Template synthesis of mesoporous nanofilms and nanowires and their applications

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2013

Xue, T. (2013). Template synthesis of mesoporous nanofilms and nanowires and their applications. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54767>

<https://doi.org/10.32657/10356/54767>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**TEMPLATE SYNTHESIS OF MESOPOROUS
NANOFILMS AND NANOWIRES AND THEIR
APPLICATIONS**

TONG XUE
SCHOOL OF CHEMICAL AND BIOMEDICAL
ENGINEERING
2013

TEMPLATE SYNTHESIS OF MESOPOROUS NANOFILMS AND NANOWIRES AND THEIR APPLICATIONS

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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

2013

Acknowledgements

Since I started my PhD study as the first student in our research group four years ago, I received tremendous help from many kind people. I deeply appreciate all the help and support I have received in four years. Herein, I would like to take this opportunity to express my heartfelt gratitude to those who gave me selfless assistance.

Firstly, I would like to express my deepest gratitude to my supervisor, Asst. Prof. Lee Jong Min, for his guidance and mentoring throughout the span of these projects. He has spent valuable amount of time and given brilliant ideas to follow up the progress of the projects.

Secondly, I express my heartfelt gratitude to all my friends who gave me help and support in my project, especially recommend Dr. Sun Zhi Peng, who gave me unreturnable assistance in my experiments. There is no word can express my unlimited thanks. I am thankful to Chunping Chen, Hong Wang, Jingdui Hong, Wenjin Yan, Guoyi Chi, Rongmei Si, Yabo Wang, Jing Liu, Wenchao Jiang, Jibin Song, Yilei Wang, Zhihong Yang, Ke Huang, Dr. Li Wei and Dr. Wei Zhang for their valuable help and support on my research. I also would like to express my thanks to the members in our group: Dr. Piyarat Weerachanchai, Dr. Zhenjian Chen, Ms. Linlu Bai and Mr. Duc Tai Dam.

Last, but not least, I want to express gratitude to my beloved family: my parents and husband. Thanks for their support without taking.

List of Abbreviations

LLC	Lyotropic Liquid Crystalline (Crystal)
LC	Liquid Crystal
TLC	Thermotropic Liquid Crystal
PAA	Porous Anodic Alumina
PC	Polycarbonate
PANI	Polyaniline
MCNWs	Mesoporous Carbon Nanowires
CNTs	Carbon Nanotubes
CNFs	Carbon Nanofibres
CPP	Critical Packing Parameter
POM	Polarized Optical Microscopy
XRD	X-ray diffraction
FESEM	Field Emission Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy
UV-Vis	Ultraviolet-Visible
ICP	Inductively Coupled Plasma
CV	Cyclic Voltammetry
SCE	Saturated Calomel Electrode
EDLCs	Electrochemical Double Layer Capacitors

ECs

Electrochemical Supercapacitors

SSA

Specific Surface Area

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Summary

This thesis focuses on the template synthesis of ordered mesoporous nanofilms and nanowires for their applications in semiconductors, supercapacitors and electrochemical catalysts. Synthesis of ordered nanomaterials with a high specific surface area has received continuous interest, because they have great potential to apply in catalysis, biosensors, semiconductors and electrochemical devices. With the development of nanoscaled fabrication, template synthesis has received much attention for flexibility and stability in ordered nanomaterials synthesis. The template could be considered as a nanoscale reactor for the synthesis of the desired materials (metal, metal oxide, and non-metal) by chemical or physical method. Therefore, structure of ordered mesoporous nanomaterials can be controlled easily and effectively by template synthesis. In templates, lyotropic liquid crystalline (LLC) phases as a soft template are most widely used to prepare mesoporous materials with repeat distances ranging from 2 to 10 nanometers. The porous anodic alumina (PAA) template as a hard template is frequently used to prepare ordered nanowires and nanotubes with a uniform diameter and length to fabricate nanostructure devices.

Firstly, mesoporous dual layers of polyaniline (PANI) supported Cu_2O films have been designed and synthesized by the electrochemical method in the LLC template. Both potential and pH values for the electrodeposition were discussed to show optimized conditions to synthesize the target composite films. The band gap

of mesostructure Cu₂O/PANI dual layers (1.86 eV) was narrower as compared with the band gap of the mesoporous Cu₂O single layer (2.41eV). The decrease of the band gap (i.e. 0.55eV) by introducing PANI as a supporting layer explicitly indicates that electron transfer between conductive band and covalent band is much easier. As the results show, mesoporous Cu₂O/PANI bilayer film could be a promising material which can be used in some specific fields, such as photocatalysis, solar cells and chemical sensors.

Secondly, in order to verify the contribution of the mesoporous PANI layer on band gap, mesoporous Se_{0.5}Te_{0.5}-PANI dual-layer films were synthesized in the LLC template. The concentration of Te in Se_xTe_{1-x} could also affect the band gap and optical property. Se_{0.5}Te_{0.5} was selected in this study. The band gaps of mesoporous Se_{0.5}Te_{0.5} alloy and mesoporous Se_{0.5}Te_{0.5} /PANI are proved to be 1.3eV and 0.8eV, respectively.

Thirdly, the confined LLC phase in cylindrical pores of PAA membrane has been demonstrated to be a promising way to synthesize mesoporous nanowire structures. The chronopotential results showed the relatively high specific capacitance of 993 F g⁻¹ at current density of 1A g⁻¹ has been achieved. The mesoporous Co(OH)₂ nanowires have a potential application in supercapacitors as an electrode material.

Furthermore, optimized synthesis conditions of mesoporous Co(OH)₂ have been investigated and show that the electrochemical deposition should be carried out at a constant potential of -0.75V in LLC phase at 50°C without any heat treatment. The discharge curves show the highest capacitance of 1180F g⁻¹ was

obtained at a current density of 4 A g^{-1} . The chemical state and detailed structure of $\text{Co}(\text{OH})_2$ were examined by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) respectively. It reveals the capacitance of mesoporous $\text{Co}(\text{OH})_2$ nanowires depends on not only the oxygen atomic ratio of $\text{Co}(\text{OH})_2$ to CoO chemical state, but also the packed density of interlaced nanostructure.

Finally, in order to investigate mesoporous nanowire structure on electrochemical catalysis, the one-step methodology has been utilized to fabricate platinum catalysts on well-aligned mesoporous carbon nanowires (Pt/MCNWs) in dual templates, which are the combination of porous anodic alumina (PAA) as the hard template and triblock polymer ethanol solution as the soft template with evaporation-induced self-assembly technique. From electrochemical measurements, the MCNWs have been proved to be a good carbon support, and the Pt/MCNWs show a high active surface area and excellent electrocatalytic activity with an enhanced carbonaceous species tolerance, which have the potential application to be utilized as an electrocatalyst in methanol oxidation.

Keywords: Porous anodic alumina; Lyotropic liquid crystal; Dual templates; Cuprous oxide; Selenium; Tellurium; Cobalt hydroxides; Mesoporous carbon nanowires; Platinum; Semiconductor; Capacitor; Catalyst; electrodeposition;

Chapter 1 Introduction

In recent years, nanostructured materials which have potential applications in various fields such as energy storage, magnetism, optics, electronics, electrochemistry and bioscience etc. have attracted much more attention from many researchers[1]. Much effort has been taken on further improvement of performance and reduction of the cost for materials by using high specific surface materials. In the past decades, there are many methodologies such as sol-gel synthesis, chemical or physical vapor deposition, hydrothermal method, template-based synthesis, lithography and self-assembly etc. to be developed in order to synthesize nanoscaled materials with restricted structure [2]. Among all methodologies for nanostructured materials fabrication, template synthesis is a fascinating and versatile way which can create controllable shape and size-uniform nanostructure from simply casting procedure [3].

1.1 Template synthesis

1.1.1 Concept of template synthesis

In template synthesis, at first, templates with special and controllable nanostructure are employed to synthesize target materials on the surface or inside of the patterns by using physical or chemical methodologies. And then, the templates are removed, the resulting materials which duplicate the reverse morphology and shape of template will be produced. Since C. R. Martin

(Department of chemistry, Colorado state university) synthesized conductive polypyrrole by using electropolymerization method in polycarbonate template in 1985, template synthesis was proposed to be a promising way for synthesizing nanostructure materials [4]. By using this approach, series materials such as Au, TiO₂ and carbon tubules etc. have been synthesized [5-7]. Subsequently, much more research [8-12] has been carried out in the field of template synthesis according to C. R Martin's theory which generates great development in the past decades.

1.1.2 Advantages of template synthesis

Template-based growth is an inexpensive and practicable methodology which could produce various types of materials and controllable structure such as pore size, wire length and packing density [3, 13]. It is also environmentally benign for the advantage of low pollution.

With the aid of templates, a variety of functional materials with diverse structures and morphologies such as zero-dimensional, one-dimensional (1D) nanostructures, 2D films, and 3D porous frameworks have been synthesized by using bottom-up synthetic pathway[14, 15].

Although the template removal in synthesis procedure could lead to the aggregation and destruction of nanostructures, researchers still paid much attention to template synthesis because of its remarkable advantages.

Templated synthesis offers many advantages over other methods for the synthesis of ordered and porous materials[3]: i) template synthesis can be

performed to synthesize various types of materials such as metal, alloy, semiconductor, conductive polymer, metal/nonmetal oxides and carbon etc.; ii) well-dispersed nanoparticles, nanowires, nanotubes, porous films and other composite structure can be synthesized by using this approach; iii) template structural parameters could be tuned to change the detailed structures such as the length/radius ratio of nanotubes or nanowires, pore size of porous films, orientation and dimensions of the materials; iv) ordered nanoarrays can be obtained; V) the performance of nanomaterials can be adjusted by controlling technical parameters (such as concentration, potential, frequency and time etc.). Therefore, this innovative technique is the fundamental to develop and design next generation of nanodevices.

1.1.3 Type of template

Templates can be classified into two main types: i) hard template and ii) soft template [13, 16]. In hard template method, the nanostructures growth is confined in pores offered by porous films. The morphology and pore size of template entirely determine the resulting structure of desired materials. In soft template method, the mesoporous nanostructure forms with self-assembly controlled molecular interactions (such as Van der Waals force, hydrogen bonds and electrostatic interactions etc.). The soft template method does not need to prepare the template before synthesis, and also, use special method to remove template after synthesis. However, the structure of soft template is always decided by the ingredient, pH value, and temperature etc. Hence, the soft templates cannot be well

controlled as comparing with hard template. Nevertheless, the less controllability means the more flexibility. Hence, soft template methodology could challenge the special structure synthesis by self-assembly method. The hard template method limits the variety of synthesized structures because of unchangeable morphology of porous membranes. As mentioned above, both templates can supply shaped spaces as nanoreactors that allow the desired materials synthesized. The soft template has dynamic pore, the particles can across through the pore-wall. Whereby the hard template supplies stable circumstances for reaction, and the structure of synthesized material could be fully controlled.

In hard template family, widely used porous anodic alumina (PAA) membranes and polycarbonate (PC) membranes have attracted much attention. Besides, other new type of membranes, such as porous alumina silicate [8], mesoporous zeolites [17], carbon nanotubes [18], micro-porous polymeric filtration membranes [19] and DNA [20] have been also employed. And in soft template family, block polymer with spherical, cylindrical and lamellar structures [21], super-molecular self-assembled hexagonal cylindrical structures [22], surface micelles [23], liquid-crystalline phases [24, 25] and soap bubbles [26, 27] have been reported to synthesize nanoscaled materials in various fields.

In template synthesis, structure of template is reversely duplicated by synthesizing materials. As choosing the new templates to produce structures, the stability and uniformity of templates are the crucial factors need to be considered. Furthermore, the interaction between template and precursors for synthesized

materials need to be studied [28]. And finally, the template should be easily removed by solvent or heat treatment.

The template fully satisfied with above requirements is PAA template. PAA membranes can be electrochemically prepared from aluminum metal by using two-step anodization [29-31]. Their pores are arranged in regular hexagonal lattice with pore density of 10^{11} - 10^{13} pores/cm² and pore diameter of around 4-420nm [32]. The diameter and density of pores can be easily adjusted by species and concentration of electrolyte, temperature, potential and time of oxidation. Another one is the lyotropic liquid crystalline (LLC) template[33] which can be obtained by mixing nonionic surfactant and solvent together with self-assembly process. With this versatile approach, nanowires, nanotubes, nanofilms and 3D structures with 2-10nm mesopores could be obtained.

1.2 Lyotropic liquid crystalline (LLC) template

1.2.1 The concept of liquid crystal (LC)

Liquid crystal is an anisotropic fluid. It represents the thermodynamically favorable phases that are located between the ordinary isotropic liquid and the anisotropic crystal solid[34]. The liquid crystal phase occurs between the liquid phase and the conventional crystal phase. It possesses both continuity and fluidity of liquid and anisotropy of crystal. It is considered the fourth state besides solid, liquid and gas. Commercial applications of liquid crystal include display systems, drug delivery vehicles, optical elements, sensors and photonic band gap structures [35].

There are two basic classifications of liquid crystals[36]: thermotropic and lyotropic liquid crystalline phases. Thermotropic liquid crystal (TLC) which normally used in displays, is formed from one compound and exhibits different phases as a function of temperature. For lyotropic liquid crystal (LLC), the phase transition is a function of both the temperature and the concentration. It shows long-range periodicity and rich polymorphism with a typical period ranging from 2-10nm. In our study, only LLC template has been discussed and utilized in order to synthesize of mesoporous materials.

1.2.2 Formation of lyotropic liquid crystalline (LLC) phases

Lyotropic liquid crystal (LLC) normally consists of amphiphilic surfactant and polar solvent these two components. The amphiphilic surfactant molecule is defined a compound which is composed of a hydrophilic “head” and a hydrophobic “tail” as shown in Figure 1-1. According to type of “head” functional group, it can be classified into anionic (with negative charge), cationic (with positive charge) and nonionic (without charge) surfactants.

Figure 1-1 Schematic of amphiphilic surfactant

In polar solvent, the amphiphilic surfactant molecules aggregate to form micelles when the concentration of the surfactant molecules increases above critical micelle concentration (CMC) [37].

Figure 1-2 Surfactant micelles: a) micelles and b) reverse micelles

As shown in Figure 1-2a, the hydrophobic groups are shielded by the hydrophilic “head” of the surfactant from the polar solvents. That is because the existing of hydrophobic groups could disrupt the continuity of the solution and induce the free energy increasing. Hence, the contact between the hydrophobic groups and the solvent should be limited to reduce free energy. At the same time, the hydrophilic groups of the surfactant prevent the molecules from being expelled by polar solvent. The free energy can be reduced when the surfactant molecules aggregate into micelles, where the interior core of the micelles comprises of the hydrophobic groups which have limited contact with the polar solvent. Similar explanation holds when surfactant molecules are introduced into non-polar solvent (shown in Figure 1-2b). The interior of the micelles is made up of the hydrophilic group and the outer region comprises of hydrophobic groups. It is so-called reverse micelles.

Between micelles and reverse micelles, there still exist other liquid crystalline phases with introducing various amount of amphiphilic molecule into polar solvent (typically water).

Figure 1-3 Structure of different lyotropic liquid crystalline phases. Reproduced from [38], by permission from John Wiley & Sons, Copyright 2012)

With the concentration of the surfactant molecules increasing, the micelles start to form anisotropic patterns. The first liquid crystal structure formed from individual micelles is the hexagonal crystal phase. The surfactant micelles aggregate to form parallel rods in a hexagonal arrangement with exposing the hydrophilic surface to the polar solvent. The hexagonal crystal (H_1) phase is shown in Figure 1-3a. H_1 texture usually exists when the concentration of surfactant molecule ranges from 40 wt% to 70 wt%. As the surfactant molecules concentration is further increased, liquid crystalline phase will be changed to cubic structure (V_1 , shown in Figure 1-3b). At even higher concentration of surfactant, lamellar structure is formed with paralleled molecules. Both the hydrophobic tail and hydrophilic head of the amphiphilic molecules face outwards (L_a , Figure 1-3c). With the concentration of surfactant continuing increased, the hydrophilic heads aggregate with each other and hydrophobic tails expose to outside to produce reverse hexagonal texture (H_{II} , shown in Figure 1-3d).

1.2.3 Influence factor of liquid crystalline formation

The texture of the micelles produced in solvent is very important as it determines the phase behavior of the LLC. The driving force for assembly of amphiphilic molecule is the attraction force between water interface and hydrophilic head of surfactant molecules or repelling force between water interface and hydrophobic tail of molecules. The general factor that governs the texture of the micelles is known as the critical packing parameter (CPP) shown in Eq. 1-1 [38, 39].

$$p = \frac{V_H}{l_c a_o} \quad (1-1)$$

Where p is the dimensionless packing parameter, V_H is the volume occupied by the hydrophobic group in the micelle, l_c is the length of the hydrophobic group and a_o is the cross-sectional area occupied by the hydrophilic group at micelle to solvent interface (effective head area). The relationship between texture of micelles and CPP is given in Table 1-1.

Many experimental factors such as concentration of surfactant, temperature, presence of additive and functional group of surfactant molecule could influence CPP, which cause the conversion of LLC phase.

As mentioned above, with surfactant concentration increasing, the LLC texture will convert from hexagonal to cubic, lamellar and reverse hexagonal texture, respectively. That is because the enhancement of surfactant concentration decreases the number of water molecules contacting with hydrophilic head, which further lead effective head area (a_o) of micelles to decrease. Based on CPP, if the

length of hydrophobic chain was fixed, the decrease of a_0 would increase CPP value and let phase transition occur.

Table 1-1 Packing Parameter related with micelle structure. Reproduced from [38], by permission from John Wiley & Sons, Copyright 2012

Packing Parameter	$<1/3$	$1/3-1/2$	1	>1
LLC Texture	Micelles	Hexagonal	Lamellar	Reverse Micelles
micelle molecule structure

Temperature is another important factor that could be manipulated conveniently to control the texture of the micelle and investigate the phase behavior of LLC. With temperature increasing, the hydrogen bonds between polar heads and water molecules will be partially broken, and this leads to the decrease of a_0 . As a result, CPP increases to help the phase transition from hexagonal to lamellar phase.

1.2.4 Mechanism of mesoporous materials synthesis by using LLC template

Electrochemical deposition is a preferred technique to utilize electrochemical redox reaction to deposit desired materials onto the electrode combined with LLC template as its electrolyte.

Figure 1-4 Schematic diagram of LLC phase (a) and a film deposited from LLC template (b). Reprinted from[40]. Copyright (2007) with permission from Elsevier.

This process is known as direct templating method. In LLC direct casting, the materials deposited onto the electrode grow in the interspaces among the individual micelle cylinders. The as-deposited materials obtained from such system have a well-defined porous structure. Figure 1-4 shows the formation of a mesoporous solid film using LLC template [40].

In hexagonal liquid crystalline phase, paralleled cylindrical micelles disperse into continuous aqueous region and come into being stable structure with long-range periodicity. This hexagonal phase can be used in preparing 3-dimensional porous nanomaterials. As shown in the Figure 1-5a [33, 41], hexagonal liquid crystals with paralleled cylindrical rods are self-assembled on the electrode surface and the electrolyte only exists in continuous water phase. During electrodeposition, the metal ions only can access the electrode surface where is not covered by the cylindrical rods. As the thickness built up, the mesoporous film forms. The materials synthesized by LLC phase possess high specific surface area, favorable conductivity and stable chemical properties. The size of pore can be controlled by the structure of surfactant molecules, and geometric distribution is decided by

texture of LC phases which show hexagonal state. The template is reverse duplicated quite well.

Figure 1-5 Schematic diagram of the templating process of the hexagonal film (a) From [33], Reprinted with permission from AAAS Copyright 2007. Reprinted with permission from [41]. Copyright (2003) American Chemical Society. and lamellar film (b) with TEM images. Reprinted by permission from Macmillan Publishers Ltd: [Nature][42], Copyright(2009).

Lamellar liquid crystalline phases are with independent hydrophobic and hydrophilic area. Under controlling and adjusting of lamellar template, the lamellar LLC scaled mesofilms have been obtained (shown in Figure 1-5b [42]). Comparing with hexagonal LLC template, lamellar template is softer and more flowable because of its bilayers structure. Hence, its ordered structure and stability

could be easily influenced by external factors. However, lamellar phase is better for mass transfer as compared with hexagonal and reverse hexagonal LLC phase because of its fluidity. According to the “soft” structure, the synthesized mesoporous films can achieve better performance.

1.2.5 History and present situation of LLC template

In past few decades, amphiphilic surfactants and block copolymers have been paid more and more attention and obtained great achievement because they could be utilized to synthesize ordered mesoporous structure with excellent performance.

In 1990, it is the first time that hexagonal mesoporous molecular sieve of FSM-16 has been synthesized using LLC template by Yanagisawa, T. et al. [43]. A layered polysilicate kanemite need to be synthesized first, and then kanemite was slightly changed by chemical methodology. Finally, the template reagent should be added to produce hexagonal porous structure. As mentioned above, preparation procedure is quite complicated that have not obtained enough concern.

In 1992, Beck, J. S. et al. in Mobil Research and Development Co. [44] synthesized MCM-41, one member of M41S family, which possesses hexagonal array with uniform mesopores (from 1.5nm to 10nm). The hydrothermal method has been utilized for MCM-41 synthesis that surfactant liquid crystal phases serve as organic templates. The formation of the hexagonal MCM-41 is shown in Figure 1-6 [44]. Two mechanisms are proposed. The results of this study are meaningful not only because the structure and performance of molecular sieves has been

achieved, but let people know LLC soft template is a new pathway to synthesize mesoporous materials as well.

Another meaningful discovery is proposed by Stucky, G. D. research group [45]. They synthesize SBA-15 mesoporous molecular sieves series include hexagonal and cubic structures using nonionic surfactant (amphiphilic block copolymer LLC template, $\text{EO}_m\text{PO}_n\text{EO}_m$). With adjusting the molecular weight and composition (m:n) of block copolymers, the nanoscaled structure of resulting materials can be tuned in the synthesis procedure. For example, the ratio between PO and EO (n:m) could influence the porous structure of resulting mesomaterials. With the discovery of SBA-15, block copolymer template methodology became the one of the most important approaches to synthesize the mesoporous structures.

Figure 1-6 Possible mechanism for MCM-41 formation: (1) LLC template theory and (2) silicate anion induced formation. Reprinted with permission from [44].

Copyright (1992) American Chemical Society.

Besides the development of SBA series applications, Attard, G. S. et al. [46] used nonionic surfactant poly(oxyethylene) as hexagonal, lamellar and cubic templates to construct mesoporous silicas by hydrothermal treatment respectively.

