Conjugated polymer-based composites for electrochromic applications

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2019

Che, B. (2019). Conjugated polymer-based composites for electrochromic applications.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/90130>

<https://doi.org/10.32657/10220/48422>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**CONJUGATED POLYMER-BASED COMPOSITES FOR
ELECTROCHROMIC APPLICATIONS**

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**Interdisciplinary Graduate School
Energy Research Institute @ NTU**

2019

CONJUGATED POLYMER-BASED COMPOSITES FOR ELECTROCHROMIC APPLICATIONS

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INTERDISCIPLINARY GRADUATE SCHOOL

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

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Lu Xuehong

Authorship Attribution Statement

This thesis contains material from papers published in the following peer-reviewed journals where I was the first author.

Chapter 5 is published as B. Che, D. Zhou, H. Li, C. He, E. Liu, X. Lu. A highly bendable transparent electrode for organic electrochromic devices. *Organic Electronics* **66**, 86-93 (2019). DOI: 10.1016/j.orgel.2018.12.015.

The contributions of the co-authors are as follows:

- A/Prof Lu Xuehong provided the initial project direction and edited the manuscript drafts.
- Dr. Li Hui synthesized the PANI-grafted-CNTs.
- I performed all other laboratory works, analyzed the data and prepared the manuscript.
- Dr. Zhou Dan, A/Prof He Chaobin, A/Prof Liu Erjia, and A/Prof Lu Xuehong contributed their thoughts about the project in every discussion during the work.

Chapter 6 is published as B. Che, H. Li, D. Zhou, Y. Zhang, Z. Zeng, C. Zhao, C. He, E. Liu, X. Lu. Porous polyaniline-carbon nanotube composite electrode for supercapacitors with outstanding rate capability and cyclic stability. *Composites Part B: Engineering* **165**, 671-678(2019). DOI: 10.1016/j.compositesb.2019.02.026.

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Che Boyang

Abstract

Electrochromism is a phenomenon that materials are able to change its color reversibly under external potential. The mechanism of electrochromic materials is redox reactions in most of the cases. Composite materials have been widely used for electrochromic applications, as they have the potential to exhibit the advantages of both components. Conjugated polymer-based composite is a popular option due to the conductivity and flexibility of conjugated polymers. The challenge in design of a high-performance composite material is to achieve synergistic effects in desired aspects instead of getting average performance of the components. The design guidelines of electrochromic composite are not well established. Thus, the aim of the thesis is to design new conjugated polymer-based composite systems in which the conjugated polymers and the other components are complementary in certain aspects, and study how interfacial interactions affect synergistic effects of the complementary components in conjugated polymer-based electrochromic composites. The key hypothesis is that with proper structural design, strong interfacial interactions between conjugated polymers and the other components may induce significant synergistic effects, positively influencing electron transport, oxidation/reduction potentials, electrochemical stability, and/or mechanical robustness. To verify the hypothesis, two composite systems have been studied are molybdenum trioxide/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate ($\text{MoO}_3/\text{PEDOT:PSS}$) and polyaniline-carbon nanotube (PANI-CNT). The components have complementary properties in conductivities or mechanical properties. The interfacial interactions in each composite are electrostatic interaction and covalent bond, respectively. Both composites show enhanced electrochromic and electrochemical properties. It is proved that strong interfacial interactions between these two pairs of components induce significant synergistic effects. This conclusion provides a rationale for designing high-performance composite materials for electrochromic applications.

Lay Summary

Electrochromism is color change of the material under electricity. It has been utilized on windows of buildings and airplanes to protect the privacy or insulate the UV light/heat. It is also used in displays that need less energy consumption than traditional displays. Moreover, it is possible to fabricate flexible displays using electrochromic displays. Currently electrochromic materials are only used in high-end applications. The main reason is the cost of current materials and techniques. Polymer composite is a mixture of polymer and another material. They are cheap and easy to process, so they have huge market potential in the industry. The aim of this thesis is to design new electrochromic polymer composites with complementary components and find the key reasons affect the performance of such materials.

Two composite systems have been studied in the thesis. It has been proved that strong interactions between the complementary components in the composite are the key factor to high performance. With this conclusion, a critical rule has been found to design any polymer composite for electrochromic applications. The materials prepared using this rule have better performance, longer lifetime, and chance to use in flexible devices. With these advantages, less material is required to perform similarly to current products, so the total cost is reduced. Also, they are able to use in wearable and flexible electronics. The results of the thesis take a forward step to advance electrochromic devices to more potential applications.

Acknowledgements

I would like to express my sincere appreciation to my supervisor, Associate Professor Lu Xuehong, School of Materials Science and Engineering (MSE), for her invaluable guidance and patience for education throughout my PhD experience.

I would like to give my thanks to my co-supervisor, Associate Professor Liu Erjia, School of Mechanical and Aerospace Engineering (MAE), and my mentor, Prof Lam Yeng Ming, MSE, for their support in every Thesis Advisory Committee meeting.

I would like to give my thanks to technicians of MSE and all my group members for sharing their time and knowledge with me regarding to lab equipment and techniques.

I would like to thank my parents for their love, understanding and encouragement.

I would like to thank Energy Research Institute @ Nanyang Technological University, Interdisciplinary Graduate School for the financial support.

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Figure 7.3 Proposed synthesis route for covalently bonded PANI-Fe₂O₃ composite.

Abbreviations

AC	Alternating Current
A-CNT	Amine-functionalized Carbon Nanotube
APS	Ammonium Persulfate
ATR	Attenuated Total Reflectance
BE	Binding Energy
BEI	Backscatter Electron Image
CE	Coloration Efficiency
CNT	Carbon Nanotube
CSA	Camphor Sulfonic Acid
CV	Cyclic Voltammetry
DBSA	Dodecylbenzenesulfonic Acid
DWCNT	Double-walled Carbon Nanotube
EDLC	Electric Double-layer Capacitor
EDX	Energy Dispersive X-ray Analysis
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field-emission Scanning Electron Microscope
FTIR	Fourier-transform Infrared Spectroscopy
FTO	Fluorine Doped Tin Oxide
FWHM	Full Width at Half Maximum
HRTEM	High Resolution Transmission Electron Microscope
IPA	Isopropyl Alcohol
IR	Infrared
ITO	Indium Tin Oxide
IV	Current-Voltage
KE	Kinetic Energy
LABE	Low Angle Backscattered Electron
LBL	Layer-by-Layer
MWCNT	Multi-walled Carbon Nanotube
OCP	Open Circuit Potential

OD	Optical Density
PANI	Polyaniline
PC	Propylene Carbonate
PEDOT	Poly(3,4-ethylenedioxythiophene)
PEDTS	Poly(4-(2,3-dihydrothieno[3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid)
PET	Polyethylene Terephthalate
PSS	Polystyrene Sulfonate
PTA	Peroxytungstic Acid
PVDF	Polyvinylidene Difluoride
SE	Secondary Electron
SEI	Secondary Electron Image
SEM	Scanning Electron Microscope
SWCNT	Single-walled Carbon Nanotube
TEM	Transmission Electron Microscope
UV	Ultraviolet
Vis	Visible
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

In this chapter, a brief introduction to the PhD thesis is given, including the motivation, hypotheses, objectives, and scope of the PhD study. It starts with some background information about electrochromism and electrochromic materials, followed by a statement of the challenges faced in this field. Briefly, composite materials have been widely used for electrochromic applications, whereas how interfacial interactions between the components influence their synergistic effects for improving electrochromic properties are not well studied. Thus, the goal of the PhD research is to study how interfacial interactions affect synergistic effects of the complementary components in conjugated polymer-based electrochromic composites. To achieve the goals, the key hypothesis is that with proper structural design, strong interfacial interactions between conjugated polymers and inorganic components may induce significant synergistic effects, positively influencing electron transport, oxidation/reduction potentials, electrochemical stability, and/or mechanical robustness. To verify the hypothesis, two composite systems, MoO₃/PEDOT:PSS and PANI-CNT, with interfacial electrostatic interaction and covalent bond, respectively, have been studied. The detailed objectives and scope of the PhD work are then presented, and the overview of each chapter is given. The original and significant findings and outcomes are highlighted in the last section.

1.1 Background and Motivation

Electrochromism is a phenomenon that materials are able to change its color reversibly under external potential. It has been used on electrochromic windows, self-dimming rear mirrors, and displays with lower energy consumptions.[1] The mechanism of electrochromic materials is redox reactions in most of the cases. The electrochromic materials are either oxidized/reduced under the insertion of ions and charges, so that the optical properties of the materials change, leading to the change in color. A material that is colored at reduced state is a cathodically colored material and a material colored at oxidized state is an anodically colored material. A typical electrochromic device is made up of three components: electrode, electrochromic material and electrolyte. Electrochromic materials are coated on the electrodes and separated by electrolyte in the electrochromic device. Optical contrast, which is the difference in transmittance between colored and bleached states, is the most important parameter of an electrochromic device. Other parameters like switching time and long-term stability are also concerned in electrochromic applications.

Two types of commonly used electrochromic materials are transition metal oxides and conjugated polymers. Transition metal oxides, like WO_3 and MoO_3 , are well studied for electrochromism. The transfer between different valence states of transition metals enables them a promising option for electrochromism. They usually have high optical contrast and good long-term stability due to their crystallinity and environment stability, but longer switching time due to their poor conductivity.[2] Conjugated polymers, like polyaniline (PANI) and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), are also electrochromic, as they have different oxidation states showing different colors. Comparing to transition metal oxides, electrochromic conjugated polymers have advantages like faster switching speed, flexibility, multi-color and low cost.[3] However, they usually suffer from stability issue due to over-oxidization.[4]

Since each type of material has its own strength and drawback, a composite material is a good option with the potential to exhibit the advantages of both components. Conjugated polymer-based composites have been widely studied for electrochromic applications. The

prime reason is to utilize the conductivity and flexibility of conjugated polymers. For example, the charge transfer of $\text{WO}_3/\text{poly}(4-(2,3\text{-dihydrothieno}[3,4\text{-}b]-[1,4]\text{dioxin-2-yl-methoxy})-1\text{-butanesulfonic acid})$ (PEDTS) composite has been found to be improved due to the good conductivity of PEDTS.[5] A flexible electrode, Ag grid/PEDOT:PSS, has been prepared and used in bendable electrochromic applications.[6] The motivation of this PhD work is to further improve electrochromic properties of conjugated polymer-based composite materials through rational design so that their application potentials in certain areas can be further enhanced.

1.2 Research Gap and Hypotheses

The challenge in design of a high-performance composite material is to achieve synergistic effects in desired aspects instead of getting average performance of the components. Though composite materials have been widely demonstrated for electrochromic applications, design guidelines for electrochromic composites are not well established. In this work, it is hypothesized that to achieve significant synergistic effects, two important issues in material design should be considered: complementary properties of the components and interfacial interactions. So far, the research focus for composite materials has been largely focused on improving the dispersion of the discrete phase in order to increase the interfacial area and enhance the interfacial interactions.[7] Different types of interfacial interactions have been examined in electrochromic composites, including covalent bond[8], coordination bond[9], electrostatic interaction[10], and hydrogen bond[11], while the above two design issues were rarely addressed simultaneously to boost the synergistic effects.

The goals of this PhD work are to design two new electrochromic conjugated polymer-based composite systems, in which the components have complementary properties in certain aspects, and study whether and how the interfacial interactions can lead to significant synergistic effects in boosting electrochromic properties. In the first system, electrostatic interaction between the two components may allow the two components, which have complementary electrical conductivity, be combined tightly together,

improving electron transport. In the second system, covalent bonds are built between the two components. With the interfacial covalent bonds, the electron transport is through direct conjugation instead of tunneling effect.[12] Moreover, the two components have complementary mechanical properties, and hence covalent bonding of the two components may also lead to robust electrochromic thin films. In summary, the thesis work test the hypothesis that strong interfacial interactions between the complementary components, like electrostatic interaction or covalent bond, may induce significant synergistic effects between the conjugated polymer and another component to improve one or more of the following parameters:

- Electron transport
- Oxidation/reduction potentials
- Electrochemical stability
- Mechanical robustness

1.3 Objectives and Scope

To verify the hypotheses proposed in the previous section, three pieces of work have been designed to study how strong interfacial interactions affect the properties of conjugated polymer-based composites used in electrochromic applications.

A MoO_3 /PEDOT:PSS composite material has been prepared utilizing the electrostatic interaction between the MoO_3 nanoparticles with negative charged surface groups and positive charged PEDOT. The objective of the work is to study if the electrostatic interaction can facilitate the electron transport and improve the long-term stability of the electrochromic films.

A polyaniline-carbon nanotube/polyethylene terephthalate (PANI-CNT/PET) flexible electrode has been prepared by chemically grafting PANI on CNTs for fabrication of flexible electrochromic films. The objective is to study if the chemically grafted PANI on CNTs can enhance the conductivity of the electrode, as well as make both the electrode and the resultant electrochromic films highly bendable.

Porous PANI-grafted-CNTs has also been prepared as the electrode material of an electrochromic supercapacitor. The objective is to study the electron transport improved by covalent bond between PANI and CNT and the ion transport improved by the porous morphology. Also, the oxidation/reduction potentials and electrochemical stability are studied. The electrochromic supercapacitor is explored by using PANI as both supercapacitor electrode and electrochromic indicator of charging state.

1.4 Dissertation Overview

The thesis addresses conjugated polymer-based composites and their electrochromic applications. The thesis focuses on utilizing the strong interfacial interactions between the conjugated polymer and another complementary component in the composite to improve the electrochemical properties, thus enhance the performances of the electrochromic applications. The overview of each chapter is stated as the following.

Chapter 1 gives a brief introduction to the PhD thesis, including the motivation, hypotheses, objectives, and scope of the PhD study. It starts with some background information about electrochromism and electrochromic materials, followed by a statement of the challenges faced in this field. Briefly, composite materials have been widely used for electrochromic applications, whereas how interfacial interactions between the components influence their synergistic effects for improving electrochromic properties is not well studied. Thus, the goal of the PhD research is to study how interfacial interactions affect synergistic effects of the complementary components in conjugated polymer-based electrochromic composites. To achieve the goals, the key hypothesis is that with proper structural design, strong interfacial interactions between conjugated polymers and inorganic components may induce significant synergistic effects, positively influencing electron transport, oxidation/reduction potentials, electrochemical stability, and/or mechanical robustness. To verify the hypothesis, two composite systems, $\text{MoO}_3/\text{PEDOT:PSS}$ and PANI-CNT, with interfacial electrostatic interaction and covalent bond, respectively, have been studied. The detailed objectives and scope of the PhD work are then presented, and the overview of each

chapter is given. The original and significant findings and outcomes are highlighted in the last section.

Chapter 2 provides a literature review concerning electrochromic conjugated polymer-based composite materials. Firstly, a brief introduction to electrochromism is given, including the concept, applications and principles of electrochromism. Then, key parameters of electrochromic devices and types of electrochromic materials are discussed. Next, several specific electrochromic materials that are closely related to the materials studied in this PhD work, including MoO_3 , PEDOT and PANI, are discussed in detail, to show the state of art, critical issues and research gap in this field. Moreover, the concept of electrochromic supercapacitors is introduced, and literatures about supercapacitor electrode materials, especially CNT, PANI and their composites, are reviewed to describe the potential and issues of these materials for electrochromic supercapacitors.

Chapter 3 discusses the principles underlying the different characterization techniques used to study the dispersion of the discrete phase and interfacial interactions between the components, which are very important factors affecting the properties of the composites. Techniques discussed include scanning electron microscope, X-ray photoelectron spectroscopy, and Raman spectroscopy. Other similar techniques are compared with them and the reasons why such techniques are chosen in the specific work are clarified. Furthermore, varied characterization methods used in electrochemistry are discussed.

Chapter 4 elaborates the first major set of results, regarding to facile preparation of molybdenum trioxide/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate nanocomposites for enhancement of electrochromic properties.

Chapter 5 elaborates the second major set of results, regarding to a highly bendable and flexible PANI-CNT/PET electrode used in organic electrochromic devices.

Chapter 6 elaborates the third major set of results, regarding to a porous PANI-CNT composite electrode for supercapacitors with outstanding rate capability and cyclic stability.

Chapter 7 draws a conclusion of the thesis. Two conjugated polymer-based composite systems, $\text{MoO}_3/\text{PEDOT:PSS}$ and PANI-CNT, are summarized respectively and the hypothesis is discussed. Reconnaissance work related to electrochromic supercapacitor based on PANI is reported. Recommendations to future studies are also presented.

1.5 Original and Significant Findings

This research led to two significant and novel findings:

1. MoO_3 is an electrochromic material that exhibits higher apparent contrast and better open circuit memory than most commonly used WO_3 . However, MoO_3 is not widely used as the main component of an electrochromic material due to its low conductivity at fully oxidized state, slow Li^+ transport and poor long-term stability. So far, electrochromic materials based on MoO_3 only demonstrate stability of about 100 cycles. In this work, for the first time, a $\text{MoO}_3/\text{PEDOT:PSS}$ electrochromic composite is facilely fabricated by adding PEDOT:PSS into MoO_3 aqueous dispersion with electrostatic interactions between MoO_3 and PEDOT. The composite prepared shows long-term stability up to more than 500 cycles. It better utilizes complementary-conductivity strategy by combining PEDOT:PSS with semicrystalline MoO_3 nanoparticles of size of about 10-30 nm, bringing extensive interfacial interactions. As a result, the composite demonstrates enhanced long-term stability. This study significantly improves the stability issue of MoO_3 , and enhances the potential of MoO_3 -based materials for electrochromic applications.

2. A novel flexible transparent electrode for electrochromic applications has been prepared by chemically grafting PANI on CNTs to form covalent bonds between PANI and CNTs. PANI provides the flexibility of the electrode and robust interface with electrochromic layer, while the grafted CNTs improves the mechanical robustness of the electrode and the resultant electrochromic film, as well as enhances redox stability of the composite. It is found that failure of the interface between the indium tin oxide (ITO) electrode, which is the most commonly used traditional transparent electrode, and

electrochromic PANI layer is the key factor responsible for the bending-induced deterioration of electrochromic films prepared on ITO/PET electrode. By contrast, both the new PANI-CNT/PET electrode and the interface between the electrode and the electrochromic layer is robust when subjected to severe bending. This important finding may facilitate the development of highly bendable conjugated polymer-based electrochromic devices.

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Chapter 2

Literature Review

In this chapter, the literatures concerning electrochromic conjugated polymer-based composite materials are reviewed. Firstly, a brief introduction to electrochromism is given, including the concept, applications and principles of electrochromism. Then, key parameters of electrochromic devices and types of electrochromic materials are discussed. Next, several specific electrochromic materials that are closely related to the materials studied in this PhD work, including MoO_3 , PEDOT and PANI, are discussed in detail, to show the state of art, critical issues and research gap in this field. Moreover, the concept of electrochromic supercapacitors is introduced, and literatures about supercapacitor electrode materials, especially CNT, PANI and their composites, are reviewed to describe the potential and issues of these materials for electrochromic supercapacitors.

2.1 Electrochromism and Electrochromic Materials

2.1.1 Introduction

Electrochromism is a phenomenon where the material is able to reversibly change its optical properties under external voltage. Electrochromic devices can be categorized into two types: reflective and transmissive. It corresponds whether the electrochromic device changes its reflectance or transmittance under the potential applied. The change in reflectance and transmittance is actually the reason why the color of the material changes and also the characteristic of electrochromic device that is significant and can be utilized.

