with permission from Reference 104. © 2015 Nature Publishing Group.)

Similarly, foldable electrochromic devices are also scarcely developed due to the lack of development of foldable electrode that maintains conductivity through extreme bending. Correspondingly, compatible electrochrome and the electrolyte also need to be carefully handled. Apart from our pioneer work for the foldable electrochromic nanopaper,⁴⁰ Han⁴³ reported the use of ultrathin PET of only 1.8 μm thick as the substrate for foldable electrochromic devices. The electrode is sputtered with ITO of 100 nm. Due to the intrinsic brittleness of ITO, the substrate needs to be ultrathin so as to reduce the tensile strain ITO suffers during folding. The study finds that the substrate thickness is critical to determine the foldability of the ITO layer. If the plastic substrate exceeds 15 μm and is folded to a radius of 350 μm , ITO would break and result in loss of conductivity. Sputtered WO_3 nanoparticle of 500 nm thickness was adopted as the electrochrome. The subsequently assembled device survived two folding cycles without loss of optical contrast. Since the substrate is too thin and loses mechanical strength due to low Young modulus, it cannot be handled without a backing. The thin PET was stuck to some backing support leaving the intended crease area free, thus the whole device is not freely

foldable. (Figure 2.19) Besides, the intrinsic brittleness of ITO restricts the device foldability from reaching a lower folding radius.

Figure 2.22 a) schematic of the foldable EC device; b) photographs of the patterned EC device that maintains the working function through folding. (Reprinted with permission from Reference 43. © 2015 John Wiley and Sons.)

A table summarizing the performance of flexible and deformable electrochromic devices as well their distinctive highlighted deformation ability is shown in table 2.3.

Table 2.3 Summary for flexible and deformable electrochromic devices

Material	Electrode	Key Performance	Comparative Deformation Ability
WO_3^{92}	ITO/PET	$\Delta T=48\%$	Functioning while slightly bent
PproDOT-Me ₂ ⁹³	ITO/PET	$\Delta T= 53\%$	Functioning under 3 mm bending radius
Viologen ⁹⁴	ITO/PET	$\Delta T=50\%$	On mild bending, device functioning with $\Delta T=15\%$
WO_3^{39}	Ag/Pedot/PET	$\Delta T=81.9\%$	Maintains 90% contrast through 1200 bending cycles to a radius of 20 mm
WO_3^{98}	Graphene/PET	$\Delta T= 31.2\%$	Functioning under mild bending
Graphene ⁹⁹	Graphene/PVC	$\Delta T= 55\%$	Functioning under 1 cm bending radius

P3HT ¹⁰⁴	SWCNT/PDMS	$\Delta A \approx 0.3$	Functioning at 20% strain
WO ₃ ⁴³	ITO (100nm)/PET (1.8 μ m)	- -	Functioning after folding

2.3 Challenges in deformable electrochromics

Components that consist of a regular electrochromic device comprise of working and counter electrode, electrochrome and electrolyte. To realize deformable electrochromic devices, or to be more specific in our context of study, stretchable and foldable electrochromic devices, each component needs to be carefully designed and compatibly selected to pair into functioning devices.

The most stringent requirement falls on the deformable electrode itself. How to produce an electrode that possesses good conductivity with good mechanical compliance so as to avoid incomplete redox reacting and poor optical modulation remains to be settled. Excellent stability of the electrode and strong preservation of the high conductivity surviving repeated stretching or folding needs to be guaranteed so as to maintain the function of the device under deformation. As for transmissive electrochromic devices, extra care needs to be given on transparency. It is still quite challenging for a good design that facilely produces electrodes with high quality of $< 10 \Omega/\text{sq}$ and $> 90\%$ transparency, which is also beneficial for high contrast EC performance and low power consumption and ideal integration into large scale devices.

On the other hand, though the material selection for the electrochrome and electrolyte can be quite versatile, a good compatibility with the adopted electrode to avoid electrode failure and electrolyte decomposition needs to be considered. Besides, the structure of the electrochrome also needs to be carefully designed so that the electrochrome can have intimate contact with the electrode to facilitate charge transfer and at the same time it can sustain deformation like stretching and folding.

To date, the development in deformable electrochromics has been quite sluggish with scarcely reported results and proposals due to the lack of study for the specific working components and subsequently assembling them into a device. A good design for a deformable electrochromic device with acceptable performance under deformation still

remains to be accomplished.

2.4 Ph.D studies in context of literature

As mentioned earlier, the realization of a deformable electrochromic device requires a systematic study from the deformable electrode to the electrochrome and the assembly of them into functioning devices. My Ph.D study targets two types of deformable electrochromics, which are stretchable, wearable electrochromic display and foldable electrochromic display.

For stretchable and wearable electrochromic display, efforts were made towards high performance stretchable display. The currently reported stretchable electrochromic devices are of poor quality with very faint color switch due to the poor conductivity of the stretchable electrode. Ag nanowires network with high conductivity embedded in a stretchable PDMS matrix was utilized as the electrical current support. WO₃ islands were grown along Ag nanowires and functioned as the electrochrome with good contrast. The isolated structure allows the display to maintain optical modulation even under stretching. The stretchable display can be fused onto fabric textile for wearable display applications. For foldable electrochromics, we reported the first freely foldable electrochromic nanopaper. Nanopaper with its unique property of transparency, foldability and high surface energy was adopted as a novel substrate to support the electrochromic device. A nanopaper transfer method was discovered that facilitated the highly transparent conducting Ag nanowire percolating network. Thin coating of WO₃ was adopted as the electrochrome layer. Unlike the reported foldable ITO which folds to 0.3 mm radius and cracks, the metallic network was able to fold below 10 μm . The electrochromic nanopaper shows a reversible switching function even after 50 folding cycles.

To further improve the concept of foldable electrochromics, a transparent solid state electrochromic device was fabricated. Small molecule electrochrome as well as the electrolyte were embedded into a solid state slime matrix. The assembled device was fully foldable with each component of no folding constraints. The device maintains a good function after 100 folding cycles. The concept of camouflage wearables was demonstrated with the electrochromic nanopaper device mounted onto human hands.

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Chapter 3

Experimental Methodology

In this chapter, the underlying principles for the optical modulation of type I ethyl viologen and type III WO₃ as well as the dynamic switching process are discussed to understand their functionality and feasibility for deformable display applications. This detailed discussion also serves as an instructive guidance for the accurate analysis of device performance change upon external deformation. Following this, the synthesis methods for the samples in this study are discussed. Subsequently, the important equipment for detail characterization of the samples and devices are introduced with their corresponding working principles. Finally, the fabrication procedures leading to well-functioning deformable devices are elaborated.

3.1 Working principles for selected electrochromic materials

3.1.1 Viologen as type I electrochrome

As mentioned earlier, electrochromism is defined as the reversible optical modulation under external supplied voltage.¹ For most cases, electrochromism requires the existence of reversible redox molecules that deliver different redox states in response to the driven voltage. At different redox stages, the existence of optical intervalence charge transfer is believed to be the main cause of different colors exhibited by the electrochrome.² A general expression for this mechanism is listed below, where electrons at site i of electrochrome E of redox state a is excited to an adjacent molecular orbital at site j of electrochrome E of redox state b by absorbing the excitation energy of $h\nu$ from the photon. The color that is delivered by the electrochrome is the complementary of the absorbed. Excessive energy gained by the whole systems is dissipated as heat.

Based on the physical property before and after the redox reaction, electrochromic materials are generally classified into three different types.²

A type-I material remains dissolved in the solvent before and after the redox reaction. A typical example is ethyl viologen (EV) with the molecular structure shown below.

Figure 3.1 the molecular structure of ethyl viologen diperchlorate.

The viologen forms intensely colored water soluble radicals cation when reduced.

The injected electron would be delocalized throughout the π framework and the Nitrogen (N) bears the positive charge. The intense color of the radical cation origins from the intervalence charge transfer between the +1(nominally) and 0 (nominally) charge nitrogen in a simplified view. However, as mentioned earlier the electron would be delocalized, it should be more technically viewed as an intramolecular photo-effected electronic excitation and thus the substituents on the nitrogen would also affect the color demonstrated.³

When a cathodic over-potential is exerted, the viologen dication would be reduced leading to a surface concentration depletion of the electrochrome. Diffusion caused mass transfer brings the dication in the bulk to the electrode/electrolyte interface for continuous reaction. The diffusion controlled current can be estimated from Cottrell equation:^{4, 5}

$$I(t) = nFAc \sqrt{\frac{D}{\pi t}}$$

F is the Faraday constant, c is the concentration of the electroactive species in the bulk solution, D is its diffusion coefficient and n is the number of electrons consumed for the redox reaction.

The rate of coloration of the electrochrome is a linear function of the reaction current $I = dQ/dt$. Since the optical absorbance *Abs* is proportional to *Q*, $dAbs/dt$ should also have $t^{-0.5}$ dependence. The integration of this results in *Abs* being proportional to $t^{0.5}$.⁶

Being a small molecule electrochrome, ethyl viologen has distinct advantages without the concerns for mechanical failure over solid electrochromic films. This is beneficial for an easy integration into a deformable device, which would be discussed later.

3.1.2 WO₃ as type III electrochrome

Different from type I materials, this group of electrochrome remains solid and insoluble in the electrolyte throughout the redox reaction. WO₃ as an inorganic transition metal oxide exemplifies as a type III electrochrome. The electrochromic redox reaction can be simplified as:

M^+ is a cation counter ion like H^+ , Li^+ , Na^+ etc. intercalated from the electrolyte to preserve the electroneutrality of the oxide film.

After the reduction reaction, intervalence charge transfer between W^{5+} and W^{6+} results in a blue color.⁷ Another widely accepted theory explaining the color formation of WO₃ by Mott⁸ and Emin⁹, similar to the intervalence charge transfer theory but more specifically explained with the energy absorption by quantum mechanics is called small polaron hopping mechanism. Briefly, injected electrons would localize to one lattice site forming small polarons and constrained wave functions. A small overlap between wavefunctions corresponding to adjacent sites becomes conducive to the small polarons under the

excitation of photon:^{10, 11}

The polaron hopping coupled with the absorption of photons leads to the characteristic optical modulation.

The inorganic film keeps electroneutrality by intercalating/ egressing counter-ions from the electrolyte during cathodic/anodic reactions. An electron-counter ion double injection /removal mechanism during redox reactions applies for the redox reaction as illustrated below:

Figure 3.2 The schematic for the electron-counter ion injection/removal process during a) coloring and b) bleaching.

At the beginning of electron injection, fully oxidized WO_3 is a poorly conducting semiconductor¹² and electron conduction is believed to occur through site-to-site hopping.^{2, 13} With inserted electrons gradually charging to the conduction band, the conductivity of WO_3 would experience a huge jump as shown in the figure below.¹⁴

Figure 3.3 Conductivity of H_xWO_3 as a function of insertion coefficient. (Reprinted with permission from Reference 13. © 1978 Elsevier.)

However, for electrochromic applications, deep electron insertion by large over-potential should be avoided due to the irreversible reaction that is unable to remove inserted electrons.²

A small size of the counter-ion is preferred for a rapid optical modulation with protons more favored than Li^+ in terms of switching speed. Besides that, intercalated ion would stress the oxide matrix lattice with the stress in a film approximated linear to the insertion coefficient.¹⁵

The motion of the intercalated ion inside the matrix is determined by the chemical diffusion coefficient $\bar{D}$, which should be differentiated from the true diffusion D as discussed earlier in section 3.1.1. The chemical diffusion coefficient $\bar{D}$ is a gauge of the rapidity of movement of the counter-ion inside the inorganic matrix. When the ions channel through the bulk, it would be affected both by diffusion and migrations.¹⁶ Both of the factors are energy activated process with the diffusion more sensitively affected by temperature. The combined influence of these factors leads to the so called chemical diffusion which could be related to the true diffusion of ions by Wagner factor as in:

$$\bar{D} = WD$$

The Wagner factor was derived as:¹⁷

$$W = t_{(\text{electron})} [\partial \ln a_{(\text{ion})} / \partial \ln c_{(\text{ion})} + z_{(\text{ion})} \partial \ln a_{(\text{electron})} / \partial \ln c_{(\text{ion})}]$$

a and c refer to activity and concentration respectively. $z_{(\text{ion})}$ denotes the charge on the ion and $t_{(\text{electron})}$ is electron transport number. The chemical diffusion coefficient can be varied from different preparation methods and testing conditions.

In actual redox reactions, both the ion and electron are injecting inside the matrix, it is thus the slower moving part that determines the overall reaction rate.¹⁸ Currently, there are several models established to describe the coloring/bleaching process. However, due to the complexity of the reaction involved, there is no universal model yet that can be applied to cover a random system. Some tenable and classical models are here discussed which saw some success in characterizing the complex kinetics.

Faughnan and Crandall proposed a semi-empirical model for WO_3 coloring and bleaching.¹⁹⁻²³ In this model, assumptions are made to simplify the process, such as that

there is no concentration gradient of the ion inside the inorganic matrix; the rate limiting motion merely comes from the ion that enters WO_3 ; and that there is an empirically characterized back-potential which exists at the WO_3 electrolyte interface. The invoked back potential is caused by the increased chemical potential of the intercalated ion that is unfavorable energetically. In detail, the magnitude of the current would thus be controlled by two energy barriers, with the first barrier at the electrolyte interface for the ion charge transfer to WO_3 and a second barrier affected by the insertion coefficient x , as described in the function below:

$$i_c = i_0 (1-x/x) \exp(-10x) \exp(V_a e/2RT)$$

i_0 is the exchange current at equilibrium and V_a is the overpotential.

When introducing an empirical time related factor relating film thickness and ion diffusion (true diffusion), we can arrive at:

$$i_c = i_0 (\tau_0/t)^{0.5} \exp(V_a e/4RT)$$

The semi-empirical model was fit for some WO_3 systems for a limited range of insertion coefficient.²⁴⁻²⁶ Though the treatment in this model and the derived equation has met some corroboration from the experiment, the kinetic process treated here is based on empirical fitting and did not quite depict a clear picture. Green and co-workers put forth a model under low potential Galvano static condition. Instead of a uniform distribution of the ions as in Faughnan and Crandall's model, he suggests a concentration gradient of the intercalated ion inside the matrix. By analogy with heat conduction through solids,²⁷ Green derived the ion concentration function:²⁸

$$c(y, t) = J_0 t/l + J_0 l F(y,t)/\bar{D}$$

J_0 is the constant ionic flux of the ion from the electrolyte to the interface; l is the thickness of the WO_3 layer. The flux of the ion penetrates the matrix to a distance of y . At position $y=l$, there exists the WO_3 electrolyte interface while $y=0$ refers to the position for electron injection. c_0 refers to the concentration of the ion at the interface. As can be seen from this equation, $c(y,t)$ would be independent of the position if $\bar{D}$ is large, which renders the distribution of the ion uniform within the matrix. Then this would agree with Faughnan and Crandall's hypothesis. But if $\bar{D}$ is only moderate, the term $J_0 l F(y,t)/\bar{D}$ could then be regarded as a correction term for the diffusion limited process. The mass transfer function $F(y,t)$ is calculated and plotted against y/l as shown in Figure 3.4:

Figure 3.4 $F(y,t)$ as a function of film position at different time. The numbers on the right in the figure refer to the values of $\bar{D}t/l^2$. (Reprinted with permission from Reference 28. © 1976 Elsevier.)

$F(y,t)$ is helpful for understanding the evolution of the distribution of ions inside the bulk over time. One can expect from the Green's equation that at the beginning of coloration ions predominantly reside at the interface and the concentration of ions at $y=0$ would almost equal to 0; while with time progressing, the concentration gradient would gradually be flattened.

As for the bleaching process, Faughnan and Crandall assume a space charge limited current. In their model, a distinct interface exists between the bleached and the intercalated WO_3 , with a moving interface front starting at the WO_3 electrolyte interface and progressing towards the conductor side.

The length for the proton depleted region is described as $l(t)$. The bleaching time is derived by solving the differential equation for the time-dependent diffusion travelling $l(t)$, described as:

$$i(t) = (p^3 \epsilon \mu_H^+)^{0.25} V_a^{0.5} / (4t)^{0.75}$$

ϵ is the permittivity of WO_3 , μ_H^+ is proton mobility, p is proton volume charge density and V_a is the over-potential.

The calculated data based on this empirical assumption has met some agreement with a few studies that show the time dependent behaviors in a certain range as shown below:²⁹⁻

Figure 3.5 Bleaching current of Li_xWO_3 as a function a time. (Reprinted with permission from Reference 30. © 1978 The Electrochemical Society.)

When WO_3 is fully bleached $I(t)$ would equal to the thickness of the film d . Under this boundary condition, t_b is derived as:

$$t_b = \frac{\rho d^4 x}{4 \mu V_a^2 \epsilon}$$

ρ is the density of W atoms and x is the insertion coefficient at the beginning of bleaching.

For Green's model on the bleaching process, he adopted the same manner as in the coloring process by assuming the existence of counterion concentration gradient across the film thickness, which was simulated by taking analogous functions to heat flow. He also assumes that the counter-ion would instantly be removed at the WO_3 electrolyte interface so that $c(y=1, t>0) = 0$. The concentration gradient of counter-ion inside the inorganic matrix is theoretically calculated based on the established model in figure 3.6:

Figure 3.6 Concentration distribution of the counterion inside WO_3 . The numbers on the curve refer to the value of $\bar{D}t/d^2$. (Reprinted with permission from Reference 28. © 1976 Elsevier.)