This kind of templates also shows the same importance comparing with block copolymers.

As mentioned above, only silicas and silicate materials have been synthesized. Developing mesoporous non-silicon-based materials became necessary in mesoporous field. Tracking back to 1993, Monnier, A. et al. have already considered that model of silicate synthesis could be generalized into the synthesis of other nonsiliceous materials as well [47].

In 1994, Huo, Q. et al. [48] reported synthesis of non-silicon-based mesophase materials using cationic and anionic surfactants firstly. Not mesoporous materials, but only mesophases were obtained because the templates could hardly be removed.

In 1995 and 1996, Antonelli, D. M. et al. [49] and Ciesla, U. et al. [50] synthesized non-silicon mesoporous materials individually. They started a new period to synthesize mesoporous materials by using LLC phases as templates.

In 1997, Attard, G. S. et al. [33] have proved long-range periodic hexagonal nanostructured Pt films can also be achieved by using LLC template with high surfactant concentrations (>30 wt%). The diameter of cylindrical holes is around 2.5nm and wall thickness is nearly to 2.5nm either. And also, they synthesized series mesoscaled nanofilms such as Pd, Ni/NiO, Co, Se, Te, Sn and so on [51-56]. Bartlett, P. N. et al. [41] fabricated Pd/Rh double layers that outer pores (H1-Rh film) and inner pores (H1-Pd) are connecting with each other, hence, the continuous pores pass through both metal layers in the structure. Luo, H. M. et al. [57] used hexagonal LLC phases formed from similar nonionic surfactant to

electrodeposit n-type ZnO and p-type Cu₂O films, which could be applied in solar cells, photocatalysts and chemical sensors.

In 1998, Yang, P. D. et al. [58] have used amphiphilic block copolymers as template in non-aqueous solutions to form the network of metal-oxide species. The mechanism combines self-assembly of block copolymer with complexation of inorganic species. A series of metal oxides and doped oxides have been fabricated. Ethanol was utilized to replace the water as solvent to reduce the hydrolysis and condensation of the inorganic species. That is because they have strong tendency to precipitate and aggregate into bulk oxide phases in aqueous media.

In 1999, Ryoo, R. et al. [59] started up a new technical for ordered carbon molecular sieves synthesis using mesoporous silica molecular sieves as the template. The structure was not simply a reverse replica of the used silica template. The mechanism of synthesis involved unique transformation, which could turn into a new ordered array that was triggered by the removal of silica frameworks. Using silica sieves to synthesize mesoporous carbon is not only a new application of LLC template, but giving an efficient way to prepare ordered porous carbon as well.

Huang, L. et al. fabricated Cu₂O [60] and Ag [61] nanowires by lyotropic reverse hexagonal liquid crystalline phase with one-dimensional aqueous channels as space-confined microreactors.

Braun, P. V. et al. [62, 63] produced ZnS, CdS and CdSe superlattice hexagonal structure by flowing hydrated H₂S over metal salt-doped liquid crystals. And they have utilized cubic and lamellar phases to synthesize hollow spheres and lamellar superlattice respectively.

Jiang, X. et al. [64] proposed a novel simultaneous in situ formation (SISF) technique to synthesize ordered ZnS nanowire by γ -irradiation in a reverse hexagonal liquid crystalline template. It was found that the ZnS nanowires disperse well before and after removal of the liquid crystal template and the bundle of ZnS nanowires duplicated the structure of the inverted hexagonal liquid crystal phases. The previous surfactant templating processes are almost exclusively a single ionic or nonionic surfactant. Furthermore, Kijima, T. et al. [65] revealed that lyotropic media of nonionic-ionic mixed surfactant was effective for the preparation of nanowires.

Despite the mesoporous materials have been fabricated for various applications, but they all confirmed the structural controllability of LLC templates. The development of template synthesis for preparing mesoporous materials approximately experienced following steps: i) from traditional silicate materials to Al, Fe, Mn, Zn, Cu, V, Ti, Mo doped silicate materials; ii) non-silicate materials such as TiO_2 , ZrO_2 , SnO_2 , Al_2O_3 , Nb_2O_5 and GeO_2 etc. ; iii) surfactants mixture replaced single surfactant as templates [66]. The utilization of mixed surfactants could change the texture and size of micelles, and on the other hand, the amount of nonionic surfactant could be reduced by cationic and anionic surfactants adding.

1.3 Porous anodic alumina (PAA) template

1.3.1 Background of PAA template research

The study of aluminum oxidation started from 1930s [67]. At the beginning, the anodic oxidation of aluminum was only utilized as protective and decorative

material because of its chemical stability. In 1953, Keller F. et al. [68] described the porous structure of alumina, it has hexagonally close-packed duplex structure with cylindrical porous and barrier layers. In 1995, Masuda et al. [32] designed the two-step anodization technology to fabricate aluminum oxide with honeycomb structure. The highly ordered porous structure with a hexagonal arrangement has been fabricated by this technique, which is a milestone in template development. Since then, the porous anodic alumina (PAA) became the most important candidate with highly ordered structure to be used as template in synthesis of nanoscaled materials.

Figure 1-7 Ideal model of porous anodic alumina (PAA). Reproduced with permission from [69]. Copyright (2007) Taylor & Francis.

The role of the PAA within the nanostructure fabrication domain can be divided basically in two types: i) well-aligned porous structure as template to fabricate nanodevice[70, 71]; and ii) acting as a nanodevice itself [72]. Nowadays, PAA has already been a dominating template in nanomaterials synthesis. That is because the structure of PAA could be duplicated accurately and easily.

Furthermore, a large number of materials [71, 73, 74] such as metal, metal oxide and carbon nanotubes etc. could be fabricated by utilizing this versatile nanoreactor which has uniform diameter and ordered nanostructures. As shown in Figure 1-7 [69], the framework of porous alumina with honeycomb structure and fine channels is represented as a schematic diagram. The hexagonal cells are close-packed with each other with cylindrical pore located at the center.

1.3.2 Mechanism of PAA template electrosynthesis

In principle, the formation of porous alumina should include following steps: i) multiphase transfer and kinetic control; ii) chemical reaction of PAA; iii) nucleation process. PAA is obtained by anodic oxidization of Al. The film formation is a dynamic process, the dissolution and formation of aluminum oxides occur at the same time. The membrane thickness always increases with extension of electro-oxidation time. However, how pores initiate, where electrolyte anions play and why aluminum shows this particular behavior, are not fully understood.

Heber K. V. [75] in his colloidal precipitation model shows porous alumina is generated from decomposition of $Al(OH)_3$ colloid which is anodized from Al. The chemical reactions are as followings:

This model is based on the postulate of ‘pockets’ locating on the colloidal interfacial layer. In the first step, acid erodes Al or its natural skin of Al_2O_3 . Secondly, under appropriate conditions, a hydroxide forms. In aqueous solution, the hydroxide generally forms a colloidal layer with densely arranged pockets. These pockets are the nuclei for pore formation. On further anodization, the pockets become bigger as the whole layer grows. Thirdly, when the pockets open, the electrolyte will contact with pore inner to induce coagulation of the colloid. And finally, newly formed colloid coagulates very fast from anodization process. Among all dimensions of pore, the pore only grows in perpendicular direction. It means the so-called ‘open pockets’ continue moving to the metal to produce the cylindrical channels. During this process of pore growth, a balance between formation and dissolution is set up. The thickness of the bottom layer (barrier layer) won’t change. The barrier layer continues moving inward and the moving rate is decided by Faraday’s law.

Figure 1-8 (a) Potentiostatic I-t curve and (b) schematic diagram of the kinetics growth of PAA. Reprinted with permission from [30]. Copyright (1992) IOP publishing.

Parkhutik, V. P. et al. [30] proposed steady-state pore growth mechanism according to current changes during experiments. As shown in Figure 1-8, in stage I, a barrier layer (aluminum oxide) appears with power on. And in stage II, precursors of true pores are formed at the surface region of the barrier layer. In stage III, further anodization leads to electrons movement towards the barrier layer with real pores formation. Finally, at stage IV, a balance (steady-state) has been set up to form a closely packed hexagonal alignment, with cylindrical pores located at the center and barrier layer situated between pores and aluminum film.

In our experiment, as shown in Figure 1-9, the first three stages are as same as Parkhutik, V. P. et al. mentioned in this chapter. In the IV stage, the curves show the different tendency. The current of PAA obtained from pure Al plate reached a platform, but the current obtained from anodization of Al/Ti/Si substrate faced a continuous decrease. It is considered that the thickness of Al layer in Al/Ti/Si template is only 2000nm. The reaction won't last too long. Therefore, the current decrease is quite obvious as compared with commercial Al plate. The conductivity decreases step by step until current reaches the lowest point, the growth of Al_2O_3 stops, all Al convert into Al_2O_3 membrane with barrier between pores and Ti layer.

Figure 1-9 Potentiostatic I-t curve of anodization of Al/Ti/Si substrate at the beginning 30 mins

During porous structure formation, the mechanism of ions and molecules transfer also need to be explored. According to place-exchanged mechanism proposed by Parkhutik, V. P. et al., aluminum ions migrate outwards during the oxidation procedure to which leads alumina growth to external boundary. This boundary could be dissolved by electrolyte species as a result of interaction with the alumina surface. Finally, the alumina/aluminum interface shifts inwards to produce pore structure due to alumina formation/dissolution equilibrium.

Theoretically, chemical reactions involved to porous alumina growth consist of three steps:

As indicated in Eq. 1-5, Al^{3+} ions are produced with losing three electrons at the metal/oxide interface and then transfer to the external layer with oxide exist. Eq.

1-6 shows that water molecule split into hydrogen ion and O^{2-} (oxide) with assistance of electric field, and then obtained O^{2-} (oxide) combines with Al^{3+} from the first step to form Al_2O_3 .(as shown in Eq. 1-7).

In exploring PAA formation mechanism, Müller, F. et al. [76] suggested a reasonable self-organized arrangement of neighboring pores mechanism. As shown in Figure 1-10 [28], volume expansion during alumina formation was observed. In order to obtain ordered pores in PAA membrane, a proper expansion of aluminum is necessary. No expansion or strong volume expansion will lead the pores to be less ordered. The balance between mechanical stress force arising from expansion of the aluminum and repulsive forces among neighboring pores lead to formation of self-organized hexagonal pores array.

Figure 1-10 Expansion of aluminum during anodic oxidation; On the left the level of metal surface is depicted. Reprinted from [28], Copyright(2008), with permission from Elsevier.

Besides the mechanisms mentioned above, there are still many other models proposed to explain PAA formation mechanism. It is hoped the real mechanism could be found in not far future.

1.3.3 Synthesis of PAA template on hard substrate

PAA templates grow continuously in acid solutions with aluminum anodized under an assistance of direct current supply. Electrolytes for aluminum anodization normally are phosphoric acid (H_3PO_4), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and sulphuric acid (H_2SO_4), these three types. Diverse pore size and interpore distance can be produced via different electrolytes. Table 1-2 shows phosphoric acid induces the largest pore and sulphuric acid supplies the smallest one. Pore diameter and interpore distance of PAA membrane are decided by the types of electrolyte and the applied voltage both.

Table 1-2 Summary of pore diameter and inter-pore distance corresponding to different electrolytes and various anodized potentials

Electrolyte	Pore diameter(nm)	Inter-pore distance(nm)	Voltage(V)
Sulphuric acid(H_2SO_4)	20-30	60-70	25
Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$)	50-60	100-140	40
Phosphoric acid (H_3PO_4)	150-200	250-500	195

PAA has been frequently used for the template synthesis of nanowires and nanotubes, since this porous membrane consists of uniformly parallel channels. With filling the channels and removing PAA membrane, aligned nanowires with uniform size, could be produced. However, PAA has some severe disadvantages that limit the application [77]: PAA is a fragile ceramic membrane. Great care is needed in preparation procedure. Otherwise, PAA films will have defects which are

not satisfied with the requirement of uniform nanowires and nanotubes. Furthermore, there is an alumina barrier layer between the porous membrane and the aluminum substrate (as shown in Figure 1-11a).

The pore and the substrate could not connect with each other because the existence of barrier. In order to open the pores, the aluminum substrate and exposed barrier layer need to be etched away, and then blocked ends of cylindrical arrays could be opened. However, unsupported PAA membrane will be left after removed substrate, the membrane is fragile and unfit for application. It is necessary to improve and develop practicability of PAA template. Hence, the rigid substrates have been introduced as a support media for PAA membrane. By using this technology, nanowires array on rigid substrate could be obtained and directly utilized into electrochemical devices such as battery, capacitors, sensors and catalysts. PAA template used in our study is the one with rigid substrate which has three layers: silicon wafer as hard supporting substrate, titanium coating as conductive layer and PAA layer on top as nanowires directing mold (PAA/Ti/Si) as displayed in Figure 1-11b.

Figure 1-11 Schematic diagrams of a conventional PAA film (a) and PAA/metal/silicon template with open channels without barrier (b). Reproduced from [77], Copyright (2003), with permission from John Wiley & Sons.

In our experiment, Al/Ti/Si substrate was prepared firstly. The pure Al film as the second layer (3000nm) was magnetron sputtered on a (111) silicon substrate with Ti (around 300 nm) coated as first layer. Al/Ti/Si substrate was anodized in 0.3M oxalic acid aqueous solution for 2-8 hrs by using 40 V direct current supply(as shown in Figure 1-12), and then 5 wt% H_3PO_4 was used to remove the barrier at 45° C for 5mins.

I. One-step anodization

Normally, synthesis of PAA template is two-step method. That because aluminum foil surface is rough, the first-step anodization is necessary to smooth the aluminum surface. However, in our case of the Al/Ti/Si substrate, the surface is very glossy so that one-step anodization can achieve the ordered pore arrays directly. The growth of pore would reach to a balance between formation and dissolution of alumina according to steady-state pore growth mechanism.

Figure 1-12 Installation for PAA template synthesis

At the end of anodization, not aluminum, but only barrier layer exists, since all the aluminum has been anodized into alumina. After use 5 wt% H_3PO_4 to remove the barrier, Ti layer will be exposed as the conducting layer. Then the PAA/ Ti/Si substrate could be directly used as the electrode. The average pore diameter is about 50-60 nm and the interspaces is about 60-80 nm. However, their arrangement has lower order comparing with PAA from bulk Al, due to smaller grains, thinner aluminum films and shorter anodization time.

II. Effect of anodizing time, temperature and pore expansion time (PET)

There are many factors such as anodization time, temperature and pore expansion time et al. could influence the morphology and arrangement of resulting films. Anodization time is an important factor in PAA template synthesis. The PAA structures shown in Fig. 1-13a-c are prepared in 0.3M $\text{H}_2\text{C}_2\text{O}_4$ aqueous solution under 40V direct current for 2 hrs (c), 3 hrs (d) and 4 hrs (e) at room temperature. It shows, with the time increasing, the density and diameter of pores is enhanced. And yet, as oxidation time reaches to 4 hrs, the PAA is partially broken.

For the PAA template prepared at 0-4° C, the 4hrs template (shown in Fig. 1-13g) shows smooth pores, and 8 hrs one also displays the fine texture (shown in Fig. 1-13h) with larger pores as compared with 4hrs one. The defects of 8 hrs one synthesized at 0-4° C are even less than 4 hrs room temperature one. It investigates the anodization process is stable at low temperature.

Figure 1-13 SEM images of PAA template obtained in different conditions

After anodization, the template needs to immerse into 5% H_3PO_4 to broaden the pores and remove the barrier between template and conductive layer. The pore expansion time (PET) is normally around 5 min. When the template immersed into H_3PO_4 for 30mins, the porous structure disappears (shown in Fig. 1-13f). It means the PAA template is dissolved by H_3PO_4 .

1.4 LLC and PAA combined dual-template synthesis

In order to further improve the performance of synthesized materials, a novel mesoporous nanowire structure has been paid much attention recently. It has been confirmed the mesoporous nanowires have remarkable performance as compared with bulk ones.

Yamauchi, Y. et al. [78] have synthesized mesoporous Pt nanofibers successfully in 2008 by filling LLC phase into PAA templates with assistance of self-assembly and chemical reduction. The pores were well-ordered and showed stacked donut-like mesostructure with enhanced surface area.

Mesoporous Pt nanowires have been produced by Zhong, Y. et al. [79] with confining the LLC phase in PAA cylindrical pores via electrodeposition in the same year.

The electrode shows the enhanced CO tolerance, excellent activity for catalysis, and relatively high stability.

Manganese dioxide with mesoporous nanowire structure has been synthesized by Xu, C. et al. [80] The mesoporous manganese wires displayed the excellent electrochemical behavior with capacitance of 493 F g^{-1} at current density of 4 A g^{-1} . And only 2.7% capacitance lost after charge-discharge of 800 cycles.

Zheng, M. et al. [81, 82] have obtained mesoporous carbon nanofibers utilizing evaporation-induced self-assembly method via dual-template. The specific surface area of synthesized carbon nanofibers is as high as $1424 \text{ m}^2 \text{ g}^{-1}$, and pore volume has achieved $327 \text{ cm}^3 \text{ g}^{-1}$. And also, it shows the good capacitor behavior.

In our study, we have successfully synthesized mesoporous $\text{Co}(\text{OH})_2$ nanowires [83] and ordered mesoporous carbon nanowires with Pt loading. Both have shown excellent electrochemical performance.

As mentioned above, PAA has been used as the template of nanowires synthesis frequently, since this porous template consists of uniformly sized parallel channels. It could be utilized as the electrode directly after nanowire synthesis. Surfactant is a kind of nonionic surfactant contains hydrophilic headgroups and hydrophobic chains. As mixing the Brij56 with the aqueous solution, the hydrophilic “head” are dissolved in the water where the hydrophobic “tails” tend to aggregate with each other to form liquid crystalline phase. The metal salts exist in the aqueous solution only. After electrodeposition and remove the surfactant, the porous structure will be produced in purpose. Most interesting aspect for this study is to utilize both porous anodic alumina (PAA) as hard template and surfactant as soft template to synthesize the mesoporous nanowire structure. As Brij56 combine with PAA templates, the nanowires with porous structure aligned on substrate will be the ultimate architecture. The schematic diagram of porous nanowire synthesized procedure is shown in Figure 1-14.

Figure 1-14 Schematic diagram of mesoporous nanowires synthesis

1.5 Advantages of electrochemical deposition in template synthesis

In template synthesis, template is only the mold to restrict and define the structure and size of material, the other techniques such as sol-gel method, chemical deposition, chemical or physical vapor deposition, injection, catalysis induced growth, hydrothermal and electrochemical method etc. are still required as an assistant to synthesize nanoscaled structures. Among these techniques, electrochemical method is one of the most attractive methods because of its environmental friendliness, low cost, relatively high growth rate and flexibility of tuning the size and dimensions of materials [84].

Electrochemical method includes electrodeposition, electrohydrolysis and electropolymerization. Electrodeposition is a process to coat conductive films (such as metal, alloy and metal oxides etc.) on the electrode surface with electrons transfer. The deposition need to occur in electrolyte system which contains the salt precursor. The salt could convert into metal or metal oxide depends on negative or positive charges loading. During the deposition process, an object should be immersed into the electrolyte to collect deposits. If the object carried negative charge, the metallic ions would be attracted by the object easily because of their positive charge. And the object could provide electrons to reduce the positively charged ions to metallic form. And now it also can be used in synthesizing the oxides by anodic oxidation, so various materials including metals, metal oxides, non-metal oxides and metal hydroxides have been achieved in this versatile method. The amount of resulting materials can be adjusted by accurately controlling the electrodeposition time and charges. Hence, the length, and length/radius ratio can

also be manipulated[85]. Comparing with traditionally chemical method, electrochemical method is a promising way to synthesize and assemble nanoparticles with restricted and controllable size or morphology.

1.6 Equipments and Characterization

The Lyotropic liquid crystalline (LLC) phase with particular optical texture was investigated by polarized optical microscopy (POM, XJP400T, KOZO) equipped with a KER-3100-08S heating stage and temperature control unit. Figure 1-15 shows typical optical textures of lyotropic liquid crystalline (LLC) phases [hexagonal (a), lamellar (b) and reverse hexagonal (c) phases]. In cubic systems, there is no birefringence as light interacts with the material in a similar manner whatever the orientation. Micellar solutions are isotropic and therefore, appear black under the polarizing microscope.

Figure 1-15 POM images of LLC phase: hexagonal phase (a); Lamellar phase (b); Reverse hexagonal phase

Low-angle X-ray diffraction (XRD) recorded on a Bruker D8 Advance diffractometer with Cu-K α as the radiation source ($\lambda=0.154\text{nm}$) over the 2θ range of 0.8° - 5° was used to provide primary evidence for the formation of the liquid crystalline phases in template mixture and mesoporous structures in synthesized

nanofilms or nanowires. The diffraction peak presenting in low-angle region means the existence of mesoporous structures.

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu-K α as the radiation source ($\lambda=0.154\text{nm}$) to determine the crystal structure of synthesized materials.

Field emission scanning electron microscopy (FESEM) was carried out with a JEOL-JSM-6700F microscope operated at 5 kV to determine the surface morphology of nanofilms and nanowires on the substrate.

Transmission electron microscopy (TEM) was carried out with JEOL-2010 microscopes operated at 300 kV for the detailed nanostructure of deposited mesoporous films and nanowires feature.

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS Ultra HAS spectrometer equipped with a monochromatized Al K α X-ray source to study the chemical state of electrodeposited films.

Raman spectra were obtained on a Renishaw Raman spectrometer under a 633 nm excitation laser to determine the existence and defect of synthesized materials.

Optical properties of semitransparent films were measured for calculation of band gap under normal absorption mode by a Varian-5000 ultraviolet-visible (UV-Vis) spectrophotometer.

The content of elements was measured by inductively coupled plasma (ICP) optical emission spectroscopy on a Perkin Elmer ICP Optima 2000DV.

The electrochemical deposition and measurements such as cyclic voltammetry (CV), chronopotentiometry and impedance were performed on potentiostat

(CHI660d, CH instrument) in three-electrode system(ITO glass or Ti/Si substrate as working electrode, Ag/AgCl electrode or saturated calomel electrode (SCE) as reference electrode and platinum plate as counter electrode).