There are several applications of electrochromic devices in daily lives. One is on car rear-view mirrors.[1] (Figure 2.1a) The mirror-reflected glare caused by the strong lights from other automobiles may cause an “after image” to stay on human’s eye’s retina. This could result in safety issues during driving. If using anti-glare car rear-view mirrors made by electrochromic devices, the mirrors can darken by turning on the switch and thus minimize the effect of the glare. Another application of electrochromic devices is on displays.[2] The electrochromic displays require less energy consumption to maintain the image than currently used display electronics. It is also possible to fabricate flexible displays based on electrochromic devices. (Figure 2.1b) The most widely used electrochromic devices are electrochromic windows.[3] Figure 2.1c is electrochromic windows on Boeing 787 Dreamliner flight. These windows can easily block the sunlight by darkening its colors to reduce the transmittance. Also, the color is adjustable so that the view outside can be seen.

Figure 2.1 Varied applications of electrochromic devices: (a) car rear-view mirror[4] (b) electrochromic display[5] (c) electrochromic windows[6].

Figure 2.2 shows a typical structure of an electrochromic device. An electrochromic device is made up of three components: electrodes, electrochromic materials and electrolyte. A full device has a symmetric multi-layer structure. Glasses are usually used as the substrates of the device to provide a basic support. The first layer is the electrode layer. It is a transparent electrode so that it will not influence the color of the device and provide a place to connect the circuit to apply the voltage. The second layer is the electrochromic material, where the color of this layer changes during operation. In between the two electrochromic materials is the electrolyte, where ions (H^+ , Li^+ etc.) are stored inside. When an external potential is applied on the electrodes, an electric field is created in the electrolyte. Under the electric field, ions move to one of the electrochromic materials. The redox reaction occurs at this layer and the color of the material changes. When an opposite potential is applied, ions move to the opposite direction. The material returns to its original state and the color also returns. Thus, to maximize the performance of the device, usually one electrochromic material is cathodically colored material, another one is anodically colored

material. During the operation, as one layer is in reduced state and one layer is in oxidized state, the two materials are either in colored state or bleached state simultaneously, so that the difference between the two states is maximized.

Figure 2.2 Typical structure of an electrochromic device.

2.1.2 Key Parameters of Electrochromic Devices

The performance of an electrochromic device can be described by the following key parameters:

Optical contrast

Optical contrast can quantitatively determine the color change of an electrochromic device. For a transmissive electrochromic device, optical contrast is the difference of transmittance/absorbance in bleached state and colored state.

$$\Delta T = T_b - T_c$$

or

$$\Delta A = A_c - A_b$$

where T is transmittance, A is absorbance, subscript b represents bleached state and subscript c represents colored state.

In the thesis, ΔT at a specific wavelength is usually used to describe the optical contrast. For different practical applications, the maximum ΔT may occur at different wavelength range. For electrochromic windows to protect the privacy, the maximum ΔT should be at visible light region. For applications that insulate the heat, the maximum ΔT should be at infrared (IR) region.

Coloration efficiency (CE)

This parameter measures the efficiency of an electrochromic layer. It is defined as

$$CE = \frac{\Delta A}{q}$$

where ΔA is the optical absorbance change and q is the injected charge per unit area.

Sometimes change in optical density (ΔOD) is used to replace ΔA in the equation

$$CE = \frac{\Delta OD}{q}$$

where OD is an expression of transmittance (T) and is defined as

$$OD = \log_{10} \frac{1}{T}$$

Coloration efficiency is an efficient tool to measure the power requirement of electrochromic materials. The material with higher coloration efficiency means it requires less charge to obtain the same color change. Organic materials generally have higher coloration efficiency than inorganic ones due to higher molar absorption.[7]

Switching time

It is the time required to switch between the colored and bleached states. Usually time required to reach 90% of its highest contrast is recorded for convenience. It includes both the time needed for an electrochromic device to color from its bleached state and the time needed to bleach from its colored state. The switching speed of an electrochromic material

depends on many factors, like ion diffusion in thin films, ionic conductivity of the electrolyte, morphology of the film, film thickness, and magnitude of the applied potential.

Cycle life

If an electrochromic device switches between its colored and bleached state, after a certain amount of cycles the device will eventually fail. This may be due to induced stress or over-oxidization of the materials. The cycle life is the maximum number of cycles where the device retains its optical contrast. It is usually used to describe the long-term stability of the device.

There are also other parameters related to electrochromic devices, such as write-erase efficiency, defined as the percentage of the originally formed coloration that can be subsequently bleached; open-circuit memory, which can be described as the time lasted to retain the color after the external potential is removed at colored state.

2.1.3 A Few Important Types of Electrochromic Materials

2.1.3.1 Transition Metal Oxide

Transition metal elements are those with a partially filled d sub-shell, which can provide cations with different oxidation states according to the loss of electrons. Many types of transition metal oxides are found to be electrochromic because these materials possess different colors at different oxidation states, including WO_3 , [8] MoO_3 , [9] TiO_2 , [10] V_2O_5 , [11] Nb_2O_5 , [12] MnO_2 , [13] NiO , [14] SnO_2 , [15] Fe_2O_3 , [16] etc. WO_3 is the most widely used transition metal oxide for electrochromic device now due to its good contrast and long-term stability, as well as mature manufacturing techniques.

Currently the most acceptable principle of the electrochromism of transition metal oxides is simultaneous injection/extraction of electrons and ions. [17] Taking WO_3 as an example, the reversible redox process can be represented by the following reaction:

WO₃ thin film with W^{VI} is colorless. When cations (H⁺, Li⁺ or other alkali metal ion) and electrons are inserted simultaneously, some W^{VI} are reduced to W^V, and the color of the material changes to blue. When the cations and electrons are extracted, this reaction is reversed. W^V are oxidized to W^{VI} and the color returns to colorless.

There are varied methods to prepare an electrochromic transition metal oxide. Physical vapor deposition, like sputtering, is a common method to produce high quality transition metal oxides with highly ordered structure.[18, 19] However, the cost of the material is high prepared by such technique and a highly crystal structure limits the performance. Electrodeposition is another technique used for those with proper precursors.[20, 21] However, the size of the material is limited to the size of the cell and it is hard to control the microstructure. Sol-gel method is used lately as its low cost and control on microstructure.[8, 22] A drop casting/dip coating/spin coating process is to coat the material on the substrate and an annealing process is usually required.

2.1.3.2 Conjugated Polymers

A conjugated polymer is an organic macromolecule with a backbone chain of alternating single and double bonds. Their overlapping p-orbitals combine with each other to form a delocalized band of π -electrons. The high mobility of the electrons in this band contribute to the electrical conductivity of the conjugated polymers. Conjugated polymers can be either conductor or semiconductor, and the conductivity can be improved by doping. Now most research on conjugated polymers have been shifted to those with aromatic and heterocyclic aromatic structures.[23] Among varied types of conjugated polymers, three of them are deeply studied for electrochromic applications. They are polythiophenes, polypyrroles, and polyanilines. The repeating units of each type are shown in Figure 2.3.

Figure 2.3 Repeating units of different types of electrochromic conjugated polymers.

The electrochromism of conjugated polymers is the result of redox reactions, which is a p-doping/dedoping process.[7] In the oxidized state, the conjugated polymer is doped (p-doping) with counter anions and have a delocalized π -electron band. Upon reduction, the exit of counter anions or the incorporation of cations (dedoping) recovers the band structure of the conjugated polymer. Therefore, the redox reactions of conjugated polymers create and remove the new optical absorption band, causing color changes. Electrochromic conjugated polymers have advantages like high contrast, fast switching speed, flexibility and good processability.[24-26]

2.1.3.3 Composite/Hybrid Materials

Composite/hybrid materials have gained a lot of research interest. The prime reason is the potential to fabricate a material with advantages from both components. Conjugated polymer-based composites have been intensively studied for electrochromic applications. Many composites of conjugated polymers with transition metal oxides like WO_3 , [27] MoO_3 , [28] NiO , [29] TiO_2 , [30] etc. have been reported. Moreover, conductive nanoparticles like Au, [31] Ag, [32] and carbon materials like carbon nanotubes [33] and graphene [34] have been composited with conjugated polymers to enhance the electrochromic properties. Generally conjugated polymer/inorganic material composites exhibit higher coloration efficiency and faster switching speed. The higher coloration efficiency is attributed to the bridging effect of conductive particles as well as CNT and graphene, leading to a reduced charge transfer resistance. The faster switching speed is attributed to the shorter diffusion length due to the porous structure caused by the inorganic materials.[7] The challenge to fabricate a conjugated polymer-based composite with a

boosted electrochromic performance is to achieve synergistic effects of the two components. The design guidelines to deal with it could be to increase the interfacial area and/or improve the interfacial interactions.

To increase the interfacial area, the dispersion of nanoparticles in the polymer matrix needs to be improved. Zhu et al. used chlorosulfonic acid to disperse WO_3 nanoparticles and also as dopants of the conjugated polymer.[27] WO_3 is found to uniformly disperse in the polymer matrix and serve as a more efficient polymer intra-chain electron transfer pathway, resulting in a better conductivity and higher optical contrast. Zhang et al. used peroxotungstic acid (PTA) as the dopant for in-situ polymerization.[35] Later, PTA was converted to WO_3 and such preparation process led to good dispersion and large interfacial interaction. Faster switching speed and good long-term stability is obtained.

To improve the interfacial interactions between the components, different methods have been used to obtain different types of interfacial interactions. Covalent bond is a chemical bond that involves the sharing of electron pairs between two atoms. It has the highest bond energy among all types of interfacial interactions. The key improvement is reflected on the electron transport between the two components, from indirect inter-chain jumping to direct conduction along molecular chain.[36] To form covalent bond between the organic and inorganic components, a bridging functional group is usually required in the inorganic component. Xiong et al. functionalized single-walled CNT (SWCNT) to SWCNT-COOH and covalently grafted with PANI.[37] Due to the good conductivity of CNT and covalent bond between CNT and PANI, an effective conductive network is formed in PANI matrix, thus the redox process are easily proceeded and electrochromic performances are enhanced. Coordination bond is a special covalent bond, where a lone pair of electrons from ligand occupy the empty orbital of central atom. In a typical electrochromic coordination complex, transition metal atoms act as the central atom and derivatives of pyridine act as the ligand. The electrochromism of such material comes from the redox process of the transition metal and the metal to ligand charge transfer.[38] For instance, Hsu et al. prepared an electrochromic coordination complex with Co ion and 4'-4''-(1,4-phenylene) bis(2,2':6',2''-terpyridine).[39] It demonstrates high optical contrast and fast switching

speed because the charge transfer between central atom and ligand is enhanced by the coordination bond. Electrostatic interaction is commonly existed interaction caused by attractions between positive and negative charges. It can be utilized in the layer-by-layer (LBL) assembly of electrochromic multilayer films. A LBL assembled PANI/Prussian blue composite was prepared by alternating adsorbing polyanion and polycation.[40] The alternately arranged polyanion and polycation act as ion storage reciprocally, thus the ion transport distance is shortened and a fast switching speed is obtained. Hydrogen bond is the interaction between a hydrogen atom that is adjacent to an electronegative atom and another electronegative atom. Akpinar et al. studied the influence of hydrogen bond on electrochromic performance and found that it was important to control the quantity of hydrogen bond as it directly affected the polymer conformation.[41] Varied types of interfacial interactions have been studied and found helpful in improving electron and ion transport, as well as electrochemical properties.

2.2 Specific Electrochromic Materials Closely Related to This Work

2.2.1 Molybdenum Oxide (MoO_3)

MoO_3 is one of the transition metal oxides that are studied for electrochromic applications. MoO_3 has three crystal phases, orthorhombic α - MoO_3 , monoclinic β - MoO_3 and hexagonal h - MoO_3 . (Figure 2.4) Most of studies focus on conventional thermodynamically stable phase α - MoO_3 . It consists of MoO_6 octahedra arranged in a variety of corner-sharing and edge-sharing arrangements, resulting in zigzag chains and unique layers parallel to the (010) plane structure, presenting open channels for H^+ or Li^+ ion intercalation.[42] H - MoO_3 has also been studied as it has large tunnel structure which can serve as conduits and intercalation sites for mobile ions.[43]

Figure 2.4 Three MoO_3 crystal phases: orthorhombic $\alpha\text{-MoO}_3$, monoclinic $\beta\text{-MoO}_3$ and hexagonal h-MoO_3 . [44]

The principle of electrochromism for MoO_3 is similar to WO_3 . During the simultaneous injection of electrons and ions, Mo^{VI} is reduced to Mo^{V} and the color of the material changes from colorless to blue. Upon reduction, the electrons and ions are extracted and the color returns. The reversible reaction can be represented by the following equation:

MoO_3 can be prepared by sputtering [45], hydrothermal method [46], electrodeposition [47] and sol-gel method [48]. Comparing with commonly used WO_3 , MoO_3 has its unique advantages. It shows apparent contrast as its highest contrast occurs at the wavelength that is more sensible to human eyes. [43] Also, MoO_3 shows better open circuit memory, that the color could remain longer time after the removal of external potentials. [9] However, MoO_3 has relatively poor long-term stability. Li^+ intercalation process may lead to structural distortion and non-uniform coloration. [47] During cycling, some Li^+ ions are trapped in the film and cracks occur on the surface. [49] Recently, electrochromic MoO_3 film was prepared by pulsed laser deposition with high optical contrast, but the long-term stability remained as an issue of MoO_3 . [50] The number of work on electrochromic materials with MoO_3 as major component is limited by its drawbacks, especially over the past decade.

2.2.2 Poly(3,4-ethylenedioxythiophene) (PEDOT)

Due to the two electron-donating oxygen atoms adjacent to the thiophene unit, PEDOT has relatively lower bandgap about 1.6 eV.[51] PEDOT has good stability at its doped state and high electronic conductivity. The monomer EDOT and polymer PEDOT are not soluble in water. This issue could be solved by the addition of water-soluble dopant poly(styrene sulfonate) (PSS). PEDOT:PSS is composed of positively charged conjugated PEDOT and negatively charged PSS dopant, which is commercially available aqueous dispersion. (Figure 2.5)

Figure 2.5 Chemical structure of PEDOT:PSS, where PEDOT is doped with PSS.

PEDOT has a molecular weight of about 1,000-2,500 g mol⁻¹, while PSS is about 400,000 g mol⁻¹. [52] PEDOT chains are much shorter than PSS chains. PEDOT and PSS chains are attached together due to electrostatic interactions. As a result of the hydrophobicity of PEDOT and hydrophilicity of PSS, PEDOT:PSS has a necklace structure.[53] (Figure 2.6) Each blob has a core/shell structure with PEDOT in the core and PSS in the shell. The excess PSS that is not doped with PEDOT dissociate into protons and anions. The linear conformation minimizes the repulsion between anions and the repulsion separates each

blob. Such structure results in PEDOT-rich domain and PSS-rich domain, which leads to non-uniform distribution of conductivity in PEDOT:PSS.

Figure 2.6 Conformation structure of PEDOT:PSS. The black chain represents PSS and the blue chains represent PEDOT.

PEDOT:PSS is electrochromic as it has reversible electrochemical oxidation and reduction. (Figure 2.7) The color of PEDOT:PSS can change from transparent light blue to dark blue reversibly. Kawahara et al. reported an electrochromic device with contrast about 42% built by controlling the thickness of PEDOT:PSS.[54] Tehrani et al. prepared PEDOT:PSS based electrochromic paper display, utilizing the flexibility of PEDOT:PSS.[55] Gomes et al. increased the conductivity of PEDOT:PSS used in the electrochromic applications by adding conductive particles to enhance the performances.[56] Generally, the optical contrast could be improved by increasing the thickness, but the switching time is influenced as the ionic transport is hindered by the stodgy morphology.

Figure 2.7 Chemical structure of PEDOT in colored and bleached state.

2.2.3 Polyaniline (PANI)

PANI is a type of conjugated polymer with good environmental stability, cheap monomer, unique redox states and doping/dedoping properties.[57] Its unique redox properties reflect on its multiple oxidation states. Unlike PEDOT which only has two major oxidation states, PANI has three major oxidation states, named leucoemeraldine (fully reduced), emeraldine (half-oxidized) and pernigraniline (fully oxidized). (Figure 2.8) The difference between these states can be determined by the number of benzenoid and quinoid units in polyaniline structurally.[57] If only benzenoid rings in the undoped form are present, polyaniline is in its leucoemeraldine state. If there are two quinoids every 8 monomer units, polyaniline is in emeraldine state. If there are four quinoids every 8 monomer units, with every alternating ring being a quinoid, polyaniline is pernigraniline state. The emeraldine base can be doped to emeraldine salt by protonic acid, which is the most conductive state of polyaniline. Polyaniline exhibits different colors at different oxidation states. The reversible electrochromism of polyaniline is to change from yellow to green, between leucoemeraldine and emeraldine salt state.

leucoemeraldine (yellow)

emeraldine salt (green)

emeraldine base (blue)

pernigraniline (black)

Figure 2.8 Different oxidation states of polyaniline.

The common preparation methods of polyaniline are electrochemical polymerization and chemical oxidative polymerization.[58] PANI was electrodeposited on the substrate in the aniline solution to prepare electrochromic films.[59] Both potentiostatic and potentiodynamic techniques could result in continuous and fast-grow PANI films. Under chemical oxidative polymerization, aniline is polymerized in the presence of oxidant, like ammonium persulfate (APS).[60] Such PANI prepared by chemical oxidative polymerization has longer chains with better long-term stability. As the fact that PANI has different oxidation state, a multi-color electrochromic device is able to build using PANI-based composite. PANI/graphene oxide[61], PANI/TiO₂[62], and PANI/Prussian blue[40]

have been studied for multi-color electrochromism. The disadvantage of PANI in electrochromic application, which is similar to other conjugated polymers, is the over-oxidation issue during the cyclic electrochemical process. The degradation caused by relative high potentials gradually influences the conductivity and electrochromic performances.[63, 64]

2.3 Flexible Electrochromic Devices

Flexible electronics have attracted lots of research interest recently due to ever-growing demands for flexible and wearable devices. Flexible electronics can be bended, folded or rolled, which can easily achieve what traditional hard electronics cannot achieve owing to their lighter weight, improved comfort, and higher space efficiency.[65] Flexible displays are required for the fabrication of next-generation e-papers that can possibly be folded like a regular paper. Flexible electrochromic devices are potentially fabricated as flexible displays for smart clothes and implantable display applications.[66]

To fabricate a flexible electrochromic device, rigid components in the typical electrochromic device need to be replaced by flexible components. Bulk electrochromic materials have been changed to nano-sized ones to increase the flexibility of the materials. For instance, WO_3 nanoparticles and nanosheets have been used in flexible electrochromic devices and demonstrated some degree of cyclic stability under bending condition.[67, 68] Also, gel-electrolyte based materials have been studied for flexible electrochromic device.[69, 70] Organic materials are the most common and promising candidates for highly bendable electrochromic device.[71, 72]

Another point is to increase the flexibility of the electrode used in the electrochromic device. Instead of glass, polyethylene terephthalate (PET) is the most commonly used substrate in flexible electronics due to its low cost, good transparency, flexibility and barrier properties. A thin layer of ITO can be deposited on a PET sheet to make it conductive. However, unlike highly conductive ITO glass, it is difficult to obtain high-quality ITO coatings on a plastic substrate due to reduced activation efficiency of the tin

dopant and highly defected microstructure, which is caused by the poor thermal stability of the polymer substrate and high deposition rate[73]. To address this issue, other materials with both good conductivity and flexibility have been studied as alternatives of ITO. For example, metal nanowires or nanopatterns, such as Ag nanowires[74] and Cu nanopatterns[75], deposited on transparent polymer films have been intensively investigated because of their excellent electrical conductivity. Owing to their low percolation thresholds, the conductive networks formed on transparent polymer films showed good transparency and flexibility[74]. However, the undesirable surface toughness[76], the junction resistance between distinct nanowires[77], and especially the oxidation and corrosion of the metals under positive voltage[78] could deteriorate the performance and stability of the conductive networks, reducing life-time of the flexible electrochemical devices. Carbon nanotubes (CNTs) are another promising material with good electrical conductivity and flexibility[79]. Flexible polymer films with deposited CNT random networks could be highly bendable. For instance, light emitting diodes built on CNT electrodes could be bended to 2.5mm radius without failure[80]. By hybridizing a polymer into the system, though the resistance increases slightly, the flexibility of the electrode can be further improved[81]. More importantly, CNTs exhibit excellent electrochemical stability, making them more suitable for electrochemical device applications.