As shown in the figure, the concentration front at the electrolyte side equals to 0 at all times and the gradient would gradually be smoothed out as the bleaching process goes on.

As a conclusion for the kinetics of WO_3 during color switching, we could see the dynamic switching process is very complicated. An accurate model needs to involve migration and diffusion at the same time and consider the relative rate between electron and ion transportation. Although up till now there is no universally applied model established yet, the discussion above for the two classical models serves as a good guidance for a basic and simplified understanding of how the color changes over time.

In chapter 4 and 5, reflective modulation of WO_3 will be studied. To correctly characterize such reflective device by appropriate parameters, the modulation principles are briefly discussed. Reflective modulation is similar to the transmissive type but more complex, we shall start with the transmissive type first and then discuss the reflection by drawing justified analogies.

The incident light with intensity I_0 hits normally on a sample surface and travels through the sample with thickness of t . The finally attenuated intensity I can be described $I = I_0 e^{-A}$,

A is called absorbance of the sample. The absorbance is proportion to the sample thickness t and the characteristic absorptivity α . The reason a certain material gives a unique color is that the characteristic α that governs the absorption is band structure dependent which lead to the wavelength dependency. A strong absorption at a certain wavelength will finally give rise to a complementary color other than absorbed color for a certain material. At the same time, the intensity of α as well as the thickness of the sample determines how much the incident light attenuates. Meanwhile, the transmittance defined as $T = I/I_0$, can thus be related to A by $A = \log (1/T)$. Accordingly to Beer-Lamber law,³² the absorbance could also be defined as $A = \epsilon lc = \beta c$, where ϵ is the molar absorption coefficient and c is the concentration of the dispersed sample and l is the light path which could be equivalent to sample thickness t and β equals to ϵl which is material dependent.

For a specific electrochrome, the thickness t remains constant and the electrochrome could switch its absorption property through redox reactions between the bleach and color state. The overall expression for its absorbance thus goes to $A = \beta_b c_b + \beta_c c_c$. Since the concentration of the bleached electrochrome is directly related to the colored electrochrome through redox reaction, if we assume a single electron transfer reaction then $dc_b = -dc_c$ and if we further assume that the total amount of the material $c_b + c_c = 1$, then the absorbance of the electrochrome could be simplified as $A = \beta_b c_b + \beta_c (1 - c_b)$. During redox reactions, the electrochrome would be switched between the bleached state of absorption coefficient β_b and the colored state of β_c , for WO_3 a small absorption exists at the red light wavelength (633 nm), but when it is reduced to H_xWO_3 a strong absorption occurs and thus a large contrast at this wavelength could be observed. It is the absorption of the red component of the incident that leads to the observed blue tint of the cathodically obtained product. The extent for the change of absorbance is thus described $\Delta A = (\beta_b - \beta_c) \Delta c_b$. Both β_b and β_c are wavelength dependent, the choice of wavelength for characterizing the optical modulation is such that ΔA and $\beta_b - \beta_c$ is around the maximum where in the transmittance spectrum $\Delta A = A_c - A_b = \log T_b/T_c$, in which ΔA is also called change of optical modulation ΔOD and T_b/T_c is defined as contrast ratio.^{1,2} Furthermore, Δc_b is proportional to the charge consumed Q during the redox reaction, thus $\eta = \Delta OD/(Q/\text{area})$ is proportional to $\beta_b - \beta_c$; η is also called coloration efficiency which is used

to reflect how readily a certain system changes its absorption (color) under unit charge density. Higher coloration efficiency indicates a more energy efficient performance. However, for a real testing device, the linearity is usually limited within a short charge intercalation range because the absorbance maximum is shifting and the absorptivity coefficient would vary during intercalation.¹ The way to characterize coloration efficiency thus goes to the slope for the linear region.²

The situation for reflectance is more complex, unlike the relationship between transmittance and absorbance; there is no linear relationship between reflectance and absorbance since absorption + reflectance + transmittance = 1.³³ However, for thick reflective sample testing, the transmittance can be neglected and this goes to absorption + reflectance = 1. By drawing analogy to the transmissive discussion, $\log(1/R)$ is adopted and called apparent absorbance³⁴ since it is not the real absorbance, and it could be mathematically treated through regression and fitted to $A = B_0 + B_1 \log(1/R)$.³⁵ This would lead to a similar strategy to characterize the reflective result that ΔA is proportional to $\log(R_b/R_c)$, where again the ratio between reflectance at different states is called the contrast ratio.

Apart from the calibrated apparent absorbance, a model based on Kubelka-Munk (K-M)³⁶ theory was established. The diffusive reflectance is reported to be determined by the ratio of absorption coefficient (K) to the scattering coefficient (S): $K/S = (1-R)^2/2R = F(R)$. The absorption coefficient is proportional to absorbance and for some systems, the scattering coefficient is found to be a material structure constant that is independent of incident wavelength;^{33, 34} this results in absorbance being proportional to the function $F(R)$. Both the calibrated apparent absorbance $\log(1/R)$ and K-M absorbance have been well accepted and adopted for the monitoring of absorbance for reflective samples.³⁵ The apparent absorbance method was adopted to better represent the contrast ratio for electrochromic applications.^{37, 38} Based on the discussions, we might now derive that $\eta = \Delta OD/(Q/\text{area})$, $\Delta OD = \log(R_b/R_c)$. Thus the reflective modulation could be similarly characterized as in the transmissive modulation.

Finally, in terms of the application for deformable display, WO_3 is especially selected due to its large contrast and facile deposition on our deformable electrode. Besides, the

electrochemical deposition from its precursor allows the control of its morphology and thickness for desired deformation applications. Furthermore, the narrow switching window of WO_3 permits a safe switching condition for Ag based electrodes, which would be discussed in detail in the following chapters.

3.2 Synthesis

3.2.1 Hydrogen bond electrochromic slime

A solid state electrochrome is prepared by dissolving ethyl viologen inside a hydrogen bonded slime matrix constructed from the interaction between borax and PVA.

When Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is dissolved in water, it would hydrolyze to form boric acid ($\text{B}(\text{OH})_3$) buffer solution. Subsequently, $\text{B}(\text{OH})_3$ maintains equilibrium in the solution through the following reaction:³⁹

PVA is a water soluble polymer with abundant hydroxyl groups on the polymer chain. Both $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ are able to form hydrogen bonds with PVA while only $\text{B}(\text{OH})_4^-$ is assumed to be majorly responsible for an effective three dimensional cross-linking that determines the viscoelastic nature of the slime. This is due to the geometry difference between these two species with $\text{B}(\text{OH})_3$ showing a coplanar structure that is efficient in bonding with adjacent hydroxyl groups on the same polymer chain while $\text{B}(\text{OH})_4^-$ showing a tetrahedral structure is more easily connected three dimensionally with surrounding hydroxyl groups as shown in the figure below.⁴⁰

Figure 3.8 a) Coplanar structure of $\text{B}(\text{OH})_3$; b) tetrahedral structure of $\text{B}(\text{OH})_4^-$

The schematic that shows the formation of hydrogen bonding is shown below:

Figure 3.9 Cross linking between $B(OH)_4^-$ and PVA through hydrogen bonding.

The slime shows a viscoelastic property due to the enhanced immobilization of the polymer chains by the numerous bonding. On the other side, the slime is extremely soft and flexible due to the low bonding strength from hydrogen bonding which dynamically breaks and reforms the bond at extreme physical conditions.³⁹

The soft physical property and polar matrix environment is well leveraged for deformable electrochromic applications by incorporating the electrochrome into the matrix.

Electrochromic small molecule redox pairs of Ethyl Viologen Diperchlorate ($15 \text{ mmol} \cdot \text{L}^{-1}$) and Sodium Anthraquinone-2-sulfonate ($5 \text{ mmol} \cdot \text{L}^{-1}$) in combination with KCl ($20 \text{ mmol} \cdot \text{L}^{-1}$) were dissolved in 4 wt% PVA in DI solution. This was subsequently mixed with 4 wt% borax in DI solution in a volume ratio of 4:1 to form the hydrogen bonded slime. Sodium Anthraquinone-2-sulfonate (AQS) was added as a redox mediator. During the coloring process at the working electrode, ethyl viologen undergoes reduction while AQS balance the charge by going through the oxidation process. When voltage is switched off, a spontaneous chemical reaction between oxidation AQS and the reduced viologen would occur, which leads to an efficient bleaching of the electrochromic slime. Detailed device performance would be discussed later in the following chapters.

3.2.2 Ag nanowire synthesis

The Ag nanowires from Seashell have a dimension of around 114 nm in diameter and 31.2 μm in length. The synthesis of Ag nanowires has become universal and commercialized. The synthesis mechanism was suggested by Sun⁴¹ and has become

widely accepted.

Since most metals prefer to be crystalized with symmetric cubic lattices, the isotropic growth behaviors makes it difficult to evolve into one dimensional structure. To conquer this, capping agents need to be adopted to manually confine the growth rate in certain crystal facets. It is a popular method for Ag nanowire growth by reducing silver nitrate with ethylene glycol with the growth rate controlled by poly (vinyl pyrrolidone) (PVP). In the presence of Ag nanoparticles as the seeds, the nanoparticles would first grow into a twinned structure with 5 fold symmetry with facets of $\{111\}$ to reduce the surface energy. The twin boundaries as the sites with the highest energy would then direct the diffusion of Ag atoms to crystalize around the boundaries. Instead of growing into bigger particles, the twin plane would be confined which results in the hampered growth of the $\{100\}$ facets because of the preferred adsorption of PVP on these planes that passivates the growth in this direction. On the other hand, the growth rate at the $\{111\}$ facets is much higher and this leads to the one dimensional controlled growth of Ag nanowires as shown in figure 3.10.

Parameters such as the PVP concentration and growth temperature play important roles on the final morphology. If PVP is too dense, Ag nanoparticles would be obtained due to the coverage on $\{111\}$ planes also that leads to isotropic growth. If PVP is dilute, insufficient passivation causes the $\{100\}$ plane to growth with a final needle shape structure obtained. Appropriate concentration is required for the growth of uniform 1D nanostructure. Temperature also affects the morphology with below 110 °C leading to nanoparticle morphology. The reason is suggested that a high temperature is needed for the activation or slightly melting of $\{111\}$ facets for a higher reactivity to facilitate growth along those planes.

Figure 3.10 The schematic showing the growth of Ag from a) nanoparticle seed to b) nanowire due to side surface passivation.

3.2.3 Synthesis of nanocellulose

The nanocellulose involved in the studies was obtained from liberation of normal softwood cellulose fibers. Nanocellulose or cellulose nanofibril is defined as nanoscale sized fiber (like cellulose nanocrystal with both diameter and length < 100 nm) or micron scale sized fiber with a cross sectional diameter < 100 nm.⁴²

The wood fiber is usually pulped first with sodium hydroxide and sodium (Kraft pulp)⁴³ sulfide to remove impurities like lignin to form cellulose based slurries. The pulp could then be subject to the liberation process in high pressure homogenizer or high pressure micro fluidizer to separate the microfibrils by forcing the hydrogen bonded nanofibrils apart. The large hydrostatic pressure inside the working chamber will “explode” the microfibrils when passing through the restriction-to-flow valve causing the split of the bundled cellulose fibers.

The bonding strength in the micro sized cellulose fiber is strong, which causes a large energy input to facilitate the liberation.⁴⁴ It is also difficult to fully separate the fibers physically to get uniform nanocellulose without multiple passes conducted. To achieve uniform fine fibers with suppressed energy consumption and high production consistency, surface charge induction could be leveraged for this purpose. The charges on the microfibrils would cause swelling and reduce the cell wall adhesion of the fibers. These are beneficial for facile liberation of the microfibrils into nanofibrils.^{45, 46}

Isogai⁴⁷ suggested a TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) mediated oxidation

of microfibrils to selectively oxidize the C6 hydroxyl group into carboxylate group under the catalytic effect from TEMPO and NaBr. The swelled microfibrils could easily be liberated into cellulose nanofibrils with diameter < 10 nm and length > 2 μm. The plausible synthesis route is shown in figure 3.10.

Figure 3.11 Suggested reaction route for the production of carboxylate cellulose. (Reprinted with permission from Reference 47. © 2010 American Chemical Society.)

3.3 Characterization

3.3.1 SEM

SEM is utilized for nanostructure and morphology analysis. Compared to optical microscopy, SEM could give us more details of a sample at much higher magnifications. This is because the resolution of SEM determined from the minimum distinguishable distance could be very high as predicted from Abbe's equation:⁴⁸

$$d = 0.612 \lambda / NA$$

d is the resolution, λ is the radiation wavelength of the travelling electron, and NA is called numerical aperture which is an equipment constant.

Normally, SEM could have a resolution down to 3 nm with the important working components shown in the schematic below.

Figure 3.12 The schematic showing the traveling of electron beam inside an SEM equipment.

The electron gun generates electrons that is accelerated under potentials and pass through the condenser lens which is an electromagnetic lens that controls the size of the electron beam. A larger size leads to a higher signal to noise ratio but a lower resolution and vice versa. Then the objective lens focuses the beam onto the sample. The scan coils deflects the electron beam by applying potentials to drive it. The deflected beam thus could scan on the sample surface to generate location dependent signals to reflect the sample morphology.

The electron beam hits on the sample surface and interact with the sample. It is the interaction that gives us clues on the sample morphology. Secondary electrons and backscattered electrons are typically the most useful electrons that results in the contrast. Secondary electrons are generated from inelastic collision between the electron beam and the shell electron from the sample. Secondary electrons are low in energy and need to be collected by a positively polarized plate. Secondary electrons are very sensitive to surface roughness and they are efficient for capturing the morphology. Backscattered electrons come from the collision between the primary electron beam and the sample atom nucleus. The back scattered electrons are thus sensitively affected by the sample density or atomic weight and will bring a large contrast between samples of different compositions.⁴⁹

3.3.2 Uv-vis Spectrophotometer

Uv-vis Spectrophotometer is used for characterizing the optical properties of the measured sample like transmittance and reflectance. The principle for measuring transmittance/reflectance is based on the calculated percentage of the transmitted or reflected light intensity with reference to the incident light intensity.

The basic configuration of a spectrophotometer is shown below:

Figure 3.13 Configuration of a spectrophotometer

The light source generates a range of light wavelength. Typical light sources are halogen lamp and deuterium lamp. Since the generated light is a combination of different wavelengths, monochromator is needed to split them into separate components for single wavelength characterization. A prism or nowadays a popular choice of diffraction grating can work as the monochromator to split light to different exit slits. Samples are placed inside the sample holder in the sample compartment with the investigating area of the sample exposed in the light path to interact with the light source. Finally, photodetectors such as photomultiplier or silicon photodiode works as the detector to gauge the intensity of the remaining light beam.

In order to determine the diffusive reflectance, an integrating sphere attachment is settled in the sample compartment. The reason such a sphere attachment is needed is because of the difficulty to collect the randomly scattered diffusive light in a natural way. The introduction of integrating sphere allows the equal distribution of the diffusively scattered light across the sphere surface. Hence, it is possible for the detector to correctly gauge the reflected light intensity. This way of characterization necessitates reflectance to be measured in a relative value because the relative reflectance is calculated based on the regulating reflectance of a background sample. However, the relative reflectance could be close to the absolute reflectance if the background sample is low in absorption and highly diffusive like BaSO₄ or PEFE plates.^{50, 51}

Figure 3.14 Structure of an integrating sphere attachment.

The schematic for the reflectance measurement is shown above. When the light beam hits on the sample surface, it will reflect randomly to every possible direction. The reflected light will travel inside the sphere and bounce indefinitely on the sphere surface. The reflected light intensity would thus be averaged on every point of the integrating sphere surface. A detector is placed inside the sphere chamber to count the light intensity. With a reference value established first, the relative reflectance value can then be calculated as discussed before.

3.3.3 Four point probe test

The four point probe is adopted to obtain the sheet resistance of fabricated electrodes. The schematic for the four point probe configuration is shown below:

Figure 3.15 Configuration of a four point probe.

The four point probe consists of four points that touches the surface of a conductor with the current measured from the outer two probes and the voltage measured from the inner

two.

For a thin film conductor with thickness t , current travels in a ring form distribution inside the conductor.⁵² The resistance can thus be expressed as:

$$R = \int_{x_1}^{x_2} \rho \frac{dx}{\pi x t} = \frac{\rho}{\pi t} \ln(x) \Big|_{x_1}^{x_2}$$

The spacing between each probe is constant, thus $x_2 = 2x_1$, and $R = \frac{\rho}{\pi t} \ln 2$.

Since $R = V/I$, $\rho = \frac{\pi t}{\ln 2} \frac{V}{I}$ is obtained.

Sheet resistance $R_s = \rho/t$ is thus expressed as $R_s = \frac{\pi}{\ln 2} \frac{V}{I}$.

3.3.3 Electrochemical workstation

The electrochemical workstation is an important tool for electrochemical studies. It is the source, like a battery, to power the devices. The most important components for the workstation are reference, counter and working electrode.

The reference electrode has a fixed, known potential usually determined from Nernst equation. The stability of the reference electrode comes from the constant activity of the redox elements. A typical example is Ag/AgCl in saturated KCl solution. During electrochemical reactions, reference electrode is inert and no current passes through it which guarantees an absolute constant potential of the reference electrode. This is achieved by designing high input impedance for the reference port on the workstation.⁵³

The current would thus only travel between the working and counter electrode.

