Synthesis of nanomaterials and design of nanostructures for energy storage application

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**SYNTHESIS OF NANOMATERIALS AND DESIGN OF
NANOSTRUCTURES FOR ENERGY STORAGE APPLICATION**

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

2014

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SCHOOL OF CHEMICAL AND BIOMEDICAL ENGINEERING

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Nomenclatures

AFCs	Alkaline fuel cells
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CBD	Chemical bath deposition
CNTs	Carbon nanotubes
CNFs	Carbon nanofibres
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
DI	De-ionized
ECs	Electrochemical supercapacitors
EDLCs	Electrochemical double layer capacitors
EDLs	Electrical double layers (EDLs)
EDS	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
fcc	Face-centered cubic

FESEM	Field emission scanning electron microscopy
FFT	Fast Fourier transform
FT-IR	Fourier transform infrared
GC	Glassy carbon
GO	Graphene oxide
HR	High-resolution
ITO	Indium-tin oxide
ITO NWs	Indium-tin oxide nanowires
LLC	Lyotropic liquid crystalline (Crystal)
LC	Liquid Crystal
MCFCs	Molten-carbonate fuel cell
MEA	Membrane electrode assembly
MO	Metal oxide
MWCNT	Multi-walled carbon nanotube
NF	Nanoflake
PAFCs	Phosphoric-acid fuel cells
PANI	Polyaniline

PEMFCs	Polymer electrolyte membrane fuel cells
POM	Polarized optical microscopy
PTFE	Polytetrafluoroethylene
PVP	Polyvinylpyrrolidone
rGO	reduced graphene oxide
SAED	Selected-area electron diffraction
SCCM	Standard cubic centimeters per Minute
SCE	Saturated Calomel Electrode
SEI	Solid-electrolyte-interface
SEM	Scanning electron microscopy
SOFCs	Solid-oxide fuel cells
SSA	Specific Surface Area
TEM	Transmission electron microscopy
TGA	Thermogravimetric analysis
TMO	Transition metal oxide
UV-Vis	Ultraviolet-Visible
VLS	Vapor-liquid-solid

VGCF	Vapour-grown carbon fibre
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray diffraction

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Abstracts

This thesis aims to develop nanostructures/nanomaterials by various approaches and investigate their potential applications in the field of energy storage. Synthesis of porous nanomaterials with large active surface area and suitable pore size distribution has drawn considerable attention from scientific society owing to their great potential application and the fields of catalysis, biosensor, energy storage and conversion. The thesis mainly focuses on energy storage system (i.e. supercapacitor) and comprises of 3 major parts.

The first part (chapter 1) provides background to common energy storage system of supercapacitor. In this part, the author would also like to elaborate on different type of active materials used in fabrication of supercapacitor electrode. Transition metal oxides/hydroxides such as Co(OH)_2 , NiO and MnO_2 has captured considerable attention from scientists and has been investigated in many studies. This first part of thesis also highlights the major problems associated with this particular system. Those limitations include narrow operating potential window, inadequate cycle life and high electrode resistance. More important, some potential approaches to overcome addressed issues are also proposed.

The second part (chapters 2, 3 and 4) of this thesis focuses on the synthesis of composite materials of ITO nanowire and different mesoporous metal oxides/hydroxides such as Co(OH)_2 , NiO and MnO_2 . Beside kinetics of oxidation/reduction reactions, electron transport and electrolyte diffusion are two key processes which are crucial in

performance of supercapacitor electrode. Therefore, as an attempt to enhance above processes, ITO nanowire array is incorporated into electrode design. ITO nanowire is chosen as structure-directing agent due to its high conductivity which would address issue of high electrode resistance. On top of that, the introduction of ITO microarray enhances stability of composite electrode, resulting in larger operating window and prolonged cycle life. Two main techniques are utilized for preparation of those composite nanostructures. Conventional chemical vapor deposition (CVD) is carried out to grow ITO nanowire array on titanium substrate and potentiostatic electrodeposition is performed to coat mesoporous metal oxides/hydroxides along ITO nanowires. Another highlight in coating process is the advantage of using hexagonal lyotropic liquid crystalline (LLC) phase as soft template to generate mesoporous structures of different morphologies. This approach results in enlarged surface area and enhanced specific capacitance. It is worth noting that even electrodeposition technique is employed to coat all three active materials along ITO nanowire, three different morphologies are achieved. Field emission scanning electron microscopy (FESEM) allows us to confirm the morphologies of Co(OH)_2 , NiO and MnO_2 are nanosheets, nanoflakes and nanofiber, respectively. It is experimentally and scientifically proven that open spaces between ITO nanowires allow better diffusion of electrolyte species into nanosheet network, resulting in lower electrode internal resistance, more effective electrolyte diffusion and enhanced supercapacitor performance. Consequently, $\text{Co(OH)}_2/\text{ITO}$, NiO/ITO and MnO_2/ITO systems exhibit superior electrochemical performances as compared to Co(OH)_2 , NiO and MnO_2 thin films, respectively. The specific capacitance values of $\alpha\text{-Co(OH)}_2/\text{ITO}$, NiO/ITO, MnO_2/ITO electrodes are calculated to be 1128,