2.4 Supercapacitors and Electrochromic Supercapacitors

2.4.1 Types of Supercapacitors and Electrode Materials

Supercapacitors are energy storage devices that have higher capacitance than traditional capacitors, and have higher power density and longer cycle life than batteries.[82] Depending on the storage mechanism, there are two types of supercapacitors: electric double-layer capacitors (EDLC) and pseudocapacitors. EDLC stores electrical energy by the electrostatic adsorption and desorption of ions in the conductive electrolyte, thus creating the double layers at the electrode and electrolyte interface. Pseudocapacitors store

energy through the redox reactions occurring at the electrode surface, which usually has higher capacitance than EDLC.

There are mainly three types of commonly used electrode materials for supercapacitors: carbon-based materials, metal oxides and conjugated polymers. Carbon based materials, as EDLC materials, have advantages of low cost, good conductivity, ease of processability and good stability due to inert electrochemistry.[83] Activated carbon,[84] carbon nanotubes,[85] graphene[86] and mesoporous carbon[87] have been used for supercapacitors electrodes. Metal oxides are commonly used pseudocapacitor materials, which have high specific capacitance, such as RuO_2 , [88] MnO_2 , [89] IrO_2 , [90] NiO , [91] Co_2O_3 , [92] V_2O_5 [93] etc. RuO_2 is the most studied metal oxide, which has high specific capacitance, wide potential window, good thermal stability, long cycle life, metallic type conductivity.[94] However, the material cost is too high. MnO_2 is a good alternative to RuO_2 due to low cost, good environmental safety and good specific capacitance.[95] However, metal oxides are rigid materials which limit the applications in flexible devices. Conjugated polymers are another type of pseudocapacitor materials and are more flexible than metal oxides. Conjugated polymers usually have advantages of low cost, good conductivity, and flexibility,[96] but have the drawbacks like poor long-term stability caused by swelling and shrinking.[82]

2.4.2 Key Parameters of Supercapacitors

Capacitance is the key performance of a supercapacitor. It is related to the nature of the electrode material, the capability to storage the charges, the electronic conductivity and ionic conductivity of the material. The specific capacitance is usually used to evaluate a supercapacitor, which is the capacitance per unit mass of the electrode material. It can be measured via either a discharge curve or a cyclic voltammetry.

From a discharge curve, the specific capacitance is calculated as

$$c = \frac{It}{m\Delta V}$$

where I/m is the discharge current density, t is the discharge time, ΔV is the potential window.

From a cyclic voltammetry, the specific capacitance is calculated as

$$c = \frac{A}{vm\Delta V}$$

where A is the area enclosed by CV diagram, v is the scan rate, m is the mass of the material, ΔV is the potential window.

Rate capability is another interested performance of supercapacitors. Basically, it compares the specific capacitance at different current density. Usually the calculated specific capacitance drops as the current density increases due to limitation on kinetics. A supercapacitor with good rate capability has a similar specific capacitance at high current density than that at low current density, which indicates the discharging current density does not influence on the performance obviously. Such supercapacitors can function well under high current density, providing more potential applications.

Cyclic stability is a long-term performance of supercapacitor after charge/discharge cycles. The specific capacitance usually decreases as the cycle number increases. This may be caused by over-oxidization or physical damage during the cycling process. The ability of the supercapacitor to retain the specific capacitance as its first cycle determines the lifetime of the supercapacitor.

2.4.3 Carbon Nanotube (CNT) for Supercapacitors

CNT is a long and slender fullerene where the walls of the tubes are hexagonal carbon and often capped at each end,[97] which can be visualized as a sheet of graphite rolling into a tube. The unique structure of CNT has brought unusual properties. CNTs demonstrate excellent mechanical, thermal and electric properties. CNTs can be categorized as single-walled CNT (SWCNT) and multi-walled CNT (MWCNT). Both of them have been widely used in supercapacitors. CNTs are regarded as a popular choice in supercapacitor electrode

material because of their good electrical conductivity and readily accessible surface area. Moreover, their high mechanical strength and open tubular network make them a good support for other active materials.[83] In the early study, neat CNT supercapacitor electrode was prepared and it had a specific capacitance of 102 F g^{-1} in an acidic electrolyte.[98] To deal with the entanglement of CNTs and increase the surface area, a densely packed aligned SWCNT supercapacitor electrode was prepared and showed a better energy density of 35 Wh kg^{-1} and good rate capability.[99]

On the other hand, CNTs are used in composites to incorporate a nanotubular backbone coated by other pseudocapacitive materials with higher capacitance, like CNT/metal oxide composite. For example, MWCNT/RuO₂ composite has been studied for its capacitive performance, and it showed a significant increase comparing to pristine MWCNTs.[100] MnOx/CNT/Ni nanocomposite electrodes showed good electrochemical reversibility and a high capacitance of 415 F g^{-1} at 5 mV s^{-1} . [101] Some basic reasons why such material is preferred are: (1) the percolation of the metal oxide particles is more efficient with CNTs than traditional carbon materials; (2) the entanglement of nanotubes forms an open mesoporous network, allowing the ions to easily diffuse to the active sites of the composite; (3) the strength of CNTs enable the composite electrodes easily adapt to the volumetric changes during charge/discharge process, improving the cyclic stability.[102]

2.4.4 Polyaniline in Supercapacitors

PANI is an intensely studied material for supercapacitors. Though as a conjugated polymer it has the advantages mentioned previously, it also faces several challenges as a supercapacitor electrode material. Firstly, the conductivity of PANI at reduced state is lower than that at its oxidized state.[37] The relatively low conductivity at reduced state hinders electron transport in the redox process of PANI, leading to slower kinetics of oxidation, and therefore limiting its specific capacitance. In addition, polymer binders are typically mixed with active materials in supercapacitors to bind the active materials to the substrates.[103] The binder added, such as polyvinylidene difluoride (PVDF), is typically electrochemically inert and non-conductive, which may further reduce the conductivity of

the electrodes. Secondly, owing to its molecular nature, bulk PANI exhibits a compact morphology.[104] This hinders ion transport in PANI in redox processes, and hence the regions that are not directly exposed to electrolyte are difficult to undergo redox reactions, leading to less active units. Furthermore, during the charge/discharge process some PANI units may be over-oxidized at relatively high potentials and hence a small portion of oxidized PANI units could not be reduced back, causing decay of capacitance in a long-term cyclic process.

To address the aforementioned issues, various approaches have been explored. To increase the conductivity of PANI, the combination of PANI with carbon nanomaterials is a popular approach. Yan et al. mixed PANI with graphene and demonstrated enhanced electrochemical properties.[105] Li et al. chemically grafted PANI onto CNTs to extend the conjugation length of PANI and achieved a high conductivity of 3009 S cm^{-1} for the PANI/CNT composite with CNT content of 70 wt%.[106] To enhance ion transport, Yan et al. prepared a graphene nanosheet/PANI composite via in situ polymerization.[107] The good performance was attributed to excellent electrical conductivity and unique microstructure, in which the dispersion of nanoscale PANI particles on graphene nanosheets reduces the diffusion length of ions. It was also reported that vertically aligned PANI nanowire arrays exhibited a capacitance of 950 F g^{-1} at a current density of 1 A g^{-1} . [108] The aligned arrays of PANI enabled high specific surface area and short ion diffusion path, which benefit the improvement of the specific capacitance of PANI, whereas to improve the electrochemical stability of PANI, a more effective approach is to utilize the interfacial interactions between sp^2 carbon and PANI to stabilize the conjugated structure. For example, PANI deposited on MWCNTs could reach a capacitance of 1065 F g^{-1} at a current density of 0.5 A g^{-1} and good cyclic stability up to 1000 cycles.[109] Although the aforementioned approaches could effectively boost the performance of PANI-based supercapacitors in certain aspects, so far high capacitance were typically achieved at relative low current density, and simultaneous enhancement of electrical conductivity, ion transport and electrochemical stability remains a challenge.

2.4.5 Electrochromic Supercapacitor

It is helpful to integrate electrochromism with other functions into one device with attractive applications. Integration of electrochromic devices and energy-storage devices becomes more and more popular.[110] WO_3 -based electrochromic energy-storage windows are readily studied.[111, 112] Electrochromic energy-storage smart windows are able to not only adjust the sunlight and solar heat through the windows, but also can be used as energy-storage devices at the same time. Moreover, the level of energy stored in the window can be monitored by the color variations. Electrochromism has been integrated with sensors also. A ribonuclease B sensor is built together with Prussian blue electrochromic device, in which the detection limit of ribonuclease B is as low as 0.12 pM and it is reflected on the color change of Prussian blue.[113]

The term “electrochromic supercapacitor” was first mentioned in 2012 when Wei et al. fabricated a freestanding vanadia network by electrodeposition into a voided block copolymer template that had self-assembled into the double-gyroid morphology.[114] Such material exhibit a specific capacitance of 155 F g^{-1} and a color change from green/gray to yellow. The key concept of electrochromic supercapacitor is that the charging state of the supercapacitor can be demonstrated by the color of the material based on electrochromism. The same material that is electrochromic and able to perform good capacitive properties is the key factor to make an electrochromic supercapacitor.

2.5 Concluding Remarks

MoO_3 is an electrochromic transition metal oxide that has more apparent optical contrast and better memory effect than currently widely used WO_3 . However, MoO_3 is not widely used due to its low conductivity and poor long-term stability. The deterioration of MoO_3 is caused by Li^+ trapping in the active sites and induced stress during Li^+ intercalation/deintercalation process. MoO_3 /conjugated polymer composite has the potential to improve the mentioned issue in order to get a stable electrochromic performance.

PANI is a conjugated polymer with good conductivity, cheap monomer, and flexibility. Conjugated polymer is a common electrochromic material used in flexible electrochromic device. However, the flexible electrode currently used is either ITO/PET that suffers under bending condition, or Ag/Cu nanowires and nanopatterns that suffer oxidation under oxidation/reduction-based applications. A flexible electrode that is more suitable for electrochromic applications is absent. In terms of stability under electrochemical reactions, carbon materials such as CNT based materials have more potential to use as the electrode in flexible electrochromic devices. PANI is also a good supercapacitor electrode material with high capacitance due to its pseudocapacitance. Therefore, the idea of electrochromic supercapacitor is able to realize using PANI as both the supercapacitor electrode and electrochromic indicator. The challenge of PANI as a supercapacitor electrode material includes the relatively low conductivity at reduced state, poor ion transport due to compact morphology and over-oxidation issue.

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Chapter 3

Experimental Methodology

For the composite materials studied in this thesis, the dispersion of the discrete phase and interfacial interactions are very important factors affecting the properties of the composites. Thus, in this chapter, the principles underlying the different characterization techniques used to study the dispersion in the composites and interfacial interactions between the components, such as scanning electron microscope, X-ray photoelectron spectroscopy, and Raman spectroscopy, are discussed. Other similar techniques are compared with them and the reasons why such techniques are chosen in the specific work are clarified. Furthermore, important electrochemical characterization methods used in this work are discussed.

3.1 Overview

Various experiment techniques have been used in this thesis work. In terms of the purpose, most of the techniques used can be classified into two major categories: (1) techniques used to characterize the materials, (2) techniques used to test the electrochemical properties. In the first category, to characterize the materials, the techniques used involve scanning electron microscope, transition electron microscope, X-ray diffraction, Fourier-transform infrared spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, dynamic light scattering, etc. They can provide the material information such as morphology, composition, crystal structure, chemical structure, particle size, zeta potential, etc. In section 3.2, several techniques are discussed in detail as they can be used to study the dispersion in the composite and interfacial interactions between the two components of the composite, which are the most important factors to the performance of the composite. In the second category, to test the electrochemical performances of the composites, some electrochemistry techniques are conducted to probe the electrochemical and electrochromic properties of the composite, such as in situ spectroelectrochemical test, cyclic voltammetry, and electrochemical impedance spectroscopy. The principles of the mentioned techniques are discussed in section 3.3.

3.2 Techniques Used to Study Composite Structures and Morphologies

3.2.1 Scanning Electron Microscope (SEM)

SEM is an instrument of which the specimen surface is scanned by a focused beam of electrons, where the signals generated from electron sample interaction forms image, showing the surface morphology of the specimen. Comparing to optical microscope, SEM has higher resolution that is defined as the smallest distance at which two objects can be distinguished and recognized as individual objects. According to Abbes equation, the resolution d is calculated as

$$d = \frac{0.61\lambda}{NA}$$

where λ is the wavelength of the energy source, NA is a constant called Numerical aperture. The resolution is proportional to the wavelength. Smaller wavelength of the energy source gives better resolution. The wavelength of an electron beam is related to the accelerating voltage of the electron beam.

$$\lambda = \frac{h}{\sqrt{2meV}}$$

where h is the Planck's constant, m is the mass of electron, e is the electronic charge of electron, V is the accelerating voltage.

The wavelength of the electron beam with accelerating voltage of 5 kV is about 0.173 Å, which is much smaller than the wavelength of light (about 4000 Å). This leads to a higher resolution of SEM (10.55 Å) than optical microscope (2400 Å).

When the electron beam scans the surface of the specimen, the electron beam interacts with the coulomb field of both the specimen nucleus and electrons. These interactions result in multiple signal types. (Figure 3.1) Backscattered electrons are caused by elastic scattering events that affect the trajectories of the electron beam without changing the kinetic energy of the electrons. Inelastic scattering events that result in transfer of energy from the beam electrons to the atoms of the specimen cause secondary electrons and X-rays. If an electron is expelled from the atom, it is a secondary electron. If the vacancy due to the creation of a secondary electron is filled by another electron from a higher-level orbital, a characteristic X-ray of that energy transition is produced. By collecting these three different types of signals, there are three modes in SEM: secondary electron imaging (SEI), backscatter electron imaging (BEI), and energy dispersive X-ray analysis (EDX).

Figure 3.1 Multiple types of signals from electron sample interactions.

SEI is used to provide morphology information of the specimen with the highest resolution. BEI is used to distinguish different components in a multi-component material. This is because contrast observed in BEI is proportional to atomic number. Elements with higher atomic number will appear brighter than element with lower atomic number. EDX is used to analyze elements in the specimen as each element emits a characteristic set of wavelengths. EDX can also be used for quantitative analysis as peak intensity is proportional to the amount of the element.

EDX is a common technique to study the element distribution in the composite material under mapping mode. However, in Chapter 4, SEM-EDX is not used to study the dispersion of MoO_3 nanoparticles in PEDOT:PSS. The reason is that the characteristic X-ray of Mo (2.293 keV) has very similar energy to S (2.307 keV). (Figure 3.2) This leads to the mapping images of Mo and S element almost fully overlap, which cannot provide information about the dispersion of MoO_3 nanoparticles in PEDOT:PSS. Therefore, in Chapter 4, low angle backscattered electron (SEM-LABE) mode is used. As MoO_3 has higher average atomic number, it is brighter in the SEM-LABE image, thus shows the dispersion of MoO_3 nanoparticles in PEDOT:PSS.

Figure 3.2 EDX spectrum of MoO₃/PEDOT:PSS composite.

Transmission electron microscope (TEM) is another option to study the material composition. TEM is also an imaging technique in which the specimen is scanned by a beam of high energy electrons and the signals that transmitted through are collected. TEM operates on the same basic principles as the optical microscope but uses electron instead of light. When an electron beam passes through the specimen, electrons are scattered. A sophisticated system of electromagnetic lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano-analytical spectrum, depending on the mode of operation. In TEM image, the contrast is determined by the absorption of electrons by the material. A heavier atom is darker in TEM image, thus the dispersion of MoO₃ nanoparticles can be exhibited in TEM image. However, the sample preparation of TEM requires the sample must be very thin (less than 100 nm). As a result, the sample is usually dispersed in solvent by ultrasonication and then dropped on the Cu grid sample holder. This sample preparation process may damage the original structure of MoO₃/PEDOT:PSS, so the TEM image observed is not the true morphology of the composite. Therefore, TEM is not used in Chapter 4 to study the dispersion of MoO₃ nanoparticles in the composite.

However, TEM is used to observe the particle size of MoO₃ nanoparticles and lattice is observed under TEM to confirm the crystallinity.

In Chapter 5, SEM-SEI is used to study the morphology of PANI-CNT. CNTs have different morphology to PANI, so the dispersion of CNTs at the surface can be observed in the image. As the scanning time increases, PANI is gradually burned by the accumulating charges, thus CNTs underneath can be observed. The 3D network of CNTs is observed under SEM-SEI. EDX is not able to study the dispersion in this case because carbon as the main component of CNT exist in both components.

In Chapter 6, the surface morphology is observed by SEM-SEI and the etching process of porous PANI-CNT composite is monitored by SEM-EDX. The pores are created by removing CaCO₃ nanoparticles in the composite via acid etching. The mapping image of Ca element before etching process exhibits the dispersion of CaCO₃ nanoparticles in the material. The mapping image of Ca element after etching process certifies the successful removal of CaCO₃ nanoparticles. The elemental analysis by EDX enable it a useful technique in the work. SEM-SEI is used to study the morphology at the cross-section, to observe the porous structure inside PANI-CNT.

3.2.2 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface analytical technique that measures the elemental composite, chemical state and electron state of the elements in the material. The principle of XPS is photoelectric effect. The sample in XPS is irradiated with a beam of X-rays and the energies of the resulting photoelectrons are measured. The photoemission process can be described by the formula

$$KE = h\nu - (BE + \phi)$$

where KE is the kinetic energy of the photoelectron measured by the analyzer, BE is the binding energy of each core atomic orbital of each element, $h\nu$ is the X-ray photon energy depended on the X-ray source, ϕ is the instrumental work function.

The binding energy is the characteristic of the core electrons for each element. The intensity of signal at different binding energy is plotted in the spectrum. Each peak represents photoelectrons emitted from a particular core level with a characteristic BE.

$$BE = h\nu - (KE + \phi)$$

Since each element has a unique set of core levels, binding energy can be used as fingerprint for an element.

XPS can not only help to identify what elements exist in the sample, but also give the information about the chemical state of the element. The exact binding energy of an electron mainly depends on the level where photoemission occurs, but the change in the oxidation state of the element gives rise to small shifts in the peak position. The chemical shift is the change in binding energy of a core electron of an element due to a change in the chemical environment.

The interfacial interaction within a composite, like electrostatic attraction, will influence on the binding energy. The strong interactions between two components make electrons required more energy to escape from the nuclei, so a chemical shift is present for the component in the composite that has interactions with others. XPS can be used to study the interfacial interactions within the composite and it provides solid evidence for the presence of strong interactions between MoO₃ and PEDOT:PSS in Chapter 4.