The working electrode is where reaction of interest is investigated and the counter electrode, also known as auxiliary electrode, can be an inert noble metal like Pt, Au to close the current circuit.

The voltage or current is constantly monitored inside the electrochemical work station in order to provide requested energy input. For example, during potentiostatic output, control amplifier connected with counter electrode would force current to flow through the cell and change the potential for the working electrode. At the same time, the sensor port in connection with working electrode would be constantly checking the potential difference with the reference electrode. An accurate controlled voltage is achieved through a negative feedback mechanism to obtain the required potential difference.⁵³

Similarly, for galvanostatic output, the current travelling between the working and counter electrode would be constantly monitored by current follower or shunt to obtain

the user specified value.

3.4 Device fabrication

3.4.1 Embedded Ag NW as a stretchable electrode

To fabricate an electrochromic device, the electrode through which electrons are injected or retracted is indispensable. For a stretchable electrochromic device, the substrate as well as the conducting material has to be carefully designed to achieve this function.

PDMS composed of alternatively occurring silicon and oxygen groups is an intrinsically stretchable polymer due to the soft bonding that allows for extension of the polymer chain under strain. Ag nanowire as one dimensional conductive element has good compatibility with the stretchable substrate due to its large aspect ratio of the nanowire and the inter-sliding between wires that guarantees constant interconnection under strain so that the overall conductivity can be preserved.

To integrate the conductive Ag nanowires network with the stretchable substrate, an embedding transfer technique was adopted for fabrication of the stretchable electrode. The schematic for the fabrication process is shown in Figure 3.14.

Figure 3.16 a) Filtration of the Ag nanowires suspension onto filter membrane; b) PDMS covering the conductive layer; c) peeling of the PDMS layer after curing; d) PDMS with the Ag nanowires network embedded and the top layer exposed for electrical conduction.

The fabrication process starts with the filtration of Ag nanowires suspended in IPA onto polycarbonate filter membranes to form the first conductive layer. Following this, Polydimethylsiloxane (PDMS) precursor mixed with curing agent is gently poured over the conducting area. Subsequently, the whole system is put into a vacuum pumped desiccator to remove trapped air bubbles in the PDMS matrix and fully impregnate PDMS in between each Ag nanowire. Then thermal treatment at 60° for 2h is practiced to cure the PDMS into solid form. After this, the cured PDMS can be peeled off from the membrane and the Ag nanowires are embedded into the matrix with a fraction of the Ag nanowires tips out to form conductive pathways. Typical FESEM images of the embedded stretchable conductor are shown in Figure 3.15.

Figure 3.17 FESEM images of the embedded Ag nanowires inside PDMS matrix with a) top view and b) cross sectional views (inset is a magnified view with scale bar of 500 nm).

3.4.2 Stretchable electrochromic device

With the stretchable conductor and electrochemically deposited WO_3 as the electrochrome, the stretchable device testing is facilitated by settling the electrochromic electrode inside a home-made PDMS casing with injected H_2SO_4 as the electrolyte. To complete the circuit, an inert Pt wire is inserted into the electrolyte. The device configuration is shown in Figure 3.16.

Figure 3.18 The schematic setup for the performance testing of the stretchable electrochromic device.

As shown in the schematic, a casing is utilized to contain the electrolyte; and the stretchable electrochromic electrode is settled inside the casing and fixed by the binder clip for the on-strain electrochromic property testing.

3.4.3. Nanopaper transfer for high quality transparent conductive electrodes

Unlike the PDMS monomer chains crosslinking during curing that leads to the embedded Ag nanowire structure, nanocellulose fibers assemble together due to hydrogen bonds cohesion when water evaporates. Densification of the filtered nanocellulose gel during drying and the high surface tension of nanocellulose would enact the formation of a flat nanopaper plane. This results in an interface transfer of functional materials between the filter membrane to the nanopaper surface, which would be more complex than the embedding transfer method that utilizes the encompassed mechanical interaction described earlier. We would discuss the theory for practicable transfer detailed in later chapters.

We start with physically liberated cellulose nanofibrils for the nanopaper transfer. The schematic diagram for the transfer process is shown in Figure 3.17.

Figure 3.19 The schematic nanopaper transfer procedure.

Ag nanowires are filtered first followed by the filtration of physically liberated cellulose nanofibril (PCNF) suspension that forms a gel layer that covers the conducting areas. The whole system is then subject to heating at 105° to evaporate water and to allow for the nanofibrils assembly which is accompanied by the transfer of the conducting network. Finally, the conductive nanopaper is peeled off from the filter membrane.

A typical SEM image of a transferred conductive nanopaper is shown below.

Figure 3.20 The SEM image for a nanopaper transferred Ag nanowires network on PCNF. Apart from Ag nanowire, the nanopaper transfer method has been proven to be very versatile in successful transfer of a range of 0D, 1D, 2D nanostructures which would be discussed later.

To reduce the haze of the nanopaper and protect the Ag nanowires from dislodgement, Tempo assisted oxidized cellulose nanofibrils (TCNF) transfer for a SWCNT anchored transparent conductive electrode (TCE) is introduced. The most striking difference between PCNF and TCNF lays in their respective molecular structure. PCNF has the same structure as natural cellulose while for TCNF the C6 hydroxyl group is converted to

carboxylic group. The induced surface charge leads to facile fiber separation and uniform nanofiber composition, which contributes to better optical properties

The schematic procedure is shown as follows.

Figure 3.21 The TCNF nanopaper transfer procedure for SWCNT@Ag transparent conductive electrodes.

As shown from the procedure, SWCNT is filtered as the first layer on the filter membrane followed by the filtration of Ag nanowire. Then fine TCNF fibers form a conformal layer that intimately covers SWCNT and Ag nanowires. The drying process and the corresponding transfer finally results in the SWCNT@Ag transparent conductive electrode. Ag nanowires conducting electrodes are also fabricated using the TCNF method, the procedure is the same as the aforementioned method without filtering SWCNT layers in the first step.

The SEM for the TCNF transferred Ag TCE and the SWCNT@Ag is shown below.

Figure 3.22 a) The SEM image of the TCNF transferred Ag TCE; the SEM image of the SWCNT@Ag at b) low magnification and c) high magnification.

3.4.4. Foldable electrochromic devices

For the PCNF foldable electrochromic nanopaper, WO_3 is electrochemically deposited as the electrochrome. Reflective testing is adopted because of the haze and large scattering angle of the PCNF nanopaper. A similar testing configuration to Figure 3.16 is adopted with the PDMS casing to hold the electrochromic nanopaper and the H_2SO_4 electrolyte.

For the TCNF foldable electrochromic nanopaper, a transparent solid state foldable electrochromic device was constructed. The solid state electrochrome is obtained by embedding ethyl viologen into the slime matrix as discussed in section 3.2.2. The device schematic is shown below.

Figure 3.23 The device schematic for the solid state foldable electrochromic nanopaper device.

Due to the liability to oxidation of Ag, it is not suitable to work as an inert counter electrode. To solve this problem, carbon fiber was utilized. A strand of weaved carbon fiber was placed laterally around the working electrode. The electrochromic slime was then spread uniformly across the working and counter electrode to complete the circuit.

The detailed electrochromic performance under various folding cycles will be discussed in detail.

3.5 Overview of Methodologies

As a conclusion, this chapter starts by discussing the optical modulation mechanism of type I viologen and type III WO_3 . Subsequently, the dynamic optical modulation of viologen and WO_3 involving counter-ion/electron double injection and mass transport were reviewed to understand the color switching mechanism, which provides informative insights for deformable device performance analysis. The facile electrochemical deposition method of WO_3 is very compatible with our conductive electrode to facilitate the stretching and folding function. Meanwhile, water soluble small molecule viologen incorporated in the slimes surpasses the deformation constraints in conventional electrochromic thin films, which is promising for highly deformable devices.

The electrochemical deposition principle of WO_3 was discussed in detail by analyzing the deposition current to determine the specific component in the precursor that contributes to the effective deposition. Subsequently the slime formation mechanism for hydrogen bonded PVA/borax mixture was reviewed to better understand the structure of the electrochromic slime that is incorporated in the foldable device.

Principles underlying technique such as SEM, four point probes, Uv-vis spectrophotometer, electrochemical workstation were presented, which provide useful information on how these characterizations work a priori.

Finally, the fabrication of stretchable conductors and foldable transparent conductive electrodes were presented. Integration methods of the conductors into functional deformable electrochromic devices were then introduced.

With the working principles of electrochromes discussed, synthesis mechanism studied, characterization and device fabrication methods presented, this chapter provides theoretical understanding and a good clarification of the involved techniques and approaches for the realization of the deformable electrochromic function.

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Chapter 4

Stretchable and wearable electrochromic devices

The strategies to realize stretchable and wearable electrochromic devices are discussed in this chapter. Specifically, Ag nanowires are integrated with PDMS to form an embedded composite with excellent stretchability as the deformable electrode. Inorganic WO_3 nanoparticles islands were deposited onto the electrode to act as the electrochrome. The electrochromic device is able to function under stretching and its performance at relaxed and stretched state is analyzed. Finally, a pixel patterned stretchable device was cured onto a fabric textile which shows promising application for wearable displays.

4.1 Introduction

Conventional electrochromic devices are constructed on rigid substrates with poor mechanical compliance. Futuristic electrochromic device requires much more mechanical compliance to cater for stretching and folding applications that allows compatibility with large human motion.^{1, 2} The intricate and complex demands from the next generation devices make it a requisite to develop stretchable and wearable devices that are able to conform to curvature surface and deform easily without losing the functionality.^{3, 4}

Although organic electrochrome might serve as a good candidate for stretchable electrochromic applications due to its intrinsic flexible and soft polymer chains,^{5, 6} inorganic electrochrome like WO_3 on the other hand offers good contrast and better stability as the optical modulation layer.⁷

Conventionally, brittle WO_3 films would crack at a relatively small undertaken strain which is not very suitable for stretchable applications. For intrinsically non-stretching materials, structure engineering with creating out of plane waves or arches are very effective to endow stretchability with brittle materials.¹ A careful design for a stretchable structure needs to be developed. Besides the electrochrome, traditional electrode ITO also suffers from the same brittleness fiasco with a poor breaking strain of less than 1%.^{2, 8} Alternative electrodes need also to be discovered. Percolating Ag nanowire network serves as good candidate to fulfil the stretching function due to the open structure that permits alignment along strain while keeping the conductivity.⁹ In this study, Ag nanowire embedded elastomer serves as the stretchable electrode and discrete WO_3 islands were electrochemically deposited to serve as the electrochromic layer.

4.2 Experimental methods

4.2.1 Fabrication of the stretchable electrode

Ag nanowires with diameters of around 114 nm and lengths 31.2 μm at the concentration of 1 mg/ml were vacuum filtered onto a polycarbonate filter membrane to form a conducting network. Then PDMS with uniformly mixed curing agent at the weight ratio of 10 to 1 was poured onto the filtered Ag nanowires network followed by degassing in a desiccator until no bubble was seen. The mixture was then cured in an oven at 60 $^{\circ}\text{C}$ for 2

h to form the solid elastomer conductor which was then peeled off from the filter membrane with the Ag nanowires embedded into the elastomer matrix.

4.2.2 Fabrication of the wearable electrode

To integrate the stretchable electrode with fabric textiles, a piece of cotton fabric was settled on top of the liquid PDMS before curing. The thin interface where liquid PDMS infiltrate into cotton matrix works as the bridge to link the transferable stretchable electrode to the fabric surface after the interface was cured.

4.2.3 Electrochromic layer

WO₃ was electrochemically deposited onto the stretchable electrode in a three electrode configuration with Ag/AgCl as the reference electrode and Pt as the counter electrode. The deposition solution was prepared by dissolving 1.8 g tungsten powder into 30 wt% H₂O₂ solution to form the perexy-tungstate (PTA) acid. The electrochemical deposition was conducted at -0.5 V on an electrochemical work station.

4.2.4 Characterization:

The structure and morphology of the electrodes were investigated using FESEM. The resistance of the stretchable electrode at different tensile strain was measured by stretching the sample on a homemade stretching stage. To test the electrochromic performance, a hollow PDMS casing was adopted to contain the H₂SO₄ electrolyte, electrochromic electrode and the Pt counter electrode. A backing layer with two binder clips was placed behind the stretchable electrochromic electrode to fix it at desired tensile strain for quantitative measurement. The electrochromic performance was characterized in reflective mode inside an integrating sphere attachment on a UV-vis spectrophotometer. The device was driven between -1.8 V and -0.5 V for color switching with the voltage supplied from Solartron 1470E.

4.2.5 Diffusive reflectance testing:

Depending on the optical property of the device and the required application, both transmissive and reflective electrochromics have been highly demanded for typical applications like smart windows and paper-like displays respectively. The assembled

device was placed at the sample position of an integrating sphere attachment inside a UV-vis spectrophotometer to integrate the diffusive reflectance signal.

4.3 Results and discussions

4.3.1 Stretchable electrochromic electrode characterization

The degassing of PDMS liquid on the pre-filtered Ag nanowire network removes air bubbles that might otherwise forms cavity defects in the later solidified stretchable matrix, which severely restricts the potential stretchability due to crack growth along the defects. At the same time, the removal of the air allow PDMS liquid to infiltrate into the Ag nanowire network and encompass the conducting structure for a successful embedding effect and transfer the Ag nanowires into the elastomer matrix.⁹ The as fabricated Ag nanowire electrode in PDMS is able to be stretched without observable delamination and physical separation of the conducting elements from the elastomer matrix as shown in figure 4.1 a and b. The stretchable electrode also maintains the high conductivity throughout the stretching cycles which would be discussed later. This suggests that PDMS infiltrated into the open space between nanowires without breaking the junctions which would otherwise lead to loss of the conducting path and the overall conductivity.¹⁰
¹¹ The filtration of the conducting network followed by the embedding transfer method provides a facile and superior method to fabricating conductive composite with the conventional physical mixing method in that a highly connected conducting network could be preserved inside the composite that results in a low resistance of only 4.5 Ω while a physical mixing usually suffers from a poor conductivity due to insufficient percolation.¹ At the same time, the embedded transfer resulted in a robust electrode with the Ag nanowire network tightly integrated with the substrate matrix with high mechanical stability that allow it to survive scratching and tape peeling. This is in stark contrast with some of the bulked structure in that the loosely adhered bulked material suffers from dislodgement from the supporting substrate to accommodate the strain.^{1, 12, 13} This might impose concerns on electrode stability for a stable supply of electrical current during deformation.¹⁴ The microstructure for top and cross view of the embedded structure is shown in figure 4.1 c and d. Exposed Ag nanowire tips could be found on the

elastomer surface and this serves as the path for electron transportation. On the cross section view, a clearly embedded layer of the conductive network could be observed.

Figure 4.1 The stretchable Ag nanowire electrode at a) relaxed and b) stretched state without Ag delamination; and the SEM images for the c) top and d) cross section view of the stretchable electrode.

The schematic for the electrochromic electrode was shown in figure 4.2 a. The obtained pattern for display is realized through a lithographic filtration on patterned PDMS mask. Ag nanowires network was adopted due to its ability to realign to the tensile direction by overcoming the inter-wire sliding friction. SWCNT network as an alternative for stretching application^{15, 16} on the hand has a poor conductivity for reversible redox reactions.¹⁷ WO_3 as the electrochrome was electrochemically deposited onto the conductive electrode from the peroxy-tungstate acid (PTA) precursor solution. It was selected as the electrochrome due to its high optical contrast, good chemical and cycling stability. Like ITO and Si, WO_3 is brittle with a low tolerance for strain; a continuous film deposited, through for example sputtering and evaporation cannot be stretched. Realization of stretchability for WO_3 can be achieved through structure engineering. A controlled electrochemical deposition facilitates the formation of WO_3 along the conductive Ag nanowire tips. The surface of PDMS is hydrophobic with a low surface free energy that causes difficult wetting of the precursor and is unsuitable for the

nucleation growth of WO_3 . The combined factors lead to discrete WO_3 islands that scatter across the surface following the shape of tipped Ag nanowires as shown in figure 4.2. The finally obtained discrete WO_3 island structure was deposited at -0.5 V in a three electrode setup vs. Ag/AgCl for 200 s.

The discontinuous island structure is in turn beneficial for the stretching purpose due to the aligning of the island orientation to the tensile direction to accommodate strain instead of taking physical elongation that would result in crack formation. The electrochromic electrode shows a good mechanical compliance and can be twisted and crumpled. The robust electrode functions as a promising candidate for futuristic stretchable and wearable display applications.

Figure 4.2 a) The schematic of the stretchable electrochromic electrode; and the device being b) twisted and c) crumpled; d), e) demonstration of the functionality of the stretchable electrochromic electrode at relaxed and strained condition; SEM images of the discrete island structured WO_3 at f) top and g) tilted cross view.