1.7 Research scope and objective

In the past few decades, various one-dimensional (1D) and two-dimensional (2D) nanostructures with designed morphologies and specific architectures have been fabricated for different research field. Among a variety of physical techniques and chemical methods, the template method is the well-established strategies to achieve plenty of metal and metal oxide nanowires, nanotubes, or films. Lyotropic liquid crystalline (LLC) template was newly developed for attractive characteristics, which are self-assembly, rich polymorphism, and long range periodic nanostructure, and convenient synthesis. As pore directing reagent, LLC template was chosen to synthesize mesoporous and 2D mesostructure materials which show great improved performance in research fields. However, the studies normally focus on the single-layered mesoporous films. The mesofilms with dual-layer were seldom reported. In our study, we focus on design and synthesis of mesoporous polymer supported metal oxides dual layer films using LLC template. This kind of dual-layer film has the potential application in photocatalysis, sensors and semiconductors etc.

As known, porous anodic alumina (PAA) films as hard templates containing cylindrical pores with pore diameter ranging between 10 and 300nm can be used in templating nanowires or nanotubes over a decade year. Recently, by confined

lyotropic liquid crystalline (LLC) phases in cylindrical pores of membranes, mesoporous silica nanowires and nanotubes were fabricated. But the limited reports on non-silica ones can be reached. According to the higher specific surface area and aligned porous structure of mesoporous nanowires, particular attractions are concentrated in supercapacitors, sensors, semiconductors and catalyst applications. Furthermore, with the surface area increasing, the kinetics and mass transfer will have a corresponding enhancement at the interfaces of nanowires, thus the efficiency of chemical and electrochemical reactions could be improved. However, there remains challenge to develop an efficient and affordable method to produce porous nanowires and nanotubes with controlled morphologies. Thus, our research focuses on this novel dual templates (confined LLC phases in PAA membranes) technique to synthesize non-silica porous 1D nanowires and nanotubes. And then the as-synthesized porous nanowires or nanotubes could be employed in the field of supercapacitors and catalysts as a part of electrochemical devices.

In this thesis, 2D mesoporous porous PANI/Cu₂O composite films and Se_{0.5}Te_{0.5}/PANI dual-layer films will be introduced. Synthesis conditions and optical properties of dual layers films will be discussed in details. Furthermore, Dual-template synthesis of 1D mesoporous Co(OH)₂ nanowires and Pt loading on mesoporous carbon nanowires (Pt/MCNWs) will be studied. Electrochemical behaviors and effect of experiment conditions will be analyzed.

Chapter 2 Electrodeposition of Mesoporous

Bilayers of Polyaniline Supported Cu₂O

Semiconductor Films from Lyotropic Liquid

Crystalline Phase

Reprinted from Chemical Engineering Science, Vol 80, T. Xue, L. S. Loo, X.

Wang, S. K. Kwak, J.-M. Lee*, Electrodeposition of mesoporous bilayers of polyaniline supported Cu₂O semiconductor films from Lyotropic Liquid Crystalline phase, 452-459, Copyright (2012), with permission from Elsevier.

This chapter focuses on mesoporous dual layers of polyaniline (PANI) supported Cu₂O films synthesis via LLC template and their optical properties.

Mesoporous materials, whose characteristic pore diameters are ranged from 2 to 50 nm, are of great interest for versatile and applied fields such as supercapacitors, catalysis, magnetic storage, chemical sensors, fuel cells, and semiconductors[56]. Synthesis and characterization of those materials have been soundly developed over decades. In search of overcoming those shortcomings of other methods, a synthesis method of Lyotropic Liquid Crystalline (LLC) template was newly developed by Attard and co-workers[13, 33]. This method fully exploits the attractive characteristics of the LLC template, which are self-assembly, rich

polymorphism, and long range periodic nanostructure, and importantly conveniently synthesized. The LLC template with highly concentrated surfactant had been chosen as the pore directing reagent. In this approach, mesoporous and mesostructure materials[55-57, 86, 87] have been electrodeposited by using the similar liquid crystalline as structure-casting agents and some of them show tremendous increase in performance in specific fields[56, 88, 89]. Cuprous oxide (Cu_2O), a typical p-type inorganic semiconductor[90], is nontoxic, optically transparent, and photochemically stable[91]. Its usage already have been grown in the conversion of solar energy into electrical or chemical energy[92], photocatalysis[93] and chemical sensors. The beneficial properties have stimulated researchers to explore the applications of Cu_2O , subsequently figure out various morphologies of Cu_2O by different methodologies. Kumar P. et al.[94] reported the nanocrystalline Cu_2O was electrodeposited by using mesoporous silicon as a template. The secondary structures of Cu_2O nanoparticles were prepared in an aqueous solution by utilizing self-assembled aggregation process by Lee et al.[95] Wei et al.[96] reported the synthesis of the Cu_2O nanorod via a simply solvothermal treatment. Yanagimoto et al.[97] prepared small Cu_2O particles by the vacuum evaporation. Sonochemical method was used to obtain nanocrystalline Cu_2O by Kumar R. V. and co-workers[98]. Among these methods, electrochemical deposition[99] is a promising method due to low cost and simplicity in synthesis technique.

As a supporting material, conducting polymers have attracted very much interest and attention, especially on their synthesis and application. This is due to

their outstanding chemical and electronic properties as well as their porosity, hydrophilicity and ability to maintain dispersion of active materials[100]. The possible applications of conducting polymer supported composites are used in memory devices[101, 102], catalysts[103, 104], energy storage materials[105, 106] and electrochemical sensors[107-109]. In particular, Polyaniline (PANI) has been widely used as supporting material since it has a good conductivity that can be modulated both by the charging level and degree of protonation. It shows well defined electrochemical (redox) response, thus finds great potential applications in rechargeable batteries, corrosion protection[31], light emitting diodes, molecular sensors, electrochromic devices and microwave screening[110]. PANI/MnO₂ hybrid film was synthesized with fibrous morphology by Sun L. J. et al.[105], the specific capacitance can reach to 532 F g⁻¹, which is 26% higher than the bulk one and 76% maintained after 1200 charge/discharge cycles. Prasad K. R.[106] reported PANI/MnO₂ composite electrode with 715 F g⁻¹ specific capacitance was potentiodynamically deposited on the surface of stainless steel foil and its energy density was as high as 200 Wh kg⁻¹. Chen Z. et al.[111] has shown that Pt displayed a better catalytic reactivity and lower degree of poisoning in methanol oxidation by introducing PANI as a supporting media.

As seen from the studies above, the large specific area and hexagonal mesoporous architecture of oxide semiconductor films are quite important for applications of the composites in photocatalysis, sensors and semiconductors, and those attracted points are all featured in a potential composite film, PANI/Cu₂O. The potential capabilities of the PANI/Cu₂O composite film have been implicitly

shown, yet it has been little effort on the synthesis and property characterization of the composite film. Hence, in this study, the PANI/Cu₂O composite film is first designed and synthesized by electrochemical method in the LLC template.

2.1 Chemicals for synthesis

The nonionic surfactant Brij 56 (Polyoxyethylene (10) cetyl ether, C₁₆EO₁₀, Sigma), copper sulfate (Sinopharm Chemical Reagent Co.), lactic acid (Sinopharm Chemical Reagent Co.), sodium hydroxide ($\geq 98\%$, Sigma-Aldrich), aniline (Merck), sulfuric acid (95%, Merck) and ethanol (99.8 %, Merck) were used without further purification.

2.2 Preparation of Lyotropic Liquid Crystalline (LLC) template

2.2.1 Preparation of aniline Brij56 LLC templates

LLC templating mixtures were prepared by mixing Brij56 surfactant with aniline aqueous solution containing 0.3M aniline (C₆H₅NH₂) and 1M sulfuric acid (H₂SO₄). The proportion of the surfactant was about 30 to 70 wt%. To achieve the homogeneous liquid crystal, the liquid crystalline mixtures were sealed in capped vials separately and allowed to stand in thermostatic water bath at a temperature of 70 °C for at least 30min, followed by vigorous stirring with a vortex mixture. These two steps were repeated for at least 3 rounds, after the LLC mixtures were allowed to equilibrate at the room temperature for one day before phase characterization and electrodeposition.

2.2.2 Preparation of Brij56 LLC template for mesoporous Cu₂O

The electrolyte used in the electrodeposition of mesoporous Cu₂O was the binary system of 50 wt% surfactant Brij56 and 50 wt% aqueous solution containing 0.025M copper sulfate and 0.3M lactic acid, with 2M sodium hydroxide added to the solution till pH of metal salt solution became 9. The same heating/mixing process as mentioned above was used to achieve homogeneity.

2.3 Electrodeposition of dual-layer mesoporous Cu₂O/PANI films

The electrochemical deposition of aniline was conducted on a CHI660d electrochemical workstation (Chenhua, Shanghai), by using a conventional three electrode system composed of a 1cm² tin-doped indium oxide (ITO) glass working electrode, a 1cm² platinum counter electrode, and a standard saturated calomel reference electrode (SCE) with the aniline Brij56 LLC template as electrolyte. The electrodeposition of polyaniline onto ITO glass was carried out under potentiostatic and thermostatic control while maintaining a constant potential of 0.75V and temperature of 50°C. After the deposition, the hexagonal polyaniline films were needed to soak in ethanol for at least a day. During this period, the ethanol was replaced every 2 h until all the surfactants were removed. Subsequently, the electrodes were entirely dried in ambient atmosphere for 24 h. The electrodeposition of mesoporous Cu₂O films were carried out under the same three electrode system in Cu²⁺ Brij56 LLC electrolyte, and ITO electrodes were changed to PANI modified ITO electrodes synthesized firstly to achieve Cu₂O/PANI dual layers. The Cu₂O electrodeposition was also under potentiostatic and thermostatic

control at a constant potential of -0.4V and temperature of 50 °C. The working electrodes were cleaned by ethanol.

2.4 LLC Phase Characterization

Since the final nanostructure of mesoporous films is decided by structure of used LLC phase, it is quite important to determine the phase structure of the LLC template before the electrodeposition. Composition and temperature, as regulators for a required resulting nanostructure, were varied. The POM was used to determine the characteristic appearance and textures of phases to indicate the relative complexity of the LLC phases. Figure 2-1a and 1b show the representative POM images of aniline Brij 56 LLC phase. Figure 2-1a is an image with fan-like textures that are the clear indication of hexagonal structure and optical textures of Figure 2-1b suggest that their crystal phase belongs to the lamellar mesostructure according to the mosaic shape. Both experimental liquid crystalline phases match the patterns from a literature[112]. In our experiment, hexagonal templates containing with 50 wt% Brij56 and 50 wt% aniline aqueous solution were selected to achieve nanoscaled polyaniline films at the temperature of 50°C.

Figure 2-1 POM images of LLC mesophase: 1a.LLC mixture of 50wt% Brij56+50wt% 0.3M aniline and 1M H₂SO₄ aqueous solution at 50°C (Hexagonal); 1b. LLC mixture of 60wt% Brij56+40wt% 0.3M aniline and 1M H₂SO₄ aqueous solution at 60 °C (Lamellar); 1c.LLC mixture of 50wt% Brij56+50wt% 0.6MCuSO₄ and 3M lactic acid with sodium hydroxide added to increase pH to 9 at 50°C; 1d.LLC mixture of 50wt% Brij56+50wt% 0.6M CuSO₄ at 50°C (Hexagonal); 1e. LLC mixture of 50wt% Brij56+50wt% 0.025MCuSO₄ and 0.3M lactic acid with sodium hydroxide added to increase pH to 9 at 40 °C (Hexagonal).

For achieving hexagonal mesophase of Cu²⁺ Brij56 LLC template, a proper metal salt solution was prepared. Initially, the prepared metal salt electrolyte was according to that prepared by Luo et al.[57] : 0.6M Copper Sulfate + 3M Lactic Acid with Sodium Hydroxide added to increase pH to 9. Then the LLC phase was prepared by using 50 wt% aqueous solution as above and 50 wt% of Brij56. However, LLC structures were not clearly observed, instead, foam-like bubbles were seen (see Figure 2-1c) and phase separation was occurred even after several hours. A probable cause is the presence of lactic acid, of which structure is similar

to surfactant. Furthermore the existence of the bubbles was supposed to be another reason for the interference of the formation of LLC structures. To confirm these speculations, a POM observation on the effect of lactic acid was conducted on a sample mixture, which is free of lactic acid and sodium hydroxide and we found the signs of hexagonal LLC structures as shown in Figure 2-1d.

As lactic acid acts as a chelating agent to suppress the formation of the precipitate cupric hydroxide when sodium hydroxide is added to copper sulfate solution, it must be included in the metal salt solution. Sodium hydroxide is also required in the metal salt solution to bring the pH of the mixture to 9, as copper metal would be deposited instead of cuprous oxide if pH is lower than 7 (to be discussed in Part 2.6). To this end, the final concentration of the metal salt solution was determined to consist of 0.025M copper sulfate and 0.3M lactic acid, with sodium hydroxide added to the solution till pH of the metal salt solution became 9. We found the hexagonal mesophase, which consists of 50 wt% Brij56 and 50 wt% Cu^{2+} aqueous solutions prepared at 40°C, and it is shown in Figure 2-1e. It displays a fan-like structure, which is consistent with the optical texture of aniline one. Hence, the hexagonal phase was used as template to synthesize hexagonal mesoporous Cu_2O film.

2.5 Effect of Deposition Potential for Hexagonal PANI films

It has been demonstrated that PANI can be synthesized by the electrochemical polymerization of aniline. The electropolymerisation of aniline to PANI film on the

electrode follows a two electron-transfer process as shown in following reaction[113]:

It can exist in different oxidation states, each having different polymer structure and properties. Among the different oxidative states of PANI, the conducting emeraldine salt (ES) was the desirable state for the synthesis of polymer support[114]. In its emeraldine oxidative state, PANI is green in color and becomes electrically conducting when doped with an acid.

Figure 2-2 Cyclic voltammogram of 0.3M aniline and 1M sulfuric acid solution at scan rate of 100mV s⁻¹

Cyclic voltammogram was carried out to determine a suitable electrodeposition potential for aniline. From Figure 2-2, we observed an increase in the value of current at approximately 0.7V. This increase corresponds to the growth of polyaniline on the ITO glass electrode. Hence in the forward cycle, we find that aniline is electrochemically oxidized to form polyaniline and at the reverse cycle,

aniline undergoes the reduction reaction. During the entire cyclic voltammetric analysis, the change of the color has been observed on the ITO glass electrode as Huang et al. has[115] : blue to green, and then yellow as shown in Figure 2-3. This color change corresponds to the readings from the voltamogram (i.e. the electro-oxidation of polyaniline followed by the electro-reduction of polyaniline). Based on literature reports[116] and the cyclic voltammetric analysis, we chose 0.75V as a suitable potential to cause the electropolymerization of aniline, which is to obtain the green colored conductive PANI.

Figure 2-3 Different polyaniline forms: 3a. Emeraldine base form (Blue) 3b. Emeraldine salt form (Green) 3c. Leuco-emeraldine salt form (Yellow)

2.6 Effect of Deposition Potential and pH for Hexagonal Cu₂O Films

The following chemical equations are the likely reactions occurred for the cathodic reduction of the copper sulfate solution:

Two conditions must be considered for cuprous oxide to be electrodeposited on the substrate: i) Electrodeposition voltage to be between -0.3 to -0.5V and ii) pH to be around 9.

Figure 2-4 Wide-angle XRD pattern of cuprous oxide corresponding to electrodeposition voltage of -0.4V (a) and -0.6V (b) on ITO glass.

For the first condition, Wang et al. and Zhou et al. [117, 118] have separately conducted the deposition of Cu₂O within this range of voltage and if the applied voltage is out of this scale, copper metal will be deposited instead[119]. Figure 2-4 shows the wide-angle XRD of the films, which were deposited from the electrolyte by using different electrochemical deposition potentials. The intensity data of (a) in Figure 2-4 shows the electrodeposition of Cu₂O at -0.4 V. The three peaks with

indexes of (111), (200) and (220) can be assigned to the diffraction of Cu_2O (JCPDS No. 78-2076) except peaks labeled as ITO substrate. This finding is similar to the XRD study conducted by the other researchers [117, 118]. For the sample deposited at voltage of -0.6V, the intensity of peaks decreases and the result explicitly shows that product is changed when potential is lower than -0.5V. For the second condition, Zhou et al.[118] suggested that Eq. (2) and (4) are pH dependent. Thus, at high pH, Copper (I) Oxide is deposited in the presence of OH^- ions, while at low pH, metallic copper is deposited instead (shown in Eq. 4). Their results showed that for the films deposited at pH 7, a composite of copper and Cu_2O was obtained, and for those at pH 8-12, pure Copper (I) Oxide was obtained. Therefore, to prepare the copper sulfate solution, sodium hydroxide must be added to let pH of the solution reach around 9.

2.7 Structure Characterization by Low-angle XRD, SEM, and TEM

The phase structure of liquid crystalline mixtures was also identified by low-angle XRD. Low angle XRD patterns were used to identify the mesoporous structure of the samples. The presence of peaks in low angle XRD patterns signifies that there is formation of mesoporous structures. Each diffraction has an associated reciprocal spacing, $S_{hkl}=1/d_{hkl}$. The ratio of the reciprocal spacings of the diffraction allows powder patterns to be indexed to particular mesophase symmetries (i.e. lamellar, hexagonal or cubic for lyotropic systems). The diffraction peaks for the hexagonal liquid phase are regularly spaced as $S_{hk} = (2/\sqrt{3})(h^2+k^2+hk)^{1/2}$ ($1, \sqrt{3}, 2, \sqrt{7}, \dots$). Figure 2-5 shows the low angle XRD patterns of

LLC phases and deposited mesofilms. Liquid crystalline templating mixture of the copper sulfate aqueous solution and Brij56 (i.e. (a) in Figure 2-5) exhibits two well-resolved diffraction peaks with d-spacings of 65.8 and 35.0 Å, respectively. Similarly, aniline Brij56 LLC template (i.e. (b) in Figure 2-5) also exhibits two diffraction peaks with d-spacings of 70.0 and 36.2 Å. These d-spacings are close to the ratio 1: $1/\sqrt{3}$ and consistent with (100) and (110) diffraction planes of the hexagonal structures[55]. However, there is a slight difference between these two LLC molds. The value of 2θ of Cu^{2+} LLC shifts a little bit right than the aniline one due to the introduction of lactic acid, which has the similar functional group as Brij56.

Figure 2-5 Low-angle XRD patterns of (a) Cu^{2+} Brij56 liquid crystalline phase, (b) aniline Brij 56 liquid crystalline phase, (c) meso-PANI films, (d) meso- Cu_2O films and (e) meso- Cu_2O /PANI bilayers deposited on ITO glass from LLC template.

The intensity data (c), (d), and (e) in Figure 2-5 show the low angle XRD patterns of mesoporous PANI, Cu₂O and Cu₂O/PANI composite separately. The presence of peaks in a low angle XRD patterns also signifies that mesoporous structures are formed within the electrodeposited films, thus the synthesis of mesoporous films has been successful. For the three peaks, great intensities and narrow widths of those indicate the higher long-range order in the mesoporous structures. The 2θ angles of three peaks appearing at 0.96° (i.e. (c) in Figure 2-5), 1.1° (i.e. (d) in Figure 2-5) and 1.02° (i.e. (e) in Figure 2-5) correspond to the d-spacings of 91.9, 80.2 and 86.5 Å, respectively. The order of d-spacing size is coherent with the LLC template and the dual layer film is in the middle. It is also shown that the d-spacing of porous material is clearly larger than that of LLC phases and this result should attribute to the entire removal of the surfactant by ethanol.

The surface structures of the electrodes characterized by SEM are shown in Figure 2-6. The thicknesses of all mesoporous films are estimated to be around 1 μm . The loose sheet-layered morphology is observed for mesoporous polyaniline, it is obvious that the film deposited from aniline Brij56 LLC mesophase (Figure 2-6a) is less packed as compared to the one from the aqueous aniline solution (Figure 2-6b). The sheet of film is found to be composed of small PANI particles. It is also observed that the polyaniline particles are bonded tighter in Figure 2-6b. A close similarity of the SEM image of polyaniline deposited from the aqueous aniline solution was reported by Huang et al[25]. For Cu₂O, the rough surface obtained from Cu²⁺ Brij56 template (Figure 2-6c) is found in contrast with the cuprous film

deposited from the aqueous copper sulfate solution (Figure 2-6d), which shows a smooth surface. For the composite film (Figure 2-6e), the film seems to be electrodeposited uniformly and mesoporous Cu_2O with flower-like structure (bright particles) disperses on the sheet-layered surface (dark particles) of the porous PANI.

Figure 2-6 Scanning electron microscopy (SEM) of (a) mesoporous PANI films (with-cross section), (b) bulk PANI films, (c) mesoporous Cu_2O films (with cross-section), (d) bulk Cu_2O films and (e) mesoporous Cu_2O /PANI bilayer films (with cross-section) on ITO glass.

Figure 2-7 shows the TEM images of mesoporous PANI (a) and Cu_2O (b) films molded from Brij56 templates. Apparently, as shown in Figure 2-7a, PANI films have homogeneous mesoporous pores $2.5\pm0.8\text{nm}$ (95% confidence interval [CI]), wall thickness $2.9\text{nm}\pm0.8\text{nm}$, and pore to pore distance $5.5\pm1.6\text{nm}$. The side-view of the mesopores in the PANI films is shown in Figure 2-7b. The aligned pores can be observed but are not easy to be distinguished because of a slight difference between wall and pores. After the pores were destroyed by the electron beam (as shown in Figure 2-7c), the difference between the pore and wall is more obvious: the pores are damaged but the partially ordered mesoporous structures still remain. Mesoporous Cu_2O films in Figure 2-7b show partially aligned hexagonal pores with $2.3\pm0.8\text{nm}$ pore size, $3.1\pm0.8\text{nm}$ wall thickness and $5.6\pm1.7\text{nm}$ pore to pore distance.

Figure 2-7 Transmission electron microscopy (TEM) of (a) meso-PANI films (end-view of pores), (b) meso-PANI films (side-view of pores), (c) meso-PANI films (side-view of destroyed pores) and (d) meso- Cu_2O films.

The partially ordered hexagonal cross-section and end view of the pores also can be observed clearly. The relative larger pore parameters should be caused by lactic acid addition. The mesoporous films are expected to have relatively high specific surface area.

2.8 Optical Properties

Figure 2-8 Optical absorbance spectra for mesoporous PANI (a), mesoporous Cu₂O (b) and mesoporous Cu₂O-PANI dual layers (c)

Figure 2-8 illustrates the typical absorbance (i.e. optical density) spectra for the porous PANI (a), Cu₂O (b) and Cu₂O/PANI (c) thin films. For the PANI film spectrum, the broad band observed at wavelengths from 400nm to 800nm could be

attributed to the conjugation between the π electrons. This conjugation reduces the band gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital. For Cu_2O , the curve increases sharply from 500nm to 400nm with strong absorbance. For $\text{Cu}_2\text{O/PANI}$, the curve shows its stronger absorbance than that for the case of Cu_2O in the almost full range because of the PANI.