Other techniques that may be used is Fourier-transform infrared spectroscopy (FTIR). Spectroscopy is a group of technique that study the interaction of electromagnetic radiation with the specimen to obtain characteristic information about the material. FTIR deals with the absorption of radiation by the specimen in infrared (IR) region causing molecular vibration. Simply, it is the absorption measurement of different IR frequencies by a specimen positioned in the path of IR beam. The main goal of FTIR is to determine the chemical functional groups in the sample. Different functional groups absorb different characteristic frequencies of IR radiation. Each band/peak in the spectrum represents absorption of IR at that frequency by the sample. The change in chemical environment may also lead to a shift in the band/peak position. However, the resolution of FTIR cannot

demonstrate the influence of electrostatic interactions in MoO₃/PEDOT:PSS. Therefore, XPS is chosen to study the electrostatic interactions in the composite in Chapter 4.

3.2.3 Raman Spectroscopy

Raman spectroscopy is a technique that can provide chemical structure information like FTIR. In Raman spectroscopy, a laser light is irradiated on the specimen and an infinitesimal amount of Raman scattered light is generated and detected. The characteristic fingerprinting pattern in Raman spectrum provides information about chemical structure, phase and polymorph, crystallinity and molecular interactions.

The principle of Raman spectroscopy is based on the light scattering by the molecule. Almost all of the scattering is elastic process (Rayleigh scattering) and there is no change in energy. A very small percentage of scattering is inelastic process (Raman scattering), and the scattered light has different energy from incident light. Raman scattering can be classified as two types: Stokes Raman scattering and anti-Stokes Raman scattering. Stokes Raman scattering is a process that an electron is excited from the ground level to a vibrational level. Energy of the incident light is absorbed by the molecule, so Stokes Raman scattered light has less energy than the incident light. Contrarily, anti-Stokes Raman scattering is a process that an electron is excited from the vibrational level to the ground level. Energy is transferred to the scattered light, so anti-Stokes Raman scattered light has more energy than incident light.

Raman spectrum is plotted by intensity versus Raman shift. Raman shifts are usually in wavenumber, in the unit of reciprocal of length, and calculated as

$$\Delta\omega = \frac{1}{\lambda_0} - \frac{1}{\lambda_1}$$

where λ_0 is the excitation wavelength, λ_1 is the Raman spectrum wavelength.

A Raman spectrum contains a number of peaks and each peak corresponds to a specific molecular bond vibration. The change in intensity and position of peaks is related to the change of respective bond.

In Chapter 6, Raman spectroscopy is used to verify the chemical structure change between PANI, PANI-CNT and porous PANI-CNT. A peak in the PANI and PANI-CNT spectrum becomes a shoulder in the porous PANI-CNT spectrum, indicating some PANI that are not grafted on CNTs are removed by the washing process. This leads to an increase in the average conjugation length. FTIR is another potential technique that provides information about chemical structure. There are two reasons why FTIR is not used in the work. Firstly, FTIR is only sensitive to polar bonds. The major bonds in the composite is C-C non-polar bond. Raman signals are more abundant for such bond. Secondly, due to the hard nature of CNT, it is impossible to fabricate a homogenous pellet for FTIR transmission test. Thus, attenuated total reflectance (ATR) is the only way to get FTIR signal of the sample. However, due to the porous morphology of PANI-CNT, the reflection is highly influenced and the signal is noisy. The shift of peaks caused by the extension of conjugation length is unreadable.

3.3 Electrochemical Tests

3.3.1 Three-electrode Electrochemical Cell

To examine the performance of an electrochromic device or a supercapacitor, the device must be connected into a circuit. A two-electrode electrochemical system is a straightforward approach to do the test but it has shortcomings. Most significantly, it is difficult for an electrode to maintain a constant potential when passing current to counter redox events at the working electrode. Also, in the laboratory an electrochromic cuvette is usually used in the test. In the cuvette, only half of the electrochromic device is present. In this case, a three-electrode system is preferred, which contains working electrode, reference electrode and counter electrode. (Figure 3.3) The working electrode connects the sample and the counter electrode passes the current needed to complete the circuit. The reference electrode works as reference in measuring and controlling the working electrode's potential, with a known reduction potential. No current passes through this

electrode. All three electrodes are immersed in the electrolyte. This three-electrode cell is widely used in the following electrochemical tests.

Figure 3.3 Scheme of a three-electrode electrochemical cell.

3.3.2 In Situ Spectroelectrochemical Test

UV-Vis spectroscopy is a common technique to examine the optical property of a material. UV-Vis spectroscopy probes the electronic transitions of the sample as it absorbs light in the UV (200-400 nm) and visible regions (400-800 nm) of the electromagnetic spectrum. Either absorbance or transmittance of the sample can be measured. UV-Vis spectra are plotted as absorbance or transmittance versus wavelength (nm). Absorbance (A) is a quantitative measure of the extent to which a compound absorbs UV radiation at a particular wavelength.

$$A = \log_{10} \frac{I_0}{I}$$

where I_0 is the intensity of the incident radiation on the sample, I is the intensity transmitted through the sample.

Transmittance (T) is

$$T = \frac{I}{I_0}$$

and usually presented as a percentage.

Therefore, absorbance and transmittance could be converted by

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

The absorbance has a linear relationship with concentration according to Beer Lambert's Law:

$$A = \varepsilon cL$$

where ε is the molar absorptivity, c is the concentration, L is the pathlength through the sample.

In the thesis, the optical contrast is the change in transmittance measured by in situ spectroelectrochemical test, where the sample is connected to a potentiostat and the transmittance of the sample is simultaneously measured by UV-Vis spectroscopy at different potentials. Such technique is widely used in the electrochromic studies and it provides in situ information that both the optical and electrochemical properties at the same time. The spectra at different potentials, the switching curves, the long-term stabilities and the coloration efficiencies all can be tested by this technique.

3.3.3 Cyclic Voltammetry (CV)

CV is a powerful tool to measure electrochemical properties of materials. CV is usually tested in a three-electrode electrochemical cell. The working electrode potential is ramped linearly versus time and the current is recorded. After it reaches the set max potential, the working electrode potential drops to the initial potential at the same speed. The cyclic scan may be repeated for many times. The current measured is plotted versus the potential to get the CV diagram. Among the three electrodes, the working electrode is the interested material. The reference electrode should have a stable and known electrode potential. Ag/AgCl electrode is used in the works of this thesis. The counter electrode should be electrochemically inert and Pt is used in the works.

The wide application of CV on electrochemical studies is because of the fact that it provides information about the redox reactions. During the voltage scan, at certain ranges the redox reactions occur, leading to a sudden increase of current. Therefore, it exhibits a peak in CV

diagram where the redox reaction occurs. Peak positions provide information of oxidation/reduction potentials, which gives a guide to select suitable switching voltages for electrochromic applications. Also, the area enclosed by CV diagram represents the value of (charge * scan rate). By dividing the scan rate, the total charge in the process could be estimated. A material with a higher enclosed area implies the material has better electrochemical activity.

3.3.4 Electrochemical Impedance Spectroscopy (EIS)

Resistance is the ability of a circuit element to resist the flow of electrical current. A well-known relationship Ohm's law defines the value of resistance as the ratio of voltage E and current I:

$$R = \frac{E}{I}$$

However, this relationship is limited to only one circuit element, the ideal resistor, which has simplifying properties like the resistance is independent of frequency, as well as alternating current (AC) and voltage signals are in phase with each other. In a more practical scenario, more complex circuit elements are present and the circuit shows more complex behavior. Impedance replaces resistance in the scenario, which measures the ability of a circuit to resist the flow of electrical current, but not limited by the simplifying properties.

Electrochemical impedance is measured by applying a small sinusoidal potential of a fixed frequency. The response current should be at the same frequency but shifted in phase. The response current is also AC and the impedance is calculated as

$$Z_{\omega} = \frac{E_{\omega}}{I_{\omega}}$$

where both E_{ω} and I_{ω} are frequency dependent.

Such test will be conducted for a wide range of frequencies and the data are analyzed.

The information provided by EIS is much more than a single frequency resistance. EIS may be able to distinguish between two or more electrochemical reactions taking place.

Also, EIS can identify diffusion-limited reactions. Moreover, EIS can provide information about the electron transfer rate of reaction. It is also a convenient method that is able to use the device's own electrodes to test the component within an assembled device. Therefore, EIS is widely used in electrochemical studies. In this thesis, EIS is mainly used to study the charge transfer resistance of the materials.

Chapter 4

Facile Preparation of Molybdenum Trioxide/Poly(3, 4-ethylenedioxythiophene):Polystyrene Sulfonate Nanocomposites for Enhancement of Electrochromic Properties

In this chapter, a molybdenum trioxide/poly(3,4-ethylenedioxythiophene):polystyrene sulfonate ($\text{MoO}_3/\text{PEDOT:PSS}$) composite material is prepared via electrostatic interaction between MoO_3 nanoparticles with negative charged surface groups and positive charged PEDOT. Such composite exhibits good electrochromic performance as the conductive PEDOT:PSS facilitates the electron transport in and out the active sites of MoO_3 , mitigating the Li^+ trapping tendency of MoO_3 . The complementary conductivities of MoO_3 and PEDOT:PSS benefit the electron transport at both oxidized and reduced state. The induced stress caused by volume change of MoO_3 during Li^+ intercalation/deintercalation process is buffered by PEDOT:PSS polymer matrix. Thus, the composite has a good long-term stability. This composite material has more apparent optical contrast than currently widely used WO_3 -based materials, which means the wavelength where the maximum contrast occurs is more sensible to human eyes. This work improves the poor stability of electrochromic MoO_3 and gives MoO_3 -based electrochromic materials a potential to be used in practical applications.

4.1 Introduction

As mentioned in Chapter 2, electrochromism has been utilized to create different types of electrochromic devices such as smart windows,[1, 2] self-dimming rear mirrors,[3] and energy-saving displays[4, 5] which have the advantage of low power consumption for maintaining the devices at colored state. Tungsten oxide (WO_3) is the first well established electrochromic material and to date it is still the most commonly used cathodically coloring electrochromic material. Crystalline WO_3 exhibits relatively high optical contrast and good long-term stability due to its good environmental and electrochemical stabilities.[6, 7] Similar to WO_3 , molybdenum trioxide (MoO_3) can also be electrochromic.[8, 9] Moreover, MoO_3 has its unique advantages. It shows higher apparent contrast than most of transition metal oxides as its highest contrast occurs at the wavelength that is more sensible to human eyes,[8, 10] which is useful for some niche applications. Also, MoO_3 shows better open circuit memory,[10, 11] that the color could remain longer time after the removal of external potentials. Similar to WO_3 , MoO_3 can be prepared by physical vapor deposition,[12] hydrothermal method,[13] electrodeposition,[14] or sol-gel method[15]. Orthorhombic $\alpha\text{-MoO}_3$ is the most well studied phase for electrochromic applications. It consists of MoO_6 octahedra arranged in a variety of corner-sharing and edge-sharing arrangements, resulting in zigzag chains and unique layers parallel to the (010) plane structure, presenting open channels for Li^+ ion intercalation.[16] When electrons and ions are inserted into MoO_3 , some Mo is reduced from VI to V and the color of the material changes from colorless to blue.

Despite that MoO_3 has some unique advantages for electrochromic applications, it has mainly been used as a dopant to other electrochromic transition metal oxides, including WO_3 ,[17] Nb_2O_5 ,[18] and V_2O_5 . [19] For example, a porous tungsten molybdenum oxide ($\text{W}_{0.71}\text{Mo}_{0.29}\text{O}_3$) has been studied recently with good contrast and long-term stability.[20, 21] MoO_3 is not widely used as the main component of an electrochromic material due to three reasons: (1) the low conductivity at fully oxidized state, (2) slow Li^+ transport and (3) poor long-term stability.[22] MoO_3 has a relatively higher band gap comparing to commonly used WO_3 , and its low conductivity hinders the electron transport. Moreover,

the electrochemical stability of MoO_3 is usually demonstrated for no more than 100 cycles.[15, 23-26] It has been found that after Li^+ ions enter the film, it causes structural distortion and non-uniform coloration.[27] During cycling, some Li^+ ions are trapped in the film and cracks occur on the surface.[28] These cracks may be caused by the induced stress due to non-uniformly distributed Li^+ . Also, defects and oxygen vacancies in MoO_3 are detrimental to electrochromic performance.[9] Annealing has been found to be helpful to reduce defects and create crystalline structure,[25] but a highly crystalline MoO_3 hinders Li^+ intercalation, further slowing down the switching speed of electrochromic devices.[11]

One way to enhance the performance of MoO_3 is to use nanoparticles. Low average grain size can contribute to the ease of ion transport and better reversibility of the device.[8] To enhance the Li^+ transport, MoO_3 - TiO_2 nanorods have been prepared.[14] Faster Li^+ diffusion was achieved due to high surface area, while the cyclic stability is not reported. A high contrast has been achieved by a graphene-based MoO_3 composite prepared using hydrothermal method, but the stability of such composite was only demonstrated up to 100 cycles.[23] To improve both the conductivity and long-term stability of MoO_3 , a stacked $\text{MoO}_3/\text{Ag}/\text{MoO}_3$ film was built to form a dielectric-metal-dielectric structure, where by adjusting the thickness of each layer, good conductivity and a stability up to 150 cycles was achieved.[29] However, such layered structures were prepared by electron-beam evaporation, which requires expensive equipment. Currently a simple method to prepare a MoO_3 -based electrochromic material with good performance and long-term stability remains a challenge.

In a previous work, it has been demonstrated that $\text{WO}_3/\text{poly}(3,4\text{-ethylenedioxythiophene})\text{:polystyrene sulfonate}$ (PEDOT:PSS) composite prepared by layer-by-layer electrodeposition has enhanced electrochromic performances.[30] PEDOT:PSS, as an cathodically coloring electrochromic conjugated polymers, usually exhibits faster switching speed and higher coloration efficiency.[31, 32] Due to the existence of two electron-donating oxygen atoms, PEDOT has relatively lower band gap.[33] It exhibits high electrical conductivity and good stability at the doped state. PSS is usually used as the counter ion to dope PEDOT and it can solve the insolubility of

PEDOT in water and form dispersions in water. It forms a necklace structure where PEDOT is surrounded by PSS.[34] PEDOT:PSS possess high conductivity at oxidized state (bleached state) but relatively low conductivity at reduced state (colored state), while WO_3 possess high conductivity at reduced state but low conductivity at oxidized state. Thus in WO_3 /PEDOT:PSS system, the two components have complementary conductivity in the redox switching process.[31] However, WO_3 prepared by electrodeposition was amorphous, which was less stable; the interfacial area between the two components were also limited due to layer-by-layer structure. It is hypothesized that by using crystalline nanoparticles with small particle size, both the stability of nanoparticles and interfacial area between the two components should be improved. Furthermore, more significant interfacial interactions could help to better utilize the complementary conductivities.

In this work, the complementary-conductivity strategy is utilized to address the three critical issues for the more challenging electrochromic MoO_3 , which is also an insulator at oxidized state (bleached state) and a good conductor at reduced state (colored state). Differently, PEDOT:PSS is added into an aqueous dispersion of semicrystalline MoO_3 nanoparticles with size of only about 10-30 nm to obtain a MoO_3 /PEDOT:PSS composite due to electrostatic interactions between PEDOT and MoO_3 . The MoO_3 nanoparticles were facilely prepared by conventional sol-gel process followed by annealing and redispersion in water. This not only improves the stability of the MoO_3 nanoparticles and greatly increases interfacial area, but also addresses Li^+ ion trapping issue. The addition of PEDOT:PSS facilitates Li^+ and electron transport in MoO_3 , so that more active sites of MoO_3 could be involved in the Li^+ intercalation process. The complementary conductivities of MoO_3 and PEDOT:PSS are better utilized due to the extensive interfacial interactions, facilitating electron transport at both states. Also, PEDOT:PSS works as a polymer matrix to buffer the induced stress during cycling, which will benefit long-term stability. Therefore, such composite exhibits good electrochromic contrast and long-term stability.

4.2 Experimental Section

4.2.1 Materials

PEDOT:PSS (1.3 wt% dispersion in water, conductive grade), lithium perchlorate (LiClO_4 , ACS reagent, $\geq 95.0\%$), propylene carbonate (PC, anhydrous, 99.7%) were purchased from Sigma-Aldrich. Molybdenum powder (99%) and ethanol (99.9%) were purchased from Merck. 30% H_2O_2 was purchased from VWR. Acetone (technical grade) and isopropyl alcohol (IPA, technical grade) were purchased from Aik Moh (Singapore). All chemicals were used as received. ITO glasses were purchased from Wintek Technology with resistivity of $8 \Omega/\square$.

4.2.2 Preparation of Crystalline MoO_3 Nanoparticles

0.96 g molybdenum powder was added to 30 mL 30% H_2O_2 solution slowly under continuous stirring. 30 mL ethanol was added after 4 h stirring. The solution was kept stirred for 24 h and then a Pt sheet was placed inside the solution for 48 h to remove excess H_2O_2 and obtain the precursor. After that, the precursor was dried at 80°C for 3 h, and then annealed to 300°C for 2 h in a tube furnace with ramp of $5^\circ\text{C}/\text{min}$. The precursor without annealing was dried at 60°C as a reference sample for characterization tests.

4.2.3 Preparation of Composite Thin Films and Single Active-layer Electrochromic Devices

10 mg annealed MoO_3 nanoparticles were dispersed in 10 mL DI H_2O by ultrasonication for at least 5 h until a clear dispersion was obtained. As-received PEDOT:PSS dispersion was diluted to 1 mg/mL. 1 mg/mL MoO_3 dispersion and 1 mg/mL PEDOT:PSS dispersion were mixed at a volume ratio of 3:1. Composites with different ratios (1:1, 3:1, 5:1), neat MoO_3 and neat PEDOT:PSS were also prepared for comparison. ITO glasses were cleaned by soap water, and then ultrasonicated in DI H_2O , acetone, and IPA consequently, and dried by blowing N_2 gas. They were then cleaned using a plasma cleaner for 10 min. Freshly mixed dispersions were dropped on pre-cleaned ITO glasses at heating temperature of 70°C to get the electrochromic films. A single active-layer electrochromic device was

fabricated with sandwich configuration of ITO glass//MoO₃/PEDOT:PSS//electrolyte//ITO glass. The electrolyte used was 1 M LiClO₄ PC solution.

4.2.4 Characterization

FTIR spectra of MoO₃ precursor before annealing and MoO₃ nanoparticles after annealing were recorded on a Frontier FTIR spectrometer (Perkin Elmer Frontier) in transmission mode in the range of 400 to 4000 cm⁻¹. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance XRD. The field-emission scanning electron microscopic (FE-SEM) images of the materials were obtained on a JEOL 7600F SEM with secondary electron (SE) detector and low angle backscatter electron (LBE) detector. The high resolution transmission electron microscopic (HRTEM) images were obtained on JEOL-2100F field emission transmission electron microscope operating at 200 kV. The particle size distributions and zeta-potential were analyzed by nano particle analyzer HORIBA SZ-100. X-ray photoelectron spectroscopy (XPS) was performed using Kratos AXIS Supra. The thicknesses of the samples were measured by Surface Profiler (Alpha-Step IQ). The electrochemical properties of the samples were measured in a three-electrode electrochemical cell, using the sample, Pt, and Ag as working, counter, and reference electrode, respectively, in 1 M LiClO₄ PC solution. Cyclic voltammetry (CV) was tested from -1 V to +1 V at a scan rate of 20 mV s⁻¹ and the electrochemical impedance spectroscopy was carried out over the frequency range of 10⁵ to 10⁻¹ Hz with signal amplitude of 5 mV using an Autolab PGSTAT302 potentiostat. In situ spectroelectrochemical properties of the samples, including the UV-Vis spectra from 400 to 800 nm under different voltages and switching curves at a fixed wavelength of 600 nm, were recorded using UV-Vis spectrometer (SHIMADZU 2501).