1025 and 821 F g⁻¹, respectively. In a nutshell, this electrode engineering technique can be applied to other transition metal oxides/hydroxides to construct hierarchical structures for a large variety of applications.

The third part of this thesis (chapter 5) is designed to open up new synthetic strategy so as to further improve electrochemical behavior of existing heterostructure. In near future, we intend to develop systematic and rational techniques to fabricate stable three-dimensional (3D) microstructures of nano-building blocks. Those are highly desirable to achieve enhanced electron transport, improved ionic diffusion, excellent rate capability and great stability.

Chapter 1: Introduction of energy storage system of supercapacitor

Over the last decade, due to increasing environmental pollution and depletion of fossil fuels, considerable effort has been devoted to the development of clean and sustainable sources of energy. On top of that, latest technological advancements in market of hybrid electric vehicles and electronic devices lead to a need of alternative energy storage/conversion systems with higher powers and energy densities. As a result, electrochemical energy systems are grasping more attention as alternative energy sources. Those energy systems include batteries, fuel cells and electrochemical capacitors (ECs). All three systems share some electrochemical similarities in working principles. The first common feature is that the energy generating process occurs at the interface between electrode and electrolyte. In addition, charge transfer is one key process in which electron and ion transports are separated. As compared to batteries which are already widely commercialized in the market of consumer electronics, fuel cells and supercapacitors are still in early development stage. Fuel cells were firstly commercialized in space applications such as power generating device for satellites and capsules. Another promising future prospect for fuel cell is rapidly expanding automobile market.

Rechargeable supercapacitors, also as known as ultracapacitors, emerge as ecologically friendly sources of energy and real-world solutions to real-world problems. On top of that, ultracapacitors and recent advancement in energy storage technologies

provide flexible platform to electrochemically store and transport energy. As illustrated by Ragone plot shown in Figure 1.1, fuel cells can be considered as an alternative of combustion engine due to their high energy density and lower environmental impact. On the other hand, supercapacitors play the role of the bridge connecting conventional capacitors and batteries owing to their high power density. Supercapacitors established their usefulness in applications of portable electronic equipments and industrial power management systems.

Figure 1.1. Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion systems [1].

Specific energy or energy density is defined as amount of energy stored in one kilogram of materials (Wh kg^{-1}). On the other hand, specific power, as known as power density, indicates the rate capability of a system to deliver energy (W kg^{-1}). As such, based on above Ragone plot, capacitors can be regarded as high-power systems.

However, the main drawback of conventional capacitors is low energy density which limits their use in various applications. In the last decade, attention has been gradually shifted to next-generation supercapacitors which can deliver energy at significantly higher rate. In other words, the specific energy of electrochemical capacitor is several orders of magnitude higher than that of conventional capacitors. The main characteristics of high performance supercapacitor are large energy density (1 – 10 Wh kg⁻¹), high power density (10³ – 10⁵ W kg⁻¹) and excellent cycle life (above 100,000 cycles) [2, 3]. It is worth noting that no individual electrochemical energy storage systems can fairly take over the place of combustion engine which is capable of storing high energy and delivering high power. Nonetheless, with rapidly advancing technology in electrochemistry, one potential approach to tackle this problem is to integrate more than one electrochemical power systems into one hybrid structure.