As an important parameter, the band gap, E_g , should be obtained to analyze the optical properties of semiconductor materials. First, the absorption coefficient, α , is required to be obtained and it can be directly calculated from the absorbance. The relation between α and absorbance is given below,

$$T = A \exp(-\alpha d) \quad (2-5)$$

where T is the transmittance of the film, A is a constant and d is the film thickness in meters. A is close to unity as the reflectivity is negligible and insignificant near the absorption edge[120]. T is related to the absorbance by the following equation:

$$A = -\lg T \quad (2-6)$$

The relation between the energy of the incident photon, α , and E_g is given by the following:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (2-7)$$

where A is a constant, E_g is the band gap and n is the type of transition. The values of n could be 1/2, 3/2, 2 and 3, depending on the nature of the electronic transition during the absorption process. n equals to 1/2 and 3/2 for a direct transition and 2

and 3 for a indirect one. The electrons of Cu_2O have a direct transition, therefore a half is used in the calculation of the band gap. Figure 2-9 shows the plots of $(\alpha h\nu)^2$ vs. $h\nu$. The E_g value can be obtained by extrapolating the linear portion in the photon energy axis. For mesoporous Cu_2O , the band gap value was determined to be 2.41eV, which is similar to the reported value of 2.3 eV by using the same technique[57]. For mesostructure dual layers $\text{Cu}_2\text{O}/\text{PANI}$, the band gap value is found to be 1.86 eV. The decrease of the band gap (i.e. 0.55eV) by introducing PANI as a supporting layer explicitly indicates the better electron transfer from the valence band to the conduction band, possibly because the mesoporous dual layers $\text{Cu}_2\text{O}/\text{PANI}$ can not only produce more electron-hole pairs but also increase the recombination rate of electron-hole pairs.

Figure 2-9 Plot of $(\alpha h\nu)^2$ versus photon energy for the mesoporous Cu_2O (a) and $\text{Cu}_2\text{O}/\text{PANI}$ (b) thin films

2.9 Conclusion

In this study, we synthesized $\text{Cu}_2\text{O}/\text{PANI}$ dual layer films in Brij56 LLC phases by using an electrodeposition technique for the first time. Both the potential and pH values for the electrodeposition were discussed to show optimized conditions to synthesize the target composite films. The mesoporous structure of the films with high specific surface area was identified by Low angle XRD and TEM. For mesoporous Cu_2O , the band gap value was determined to be 2.41 eV. However, the band gap of mesostructure $\text{Cu}_2\text{O}/\text{PANI}$ dual layers was 1.86 eV. The decrease of the band gap (i.e. 0.55 eV) by introducing PANI as a supporting layer explicitly indicates that electron transfer between conductive band and covalent band is much easier. From the results, mesoporous $\text{Cu}_2\text{O}/\text{PANI}$ bilayer film could be a promising material which can be used into some specific fields such as photocatalysis, solar cells and chemical sensors.

Chapter 3 Synthesis of Mesoporous Polyaniline

(PANI)-Se_{0.5}Te_{0.5} Dual-Layer Film from

Lyotropic Liquid Crystalline Template

Reprinted from Industrial & Engineering Chemistry Research, Vol52, T. Xue, X. Wang, S. K. Kwak, J.-M. Lee*, Synthesis of mesoporous polyaniline (PANI)-Se_{0.5}Te_{0.5} dual-layer film from lyotropic liquid crystalline template, 5072-5078, Copyright (2013) American Chemical Society.

In this chapter, in order to verify the contribution of mesoporous PANI layer as mentioned in Chapter 1, mesoporous Se_{0.5}Te_{0.5}-PANI dual-layer films were synthesized in LLC template. The Se_{0.5}Te_{0.5} was selected to be supported by the PANI, because the concentration of Te in Se_xTe_{1-x} could also affect the band gap and optical property. It shows a versatile way to control band gap of synthesized materials.

Selenium (Se) is a p-type semiconductor with an indirect band gap of 2.7eV. It is used in the fabrication of chalcogenide glasses in optoelectronic devices [121]. However, pure selenium has disadvantages because of its short lifetime and low photosensitivity. To enhance the electronic and optical properties of Se, it is often synthesized with bismuth (Bi), gallium (Ga), lead (Pb) and/or tellurium (Te) [122].

These chalcogenide glasses have higher hardness and photosensitivity than those from Se [123].

Tellurium is a p-type semiconductor with the direct band gap of 0.3eV. The crystalline structure of Te is a helical chain without rings existing in crystalline type while the structure of Se is a mixture of eight closed rings and long helical chains existing in amorphous type [121]. Substitution of Te into Se could partly reduce the Se_8 ring population and increase chain fraction to stabilize the amorphous state. In addition, the concentration of Te in $\text{Se}_x\text{Te}_{1-x}$ affects its optical property. When Te concentration increases, the energy gap decreases [121, 124-128]. The reported band gap of $\text{Se}_x\text{Te}_{1-x}$ ranges from 1.01eV to 3.40eV [124, 126].

Polymer is often used as supporting media because of their porosity, hydrophilicity and ability to maintain dispersion of active materials. Incorporating semiconductors such as selenium and tellurium into conducting polymer such as PANI were carried out because the particles can be deposited onto electron conducting matrix where charges can flow efficiently. PANI acts as good support for the chalcogen alloy as it adheres to electrode surface tightly and also has durability under atmosphere. Composite compound can provide enhanced electrocatalytic activity or photoactivity [129]. The performance of these composites deposited on the polymer layer depends on not only the amount, size and location of the deposited particles but also the intrinsic properties of the polymer. Due to the promising properties of polymer-semiconductor composites, various composites have been investigated. Selenium doped polyaniline is classified into organic superconductors because they show metal-to-semiconductor

transition at low temperature [130]. Tellurium doped polyaniline has higher conductivity, glass transition temperature and enthalpy than Tellurium [131]. Fabrications of heterojunctional cadmium chalcogenides (CdX) (X=Se, Te) with polyaniline also have been carried out [132]. The incorporation of inorganic particles in conducting polymer films has the possibility to design inorganic/polymer composite materials with various properties and to develop the devices be utilized in multi-fields.

In this study, mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ -PANI dual-layer films were synthesized in LLC template by using electrodeposition [133]. Brij56, a commercially nonionic surfactant was employed to prepare the LLC template. In previous studies, it is shown that Brij56 can be utilized to produce versatile nanostructures and high-quality mesoporous nanofilms [33, 88, 89, 134]. Comparing with other surfactants, Brij56 is much easier to be operated because of its low melting point and cheap price. The band gaps of mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ and composite films are characterized by ultraviolet-visible (UV-vis) absorption spectrum.

3.1 Materials for dual-layer films synthesis

The nonionic surfactant Brij56 (Polyoxyethylene (10) cetyl ether, $\text{C}_{16}\text{EO}_{10}$), tellurium dioxide (TeO_2 , 99.9999%) and selenium dioxide (SeO_2 , 99.999%) are received from Sigma-Aldrich. Aniline (99.5%), sulfuric acid (95-97%) and ethanol (99.8 %) were purchased from Merck.

3.2 Preparation of Brij56 LLC template for mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ alloy

A solution containing Se and Te was prepared by adding concentrated H_2SO_4 in 5ml high purity water which contains SeO_2 and TeO_2 , and then diluted after SeO_2 and TeO_2 were dissolved entirely. The electrolyte used in the electrodeposition of mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ is the binary system of surfactant Brij56 and aqueous solution containing 1mM SeO_2 , 1mM TeO_2 and 0.1M sulfuric acid in different ratio. The proportion of Brij56 and mixing procedure are same as those for aniline Brij56 LLC template.

3.3 Synthesis of $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI dual layers via LLC template

The mesoporous polyaniline (PANI) was electropolymerized in aniline Brij56 LLC template by using a conventional three electrode system composed of a 1cm^2 indium tin oxides (ITO) glass working electrode, a 1cm^2 platinum counter electrode, and a standard saturated calomel reference electrode (SCE) conducted on a CHI660d electrochemical workstation. The electrodeposition of polyaniline onto ITO glass was carried out under potentiostatic and thermostatic control maintaining a constant potential of 0.75V and temperature of 50°C . After deposition, the hexagonal polyaniline films were soaked in ethanol for at least 24 hrs. During this period, the ethanol was replaced every 2 hrs until all the surfactants were removed. The electrode was dried by ambient air entirely.

The mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ films were electrodeposited under the three electrodes system in Se-Te Brij56 LLC electrolyte, and PANI modified ITO electrodes were used to achieve $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI dual layers. The $\text{Se}_{0.5}\text{Te}_{0.5}$

electrodeposition was also under potentiostatic and thermostatic control at a constant potential of -0.55V and temperature of 50 °C. The working electrode was cleaned by ethanol as described above.

3.4 Electrodeposition potential

For electropolymerization of aniline, from the preliminary experimental results and literature [116], an electrodeposition potential was set at 0.75V to achieve the green colored conductive PANI (in conducting emeraldine salt state).

For electrodeposition of $\text{Se}_{0.5}\text{Te}_{0.5}$, cyclic voltammetric (CV) was performed to investigate the suitable reduction potential. Figure 3-1 shows the first cycle of CV in Se-Te aqueous solution. The reductions of Se^{4+} and Te^{4+} occur at the potentials after -0.4V. The current hysteresis loop represents an autocatalytic character of the Se-Te reduction. A reduction peak was observed at -0.57V, in good agreement with the value reported in literature [52, 135].

In acidic aqueous solution, Se^{4+} exists in H_2SeO_3 and converts to Se with acquiring 4 electrons. The principle is given as follows:

It is well known that TeO_2 is reversible to HTeO_2^+ at $\text{pH} < 1.9$:

and also HTeO_2^+ converts to Te with accepting 4 electrons.

Figure 3-1 Cyclic voltammogram of 1mM TeO₂, 1mM SeO₂ and 1M sulfuric acid solution at scan rate of 100mV s⁻¹

The literatures reported the reduction potential of -0.50V for Se⁴⁺ and -0.35V for Te⁴⁺ [135, 136]. Thus, a potential of -0.55V was used for the electrodeposition of Se_{0.5}Te_{0.5} in this study.

The accurate ratio between Se and Te is 1:1 which was confirmed by inductively coupled plasma (ICP) measurement. From wide-angle XRD measurement (not shown here), only background peaks were observed, indicating that the Se_{0.5}Te_{0.5} composite is in amorphous or glassy-like state. Raman spectrum was used to investigate the existence of Se-Te alloy and the formation of Se-Te bond.

Figure 3-2 Raman spectra (2a) for pure Se (a-1), amorphous $\text{Se}_{0.5}\text{Te}_{0.5}$ alloys (a-2) and pure Te (a-3); XPS (2b) Se 3p and Te 3d spectra of pure Se, pure Te and $\text{Se}_{0.5}\text{Te}_{0.5}$.

As shown in Figure 3-2a-1, the pure Se shows its Se-Se vibrating peak around 250cm^{-1} , while pure Te in Figure 3-2a-3 shows its Te-Te vibrating peaks located at around 125cm^{-1} . The bond vibration of $\text{Se}_{0.5}\text{Te}_{0.5}$ is shown in Figure 3-2a-2. The vibrations of neighboring Se-Te bond found at around 190 cm^{-1} . The vanishing Se-Se vibration and decreasing Te-Te vibrating intensity indicate the existence of Se-Te alloys [124]. As shown in Fig. 3-2b, the XPS spectra were also used to confirm the formation of Se-Te alloy. Both Te 3d and Se 3p peaks are observed in the $\text{Se}_{0.5}\text{Te}_{0.5}$ spectrum. Meanwhile, the energy shifts which indicate alloy formation are distinguished. Comparing with pure Se and Te, Te 3d peaks in alloy shift to higher binding energy because of electron donating while Se 3p peaks in the alloy

shift to lower binding energy because of electron accepting during the alloy formation [137]. Hence, the formation of Se-Te alloy is confirmed by XPS.

3.5 Phase Diagram of LLC phase

Since the resulting structure of mesoporous film is influenced by the morphology of LLC phases, it is quite important to understand the phase behavior before electrochemical deposition. Figure 3-3a and 3b show the phase diagrams of Brij 56 with aniline aqueous solution and Se-Te aqueous solution respectively. Both phase diagrams were obtained by using a POM to observe the characteristic textures of the LLC phases. At low concentration of Brij56, the whole system is the L_1 (isotropic micellar solution) phase. With increasing weight ratio of surfactant, the system turns into a birefractive phase which comprises a mixture of H_I (hexagonal) and I_I (cubic spherical micellar) phase. The absolute H_I phase appears from 45 wt% to 65 wt% Brij56 over a wide temperature range from 30°C to 70°C in aniline system and from 40% wt% to 65wt% Brij56 in Se-Te system. The hexagonal phase is shown in Figure 3-3c with fan-like structure which can be identified directly by its characteristic texture under observation of POM. With decreasing temperature, the hexagonal phase turns from transparent to turbid in appearance and display homocentric circles on fan textures. This domain is marked as the coagulated hexagonal phase [H_I (S)]. ; A small region of the V_1 (isotropic cubic) phase exists between 55wt % and 65wt% Brij 56 over the temperature range of 30-65°C in aniline system.

Figure 3-3 Phase diagram of aniline Brij56 LLC phase (a) and Se-Te Brij56 LLC phase (b); And POM images of hexagonal (H_I) (c) and lamellar (L_α) (d) phase

As compared with the results for aniline system, the Se-Te surfactant mixture has a relatively large V_1 area from 45wt% to 65wt% at the temperature range 30–70°C. At higher temperatures and concentrations, lamellar (L_α) phase appears to have a floccus-shaped structure with flower-like texture (shown in Figure 3-3d). When the weight ratio of Brij56 reaches to 70wt%, the reverse micelle (L_2) can be observed in the temperature range 30–70°C. From the results, the change of LLC-phase structure follows the trend: $L_1 \rightarrow H_I \rightarrow V_1 \rightarrow L_\alpha \rightarrow L_2$ according to increasing the amount of Brij56. Desired hexagonal structure (H_I) can be easily obtained by using LLC templating system because it occupies a large area in the phase diagram. In

this study, Brij56 of 50 wt% and temperature of 50°C were selected to synthesize dual-layer films with hexagonal structure.

3.6 Structure of synthesized mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI films

The phase texture of liquid crystalline template can be characterized by low-angle XRD. Within each diffraction order, the ratio of reciprocal spacings of diffraction peaks allow powder patterns to be indexed to particular mesophase symmetry (lamellar, hexagonal or cubic for lyotropic systems). The ratio of reciprocal spacings for the hexagonal liquid phase is 1: $\sqrt{3}$: 2: $\sqrt{7}$. Figure 3-4 shows the low angle XRD patterns of LLC phases and deposited mesofilms. The liquid crystalline templating mixture of aniline Brij56 (Figure 3-4a) exhibits two well-resolved diffraction peaks with d-spacings of 70.0 and 36.2 Å. Similarly, Se-Te aqueous solution with Brij56 (Figure 3-4b) also exists two diffraction peaks with d-spacings of 60.9 and 33.9 Å, which are close to the ratio of 1: $1/\sqrt{3}$, consistent with the (100) and (110) diffraction peaks of the hexagonal structure [55]. As compared with the result for Se-Te LLC template, the 2θ of aniline LLC phase shifts to the lower 2θ angle, which can be attributed to the organic nature of aniline.

Figure 3-4c, 3-4d and 3-4e show the low angle XRD patterns of mesoporous PANI, $\text{Se}_{0.5}\text{Te}_{0.5}$ and $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI composite, respectively. The presence of peaks in low angle XRD patterns signifies that the formation of mesoporous structures within the electrodeposited films was successfully created. The narrow widths and the strong intensities of the peaks clearly indicate the existence of the highly ordered mesoporous structures. The 2θ angles of these three peaks appear at

0.96°(PANI), 1.1°(Se_{0.5}Te_{0.5}) and 1.00°(Se_{0.5}Te_{0.5}-PANI), corresponding to the d-spacings of 91.9, 80.2 and 88.2Å, respectively. The pore to pore distances of resulting materials, calculated by $d_{100}/\cos 30$, are 10.6nm, 9.3nm and 10.2nm, consistent with the results for the LLC templates.

Figure 3-4 Low-angle XRD patterns of (a) aniline Brij 56 liquid crystalline phase, (b) Se-Te Brij56 liquid crystalline phase, (c) meso-PANI films deposited on ITO substrate from LLC template, (d) meso- Se_{0.5}Te_{0.5} films deposited on ITO glass from LLC phase and (e) meso- Se_{0.5}Te_{0.5}/PANI bilayers deposited on ITO glass from template.

The surface structures of electrodes captured by scanning electron microscope (SEM) are shown in Figure 3-5. Sheet-like morphology is observed for meso-PANI (Figure 3-5a). It is obvious that the films deposited from LLC mesophase are less packed. The homogenous aggregation of the round particles is observed in Se_{0.5}Te_{0.5} (Figure 3-5b). The composite films (Figure 3-5c) seem to be uniformly

electrodeposited and the small grains of mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ disperse on the surface of porous PANI.

Figure 3-5 SEM images of (a) mesoporous PANI films, (b) mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ films and (c) mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI bilayer films on ITO glass.

Figure 3-6 shows the TEM images of meso-PANI and meso- $\text{Se}_{0.5}\text{Te}_{0.5}$ synthesized from the LLC template. The PANI films containing round-shaped pieces are shown in Figure 3-6a which is accordance with the SEM image. The homogeneous porous structure in the film has a pore diameter of 2.8nm, wall thickness of 2.7nm and pore to pore distance of 5.6nm. The electropolymerization of PANI is a chain reaction, and all chains twist together easily. Hence the pore

structures cannot be observed clearly. Mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ films in Figure 3-6b have well-ordered hexagonal pores with pore diameter of 2.25nm, wall thickness of 2.5nm and pore to pore distance of 4.75nm, which are less than those obtained from low-angle XRD patterns, due to the pore shrinkage after the surfactants were removed.

Figure 3-6 TEM images of (a) meso-PANI films, (b) meso- $\text{Se}_{0.5}\text{Te}_{0.5}$ films.

3.7 Optical Properties

In the UV-vis spectra shown in Figure 3-7, the absorbance spectra of polyaniline film and Se-Te film are consistent with those reported in literature [127, 138]. In the spectrum of PANI film, the broad band is observed at wavelength between 500nm and 1800nm. The absorbance increases from 500nm to 900nm for mesoporous PANI and $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI composite and decreases thereafter. Compared with the spectrum of mesoporous- $\text{Se}_{0.5}\text{Te}_{0.5}$, $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI composite has relatively strong absorbance due to the influence of PANI.

Figure 3-7 Optical absorbance spectra for mesoporous PANI (a), mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ - PANI dual layers (b) and mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ (c).

Currently, there is no information available for the UV-vis absorbance spectrum of $\text{Se}_{0.5}\text{Te}_{0.5}/\text{PANI}$ composite. The trend in the spectrum of $\text{Se}_{0.5}\text{Te}_{0.5}/\text{PANI}$ composite is similar to that in the spectrum of PANI, indicating that the composite is influenced more by PANI than by $\text{Se}_{0.5}\text{Te}_{0.5}$ alloy. In the other hand, PANI as a supporting media reduces the charge doping effect of $\text{Se}_{0.5}\text{Te}_{0.5}$ layer. Therefore, the absorbance of the composite locates between PANI and $\text{Se}_{0.5}\text{Te}_{0.5}$.

The energy band gap of a semiconductor material can be obtained by its absorption spectrum. In particular, the band gap is influenced by absorption coefficient (α) which can be calculated directly from the absorbance (optical density) of the mesoporous films. The relation between absorption coefficient and absorbance is given in the Equation 3-4:

$$\alpha = \frac{OD}{t} \quad (3-4)$$

where OD is the absorbance at defined thickness (t) of layer.

The relation between the energy of incident photon, absorption coefficient and band gap is given in the Equation 3-5:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (3-5)$$

where A is a constant, E_g is the band gap and n is the type of transition. The value of n could be 1/2, 3/2, 2 and 3 which depends on the nature of electronic transition during the absorption process. n equals to 1/2 and 3/2 for direct transition while n equals to 2 and 3 for indirect transition. In addition, Te has a direct band gap while Se has an indirect band gap. In a Se-Te binary system, a transition from the direct band gap of Te to the indirect band gap of Se occurs and the index used in this study is 0.5, which is confirmed by the previous studies [123, 124, 126, 128].

Figure 3-8 shows the variation of $(\alpha h\nu)^2$ with photon energy for composite films (mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI) and $\text{Se}_{0.5}\text{Te}_{0.5}$ alloy films. The value of the indirect band gap is obtained by taking the intercept on the horizontal axis. The band gaps of $\text{Se}_{0.5}\text{Te}_{0.5}$ alloy and composite are 1.4eV and 0.9eV, indicating that the incorporation of PANI into $\text{Se}_{0.5}\text{Te}_{0.5}$ enhances its electron transfer.

Figure 3-8 Plot of $(\alpha h\nu)^2$ versus photon energy for the mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ and $\text{Se}_{0.5}\text{Te}_{0.5}/\text{PANI}$ composited thin films

3.8 Electrochemical impedance measurement

The complex impedance spectra of the PANI- $\text{Se}_{0.5}\text{Te}_{0.5}$ composite and $\text{Se}_{0.5}\text{Te}_{0.5}$ are shown in Figure 3-9. The initial intersection of the semicircle with Z' is due to the electrical-resistance (R_Ω) of the electrolyte, which is around 20Ω in $0.1 \text{ M H}_2\text{SO}_4$ electrolyte. The resistance of the active electrode material (R_{ct}) is decided by the distance between two intersections of the semicircle with Z' . Hence, the resistance of the PANI- $\text{Se}_{0.5}\text{Te}_{0.5}$ composite and $\text{Se}_{0.5}\text{Te}_{0.5}$ could be assigned to 18Ω and 170Ω respectively. It indicates that PANI has a significant contribution

to the conductivity of PANI- $\text{Se}_{0.5}\text{Te}_{0.5}$ composite. For the PANI- $\text{Se}_{0.5}\text{Te}_{0.5}$ composite, the conductivity increases more than 9 times as comparing with pure $\text{Se}_{0.5}\text{Te}_{0.5}$.