4.3 Results and Discussion

4.3.1 Structures and Morphologies of the MoO₃/PEDOT:PSS Composites

The preparation process for the electrochromic films is illustrated in Figure 4.1. Briefly, Mo powder was dispersed in H_2O_2 to prepare the sol-gel precursor. The precursor was annealed to obtain semicrystalline MoO_3 nanoparticles. The MoO_3 nanoparticles were then redispersed in water and mixed with PEDOT:PSS dispersion. The mixed dispersion was used for drop casting on ITO glasses to fabricate electrochromic films and devices.

Figure 4.1 A scheme showing the preparation process of MoO_3 /PEDOT:PSS electrochromic film.

The chemical structure change of the MoO_3 precursor caused by annealing process is confirmed by FTIR spectra. (Figure 4.2a) Before annealing, the FTIR spectrum exhibits three characteristic bands corresponding to the stretching vibration of $\text{O}=\text{Mo}$ at $\sim 960\text{ cm}^{-1}$, stretching vibration of $\text{O}-\text{O}$ peroxy structure at $\sim 930\text{ cm}^{-1}$, and stretching vibration of O connected to three Mo at $\sim 560\text{ cm}^{-1}$. [35, 36] After annealing, $\text{O}-\text{O}$ band disappears, and a new band appears at $\sim 876\text{ cm}^{-1}$ corresponding to stretching vibration of $\text{Mo}-\text{O}-\text{Mo}$. [37, 38] FTIR results signify the formation of MoO_3 after annealing. The band at $\sim 1628\text{ cm}^{-1}$ and the broad band at $3400\text{--}3510\text{ cm}^{-1}$ are attributed to $\delta(\text{H}_2\text{O})$ and $\nu(\text{OH})$ respectively. [39, 40] The presence of $-\text{OH}$ on the surface of MoO_3 nanoparticles enable them to disperse in water. The morphology of these particles before and after annealing are observed by SEM, as shown in Figure 4.2c-d. Before annealing, particles are smaller and have a wider size

distribution. After annealing, MoO_3 nanoparticles form and they have a more spherical shape and diameter of about 10-30 nm. The crystal structure caused by the annealing process is studied by XRD. (Figure 4.2b) Particles derived from the precursor (before annealing) is amorphous. After annealing the precursor at 300 °C, crystallization occurs in MoO_3 (the sample is denoted by MoO_3 -300 °C) and the XRD pattern shows characteristic peaks of orthorhombic α - MoO_3 (ICDD 01-074-7912). By further increasing the annealing temperature to 500 °C, the characteristic peaks of MoO_3 -500 °C are at the same positions as those of MoO_3 -300 °C but become sharper with smaller full width at half maximum (FWHM), indicating higher crystallinity and larger crystal domains. However, MoO_3 -500 °C is not able to be redispersed in water, and hence MoO_3 -300 °C is used for later studies. The semicrystalline nature of MoO_3 -300 °C is further proved by HRTEM observation of the MoO_3 nanoparticles, as shown in Figure 4.2e-f. The particle size shown in the TEM images corresponds with SEM result and polycrystalline structure is observed under high magnification. The crystal lattices can be observed and each crystal domain is about 4-10 nm. In summary, MoO_3 nanoparticles prepared are highly crystalline with small particle diameters. The polycrystalline nature of the MoO_3 particles benefits their electrochemical stability, while their small size facilitates their effectively interactions with PEDOT:PSS.

Figure 4.2 (a) FTIR spectra of MoO₃ precursor before annealing and MoO₃ nanoparticles after annealing. (b) XRD patterns of MoO₃ precursor, MoO₃-300 °C, MoO₃-500 °C, and reference diffraction pattern of ICDD 01-074-7912. Morphology of MoO₃ nanoparticles (c) before and (d) after annealing. (e-f) HRTEM images of MoO₃-300 °C nanoparticles at different magnifications.

The SEM images showing the surface morphology of MoO₃, PEDOT:PSS and MoO₃/PEDOT:PSS prepared on ITO glasses are presented in Figure 4.3a-c. All three samples form smooth thin films. PEDOT:PSS and MoO₃/PEDOT:PSS films have more

smooth textures than the MoO_3 films as some single isolated MoO_3 nanoparticles exist on the top of the closely packed MoO_3 nanoparticles, increasing the roughness of the film. Obviously, PEDOT:PSS is able to alleviate this effect due to its flexibility and conformation. To confirm the existence and dispersion of MoO_3 nanoparticles in the composite, SEM-LABE is used to study the MoO_3 nanoparticles distribution in the composite as EDX is unable to detect the phase morphology in this case (the characteristic X-ray of Mo (2.293 keV) has very similar energy to S (2.307 keV)). Under SEM-LABE, the component with higher average atomic number appears brighter in the image. Figure 4.3f shows clear white and black contrast in the composite, where white regions should be MoO_3 -rich regions, given neat MoO_3 and PEDOT:PSS show no contrast in their SEM-LABE images (Figure 4.3d-e). Figure 4.3f implies that MoO_3 agglomerates with an average size about 100-200 nm are distributed in PEDOT:PSS.

Figure 4.3 SEM-SEI images of (a) MoO_3 , (b) PEDOT:PSS and (c) $\text{MoO}_3/\text{PEDOT:PSS}$; SEM-LABE images of (d) MoO_3 , (e) PEDOT:PSS and (f) $\text{MoO}_3/\text{PEDOT:PSS}$. The magnification for SEM and SEM-LABE images are $\times 60,000$ and $\times 40,000$, respectively. The scale bar is 100 nm for all pictures.

4.3.2 Interfacial Interactions

To establish structure-property relationship for this new composite system, the interaction between MoO_3 and PEDOT:PSS in the composite is examined. The particle size distribution in the suspension is studied to probe the interaction between MoO_3 and PEDOT:PSS particles. Under dynamic light scattering, MoO_3 suspension has an average particle size of 165 nm and PEDOT:PSS suspension has an average particle size of 750 nm. (Figure 4.4a) After mixing the two suspensions by stirring, the new suspension has a bimodal size distribution, with two peaks at particles size of 130 nm and 950 nm, respectively. The average size decrease in the first peak and increase in the second peak indicate some MoO_3 nanoparticles interact with PEDOT:PSS to form larger particles. The driving force of the interaction is likely to be electrostatic attractions[41], as MoO_3 nanoparticles are negative charged (zeta-potential: -36.3 mV) and PEDOT in PEDOT:PSS are in the form of radical cations. To further verify the interfacial interactions, the chemical environment of Mo and S is studied by XPS. (Figure 4.4b-c) For the neat MoO_3 , two bands at binding energy of 236.4 eV ($\text{Mo } 3d_{3/2}$) and 233.3 eV ($\text{Mo } 3d_{5/2}$) correspond to the oxidation state of Mo^{VI} , indicating Mo is at the highest oxidation states.[42, 43] The relatively high binding energies than the reported values for crystalline MoO_3 may be attributed to the large amount of surface groups. The MoO_3 /PEDOT:PSS composite shows two bands at 236.6 eV and 233.5 eV, which are 0.2 eV higher than neat MoO_3 . In S 2p scan of PEDOT:PSS, the two bands at lower binding energy (165.5 eV, 164.2 eV) are attributed to PEDOT and the two bands at higher binding energy (169.5 eV, 168.3 eV) are attributed to PSS.[30] For the composite, the bands of PEDOT shift to the positions of 0.2 eV higher and the bands of PSS shift to the positions of 0.4 eV higher. This is likely due to the electrostatic attractions between negative charged MoO_3 and positive charged S, resulting in a strong interaction between MoO_3 and PEDOT:PSS. The inner electrons are more difficult to escape, leading to a higher binding energy in the composite. It is worth noting that the shift in PSS is higher than PEDOT, implying that more MoO_3 may interact with PSS, which is reasonable considering the core-shell structure of PEDOT:PSS.

Figure 4.4 (a) Particle size distribution of MoO₃, PEDOT:PSS and composite tested by dynamic light scattering. XPS spectra in (b) Mo 3d region of MoO₃ and composite and (c) S 2p region of PEDOT:PSS and composite.

4.3.3 Electrochemical Properties

The electrochemical properties of MoO₃, PEDOT:PSS and composite are further studied by CV from -1 V to +1 V. (Figure 4.5) MoO₃ has a broad oxidation peak at -0.43 V and no obvious reduction peak in this range. PEDOT:PSS has an oxidation peak at -0.02 V and a reduction peak at -0.55 V. In the composite, the peak at -0.43 V becomes a shoulder and a new pair of redox peaks appear at -0.18 V/-0.09 V. Based on literatures, more than one couple of peaks have been found in CV during Li⁺ intercalation process of MoO₃, attributed to multi-step Li⁺ intercalation in interlayer and intralayer spaces of MoO₃. [44, 45] The appearance of new peaks means more active sites involved in the Li⁺ intercalation process,

which corresponds with the larger enclosed area of composite than that of MoO_3 . Moreover, the presence of peaks from both PEDOT:PSS and MoO_3 indicates both components in the composite participate in the electrochemical process.

Figure 4.5 Cyclic voltammetry of MoO_3 , PEDOT:PSS and composite from -1 V to +1 V at a scan rate of 20 mV s^{-1} .

With the above analysis, the interaction between MoO_3 and PEDOT:PSS in the composite is proposed as following. The electrostatic attraction between negative charged surface groups of MoO_3 and positive charged S in PEDOT makes them interact with each other.[41] PEDOT:PSS has a necklace structure where PEDOT is core and PSS is shell. Under the attraction, MoO_3 is attached to PSS due to its hydrophilicity and the structure that PEDOT is surrounded by PSS.[46] In the composite, PEDOT:PSS becomes a backbone and MoO_3 nanoparticles are separated and attached on the backbone. Such morphology can facilitate the Li^+ and electron transport in the material. The neat MoO_3 film is composed of packed MoO_3 nanoparticles. The Li^+ and electron transport is slow in MoO_3 , so limited active sites are involved in the reaction and mainly interlayer sites are occupied. In the composite, Li^+ and electron transport is faster in PEDOT:PSS. The average diffusion length to active sites

in MoO_3 is reduced and replaced by the route in PEDOT:PSS which has better kinetics. More active sites in the MoO_3 are involved in the reaction, including both interlayer and intralayer ones.

The enhancement in charge transport is verified by the electrochemical impedance study (EIS). The diameters of the arcs in Nyquist plots represent the charge transfer resistance R_{CT} .^[47] The smaller the arc, the better the charge transfer ability. At the bleached state, (Figure 4.6a) MoO_3 has larger R_{CT} than PEDOT:PSS, which corresponds the poor conductivity of MoO_3 at oxidized state. The composite has the lowest R_{CT} due to the good conductivity of PEDOT:PSS at oxidized state and the morphology of the composite. At the colored state, (Figure 4.6b) PEDOT:PSS has larger R_{CT} than MoO_3 , which corresponds the poor conductivity of PEDOT:PSS at reduced state. The composite exhibits two arcs: the one at high frequency region (inset in Figure 4.6b) can be attributed to MoO_3 and the one at middle frequency region attributed to PEDOT:PSS. Each arc for the composite is smaller than that for its respective neat component. The good conductivity of MoO_3 at reduced state enables it as a complementary charge carrier to facilitate the charge transport in the composite. The complementary conductivities of MoO_3 and PEDOT:PSS enhance the R_{CT} of the composite at both oxidized and reduced states, giving the composite good electrochromic performance during redox switching, as shown below.

Figure 4.6 Nyquist plots of MoO_3 , PEDOT:PSS and composite at (a) bleached and (b) colored states. (Inset in b is the detailed plot at the high frequency region.)

4.3.4 Electrochromic Performances

The electrochromic performances of the composites and each individual components are compared in Figure 4.7. Spectra of MoO₃, PEDOT:PSS, MoO₃/PEDOT:PSS at different voltages are demonstrated in Figure 4.7a-c. The as-prepared samples are denoted as 0 V. All samples are cathodically colored materials. Their colored states are denoted as -0.8 V and their bleached states are denoted as +0.8 V. It is clearly shown that, unlike PEDOT:PSS, MoO₃ is not able to fully switch back, though it has a large contrast in its first coloring process. This is similar to previous report that some Li⁺ are trapped in MoO₃ resulting in a decay of contrast. This issue is solved when PEDOT:PSS is added, that MoO₃/PEDOT:PSS is able to fully bleach to its original state. This is attributed to the addition of PEDOT:PSS facilitates the Li⁺ and electron transport as discussed before. The matrix formed by PEDOT:PSS provides routes to electrons and Li⁺ to transport in and out. Also, the composite demonstrates a relatively constant contrast over the visible wavelength range, and its maximum contrast occurs at 600 nm. This is closer to the wavelength (about 580 nm) that is the most sensible to human eyes[48], comparing to current widely used WO₃, in which the best performance contrast occurs at 720 nm.[6] Therefore, it shows more apparent contrast than WO₃. (Figure 4.7c inset) Figure 4.7d shows the switching curves of MoO₃, PEDOT:PSS, MoO₃/PEDOT:PSS at the wavelength of 600 nm after a few cycles of stabilization. MoO₃/PEDOT:PSS demonstrates the highest optical contrast of 37%, while MoO₃ and PEDOT:PSS only has optical contrast of 7% and 8% respectively. Composite samples with different ratios of MoO₃ to PEDOT:PSS (1:1, 3:1, 5:1) have been tested, and the sample with 3:1 ratio has the best contrast. (Figure 4.7e) The bleaching/coloration time of MoO₃, PEDOT:PSS, and composite is 28 s/25 s, 21 s/26 s, 12 s/17 s, respectively. The faster switching speed of composite is another evidence of improvement on electron transport. The coloration efficiency of MoO₃, PEDOT:PSS, and composite is 18.6, 72.9, and 24.4 cm² C⁻¹, respectively. (Figure 4.7f) The long-term stabilities of all three samples are compared in Figure 4.7g. MoO₃ has a very poor stability and decays obviously after 50 cycles. MoO₃/PEDOT:PSS has 14% contrast at its first cycle. However, after about 60 cycles of activation process, it gradually reaches to its max

contrast 37%. After 240 cycles, it drops to 30% and starts to maintain at this number. After 560 cycles it still retains 77% of its maximum contrast, which exhibits better long-term stability than most of the reported MoO₃-based electrochromic materials. The good long-term stability of MoO₃/PEDOT:PSS is caused by two reasons. One is PEDOT:PSS provides routes for Li⁺ transport in and out, improving the Li⁺ trapping issue in MoO₃. The other is PEDOT:PSS holds the MoO₃ nanoparticles as a matrix, which buffers the induced stress during Li⁺ intercalation process.

Figure 4.7 Electrochromic performances of MoO₃, PEDOT:PSS and composite: optical spectra of (a) MoO₃, (b) PEDOT:PSS, and (c) composite at different potentials (0V, -0.8V and +0.8 V); (d) switching curves, (f) coloration efficiencies, and (g) long-term stabilities of MoO₃, PEDOT:PSS and composite tested at $\lambda_{600\text{nm}}$ under -0.8 V, 30 s/+0.8 V, 30 s. Insets in (c) are pictures of the single active-layer device built by the composite at bleached and colored states. (e) Switching curves of MoO₃/PEDOT:PSS composite with different component ratio of MoO₃ to PEDOT:PSS=1:1, 3:1, and 5:1, respectively.

4.4 Conclusions

In summary, a novel MoO₃/PEDOT:PSS composite is facily prepared via electrostatic interactions. The small particle size of MoO₃ improves the stability of the MoO₃ nanoparticles and greatly increases the interfacial area. The addition of PEDOT:PSS facilitates Li⁺ and electron transport in and out the active sites of MoO₃, alleviating Li⁺ trapping problem and resulting more active sites in MoO₃ are involved in the Li⁺ intercalation process. The complementary conductivities of MoO₃ and PEDOT:PSS facilitate electron transport at both oxidized and reduced states, and they are better utilized due to the extensive interfacial interactions between the two components. Also, PEDOT:PSS works as a polymer matrix to buffer the induced stress during cycling, benefitting long-term stability. This study addresses the critical stability issue of MoO₃ and provides MoO₃-based materials a potential to be utilized in electrochromic applications.

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Chapter 5

A Highly Bendable Transparent Electrode for Organic Electrochromic Devices

In this chapter, a thin film of polyaniline (PANI)-grafted single-walled/double-walled carbon nanotubes (CNTs) on polyethylene terephthalate (PET) is reported as a transparent electrode for highly bendable electrochromic films. The results show that the high conductivity of the PANI-CNT/PET electrode brought by its conductive CNT network, as well as the strong conjugation between CNTs and PANI, can be well retained even after 9,000 cycles of bending with a bending radius of 0.6 cm, which is superior to that of the most widely used transparent electrode, indium tin oxide (ITO) on PET. By electrodeposition of PANI on the PANI-CNT/PET electrode, the overall electrochromic performance of the PANI-deposited PANI-CNT/PET (PANI/PANI-CNT/PET) is comparable to its PANI/ITO/PET counterpart, whereas after 100 cycles of bending, PANI/PANI-CNT/PET can much better retain its initial electrochromic performance than PANI/ITO/PET. The mechanism for the enhanced bendability is studied via impedance analysis. It shows that the enhancement is mainly due to the robust interface between the PANI-based electrode and active layer. The findings provide a new avenue for rational design of highly bendable electrodes for flexible electrochromic devices.

*This section published substantially as B. Che, D. Zhou, H. Li, C. He, E. Liu, X. Lu. *Org. Electron.* **2019**, 66, 86-93.

5.1 Introduction

Nowadays electronic devices are engaged in people's lives in a way we could have never imagined a decade ago. In particular, with the rapid growth of personal electronics, a new technology field booms, which is flexible electronics.[1-3] It started with organic polymer transistors fabricated on flexible plastic sheets.[4] Later, various types of flexible electronic, optoelectronic and electrochemical devices that can be bended, folded, or rolled have been developed.[5, 6] These flexible devices can easily achieve what traditional hard electronics cannot achieve owing to their lighter weight, improved comfort, and higher space efficiency.[7] They are attracting more and more research interest because of the ever-growing demands for flexible and wearable devices.

As discussed in Chapter 2, an electrochromic device can reversibly change its optical properties under external potentials due to the redox reactions of its active layers. For example, by controlling the voltage applied, an electrochromic device may change its light transmittance or reflectance. Thus, they can be used as energy-saving smart windows in buildings[8, 9], airplanes and vehicles[10], as well as displays in electronic devices[11]. A typical electrochromic device has a multilayered structure, consisting of transparent electrodes, electrochromic and electrolyte layers. Currently, the most commonly used electrode is indium tin oxide (ITO) on glass substrate[12, 13] and popular electrochromic materials are tungsten oxide and nickel oxide[14, 15]. All these inorganic materials are rigid. Thus, to enable highly bendable electrochromic devices, an attractive option is to use organic transparent electrodes and electrochromic materials.