4.3.2 Study of the electrochromic performance

As mentioned earlier, the reflective test was done in a two electrode configuration with the stretchable electrochromic electrode as the working electrode and Pt as the counter electrode. The electrolyte was 0.5 M H_2SO_4 . The whole device was assembled inside a

homemade PDMS casing and placed in an integrating sphere for the reflectance measurement. To drive the device for optical modulation, voltage between -1.8 V and -0.5 V was selected. One important care that needs attention is that the oxidation peak for Ag nanowire needs to be avoided. Unlike noble metals such as Au and Pt, Ag with a high activity is prone to lose its electron and get oxidized in an electrochemical reaction. The oxidation could be sensitively affected by the morphology¹⁸ as well as the electrolyte.¹⁹ In H_2SO_4 environment, the oxidation is proposed to occur through:²⁰ $\text{Ag}_2\text{SO}_4 + 2\text{e}^- \leftrightarrow 2\text{Ag} + \text{SO}_4^{2-}$. An oxidation peak at 0.15 V was observed as shown in figure 4.3 which is avoided by restricting the bleaching potential below it.

Figure 4.3 The CV curve scanned for the Ag nanowire electrode in 0.5 M H_2SO_4 electrolyte against Pt counter electrode. An oxidation peak at around 0.15 V was observed.

The relative reflectance was normalized to the bleached state of the electrochromic electrode to better reflect the relative change of optical modulation and the contrast ratio. As can be seen from figure 4.4, the reflective spectrum features two regions with enhanced reflectance from 300 to 400 nm and reduced reflectance from 400 nm upwards. This is consistent with the previous discussions that the absorption of the red light component leads to the reflected observed blue color. Since the reflection peak at 350 nm leads to a larger contrast compared to the absorbed red light region, the reflective performance was studied at this wavelength. The switching time is defined as the time required obtaining 90% optical modulation. Based on the dynamic switching curve and

enlarged view of the switching cycle in figure 4.4 b,c, a fast response of 1 s and 4 s was determined for the coloration and bleaching process respectively.

The reflectance change is due to the redox reaction coupled with proton intercalation and de-intercalation that changes the absorptivity as well as the electrochrome concentration. This leads to the absorbance to vary and correspondingly the change of the reflectance. The coloration efficiency that reflects the ease and practicability of such modulation through intercalation is determined by $\eta = \Delta OD / (Q/a)$, $\Delta OD = \log (R_b/R_c)$ where ΔOD is the change of optical density and Q/a is inserted charge density. A fitted slope for the linear region results in a coloration efficiency of $12.6 \text{ cm}^2/\text{C}$. The obtained coloration efficiency is relatively small compared to that from transparent devices ($16\text{-}100 \text{ cm}^2/\text{C}$)^{21, 22} for the reason that apparent absorbance is adopted for this characterization. The coloration efficiency can also be tuned by optimizing the deposition condition that affects the morphology and crystal structure of the electrochrome.^{21, 23, 24} The electrochemical stability of the electrochromic devices was also investigated by cycling the device between -1.8 V and -0.5 V for 100 cycles (figure 4.4 e). A good retention of 81% of the contrast could be achieved.

Figure 4.4 Study of the electrochromic performance of the stretchable device at the relaxed state. a) the reflective spectrum for contrast study; b) the switching between colored and bleached states; c) switching time study at one full cycle; d) coloration

efficiency test; e) stability over 100 cyclic switching; f) calculation of the contrast retention after 100 switching cycles.

To apply this novel device for stretchable display applications, the performance on-strain needs to be investigated. The comparison between the relaxed and strained states is conducted. To enable the tensile strain, binder clips was utilized to fix the device to the desired strain level inside the homemade casing. The schematic for the strained device was shown in figure 4.5 a. To enable better stretchability with thinner WO_3 islands, reduced deposition time to 120 s was adopted for the new devices. The digital photo for the working device subjected to reflective testing at 50% strain was shown in figure 4.5 b.

Figure 4.5 a) the schematic cross section structure for the on-strain device with the backing and binder clip to fix the strain; b) Digital photos for the stretched device with proper functionality at 50% strain.

The reflective spectra for the configured device at relaxed and 50% stretched state were collected and shown in figure 4.6. The difference in the deposition condition resulted in new spectra features due to the incurred change of wavelength and thickness dependent absorbance and correspondingly the contrast ratio. A larger contrast and contrast ratio at 633 nm absorption wavelength compared to the 350 nm reflective wavelength was observed (figure 4.6a). The contrast slightly reduced from 56% at 633 nm at relaxed state to 50% upon stretching. The reduced optical modulation is expected from the increased resistance of the underlying electrode which reduces the effective driving over-potential upon increased resistance. The larger resistance is also responsible for a slower kinetics (figure 4.6 b). The switching time was 2.25 times (from 4 s to 9 s for coloration) and 1.72

times (from 25 s to 43 s for bleaching) longer for the strained state compared to the relaxed state as reflected by the less sharp switching curve for the stretched sample.

Figure 4.6 a) Comparison of the spectra at relaxed and 50% strained state for the device; b) comparison of the switching time between these two states.

To check the variation of the electrode resistance that accounts for the slightly reduced performance, a home-build stretching stage was adopted to fix the stretchable electrode to the required tensile strain for resistance testing (figure 4.7 a,b). The stretchable electrode was progressively stretched to 50% tensile strain while the on-strain resistance was measured. A gradual increase of the resistance (figure 4.7 c) with enlarged strain was observed due to the inter-sliding of the Ag nanowire that affects the junction contacts under strain.¹¹ When tested for cyclic stretching, the resistance of the electrode at both strained and relaxed states gradually stabilized after 30 stretching cycles (figure 4.7 d). Although the resistance was observed to increase upon stretching which results in a degraded device performance, the final resistance and the increment in resistance for the embedded stretchable electrode (from an initial 5 Ω to a final 20 Ω after 100 stretching cycles) was quite small and tolerable for a relatively stable device performance compared to many other stretchable electrodes of different structures that change resistance sensitively upon strain due to insufficient contacts.²⁵⁻²⁷

Figure 4.7 a), b) Photographs for the home-build stretching stage for the characterization of the resistance for the stretchable electrode at different strain; c) the resistance variation of the electrode with different tensile strains; d) Cyclic stretching for 100 cycles of the electrode from relaxed state (0%) to 50% strain to track the electrode resistance change.

The mechanical stability of the stretchable electrochromic device against repeated stretching was also investigated. The device was stretched to 50% for 30 cycles and its performance was recorded. A more obvious drop of contrast was observed compared to the pristine sample (figure 4.9 a). During cycling, observed increase of the bleached state reflectance gradually surpassing the background baseline suggests delamination of the WO_3 islands from the electrode and this causes the gradual loss of reflective contrast in the following cycles as shown in figure 4.8 b. During stretching, the length of the device along the tensile strain direction increases while the lateral dimension reduces as determined from the Poisson ratio. This pushes the non-continuous WO_3 tighter and increases the chances of delamination off the electrode surface. Adhesion of the deposited electrochrome on the stretchable substrate needs to be enhanced in the future

through annealing, or surface functionalization²⁸ etc. for better practicability and durability of the device.

Figure 4.8 a) The reflectance of the device after 30 stretching cycles to 50%. b) Switching curve of the device at 0% and 50% strain after 30 stretching cycles to 50%.

Figure 4.9 a) The schematic structure of the implantable wearable electrochromic electrode; b) demonstration of individually addressed wearable electrochromic pixels with good mechanical compliance.

Electrochromism is highly promising for futuristic displays for due to its low power consumption and large contrast. Wearable electrochromic display with great mechanical compliance that allows compatibility with human motion and large deformation is a compelling concept for the next generation deformable displays. Often appearing in fiction movies, wearable electrochromic display is an emerging topic with popularity but insufficient development due to the rough woven fabric structure that leaves difficulty on processibility and poor electrochromic performance with little contrast.^{29, 30} With the development of the herein discussed stretchable electrochromics, implantable wearable electrochromic display with good contrast was realized. Pixels that could be individually addressed were patterned on the stretchable PDMS electrode which was successfully

implanted onto the cotton fabric textile (figure 4.9). The pixels can be switched on separately or in any directed combination. The wearable fabric was robust and maintained the functionality even after crumpling. As a proof of concept, only three pixels were included. However, it serves as a good guidance for futuristic devices that could incorporate wearable transistors and wearable electrochromic pixels for unprecedented display applications with precise control and robust mechanical stability.

4.4 Conclusions

The strategies for the realization of a well-functioning stretchable and wearable electrochromic display device were discussed. The large optical modulation of such device results from the highly conductive and stretchable electrode with the well-connected percolating Ag nanowires preserved by embedding into the elastic matrix. The electrode delivers a stable and low resistance below 20 Ω through repeated stretching cycle to 50%. Structure engineering via controlled deposition of non-continuous WO_3 islands was conducted. The reflective electrochromic device delivers fast switching response and stable cycling. The device maintains a good working condition even at 50% strain which is unreachable for conventional electrochromics. Finally a robust wearable textile with patterned display was demonstrated. The successful demonstration of the stretchable and wearable electrochromic display with the reported techniques lays a solid background for the rational design of the next generation deformable electrochromic devices that may find wide applications in areas like display, camouflage and even fashion industries.

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Chapter 5

Foldable Electrochromics Enabled by Nanopaper Transfer Method

A facile and versatile nanopaper-transfer method is discovered. This novel transfer method can be applied to transfer a broad range of functional materials by leveraging the high surface free energy of nanocellulose. With this method, Ag nanowires transparent conductors can be fabricated with a high figure of merit. The excellent mechanical compliance as well as the unique surface properties of nanopaper makes possible the realization of foldable electrochromics with excellent optical modulation capability. Furthermore, the foldable electrochromic device is able to preserve the functionality through cyclic folding. The herein reported technique along with the foldable electrochromics shows great promise and potential for the next-generation deformable displays.

5.1 Introduction

The ever growing requirements from the next-generation electronics demand more mechanical compliance with functionalities like stretchability and foldability in order to survive in harsh working conditions. The imparted foldability to electrochromics is a compelling idea and may extend the range of traditional electrochromics to applications like foldable display, camouflage coating, portable electronics etc.

As a promising conductive electrode to support electrical current to drive electrochromic devices, conductive metallic wires such as Ag nanowires based percolating network has been shown with good deformation capability. However, the reported electro-optical performance for solution processed Ag nanowires TCE with a typical value of $\sim 10 \Omega/\text{sq}$, $\sim 85\%$ as discussed in chapter 2.1.2 is still below the high quality standard ($>90\%$, $<10 \Omega/\text{sq}$)¹ to cater for the stringent requirements for futuristic large area, fast responsive, low power consumption, deformable electronics.

Besides the conductive element, the substrate to hold it also needs to be highly deformable in order to survive external disruptions for the conductor as a whole. Traditional and common flexible substrates like polycarbonate (PC) and polyethylene terephthalate (PET) have dominated the market for years. The idea of naturally derived nanocellulose and nanopaper as a new type of substrates in place of the petroleum based plastics is gaining great steam recently. The abundance source, degradability, biocompatibility and excellent mechanical strength and flexibility make it a competent candidate for foldable electronics. Cellulose is claimed to be the most abundant biomass on earth and nanocellulose could be extracted from plants like cotton linters, wood pulps, ramie fibers, hemp etc. or secreted by bacteria. Tempo assisted oxidation,² enzyme treatment³ as well as physical liberation⁴ methods have been reported so far to efficiently liberate the plant cellulose bundles into fine nanocellulose fibrils by splitting the hydrogen bond interaction originated from the hydroxyl groups on the cellulose chain as shown in chapter 2.1.3 while bacteria cellulose nanofibril could be cultured from selected strains like *Acetobacter Xylinum*. When the diameter of the fiber reduces from micrometer range to nanometer range, the increased fiber-fiber interaction leads to enhanced mechanical strength. The reduced light interactive cross section area leads to

suppressed back light scattering and enhanced transparency.⁵ Besides, the good stability under high temperature ($>180^{\circ}$) without decomposition and a low thermal expansion coefficient of $5\text{-}10\text{ ppm K}^{-1}$ makes the nanopaper compatible with a broader range of possessing techniques,⁶ which is far more superior to common plastics like PET. Moreover, the hydrophilic nature of the hydroxyl terminated nanocellulose chain is advantageous for printing and coating of functional materials that shows great promise for industrial scale up.⁷ The affinity with water has also been reported to be beneficial for enhanced electrochemical reactions with the substrate base serving as the electrolyte reservoir.^{8, 9} Furthermore, the polar hydroxyl group terminated surface endows the nanopaper with a strong adhesion property to functional materials which plays a critical role in the nanopaper transfer method for the realization of a compact high quality Ag nanowire TCE which would be discussed later. A table summarizing the above mentioned properties is shown in Table 5.1.

Table 5.1 Summary of the characteristic physical properties of nanopaper resulting from the nanoscale dimension of the assembled cellulose

Properties	Parameter value
Transparency	$\sim 90\%$ ^{10, 11}
Thermal stability	$>180^{\circ}$ ⁶
Thermal expansion coefficient	$5\text{-}10\text{ ppm K}^{-1}$ ⁶
Young's modulus	$7\text{-}21\text{ Gpa}$ ^{11, 12}
Tensile strength	$20\text{-}300\text{ Mpa}$ ¹³
Oxygen permeability	$0.0005\text{-}0.6\text{ ml.}\mu\text{m/m}^2\cdot\text{day.kPa}$ ¹⁴
Water vapor transmission rate	$167\text{-}234\text{ g/m}^2\cdot\text{day}$ ¹⁴
Printability	Excellent
Bendability	Excellent

5.2 Experimental Methods

5.2.1 Nanopaper electrode

0.5 g physically liberated nanocellulose in 3 wt% gel form was dispersed and stirred well in 100 ml DI water. Ag nanowires diluted to 0.025 mg/ml in ethanol was adopted for the deposition of the conductive layer. Vacuum filtration for the deposition of a uniform layer was utilized. Ag nanowires filtered to a polycarbonate membrane serves as the first conducting layer. Subsequently, the prepared nanocellulose suspension was gently filtered on top of the conductive layer. The two layers were then sandwiched between glass slides and subjected to heating in an oven of 105 °C to evaporate the water and assemble the nanocellulose fibrils. Finally the dried nanopaper was peeled off the filter membrane and the Ag nanowires could be successfully transferred to the nanopaper surface. The schematic for the transfer process is shown in figure 5.1a.

5.2.2 WO₃ Deposition

WO₃ was electrochemically deposited onto the conductive nanopaper surface from the PTA precursor, which was prepared by dissolving tungsten powder of 1.8 g in 30% hydrogen peroxide solution. A three electrode setup with the deposition voltage set at -0.7 V vs. Ag/AgCl reference was configured.

5.2.3 Characterization

Field Emission Scanning Electron Microscopy (FESEM) was utilized to investigate the structure and surface morphology of nanocellulose and nanopaper. Atomic Force Microscope (AFM) in tapping mode was used to measure the surface roughness of the fabricated nanopaper. The conductivity of the electrode is reflected by measuring the sheet resistance of the nanopaper electrode on a CMT-SR2000N four point probe. UV-vis spectrophotometer (Shimadzu UV-3600) with an integrating sphere attachment was used to collect the data for sample transparency.

5.2.4 Testing of the electrochromic performance

A two electrode configuration was adopted with the electrochromic nanopaper as the working electrode and Pt as the counter electrode for the performance testing. The optical modulation was switched between -1.8 V and -0.2 V in 0.5 M H₂SO₄ electrolyte. The working and counter electrode as well as the electrolyte were contained in a home-made PDMS casing for the measurement of the optical property. The electrochromic

performance was characterized in reflective mode with the relative reflectance gathered inside the integrating sphere.

5.3 Results and discussion

The physically liberated cellulose nanofibril (PCNF) can be filtered and assembled into transparent nanopaper. Apart from the vacuum filtration method, techniques like resin impregnation into nanocellulose aerogel; casting of dilute nanocellulose suspension followed by air drying; and centrifugal casting have been adopted for the fabrication of transparent nanopaper. Compared to the mentioned techniques, the vacuum filtration method shows combined advantages of fast fabrication (~ 1 h) compared to the suspension casting method that usually takes 1-3 days;⁶ facile operation and obtained higher transparency of the nanopaper as compared to the resin impregnation method which involves freeze drying followed by resin curing;^{15, 16} and no specific requirement on the concentration of the nanocellulose suspension which needs to be controlled in the centrifugal casting method to obtain a planar and smooth surface of the nanopaper.¹⁷

Due to the liberation through high pressure homogenizer, much smaller nanofibrils compared to regular cellulose fibrils can be obtained (figure 5.1 b and c). The average diameter is calculated to be around 22 nm (figure 5.1 d) while in comparison, the regular Kim Wipes cellulose fibril has a much larger diameter in the range of 15-60 μm . The phenomenal reduction in dimension is beneficial in multiple aspects. Due to reduced size and correspondingly larger fiber-fiber interaction through hydrogen bonding, the mechanical strength is much stronger with larger Young's Modulus and tensile strength compared to regular paper.^{11, 18} The smaller diameter of the fiber with much denser structure with less air cavity inside the paper matrix also leads to a smaller degree of incident light scattering¹⁵ and this helps deliver a more transparent optical property as shown by the digital photo in figure 1e while regular paper usually gives an opaque quality. The diffusive transmittance is measured to be as high as 88.1% at 600 nm which is comparable with a commercial glass slide of 90.9% (figure 5.1f) and the nanopaper obviates the short wavelength absorption that is characteristic of glass; this is beneficial for many optoelectronic applications responsive to the ultraviolet light such as photodetectors and solar cells. However, due to the existence of haze, when the

nanopaper is placed 20 mm away from the detection window the transmittance drops to 60.8%.