1.1. Conventional capacitor

The concept of capacitor was firstly introduced by Ewald Georg von Kleist in 1745 when he was fabricating a device called Leiden jar storing static electricity between two electrodes on the inside and outside of a glass jar. Since then, tremendous effort has been devoted in this field. A typical conventional capacitor comprises of two metallic plates separated by insulating or dielectric material. The capacitance can be determined by following basic equation:

$$C = \frac{\epsilon S}{d} \quad (\text{eqn 1.1})$$

where C is capacitance (μF), ϵ is dielectric constant, S is surface area of electrode and d is the thickness of dielectric layer (cm). The charge accumulating principle can be described as follows:

The electrical charge is accumulated by dielectric layer between two electrodes. The process of charge transfer from one electrode to another can be achieved by applying external power supply/circuit. During charging process, electrons are withdrawn away from one capacitor electrode due to connection to positive terminal of power source, which develops electrode deficit forming cathode. In contrast, the other capacitor electrode receives additional electrons from negative terminal of power supply, forming anode. Capacitor is fully charged when potential difference between capacitor electrodes is balanced by voltage of external power supply. The discharge takes place when capacitor is connected to external circuit and electrons flow from negative side to positive side. As mentioned earlier, the capacitance is governed by equation 1.1 and depends on chosen dielectric materials. The dielectric constants of various materials are summarized in table 1.1. In voltage range of 50 – 400 V, capacitance in the range of 0.1 – 1 μF can be achieved for traditional capacitor.

Table 1.1 Dielectric constants of various materials used in conventional capacitors [4].

Material	ϵ
Paper	1.2 – 2.6
Paraffin	1.9 – 2.4
Polyethylene	2.2 – 2.4
Polystyrene	2.5 – 2.7
Ebonite	2.0 – 3.5
Mica	5.0 – 7.0
Mineral oil	2.2 – 2.4
Polyethylene tetraphtharate	3.1 – 3.2
Sulfur	2.0 – 4.2
Steatite porcelain	6.0 – 7.0
Al porcelain	8 – 10
Water	80

1.2. Supercapacitors

Supercapacitor is the new generation of capacitor with specific capacitance several thousand times higher than that of conventional capacitor. Based on working mechanism, the supercapacitors can be divided in two categories: classical electrochemical double layer capacitors (EDLCs) and pseudocapacitors (redox capacitors) [5-7]. EDLCs store energy by adsorption/desorption of electrolyte ions onto electrode surface. In other words, these processes involve electrostatic accumulation of surface charges. Carbon-based materials (e.g. activated carbon, carbon aerogel, graphene and carbon nanotubes) have been widely utilized in fabricating EDLCs

electrodes [2, 3, 8-10]. On the other hand, electrochemical energy in pseudocapacitor arises from reversible surface reduction/oxidation reactions. The charging process is initiated by application of potential onto pseudocapacitor. As a result, fast and reversible faradaic reactions occur on electrode surface and lead to the passage of charges across the double layer. Since its first development in 1982 [11], plenty of materials have been investigated and employed as pseudocapacitor electrode materials. Those potential candidates include conducting polymers and several metal oxides/hydroxides such as RuO_2 , MnO_2 , and Co_3O_4 , NiO .

Figure 1.2. Hierarchical classification of supercapacitors.

According to equation 1.1, the capacitance of supercapacitor is inversely proportional to the thickness of dielectric layer. Therefore, capacitance can be greatly increased by decreasing the thickness. The reduction in thickness to nanoscale can be obtained by utilization of electrolyte solution instead of conventional materials reported in table 1.1. The choices of electrolyte may range from alkaline (KOH), acidic (H₂SO₄), neutral aqueous solution ((NH₄)₂SO₄) to ionic liquids. This idea triggers the generation of electrochemical double layer supercapacitors (EDLCs) vividly illustrated in Figure 1.3.

Figure 1.3. Schematic illustration of electrochemical double layer supercapacitor (EDLC).

The dielectric separator used in EDLCs is semi-permeable porous membrane which prevents charge transport. In order to quantify specific capacitance of EDLCs, equation 1.1 is modified and re-written as follows:

$$C = \frac{\epsilon_T \epsilon_0 S}{d} \quad (\text{eqn 1.2})$$

where ϵ_T is dielectric constant of electrolyte, ϵ_0 is permeability of vacuum, S is surface area of electrode and d is the effective thickness of double layer.

Due to Coulombic attraction force, charges of opposite signs tend to accumulate at the electrolyte/electrolyte interface, forming electrical double layers (EDLs), as presented in Figure 1.4. This condition is usually referred as charged state of EDLCs formed by connection to external supply. If charged EDLCs is connected to external circuit, reverse process happen and as a result, energy is released. The relevance thickness d is in nanoscale. Therefore, the use of electrolyte solution allows us to introduce the concept of supercapacitor of which capacitive performance is superior to that of conventional capacitor.

Figure 1.4. Scheme of the electrical double layer [2].