Polyethylene terephthalate (PET) is the most commonly used substrate in flexible electronics due to its low cost, good transparency, flexibility and barrier properties. A thin layer of ITO can be deposited on a PET sheet to make it conductive. However, unlike highly conductive ITO glass, it is difficult to obtain high-quality ITO coatings on a plastic substrate due to reduced activation efficiency of the tin dopant and highly defected microstructure, which is caused by the poor thermal stability of the polymer substrate and high deposition rate.[16] To address this issue, other materials with both good conductivity

and flexibility have been studied as alternatives of ITO. For example, metal nanowires or nanopatterns, such as Ag nanowires[17] and Cu nanopatterns[18], deposited on transparent polymer films have been intensively investigated because of their excellent electrical conductivity. Owing to their low percolation thresholds, the conductive networks formed on transparent polymer films showed good transparency and flexibility.[17] However, the undesirable surface toughness[19], the junction resistance between distinct nanowires[20], and especially the oxidation and corrosion of the metals under positive voltage[21] could deteriorate the performance and stability of the conductive networks, reducing life-time of the flexible electrochemical devices. Carbon nanotubes (CNTs) are another promising material with good electrical conductivity and flexibility.[22] Flexible polymer films with deposited CNT random networks could be highly bendable. For instance, light emitting diodes built on CNT electrodes could be bended to 2.5 mm radius without failure.[23] By hybridizing a polymer into the system, though the resistance increases slightly, the flexibility of the electrode can be further improved.[24] More importantly, CNTs exhibit excellent electrochemical stability, making them more suitable for electrochemical device applications.

To fabricate a highly bendable electrochromic device, the electrochromic layer also needs to be flexible. The most widely studied flexible electrochromic materials are conjugated polymers, such as polyaniline (PANI)[25] and poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS)[26]. On one hand, comparing with inorganic electrochromic materials such as transition metal oxides, conjugated polymers have advantages of flexibility, light-weight, multicoloration, relatively high coloration efficiency and switching speed, as well as ease of processing.[27, 28] On the other hand, they often suffer from poor electrochemical stabilities.[29, 30] To address this issue, conjugated polymer/CNT composites have been widely studied. The results showed that CNTs could not only exhibit excellent electron-transport property and high electrochemical stability themselves, but also interact with conjugated polymers via strong π - π interactions or extend conjugation lengths of the conjugated polymers through covalent grafting conjugated polymers on CNTs,[31, 32] leading to synergistic effects in improving electron transport and electrochemical stability of the devices. This makes

CNTs ideal candidates for fabrication of electrochromic devices in conjunction with conjugated polymers. Furthermore, if both the electrode and electrochromic layers contain conjugated polymers, an intimate interface may be achieved, which may facilitate electron transport and hinder interfacial failure, improving the performance and life time of the bendable devices.

In this work, a PANI-CNT hybrid material made by in situ polymerization of aniline with amine-functionalized CNTs was used to fabricate transparent flexible electrodes. Through the in situ grafting polymerization, a direct conjugation between the CNTs and PANI was established, leading to significantly enhanced electrical conductivity.[31, 33] This allows aniline be directly electropolymerized on the PANI-CNT coated PET electrode (PANI-CNT/PET) to form an electrochromic layer, and gives rise to favorable interactions between the electrode and electrochromic layer because they share the same base material, PANI. The PANI presents in the hybrid electrode is also electrochromic, so it can contribute to the overall electrochromic performance as well. Herein, this work demonstrates the mechanical robustness and durable electrical conductivity of such a PANI-CNT/PET electrode as well as the good electrochromic performance and excellent bendability of PANI-deposited PANI-CNT/PET (PANI/PANI-CNT/PET), which can maintain its electrochromic performance after 100 cycles of rigorous bending. The underlying mechanism for the enhanced bendability is also revealed via impedance analysis. The findings from this work will shed new light on the rational design of highly bendable electrodes for flexible electrochromic devices.

5.2 Experimental Section

5.2.1 Materials

Aniline, ammonium persulfate (APS), camphor sulfonic acid (CSA), m-cresol, dodecylbenzenesulfonic acid (DBSA), lithium perchlorate (LiClO_4), propylene carbonate (PC) and ITO/PET ($100 \Omega/\square$) were purchased from Sigma-Aldrich. Acetone and isopropyl alcohol (IPA) were purchased from Aik Moh (Singapore). Amine-functionalized carbon

nanotubes (A-CNTs) with outer diameter of 1-4 nm (i.e., a mixture of single-walled and double-walled CNTs) and length of 3-30 μm were purchased from Cheaptubes (purity > 99%). Aniline was purified by vacuum distillation prior to use. All other chemicals were used as received.

5.2.2 Preparation of PANI-CNT/PET Electrode

The PANI-CNT hybrid with PANI in emeraldine base form was prepared as described in the previous work.[31] 8 mg as-synthesized PANI-CNTs were dissolved in 2.5 mL m-cresol that also contained 4.7 mg CSA as the dopant. The solution was stirred overnight and then centrifuged to remove large particles. PET sheet was cut into the dimension of 5 cm * 0.9 cm and washed by DI water, acetone and IPA subsequently. The solution was spin-coated on the PET substrate at 400 rpm. The as-coated sample was dried in a vacuum oven at 60 °C. The coating process was repeated 3 times to get the final electrode, denoted as PANI-CNT/PET. Neat PANI was also spin-coated on PET to make PANI/PET as a reference sample for bending tests. A PET sheet was coated with pure m-cresol to study the interaction between the substrate and the solvent.

5.2.3 Electrodeposition of PANI

An aniline aqueous solution was prepared by adding 0.559 g aniline into 100 mL DI water that contained 9.79 g DBSA as the dopant. The dried PANI-CNT/PET electrode was immersed into the solution for electrodeposition. The electrodeposition was conducted at +1.3 V using a three-electrode system, where the working, counter and reference electrodes were PANI-CNT/PET, Pt, and Ag/AgCl electrodes, respectively. The resultant sample is denoted as PANI/PANI-CNT/PET. The ITO/PET electrode was also used as the control electrode to prepare PANI/ITO/PET. The deposition charge (Q) and deposition voltage (E) was set to be the same for both PANI/PANI-CNT/PET and PANI/ITO/PET.

5.2.4 Characterization

The field-emission scanning electron microscopic (FE-SEM) images of the materials were obtained on a JEOL 7600F SEM. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Kratos AXIS Supra spectrometer. The transmittance and absorbance values of the samples were measured using a UV-Vis spectrometer (SHIMADZU 2501). To estimate the thickness (t) of the PANI-CNT coating on PET, an absorbance-thickness relationship was established first by measuring the absorbance and thicknesses of PANI-CNT coatings on glass using the UV-Vis spectrometer and a surface profiler (Alpha-Step IQ), respectively. The thickness of PANI-CNT on PET was then estimated by measuring its absorbance and assuming that the absorbance is proportional to thickness (based on Beer-Lambert law). The resistance of the electrode was calculated from the IV curve obtained using Autolab PGSTAT302 potentiostat, where the current was measured as voltage was scanned from -1 V to +1 V. The conductivity (c) and sheet resistance (R_s) of the electrode were calculated using the equation (1) and (2) below, respectively:

$$c = \frac{RS}{a} = \frac{Rbt}{a}$$

$$R_s = \frac{1}{ct}$$

where R is resistance, S is cross-section area, a , b , t are the length, width and thickness of the electrode, respectively.

Bending tests were conducted at compression mode using Instron 5567. The electrochemical properties of the samples were measured in a three-electrode electrochemical cell, using the sample, Pt, and Ag as working, counter, and reference electrode, respectively, in 1 M LiClO₄ PC solution. In situ spectroelectrochemical properties of the samples, including the UV-Vis spectra from 400 to 800 nm under different voltages and switching curves at a fixed wavelength 720 nm, were recorded using UV-Vis spectrometer (SHIMADZU 2501). The impedance test was carried out over the frequency range of 10⁶ to 10⁻¹ Hz with signal amplitude of 5 mV using an Autolab PGSTAT302 potentiostat.

5.3 Results and Discussion

5.3.1 Properties of PANI-CNT/PET Electrode

The preparation process for the electrode is illustrated in Figure 5.1. The synthesis of PANI-grafted double-walled/single-walled CNTs and structural verification of the as-synthesized PANI-CNT have been reported in the previous publications.[31, 33] Briefly, aniline was polymerized in an acidic aqueous solution with dispersed A-CNTs to form PANI-grafted-CNTs, which was subsequently dedoped to obtain PANI-CNT emeraldine base. In this work, the as-synthesized PANI-CNT emeraldine base was redoped with CSA in m-cresol and centrifuged to remove large particles and bundles of CNTs. The PANI-CNT/PET electrode was then prepared by spin-coating the doped PANI-CNT suspended in m-cresol on a PET sheet.

Figure 5.1 A scheme showing the preparation process of PANI-CNT/PET electrode and PANI/PANI-CNT/PET electrochromic film.

In the electrode, the mass ratio of PANI to CNT is estimated based on the composition information provided by XPS. (Figure 5.2) There are four components in the sample: PANI, CNT, CSA, and cresol. Given the atomic ratio of elements in each component, the

composition of each element can be calculated in Table 5.1. The mass ratio of PANI to CNT is $(19.74\% \times 93.13) : (17.26\% \times 12) = 8.88 : 1$.

Figure 5.2 XPS spectrum of PANI-CNT/PET electrode with atomic percentage of each element.

Table 5.1 The composition table of each element in the electrode.

	C	O	N	S	Atomic Ratio
Total	85.05%	10.31%	3.29%	1.34%	
PANI	19.74%		3.29%		C:N=6:1
CNT	17.26%				
CSA	13.4%	5.36%		1.34%	C:O:S=10:4:1
cresol	34.65%	4.95%			C:O=7:1

In the spin-coating process, the solution could wet the PET surface very well. Moreover, after drying the adhesion between PANI-CNT and PET is very strong so as to the coating could hardly be separated from the substrate by scraping. This may be attributed to the

solvent used in the solution. As m-cresol could be used as a solvent to dissolve PET,[34] there may be slight dissolution of PET in m-cresol at the surface of the substrate. Figure 5.3 shows that the transverse grooves on the as-received PET substrate surface, which may be created due to stretching in the manufacturing process, disappear after a few drops of m-cresol spread over the surface and later being dried, providing evidence for the slight dissolution of PET surface by m-cresol. This would promote interfacial interactions between PET and PANI phases, resulting in a robust interface.

Figure 5.3 Surface of PET substrate (a) before and (b) after coating cresol and drying.

Figure 5.4a reveals the surface morphology of PANI-CNT/PET electrode. As shown, by removing large CNT bundles through centrifuge, the CNTs in the electrode are well dispersed as single tubes, which are interconnected with one another to form a network structure. This network structure improves the charge transfer ability and thus enables PANI-CNT/PET to be used as an electrode in the electrochromic device. As the SEM scanning time increases, PANI is removed due to heat caused by charging, while CNTs remain at the same position. Therefore, the morphology underneath the surface could be observed, as shown in Figure 5.4b-d. It further confirms that CNTs, which mainly exist as single tubes rather than bundles, are embedded in PANI and interconnected to a 3D network structure.

Figure 5.4 SEM images showing (a) surface morphology of PANI-CNT/PET electrode, and (b-d) morphology of PANI-CNT/PET electrode at a fixed spot as the SEM scanning time increases.

The resistance of the electrode was calculated from the slope of the IV curve shown in Figure 5.5a. Given the very thin thickness of the electrode (only 50 nm), the surface conductivity of the electrode is estimated to be about 55,000 S/m, corresponding to the sheet resistance of about $364 \Omega/\square$. The good conductivity is attributed to the CNT network structure in the hybrid and conjugation between CNT and PANI.[31] As transparency is another important property of transparent electrodes, UV-Vis spectrum of the PANI-CNT/PET electrode was also measured. Figure 5.5b shows that without external potential, the as-prepared PANI-CNT/PET electrode has two weak absorption bands in the wavelength range of 400 to 800 nm, which are centered at the wavelengths of around 445 and 700 nm, respectively, and the average transmittance is about 94%. When a small voltage of -0.4 V is applied, it can be switched to a higher transmittance state with average transmittance of 97% over the same wavelength range. The high conductivity and good transparency of the electrode makes it ideal for electrochromic applications.

Figure 5.5 (a) Current-voltage curve of PANI-CNT/PET electrode. (b) Optical transmittance of PANI-CNT/PET electrode without external potential (bottom curve) and with an external potential of -0.4 V (top curve).

To function in a flexible electrochromic device, the electrode must be bendable and the conductivity of the electrode must remain after bending. Therefore, the electrodes underwent a bending test with a bending radius of 0.6 cm. The bending was done by an Instron compression test and the set-up was provided in Figure 5.6a. The resistance was measured every hundreds of bending cycles. ITO/PET, which is one of the most popular flexible electrodes[22], was used as the control sample. Figure 5.6b compares the two types of electrodes by resistance ratio $(R/R_0) * 100\%$, where R_0 is the initial resistance before bending and R is the tested resistance after bending. The resistance of ITO/PET increases massively after bending. It is already 70 times higher than its original value after 500 bending cycles. By contrast, the resistance ratio of PANI-CNT/PET maintains in the range of 100%-120% till 9,000 bending cycles. The rapid increase on the resistance of ITO/PET is due to the crack initiated by defects or impurities. Those cracks start as early as 10 bending cycles, and later they propagate to large cracks, so the conductivity deteriorates.[35] The polymeric material like PANI is not brittle as ITO. The long chain structure of PANI enables the chains to rearrange their conformation to accommodate the bending-induced deformation, preventing the initiation and growth of cracks. Therefore, the conductivity of PANI retains after a huge number of cycles of bending. Figure 5.6c shows that after the same bending test, neat PANI-coated PET (PANI/PET) could also

retain its conductivity much better than ITO/PET, supporting the above explanation. The resistance-ratio fluctuation of PANI-CNT/PET during the bending test is, however, smaller than that of PANI/PET. This suggests that CNTs in PANI-CNT reinforce the endurance of the coating to bending. Since the conductivity of the PANI-CNT/PET electrode is not obviously influenced by bending, it has the potential to be used in a flexible electrochromic device.

Figure 5.6 (a) Bending test set-up using Instron 5567. (b) Resistance ratios (R/R_0) of PANI-CNT/PET (bottom curve) and ITO/PET (inset) as a function of bending cycle number. (c) Resistance ratios (R/R_0) of PANI/PET after bending.

5.3.2 Electrochromic Properties Using PANI-CNT/PET as Electrode

Owing to the good conductivity and transparency of PANI-CNT/PET, it was used as the electrode to deposit PANI electrochromic layer. The electrodeposition was also performed on ITO/PET to make a control sample. The deposition charge (Q) and deposition voltage (E) was set to be the same for the two electrodeposition processes on different electrodes. Therefore, the thicknesses of the PANI layers deposited on the two electrodes should be about the same. The electrochromic properties of PANI on both PANI-CNT/PET and ITO/PET electrodes were characterized. Figure 5.7a shows the transmittance spectra of the samples under different voltages. At the voltage of +0.7 V, PANI is oxidized and it colors to green. At -0.5 V, PANI is reduced and it bleaches to yellow. In the wavelength range of 620-800 nm, the transmittance of PANI-coated PANI-CNT/PET (PANI/PANI-CNT/PET) is lower than PANI-coated ITO/PET (PANI/ITO/PET) at bleached state. This is because ITO/PET electrode is more transparent than PANI-CNT/PET electrode in this wavelength range. Meanwhile, in the same wavelength range the transmittance of PANI/PANI-CNT/PET is also lower than that of PANI/ITO/PET at colored state, which means PANI/PANI-CNT/PET is darker at colored state. Besides the contribution from the initial color of the PANI-CNT/PET electrode, another reason for this is that PANI in the PANI-CNT/PET electrode is also electrochromic. Figure 5.7d shows the electrochromic switching curve of PANI-CNT/PET. A voltage of -0.5 V was applied to the PANI-CNT/PET electrode for 40 s, and then a voltage of +0.7 V was applied for 80 s. The electrode exhibits an optical contrast, i.e., the transmittance difference (ΔT) between the colored state and bleached state, of 4% at the wavelength of 720 nm. This confirms that the lower transmittance of PANI/PANI-CNT/PET at colored state is partially contributed by PANI-CNT. Figure 5.7b compares the electrochromic switching performance of PANI/PANI-CNT/PET and PANI/ITO/PET at $\lambda=720$ nm. The detailed performance parameters, including optical contrasts, switching times and coloration efficiencies, of PANI/ITO/PET and PANI/PANI-CNT/PET are listed in Table 5.2. The optical contrasts of PANI/ITO/PET and PANI/PANI-CNT/PET are very close to each other (both around 34%), which are also similar to reported values for PANI coated on ITO or FTO glass.[36-38] The switching curve of PANI/ITO/PET is slightly steeper than that of PANI/PANI-CNT/PET in both initial bleaching and coloring processes, indicating that PANI/PANI-CNT/PET has longer switching times than PANI/ITO/PET. From Table 5.2, the bleaching

time of PANI/PANI-CNT/PET (20 s) is only slightly longer than that of PANI/ITO/PET (17 s), while the coloration time of PANI/PANI-CNT/PET (40 s) doubles that of PANI/ITO/PET (20 s). This signifies that PANI plays a significant role in influencing the conductivity of the PANI-CNT/PET electrode as it could reduce contact resistance between the CNTs. Since PANI has lower conductivity at reduced state, the conductivity of PANI-CNT/PET is also lower under negative potentials, which makes the subsequent oxidation process slower. It is worth noting that this redox-induced conductivity change of PANI is reversible, which would not cause fast performance fading like those happened to metal nanowire/nanopattern-based electrodes under positive potentials. It is also worth noting that the switching time of PANI/ITO/PET measured in this work is comparable or longer than the reported values for PANI on ITO/PET[39] or ITO glasses[36, 38] as the conductivity of ITO/PET used in this study is in general lower than that of ITO glasses reported in the above references. For the same reason, the coloration efficiency of PANI/ITO/PET (Table 5.2) is also lower than the reported values for PANI coated on ITO glass.[36, 38] On the other hand, the “apparent” coloration efficiency of PANI/PANI-CNT/PET is higher than that of PANI/ITO/PET because the PANI component in the PANI-CNT electrode can also be switched to contribute to the optical contrast. Figure 5.7c shows long-term stability of PANI/ITO/PET and PANI/PANI-CNT/PET. Both could retain above 85% of their initial contrast after 200 cycles of switching. In summary, PANI-CNT/PET as an electrode could provide similar optical contrast and bleaching time as ITO/PET, as well as good long-term stability for electrochromic switching, but it gives longer coloration time.

Figure 5.7 Electrochromic properties of PANI/PANI-CNT/PET and PANI/ITO/PET: (a) transmittance spectra at voltage of -0.5 V and +0.7 V; (b) switching curves of at λ_{720} nm (-0.5 V, 40 s/+0.7 V, 80 s); (c) long-term stability at λ_{720} nm (-0.5 V, 40 s/+0.7 V, 80 s). (d) Switching curves of PANI-CNT/PET electrode at λ_{720} nm.

Table 5.2 Optical contrast, bleaching time, coloration time and coloration efficiency of PANI/ITO/PET and PANI/PANI-CNT/PET at λ_{720} nm.

	Optical contrast (%)	Bleaching time (s)	Coloration time (s)	Coloration efficiency (C/cm ²)
PANI/ITO/PET	34	17	20	11.9
PANI/PANI-CNT/PET	34	20	40	22.9

The electrochromic contrasts of PANI/PANI-CNT/PET and PANI/ITO/PET after bending are compared in Figure 5.8a. After 100 cycles of bending, the contrast of PANI/PANI-CNT/PET is well retained, while the contrast of PANI/ITO/PET decreases as the bending cycle number increases and finally drops to one third of its original value after 100 cycles. A harsher testing condition was also applied to PANI/PANI-CNT/PET. The sample was folded as shown in Figure 5.8b. It can retain 83% of its initial contrast after 50 times of folding, as shown in Figure 5.8c. These results demonstrate that PANI-CNT/PET electrode is more suitable for a flexible electrochromic device as compared with ITO/PET, especially for applications where a large degree of bending/folding is required. This is due to not only the durable conductivity of PANI-CNT under severe bending, but also the robust interface between the electrochromic layer (PANI) and electrode (PANI-CNT). Contrarily, since ITO is an inorganic material and PANI is an organic polymer, the interface between them is poor and could be easily damaged by bending. This, coupled with the larger conductivity reduction of ITO caused by bending, makes ITO/PET electrode unsuitable for highly flexible electrochromic devices with organic active layers.