Figure 3-9 Complex impedance spectra (at 0.8V) of PANI- $\text{Se}_{0.5}\text{Te}_{0.5}$ composite and $\text{Se}_{0.5}\text{Te}_{0.5}$.

3.9 Conclusion

It is the first time that mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI dual-layer films were synthesized by using electrochemical deposition methodology in Brij56 LLC template. The electrodeposition potential was determined by cyclic voltammetric analysis. The mesoporous structure of composite was characterized by low-angle XRD and TEM. The optical properties of meso-SeTe and meso-SeTe/PANI were investigated by UV-vis absorption spectra. The narrow band gaps are near 0.9eV for composite and 1.4eV for $\text{Se}_{0.5}\text{Te}_{0.5}$ alloy, indicating that the incorporation of PANI

into $\text{Se}_{0.5}\text{Te}_{0.5}$ enhances its electron transfer. Thus, mesoporous hexagonal $\text{Se}_{0.5}\text{Te}_{0.5}$ /PANI dual layer films are promising materials to be used in various optical devices.

Chapter 4 Dual-template Synthesis of $\text{Co}(\text{OH})_2$ with Mesoporous Nanowire Structure and Its Application in Supercapacitor

Reprinted from Journal of Power Sources, Vol 201, T. Xue, X. Wang, J.-M. Lee*, Dual-template synthesis of $\text{Co}(\text{OH})_2$ with mesoporous nanowire structure and its application in supercapacitor, 382-386, Copyright (2012), with permission from Elsevier.

Confined LLC phase in cylindrical pores of PAA membrane has been demonstrated to be a promising way to synthesize mesoporous nanowire structures. Hence, in this chapter, mesoporous $\text{Co}(\text{OH})_2$ nanowires have been designed and fabricated for the first time.

Electrochemical supercapacitors (ECs) are well known as attractive energy storage devices for application because of their high power energy storage ability [139]. The range of potentially practical applications of ECs extends from mobile device to electric vehicles. Based on the different nature of charge-storage mechanism, electrochemical capacitors are classified into two forms: electrochemical double layer capacitors (EDLCs) and redox capacitors (pseudocapacitors). Carbon-based materials [140, 141] with high specific surface area are widely utilized as EDLCs which exhibit a nonfaradaic reaction with

accumulation of charges at the electrode/electrolyte interface. Subsequently, conducting polymers [142, 143] and transition metal oxides and hydroxides [88, 89, 144-147] have been identified as possible electrode materials for redox capacitors which utilize the charge-transfer pseudocapacitance arising from reversible faradaic reactions occurred at the electrode surface. Redox capacitors attract much more attention than EDLCs because of their better capacitive characteristics which are not only limited by specific surface area but decided by the faradaic redox character of materials themselves as well [148]. Among all the candidates of redox electrode materials, Co(OH)_2 has generated growing research activities and extensive studies in the field for its layered structure with large interlayer spacing, great reversibility and high specific capacitance. [88, 149-152] At the beginning, precipitation methodology was used to synthesize Co(OH)_2 for supercapacitor, but it shows the very low specific capacitance in a range of 200-400 F g^{-1} . [149, 153, 154] With the development of self-assemble nanotechniques, template synthesis was paid much attention as a new kind of fabricated technology of ordered nanomaterials. One particular approach is to use porous anodic alumina (PAA) template to obtain nanowire arrays with combined lyotropic liquid crystalline (LLC) template as pore-directing agent together [79, 80, 155-157], which maintains the topology of the phase throughout the progress of the reaction and holds the ability to fabricate mesoporous nanowires with high surface area via electrodeposition. In this paper, we fabricated a novel mesoporous nanowire structure of Co(OH)_2 by confined LLC phases in cylindrical pores of PAA membranes.

4.1 Preparation of mesoporous Co(OH)₂ nanowires via dual templates

Porous anodic alumina (PAA) template was synthesized by anodizing Al/Ti/Si substrate in 0.3 mol L⁻¹ oxalic acid solution at 40 V and 4 °C for 4 hrs. Lyotropic liquid crystalline (LLC) template was prepared from mixing 50 wt% Brij56 (polyoxyethylene(10) cetyl ether, C₁₆[EO]₁₀) and 50 wt% Co²⁺ electrolyte (1.2M Co(NO₃)₂ and 0.075M NaNO₃) to achieve homogeneous mixtures. The electrochemical deposition²⁴⁻²⁶ was conducted on an electrochemical workstation (CHI660d, CH Instruments Inc., Shanghai), by using a conventional three-electrode system composed of a 0.6cm² PAA/Ti/Si working electrode, a large surface area platinum counter electrode, and a standard Ag/AgCl electrode. After electrodeposition, the electrode was immersed into ethanol to remove Brij56 for 2 hours and ethanol should be replaced at least 3 times until the surfactant was removed entirely. PAA template was removed by using 1M NaOH. Finally, the electrode was rinsed by ultrapure water and dried in ambient atmosphere.

4.2 Chemical state analysis of synthesized mesoporous Co(OH)₂ nanowires

Co(OH)₂ synthesis is carried out using potentiostatic electrodeposition method at constant cathodic potential in the range of -0.6 to -1.0V. The mechanism of Co(OH)₂ electrodeposition is proposed to be as follows:

XPS was employed to examine the chemical state of deposited Co(OH)_2 nanowires. Figure 4-1 shows the Co 2p (a) and O 1s (b) spectra of XPS deposit. As shown in Figure 4-1a, there are two main Co 2p spectrums which locate at binding energy 797eV ($\text{Co } 2p_{1/2}$) and 781.1eV ($\text{Co } 2p_{3/2}$) with satellite peaks due to plasmon losses and final state effects respectively. The distance between these two peaks ($\Delta E_b=15.9\text{eV}$) indicates Co existed as Co(OH)_2 version[152, 158]. Figure 4-1b shows the XPS spectra and curve fitting results of O 1s. Inside, the middle strongest spectrum indicates the existing of Co(OH)_2 (531.1 eV) which is the dominating form within the deposit.

Figure 4-1 XPS $\text{Co } 2p_{1/2}$, $\text{Co } 2p_{3/2}$ spectra (a) and O 1s spectra (b) of electrodeposited mesoporous Co(OH)_2 nanowires; Low-angle XRD patterns of Co^{2+} liquid crystalline phase (c-1) and mesoporous Co(OH)_2 nanowires (c-2) (upper right is POM image of hexagonal structure.); Wide-angle XRD patterns of mesoporous Co(OH)_2 nanowires (d).

The figure also shows two smaller shoulders spectrums, in which the right one can be assigned as CoO (529.8 eV) attributed to a small degree of dehydroxylation upon drying and the left one can be ascribed to structural water (532.8 eV)[159]. The crystalline structure of Co(OH)₂ was further confirmed by wide-angle XRD as shown in Figure 4-1d. The three main peaks with indexes of (100), (002) and (004) can be assigned to the diffraction of layered α -Co(OH)₂[88, 151](JCPDS No. 74-1057) except one peak labeled as Ti/Si substrate. Fig. 1c (upper right) shows the POM photo of Co(NO₃)₂ LLC phase. Its focal conic fan texture indicates the phase exists as the hexagonal form. The low-angle XRD patterns of the template mixture (Figure 4-1c-1) display two well-resolved peaks with d-spacing of 58.1 and 33.7Å at 2 θ equal to 1.52° and 2.62°, respectively, which can be indexed as the (100) and (110) planes of the P6mm space group (hexagonal structure) for reciprocal ratio of d are 1: $\sqrt{3}$. The pore to pore distance of this hexagonal LLC template, calculated by $d_{100}/\cos 30^\circ$, is 6.7nm. Meanwhile, the resulting mesoporous Co(OH)₂ nanowire(Figure 4-1c-2) also shows a strong reflection peak at 2 θ equals to 1.24°. The peak is also assigned to d_{100} plane of the P6mm space group with d-spacing of 71.2Å and pore to pore distance of 8.2nm. This result suggests the liquid crystalline structures were still retained after the electrosynthesis. The presence of diffraction peak indicates that the ordered mesophase structure in the template is preserved in the deposited film.

4.3 Morphology of synthesized mesoporous $\text{Co}(\text{OH})_2$ nanowires

The surface morphologies of PAA template and porous $\text{Co}(\text{OH})_2$ nanowire were examined by FESEM as shown in Figure 4-2. From surface (Figure 4-2a) and side (Figure 4-2b) images of PAA template, the pore diameter of templates was found to be around 50-65nm with fine channels. As shown in Figure 4-2c and Figure 4-2d, after removing the PAA template, the diameter of templated $\text{Co}(\text{OH})_2$ nanowires still kept as 65nm, which means the fully duplicated procedure was processed.

Figure 4-2 SEM images of PAA templates (end view (a) and cross view (b)) and mesoporous $\text{Co}(\text{OH})_2$ nanowire (end view (c) and side view (d)); TEM images of mesoporous $\text{Co}(\text{OH})_2$ nanowires (e,f). (g) and (h) are the end view and side view of the pores respectively.

The rough wall of nanowires indicates pores existing and a few structural defects. The wires are inclined to agglutinate each other with holly structure at topside. It can be explained by nanosheet-like morphology of Co(OH)_2 films reported from Zhou et al.[88] The growth of nanowires still obeys the rules of sheet packing. This loose packed structure causes weak holding strength between nanowires and substrate, and then leads to wires aggregation

The sheet packed structure was further confirmed by TEM as shown in Fig. 2. Fig. 2e and 2f show the nanowire structures of Co(OH)_2 at different magnifications. As expected, the ordered porous morphologies on the nanosheets of Co(OH)_2 wires were observed by TEM shown in Fig. 2g and 2h. The light regions correspond to pores left after removal of the surfactant template from the electrodeposited wires and the dark areas represent the electrodeposited Co(OH)_2 . The uniform and well-ordered hexagonal pores with cylindrical channels of about 3.6nm in diameter were observed. The pore to pore distance is around 7.9nm and the pore wall thickness is about 4.3nm, which are consistent with 100 peak appeared in the low-angle XRD patterns.

4.4 Electrochemical behavior

Both cyclic voltammetry (CV) curve and chronopotential charge-discharge methods were used to investigate capacitor behavior of the materials. For both electrochemical measurements of Co(OH)_2 , 1M KOH aqueous solution was used as electrolyte. In this electrochemical system, two reversible redox reactions can

occur during potential sweep of synthesized Co(OH)_2 electrode. The reactions can be expressed as follows [160],

As shown in Fig. 3a, the CV curves of mesoporous Co(OH)_2 nanowires measured at scan rates of 100, 50 and 10 mV s^{-1} were displayed respectively. One pair of redox peaks can be observed from the cycles at scan rate of 100 and 50 mV s^{-1} , indicating that the mechanism of capacitance generation is based on redox capacitor because of electron-transfer process which is distinct from an ideal rectangular shape produced by electric double-layer capacitors. During the electron transfer procedure, only one oxidation peak, appeared at around 0.4V, possibly due to the production of CoOOH as an intermediate form which just existed for quite short time and then converted into CoO_2 rapidly. The actual reversible reaction at scan rate of 100 and 50 mV s^{-1} can be written as follows,

At scan rate decreasing to 10 mV s^{-1} , two oxidation peaks appear, proving that Co(OH)_2 has enough time to remain in CoOOH form which can be changed into CoO_2 .

Figure 3b shows the discharge curves of the ordered mesoporous $\text{H}_1\text{-Co(OH)}_2$ nanowire array electrode measured at different discharge current densities within potential window of -0.1 to 0.5V. The specific capacitance values were calculated to be 993, 922, 873 and 810 F g^{-1} corresponding to the discharging current densities of 1, 5, 10 and 20 A g^{-1} , respectively. The highest capacitance of 993 F g^{-1} was

obtained at discharge current density of 1 A g^{-1} . Co(OH)_2 mesoporous nanowire array has a slightly lower capacitance than mesoporous film[88], possibly due to the collapse of the end parts of nanowires under different synthesis conditions (e.g. electrodeposition potential, drying method and electrode working area). Further work is needed to solve the problems and enhance its performance. Figure 3b also summarized the capacitance retained ratios of the electrodes prepared in this study as a function of current density.

Figure 4-3 Electrochemical properties of ordered mesoporous Co(OH)_2 nanowire electrode, (a) CV curves at different scan rates and (b) discharge curves at different current densities in potential range of -0.1V to 0.5V vs Ag/AgCl.

Using capacitance obtained at 1 A g^{-1} as 100% retention, when the current density was increased from 1 to 20 A g^{-1} , the capacitance of mesoporous Co(OH)_2 nanowire array electrodes reserved 100%, 92.8%, 87.9% and 81.5%, respectively, indicating that the capacitance of the Co(OH)_2 wires is not significantly influenced with increasing of the current density. From the results, mesoporous nanowires obtained from the dual templates behave excellent performance which can be attributed to the high porosity and well dispersion of Co(OH)_2 . These structural factors increase ionic transport, shorten electron traveling distance and reduce interface resistance.

4.5 Conclusion

In summary, we have demonstrated a novel approach for electrosynthesis of mesoporous Co(OH)_2 nanowire array electrode via PAA templates with Brij56 LLC templates as pore-generated agent. The results of TEM and low angle XRD indicate the presence of ordered porous nanostructures and supported a direct templating mechanism for the electrodeposition of mesoporous Co(OH)_2 wires. The electrochemical results show the attractive specific capacitance of 993 F g^{-1} at current density of 1 A g^{-1} which has potential application to be used as electrode material in supercapacitors.

Chapter 5 Effects of Experimental Parameters on The Capacitive Behavior of Mesoporous Co(OH)₂ Nanowires

Reprinted from Journal of Power Sources, Vol 245, T. Xue, J.-M. Lee*,
Capacitance behavior of mesoporous Co(OH)₂ nanowires, Journal of Power
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Dual-template synthesis has been demonstrated a promising way to fabricate the mesoporous Co(OH)₂ nanowires with capacitance of 993F g⁻¹ at current density of 1A g⁻¹. In order to improve the capacitance of Co(OH)₂, optimized synthesis condition is in great need. For electrochemical synthesis, electrodeposition potential, heat treatment and water bath temperature can be accurately controlled to find the best synthesized condition of mesoporous Co(OH)₂ nanowires [33].

In this paper, the mesoporous Co(OH)₂ nanowires was successfully synthesized via dual-template method. The optimized synthesis conditions of mesoporous Co(OH)₂ nanowires have been investigated that electrochemical deposition should be carried out at -0.75V constant potential in 50°C LLC phase without any further heat treatment. The discharging curves show the highest capacitance of 1180F g⁻¹ was obtained at current density of 4A g⁻¹.

5.1 Chemicals for synthesis

The nonionic surfactant Brij 56 (polyoxyethylene(10) cetyl ether, $C_{16}[EO]_{10}$, Sigma-Aldrich), $Co(NO_3)_2$ (99.9%, Sinopharm Chemical Reagent Co.), $NaNO_3$ (Sinopharm Chemical Reagent Co), $NaOH$ ($\geq 98\%$, Sigma-Aldrich), oxalic acid (98%, Aldrich), isopropanol (99.8 %, Merck) and phosphoric acid (85%, Sigma) were used as received without further purification.

5.2 Preparation of porous anodic alumina (PAA)/Ti/Si template and lyotropic liquid crystalline (LLC) template

PAA/Ti/Si preparation has three steps: Firstly, highly pure Al film (99.999%, 2000nm) was deposited on (111)-type silicon substrate coated with a Ti film by magnetron sputtering. Secondly, the anodization was carried out in a 0.3 mol L^{-1} oxalic acid solution at 4°C at 40 Volts for 4 hrs. Finally, the plate was immersed into 5 wt% H_3PO_4 aqueous solution for 5min at 45°C and cleaned with distilled water.

Lyotropic liquid crystalline (LLC) template is a binary system with 50 wt% Brij56 and 50 wt% aqueous solution (including 1.2M $Co(NO_3)_2$ and 0.075M $NaNO_3$). In order to achieve a homogeneous state, the mixture was sealed in a vial at 75°C for 30min, followed by vigorous stirring by vortex. The heating and mixing process was repeated four times.

5.3 Electrodeposition of mesoporous Co(OH)₂ nanowires in different conditions

Electrochemical deposition of mesoporous Co(OH)₂ nanowires was carried out by electrochemical workstation (CHI660d, CH Instruments Inc.) with a conventional three-electrode system (a 0.6cm² PAA/Ti/Si working electrode, a large surface area platinum counterelectrode and a standard Ag/AgCl electrode) at a constant cathodic potential. LLC template was used as an electrolyte to produce a porous structure. The mesoporous Co(OH)₂ nanowires were deposited at -0.6, -0.7, -0.75, -0.8, -0.9 and -1.0V, respectively at 50 °C to study the effect of deposition potential. To study the effect of deposition temperature, the electrodeposition was carried out at 30°C, 50°C and 70°C at a fixed potential of -0.75V. To determine the effect of annealing temperature, the Co(OH)₂ nanowires were prepared at a potential of -0.75V in a water bath at 50°C and then heated under a vacuum condition at temperatures of 120°C and 250°C. After the electrodeposition, the electrode was immersed into isopropanol to remove Brij56 for 2 hours and the isopropanol was replaced at least 3 times until the surfactant was removed entirely. Finally, the electrode was dipped into a 1M NaOH to remove the PAA template for measurements.

In the dual-template synthesis, PAA was used as a template of nanowire synthesis and LLC was used to make uniformly sized parallel channels. PAA plays an important role in supporting nanowire growth and making it suitable for device fabrication. Such a technology would integrate parallel nanowires as active

components. Hence, the PAA template used in our study is one with rigid substrate which has three layers: a silicon wafer as hard supporting substrate, a titanium coating as conductive layer and a PAA layer on top as nanowires directing mold (PAA/Ti/Si). It can be utilized as the electrode directly after the nanowire synthesis. Brij56 is a kind of nonionic surfactant containing hydrophilic headgroups and hydrophobic chains. When mixing Brij56 with an aqueous solution containing metal salts, the hydrophilic “heads” are dissolved in the water where the hydrophobic “tails” tend to aggregate with each other to form a liquid crystalline phase. Thus, a desired mesoporous nanowire structure can be synthesized by the dual-template method.

The mechanism of Co(OH)_2 electrodeposition is well established as follows:

The whole process includes a reversible redox reaction (Eq.1) and a precipitated reaction (Eq.2). The mass of deposited mesoporous Co(OH)_2 nanowires was estimated by the Faraday's law with an assumption that faraday current efficiency for deposition is 100 %. In this study, a total passed charge of 0.15C was used for all samples during the electrodeposition.

5.4 The effect of electrodeposition potential on mesoporous Co(OH)_2 nanowires

In order to study the effect of electrodeposition potential on mesoporous Co(OH)_2 nanowires, synthesis of mesoporous Co(OH)_2 nanowires was carried out

in an LLC phase at 50°C by using a potentiostatic electrodeposition method at constant potentials of -0.6V, -0.7V, -0.75V, -0.8V, -0.9V and -1.0V, respectively, without heat treatment. TEM images of mesoporous Co(OH)_2 nanowires deposited at -0.6V, -0.75V, -0.8V and -1.0V are shown in Figure 5-1 to investigate the influence of the electrodeposition potential on Co(OH)_2 morphology. It is apparent that all the mesoporous nanowires have a nanosheet packed structure and the diameter of the nanowires is around 60nm. However, the structure of mesoporous Co(OH)_2 nanowires slightly varies with deposition potential. In fact, the density of interlaced nanosheets becomes higher when deposition potential increases from -0.6V to -1.0V.

Figure 5-1 TEM images of mesoporous Co(OH)_2 nanowires deposited from potentials of -0.6V(a), -0.75V(b), -0.8V(c) and -1.0V(d)

In Figure 5-1a, 1b and 1c, the nanowires deposited at potentials of -0.6V, -0.75V and -0.8V, respectively, show layered nanosheets which are aligned regularly, while the nanowires deposited at -1.0V (Figure 5-1d) show a cotton-like structure with closely and disorderedly packed nanosheets. It can be understood by considering that the electrodeposition at the potential ranges of 0.6V to -0.8V could be controlled by both mass transfer and reaction kinetics, while the electrodeposition at -1V could be controlled mainly by mass transfer, which limits access of ions to the electrode surface and causes the defect of nanowires [161].

Figure 5-2 XPS Co 2p_{1/2}, Co 2p_{3/2} spectra of mesoporous Co(OH)₂ nanowires deposited at various electrodeposition potentials

The chemical state and oxygen atomic ratio of Co(OH)₂ to CoO states of Co(OH)₂ nanowires were examined by XPS. Figure 5-2 shows the Co 2p spectra at electrodeposition potentials of -0.6V, -0.7V, -0.75V, -0.8V, -0.9V, -1.0V, respectively. Two main Co 2p spectrums exist and the locations of two peaks are nearly the same at all the electrodeposition potentials. The peak positions located at binding energies of 797eV (Co 2p_{1/2}) and 781.1eV (Co 2p_{3/2}), and the distance between the two peaks is 15.9eV (ΔE_b). There are still satellite peaks which are associated with plasmon losses and final state effects. The results illuminate the presence of Co mainly in Co(OH)₂ state [152, 158].

Figure 5-3 shows XPS spectra and curve fitting results of O 1s at different deposition potentials. The spectrum is split into 3 main peaks for curving fitting. It is considered that the middle strongest spectrum is the Co(OH)₂ which dominates the deposit.

There are also two smaller shoulder spectrums. The right one is associated with CoO due to dehydration of Co(OH)₂ upon drying in a small degree. The left one is assigned to structural water [159]. However, an amount of CoO from the dehydration of Co(OH)₂ deposited at various potentials could be different. In order to investigate the relative concentration of various chemical states, peak area and peak height sensitivity factors were utilized to quantify the XPS measurements[162]. The atomic ratio of the two elements in one composition is determined by Equation 5-3:

$$\frac{n_1}{n_2} = \frac{I_1/S_1}{I_2/S_2} \quad (5-3)$$

Figure 5-3 XPS O 1s spectra of mesoporous Co(OH)_2 nanowires deposited at various electrodeposition potentials

Here n is atomic number, I is the number of photoelectrons in a specific spectra peak (equal to peak area) and S is atomic sensitivity factor based on empirical data. In this study, the oxygen atomic ratio between Co(OH)_2 and CoO is determined by the Eq. 3. n_1 and n_2 are replaced by $O_{\text{Co(OH)}_2}$ and O_{CoO} as atomic number of Co(OH)_2 and CoO respectively. I_1 and I_2 are replaced by $I_{\text{Co(OH)}_2}$ and

I_{CoO} as the peak area of $Co(OH)_2$ and CoO respectively. S_1 equals to S_2 because both of them refer to the oxygen atom. The ratio of $O_{Co(OH)_2}$ to O_{CoO} is summarized in Table 5-1. The atomic ratio of $O_{Co(OH)_2} / O_{CoO}$ is 6.62, 7.79, 9.23, 8.51, 7.19 and 5.43 according to various deposition potentials of -0.6V, -0.7V, -0.75V, -0.8V, -0.9V and -1.0V respectively. The atomic ratio of $O_{Co(OH)_2} / O_{CoO}$ is 6.62, 7.79, 9.23, 8.51, 7.19 and 5.43 according to various deposition potentials of -0.6V, -0.7V, -0.75V, -0.8V, -0.9V and -1.0V, respectively. It clearly shows that the atomic ratio of $O_{Co(OH)_2} / O_{CoO}$ increases first with an increase of negative deposition potential until potential reaches to -0.75V, while the atomic ratio decreases gradually when potential becomes more negative than -0.75. Hence, mesoporous $Co(OH)_2$ nanowires deposited at -0.75V have the highest $O_{Co(OH)_2} / O_{CoO}$ ratio.