1.3. Carbon-based materials for EDLCs

As mentioned above, the capacitance of supercapacitor is inversely proportional to thickness of double layer. Therefore, capacitance can be enhanced if thickness of double layer is reduced. This objective can be achieved by employing aqueous electrolyte. Carbonaceous materials have been commonly employed to fabricate

electrode for EDLCs. This is largely due to the high surface area offered by the porous structure of carbon-based electrode and the small charge separation ($\sim 1\text{nm}$). In the case of capacitor electrode fabricated from carbonaceous materials, the specific capacitance is typically ranging from 5 to 20 $\mu\text{F cm}^{-2}$ [12]. Typical cyclic voltammetric and chronopotentiometric curves of EDLCs resemble symmetrical and quasi-rectangular and quasi-triangular shapes [13], as illustrated in figure below.

Figure 1.5. (a) Cyclic voltammetry curves of an activated meso-carbon microbeads (AMCMBs)/CNTs compound electrode at different scan rates. (b) galvanostatic charge–discharge curves of the AMCMBs/CNTs compound electrode (Reprinted from reference [14] with permission from Elsevier).

Recently, scientists have been trying to explore various synthetic and fabrication techniques to further enhance electrochemical performance of EDLCs. For instance, a variety of carbon materials have been employed to fabricate electrodes in EDLCs. Those carbon-based materials include carbon aerogels, activated carbon and carbon nanotubes, graphene and so on [2, 15-18]. It is theoretically believed that specific capacitance of an activated carbon is directly proportional to the surface area. Nonetheless, it is not necessarily true in all cases. For instance, M-30 with surface area

of $2130 \text{ m}^2 \text{ g}^{-1}$ measured by BET technique give a larger specific capacitance (100 F g^{-1}) as compared to 62.9 F g^{-1} of M-30 with surface area of $2571 \text{ m}^2 \text{ g}^{-1}$ [19, 20].

1.4. Metal oxides/hydroxides for pseudocapacitors

Metal oxides/hydroxides provide a promising alternative electrode material because owing to their ability to deliver higher energy density and better electrochemical stability which are the main characteristics of next-generation supercapacitors. The mechanism of storing electrochemical energy is governed by reversible faradaic reactions between electrode materials and ions within appropriate potential windows [7, 21]. The fundamental requirement for a particular metal-based material to be electrochemically active is the existence of at least two oxidation states without structural changes. Up to date, electrochemical properties of oxides and hydroxides of many transition metals (i.e. ruthenium, manganese, cobalt, nickel and vanadium) have been investigated and so as to explore their potential applications in supercapacitors.

The most extensively researched metal oxide known to give very high capacitance is ruthenium oxide (RuO_2). This is largely due to its well-defined reversible redox reactions, wide potential window of 1.2 V , mixed electron-proton conductor, high specific capacitance of 1580 F g^{-1} reported in [22] and good cyclic stability. However, the toxic nature and rarity of RuO_2 are the major factors which shift the attention toward development of other transition metal oxides and hydroxides.

1.4.1. Co_3O_4 and $\text{Co}(\text{OH})_2$

The pseudocapacitive behavior of Co_3O_4 seems to arise from following redox reactions [23, 24]:

Co_3O_4 is an important transition metal oxide utilized in various applications such as heterogeneous catalysts, sensors, and electrochromic devices. Recently Co_3O_4 has been inspected as potential new-generation material for supercapacitor application. This is owing to its high surface area, good conductivity, excellent long-term performance and good stability in corrosive media [25-27]. Various techniques were utilized to prepare a large variety of Co_3O_4 micro/nano-structures. For instance, L. Wang et al. managed to synthesize mesoporous crater-like Co_3O_4 microspheres with the aid of silica template [28] delivering specific capacitance of 102 F g^{-1} . On the other hand, chemical coating technique [29, 30] was also employed to obtain Co_3O_4 thin films on all sorts of substrates. However, the major limitation of this coating method is that only small specific capacitance of supercapacitor electrode can be achieved due to amorphous nature of cobalt oxide. Y. Shan et al. tried to further improve specific capacitance of Co_3O_4 to 200 F g^{-1} by integration of MWCNT, as reported in [23]. Co_3O_4 nanowire arrays prepared on nickel foam demonstrates maximum specific capacitance of 746 F g^{-1} at discharge current of 5 mA cm^{-2} [31]. With an aim to enhance surface area, M.-B. Zheng and his colleagues tried to integrate mesopores into Co_3O_4 nanoparticles with mesoporous silica used as template [32]. It was found out that calcination temperature did not obviously affect the textural parameters of Co_3O_4 sample and the BET surface areas of Co_3O_4 samples could be regulated by the choice of template. The surface area and maximum specific capacitance of as-prepared structure were measured to be $184.8 \text{ m}^2 \text{ g}^{-1}$ and 370 F g^{-1} , respectively. In addition, mesoporous cobalt oxide aerogel was also successfully synthesized from cobalt salt