Figure 5.8 (a) Electrochromic contrast of PANI/ITO/PET (left column) and PANI/PANI-CNT/PET (right column) at $\lambda_{720\text{ nm}}$ (-0.5 V, 40 s/+0.7 V, 80 s) after bending. (b) Folding test condition of the sample. (c) Performance of PANI/PANI-CNT/PET after cycles of folding.

5.3.3 Impedance Analysis on Bending Failure

To further clarify what the dominant failure mechanism is caused by bending, the electrochemical impedance spectroscopic studies were conducted on (a) ITO/PET, (b) PANI-CNT/PET, (c) PANI/ITO/PET and (d) PANI/PANI-CNT/PET after 0, 10, 30, 50, and 100 bending cycles, respectively. Nyquist plots of each sample are shown in Figure 5.9. Based on studies reported in literature, in high frequency region, the first and second semicircles can be assigned to the electron transfer at the Pt counter electrode and the

charge transfer at the working electrode/electrolyte interface, respectively, while the straight line in low frequency region is related to a diffusion process, which is influenced by ion transport in the electrolyte.[40, 41] The charge transfer resistances (R_{CT}) can be determined from the diameters of the semicircles in the Nyquist plots.[42] From Figure 5.9, we can see that after bending, the starting point of each spectrum shifts rightwards. This indicates an increase in resistance of the electrode after bending. Also, there is an increase in the diameter of the first semicircle after bending. This decrease in the charge transfer ability at the counter electrode may be due to the reduced potentials used in the tests, as all tests were conducted at open circuit potentials (OCP) and OCPs decrease after bending. The diameter of the second semicircle, which represents the R_{CT} at electrode/electrolyte interface, has limited change after bending for both ITO/PET and PANI-CNT/PET electrode (Figure 5.9a, b). However, after deposition of PANI on the two electrodes, their behaviors become very different. PANI/ITO/PET exhibits only one large semicircle and a straight line (Figure 5.9c), while PANI/PANI-CNT/PET shows a similar pattern to that of PANI-CNT/PET (Figure 5.9d). The diameter of the semicircle in Figure 5.9c increases with the number of bending cycles and doubles after 100 bending cycles. This is not observed in other three spectra, so it may be attributed to the PANI/ITO interface. The large value of the diameter shows the charge transfer at the PANI/ITO interface is poor, and it further deteriorates quickly in the bending process. Since the interface between ITO and PANI is weak, delamination may occur in bending process. As the number of bending cycle increases, more and more PANI is delaminated from ITO/PET. Therefore, the charge transfer at the interface between PANI and ITO becomes more difficult, causing the quick drop of the electrochromic performance of PANI/ITO/PET after bending. Differently, the R_{CT} corresponding to PANI/PANI-CNT interface only increases slightly after bending (Figure 5.9d), suggesting that the charge transfer ability between the electrode and electrochromic layer is well retained after bending. Comparing with the PANI-CNT/PET electrode (Figure 5.9b), after the deposition of PANI on it, the Nyquist plot pattern looks similar. This implies that no new interface is introduced into the system after the deposition, which explains why PANI/PANI-CNT/PET is more robust under repeated bending. The impedance studies, therefore, suggest that the failure of the interface between the ITO electrode and electrochromic PANI layer is the key factor responsible for the bending-

induced deterioration of electrochromic performance of PANI/ITO/PET. It is also demonstrated that using highly conductive CNT-grafted conjugated polymers as electrodes is a useful strategy to overcome this issue, paving the way to highly bendable electrochromic devices.

Figure 5.9 Nyquist plots of (a) ITO/PET electrode, (b) PANI-CNT/PET electrode, (c) PANI/ITO/PET, and (d) PANI/PANI-CNT/PET before and after bending.

5.4 Conclusions

In summary, a PANI-CNT hybrid material where PANI is covalently grafted to CNTs is readily processed to a flexible transparent electrode. The formation of CNT network and strong conjugation between PANI and CNTs lead to high conductivity of the PANI-CNT/PET electrode prepared. It also exhibits excellent bendability, i.e., its initial conductivity can be well retained even after 9,000 cycles of bending, which is superior to

that of ITO/PET. By electrodeposition of PANI on the PANI-CNT/PET electrode, the overall electrochromic performance of the PANI/PANI-CNT/PET is comparable to its PANI/ITO/PET counterpart, whereas after 100 cycles of bending, PANI/PANI-CNT/PET can much better retain its initial electrochromic performance than PANI/ITO/PET. The mechanism for the enhanced bendability is studied via impedance analysis. It shows that the enhancement is mainly due to the robust interface between the PANI-based electrode and active layer. The findings provide a new avenue for rational design of highly bendable electrodes for flexible electrochromic devices.

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Chapter 6

Porous Polyaniline-Carbon Nanotube Composite Electrode for Supercapacitors with Outstanding Rate Capability and Cyclic Stability

The PANI-CNT composite in last chapter was further studied for supercapacitor applications. PANI has advantages such as good environmental stability and low cost, whereas it is difficult to achieve high capacitance, good rate capability and long cycle life simultaneously. In this chapter, a series of porous PANI-CNT composite materials are prepared by chemically grafting PANI on CNTs and creating interpenetrating pores via templating using CaCO_3 nanoparticles. As PANI is covalently grafted on CNT networks formed in the electrode, the delocalization of electrons improves electron transport in the electrode and the stability of PANI in redox cycling process. The porous morphology created provides sufficient channels for the transport of ions. As a result, the optimized PANI-CNT composite exhibits a high capacitance of 1266 F g^{-1} at a current density of 1 A g^{-1} . Even at a current density of 128 A g^{-1} the specific capacitance could reach 864 F g^{-1} . The excellent rate performance and cycle stability of the porous PANI-CNT composite makes it a promising high-performance electrode material for supercapacitors.

*This section published substantially as B. Che, H. Li, D. Zhou, Y. Zhang, Z. Zeng, C. Zhao, C. He, E. Liu, X. Lu. *Compos. B Eng.* **2019**, 165, 671-678.

6.1 Introduction

As mentioned in section 2.2.3 and 2.4.4, polyaniline (PANI) is one of the most widely used conjugated polymers because of its relatively high electrical conductivity, good environmental stability, low-cost monomer and ease of synthesis.[1, 2] PANI can be readily synthesized using different methods, including oxidative polymerization[3-5], electrochemical deposition[6-8], enzymatic polymerization[9-11] and photo polymerization[12, 13]. In addition, using approaches like in situ polymerization[14-18], PANI could be easily combined with inorganic materials to form nanocomposites or covalently bonded hybrids with further improved functional properties. As a result, PANI-based materials have been widely used as active components in various electrochemical devices like sensors[19-21], electrochromic devices[22-24], and different types of energy storage devices, including rechargeable battery[25], flow battery[26] and supercapacitors[8, 15, 27]. In particular, owing to their high specific capacitance, good flexibility and low cost, PANI-based redox materials have shown great promise for supercapacitor applications.[28]

Comparing with other energy storage devices, such as lithium-ion battery, supercapacitors have the advantages of high power density and long cycle life. They have higher capacitance than traditional capacitors due to their enlarged surface area of the electrode and the decreased distance between two charged layers.[29] Supercapacitors utilize either electrostatic double-layer capacitance (EDLC) or pseudocapacitance. EDLC stores electrical energy by the electrostatic adsorption and desorption of ions in the conductive electrolyte, thus creating the double layers at the electrode and electrolyte interface. Pseudocapacitor stores energy through the redox reactions between electrode and electrolyte. As PANI has many oxidation states, it is a typical pseudocapacitor material. Comparing with common inorganic pseudocapacitor materials, such as metal oxides, PANI has advantages like good conductivity, ease of synthesis, flexibility, and low cost.[2, 29] It, however, also faces several challenges as a supercapacitor electrode material. Firstly, the conductivity of PANI at reduced state is lower than that at its oxidized state.[23] The relatively low conductivity at reduced state hinders electron transport in the redox process

of PANI, leading to slower kinetics of oxidation, and therefore limiting its electrochemical properties, such as specific capacitance. In addition, polymer binders are typically mixed with active materials in supercapacitors to bind the active materials to the substrates.[30] The binder added, such as polyvinylidene difluoride (PVDF), is typically electrochemically inert and non-conductive, which may further reduce the conductivity of the electrodes. Secondly, owing to its molecular nature, bulk PANI exhibits a compact morphology.[27, 31] This hinders ion transport in PANI in redox processes, and hence the regions that are not directly exposed to electrolyte are difficult to undergo redox reactions, leading to less active units. Furthermore, during the charge/discharge process some PANI units may be over-oxidized at relatively high potentials[32] and hence a small portion of oxidized PANI units could not be reduced back, causing decay of capacitance in a long-term cyclic process.

To address the aforementioned issues, various approaches have been explored. To increase the conductivity of PANI, the combination of PANI with carbon nanomaterials is a popular approach. Yan et al. mixed PANI with graphene and demonstrated enhanced electrochemical properties.[33] Xiong et al. grafted PANI onto carbon nanotubes (CNTs)[23] and fullerene[22], respectively, via in situ polymerization and found that the covalent bonding between PANI and carbon material enhances electronic and ionic conductivity and the hybrid has larger charge-storage capacities and improved redox activity. Li et al. chemically grafted PANI onto CNTs to extend the conjugation length of PANI and achieved a high conductivity of 3009 S cm^{-1} for the PANI-CNT composite with CNT content of 70 wt%.[34] To enhance ion transport, Yan et al. prepared a graphene nanosheet/PANI composite via in situ polymerization, which could reach a capacitance of 1046 F g^{-1} at a scan rate of 1 mV s^{-1} . [17] The good performance was attributed to excellent electrical conductivity and unique microstructure, in which the dispersion of nanoscale PANI particles on graphene nanosheets reduces the diffusion length of ions. Wang et al. reported that by growing whisker-like PANI on mesoporous carbon, the capacitance could reach 900 F g^{-1} at a current density of 0.5 A g^{-1} . [35] It was also reported that vertically aligned PANI nanowire arrays exhibited a capacitance of 950 F g^{-1} at a current density of 1 A g^{-1} . [36] The aligned arrays of PANI enabled high specific surface area and short ion diffusion path, which benefit the improvement of the specific capacitance of PANI,

whereas to improve the electrochemical stability of PANI, a more effective approach is to utilize the interfacial interactions between sp² carbon and PANI to stabilize the conjugated structure. For example, PANI deposited on multi-walled CNT (MWCNT) could reach a capacitance of 1065 F g⁻¹ at a current density of 0.5 A g⁻¹ and good cyclic stability up to 1000 cycles.[37] Although the aforementioned approaches could effectively boost the performance of PANI-based supercapacitors in certain aspects, so far high capacitance were typically achieved at relative low current density, and simultaneous enhancement of electrical conductivity, ion transport and electrochemical stability remains a challenge.

To simultaneously boost specific capacitance, rate capacitance and cycle life of PANI-based supercapacitors, in this work, a binder-free porous electrode is fabricated using PANI-grafted single-walled CNTs (SWCNT) derived from in situ oxidative polymerization of aniline in the presence of SWCNTs with amino groups (A-CNT). The motivation was to improve both the conductivity and electrochemical stability by establishing intimate interactions between CNTs and PANI through grafting, as well as via binder-free approach, while simultaneously enhancing ion transport by reducing the ion diffusion path via creating interpenetrating pores. Herein it is demonstrated that the optimized porous PANI-CNT composite exhibits a capacitance of 1266 F g⁻¹ at a current density of 1 A g⁻¹, and even at a high current density of 128 A g⁻¹ the specific capacitance could reach 864 F g⁻¹. Moreover, it can remain 83% of its capacitance at first cycle after 10,000 cycles. The underlying mechanisms for the impressive properties are also discussed.

6.2 Experimental Section

6.2.1 Materials

Aniline, ammonium persulfate (APS), m-cresol, camphor sulfonic acid (CSA) and hydrochloric acid (HCl) were all purchased from Sigma-Aldrich. Sulphuric acid (H₂SO₄) was purchased from Honeywell. Aniline was purified by vacuum distillation before use. All other chemicals were used as received. Amine-functionalized SWCNT/DWCNT (A-CNT) was purchased from Cheaptubes (purity > 99%, outer diameter 1-4 nm, length 3-30

μm). Calcium carbonate (CaCO_3) nanoparticles were purchased from NanoMaterials Technology, with average diameter of ~ 100 nm.

6.2.2 Preparation of Porous PANI-CNT Electrode

PANI-CNT composites with 0, 30 and 50 wt% CNTs in emeraldine base form were prepared as described in the previous work.[34] To dope PANI-CNT with CSA, in a typical process, 4 mg as-synthesized PANI-CNT was dissolved in 1 mL m-cresol consisting of 2.35 mg CSA as the dopant. CaCO_3 cresol dispersion was also added into the solution. CaCO_3 cresol dispersion was prepared by adding 5 mg CaCO_3 nanoparticles into 1 mL m-cresol, and dispersed by ultrasonication for 1 h. The as-prepared PANI-CNT/ CaCO_3 cresol solution was dropped on graphite paper and dried in vacuum oven at 60°C . After that the sample was immersed into 1 M HCl solution for 12 h to remove CaCO_3 nanoparticles, and then washed by DI water for 2 h to remove excess HCl. The washed sample was dried in vacuum oven at 60°C . Sample without CaCO_3 nanoparticles was also prepared as a reference.

6.2.3 Characterization

The field-emission scanning electron microscopic (FE-SEM) images of the materials and elemental mapping were obtained on a JEOL 7600F SEM with an energy dispersive X-ray (EDX) detector. Raman spectra was recorded on a Renishaw inVia Raman Microscope ($\lambda_{\text{exp}}=514$ nm). The electrochemical performances of the as-prepared samples were tested by Autolab PGSTAT302 potentiostat. Cyclic voltammetry (CV), galvanostatic charge/discharge, and electrochemical impedance spectroscopy (EIS) were carried out in a three-electrode cell. The working electrode was as-prepared PANI-CNT electrode on graphite paper. A platinum sheet was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. A 0.5 M H_2SO_4 solution served as the electrolyte at room temperature. The potential window of CV measurement ranged from -0.2 to 0.6 V at 5 mV s^{-1} scan rate. The galvanostatic charge/discharge tests were also

recorded between -0.2 and 0.6 V at different current densities. The specific capacitance was calculated from the charge/discharge curves using the following equation:

$$c = \frac{It}{m\Delta V}$$

where I/m is the current density used for charge/discharge process, t is the discharge time, and ΔV is the voltage interval of discharging process. The EIS measurements were carried out in the frequency range from 100 kHz to 0.1 Hz at open circuit potential with an AC perturbation of 5 mV.

6.3 Results and Discussion

6.3.1 Porous Morphology and Effect on Ion Transport

The preparation process for the porous PANI-CNT composites is illustrated in Figure 6.1. The synthesis and structural verification of the PANI-grafted-CNTs have been reported in the previous publications.[34, 38] The electrical conductivities of the composites with 30 and 50 wt% CNTs could reach 1100 and 2350 S cm⁻¹, respectively, which are much higher than that of the corresponding neat PANI.[34] In this work, instead of simply doping the PANI-grafted-CNTs in emeraldine base form with CSA in *m*-cresol, CaCO₃ nanoparticles were also added in as sacrificial templates. After etching with HCl, porous morphology is generated by removal of CaCO₃ nanoparticles. In the etching process, CO₃²⁻ anion could react with HCl to form carbon dioxide and water, while Ca²⁺ cation could diffuse out, creating thin channels to facilitate ion transport in the redox process.

Figure 6.1 Schematic of preparation process of porous PANI-CNT electrode.

The surface morphologies of PANI-CNT and porous PANI-CNT are shown in Figure 6.2. It is clear that PANI-CNT exhibits a compact morphology, i.e., the regions between the CNTs are fully filled with PANI (Figure 6.2a). The implication of this compact morphology is that the electrolyte may penetrate into PANI only in near surface regions, hardly reaching the region close to the current collector (graphite paper). As a result, the ion transport could be hampered by the inner stodgy morphology, and the PANI chains deep inside the electrode could not be effectively utilized as active units. By contrast, the porous PANI-CNT composite shows numerous pores with size of around 100 nm (Figure 6.2b). Moreover, the cross-sectional image (Figure 6.2c) shows that the pores exist not only at the surface, but also in the inner part of the PANI-CNT composite electrode. EDX elemental mapping of the distribution of calcium before and after etching are shown in Figure 6.2d-i. Before etching, the SEM image only shows some small aggregates of CaCO_3 nanoparticles on the surface (Figure 6.2d) as the CaCO_3 nanoparticles embedded in the PANI-CNT could not be observed. The corresponding EDX mapping image, however, shows relatively homogeneous distribution of Ca element (Figure 6.2e), implying that a substantial amount of CaCO_3 nanoparticles are embedded in the PANI-CNT matrix. After etching, a porous surface is observed (Figure 6.2g). Moreover, Ca is not detected as a present element, as shown by the EDX mapping image in Figure 6.2h, which confirms the

decomposition of the embedded CaCO_3 nanoparticles and the successful removal of the resultant Ca^{2+} cations. Since the pores are created by etching process, it is reasonable to deduce that the removal of the Ca^{2+} cations in the etching process have created ion channels that connect the pores to surface. Such interpenetrating pores help to expose the regions deep inside the PANI electrode to the electrolyte, shortening the pathways for the ion transport. It is also worth noting that redox reactions of PANI involves H^+ while the size of Ca^{2+} is much larger than that of H^+ . SEM and EDX data together prove the formation of porous morphology and ion transport channels in the porous PANI-CNTs, facilitating redox reactions. Besides, from Figure 6.2b, we can also see that the CNTs in PANI-CNT composite are distributed fairly uniformly, forming networks, which would act as effective conductive frameworks.

Figure 6.2 SEM images of (a) PANI-CNT, (b) porous PANI-CNT and (c) cross-section of porous PANI-CNT composite. SEM-EDX elemental mapping of porous PANI-CNT for calcium and oxygen (d-f) before and (g-i) after etching.