Capacitive behaviors of the mesoporous $Co(OH)_2$ nanowires were investigated by both cyclic voltammetry (CV) and chronopotential charge-discharge methods in a 1M KOH aqueous solution. According to the literature[160], the redox reaction of $Co(OH)_2$ electrode can be expressed as follows:

Figure 5-4a shows CV curves of mesoporous $Co(OH)_2$ nanowires deposited at different potentials at a scan rate of 100 mV s^{-1} . During the measurements for mesoporous $Co(OH)_2$ nanowires deposited at -0.75V, one pair of redox peaks where the oxidation peak locates at around 0.45V and reduction peak locates at around 0.15V was observed.

Table 5-1 Summary of oxygen atomic ratio of Co(OH)₂ to CoO states, and specific capacitance of mesoporous Co(OH)₂ nanowires at various electrodeposited potentials, annealing and electrodeposited temperatures

Deposited potential(V)	Annealing temperature(°C)	Deposited temperature(°C)	XPS $O_{Co(OH)_2} : O_{CoO}$	Specific capacitance (F g ⁻¹)
-0.6 V	N.A.	50	6.62	579
-0.7 V	N.A.	50	7.79	921
-0.75 V	N.A.	50	9.23	1180
-0.75 V	120	50	8.01	1086
-0.75 V	250	50	3.24	461
-0.75 V	N.A.	30	-	986
-0.75 V	N.A.	70	-	984
-0.8 V	N.A.	50	8.51	1042
-0.9 V	N.A.	50	7.19	903
-1.0 V	N.A.	50	5.43	824

As compared with the results for mesoporous Co(OH)₂ nanowires deposited at -0.75V, the redox reactions of Co(OH)₂ deposited at all the other potentials (i.e. -0.6V, -0.7V, -0.8V, -0.9V and -1.0V) occur at more negative potentials. As

combined with the XPS analysis of the chemical state, mesoporous $\text{Co}(\text{OH})_2$ nanowires deposited at -0.75V have the highest ratio of $\text{Co}(\text{OH})_2$ to CoO . Hence, the amount of CoO state could influence the position of redox peaks because of side reactions.

Figure 5-4 Cyclic voltammetry (CV) curves at the scan rate of 100 mV s^{-1} (a) and discharge curves at current density of 4 A g^{-1} (b) of mesoporous $\text{Co}(\text{OH})_2$ nanowire electrode deposited at potentials of -0.6V , -0.7V , -0.75V , -0.8V , -0.9V and -1.0V , respectively.

Discharge curves of the mesoporous $\text{Co}(\text{OH})_2$ nanowire electrodes were measured at a current density of 4 A g^{-1} as shown in Figure 5-4b. The specific capacitance values were calculated to be 579, 921, 1180, 1042, 903 and 810 F g^{-1} (in Table 5-1) corresponding to the deposition potentials of -0.6V , -0.7V , -0.75V , -0.8V , -0.9V and -1.0V , respectively. The highest capacitance of 1180 F g^{-1} was obtained at a deposition potential of -0.75V with the highest $O_{\text{Co}(\text{OH})_2} / O_{\text{CoO}}$ atomic ratio of 9.23. Specific capacitance was clearly improved with an increase of the $O_{\text{Co}(\text{OH})_2} / O_{\text{CoO}}$ ratio. As the $O_{\text{Co}(\text{OH})_2} / O_{\text{CoO}}$ decreases to 5.43, the capacitance also

decreases to 824 F g^{-1} at a deposition potential of -1.0V . However, the lowest capacitance of 579 F g^{-1} was obtained at a deposition potential of -0.6V with the $O_{\text{Co(OH)}_2} / O_{\text{CoO}}$ ratio of 6.62, which is higher than 5.43, possibly because the nanosheets of nanowire were loosely packed as described in the TEM analysis. The structural defect and weak binding force with the substrate could be other reasons that lead to decreased capacitance. Therefore, the capacitance of mesoporous Co(OH)_2 nanowires depends on not only the $O_{\text{Co(OH)}_2} / O_{\text{CoO}}$ atomic ratio, but also the packed density of interlaced nanostructure.

5.5 Effect of heat treatment temperature

In order to investigate the influence of heat treatment, the mesoporous Co(OH)_2 nanowires deposited at -0.75V were annealed at 120°C and 250°C individually under a vacuum condition to prevent the dehydration of Co(OH)_2 . The effects of heating temperature on the chemical states of mesoporous Co(OH)_2 nanowires were studied by analyzing the XPS spectra as shown in Figure 5-5. Figure 5a shows Co 2p spectra of the mesoporous nanowires with no heat treatment and heat treated at 120°C and 250°C . The locations of Co 2p spectrum at a binding energy of 797eV are fixed among all the heat treatment temperatures. The distance between the two peaks ($\Delta E_b \sim 15.9\text{eV}$) doesn't change with an increase of temperature in the ranges, implying that Co exists mainly in Co(OH)_2 state.

Figure 5-5 XPS Co 2p_{1/2}, Co 2p_{3/2} spectra (a) and O 1s spectra of mesoporous Co(OH)₂ nanowires without heat treatment (b) and at annealing temperature of 120 °C(c) and 250 °C(d)

Figure 5-5b, 5c and 5d show the XPS spectra and curve fitting results of O 1s of the mesoporous nanowires with no heat treatment and heat treated at 120 °C and 250 °C. As calculated in Table 1, the atomic ratio of $O_{Co(OH)_2} / O_{CoO}$ is 9.23, 8.01 and 3.24 according to no heat treatment and heat-treated temperatures of 120 °C and 250 °C. The dehydration Co(OH)₂ to CoO increases with an increase of heat treatment temperature, resulting in a gradual decrease of the $O_{Co(OH)_2} / O_{CoO}$ ratio.

The decomposition of $\text{Co}(\text{OH})_2$ to CoO by removal of chemisorbed water is shown in Eq. 5 [146]:

The electrochemical behaviors of the mesoporous nanowires with no heat treatment and heat treatment at 120°C and 250°C were carried out by CV and charge-discharge measurements as shown in Figure 5-6.

Figure 5-6 CV curves at the scan rate of 100 mV s^{-1} (a) and discharge curves at current density of 4 A g^{-1} (b) of mesoporous $\text{Co}(\text{OH})_2$ nanowire without heat treatment (b) and at annealing temperature of 120°C (c) and 250°C (d)

In Figure 5-6a, CV curves of the three mesoporous $\text{Co}(\text{OH})_2$ nanowires measured at a scan rate of 100 mV s^{-1} were displayed. The position of oxidation and reduction peaks without heat treatment (RT) and with heat treatment at 120°C were observed nearly at the same position. With a heat temperature at 250°C , the oxidation peak located at 0.45 V vanishes and a new peak appears at around 0.1 V , due to the dehydration of a large amount of $\text{Co}(\text{OH})_2$ to CoO . Figure 5-6b shows

discharge curves of the heat-treated mesoporous Co(OH)_2 nanowires measured at a current density of 4 A g^{-1} . The specific capacitance values were calculated to be 1180, 1086, and 461 F g^{-1} (in Table 5-1) corresponding to no heat treatment and heat-treated temperatures of 120°C and 250°C . Thus, an increase of heat treatment for the mesoporous Co(OH)_2 nanowires decreases the $O_{\text{Co(OH)}_2} / O_{\text{CoO}}$ atomic ratio, resulting in a decrease of the specific capacitance.

5.6 Effect of electrodeposition temperature

Mesoporous Co(OH)_2 nanowires were deposited at a deposition potential of -0.75V at different temperatures of 30°C , 50°C and 70°C to investigate the effect of electrodeposition temperature.

Polarized optical microscope (POM) was used to determine characteristic appearances and textures of the LLC phases. Figure 5-7 shows POM images of $\text{Co(NO}_3)_2$ LLC phases at the temperatures of 30°C , 50°C and 70°C , respectively. Figure 7a is the POM image at 30°C which shows focal conic textures with homocentric circles. This domain is called a solidified hexagonal phase. With the temperature increasing to 50°C , the homocentric circles disappeared and only smooth fan-like textures appeared (as shown in Figure 7b), which is a clear indication of hexagonal structure. In figure 7c, the LLC phase at 70°C exhibits a lamellar mesostructure according to the mosaic shape[112].

Figure 5-7 Polarized optical microscopy (POM) images of LLC phase at temperature of 30 °C, 50 °C and 70 °C

The structures of mesoporous nanowires deposited at 30 °C, 50 °C and 70 °C are displayed in Figure 5-8. All the mesoporous nanowires deposited from the different textures of the LLCs have the interlaced nanosheet structure. However, with increasing temperature, the density of the interlaced nanosheets becomes lower. The interlaced nanosheets became quite loosely packed at 70 °C as compared with those at 30 °C, implying that the packing of nanosheets has a dependence on the fluidity of the LLC.

Figure 5-8 TEM images of mesoporous Co(OH)_2 nanowires deposited in 30 °C, 50 °C and 70 °C

Figure 5-9a shows CV curves of mesoporous Co(OH)_2 nanowires deposited at a potential of -0.75V at temperatures of 30 °C, 50 °C and 70 °C, at a scan rate of 200

mV s^{-1} . The redox peak currents and potentials do not considerably vary with deposition temperature in the ranges of 30°C to 70°C . Discharge curves of the $\text{Co}(\text{OH})_2$ nanowires deposited at 30°C , 50°C and 70°C at a current density of 4 A g^{-1} are shown in Figure 5-9b. The specific capacitance values were calculated to be 986, 1180, and 984 F g^{-1} (in Table 1) corresponding to the deposition temperatures of 30°C , 50°C and 70°C respectively. The mesoporous $\text{Co}(\text{OH})_2$ nanowire deposited at 50°C shows the highest capacitance. This result may come from proper packing density of interlaced nanosheets at the temperature.

Figure 5-9 CV curves at the scan rate of 200 mV s^{-1} (a) and discharge curves at current density of 4 A g^{-1} (b) of mesoporous $\text{Co}(\text{OH})_2$ nanowires deposited in 30°C , 50°C and 70°C LLC phase

5.7 Characterization of mesoporous $\text{Co}(\text{OH})_2$ nanowire at an optimized condition

Based on the above results, an electrodeposition potential of -0.75 V and an electrodeposition temperature of 50°C were selected as an optimal condition for

mesoporous $\text{Co}(\text{OH})_2$ nanowire synthesis. Heat treatment was not carried out for the mesoporous $\text{Co}(\text{OH})_2$ nanowires.

Figure 5-10 Wide-angle XRD patterns (a), Low-angle XRD patterns (b), side-view (c), top-view (d) SEM images and TEM images (e) of mesoporous $\text{Co}(\text{OH})_2$ nanowires obtained at an optimized condition

Figure 5-10a shows XRD pattern of the $\text{Co}(\text{OH})_2$ nanowires. There are two peaks with indexes of (002) and (004) which are assigned to the diffraction of crystalline $\alpha\text{-Co}(\text{OH})_2$ [88, 151] (JCPDS No. 74-1057). Figure 5-10b displays low-angle XRD patterns of the LLC phase and deposited mesoporous $\text{Co}(\text{OH})_2$ nanowires. The two well-resolved peaks indexed as the (100) and (110) planes are shown in the XRD pattern of the LLC phase. The peaks located at 2θ of 1.51° and 2.64° corresponding to d-spacings of $58.4\text{\AA}$ and $33.4\text{\AA}$ respectively. The reciprocal

ratio of d-spacings is $1:\sqrt{3}$ that indicates a presence of hexagonal structure. A strong reflection peak at 2θ of 1.23° indexed as (100) plane is shown in the pattern of the synthesized mesoporous $\text{Co}(\text{OH})_2$ nanowires. The peak has a d-spacing of $71.7\text{\AA}$ and lattice parameter of 8.3nm .

The side-view and top-view FESEM images of mesoporous $\text{Co}(\text{OH})_2$ nanowires are shown in Figure 5-10c and Figure 5-10d. In Figure 5-10c, the nanowires were connected with the Ti/Si substrate tightly and leaned upon each other. The diameter of $\text{Co}(\text{OH})_2$ nanowires was observed to be around 65nm , which indicates the reverse duplication of the PAA template (in Figure 5-10d). Figure 5-10e shows the detailed structure of mesoporous $\text{Co}(\text{OH})_2$ nanowire by TEM. The interlaced nanosheets packed nanowire was clearly displayed. The upper-right image in Figure 5-10e shows the open-end and side-view of mesopores in the $\text{Co}(\text{OH})_2$ nanosheets. The light regions represent the pores, while the dark areas represent the electrodeposited $\text{Co}(\text{OH})_2$. The diameter of pores is around 3.5nm and the thickness of the pore wall is around 4.5nm . The lattice parameter is estimated to be around 8nm , which is consistent with the value obtained from the low-angle XRD patterns.

CV curves of the mesoporous $\text{Co}(\text{OH})_2$ nanowires measured at scan rates of 200, 100, 50 and 10 mV s^{-1} , respectively, are displayed in Figure 11a. In each scan rate, a pair of redox peaks was observed. Chronopotential measurements were also carried out at discharge current densities of 20A g^{-1} , 10A g^{-1} and 4A g^{-1} to characterize the capacitance of the mesoporous $\text{Co}(\text{OH})_2$ nanowire electrodes, as shown in Figure 11b. The specific capacitance was calculated to be 1112, 1158

and 1180 F g^{-1} at the current densities of 4, 10 and 20 A g^{-1} , respectively, indicating that the current density in the ranges does not considerably influence the capacitance of the mesoporous Co(OH)_2 wires.

Figure 5-11 CV curves at different scan rate (a) and discharge curves at different current density (b) of mesoporous Co(OH)_2 nanowires obtained at optimized condition

The cycle life of the mesoporous Co(OH)_2 nanowires was examined by charge-discharge measurements at a current density of 4 A g^{-1} as shown in Figure 5-12a. After 1000 cycles, the specific capacitance still kept 613 F g^{-1} , which is still high as compared with those for Co(OH)_2 obtained from other methods [149, 153, 154]. XPS was utilized to analyze the chemical state of mesoporous Co(OH)_2 nanowires after 1000 cycles. Figure 5-12b shows the Co 2p spectra of as-prepared and used (after 1000 cycles) Co(OH)_2 nanowires. After 1000 cycles, two main Co 2p spectrums still existed, while the peaks shifted to lower binding energy, which are from 797 eV ($\text{Co } 2p_{1/2}$) and 781.1 eV ($\text{Co } 2p_{3/2}$) to 795.4 eV ($\text{Co } 2p_{1/2}$) and 780.4 eV ($\text{Co } 2p_{3/2}$). The distance between the two peaks decreased from 15.9 eV (ΔE_b) to

15.0eV. Moreover, the satellite peaks, which indicate plasmon losses and final state effects, shifted to higher binding energy.

Figure 5-12 Cycle life of mesoporous Co(OH)₂ nanowires obtained at optimized condition(a); XPS Co 2p_{1/2}, Co 2p_{3/2} spectra of as-prepared and used Co(OH)₂ nanowires (b); O1s spectra of as-prepared (c) and used (d) Co(OH)₂ nanowires.

The results may come from the dehydration of Co(OH)₂ during the charge-discharge process. During the process, Eq. 5-4 could be divided into two steps:

The dehydration process could happen in the steps. Thus, after 1000 cycles, the composition of nanowires could contain Co(OH)₂, CoOOH and CoO chemical

states. The presence of CoOOH and CoO may cause the change of Co(OH)₂ spectrum [162]. Figure 5-12c and 5-12d show XPS of O 1s spectra and curve fitting results of as-prepared and used (after 1000 cycles) Co(OH)₂ nanowires. The atomic ratio of $O_{Co(OH)_2} / O_{CoO}$ is calculated to be 2.02 for the used nanowires and 9.23 for the as-prepared nanowires. The $O_{Co(OH)_2} / O_{CoO}$ ratio significantly decreased after 1000 cycles, indicating that the dehydration of Co(OH)₂ is a major reason for the capacitance fading. In addition, the loss and collapse of the soft mesoporous nanowires could also cause the capacitance fading.

5.8 Conclusion

Mesoporous Co(OH)₂ nanowires have been successfully synthesized by a dual template method at various conditions. From the results, it was found that electrodeposition potential and heat treatment temperature have crucial effects on the chemical states and capacitance of the mesoporous nanowires, while electrodeposition temperature has a slight influence on the structure of the nanowires. The maximum supercapacitance is 1180F g⁻¹ at a current density of 4A g⁻¹. Thus, the mesoporous Co(OH)₂ nanowires have the potential to be utilized as electrodes for supercapacitors.

Chapter 6 One-step Dual-template Synthesis of Platinum on Mesoporous Carbon Nanowires for Electrocatalysts

Reprinted from International Journal of Hydrogen Energy, Vol38, T. Xue, Z. P. Sun, L. Wei, X. Wang, J.-M. Lee, One-step dual-template synthesis of Platinum on mesoporous carbon nanowires for electrocatalysts, 2754-2759, Copyright (2013) Hydrogen Energy Publications.

In order to investigate the assistance of mesoporous nanowires structure on electrochemical catalysis, the one-step methodology has been utilized to fabricate platinum catalysts on well-aligned mesoporous carbon nanowires (Pt/MCNWs) in dual templates which are the combination of porous anodic alumina (PAA) hard template and triblock polymer ethanol solution as soft template with evaporation-induced self-assembly technique.

Over the few past decades, electro-catalysts as electrode materials have been attracting much attention for application in small portable electronic devices [163-165].

For methanol oxidation, catalysts have several issues which need to be overcome: for example, carbon monoxide generated from methanol oxidation blocks the active sites of catalysts to prevent the further oxidation of methanol[166].

In order to improve the poison resistance of catalysts, many efforts such as metal doping[167], materials supporting[168], and surface area extending[79] have been attempted extensively.

Among all the candidates of electrode materials, carbon-supported catalysts have been investigated with good catalytic performance because carbon supports have a high surface area, ordered structure, and good stability [169]. There is a wide range of potentially useful carbon supports, such as; carbon black[170], active carbon[171], carbon nanotubes (CNTs)[172], carbon nanofibres (CNFs)[173], mesoporous carbon[174, 175] and graphene[176] etc., that have already been investigated in the utilization as electrode materials in methanol oxidation. As compared with other carbon supports, carbon nanotubes (CNTs) have been given much attention as a catalyst support due to the good electrochemical conductivity, stability and large specific surface area (SSA). Fabrication of electrocatalyst for fuel cells with carbon nanotubes as support has been investigated by many researchers and has shown good performances[172]. Nevertheless, the multi-wall carbon naotubes (MWCNTs) have a superior conductivity with a low SSA, and single-wall carbon nanotubes (SWCNTs) have a large SSA but with a low conductivity, which limit the development of electrocatalysts. Ordered mesoporous carbons (MCs) as supporting materials have also been of great interest recently because of their high SSA, ordered pore structures, uniform pore size, and interconnected pore networks. It has been proved that the ordered MCs present a high catalytic activity towards the CO oxidation and the methanol oxidation as comparing with the commercial catalysts [174, 175]. In order to combine the

advantages of CNTs and ordered MCs together, mesoporous carbon nanowires (MCNWs) characterized with high specific surface area and good gas permeability have recently been developed by researchers. These advantages would let them to be good support candidates for electrocatalysts[81, 82, 177, 178].

In this paper, we fabricated a mesoporous carbon nanowires with loading Pt particles (Pt/MCNWs) by confined soft template in cylindrical pores of porous anodic alumina (PAA) membranes with evaporation-induced self-assembly synthesis[179]. The Pt reduction and MCNWs formation were occurred in the one-step method. Pt nanoparticles were dispersed homogeneously on the supporting MCNWs without changing the formation or quality of MCNWs. TEM confirmed the ordered porous nanowires structures with homogeneous Pt particles dispersed thereon. The electrochemical properties of the Pt/MCNWs as electrode materials were investigated by cyclic voltammetry (CV) techniques. The peak currents ratio (I_f/I_b) between forward (I_f) and backward (I_b) currents is as high as 2.06 for 10wt% Pt/MCNWs, which reveals the excellent poison resistant properties. It indicates the Pt/MCNW is a promising material in electrocatalysis application.

6.1 Resol preparation

A soluble phenolic resin (resol) with a low-molecular-weight ($MW \leq 500$), as a carbon precursor, was prepared using a typical polymerization method reported previously.[180] Phenol (0.61 g) was melted at 40–42° C while adding 20wt% NaOH (0.13 g) and mixed with formalin (37 wt%, 1.05 g) at 70° C for 1 h while

stirring. After the mixture was cooled to room temperature, 0.6M HCl was used to adjust pH to neutral (7.0). Water was then removed under vacuum below 50° C.

6.2 Block copolymer LLC and AAO templates preparation

Triblock copolymer poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (EO₁₀₆-PO₇₀-EO₁₀₆, Pluronic 127; 1.00 g) was dissolved in ethanol (20.0 g), and then was mixed with resol precursors by stirring for 10 min to form a homogeneous solution with the molar composition of F127/phenol/formaldehyde of 0.010-0.015: 1: 2. Chloroplatinic acid (H₂PtCl₆·6H₂O) was added in proper amounts with different weight percentages.

Porous anodic alumina (PAA) template with 50-60nm pore diameter was synthesized by anodizing Al/Ti/Si substrate in 0.3 mol L⁻¹ oxalic acid solution at 40 V and 4 °C for 4 hrs.