Figure 5.1 a) The schematic procedure for the nanopaper transfer process for the fabrication of transparent conductors; b) the SEM image of the PCNF nanopaper; c) the SEM image of a Kim Wipes regular paper with diameter in the range of 15 to 60 μm; d) measurement of the nanofibril average diameter; e) a digital photograph demonstrating the transparency of the PCNF nanopaper; comparison of the transparency between PCNF nanopaper and a commercial glass slide at f) 0 mm from the detector and g) 20 mm from the detector.

The existence of haze is strongly dependent on the nanopaper surface roughness,¹² through the tuning of which nanopaper could be changed from a hazy to clear texture. The root mean square (RMS) of the PCNF nanopaper was measured on an AFM. The area scanned increased from $1 \times 1 \mu\text{m}^2$ to $10 \times 10 \mu\text{m}^2$ (figure 5.2). The data indicates that

when the scanned area is small (1×1), the RMS could be as low as 5.5 nm which is even comparable to plastic PET.⁵ However, when the scanned area increases, the RMS sharply rises to 33.0, 65.6, 68.1 nm for $3 \times 3 \mu\text{m}^2$, $5 \times 5 \mu\text{m}^2$ and $10 \times 10 \mu\text{m}^2$ respectively. The not fully liberated large fibers were found to be included with enlarged scanning area and they contributed to the large surface roughness. Depending on the purpose for specific applications, haze property is considered differently in its value with high clarity display requiring minimum haze ($< 20\%$) while solar cell and reflective panel favors a larger haze ($> 60\%$) for better performance.^{5, 18}

Figure 5.2 RMS measurement for areas scanned by a) 1×1 ; b) 3×3 ; c) 5×5 ; d) $10 \times 10 \mu\text{m}^2$.

A high haze value of 83.7% was measured for the PCNF nanopaper. To visually reflect the haze of the prepared PCNF nanopaper, the scattering angle was estimated. A laser point was projected through the nanopaper surface and it left a scattered circle on the background. The laser point is 0.3 cm in diameter and the PCNF nanopaper was held parallel 30 cm away from the background. The scattered ring has a diameter of 11.75 cm, which leads to a calculated scattering angle of 21.6° (figure 5.3).

Figure 5.3 The digital image of the created scattered ring for the scattering angle measurement.

The conductive element has to be included onto the PCNF surface to make it into a transparent conductor. Superior to the traditional transfer technique, a donor substrate with very low surface free energy was used to facilitate an effective transfer (while in most cases, PDMS stamp is used).¹⁹⁻²² The nanopaper transfer method discovered is able to work with a broader range of surfaces with different surface energies and still guarantee a successful transfer of the functional materials to the destination substrate. The mechanism is herein discussed. The work of adhesion of a certain functional material layer on a specific substrate can be described by the Dupre equation,^{23, 24} $W_{FD} = \gamma_F + \gamma_D - \gamma_{FD}$, where γ_F refers to the surface free energy of the functional material, γ_D refers to the donor substrate surface free energy and γ_{FD} refers to the interfacial free energy between the donor and the functional materials. To simplify the model by only considering London Dispersion force that characterizes intermolecular forces,^{20, 25} γ_{FD} could then be expressed as $\gamma_{FD} = \gamma_F + \gamma_D - 2\sqrt{\gamma_F \gamma_D}$. Thus the work of adhesion can be reorganized into $W_{FD} = 2\sqrt{\gamma_F \gamma_D}$.

To ensure an effective transfer, the work of adhesion of the functional material on the donor substrate needs to be smaller than that of the functional material on the target substrate. This necessitates a larger surface free energy of the target substrate than the donor substrate.

The structure of the nanocellulose polymer chains with abundant hydroxyl terminals determines a potentially good target substrate. The polar hydroxyl group is regarded as a

good contributor to high surface energy with exceptional wetting ability.^{26, 27} The disintegration of regular cellulose fibers into individual cellulose nanofibril further enhances the surface density of the polar terminals. Furthermore, the removal of part of the amorphous regions during fiber liberation further enlarged the surface free energy of the resulted nanofibrils. The surface free energy value of surfaces commonly dealt with in the lab was compared with nanocellulose (Table 5.2) to reflect the efficiency and potential of such target substrate for transfer applications.

Table 5.2 The surface free energy of some frequently adopted surfaces.

Material	γ_s (mJ/m ²)
Nanocellulose ^{26, 28}	> (53 – 116)
Polydimethylsiloxane (PDMS) ²⁹	19.8
Polycarbonate (PC) ³⁰	42.3
Polytetrafluoroethylene (PTFE) ²⁵	21.8
Polyethylene terephthalate (PET) ³¹	44.0
Polyvinyl acetate (PVA) ³²	38.5
Polyvinyl pyrrolidone (PVP) ³³	46
Polyvinylidene fluoride (PVDF) ³⁴	25.7
Polymethyl methacrylate (PMMA) ²⁰	38
Aluminum foil ³⁵	39.4

Notably, the demonstration of the nanopaper transfer in this study is based on polycarbonate as the donor substrate of a high surface energy around 42 mJ/m², which is more than doubled of PDMS surface energy. As a control experiment to study the importance of surface free energy in the determination of the effectiveness for the transfer, SWCNT or graphene was adopted as the functional material for the transfer test. They were selected because they tend to aggregate into dense films after filtration which prevents PDMS or nanocellulose to infiltrate inside, which causes physical entanglement that complicates the transfer mechanism. When liquid PDMS was poured onto the filtered SWCNT/graphene forming a conformal surface followed by curing, the thin graphene would remain intact on the polycarbonate surface (schematic shown in figure

5.4 a). This demonstrates the difficulty of transferring from high energy donor to low energy target. On the other hand, to prove the ease of transfer from low energy donor to high energy target, Ag nanowires were deposited onto PTFE followed by a simple contact on the nanopaper surface initiated by a normal writing pressure and this could easily result in a successful transfer (schematic shown in figure 5.4 b).

Figure 5.4 a) Transfer test from high energy donor to low energy target; b) transfer test from low energy donor to high energy surface.

As a result of the high surface energy of nanocellulose and the transfer kinetics that creates a conformal contact through bottom up manner by forming a seamless interface through vacuum filtration, the nanopaper transfer method was proven to be versatile and effective for a broad range of functional material transfer. Structures that span from 0D to 2D were shown in figure 5.5 with exemplary materials of SWCNT nanotube, graphene nanosheet and ZnO nanoparticles.

Figure 5.5 Structures transferred to the PCNF using the nanopaper transfer method with SWCNT, graphene and ZnO shown respectively.

Figure 5.6 a) the spectra of the nanopaper TCEs of varied sheet resistance; b) the electro-optical performance of the obtained TCEs; c) the comparison in transparency between the nanopaper electrode of 5.83 Ω/sq and commercial ITO/glass of 15 Ω/sq ; d)-f) the FESEM images of the Ag nanowires on nanopaper TCEs at various resistance.

When Ag nanowires percolating network is transferred to PCNF, transparent conductive electrodes can be obtained. Ag nanowires of various amount and areal densities were transferred and the sheet resistance spans across 630 Ω/sq to 0.75 Ω/sq with a denser network showing a lower resistance due to more continuous electron pathway; and a lower transmittance due to stronger absorption, the trend of which was shown in figure 5.6 a, b. The spectra of various PCNF electrode of different sheet resistance was recorded in figure 5.6 a. The hump at around 330 nm for the spectra is related to the characteristic Plasmon resonance of Ag.³⁶ Typical SEM images showing the transferred Ag of different resistance was shown in figure 5.6 d-f. The obtained PCNF electrode with 5.83 Ω/sq was compared with a commercial ITO/glass of 15 Ω/sq (figure 5.6 c). The nanopaper electrode shows a comparable transmittance level in the visible range and a much higher conductivity, which makes it a promising ITO substitute with excellent electro-optical properties.

The transparency of various samples of accordingly different resistance at 600 nm was tabulated in table 5.3 and shown in figure 5.6 b previously. It could be observed that at the less conducting region, a small sacrifice of transparency is able to bring in a large

reduction in sheet resistance because the Ag network of low percolating intensity is sensitive to the construction of new electron pathways and the effective conductivity of the network would be gradually approaching the bulk conductivity of the final film.^{37, 38} After the transition from percolating network to bulk film, the conductivity enhancement levels off and the conductor enters the second region where a small reduction in resistance contributes to exponential reduction in transparency. The trend figure is helpful for the choice of conductor of desired property.

Table 5.3 The opto-electrical properties for samples of different sheet resistance.

Sample Ω/sq	0.75	1.45	4.2	5.83	30.6	59.7	630
Transparency %, 600 nm	55.9	68.8	79.4	81.9	83.9	84.5	84.9
Transparency subtracting nanopaper background %, 600 nm	63.5	78.1	90.1	92.9	95.2	95.9	96.4
f.o.m	986.0 Bulk	988.2 bulk	838.8 percolative	862.0 percolative	247.4 percolative	149.3 percolative	16.2 percolative

The quality of a transparent conductive electrode can be reflected by its figure of merit (F.O.M). There are various forms F.O.M among which the contemporary electro-dynamically derived σ_{dc}/σ_{op} as the figure of merit is receiving good popularity and offering insightful assessment of the electrode, where σ_{dc} and σ_{op} refer to DC conductivity and optical conductivity respectively. The figure of merit can be obtained from the following equation: $T = (1 + \frac{188.5}{Rs} \frac{\sigma_{op}}{\sigma_{dc}})^{-2}$,³⁷⁻³⁹ where σ_{dc}/σ_{op} is a dimensionless figure with a larger value indicating a better quality.

The calculated figure of merit value for each sample is shown in table 5.3, a high value of 988 is obtained which is superior to the previously reported best value of 500, which was obtained from Ag nanowires network filtrated on ester membranes followed by etching the membrane and transfer of the network to PET.³⁷ The excellent performance results from the nanopaper transfer process in which a conducting network that keeps a good interconnection was first formed on the filter paper; the nanocellulose then forms a conformal ‘cake’ to cover the conductive network; after this the drying process

evaporates the water and initiates the compact nanopaper formation due to the strong hydrogen bond interaction during the transfer and this results in the compact structure of the conductive layer. Based on the sample of $0.61 \Omega/\text{sq}$, a sheet resistance reduction of 38.6% was observed after nanopaper transfer from the PC membrane. Compared to the traditional roll coated,⁴⁰ spin coated⁴¹ or spray coated⁴² electrode with the Ag nanowires connected after solvent evaporation where the junction resistance issue impedes good conductivity, the nanopaper transfer method with the formation of a compact structure is believed to be beneficial for such a good figure of merit.

A few things to be noted for the figure of merit, it is a constant dimensionless value for a certain system as determined by the deposition method and the conductive material itself, thus it is a good indicator to assess the electrode quality. However, the figure of merit value is calculated when bulk conductivity is obtained; and for the percolating type network if the conductivity is still in the percolating region, the calculated figure of merit would keep increasing and finally saturates until the percolation to bulk transition is completed.³⁸ As a result, the calculated data in table 5.3 has been differentiated and stipulated as bulk/percolation for distinction.

Now that the electrode is fabricated through the transfer method, the mechanical deformation ability needs to be investigated. The foldability of transferred electrode is studied through cyclic folding. The nanopaper electrode with a thickness of $15 \mu\text{m}$ as shown in figure 5.7 a is folded to a radius as small as $5 \mu\text{m}$ (figure 5.7 b).

Figure 5.7 a) the cross section of the fabricated nanopaper ; d) the nanopaper was able to be folded to an extremely small radius of $5 \mu\text{m}$.

The protocol for the folding procedure is defined (figure 5.8 a). When the nanopaper is folded in a way Ag nanowires are pressed face to face, it is defined by -180° . On the other hand, if back to back, $+180^\circ$ is defined. The cyclic foldability test was conducted in a sequential manner in which -180° folding was conducted for 100 cycles followed by another 100 cycles at $+180^\circ$ (figure 5.8 d). The sample before folding bears a sheet resistance of $0.68 \Omega/\text{sq}$, and after 200 continuous folding cycles a high conductivity below $1 \Omega/\text{sq}$ could be maintained. In comparison with the brittle ITO, even a mild bending to 10 mm could be fatal for the maintenance of the conductivity.¹ The origin for the maintained low resistance of the nanopaper electrode is reflected from the SEM images for the foldable electrode. Ag nanowires with a malleable nature is able to deform with the foldable nanopaper substrate and the adhesion of the conductive elements is observed to be strong enough to avoid dislodgement even after the crease is formed; the high aspect ratio of the nanowire is also positive for constant inter-wire connection for good deformation ability. The combined factors lead to the observed strong endurance to repeated folding. The foldability of the conductor was demonstrated visually by connecting the conductor to LED circuits and observing the light before and after folding. Constant light could be seen after even crumpling of the nanopaper electrode (figure 5.8 e,f).

Figure 5.8 a) the schematic for the folding procedure of the nanopaper electrode; SEM images for the folded electrode at b) -180° and c) $+180^\circ$; d) Variance of the electrode sheet resistance against cyclic foldings; The nanopaper electrode connected with LEDs e) before and f) after crumpling the electrode.

The deformation ability of the nanopaper electrode with its strong preservation of the conductivity makes it an appealing component for foldable electronics. The concept of foldable electrochromics is realized based on the prepared electrodes with proper functionality. Patterned shape of the electrode from PDMS mask controlled filtration leads to designed shape of the electrochromic display after electrochemical deposition of WO_3 . The digital photo exhibiting the functionality of the non-emissive display is shown in figure 5.9 a, b.

Figure 5.9 The digital photos for patterned electrochromic nanopaper display in a) and b); c) the reflective spectra for the bleached and colored WO_3 device; d) long term cycling study of the device; e) enlarged cycles for switching time measurement; f) coloration efficiency test; and the study of folding cycles on g) reflective contrast and h) switching time.

WO_3 as the electrochrome has the ability to change its optical modulation ability through redox reactions that induces the change of its absorption behavior. The change in absorption leads to the variance of its reflectance. The equation to describe the reversible redox reaction is as follows: $\text{WO}_{3(\text{bleached})} + n \text{H}^+ + n \text{e}^- \leftrightarrow \text{H}_n\text{WO}_{3(\text{colored})}$. Relative

reflectance is required to characterize diffusive reflectance in an integrating sphere. WO_3 in the bleached state was referenced as the background so as to better reflect the contrast ratio and spectra shift as a result of the redox reaction.

The blue tint of the reduced WO_3 is due to the absorption of the red incident light and reflection of the short wavelength light, which leads to two distinct regions in the reflective spectra where the reflectance intensity was reduced from 400 nm to 800 nm and the reflectance was enhanced from 300 nm to 400 nm as shown in figure 5.9 c. The contrast was taken at 633 nm which represents a typical red wavelength and around which strong absorption takes place.⁴³ A good contrast of 41% could be observed.

The switching kinetic is studied by measuring the switching time which is determined as the time required for 90% optical modulation. The calculated result from an enlarged switching cycle in figure 5.9 e was obtained with a fast switching of 11.8 s for coloration and 20.1s for bleaching.

Cycling stability of the electrochromic nanopaper was studied by switching the device between -1.8 V and -0.2 V continuously for 500 cycles. For brittle inorganic materials, one the common issues involved during counter-ion electrolyte intercalation and de-intercalation is the expansion of the inorganic matrix which could result in peeling-off of the inorganic matrix from the conductive substrate.⁸ The cycling stability was regarded as an important factor in many electrochemical energy storage applications like supercapacitor and battery, apart from electrochromics. The ways to improve the cycling stability would thus be an interesting topic to push the devices closer for practical applications. Cellulose fiber with the hydrophilic nature and softness in water allow it to form wrinkled structures which is regarded effective in suppressing the internal stress from intercalation for better cycling stability.^{8, 9} The schematic for such process was shown in figure 5.10 a and b. The cyclic data (figure 5.9 d) shows a stable performance with 22% loss in contrast after 500 cycles. In comparison, the cycling test on elastic PDMS substrate suffers a relative quicker degradation in contrast with 20% contrast loss in only 100 cycles.⁴⁴

Figure 5.10 The schematics showing the formation of wrinkled structure for the alleviation of internal stress caused by intercalation in a) and b); c) the schematic demonstrating the two injection pathways for the electrolyte.

Besides the enhanced cycling stability, the hydrophilic nanocellulose fiber offers additional advantages for a better electrochromic display application such as the deposition coverage and the coloration efficiency. Compared to the hydrophobic PDMS substrate, a much more continuous film deposition could be obtained. Different from the previously obtained discrete WO_3 islands on PDMS, the insulating space between nanowires on nanocellulose were also covered by the WO_3 film as shown in figure 5.11 a, b. Although the discrete structure is beneficial for enhanced stretchability, a uniform deposition is favored for high resolution display application. The nanopaper surface with affinity to the aqueous precursor could sufficiently wet and even stores the precursor. The good wetting also facilitates the deposition and adhesion of the newly formed WO_3 seeds on the paper surface. At the cathodic deposition condition, WO_3 deposited would be spontaneously charged with a great rise in conductivity.^{45, 46} This further promotes lateral growth of the deposited film, which leads to the full coverage across the whole nanopaper surface.

Similarly, the hydrophilic nanopaper matrix is also beneficial for good coloration efficiency, which is defined $\eta = \Delta\text{OD}/q$; $\Delta\text{OD} = \log(R_{\text{bleach}}/R_{\text{colored}})$.