To confirm the effect of the porous morphology on ion transport, cyclic voltammetry studies were carried out. Figure 6.3a shows the cyclic voltammetry of neat PANI, PANI-CNT30% and porous PANI-CNT30%, where 30 wt% is the feed content of CNT in the composite. PANI exhibits two pairs of oxidation reduction peaks in CV. At a lower potential, the first pair of oxidation reduction peaks is attributed to the redox transition of PANI between leucoemeraldine form and emeraldine form.[16, 39, 40] At a higher potential, the second pair of peaks is attributed to the transition of emeraldine to pernigraniline state.[16, 39, 40] Comparing with neat PANI, PANI-CNT30% has the same two pairs of peaks but the second oxidation peak shifts to a slightly lower potential while the second reduction peak shifts to a slightly higher potential. As band gap can be estimated by the difference of oxidation and reduction potentials, the slight changes in oxidation and reduction potentials imply that PANI-CNT30% may have a slightly lower band gap than PANI. The likely reason is that the conjugation length of PANI could be extended by chemically connecting CNTs to PANI.[34, 41, 42] Porous PANI-CNT30% shows even lower oxidation potential and higher reduction potential for the second pair of redox peaks, which could be attributed to the acid etching process in preparation of porous PANI-CNT30%. During etching, some PANI chains that are not covalently grafted to CNTs may be washed out, while the PANI chains grafted to CNTs would all remain in the composite, resulting in a higher average conjugation length. The effect of the porous morphology produced by etching is further proved by the strikingly larger area inside the CV curve of the porous PANI-CNT30% than those of PANI and PANI-CNT30%. As pores and H^+ transport channels are created in the porous morphology, the PANI chains deep inside can easily take part in redox reactions. Thus, comparing with PANI and PANI-CNT30%, porous PANI-CNT30% has more active PANI units, resulting in a much larger area enclosed in the CV. Raman study was also conducted to further probe the chemical structural differences among PANI, PANI-CNT30% and porous PANI-CNT30% (Figure 6.3b). For neat PANI, four main peaks including C-H bending of the quinoid/benzenoid ring ($\sim 1191\text{ cm}^{-1}$), weak C-N stretching ($\sim 1249\text{ cm}^{-1}$), C-N stretching of the cation radical species ($\sim 1334\text{ cm}^{-1}$) and C-C stretching of the benzenoid rings ($\sim 1622\text{ cm}^{-1}$) are observed in the Raman spectrum.[41, 43, 44] PANI-CNT30% exhibits a strong peak at $\sim 1601\text{ cm}^{-1}$,

which can be attributed to the G band of the CNTs.[38] After the etching process, the sharp band at $\sim 1622\text{ cm}^{-1}$ for PANI-CNT30% becomes a shoulder for the porous PANI-CNT30%. This is another proof that some ungrafted PANI chains are washed out and hence more CNT-grafted chains are present in the porous film. In addition, the band at $\sim 1191\text{ cm}^{-1}$ corresponding to C-H bending of the quinoid/benzenoid ring becomes a doublet with a sister band at $\sim 1170\text{ cm}^{-1}$, which might be related to the PANI aromatic ring that is directly attached to the CNTs. The CV and Raman data verify the greatly enhanced ionic transport in porous PANI-CNT30% as well as the increased average conjugation length caused by grafting PANI chains on CNTs, which will benefit both electrical and ionic conductivity, as well as electrochemical stability of PANI.

Figure 6.3 (a) Cyclic voltammetry of PANI, PANI-CNT30% and porous PANI-CNT30% scanned from -0.2 V to +0.6 V at a scan rate of 5 mV/s. (b) Raman spectra ($\lambda_{\text{exp}}=514\text{ nm}$) of PANI, PANI-CNT30% and porous PANI-CNT30%.

6.3.2 Electrochemical Properties as Supercapacitor

The supercapacitor performance was examined by galvanostatic charge/discharge tests. Figure 6.4a shows charge/discharge performances of PANI-CNT30% and porous PANI-CNT30%. It is clear that porous PANI-CNT30% has a much higher specific capacitance up to 1266 F g^{-1} at a current density of 1 A g^{-1} than non-porous one. The high capacitance can be attributed to improved electron and ion transport brought by grafting PANI chains

to CNTs and the formation of CNT network, as well as the interpenetrating pores in the porous material. Since CNTs act as conductive framework in the composite material, the content of CNTs also directly affects the electrochemical performance of the composites. Therefore, composites with different contents of CNTs (0, 30 and 50 wt%) were prepared. The charge/discharge curves of porous PANI, porous PANI-CNT30% and porous PANI-CNT50% are also compared in Figure 6.4a. Porous PANI-CNT30% exhibits the highest capacitance of 1266 F g^{-1} , where porous PANI is 787 F g^{-1} and porous PANI-CNT50% is 1062 F g^{-1} . The likely reasons are that porous PANI-CNT30% is more conductive than porous PANI but contains more pseudocapacitive material, PANI, than porous PANI-CNT50%, while the double layer capacitance provided by the SWCNT/DWCNT used in this work is relatively small[45-47].

Figure 6.4 (a) Charge/discharge curves of PANI-CNT30% and porous PANI-CNT with different contents of CNTs at the current density of 1 A g^{-1} ; (b) Charge/discharge curves of porous PANI-CNT30% at different current densities from 1 A g^{-1} to 128 A g^{-1} (Inset is the detail plots at

16, 32, 64, 128 A g⁻¹); (c) Specific capacitance of PANI-CNT30% and porous PANI-CNT30% at different current densities; (d) Cyclic stability of porous PANI-CNT30% at the current density of 16 A g⁻¹.

Porous PANI-CNT30% was also tested at current densities of 1, 2, 4, 8, 16, 32, 64, and 128 A g⁻¹, respectively, to examine its rate performance. The corresponding charge/discharge curves are shown in Figure 6.4b. Figure 6.4c shows the capacitances of porous PANI-CNT30% calculated from the charge/discharge curves shown in Figure 6.4b in comparison with the rate capacitances of PANI-CNT30% at the same current densities. It is striking to see that at a very high current density of 128 A g⁻¹, porous PANI-CNT30% still exhibits a capacitance of 864 F g⁻¹ and it is about 68% of the value at 1 A g⁻¹. This demonstrates the outstanding rate performance of porous PANI-CNT30%. It is worth noting that the rate performance of PANI-CNT30% is much poorer than that of its porous counterpart, indicating that the electrical conductivity is not the only reason for the good rate performance; the porous morphology, which can facilitate the ion transport, is also a key factor.

The cycle stability of porous PANI-CNT30% capacitor was studied by charge/discharge cycle test at 16 A g⁻¹ (Figure 6.4d). After 10,000 cycles, it can retain 83% of its capacitance at the first cycle. The good cycle stability of the material is a result of the direct conjugation between PANI and CNTs. As discussed earlier, the improved delocalization of electrons caused by grafting PANI chains on CNTs reduces the oxidation potential of the grafted PANI and the acid etching process has removed substantial amount of ungrafted PANI. This would facilitate the oxidation of PANI, reduce the voltage loss across the capacitance material and make the potential more evenly applied, reducing the possibility of over-oxidation of PANI during redox cycling and hence benefiting the long-term stability of the capacitor. In addition, the CNT network also acts as a mechanical support, which may also contribute to the good cyclic stability of the composite.

To further verify the mechanism for the greatly enhanced electrochemical performance of porous PANI-CNT30%, electrochemical impedance spectroscopy (EIS) was used to study

the charge transfer in the composite materials. Figure 6.5 shows a comparison of the charge transfer resistances of PANI, porous PANI, PANI-CNT30% and porous PANI-CNT30%. The charge transfer resistance (R_{CT}) is determined from the diameters of the arcs in the Nyquist plots.[23] For all four samples, R_{CT} at oxidized state is always lower than that at reduced state. This is because PANI is more conductive at oxidized state.[23] Porous PANI-CNT30% has the lowest R_{CT} values among the four samples, which corresponds with its much higher specific capacitance and outstanding rate performance. Furthermore, the ratio of $R_{CT}(-0.2V)/R_{CT}(+0.6V)$ is in the range of 2.11 to 2.19 for PANI, porous PANI and PANI-CNT30%, whereas this ratio is only about 1.56 for porous PANI-CNT30%, implying that electrochemical oxidation of porous PANI-CNT30% may become much easier. Since the oxidation of PANI is usually slower owing to the lower conductivity at reduced state, the much improved R_{CT} of porous PANI-CNT30% at reduced state could be a key factor for its outstanding rate performance. R_{CT} of a redox material is influenced by both its electron and ion transport properties, and often the much sluggish one would be the major limiting factor. By creating interpenetrating pores in neat PANI, the ionic conductivity should be increased, whereas by comparing the R_{CT} values of PANI and porous PANI in Figure 6.5, we can see that the R_{CT} increases slightly, instead of decreasing. On the other hand, by grafting CNTs onto neat PANI, the electrical conductivity should be increased, while by comparing the R_{CT} values of PANI and PANI-CNT30%, as expected, the R_{CT} indeed decreases. The above observation indicates that the electron transport is the limiting factor for neat PANI. Only improving the ion transport in neat PANI cannot improve the charge transfer resistances effectively. When the electron transport of PANI is improved by grafting PANI on CNTs, the R_{CT} is effectively decreased, and then the ionic transport becomes the limiting factor for PANI-CNT30%. Thus, by creating pores and ion channels in PANI-CNT30%, the ionic transport is also improved, so porous PANI-CNT30% has the lowest R_{CT} . This may explain why porous PANI-CNT30% possess much enhanced capacitance and rate performance.

Figure 6.5 Charge transfer resistance of PANI, PANI-CNT30%, porous PANI, and porous PANI-CNT30% at oxidized (+0.6V) and reduced (-0.2V) state. (Insets are the original Nyquist plots at (a) oxidized states and (b) reduced states.)

6.4 Conclusions

In summary, a porous PANI-CNT composite in which PANI is covalently grafted on CNTs was successfully prepared. As increasing the conductivity and enhancing ion transfer to more active material are key factors to fully realizing excellent electrochemical performance, in this work, the electron transport is improved by extending the conjugation length of PANI through grafting with CNTs, and the ion transport is enhanced by creating interpenetrating pores and channels to facilitate ion transport to more active units. Thus, with the improvement of both the electron and ion transport, the optimized porous PANI-CNT composite exhibits a capacitance of 1266 F g^{-1} at 1 A g^{-1} . At a high current density of 128 A g^{-1} , the specific capacitance could reach 864 F g^{-1} . This material also has a good cyclic stability up to 10,000 cycles. The excellent electrochemical properties of porous PANI-CNT composite make it a promising electrode material for high performance supercapacitors.

Since porous PANI-CNT has such promising supercapacitor performance and PANI itself is a good electrochromic material, it is possible to fabricate a PANI-based electrochromic supercapacitor, which is an integration of electrochromic device and supercapacitor. Working as one device, the supercapacitor component and electrochromic component undergo redox reaction together, so the charging state of the supercapacitor could be indicated by the color of electrochromic PANI, and this small portion of PANI could also contribute to the overall capacitance. One option of the electrode used in such device could be PANI-CNT electrode studied in Chapter 5. Thus, all components of the electrochromic supercapacitor contain PANI, the interface between different layers are expected to be strong, which may lead to a good performance and flexibility. There are some preliminary results on the topic and they are reported in detail in the next chapter.

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Chapter 7

Conclusions and Future Work

This chapter draws a conclusion of the thesis. Two conjugated polymer-based composite systems, $\text{MoO}_3/\text{PEDOT:PSS}$ and PANI-CNT, are summarized respectively and the hypothesis is discussed. Reconnaissance work related to electrochromic supercapacitor based on PANI is reported. Recommendations to future studies are also presented.

7.1 Conclusions

A MoO₃/PEDOT:PSS composite is prepared as an electrochromic film via electrostatic interactions between negative charged surface groups of MoO₃ nanoparticles and positive charged PEDOT. The electron transport is enhanced by the addition of PEDOT:PSS and strong binding between MoO₃ and PEDOT:PSS. The electrons are easier to transport in and out to the active sites of MoO₃, alleviating Li⁺ trapping problem and resulting more active sites in MoO₃ are involved in the Li⁺ intercalation process. The complementary conductivities of MoO₃ and PEDOT:PSS facilitate electron transport at both oxidized and reduced states, and they are better utilized due to the extensive interfacial interactions between the two components. Meanwhile the PEDOT:PSS matrix holds MoO₃ nanoparticles and buffers the induced stress, so the long-term stability is enhanced to more than 500 cycles.

A PANI-CNT composite material where PANI is covalently grafted to CNTs is prepared for a flexible transparent electrode. The conductivity of PANI-CNT/PET is high as the direct conjugation between PANI and CNT provides route for electron transport. As a result, the flexible electrode has compared electrical performance as commercial ITO/PET electrode. The complementary mechanical properties of PANI and CNT provide the PANI-CNT electrode flexibility. The electrochromic films prepared on the flexible electrode has strong interface between the electrode and the electrochromic layer, so the robustness under bending is highly enhanced. Pores and channels are further created in the material to fabricate a supercapacitor electrode. The oxidation/reduction potential is reduced as the conjugation length is extended and electrons are more delocalized. The possibility of over-oxidization is reduced and the long-term stability is also enhanced. The supercapacitor electrode has a high specific capacitance of 1266 F g⁻¹ at 1 A g⁻¹ and good rate capability, that at a high current density of 128 A g⁻¹ the specific capacitance could reach 864 F g⁻¹. The good cyclic stability is up to 10,000 cycles.

In the thesis, two systems of conjugated polymer-based composites are prepared by purposely designing the interfacial interactions between the two complementary

components of the composites. In $\text{MoO}_3/\text{PEDOT:PSS}$ system, it is electrostatic interaction; in PANI-CNT system, covalent bond is formed between PANI and CNT. Based on the results of the three chapters, strong interactions such as electrostatic interaction and covalent bond, facilitate the electron transport, oxidation/reduction potentials, long-term stability and mechanical robustness. The synergistic effects could be achieved by one or more of the above properties enhanced, which reflects on high performance of the electrochromic applications, such as conductivity, long-term stability and flexibility. The hypothesis of the PhD study is proved. This conclusion provides a rational strategy to design conjugated polymer-based composite materials for electrochromic applications. It is a primary point that the two components of the composite have complementary properties. The interfacial interactions between the complementary components in the composite is a key factor to the synergistic electrochromic performances. A simple physical mixing of two components should be avoided. Instead, a strong interfacial interactions should be favored to fully boost the potential of the two complementary components. This is also applied to other electrochemical applications such as supercapacitors.

7.2 Reconnaissance Study

The porous PANI-CNT30% supercapacitor electrode prepared in Chapter 6 was integrated with electrochromic PANI to fabricate an electrochromic supercapacitor. The PANI-CNT electrode prepared in Chapter 5 was used as the current collector. Both porous PANI-CNT30% and electrochromic PANI were coated on this electrode. (Figure 7.1a) Therefore, this device contains two functions: supercapacitor of porous PANI-CNT30% and electrochromism of PANI. And they function together as they are deposited on the same electrode. Working as one device, the supercapacitor component and electrochromic component undergo redox reaction together, thus the charging state of the supercapacitor could be indicated by the color of electrochromic PANI, and this small portion of PANI could also contribute to the overall capacitance. All the three components, supercapacitor, electrochromic layer and electrode, have PANI as main component, so the interaction between them are strong, leading to a potential of enhanced performance and flexibility. Figure 7.1b shows the charge/discharge curve of the electrochromic supercapacitor. The

specific capacitance is about 250 F g^{-1} at 0.5 A g^{-1} . This capacitance is lower comparing to the one tested on the graphite paper, because of the lower conductivity of the PANI-CNT electrode. The color of the electrochromic PANI is dark green at charged state ($+0.8 \text{ V}$) and yellowish green at discharged state (-0.4 V). Different color is demonstrated at different charging state. Thus, the electrochromic supercapacitor based on PANI is explored, providing the possibility of a bi-functional device built by the materials.

Figure 7.1 (a) Device structure of the electrochromic supercapacitor. (b) Charge/discharge curve of the electrochromic supercapacitor at 0.5 A g^{-1} .

7.3 Recommendations to Future Work

1. Though the specific capacitance of porous PANI-CNT is excellent on the graphite paper in Chapter 6, the specific capacitance of it in the electrochromic supercapacitor is not impressive. The difference is caused by the different current collector used in the electrochromic supercapacitor. Graphite paper is a normally used current collector in supercapacitors, but in the electrochromic supercapacitor a transparent electrode is required. In this case, the transparent PANI-CNT electrode prepared in Chapter 5 is used in the device, but the conductivity of the electrode is much lower than graphite paper. The low conductivity of the current collector limits the capacitance of porous PANI-CNT. Therefore, several methods to increase the conductivity of the electrode are proposed:

(1) By increasing the CNT content in the PANI-CNT electrode, the conductivity of the electrode will increase. Currently the CNT content is about 10wt% in the composite, there is a large potential to increase CNT content. However, there is a compromise between the conductivity and transparency of the electrode. More CNT content will lead to decrease in the transparency of the electrode.

(2) Another way is to precisely control the ratio of quinoid and benzenoid rings in PANI. A perfect emeraldine base could reach a high level of conductivity. A partial reduction of over oxidized PANI can modify the ratio of quinoid and benzenoid and improve the conductivity dramatically.[1]

(3) Moreover, the crystallinity of PANI also affects the conductivity. The probability of inter-chain hopping of charge carriers is increased with the decrease in the d-spacing and inter-chain separation.[2] Thus the conductivity is improved if more ordered PANI with smaller d-spacing could be prepared.

With the increased conductivity of PANI, the specific capacitance of the electrochromic supercapacitor could be further improved.

2. Energy storage electrochromic window is a newly proposed integrated bi-functional device. It integrates supercapacitor and electrochromic window, by storing the energy during the Li^+ intercalation process of the electrochromic window, and providing the energy during the deintercalation process. A WO_3 nanoparticle coated Ag/PEDOT:PSS demonstrates electrochromism and a specific capacitance of 221 F g^{-1} at 1 A g^{-1} . [3] MoO_3 has higher specific capacitance than WO_3 due to lower molar mass. Therefore, $\text{MoO}_3/\text{PEDOT:PSS}$ has a higher potential specific capacitance than $\text{WO}_3/\text{PEDOT:PSS}$. In Chapter 4, it has been found that the electron transport in MoO_3 is enhanced by the addition of PEDOT:PSS. Also, it is proved in Chapter 6, that both electron and ion transport play an important role in the capacitive performance. Thus, a modification on the $\text{MoO}_3/\text{PEDOT:PSS}$ system to facilitate its ion transport would be helpful to enhance its capacitive performance. It is an effective way to create porosity in the composite in order

to facilitate the ion transport. Some preliminary results show that the electropolymerization of EDOT in the presence of PSS and MoO₃ nanoparticles gives a porous morphology to the composite. (Figure 7.2) Comparing to the morphology of MoO₃/PEDOT:PSS prepared in Chapter 4, this composite clearly demonstrates pores with size about 30-100 nm. It is proposed that the presence of MoO₃ nanoparticles hinders the polymerization of PEDOT chains and fast electropolymerization process creates defects in the structure. In the future study, the control on the density and sizes of the pores and the content of MoO₃ in the composite should be considered.

Figure 7.2 Morphology of MoO₃/PEDOT:PSS prepared.

3. The hypothesis of the thesis has been proved, that strong interactions between the conjugated polymer and the other complementary component in the composite lead to synergistic effect. Therefore, a covalent bond between conjugated polymer and transition metal oxide is a good design in terms of the electron transport between the two components. Moreover, the polymer matrix holds the transition metal oxide particles and buffers the induced stress as transition metal oxides usually suffer from the volume change during the Li⁺ intercalation/deintercalation process, so the long-term stability of the material is enhanced. A covalently bonded PANI-TiO₂ has been prepared via sol-gel process and oxidative polymerization using a bridging compound, meanwhile the electrochromic performance of the composite was studied.[4] However, TiO₂ is a cathodically colored

material and PANI is an anodically colored material. They are not complementary components that color at the same potential, so the electrochromic contrast is influenced by each other. PANI-Fe₂O₃ is a better composite with two anodically colored materials. A similar synthesis route is proposed to get covalently bonded PANI-Fe₂O₃. (Figure 7.3) Other anodically colored transition metal oxides, such as MnO₂, Cr₂O₃ and NiO, can also be considered if there is a reasonable synthesis route for the hybrid.

Figure 7.3 Proposed synthesis route for covalently bonded PANI-Fe₂O₃ composite.

References

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