6.3 Electrode preparation

PAA/Ti/Si plate was immersed into the prepared triblock copolymer solution and let the ethanol to evaporate at room temperature for 24 h. The viscous surface of PAA was cleaned with ethanol to prevent blocking. The PAA template with resol monomers was then heated in an oven at 100° C for 24 h to thermopolymerize the phenolic resins. The resulting products were calcined at 350° C under hydrogen atmosphere with a flow rate of 50 ml·min⁻¹ for 5 h with a temperature increase rate of 1° C min⁻¹ in a tube furnace. The purpose is to obtain the porous structure and to decompose the amphiphilic triblock copolymer. Further carbonization was carried

out with a temperature increase rate of $2^{\circ}\text{C min}^{-1}$ to 600°C for 5 h. Finally, the PAA template was removed by using 1M NaOH and the samples were dried in an ambient atmosphere as electrode for directly electrochemical measurement.

6.4 Structure and morphology analysis

In this project, one-step strategy is employed to synthesize the Pt/MCNWs, hence, hydrogen gas is selected to be not only a reducing agent to convert $(\text{PtCl}_6)^{4-}$ into Pt^0 , but a protector to prevent carbon from further oxidization under a high temperature in a tubular reactor. The reactions are as follows:

Figure 6-1 X-ray Diffraction patterns of mesoporous 10 wt% Pt on mesoporous carbon nanowire (MCNW) and pure MCNW

XRD was employed to investigate carbon and Pt crystalline structures as shown in Figure 6-1. The five main peaks with indexes of (111), (200), (220), (311) and (222) can be assigned to the diffraction peaks at 39.7° , 46.2° , 67.4° , 81.3° and 85.7° of fcc Pt [181, 182] (JCPDS No. 04-0802) respectively and one low-intensity peak at 20° is labeled as (002) planes of FDU-15 graphitic carbon[180].

Figure 6-2 Raman spectra of mesoporous carbon supported Pt in different weight percentage, pure carbon nanowire, and 10wt% Pt/Vulcan XC-72

Figure 6-2 shows the Raman spectrum of MCNW, Pt/MCNWs, and 10wt% Pt/Vulcan XC-72. There are two characteristic vibration bands corresponding to defect-related band (D band) and graphite-like band (G band). The existing D band at 1367 cm^{-1} indicates the structural defects in MCNW. G band overlapped with D

band at 1592 cm⁻¹. This corresponds to planar vibrations of carbon atoms and is present in most graphite-like materials[183]. The relative intensities of G band to D band indicate that the synthesized MCNWs have high graphitization degree as compared with the commercial XC-72. With increasing of Pt weight percentage, the intensity of Raman spectrums decreases gradually. The decreasing rate of intensity is summarized in Table 6-1 and estimated by the following equation:

$$\frac{MCNW \text{ Intensity} - Pt / MCNW \text{ Intensity}}{MCNW \text{ Intensity}} \times 100\% \quad (6-3)$$

As comparing G band with D band, the decreasing rate of intensity at different Pt percentage (as shown in Table 6-1) is consistent. All the MCNWs show a constant ratio of the two bands, implying that the addition of Pt doesn't change the structure and graphitization degree of MCNWs. The Pt coverage leads to the decrease in the Raman intensity of MCNW.

Table 6-1 Decreasing rate of Raman spectrum intensity

	Decreasing rate	Decreasing rate
	Estimated by D band	Estimated by G band
MCNW	0	0
5%Pt/MCNW	20.1%	19.9%
10%Pt/MCNW	30.9%	27.3%
20%Pt/MCNW	50.8%	50.0%

The surface morphologies of Pt/MCNW were examined by FESEM as shown in Figure 6-3. Well-aligned nanowire structures can be observed clearly from a top view (Figure 6-3a) and a side view (Figure 6-3b) of images. The outer walls of the MCNWs partially decoil and connect with each other. The diameter of the Pt/MCNWs ranges from 55nm to 85nm after removing the PAA template with pores diameter of around 50-60nm.

Figure 6-3 SEM images of 10wt%Pt/MCNW nanowires: (a) top view and (b) side view.

The diameter extension induced by decoiling could be explained as the restriction effect from hard templates proposed by Zheng M. et al. [82] Since the hydroxyl groups exist both in the phenolic resin and inner surface of PAA pores, the interactive force between resin and PAA would influence the structure construction of MCNWs during the carbonization process.

With temperature increasing in the heat treatment process, the soft template was removed leaving the mesopores behind and phenolic resin was carbonized with shrinkage. The phenolic resin could not shrink freely due to the interaction with the PAA. Hence, the core of the nanowires shrunk and the shell still connected with PAA template. It would leave the inner mesopores smaller than the outer ones.

After removing the PAA template, the shell lost the restriction, and it would extend on account of lacking attractive force with core of nanowires.

Figure 6-4 TEM images of (a) MCNW, (b) 5wt% Pt/MCNW, (c) 10wt% Pt/MCNW and (d) 20wt%Pt/MCNW in different magnification.

This phenomenon was further illustrated by TEM as displayed in Figure 4. Figure 4a, 4b, 4c and 4d show the structural details of MCNWs, 5wt% Pt/MCNWs, 10wt% Pt /MCNWs and 20wt% Pt/MCNWS at different magnifications individually. The uniform black dots on the surface of MCNWs are the Pt particles. It can be distinguished that the density of Pt particles becomes higher with increasing the weight percentage of Pt, and even, the particles of 20 wt% Pt partially cover the pores of MCNWs because of its high density. The pores at the edge of the MCNWs are bigger than pores in the interior part apparently. Therefore, it further proves the interaction exists between MCNWs and the PAA template as shown in SEM. The width of mesopores at the edge of MCNWs decreases at least 2 nm with the weight percentage of Pt increasing from 0wt% to 10wt%. In Fig. 4d, there are no size differences between the edge pores and middle pores in the 20 wt% Pt/MCNWs, indicating that adding Pt reduces the hydroxyl group number of resin to weaken the attractive force between the wires and hard template.

6.5 Electrochemical properties

To roughly estimate the active surface area of Pt/MCNWs, the electrochemical method was utilized (because of its advantages for proving the catalytic activity of surface) instead of BET method (which only evaluates the specific surface area of materials physically).

Figure 6-5 shows the cyclic voltammograms (CV) of Pt/MCNWs with different Pt weight percentages measured in 1.0M H₂SO₄ aqueous solution at a scan rate of 100 mV s⁻¹. The CV curves display the typical feature of the

polycrystalline nature of Pt. On the basis of the Pt weight measured by ICP and the assumption that a monolayer of hydrogen corresponds to an adsorption charge of $210 \mu\text{C}\cdot\text{cm}^{-2}$, the electrochemically active surface areas (EASA) of the different Pt weight percentages in MCNWs were estimated to be $23.4 \text{ m}^2 \text{ g}^{-1}$, $46.7 \text{ m}^2 \text{ g}^{-1}$ and $56 \text{ m}^2 \text{ g}^{-1}$ which correspond to 5 wt% Pt, 10 wt% Pt and 20 wt% Pt respectively. It could attribute to the good dispersion of Pt particles and the high graphitization degree as compared with the commercial Pt/Vulcan XC-72 ($29 \text{ m}^2 \text{ g}^{-1}$, 10wt%Pt).

Figure 6-5 Cyclic voltammetry (CV) curves for Pt/MCNW and commercial 10wt% Pt/Vulcan XC-72 in 1M H_2SO_4 aqueous solution at 100mV s^{-1} . H_a : hydrogen adsorption, H_d : hydrogen desorption, O_a : formation of Pt-O, O_d : reduction of Pt-O.

Figure 6-6 shows the electrocatalytic activity of Pt/MCNWs for the methanol oxidation which was investigated in a 0.5M H₂SO₄ aqueous solution containing 1M CH₃OH by using CV technique. It shows the 20wt% Pt/MCNWs possess the highest peak current density compared with 10wt% Pt and 5wt% Pt/MCNWs, which means the improvement of catalytic activity and efficiency is dependent on increased Pt amounts. There are two anodic peaks (forward and backward peaks) existing in the CV curves. The peak currents for these two peaks are marked as I_f and I_b accordingly. I_f is assigned to be the forward peak current of methanol oxidation and I_b is due to the backward anodic peak current produced by oxidized methanol.

Figure 6-6 Cyclic voltammetry (CV) curves of Pt/MCNW and 10wt% Pt/Vulcan XC-72 in 0.5 M H₂SO₄ + 1 M CH₃OH aqueous solution at 100mV s⁻¹

The I_f/I_b ratio is a very important factor to evaluate the tolerance of the catalysts to the carbonaceous species accumulation. A higher I_f/I_b value implies more completed oxidation of methanol with less excessive accumulation of residual carbonaceous species on the catalyst surface. The mechanism of methanol electro-oxidation on Pt catalyst can be explained as follows:[184, 185]

In the catalytic process, carbon monoxide, as the most abundant surface intermediate chemisorbing on the Pt surface, leads to a decreased activity of the catalyst surface. From Fig. 6, the I_f/I_b ratio of 5wt% Pt, 10wt% Pt, 20wt% Pt and 10wt% Pt/Vulcan XC-72 is obtained to be 1.88, 2.06, 1.07 and 1.09 at scan rate of 100mV s^{-1} respectively. The 10 wt% Pt/MCNWs achieve the highest I_f/I_b value, which is significantly higher than the corresponding value (~ 1.09) for the commercial Pt-XC72 and the bulk Pt nanowires[79]. The I_f/I_b value of 2.06 measured for the 10wt% Pt/MCNWs catalyst has also been found to be higher than 1.42 for Pt-CNT samples prepared in a supercritical fluid[186] and 1.18 for the Pt-MCNTs[185] reported previously. Even, the I_f/I_b value of 2.06 we obtained is still higher than 1.83 for the Pt-CNT-Pt[181] and 1.77 for the mesoporous Pt nanowire[79], indicating that methanol is almost completely oxidized into carbon dioxide and the concentration of intermediate species on the mesoporous Pt/C nanowires is relatively low. Hence, MCNWs could be an excellent supporting media to reduce $(CO)_{ads}$ accumulation on the catalyst and enhance the efficiency of

Pt particles. After CV scanning for hundreds of cycles, the peak current of Pt/MCNWs still has been kept with the replacement of the fresh methanol electrolyte. It further illustrates the good long-term stability of Pt/MCNWs.

6.6 Conclusion

In this paper, one-step dual template method has been introduced to synthesize Pt/MCNWs with outstanding catalytic activity. The well dispersed Pt particles on unique mesoporous carbon nanowires was investigated by TEM. From the electrochemical measurements, the MCNWs have been proved to be a good carbon support, and the Pt/MCNWs show a high active surface area and excellent electrocatalytic activity with an enhanced carbonaceous species tolerance, which have the potential application to be utilized as an electrocatalyst in methanol oxidation.

Chapter 7 Conclusion and Future Research

In recent years, synthesis of ordered nanomaterials with high specific surface area has received increasing interest because of their potential applications in catalysis, selective separation and electrochemical devices. Among all fabrication methods for synthesizing nanostructured materials, template synthesis has been investigated to be a fascinating and versatile way for its simple casting procedure which can create shape- and size-uniform nanoarrays. The corresponding template can be looked as a nanoscaled mold to transfer the structures from templates to desired materials. Therefore, morphology of aimed nanomaterials can be controlled easily and effectively by template synthesis. In the candidates of templates family, porous anodic alumina (PAA) templates as hard templates are most famous to be used in fabricating ordered nanowire and nanotube arrays, and while the lyotropic liquid crystalline (LLC) phases of surfactant as soft templates are versatile to use in synthesizing mesoporous films.

In this thesis, mesoporous dual layers of polyaniline (PANI) supported Cu_2O films have been designed and synthesized for the first time. The band gap of mesostructure Cu_2O /PANI dual layers (1.86 eV) has been proved to be narrower than mesoporous Cu_2O single layer (2.41 eV). This decrease indicates PANI as a supporting layer enhances efficiency of electron transfer. $\text{Se}_{0.5}\text{Te}_{0.5}$ was selected to be supported by the PANI, because band gap of $\text{Se}_x\text{Te}_{1-x}$ also can be adjusted with changing the ratio of Te to Se. It shows a versatile way to control band gap of

synthesized materials. The contribution of mesoporous PANI layer has been confirmed further in mesoporous $\text{Se}_{0.5}\text{Te}_{0.5}$ -PANI dual-layer films. Hence, PANI support dual-layer mesoporous films are promising materials which can be applied into photocatalysis, solar cells and chemical sensors.

In our studies, mesoporous nanowires are expected to be synthesized by the dual templating method with combining LLC phase and PAA membrane. This synthetic approach is considered to have wide application in extensive area because of its feasibility not only including catalysis, supercapacitors, but semiconductors, magnetic storage and fuel cells etc. as well. In this thesis, mesoporous $\text{Co}(\text{OH})_2$ nanowires have been produced with high specific capacitance of 1180F g^{-1} at current density of 4A g^{-1} . The optimized synthesis conditions of mesoporous $\text{Co}(\text{OH})_2$ nanowires have been investigated. XPS and TEM were employed to explore effects of experimental conditions such as temperature and deposition potentials etc. Well-aligned mesoporous Pt/MCNWs were synthesized in dual templates which combine PAA hard template and triblock polymer as soft template. Pt/MCNWs show enhanced catalytic performance as compared with commercial one. All of above indicate both large specific area and mesoporous architecture of nanowire are key factors to affect the electrochemical behaviors.

As mentioned above, we have designed and synthesized Pt/MCNWs, which have been proved a promising candidate to utilize in methanol oxidation with enhanced carbonaceous species tolerance. However, Pt exists everywhere in MCNWs, including inside and outside, which could decrease the efficiency of Pt. In order to improve the electrochemical performance, Pt loading on mesoporous

carbon nanotubes (Pt/MCNTs) was designed. Pt/MCNTs are supposed to have higher active surface area comparing with Pt/MCNWs. And now, we are still working on this project.

The dual template methodology is a quite convenient method to achieve mesoporous nanowires with high specific surface area and enhanced electrochemical performance. In the future, we will still focus on this field.

Firstly, in our previous study, electrode materials related to capacitors have been focused, but only mesoporous $\text{Co}(\text{OH})_2$ nanowires have been synthesized and characterized successfully. The other capacitor materials such as $\text{Ni}(\text{OH})_2$, MnO_2 , RuO_2 etc. need to be developed and studied further.

Secondly, it is well-known that pure nanoscaled Pt do not fit for commercial applications (e.g. Direct Methanol Fuel Cell), hence, Pt need to be partially replaced by other materials such as Ru, Pd, Fe etc to form PtX alloy (M=Ru, Pd, Fe etc.). In our current study, Pt/MCNWs and Pt/MCNTs have been synthesized. In order to utilize the synthesized materials into practical applications, PtX/MCNTs will be designed and synthesized later.

Thirdly, all of our electrochemical testing has been operated in three-electrode system. In order to reflect the real capacitance of the capacitor materials, the two-electrode devices will be designed and set up for further investigation.

Finally, we shall enlarge the research fields into semiconductors and magnetic storage. Besides PAA/Ti/Si template, we still have paid much attention to conductive ITO glass supporting PAA (PAA/ITO) templates. That is because semiconductive nanowires loaded on ITO glass have potential to be applied in solar

cells, photocatalysis and chemical sensors etc. In our previous research, it is not easy to coat Al on the surface of ITO glass tightly. During the oxidation procedure of Al to Al_2O_3 , the Al surface separates with ITO glass continuously. Hence, to seek a new coating technique is necessary. If this problem could be solved, the mesoporous semiconductive nanowires would be synthesized and characterized in the future.

References

- [1] A.A.S. Edelstein, R.R.C. Cammarata, Nanomaterials: Synthesis, Properties and Applications, Second Edition, Taylor & Francis Group, 1998.
- [2] G.Z. Cao, Y. Wang, Nanostructures and Nanomaterials: Synthesis, Properties, and Applications (2Nd Edition), World Scientific, 2011.
- [3] B. Bhushan, Springer Handbook of Nanotechnology, Springer Science+Business Media, Incorporated, 2007.
- [4] R.M. Penner, C.R. Martin, J. Electrochem. Soc., 133 (1986) 2206-2207.
- [5] C.R. Martin, Science, 266 (1994) 1961-1966.
- [6] C.R. Martin, Acc. Chem. Res., 28 (1995) 61-68.
- [7] J. C. Hulteen, C.R. Martin, J. Mater. Chem., 7 (1997) 1075-1087.
- [8] C.-G. Wu, T. Bein, Science, 264 (1994) 1757-1759.
- [9] W. Cahalane, M.M. Labes, Chem. Mater., 1 (1989) 519-522.
- [10] C.G.J. Koopal, B. de Ruiter, R.J.M. Nolte, J. Chem. Soc., Chem. Commun., 0 (1991) 1691-1692.
- [11] R.P. Burford, T. Tongtam, J Mater Sci, 26 (1991) 3264-3270.
- [12] M. Granström, O. Inganäs, Synth. Met., 55 (1993) 460-465.
- [13] G.S. Attard, J.C. Glyde, C.G. Göltner, Nature, 378 (1995) 366-368.
- [14] T.L. Wade, J.-E. Wegrowe, The European Physical Journal - Applied Physics, 29 (2005) 3-22.
- [15] R. Liu, J. Duay, S.B. Lee, Chem. Commun., 47 (2011) 1384-1404.
- [16] M. Wan, Conducting Polymers with Micro Or Nanometer Structure, Springer London, Limited, 2008.
- [17] J. Zhou, M.J. Scott, Z. Hu, G. Peng, E. Munck, R.H. Holm, J. Am. Chem. Soc., 114 (1992) 10843-10854.
- [18] L. Cao, H.Z. Chen, H.B. Zhou, L. Zhu, J.Z. Sun, X.B. Zhang, J.M. Xu, M. Wang, Adv. Mater., 15 (2003) 909-913.

- [19] M. Fu, Y. Zhu, R. Tan, G. Shi, *Adv. Mater.*, 13 (2001) 1874-1877.
- [20] Y. Ma, J. Zhang, G. Zhang, H. He, *J. Am. Chem. Soc.*, 126 (2004) 7097-7101.
- [21] F.S. Bates, G.H. Fredrickson, *Annu. Rev. Phys. Chem.*, 41 (1990) 525-557.
- [22] H. Kosonen, J. Ruokolainen, M. Knaapila, M. Torkkeli, K. Jokela, R. Serimaa, G. ten Brinke, W. Bras, A.P. Monkman, O. Ikkala, *Macromolecules*, 33 (2000) 8671-8675.
- [23] A.D.W. Carswell, E.A. O'Rea, B.P. Grady, *J. Am. Chem. Soc.*, 125 (2003) 14793-14800.
- [24] J.F. Hulvat, S.I. Stupp, *Angew. Chem. Int. Ed.*, 42 (2003) 778-781.
- [25] L. Huang, Z. Wang, H. Wang, X. Cheng, A. Mitra, Y. Yan, *J. Mater. Chem.*, 12 (2002) 388-391.
- [26] L. Qu, G. Shi, F.e. Chen, J. Zhang, *Macromolecules*, 36 (2003) 1063-1067.
- [27] L. Qu, G. Shi, *Chem. Commun.*, 0 (2003) 206-207.
- [28] M. Lai, D.J. Riley, *J. Colloid Interface Sci.*, 323 (2008) 203-212.
- [29] H. Masuda, F. Hasegawa, S. Ono, *J. Electrochem. Soc.*, 144 (1997) L127-L130.
- [30] V.P. Parkhutik, V.I. Shershulsky, *J. Phys. D: Appl. Phys.*, 25 (1992) 1258.
- [31] A. Sugawara, D. Streblechenko, M. McCartney, M.R. Scheinfein, *Magnetics, IEEE Transactions on*, 34 (1998) 1081-1083.
- [32] H. Masuda, K. Fukuda, *Science*, 268 (1995) 1466-1468.
- [33] G.S. Attard, P.N. Bartlett, N.R.B. Coleman, J.M. Elliott, J.R. Owen, J.H. Wang, *Science*, 278 (1997) 838-840.
- [34] P.J. Collings, *Liquid Crystals: Nature's Delicate Phase of Matter*, Princeton University Press, 2002.
- [35] C. Koughia, S. Kasap, P. Capper, *Springer Handbook of Electronic and Photonic Materials*, Springer, 2007.
- [36] P.J. Collings, M. Hird, *Introduction to Liquid Crystals: Chemistry and Physics*, CRC PressINC, 1997.

- [37] M.J. Rosen, *Surfactants and Interfacial Phenomena*, Wiley, 2004.
- [38] N. Garti, *Self-Assembled Supramolecular Architectures: Lyotropic Liquid Crystals*, Wiley, 2012.
- [39] J.N. Israelachvili, 20 - Soft and Biological Structures, in: *Intermolecular and Surface Forces (Third Edition)*, Academic Press, San Diego, 2011, pp. 535-576.
- [40] F. Bender, T.C. Chilcott, H.G.L. Coster, D.B. Hibbert, J.J. Gooding, *Electrochim. Acta*, 52 (2007) 2640-2648.
- [41] P.N. Bartlett, J. Marwan, *Chem. Mater.*, 15 (2003) 2962-2968.
- [42] M. Sofos, J. Goldberger, D.A. Stone, J.E. Allen, Q. Ma, D.J. Herman, W.W. Tsai, L.J. Lauhon, S.I. Stupp, *Nature Materials*, 8 (2009) 68-75.
- [43] T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.*, 63 (1990) 988-992.
- [44] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, *J. Am. Chem. Soc.*, 114 (1992) 10834-10843.
- [45] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, *Science*, 279 (1998) 548-552.
- [46] N.R.B. Coleman, G.S. Attard, *Microporous Mesoporous Mater.*, 44-45 (2001) 73-80.
- [47] A. Monnier, F. Schüth, Q. Huo, D. Kumar, D. Margolese, R.S. Maxwell, G.D. Stucky, M. Krishnamurty, P. Petroff, A. Firouzi, M. Janicke, B.F. Chmelka, *Science*, 261 (1993) 1299-1303.
- [48] Q. Huo, D.I. Margolese, U. Ciesla, P. Feng, T.E. Gier, P. Sieger, R. Leon, P.M. Petroff, F. Schuth, G.D. Stucky, *Nature*, 368 (1994) 317-321.
- [49] D.M. Antonelli, J.Y. Ying, *Angewandte Chemie International Edition in English*, 34 (1995) 2014-2017.
- [50] U. Ciesla, S. Schacht, G.D. Stucky, K.K. Unger, F. Schüth, *Angewandte Chemie International Edition in English*, 35 (1996) 541-543.
- [51] P.N. Bartlett, B. Gollas, S. Guerin, J. Marwan, *PCCP*, 4 (2002) 3835-3842.