η refers to the coloration efficiency, ΔOD refers to the change in optical modulation which can be further expressed as a function of the contrast ratio and q is the charge density. A higher coloration efficiency represents a lower power consumption to obtain a certain color modulation and better practicability. The coloration efficiency is determined to be $34.8 \text{ cm}^2/\text{C}$, which is 3 times of the PDMS reflective device.⁴⁴ The enhanced coloration efficiency derives from the way counter-ions intercalate inside the

electrochrome.⁹ Distinct from other substrates, the nanopaper is hydrophilic and is able to function as an electrolyte reservoir to hold the counter-ions in the nanopaper matrix. The electrolyte counter-ion thus is able to infiltrate inside the electrochrome from inside and outside at the same time as shown by the schematic in figure 5.10 c. The two-way injection of the counter-ion would be beneficial for the chemical diffusion of the counter-ion and thus a better coloring condition.

The foldability of the electrochromic nanopaper as well as the folding influence on its electrochromic performance was studied. To enhance the foldability, the thickness of the WO_3 layer was reduced by controlling the deposition time to 30 s and this reduced the film from its original 3.4 μm to 1.6 μm as shown in figure 5.11 c and d. The folding pattern was fixed to -180° folding as shown in figure 5.10 g for cyclic folding test. The electrochromic performance was then tracked after 0, 5, and 50 cycles respectively. The pristine device (0 folding) gives a contrast of 23.2% and the smaller contrast compared to the previous study is due to reduced thickness. After 5 folding cycles, the contrast shows almost no change with a measured value of 22.9%. Repeated folding after 50 cycles leaves the device with a final contrast of 21.4% which shows its preserved functionality and only a small degradation of the optical modulation ability (figure 5.9 g).

The switching time at each recorded folding cycles was also investigated. Consistent with the contrast study, the switching kinetics for the pristine and 5 folding sample almost overlaps with T_{coloring} of 4.5 s and $T_{\text{bleaching}}$ of 11.2 s for the pristine sample and T_{coloring} of 4.8 s, $T_{\text{bleaching}}$ of 11.4 s for the device folded for 5 times. Even after 50 folding cycles, a slightly reduced switching rate was observed with T_{coloring} of 6.8 s and $T_{\text{bleaching}}$ of 13.2 s for the tested device.

The morphology of the folded electrochromic nanopaper was checked to understand the folding influence on its performance. WO_3 after the electrochemical deposition forms a rigid thin film over the underlying Ag nanowires. Unlike ductile Ag nanowire that is shown able to deform with the nanopaper, WO_3 is much more rigid and cracks upon the crease formation. After 5 folding cycles, a shallow crack can be distinguished shown in figure 5.11 e, though this has little effect on the electrochromic performance. However, after 50 folding cycles, WO_3 along with the underlying Ag nanowires were found to be

delaminated from the substrate. This delamination is probably caused by the protrusion of the rigid WO_3 that wraps around the Ag nanowires. The delaminated region as indicated by circles shown in figure 5.11 f results in some loss of active electrochrome as well as the conductivity across the crease. This causes the observed reduced contrast and slightly retarded kinetics. Overall, the influence of repeated folding on the degradation of the electrochromic performance is acceptable with the functionality of the foldable device well maintained.

Figure 5.11 a) the SEM image showing the uniform coverage of WO_3 on the nanopaper electrode; b) the magnified SEM view of the coated WO_3 ; c) the cross section view of the sample under 100 s deposition; d) the cross section view of the sample under 30 s deposition; e) the morphology of the sample after 5 folding cycles; f) the morphology of the sample after 100 folding cycles; g) the schematic for the folding of the electrochromic nanopaper.

5.4 Conclusion

In this chapter, a versatile and efficient nanopaper transfer method was discovered. This reported technique exploits an effective transfer method based on the surface free energy difference. This necessitates a larger surface free energy of the target substrate than the donor substrate, which is achievable with the hydroxylated fibrillated nanocellulose as the target. This nanomaterial transfer method provides tremendous opportunities for applications like conducting electrodes, sensor and display etc. Transparent conductive electrodes based on transferred Ag nanowires network with high quality and figure of merit was demonstrated. The electrode is foldable and maintains the excellent conductivity through cyclic folding. Finally, the concept of foldable electrochromic nanopaper was realized based on the foldable nanopaper electrode. The device shows a good performance in stability and coloration efficiency owing to the unique surface properties of the nanopaper. The electrochromic nanopaper was demonstrated to be properly working with good retention of its functionality even after 50 folding cycles. The presented nanopaper transfer technique as well as the foldable electrochromic nanopaper is promising for the development of the next generation deformable displays for e-paper and camouflage applications.

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Chapter 6

Highly Transparent Conducting Nanopaper for Foldable Solid State Electrochromic Devices

It is very challenging for the successful development of transparent solid state electrochromic device that could be folded at the whole device level. To realize such a device, every component in the electrochromic device has to be transparent and mechanically compliant to cater for folding applications. Nanocellulose is an attractive candidate as the substrate with excellent foldability, transparency and tailorable surface properties for the deposition of functional materials. In this chapter, transparent conductors made with nanocellulose/metallic nanowires deliver improved junction resistance from the nanopaper transfer method. Subsequently, a solid state slime containing the electrochrome was utilized as the optical modulating layer, the viscoelastic slime constructed from dynamic hydrogen bond breaking and formation removes physical constraints that might cause mechanical failure during folding. Finally, the concept of camouflage wearables on glove based on the foldable electrochromic device was demonstrated.

6.1 Introduction

Foldability of electronics as the limit of flexibility is under rigorous development recently as a valuable functionality aimed for portable futuristic devices, like foldable smart phone.¹ Some efforts from the deformable electronics research community have been observed in the development of foldable electronics like foldable circuit board prepared by thermal evaporation of metal thin films on conventional paper;² and foldable OLED based on Ag/graphene hybrid electrode on paper;³ and freestanding CNT film based Li-S battery etc.⁴ While demonstrated for the foldable purpose, issues like fast degradation of device performance with folding;³ low transparency of the foldable electrode⁵ and poor folding resistance² etc. need to be resolved for high performance foldable optoelectronic devices.

Electrochromic devices bear appealing attributes like low power consumption and large contrast ratio for display applications. It is thus of great interest to develop a freely foldable solid state transparent electrochromic device to cater for the stringent requirements for futuristic displays. The realization of such devices could bring value to many potential applications like foldable displays, camouflage wearables and even fashion industries.

To realize this concept of foldable electrochromic device, two major components require careful designs. The first one is the production of the transparent conductive electrode (TCE). As shown in the previous chapter, percolating metallic networks with the exemplary Ag nanowires network electrode shows great promise due to its potential high conductivity with its high carrier mobility and density. In addition, the formed ductile network shows a great resistance to mechanical rupture through inter-wire sliding^{6, 7}, which makes it compatible with folding and stretching applications. However, it has been pointed out that the large inter-wire junction resistance imposes great limitation to the overall conductivity. Approaches to address this for high quality conductors need to be developed. Furthermore, the low adhesion issue of the deposited network usually results in failure in devices applications due to loss of the conductive path from electrode delamination⁸. Facile and effective methods to address this also need to be discovered especially for deformable electronic applications.

The second component refers to the substrate that holds the conductive network. The substrate is required to possess high transparency, excellent mechanical strength and great deformation ability (such as foldability or stretchability depending on the applications). As discussed in chapter 5, nanocellulose and the derived nanopaper demonstrates great promise as a foldable substrate with excellent transparency, great mechanical strength, outstanding thermal stability and biodegradability, which makes the concept of adopting such renewable biomass for emerging electronics irresistible, in replacement of the otherwise unsustainable petroleum based plastics. Physically liberated cellulose nanofibrils (PCNF) were utilized for the preparation of nanopaper in the previous chapter. It was shown that the presence of ineffectively liberated coarse fibers led to the increased surface roughness and scattering angle. In this chapter, Tempo assisted oxidized cellulose nanofibril (TCNF) with finely exfoliated cellulose nanofibrils due to incorporated surface charge (figure 6.1) would be investigated to attain lower light scattering, high clarity nanopaper for transmissive mode electrochromic device application.

Figure 6.1 The comparison in molecular structure between pristine cellulose (left) and tempo mediated oxidized cellulose (right) where in the C₆ carbon position, the hydroxyl group is converted to carboxylic group.

6.2 Experimental methods

6.2.1 Fabrication of the nanopaper electrode

P3 SWCNT with carboxylic group was first diluted in DI to 1wt%, the suspension was subject to centrifugation at 10000 r/min for 5 mins. This process was repeated for 3 times before the top 10% supernatant was taken out. 0.5 ml of the taken clear suspension was further diluted in 20 ml DI water and mixed and stirred well with 0.25wt% sodium dodecyl sulfate for a better dispersion of the SWCNT induced by the surface charge from the surfactant. The obtained stable SWCNT has a nominal concentration of 0.024 wt%.

Ag nanowires dispersed in IPA with a diluted concentration of 0.025 mg/ml was adopted for the formation of the conductive layer. The SWCNT suspension was first filtered onto the polycarbonate filter membrane to form the first layer followed by the filtration of Ag nanowires to form the second conductive layer. Then tempo assisted oxidized cellulose nanofibril (TCNF) suspension was filtered to cover the previously obtained double layer. To control the nanopaper thickness, 0.5 g of 0.1 wt% TCNF gel diluted in 10 ml DI was used and filtered to form the nanopaper layer. Subsequently, after the filtration work was done the filter membrane along with the filtered structures were sandwiched between two glass slides and placed in an oven at 105 °C to evaporate the water and facilitate the nanopaper transfer process. After the nanopaper was dried, it could be peeled off from the filter membrane with the SWCNT@Ag structure transferred to the nanopaper surface. Alternatively, to obtain the neat Ag nanowire based electrode, SWCNT was excluded from the filtration step with the rest of the procedures kept the same. (The schematic was shown in figure 6.2) Notably, compared to the nanopaper transfer method discussed in Chapter 5, figure 5.1 a, two distinct changes are made: 1. TCNF instead of PCNF was utilized for the transfer process and 2. SWCNT was introduced for the creation of a hybrid SWCNT@Ag electrode. The resulted enhanced performance would be discussed in the following results and discussion section.

Figure 6.2 the schematic for the nanopaper transfer method to obtain the double layered transparent conductor, the inset represents a schematic of the SWCNT anchoring and bridging the underlying Ag nanowires network.

6.2.2 SWCNT amount optimization

The SWCNT suspension with a concentration of $c=0.024$ wt% was used with different volumes filtered to obtain various areal densities. The area for the filtered SWCNT was kept the same and confined by a PDMS mask of $A=1.5\text{ cm}\times 1.5\text{ cm}$. The areal density for the Ag nanowires filtered was also kept the same while only that of SWCNT was varied. The areal density (D) of 1 ml SWCNT filtered was expressed by $D=1\text{ ml}\cdot c/A$. SWCNT areal densities of $0, 0.25D, 0.5D$ and $1D$ were prepared while tracking their respective sheet resistance of the prepared electrode.

6.2.3 The foldable solid state electrochromic device fabrication

Ethyl viologen dipherchlorate of 15 mmol/L and sodium anthroquinone-2-sulfonate of 5 mmol/L along with KCl of 20 mmol/L were dissolved in 4wt% PVA-DI solution. 4 wt% borax in DI solution was separately prepared. The two solutions were mixed in 4 to 1 ratio to initiate the hydrogen bond formation to produce the electrochromic slime. Carbon fibers were weaved in a strand and placed laterally along the working electrode and the lateral position was fixed by double sided tape. Then the prepared solid state electrochromic slime was spread uniformly to bridge the working and counter electrode and close the circuit. The illustration of the device structure was shown in figure 6.3.

Figure 6.3 The schematic of the assembled electrochromic device structure

6.2.4 Characterization

FESEM 7600 was utilized to investigate the surface morphologies of samples. AFM was used to measure the sample surface roughness. The sheet resistance of the prepared electrode was collected on a CMT-SR2000N four point probe. The transmittance of the sample was gathered from an integrating sphere attachment on a UV-vis spectrophotometer. The voltage supply between -2 V and 0 V to reversible drive the optical modulation of the electrochromic device was from an electrochemical workstation (Solartron 1470E).

6.3 Results and discussion

TCNF as the source for nanocellulose and nanopaper was adopted. The TCNF was very finely liberated with a nanofiber diameter of around 10 nm as shown in figure 6.4. This is beneficial for reduced light scattering on a single fiber⁹ and at the same time the fine fiber tends to form a much denser film that excludes the air cavity pore and this further suppresses the light scattering inside the matrix¹⁰. The combined factors lead to a nanopaper (8 μm in thickness) of high transparency as shown in figure 6.4 c and d. The transmittance level at 600 nm is 90.2% and can even be compared to a commercial glass slide of 90.8%. Compared to the PCNF¹¹, the TCNF is more easily separated due the incorporation of carboxylic surface charge¹² that facilitates the liberation process and this results in TCNF nanopaper with a much smoother surface with low surface roughness and small scattering angle.

The surface roughness of TCNF nanopaper and PCNF nanopaper was compared and measured with an AFM. The scanned surface area was fixed to $5 \times 5 \mu\text{m}$ for both samples. There is no obvious large and coarse fiber seen on the TCNF paper which was clearly observed on the PCNF nanopaper (figure 6.5 a and b). The resulted root mean square roughness (RMS) for TCNF nanopaper was only 6.3 nm while the PCNF nanopaper has a value as high as 65.6 nm. It has been suggested that the RMS of nanopaper to a large extent determines the light scattering angle.¹³ The test of scattering angle was conducted by projecting a laser point of a diameter of 3 mm through the TCNF nanopaper which was held parallel to the background. The background was 30 cm away from the nanopaper surface and this geometry leads to a calculated scattering angle of only 1.06 °,

which was as high as 21.6° for PCNF nanopaper.¹¹ Correspondingly, the measured haze for the TCNF nanopaper is only as small as 3.6% as compared to the hazy PCNF nanopaper of 83.7%. The stark difference in scattering angle agrees well with the prediction from the RMS testing. The low scattering angle makes the TCNF nanopaper ultra-clear, a deep view through this nanopaper to observe the background was possible as shown in figure 6.6 b, while for the hazy PCNF nanopaper the background becomes obscure even when the nanopaper was lifted a short distance away (figure 6.6 c).

Figure 6.4 The SEM images for the a) fine TCNF nanopaper and b) a regular kim wipes paper; c) the digital photo of a fabricated clear TCNF nanopaper; d) the comparison in spectrum between the nanopaper and a commercial glass slide.

Figure 6.5 The measurement of surface roughness on TCNF and PCNF nanopaper in a) and b) respectively.

Figure 6.6 a) measurement of the scattering angle of TCNF nanopaper; b) a digital photo showing a clear deep view through the TCNF nanopaper; c) a digital photo showing the hazy PCNF nanopaper in comparison.

The high transparency and foldability of the nanopaper makes it a potential substrate for deformable electrodes. The conductive network could be transferred to the nanopaper surface utilizing the nanopaper transfer technique with the schematics as shown in figure 6.2. By incorporating a top layer of SWCNT during the transfer, a double layered SWCNT@Ag TCE could be obtained. If only Ag nanowires are used, a kinked structured Ag TCE was formed with the conformality in the TCNF transfer process. Strongly interacting Ag nanowires with one pressing tightly over another forms a special kinked structure at the interacting junctions was indicated by the circles in figure 6.7 a. The SWCNT@Ag with similar kinked morphology was also observed. Besides this, at high magnification, SWCNT was found to mount over the underlying Ag nanowires and anchor the Ag nanowires tightly to the nanopaper substrate. The SWCNT also links adjacent Ag nanowires laterally for a better construction of the conduction pathway. As discussed earlier the junction resistance more often than not limits the overall conductivity and performance of a percolating TCE. Techniques to improve the junction issues include laser welding¹⁴, GO wrapping at the junction¹⁵, hybrid electrode construction by over-coating graphene¹⁶ etc. The already explored methods are either too complex to operate or not efficient for the realization of TCEs of high quality, which is defined by an electro-optical parameter of $T > 90\%$ and $R_s < 10 \Omega/\text{sq}$ ¹⁷. In this study, a facile and effective nanopaper transfer method involving the use of TCNF was achieved without any post-treatment owing to the formation of the strongly interacting kinked structure to reduce junction resistance. The formation mechanism of such kinked structure was illustrated using the schematics shown in figure 6.7 d-f.

Figure 6.7 SEM images for a) kinked Ag TCE and b) SWCNT@Ag TCE and c) SWCNT@Ag TCE at high magnification; d-f) the schematics demonstrating the formation process for the kinked structure with the highly conformal TCNF.

Figure 6.8 a) the optimization of SWCNT amount by tracking the sheet resistance against SWCNT areal density at fixed Ag nanowires densities of M_1 (83 mg/m²) and M_2 (111 mg/m²) respectively; b) the spectra for various TCEs at different sheet resistance in which the areal density of Ag nanowires adopted is indicated in the figure and the SWCNT is fixed at 0.5D for all SWCNT@Ag TCEs.