with addition of epoxide, showing a high capacitance of 600 F g^{-1} [33]. In the recent decade, electrodeposition has drawn considerable attention as promising technique to prepare supercapacitor electrode due to its ability to control the morphology and structure of active material [34, 35]. As such, this approach was employed to prepare Co_3O_4 thin films displaying a specific capacitance of 235 F g^{-1} at a scan rate of 20 mV s^{-1} and specific power densities of 1.33 kW kg^{-1} [36]. On the other hand, J. Xu et al. successfully exploited AAO template to electrochemically deposit cobalt hydroxide and thermally convert to Co_3O_4 , forming nanotubes with diameter of 300 nm [37]. This nanostructure exhibits specific capacitance of 574 F g^{-1} at current density of 0.1 A g^{-1} .

In recent years, Co(OH)_2 has appeared as another intriguing material possessing layered structure with large interlayer spacing. The spacing between layers would allow electrolyte species to diffuse in and out and come in direct contact with innermost layers. This unique characteristic of Co(OH)_2 resulted in high surface area and a rapid ion transport, as experimentally proven in [38-41]. Once the alkaline electrolyte species come into contact with cobalt hydroxide, two reversible faradaic reactions [42] can occur, as follows:

Due to attractive chemical and physical properties mentioned above, many studies have been conducted on Co(OH)_2 for electrochemical supercapacitor application. Hydrothermal technique has been usually employed to fabricate cobalt hydroxide nanostructures of different morphologies owing to its simplicity and scalability. For

instance, Y. Shao's group succeed to prepare one dimensional hierarchical α -Co(OH)₂ nanocolumns through one-step hydrothermal procedure with hydrazine hydrate and Na₃PO₄ as morphology directing agents. Co₃O₄ with retained morphology was obtained upon complete thermal conversion at elevated temperature [43]. On the other hand, electrodeposition can also be effectively utilized to synthesize cobalt hydroxide nanostructures such as porous Co(OH)₂ film (651 F g⁻¹) on stainless steel plate [44], Al-substituted α -cobalt hydroxide (843 F g⁻¹) [45], ordered mesoporous cobalt hydroxide films (2646 F g⁻¹) [46] on nickel mesh.

The high specific capacitance reported in [46] results from lyotropic liquid crystalline phase of Brij56 as soft template. The major advantage of this approach is the generation of special ordered mesoporous nanostructure of Co(OH)₂. The authors also performed characterization on phase behavior of the deposition system.

Figure 1.6. (A) Phase diagram for Brij 56 mixed with an aqueous solution containing 0.9 M $\text{Co}(\text{NO}_3)_2$ and 0.075 M NaNO_3 and (B) POM image of a hexagonal (H_1) liquid crystalline phase for the prepared deposition electrolyte (Reprinted from reference [46] with permission from Elsevier).

Figure 1.7. Electrochemical properties of the ordered mesoporous Co(OH)₂ film electrodeposited on foamed Ni mesh: (A) CV curves at different scan rates and (B) discharge curves at different discharge current densities (Reprinted from reference [46] with permission from Elsevier).

It seems that cobalt hydroxide exhibits generally larger specific capacitances than cobalt oxide. On top of that, it is noticed that maximum capacitance, energy density and power density are usually achieved in low potential window of -0.1 – 0.4 V. Therefore, the key challenge of development of Co(OH)₂ as potential supercapacitor electrode is an increase in the energy stored at higher potential range.

1.4.2. NiO and Ni(OH)₂

As a new potential electrode material, nickel oxide (NiO), is drawing intensive attention. This is largely due to its synthetic simplicity, high specific capacitance in alkaline electrolyte, environmentally friendly nature and abundant resource [47-50]. NiO possesses a very high theoretical specific capacitance of 3750 F g⁻¹. Nickel oxide is typically active in alkaline solution and the energy can be charged and discharge through following redox reactions [51-53]:

It was reported that electrochemical activity greatly depends on crystallinity which, in turn, could be tuned by temperature of calcination process. At elevated temperature, the structure of NiO becomes more crystallized and specific capacitance is significantly increased [54]. There is an optimal temperature at which maximum specific capacitance can be achieved. If the sample is heated beyond this optimal temperature, the crystal size can be increased, which decreases the active surface area and possibly leads to capacitance drop.