- [52] I. Nandhakumar, J.M. Elliott, G.S. Attard, *Chem. Mater.*, 13 (2001) 3840-3842.
- [53] T. Gabriel, I.S. Nandhakumar, G.S. Attard, *Electrochem. Commun.*, 4 (2002) 610-612.
- [54] A. H. Whitehead, J. M. Elliott, J. R. Owen, G. S. Attard, *Chem. Commun.*, (1999) 331-332.
- [55] P.N. Bartlett, P.N. Birkin, M.A. Ghanem, P. de Groot, M. Sawicki, *J. Electrochem. Soc.*, 148 (2001) C119-C123.
- [56] P.A. Nelson, J.M. Elliott, G.S. Attard, J.R. Owen, *Chem. Mater.*, 14 (2002) 524-529.
- [57] H. Luo, J. Zhang, Y. Yan, *Chem. Mater.*, 15 (2003) 3769-3773.
- [58] P. Yang, D. Zhao, D.I. Margolese, B.F. Chmelka, G.D. Stucky, *Nature*, 396 (1998) 152-155.
- [59] R. Ryoo, S.H. Joo, S. Jun, *The Journal of Physical Chemistry B*, 103 (1999) 7743-7746.
- [60] L. Huang, H. Wang, Z. Wang, A. Mitra, D. Zhao, Y. Yan, *Chem. Mater.*, 14 (2002) 876-880.
- [61] L.M. Huang, H.T. Wang, Z.B. Wang, A. Mitra, K.N. Bozhilov, Y.S. Yan, *Adv. Mater.*, 14 (2002) 61-64.
- [62] P.V. Braun, S.I. Stupp, *Mater. Res. Bull.*, 34 (1999) 463-469.
- [63] P.V. Braun, P. Osenar, V. Tohver, S.B. Kennedy, S.I. Stupp, *J. Am. Chem. Soc.*, 121 (1999) 7302-7309.
- [64] X. Jiang, Y. Xie, J. Lu, L. Zhu, W. He, Y. Qian, *Chem. Mater.*, 13 (2001) 1213-1218.
- [65] T. Kijima, T. Yoshimura, M. Uota, T. Ikeda, D. Fujikawa, S. Mouri, S. Uoyama, *Angew. Chem. Int. Ed.*, 43 (2004) 228-232.
- [66] F. Chen, L. Huang, Q. Li, *Chem. Mater.*, 9 (1997) 2685-2686.
- [67] J.W. Diggle, T.C. Downie, C.W. Goulding, *Chem. Rev.*, 69 (1969) 365-405.
- [68] F. Keller, M.S. Hunter, D.L. Robinson, *J. Electrochem. Soc.*, 100 (1953) 411-419.

- [69] W.B. Yang, Y.L. Zhou, X.H. Tang, B.J. Zhang, G. Lei, *Journal of Experimental Nanoscience*, 2 (2007) 207-214.
- [70] X. Li, G. Meng, Q. Xu, M. Kong, X. Zhu, Z. Chu, A.-P. Li, *Nano Lett.*, 11 (2011) 1704-1709.
- [71] N. Kumar, G.D. Varma, R. Nath, A.K. Srivastava, *Appl. Phys. A*, 104 (2011) 1169-1174.
- [72] P.D. Q Ashton Acton, *Advances in Nanotechnology Research and Application: 2011 Edition*, Scholarly Editions, 2012.
- [73] L. Yuan, S. Meng, Y. Zhou, Z. Yue, *Journal of Materials Chemistry A*, (2013).
- [74] J.Y. Miao, Y. Cai, Y.F. Chan, P. Sheng, N. Wang, *The Journal of Physical Chemistry B*, 110 (2006) 2080-2083.
- [75] K.V. Heber, *Electrochim. Acta*, 23 (1978) 127-133.
- [76] O. Jessensky, F. Müller, U. Gösele, *J. Electrochem. Soc.*, 145 (1998) 3735-3740.
- [77] O. Rabin, P.R. Herz, Y.M. Lin, A.I. Akinwande, S.B. Cronin, M.S. Dresselhaus, *Adv. Funct. Mater.*, 13 (2003) 631-638.
- [78] Y. Yamauchi, A. Takai, T. Nagaura, S. Inoue, K. Kuroda, *J. Am. Chem. Soc.*, 130 (2008) 5426-5427.
- [79] Y. Zhong, C.-L. Xu, L.-B. Kong, H.-L. Li, *Appl. Surf. Sci.*, 255 (2008) 3388-3393.
- [80] C. Xu, Y. Zhao, G. Yang, F. Li, H. Li, *Chem. Commun.*, (2009) 7575-7577.
- [81] M. Zheng, J. Cao, X. Ke, G. Ji, Y. Chen, K. Shen, J. Tao, *Carbon*, 45 (2007) 1111-1113.
- [82] M. Zheng, G. Ji, Y. Wang, J. Cao, S. Feng, L. Liao, Q. Du, L. Zhang, Z. Ling, J. Liu, T. Yu, J. Cao, J. Tao, *Chem. Commun.*, (2009) 5033-5035.
- [83] T. Xue, X. Wang, J.-M. Lee, *J. Power Sources*, 201 (2012) 382-386.
- [84] S.S. Djokic, *Electrodeposition: Theory and Practice*, Springer New York, 2010.

- [85] Y.D. Gamburg, Theory and Practice of Metal Electrodeposition, Springer New York, 2011.
- [86] Q. Xu, J.-J. Zhu, X.-Y. Hu, Anal. Chim. Acta, 597 (2007) 151-156.
- [87] J.M. Elliott, L.M. Cabuché, P.N. Bartlett, Anal. Chem., 73 (2001) 2855-2861.
- [88] W.-j. Zhou, J. Zhang, T. Xue, D.-d. Zhao, H.-l. Li, J. Mater. Chem., 18 (2008) 905-910.
- [89] D. Zhao, W. Zhou, H. Li, Chem. Mater., 19 (2007) 3882-3891.
- [90] Y. Yu, F.-P. Du, J.C. Yu, Y.-Y. Zhuang, P.-K. Wong, J. Solid State Chem., 177 (2004) 4640-4647.
- [91] W. Siripala, A. Ivanovskaya, T.F. Jaramillo, S.-H. Baeck, E.W. McFarland, Sol. Energy Mater. Sol. Cells, 77 (2003) 229-237.
- [92] B. Richard N, Sol. Energy Mater. Sol. Cells, 27 (1992) 361-368.
- [93] P. E. de Jongh, D. Vanmaekelbergh, J. J. Kelly, Chem. Commun., (1999) 1069-1070.
- [94] P. Kumar, P. Huber, J. Electrochem. Soc., 157 (2010) D172-D176.
- [95] W.-r. Lee, L. Piao, C.-H. Park, Y.S. Lim, Y.R. Do, S. Yoon, S.-H. Kim, J. Colloid Interface Sci., 342 (2010) 198-201.
- [96] M. Wei, J. Huo, Mater. Chem. Phys., 121 (2010) 291-294.
- [97] H. Yanagimoto, K. Akamatsu, K. Gotoh, S. Deki, J. Mater. Chem., 11 (2001) 2387-2389.
- [98] R.V. Kumar, Y. Mastai, Y. Diamant, A. Gedanken, J. Mater. Chem., 11 (2001) 1209-1213.
- [99] E.W. Bohannon, M.G. Shumsky, J.A. Switzer, Chem. Mater., 11 (1999) 2289-2291.
- [100] Z. Qi, J. Shan, G. Pickup Peter, Conducting Polymer-Supported Fuel Cell Catalysts, in: Conducting Polymers and Polymer Electrolytes, American Chemical Society, 2002, pp. 166-183.
- [101] A.Z. Sadek, W. Wlodarski, K. Shin, R.B. Kaner, K. Kalantar-Zadeh, Nanotechnology, 17 (2006) 4488-4492.

- [102] C.O. Baker, B. Shedd, R.J. Tseng, A.A. Martinez-Morales, C.S. Ozkan, M. Ozkan, Y. Yang, R.B. Kaner, *ACS Nano*, 5 (2011) 3469-3474.
- [103] B.J. Gallon, R.W. Kojima, R.B. Kaner, P.L. Diaconescu, *Angew. Chem. Int. Ed.*, 46 (2007) 7251-7254.
- [104] H.H. Zhou, S.Q. Jiao, J.H. Chen, W.Z. Wei, Y.F. Kuang, *J. Appl. Electrochem.*, 34 (2004) 455-459.
- [105] L.-J. Sun, X.-X. Liu, *Eur. Polym. J.*, 44 (2008) 219-224.
- [106] K.R. Prasad, N. Miura, *Electrochem. Solid-State Lett.*, 7 (2004) A425-A428.
- [107] X. Feng, C. Mao, G. Yang, W. Hou, J.-J. Zhu, *Langmuir*, 22 (2006) 4384-4389.
- [108] A.K. Wanekaya, W. Chen, N.V. Myung, A. Mulchandani, *Electroanalysis*, 18 (2006) 533-550.
- [109] J.J. Langer, M. Filipiak, J. Ke, cińska, J. Jasnowska, J. Włodarczak, B. Buładowski, *Surf. Sci.*, 573 (2004) 140-145.
- [110] G. Inzelt, M. Pineri, J.W. Schultze, M.A. Vorotyntsev, *Electrochim. Acta*, 45 (2000) 2403-2421.
- [111] Z. Chen, L. Xu, W. Li, M. Waje, Y. Yan, *Nanotechnology*, 17 (2006) 5254-5259.
- [112] K. Holmberg, *Handbook of applied surface and colloid chemistry*, John Wiley & Sons Inc, 2002.
- [113] K. Rajendra Prasad, N. Munichandraiah, *Synth. Met.*, 123 (2001) 459-468.
- [114] C.M.S. Izumi, A.M.D.C. Ferreira, V.R.L. Constantino, M.L.A. Temperini, *Macromolecules*, 40 (2007) 3204-3212.
- [115] W.-S. Huang, B.D. Humphrey, A.G. MacDiarmid, *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, 82 (1986) 2385-2400.
- [116] V. Gupta, N. Miura, *Electrochem. Commun.*, 7 (2005) 995-999.
- [117] L.C. Wang, N.R. de Tacconi, C.R. Chenthamarakshan, K. Rajeshwar, M. Tao, *Thin Solid Films*, 515 (2007) 3090-3095.

- [118] Y. Zhou, J.A. Switzer, *Scripta Mater.*, 38 (1998) 1731-1738.
- [119] T.D. Golden, M.G. Shumsky, Y. Zhou, R.A. VanderWerf, R.A. Van Leeuwen, J.A. Switzer, *Chem. Mater.*, 8 (1996) 2499-2504.
- [120] S.T. Tan, B.J. Chen, X.W. Sun, X. Hu, X.H. Zhang, S.J. Chua, *J. Cryst. Growth*, 281 (2005) 571-576.
- [121] K.V. Reddy, A.K. Bhatnagar, *J. Phys. D: Appl. Phys.*, 25 (1992) 1810.
- [122] K. Li, X. Meng, X. Liang, H. Wang, H. Yan, *J. Solid State Electrochem.*, 10 (2006) 48-53.
- [123] A.E. Bekheet, N.A. Hegab, M.A. Afifi, H.E. Atyia, E.R. Sharaf, *Appl. Surf. Sci.*, 255 (2009) 4590-4594.
- [124] A. Mendoza-Galván, E. García-García, Y.V. Vorobiev, J. González-Hernández, *Microelectron. Eng.*, 51–52 (2000) 677-687.
- [125] A.L. Dawar, J.C. Joshi, L. Narain, *Thin Solid Films*, 76 (1981) 113-118.
- [126] K. Tripathi, A.A. Bahishti, M.A. Majeed Khan, M. Husain, M. Zulfequar, *Physica B: Condensed Matter*, 404 (2009) 2134-2137.
- [127] H. El-Zahed, A. El-Korashy, M. Dongol, *Thin Solid Films*, 259 (1995) 203-211.
- [128] Z.H. Khan, M. Husain, *J. Alloys Compd.*, 486 (2009) 774-779.
- [129] V. Tsakova, D. Borissov, B. Rangelov, C. Stromberg, J.W. Schultze, *Electrochim. Acta*, 46 (2001) 4213-4222.
- [130] E. Bormashenko, R. Pogreb, S. Sutovski, A. Shulzinger, A. Sheshnev, A. Gladkikh, *Synth. Met.*, 139 (2003) 321-325.
- [131] S. Kazim, V. Ali, M. Zulfequar, M.M. Haq, M. Husain, *Curr. Appl. Phys.*, 7 (2007) 68-75.
- [132] S.S. Joshi, C.D. Lokhande, *J Mater Sci*, 42 (2007) 1304-1308.
- [133] J.-M. Lee, H. McCrabb, E. Jennings Taylor, R. Carpio, *J. Electrochem. Soc.*, 153 (2006) C265-C271.
- [134] B. Dong, T. Xue, C.-L. Xu, H.-L. Li, *Microporous Mesoporous Mater.*, 112 (2008) 627-631.
- [135] C. Bhattacharya, J. Datta, *J. Solid State Electrochem.*, 11 (2007) 215-222.

- [136] Y.A. Ivanova, D.K. Ivanou, E.A. Streltsov, A.K. Fedotov, *Materials Science and Engineering: B*, 147 (2008) 271-275.
- [137] H.E. Maliki, S. Marsillac, J.C. Bernède, E. Faulques, J. Wery, *J. Phys.: Condens. Matter*, 13 (2001) 1839.
- [138] M. Nandi, R. Gangopadhyay, A. Bhaumik, *Microporous Mesoporous Mater.*, 109 (2008) 239-247.
- [139] B.E. Conway, *Electrochemical supercapacitors*, in, Kluwer Academic Publishers, New York, 1999.
- [140] E. Frackowiak, F. Béguin, *Carbon*, 39 (2001) 937-950.
- [141] C. Lin, B.N. Popov, H.J. Ploehn, *J. Electrochem. Soc.*, 149 (2002) A167-A175.
- [142] A. Rudge, J. Davey, I. Raistrick, S. Gottesfeld, J.P. Ferraris, *J. Power Sources*, 47 (1994) 89-107.
- [143] A. Rudge, I. Raistrick, S. Gottesfeld, J.P. Ferraris, *Electrochim. Acta*, 39 (1994) 273-287.
- [144] J.P. Zheng, P.J. Cygan, T.R. Jow, *J. Electrochem. Soc.*, 142 (1995) 2699-2703.
- [145] A.A.F. Grupioni, E. Arashiro, T.A.F. Lassali, *Electrochim. Acta*, 48 (2002) 407-418.
- [146] C. Lin, J.A. Ritter, B.N. Popov, *J. Electrochem. Soc.*, 145 (1998) 4097-4103.
- [147] V. Srinivasan, J.W. Weidner, *J. Electrochem. Soc.*, 147 (2000) 880-885.
- [148] B.E. Conway, *J. Electrochem. Soc.*, 138 (1991) 1539-1548.
- [149] Z. Hu, L. Mo, X. Feng, J. Shi, Y. Wang, Y. Xie, *Mater. Chem. Phys.*, 114 (2009) 53-57.
- [150] T. Zhao, H. Jiang, J. Ma, *J. Power Sources*, 196 (2011) 860-864.
- [151] V. Gupta, T. Kusahara, H. Toyama, S. Gupta, N. Miura, *Electrochem. Commun.*, 9 (2007) 2315-2319.
- [152] J.-K. Chang, C.-M. Wu, I.W. Sun, *J. Mater. Chem.*, 20 (2010) 3729-3735.

- [153] E. Hosono, S. Fujihara, I. Honma, M. Ichihara, H. Zhou, J. Power Sources, 158 (2006) 779-783.
- [154] C. Yuan, X. Zhang, B. Gao, J. Li, Mater. Chem. Phys., 101 (2007) 148-152.
- [155] S. Baber, et al., Nanotechnology, 21 (2010) 165603.
- [156] A. Takai, T. Saida, W. Sugimoto, L. Wang, Y. Yamauchi, K. Kuroda, Chem. Mater., 21 (2009) 3414-3423.
- [157] A. Foyet, A. Hauser, W. Schäfer, J. Solid State Electrochem., 12 (2008) 47-55.
- [158] L. Li, H. Qian, J. Ren, Chem. Commun., (2005) 4083-4085.
- [159] R. Xu, H.C. Zeng, Chem. Mater., 15 (2003) 2040-2048.
- [160] L. Cao, F. Xu, Y.Y. Liang, H.L. Li, Adv. Mater., 16 (2004) 1853-1857.
- [161] P. Bernard, C. Gabrielli, M. Keddad, H. Takenouti, J. Leonardi, P. Blanchard, Electrochim. Acta, 36 (1991) 743-746.
- [162] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, in: J. Chastain (Ed.), Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1979.
- [163] H. Dohle, J. Mergel, D. Stolten, J. Power Sources, 111 (2002) 268-282.
- [164] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, Science, 280 (1998) 1735-1737.
- [165] X. Ren, M.S. Wilson, S. Gottesfeld, J. Electrochem. Soc., 143 (1996) L12-L15.
- [166] N. Jung, Y.H. Cho, M. Ahn, J.W. Lim, Y.S. Kang, D.Y. Chung, J. Kim, Y.E. Sung, Int. J. Hydrogen Energy, 36 (2011) 15731-15738.
- [167] D. Bokach, J.L.G. De La Fuente, M. Tsyppkin, P. Ochal, I.C. Endsjø, R. Tunold, S. Sunde, F. Seland, Fuel Cells, 11 (2011) 735-744.
- [168] A. Santasalo-Aarnio, M. Borghei, I.V. Anoshkin, A.G. Nasibulin, E.I. Kauppinen, V. Ruiz, T. Kallio, Int. J. Hydrogen Energy, 37 (2012) 3415-3424.
- [169] A. Ermete, Applied Catalysis B: Environmental, 88 (2009) 1-24.
- [170] Y.H. Cho, H.S. Park, I.S. Park, Y.E. Sung, Fuel Cells Bulletin, 2008 (2008) 12-16.

- [171] H.Y. Lee, W. Vogel, P.P. Chu, ECS Transactions, 19 (2009) 127-142.
- [172] A.Y. Lo, N. Yu, S.J. Huang, C.T. Hung, S.H. Liu, Z. Lei, C.T. Kuo, S.B. Liu, Diamond Relat. Mater., 20 (2011) 343-350.
- [173] S.M. Park, D.H. Jung, S.K. Kim, S. Lim, D. Peck, W.H. Hong, Electrochim. Acta, 54 (2009) 3066-3072.
- [174] J.R.C. Salgado, F. Alcaide, G. Álvarez, L. Calvillo, M.J. Lázaro, E. Pastor, J. Power Sources, 195 (2010) 4022-4029.
- [175] F. Su, J. Zeng, X. Bao, Y. Yu, J.Y. Lee, X.S. Zhao, Chem. Mater., 17 (2005) 3960-3967.
- [176] S.H. Lee, N. Kakati, S.H. Jee, J. Maiti, Y.S. Yoon, Mater. Lett., 65 (2011) 3281-3284.
- [177] L. Liao, M. Zheng, Z. Zhang, B. Yan, X. Chang, G. Ji, Z. Shen, T. Wu, J. Cao, J. Zhang, H. Gong, T. Yu, Carbon, 47 (2009) 1841-1845.
- [178] Y. Wang, M. Zheng, H. Lu, S. Feng, G. Ji, J. Cao, Nanoscale Research Letters, 5 (2010) 913-916.
- [179] C.J. Brinker, Y. Lu, A. Sellinger, H. Fan, Adv. Mater., 11 (1999) 579-585.
- [180] Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein, D. Zhao, Chem. Mater., 18 (2006) 4447-4464.
- [181] Z. Wen, Q. Wang, J. Li, Adv. Funct. Mater., 18 (2008) 959-964.
- [182] N. Tsiouvaras, M.V. Martínez-Huerta, O. Paschos, U. Stimming, J.L.G. Fierro, M.A. Peña, Int. J. Hydrogen Energy, 35 (2010) 11478-11488.
- [183] P.C. Eklund, J.M. Holden, R.A. Jishi, Carbon, 33 (1995) 959-972.
- [184] W.L. Holstein, H.D. Rosenfeld, The Journal of Physical Chemistry B, 109 (2004) 2176-2186.
- [185] G.-W. Yang, G.-Y. Gao, G.-Y. Zhao, H.-L. Li, Carbon, 45 (2007) 3036-3041.
- [186] Y. Lin, X. Cui, C. Yen, C.M. Wai, The Journal of Physical Chemistry B, 109 (2005) 14410-14415.

Appendix

Journal publications

1. **Tong Xue**, Xin Wang, Jong-Min Lee*, Dual-template synthesis of $\text{Co}(\text{OH})_2$ with mesoporous nanowire structure and its application in supercapacitor, Journal of Power Sources, 2012, 201, 382-386
2. **Tong Xue**, Leslie S. Loo, Xin Wang, Sang Kyu Kwak, Jong-Min Lee*, Electrodeposition of mesoporous bilayers of polyaniline supported Cu_2O semiconductor films from Lyotropic Liquid Crystalline phase, Chemical Engineering Science, 2012, 80, 452-459
3. **Tong Xue**, Zhi Peng Sun, Li Wei, Xin Wang, Jong-Min Lee*, One-step dual-template synthesis of Platinum on mesoporous carbon nanowires for electrocatalysts, International Journal of Hydrogen Energy, 2013, 38, 2754-2759
4. Zheng Jian Chen, **Tong Xue**, Jong-Min Lee, What causes the low viscosity of ether-functionalized ionic liquids? Its dependence on the increase of free volume, RSC Advances, 2012, 2, 10564-10574
5. **Tong Xue**, Xin Wang, Sang Kyu Kwak, Jong-Min Lee*, Synthesis of mesoporous polyaniline (PANI)- $\text{Se}_{0.5}\text{Te}_{0.5}$ dual-layer film from lyotropic liquid crystalline template, Industrial & Engineering Chemistry Research, 2013, 52, 5072-5078
6. **Tong Xue**, Jong-Min Lee*, Capacitance behavior of mesoporous $\text{Co}(\text{OH})_2$

nanowires, Journal of Power Sources, 2014, 245, 194-202.

Conference presentations

7. **Tong Xue**, Jong-Min Lee*. Lyotropic liquid crystal (LLC) and anodic aluminum oxide (AAO) dual templates directed synthesis of hexagonal nickel hydroxide nanowires, The 17th Regional Symposium on Chemical Engineering (RSCE2010), Bangkok, Thailand, November 2010 (Oral presentation).