Figure 6.9 Comparison of the SWCNT@Ag TCE and kinked Ag TCE with some selected important works on high quality TCEs^{11, 15, 17-23}

First, the Ag nanowires after filtration loosely stacked to each other in an out of plane position relative to each other on the filter membrane. Then, the uniformly dispersed TCNF suspension forms a gel layer that covers the Ag nanowires in a conformal manner to initiate a maximum contact under the force of vacuum filtration. Finally, during the drying process, the high surface energy of TCNF promotes strong cohesion between the nanofibrils, which facilitates the formation of a flat nanopaper surface. Following this process, the nanopaper would stretch the out of plane Ag nanowire to the flat nanopaper surface formed due to hydrogen bond cohesion and this would result in the observed kinked structure.

The well fused junction through the formation of the kinked structure is beneficial for improved conductivity. The sheet resistance of TCNF Ag TCE with a low percolation areal density of 55.5 mg/m^2 is compared with a PCNF Ag TCE as shown earlier in chapter 5 (figure 6.9). The amount of Ag nanowires adopted for both electrodes is kept the same as reflected by almost equal transmittance. The sheet resistance of TCNF Ag TCE ($44.1 \text{ } \Omega/\text{sq}$, 96.6%) is almost 14 times lower than that of PCNF Ag TCE ($630 \text{ } \Omega/\text{sq}$, 96.4%). At the low percolating end, the insufficient construction of the electrical pathway with few junction numbers relies heavily on the junction resistance. TCNF Ag TCE with the kinked structure for reduced junction resistance thus shows the much superior conductivity as expected.

SWCNT top layer that bridges the underlying Ag nanowires would also be helpful for enhanced conductivity. To optimize the amount for best conductivity, SWCNT of various areal densities were transferred at a fixed Ag nanowire areal density namely, M_1 (83 mg/m^2) and M_2 (111 mg/m^2) to check the resulted sheet resistance. In each case study, SWCNT of varied densities from 0D to 1D were transferred. The results are shown in figure 6.8 a. For both M_1 and M_2 , the lowest sheet resistance was observed at 0.5D of SWCNT. Further increasing SWCNT amount resulted in a rougher surface of the SWCNT layer and loss of the close contact between the transferred Ag nanowires as shown in figure 6.10 a and b. With the increase of the SWCNT areal density, the surface becomes roughened by the randomly distributed carbon nanotubes. This deteriorates the contact between Ag nanowires and after the transfer process the close-contact kinked structure began to disappear at high SWCNT areal density of 1D (figure 6.10 b). Thus the sheet resistance began to increase, surpassing the critical point of 0.5D. In particular, for the less percolating network with a lower density in M_1 , the amplitude of improvement in conductivity was more significant. This agrees well with the previous discussion that at the low percolating extent, the overall conductivity is sensitive to junction resistance.

Figure 6.10 The SEM images for SWCNT@Ag TCE at a) 0.5D of SWCNT where the close-contact kinked structure was indicated the circles; and at b) 1D of SWCNT where the kinked structure was not observed.

For different amount of Ag nanowires transferred, the resulted TCE bears different combinations of transparency and conductivity. With the denser of the network, a lower sheet resistance and lower transmittance level could be obtained as shown in figure 6.8 b and figure 6.11.

Figure 6.11 The SEM images for SWCNT@Ag TCEs of different densities and correspondingly different sheet resistance.

The quality of the TCE could be assessed by figure of merit $\frac{\sigma_{dc}}{\sigma_{op}}$, which is obtained from

$$T = \left(1 + \frac{1}{2R_s} \sqrt{\frac{\mu_0}{\epsilon_0}} \frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2} = \left(1 + \frac{188.5}{R_s} \frac{\sigma_{op}}{\sigma_{dc}}\right)^{-2}. \quad 24-28$$

An excellent F.O.M value of 1055 was obtained for the kinked Ag TCE as shown in table 6.1. The saturation of the calculated figure of merit for the Ag TCE starting from 5.09 Ω/sq and downwards indicates a percolation to bulk transition around this point²⁷ where the effective conductivity of the percolating network equals to that of the bulk film. The addition of SWCNT leads to additional pathways for the conduction of electrons and the reduction of sheet resistance could be obtained. A factor called improvement factor (I.F) was defined by $I.F = R_{s_Ag} / R_{s_SWCNT@Ag}$. It is observed that the I.F is large at the less conducting region and gradually falls close to 1 after the bulk transition is reached due to the formation of sufficient conduction pathway of Ag nanowires that reduction of junction resistance would be less effective since. Overall, both the kinked Ag TCE (10.5 Ω/sq , 94.6%) and SWCNT@Ag TCE (7.92 Ω/sq , 90.9%) give excellent TCE performance. Their performances were benchmarked with some selected works on high quality TCE as shown in figure 6.9. It could be found that both TCEs stand out with competent performance with particularly the kinked Ag TCE showing the state of art performance. While the addition of SWCNT lowers the overall transparency level due to absorption of the overcoat, the anchoring of Ag nanowires to the nanopaper substrate offers appealing advantages for deformable electronic applications that would be discussed later.

Table 6.1 The opto-electrical performance of SWCNT@Ag TCE and kinked Ag TCE

	Sample 5	Sample 4	Sample 3	Sample 2	Sample1
R_s for kinked Ag TCE (Ω/sq)	1.16	2.41	5.09	10.5	44.1
After Incorporation of SWCNT: R_s for SWCNT@Ag TCE (Ω/sq)	1.15	2.31	4.72	7.92	27.4
Improvement Factor	1.008	1.043	1.078	1.33	1.61
Kinked Ag TCE Transmittance	75.1	86.7	93.2	94.6	96.6
Kinked Ag TCE F.O.M	1055.6	1057.5	1033.3	637.8	245.0
SWCNT@Ag TCE Transmittance	73.9	84.3	89.8	90.9	92.7
SWCNT@Ag TCE F.O.M	1003.9	915.4	722.6	487.1	178.1

The foldability of the SWCNT@Ag electrode was studied through cyclic folding to different directions. The folding angle is defined by the relative position of the folded conductive network. When the electrode is folded face to face, the angle is defined as -180° , and when the electrode is folded back to back, the folding angle is defined as $+180^\circ$. The schematic for the folding angles are shown in figure 6.12 a. The nanopaper electrode has a thickness of $8\text{ }\mu\text{m}$ and it is folded to a radius of $6\text{ }\mu\text{m}$ during the folding test. (figure 6.13 a and b).

Figure 6.12 a) the schematic defining the folding angle; b) sheet resistance of the SWCNT@Ag electrode ($12.7\text{ }\Omega/\text{sq}$ with SWCNT optimized at $0.5D$) as a function of the folding cycles at different folding angles; SEM images for the crease of the folded electrode at c) -180° and d) $+180^\circ$; digital photos showing the foldability of the nanopaper

electrode by connecting to LED circuits e) before crumpling and f) after crumpling the electrode.

Figure 6.13 SEM cross section images showing a) the thickness and b) folding radius of the nanopaper electrode.

The major change in sheet resistance for folding to both directions occurred in the first 100 cycles, after which the resistance became more or less stabilized. A small increase in sheet resistance of 8.8% and 12.7% were observed after folding for 500 cycles to an extremely small radius of 6 μm for -180° and 180° respectively (figure 6.12 b). In comparison, it is reported for ITO/PET¹⁷ bent mildly to 10 mm with 500% increase of the resistance in only 20 cycles due to its brittleness. On the contrary, ductile Ag nanowires and SWCNT were able to maintain the network conductivity by going through inter-wire sliding under deformation.¹¹ It is also observed in the SEM images for both folding directions that the ductile conductive element has a strong adhesion on the substrate that they are able to conform to the deformed substrate with no delamination (figure 6.12 c and d). The combined factors lead to the observed little change of the sheet resistance. To visually reflect the strong maintenance of the conductivity under folding for the nanopaper electrode, it is connected to LED lights in a circuit. Constant lighting of the LEDs before and after crumpling the nanopaper electrodes reflects the foldability of the soft electrode. (Figure 6.12 e and f)

A solid state foldable electrochromic device was realized on this foldable nanopaper electrode. For the active electrochrome, small molecule Ethyl Viologen Diperchlorate (EV^{2+}) was utilized; it was paired with a small molecule redox mediator, Sodium

Anthraquinone-2-sulfonate (AQS), to complete the electrochromic redox reactions which could be expressed as: EV^{2+} (colorless) + AQS $\leftrightarrow$ $EV^{+•}$ (colored) + AQS⁺

A technique for slime making^{29, 30} was leveraged to embed the electrochrome inside a solid state matrix. PVA and borax in DI solution was able to form hydrogen bond initiated slime with viscoelastic property. Since the slime matrix is polar and it allows the solvation of the adopted electrochrome, the solid state electrochromic slime could be obtained by dissolving the electrochrome first in the PVA solution followed by mixing with borax solution. The obtained electrochromic slime has great foldability since it is constructed by the dynamic hydrogen bonds that breaks and reforms in-situ with the deformation. Such soft electrochrome layer, unlike our previously reported inorganic electrochromic layer, removes the concerns on any possible mechanical failure and thus it perfectly matches with the foldable purpose of the device.

Before moving on to the device performance testing, the adhesion stability of the electrode was assessed. The previous discussion finds that the kinked Ag nanowire has an excellent electro-optical performance. However, the exposed Ag nanowires lack protection against other deforming functional layers which would cause delamination during device operation, especially for deformable applications.¹¹ The adhesion of the electrode to the nanopaper substrate was compared between kinked Ag TCE and SWCNT@Ag TCE by attaching the electrochromic slime to the electrode surface followed by peeling it off for 100 cycles. The sheet resistance at the peeled region was measured for both electrodes. It is found that for the kinked Ag TCE, the peeled region becomes insulating due to observed severe delamination of Ag nanowires and that non-covered insulating region by Ag nanowires were exposed (figure 6.14 a). In contrary, for the SWCNT@Ag TCE, the underlying Ag nanowires network stays firmly on the substrate (figure 6.14 b), and at the high magnification Ag nanowires were found to be anchored tightly by SWCNT (figure 6.14 c). The recorded stability of the sheet resistance for the SWCNT@Ag was observed to be phenomenally stabilized compared to the unprotected kinked Ag TCE as shown in figure 6.14 d.

Figure 6.14 SEM images at the peeled region for a) kinked Ag TCE and b) SWCNT@Ag TCE and c) magnified view for the SWCNT@Ag TCE; d) the sheet resistance of the SWCNT@Ag TCE at varied peeling cycles.

Instead of constructing the device using a conventional face-to-face structure with two SWCNT@Ag nanopaper electrodes sandwiching the solid state electrochrome, a laterally configured device with the counter electrode of carbon fiber was adopted because Ag is electrochemically active and easily oxidized at the counter electrode during the cathodic redox reaction at the working. The oxidized Ag electrode would subsequently become insulating and hampers the device operation, which is otherwise avoided by the choice of an inert carbon electrode. The electrochemical circuit for the laterally placed device was closed by spreading the electrochrome and bridging the two electrodes.

Figure 6.15 The schematic showing the folding direction of the whole device (-180°).

Figure 6.16 Contrast study of the device at various folding cycles based on a) SWCNT@Ag TCE and b) kinked Ag TCE; c) the switching time measurement for the SWCNT@Ag device at different folding cycles; d) the calculation of device coloration efficiency; e) cycling stability test of the electrochromic device.

Figure 6.17 Demonstration of camouflage application by attaching the solid state electrochromic device on bending hands.

The electrochromic device performances based on kinked Ag TCE and SWCNT@Ag TCE were compared. Cyclic folding was executed at the whole device level by folding to the device to -180° with the folding schematic shown in figure 6.15. The optical modulation area was confined to $1.5 \text{ cm} \times 1.5 \text{ cm}$ by patterned filtration. The device subjected to testing was driven between -2 V and 0 V for reversible color switching. An

excellent contrast of 53.9% determined at 550 nm is observed for device on SWCNT@Ag as shown in figure 6.16 a. Due to the anchoring effect from SWCNT to fix the underlying conducting network to the substrate, the device was found with a strong retention of 96.3% of the contrast after 20 repeated folding and 70.1% retention even after 100 folding cycles. As a comparison, the retention of the contrast on the kinked Ag TCE degrades to 43.9% after 20 folding cycles and only 27.2% retention could be maintained after 100 folding cycles (figure 6.16 b). The cause for the quick drop of performance was discussed earlier that the unprotected Ag nanowires delaminates from the substrate under deformation.

The switching time determined by 90% optical modulation was calculated for the SWCNT@Ag electrode based device. A fast switching with 11.5 s and 12.9 s for the coloring and bleaching process respectively could be obtained (figure 6.16 c). After 20 folding cycles, the switching rate was found almost constant with 11.8 s and 13.7 s for the coloring and bleaching process and the switching rate was only observed to be slightly degraded with 13.6 s and 17.9 s for the respective coloring and bleaching process even after continuous folding up to 100 cycles. On the contrary, the switching rate data is rather inconsistent for the kinked Ag TCE device due to delamination of the electrode and inhomogeneous coloration.

The coloration efficiency was also calculated for the SWCNT@Ag based electrochromic device based on the following questions: $\eta = \Delta OD/q$; $\Delta OD = \log (T_{\text{bleach}}/T_{\text{color}})$.³¹ A high coloration efficiency indicates a lower power consumption to achieve a certain modulation level which means a higher practicability of the device. A good coloration efficiency of 94.6 cm²/C was obtained, which is comparable to some viologen based devices^{32, 33}. The data is quite advantageous for such a solid state device considering the dense polymer matrix which impedes the free movement of embedded ion inside the bulky matrix.³⁴ A good cycling stability was also observed with 73.3% retention of the original contrast after 500 switching cycles (figure 6.16 e) and a properly working device with 31.7% retention of the contrast was obtained even after an extensive cycling to 1500 cycles. In the end, the solid state foldable device was mounted on to human hands with a bending angle of 65 ° (figure 6.17) for wearable and attachable electrochromic pads for camouflage applications. At the transparent state of the device, the texture of the skin

could be clearly observed. Upon driving the device at -2V, it gives a purple-red color that blends in with the surrounding tone from the glove and disguises the skin from being distinguished. The foldability and excellent flexibility allows the device to be applied for even larger deformation (lower bending radius) and ensures a proper working functionality. The prototype device for camouflage builds a platform for futuristic wearable camouflage devices where real time absorption modulation with multi-electrochrome mimicking dynamic surrounding change could be realized, which could provide significant value for military, display and fashion industries.

6.4 Conclusion

In conclusion, kinked Ag TCE and SWCNT@Ag TCE with outstanding electro-optical performance was achieved through the TCNF nanopaper transfer method. The formation mechanism for the kinked structure that promotes close contact between Ag nanowires during TCNF assembly was analyzed. It is suggested that by reducing the contact resistance through formation of such unique structure, high quality TCE with state of art electro-optical performance could be achieved. SWCNT plays a positive role in providing additional electron conduction pathway for enhanced conductivity as well as improving the adhesion property of Ag nanowires to the substrate through tight anchoring. The optimized density of SWCNT for the best TCE conductivity was examined and the factor that results in the level off of the conductivity enhancement after the critical point was analyzed. Then, a transparent and foldable solid state electrochromic device based on the nanopaper electrode was realized by incorporating electrochrome embedded slime of no mechanical failure constrain. The device demonstrates excellent optical modulation, coloration efficiency and cycling stability. It was mounted onto bending human hands for camouflage demonstration in the end. The discussed strategies and techniques show great potential and value for futuristic deformable electrochromic devices for camouflage and display applications.

Reference:

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Chapter 7

Discussion and Future Work

In this chapter, the threads of the whole thesis were drawn together by presenting a general discussion on the achieved results which are correspondingly checked with the initial objectives. By doing so, the accomplishments as well as the potential issues to be resolved in futuristic studies are identified followed by a detailed description of the work to be done and feasible means to carry out the studies to address the issues in deformable electrochromic display and advance its development for better deformable electrochromic devices.

7.1 General discussion

The thesis intends to realize deformable electrochromic devices for display applications and to address the involved issues and to overcome related challenges incurred in this course. Stretchable and foldable electrochromics devices are particularly investigated as the focus of this study. The approaches to accomplish the target were described starting from electrode design, moving on to unique electrochrome structure formation together with the device configuration. The strategies adopted along with the mentioned directions results in the successful demonstration of stretchable electrochromics, wearable electrochromics and foldable electrochromic display and foldable camouflage display. The specific discussion for these points can be further classified into the following sub-areas.

7.1.1 Stretchable and wearable electrochromic devices

The objective for this study is to realize stretchable and wearable electrochromic devices with fast switching rate and obvious optical modulation contrast. The identified difficulty to accomplish this task lays in the realization of highly conducting and stretchable electrodes and a compatible stretchable electrochrome with high optical modulation ability. The previously reported electrochromic spandex^{1, 2} suffers from a typical low conductivity of its PEDOT:PSS electrode and thus a small contrast. Ag nanowires embedded in PDMS behave as an excellent electrode with great metallic conductivity and excellent stretchability with a relatively small and reversible change of the resistance^{3, 4}, which makes it a good candidate for electrochromic applications. Inorganic WO₃, an exemplary electrochromic material known for its high optical contrast was adopted for the electrochromic display applications. To relieve its brittle constraint on device stretchability, discrete WO₃ islands deposited from controlled electrochemical deposition was found beneficial for the stretching purpose with a large contrast ratio demonstrated at 50% strain. The performances at both relaxed state and strained state were studied and the mechanical stability against cyclic stretching was also investigated for a better design of durable stretchable electrochromic devices. Finally, to realize the concept of wearable electrochromics, the stretchable electrochromic electrode was integrated with cotton fabrics by curing PDMS with the cotton fabrics. Then obtained wearable electrochromic fabrics with individually patterned pixels could be switched on for display at random

combinations and the wearable electrochromic display could maintain the functionality through mechanical crumpling of the device. In conclusion, the objective to realize stretchable and wearable electrochromic devices has been accomplished, while the durability of the device through cyclic stretching needs to be improved by enhancing the adhesion of the electrochrome on the conductor.

7.1.2 Nanopaper transfer method and foldable electrochromics

The objective for this study is to realize transparent nanopaper electrode with high quality and the foldable electrochromic nanopaper that is able to survive cyclic folding for foldable display application. Apart from stretchable electrochromics, foldable electrochromics also has a significant value for display applications^{5, 6}. The highly desired foldable screen on smart phone or e-book with large contrast ratio and low power consumption is one typical example of its potential applications. Nanopaper based biomass material with its abundant resource and bio-compatibility and potential cost effective manufacturing make nanopaper electronics a promising and competent candidate for futuristic deformable consumer electronics. The greatly reduced dimension of nanocellulose also brings along unique properties that is impossible to bear for regular cellulose, like high transparency^{7, 8}, outstanding mechanical strength⁹ and high level of surface free energy¹⁰. These attractive properties could be well leveraged as a novel transparent and foldable substrate to replace the currently dominating petroleum based plastics. In this study, a nanopaper transfer method was discovered utilizing the high surface free energy level of nanocellulose for an efficient and versatile transfer of various functional materials. Ag nanowires network when transferred results in the transparent conductive nanopaper electrode. It is believed that the drying process of the nanofibrils that leads to the formation of compact nanopaper structure due to strong hydrogen bond cohesion is advantageous for the transfer of a compact conductive layer with high performance. The obtained TCE delivers a high F.O.M approaching 1000 and an excellent electro-optical performance. The nanopaper as well as the reticulate Ag nanowire network demonstrates a good retention of its conductivity against 200 folding cycles. After deposition of the WO₃ electrochromic layer, its performance was studied at various folding cycles. The electrochromic performance of a thinner device could be well maintained even after 50 continuous folding cycles. The slightly degraded contrast as

well as the retarded switching rate could be attributed to the delamination of the electrochrome and conductive Ag nanowires evidenced from the FESEM surface morphology at the folded crease. In conclusion, the discovered nanopaper transfer technique serves as the basis for the realization of the high quality transparent conductive nanopaper electrode and the subsequently fabricated foldable electrochromic device. The initial objective has been accomplished and to further develop the foldable electrochromic device for more practicable application, crack-free electrochrome as well as a better integrated device for full foldability should be developed.

7.1.3 Foldable solid state electrochromic devices

As discussed in 7.1.2, to improve the foldability of the electrochromic device and assemble a fully foldable electrochromic device, some new approaches need to be developed. The objective for this study, to put it in a simple way, is to achieve a fully foldable electrochromic device. The previous study is also based on PCNF with a hazy optical property used for reflective electrochromic display. To develop into transparent high clarity display, TCNF with finer composition for low RMS nanopaper was adopted. To obviate the crack of the inorganic electrochromic film and avoid the liquid state electrolyte, a small molecule electrochrome with electrolyte was embedded into a hydrogen-bond slime for solid state electrochromics. The ductile matrix constructed from dynamic hydrogen bond formation is free from mechanical failure concern that is usually for thin films, it is even able to be stretched and healed after breaking the matrix apart. The extremely compliant slime is more than sufficient for the folding application with the electrochrome and electrolyte embedded. Furthermore, weaved carbon fibers were used as the counter electrode instead of Pt wire due to its foldability. The counter electrode was placed laterally along the working electrode for transmissive applications. The working electrode was obtained by utilizing the nanopaper transfer method to transfer a double layered electrode with SWCNT on top of Ag nanowires network. The SWCNT not only bridges adjacent nanowires for additional electron conduction pathway for enhanced conductivity but also anchors the nanowires tightly to the nanopaper substrate for better adhesion and no delamination of the electrode during device deformation. The fabricated solid electrochromic device shows an excellent transmittance modulation of around 54%, and the device was able to maintain a good 70.1% retention of the original

contrast even after 100 cyclic folding. The foldable electrochromic device was applied and attached on human hands for the demonstration of camouflage application. In conclusion, the objective for a fully foldable electrochromic device was successfully accomplished with a solid state transparent device showing well preserved electrochromic performance through repeated folding cycles.

7.2 Future work

7.2.1 Fully stretchable solid state electrochromic device

With the previous discussions on the realization of stretchable and wearable electrochromic devices, the achievements were elaborated. At the same time, issues that might cause degraded performance were also identified. To obtain stretchable and wearable electrochromic devices with better stability and practicability, the feasible approaches are herein suggested for future studies.

The first issue relates to the full stretchability of the previous stretchable electrochromic device. In the previous study, Pt wire was adopted as the counter electrode, which is not stretchable itself. The device was based on stretching the PDMS based electrochromic electrode while fixing the counter. This is not convenient for a realistic application where every component of the device needs to be stretchable for random stretching and at the same time the price for each component needs to be as low as possible especially for, say consumer electronics. To address this issue, electrochemically stable carbon fibers were used instead. The carbon fibers can be weaved into a strand with great flexibility and conductivity but it is not intrinsically stretchable. A serpentine structure can be constructed for the counter electrode to accommodate stretching strain by aligning to the tensile direction. The counter electrode could be embedded inside the stretchable PDMS matrix alongside the Ag nanowires working electrode to form a laterally configured device as shown by the schematic in figure 7.1.

The second issue concerns the delamination of the WO_3 islands during stretching due to the reduced lateral space that compresses the electrode while it is stretched. Meanwhile, the electrolyte is in aqueous solution. A solid state electrochrome and electrolyte would be much more favored for convenient device applications. To realize such concept, small molecule electrochrome slime as discussed in chapter 6 could be leveraged here. The soft

slime matrix with dynamic hydrogen bond formation could be applied for folding, stretching and self-healing, while the electrochromic property remains unaffected. The electrochromic slime could be butter-spread across the working and counter electrodes to complete the reaction circuit as shown in figure 7.1.

The assembled solid state device with every component designed to be stretchable would thus be more competent as a practicable stretchable electrochromic device. After implanting the device on fabrics by curing the PDMS base with it, a wearable electrochromic device could be obtained.³

Figure 7.1 The schematic structure of the fully stretchable solid state electrochromic device.

7.2.2 Graphene oxide overcoat for enhanced mechanical and electrical stability

Ag nanowires network when used as the conductor has weak adhesion stability on the selected substrate and may face peeling and delamination issues.^{11, 12} Meanwhile, the Ag nanowires were reported to gradually lose conductivity due to resulted oxidation of Ag in air.¹³ To protect Ag nanowires from unwanted side reactions for prolonged storage and service for device applications, an overcoat layer to protect the underlying Ag nanowires could be incorporated. The material as the overcoat layer should be selected with high affinity to the substrate to anchor the Ag nanowires tightly which is desired for deformable electronic applications where the relative displacement between the electrode and the functional materials might cause delamination of the otherwise unprotected

conductor. To obviate the oxidation process, Ag nanowires should be properly covered and isolated from the air. Graphene oxide (GO) with high polarity and strong interaction with hydrogen bond assembled nanopaper is a promising overcoat material. At the same time, GO tends to form a dense layer when dried and this results in low permeation of air through the GO layer.^{13, 14} To realize such a structure for the underlying Ag nanowires network, the nanopaper transfer method could be utilized to transfer the overcoat/conductor double layer electrode. The schematic stacked sequence for related materials before the transfer is shown in figure 7.2 a. After the transfer process, GO could be observed well coated on top of the Ag nanowires network in the preliminary experiment with the underlying Ag nanowire tightly pressed against the substrate and the majority of the nanowire was found covered with little exposure to air. The stability of the electrode will be tested and checked with the herein discussed hypothesis.

Figure 7.2 a) The filtration sequence for the overcoat and the conductive layer; b) SEM image showing the protected Ag nanowire by densely assembled GO overcoat.

7.2.3 Oxidation-proof Ag/Au alloy electrode for electrochromic devices

Ag nanowires are prone to oxidation during electrochemical redox reactions due to its high activity and correspondingly low oxidation potential.³ The oxidized Ag loses its conductivity, which is commonly seen in the reaction where the working electrode species gets reduced and the counter Ag nanowires gets oxidized to maintain the current flow. This is the reason the counter electrode was selected as stable Pt or carbon in the previously discussed chapters. The lateral device configuration using carbon as the counter electrode is a good solution to the oxidation issue but the derived electric field is not homogeneous across the working electrode and the device was observed with the

outer region switching relatively faster than the inner region due to the specifically designed device structure. This is not beneficial for large scale display where delayed response in the center would be found. To solve this issue, transparent deformable oxidation-proof electrodes need to be developed. Au or Pt as a noble metal is much more stable than Ag and often used as the counter electrode in electrochemical analysis. The growth of Au or Pt nanowire would be more difficult and much more costly compared to Ag. However, Ag nanowires could be used as the scaffold to replace Au in a galvanic replacement reaction to form Au shell, Ag core structure (figure 7.3 a). The Ag covered by the noble metal should thus be more oxidative resistant. Incorporation of an extra charge storage layer could concomitantly be exploited to further buffer the electron transportation to/from the Ag electrode. A good control of the replacement reaction position and rate might need to be taken care of in order to achieve an effective coverage of the Au shell layer. The oxidation resistance study needs to be done after obtaining the core/shell structure and later a face to face device structure could be configured for uniform optical modulation for deformable electrochromics (figure 7.3 b).

Figure 7.3 a) The schematic for the core/shell oxidation-proof Au-Ag alloy; b) a face-to-face device for the fully foldable solid state electrochromic device based on oxidation resistive electrodes for uniform optical modulation.

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Appendix

Purchased chemicals and consumables:

PDMS (Sylgard 184) is purchased from Dow Corning; Tungsten powder is purchased from Alfa Aesar, USA and H_2O_2 (30%, 60 ml) is from Tokyo Chemical Industry, Japan; Ethyl Viologen Diperchlorate, Sodium Anthraquinone-2-sulfonate, Sodium tetraborate and Poly (vinyl alcohol) (M_w 10000) are purchased from Aldrich Sigma, Singapore; Nanocellulose is purchased from University of Maine, USA and VTT, Finland; Polycarbonate filter membrane (Millipore GTTP) with pore size 220 nm is adopted for filtration; Ag nanowires is purchased from Seashell Technology LLC, USA; SWCNT (P3) is from Carbon Solutions, USA.

Equipment:

Field Effect Scanning Electron Microscopy (JEOL 7600F) is utilized for morphology characterization; Four point probe (CMT-SR2000N) is used measure the resistance of conductors; Atomic Force Microscope (NT-MDT) is used for surface roughness measurement; UV-vis spectrophotometer (Shimadzu UV-3600) is used to evaluate the optical properties; Filtration funnel (Smart Memories, Singapore) is used to filtrate Ag NW suspension; Solartron 1470E is used to drive electrochromic devices.

Ag nanowire (Seashell, USA) size characterization

The length distribution (left) with an average of 31.2 μm and major distribution between 20-35 μm and diameter distribution (right) with an average of 113.8 nm and major distribution between 110-140 nm of Ag NWs are obtained from SEM inspection of

filtered conductive Ag NWs films.

SEM images of the stretchable electrode at 50% strain:

The top (left) and cross sectional (right) SEM images of the stretchable electrode on strain at 50%. The inset is a relaxed control sample, scale bar: 500 nm. The arrow on the lower right of each image represents the strain direction.

Comparison in resistance through cycling folding between SWCNT@Ag and Ag electrode

The comparison in sheet resistance change after 500 cyclic folding between SWCNT@Ag and Ag electrode with SWCNT@Ag delivering 8.8% (-180 °) and 12.7% (+180 °) increase and Ag delivering 14.7% (-180 °) and 25.1% (+180 °) increase.

Electrochemical deposition of WO₃ nanoparticle

WO₃ would be electrochemically deposited onto conductive electrodes to form the electrochromic layer. A priori, WO₃ could be synthesized in a wide range of methods like electrochemical deposition (ECD),¹⁻³ chemical vapor deposition (CVD),⁴⁻⁷ hydrothermal reaction,⁸⁻¹⁰ Sol gel,¹¹⁻¹³ evaporation,^{11,14-16} and sputtering etc.¹⁷⁻¹⁹ The electrochemical method has gained a broad interest due to its mild coating condition at room temperature

and facile integration onto the conductive area.

The electrochemical deposition mechanism from peroxy-tungstate solution was investigated by Meulenkamp²⁰ back in 1997. The mechanism for WO₃ cathodic electrodeposition was not quite clear then since it could not be easily explained by local pH rise induced precipitation as in some metal oxide systems like ZnO²¹ and ZrO₂²² by evidence that higher pH leads to observed difficulty for its deposition.²⁰

In the investigation, peroxy-tungstate acid (PTA) was prepared by dissolving tungsten powder in H₂O₂ solution. Pt sheet was immersed in PTA to decompose excessive H₂O₂ in the bulk solution. The formation of the peroxytungstate was reported to be:²³

The peroxytungstate, W₂O₁₁²⁻, is not thermodynamically stable and decompose slowly in two possible reactions:

A rotating disk electrode (RDE) which is useful for manual control of mass transport was adopted to deposit WO₃ from the PTA solution. For a diffusion controlled reaction, the Levich equation holds:^{24,25}

$$i_{\text{diffusion}} = 0.62nFAD^{2/3}v^{-1/6}c_{\text{bulk}}\omega^{1/2}$$

A is the electrode surface area, D is the diffusion coefficient, n is the number of electrons consumed, F is the Faraday constant, c is the concentration of active materials, v is the kinematic viscosity and ω is the rotation rate.

If the system is kinetically controlled meaning mass transfer is very fast, the kinetic current limit would be:

$$i_{\text{kin}} = nFAkc_{\text{bulk}}$$

For a mixed process, the current is expressed in $i^{-1} = i_{\text{kin}}^{-1} + i_{\text{diffusion}}^{-1}$ and a nicely fitted data by $(i - i_{\text{basis}})^{-1} = i_{\text{kin}}^{-1} + i_{\text{diffusion}}^{-1}$ with current correlation coefficient larger than 0.99 was reported for WO₃ deposition.

Thus the deposition current could be reorganized into:

$$(i - i_{\text{basis}})^{-1} = i_{\text{kin}}^{-1} + \text{diff. slope}^{-1} * \omega^{-1/2}$$

i_{basis} is a fitted value and found to be independent of rotation speed. The process contributing to i_{basis} is termed process 1, while process 2 accounts for the current that

demonstrates the typical pattern which is characterized by $i_{kin}^{-1} + \text{diff. slope}^{-1} * \omega^{-1/2}$. The combined process 1 and 2 contributes to the whole WO_3 deposition current.

Since there are three major components in the PTA solution, namely peroxytungstate ($W_2O_{11}^{2-}$), H_2O_2 and polytungstate ($W_{12}O_{39}^{6-}$), it is thus necessary to find out how each component contributes to the deposition current to find out the deposition mechanism.

H_2O_2 was first singled out for a reducing test in a similar RDE setup. The reducing current shows a very small i_{basis} after fitting and the i_{basis} current is independent of H_2O_2 concentration, which rules out the possibility of its contribution to process 1 current during WO_3 deposition. On the contrary, its i_{kin} and diff.slope shows a linear relationship to H_2O_2 concentration and a similar potential dependence as in deposition from PTA solution, which proves its current responsible for process 2. Subsequently, polytungstate prepared by dissolving Na_2WO_4 in water at low pH of 1.9 that leads to the formation of $W_{12}O_{39}^{6-}$ was singled out to study its reducing current. Similarly, the percentage of the derived i_{basis} is too small but i_{kin} and $i_{diffusion}$ on the other hand shows an analogous potential dependence to that from PTA deposition. This suggests a process 2 current contribution instead of process 1 for the polytungstate reduction.

Therefore, peroxytungstate reduction current should be responsible for i_{basis} which is kinetically controlled and independent of rotating speed. To corroborate this conclusion, ECD at different rotation speed is carried out. Efficiency n that denotes how much charge was consumed for 1 W atom deposited at different deposition potentials and rotation speeds were recorded. To calculate the charge consumed, only i_{basis} is used for such calculation. The result is shown below:

Figure 3.7 Variation of deposition efficiency as a function of deposition potential and rotating speed. (Reprinted with permission from Reference 58. © 1997 The Electrochemical Society.)

Indeed, rotation speed independence on the deposition efficiency was observed with n at a certain potential remaining almost constant for all rotation speeds. This confirms that only kinetically controlled process 1 for peroxytungstate reduction is responsible for WO_3 deposition. If any process 2 current would otherwise contribute to WO_3 formation, this way of calculating n would result in an increased value at a higher rotation speed since the number for deposited W atoms would increase with a larger rotation speed in this situation.

Now after understanding how each chemical component in the precursor contributes to the deposition current, it is safe to conclude that only peroxytungstate reduction would lead to the formation WO_3 , reduction of H_2O_2 and polytungstate results in a "parasitic" current. The deposition could be thus expressed:²⁶

To note that, this expression also considers the natural chemical decomposition as in the case of $x=0$. If the deposition is only coming from cathodic reduction, then $x=8$ and all the O^{-1} atoms would be reduced to H_2O .

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