The synthesis route would certainly influence the electrochemical performance of nickel oxide [55]. Sol-gel technique was used to synthesize porous NiO xerogels demonstrating a specific capacitance of 696 F g^{-1} after being annealed at 250°C . In addition, C. Yuan et al. reported a practical and efficient strategy for preparation of spherical porous NiO superstructures [56]. The study proved that Ostwald-ripening effect was responsible for the coalescence of $\beta\text{-Ni(OH)}_2$ microspheres in alkaline solution with existence of $\text{Ni(NH}_3)_2^{2+}$ species. This superstructure is capable of delivering a capacitance of 710 F g^{-1} at 1 A g^{-1} and exhibits high capacitance retention of 98% after 2000 charge/discharge cycles. Nanosheets based mesoporous NiO microspherical structures were also successfully generated by template-free sol-gel technique with application of hexamethylenetetramine hydrolysis under a refluxing condition [57]. This NiO microstructure was reported to possess large surface area of $258.52 \text{ m}^2 \text{ g}^{-1}$ and maximum capacitance of 718 F g^{-1} .

Nonetheless, the fabrication of supercapacitor electrode made of NiO micro/nanostructures can be challenging. This is likely due to following reasons:

- (a) *Limited cyclic life*. This intrinsic property has been reported in many studies and one potential approach to overcome this issue is to integrate carbonaceous materials as support and cobalt oxide forming binary metal oxides. For examples, graphene–nickel oxide composite nanostructures synthesized by a controlled hydrothermal method demonstrated high rate capability and good life cycle [58]. On the other hand, hierarchical porous NiCo_2O_4 nanowires prepared via a facile polyethylene glycol-directed technique and thermal treatment exhibits high capacitance of 743 F g^{-1} at 1 A g^{-1} and excellent rate cycling stability with 6.2% loss after 3000 cycles [59].
- (b) *Low conductivity*. Electrochemical storage mechanism generally involves a charge transfer process. Therefore, the conductivity of the electrode certainly affects electrochemical performance. However, metal oxides are typically known to have low conductivity, which in turn will cause negative impact on electrochemical properties of electrode. With an aim to address and minimize this problem, tremendous effort was devoted to develop composite materials of NiO and highly conductive carbon-based materials (e.g. CNT, graphene, etc.) [60, 61].

As an attempt to understand the effect of morphology and structure on electrochemical performance, various nickel oxide nanostructures have been synthesized such as loose-packed nano-flakes [62], porous nanoflowers [63], spherical

structure [56], nanosheet-based nanospheres [64] (Figure 1.8), flower-like hollow nanospheres [65], nanoplatelet array [66] (Figure 1.9), etc.

Figure 1.8. TEM images of NiO nanospheres (Reprinted from reference [64] with permission from Elsevier).

Figure 1.9.(a) SEM images of the Ni(OH)_2 array film. (b) SEM image the annealed NiO array films. (c and d) the cross-sectional views of nanoarray at different magnifications (Reprinted from reference [66] with permission from The Royal Society of Chemistry).

It is commonly believed that porous and hollow structures usually result in larger active surface area and improve charge transport. Introduction of porosity into NiO network can be achieved by heat treatment which leads to dehydration and decomposition of organic species. On the other hand, template-based methods are usually employed to prepare hollowed micro/nano-structures. However, this technique is not preferred due to complex and tedious etching process which is always required to remove the template. Therefore, there is a need to develop a facile and simple one-step procedure to generate porous hollow structures.

Ni(OH)_2 is another promising nickel-based electrode material for supercapacitor application. Nickel hydroxide generally possesses higher specific capacitance than nickel oxide [63, 64, 67, 68]. H. Jiang et al. managed to synthesize Ni(OH)_2 hierarchical nanostructures, assembled from ultrathin nanoflakes (Figure 1.10) demonstrating

highest specific capacitance of 1715 F g^{-1} at a scan rate of 5 mV s^{-1} within the potential range of 0.6 V [69].

Figure 1.10. (a) XRD pattern, (b) The corresponding FESEM image (c and d) TEM images of a and (e) HRTEM image of a part of the white-boxed area of the flowerlike Ni(OH)_2 nanostructures (Reprinted from reference [69] with permission from The Royal Society of Chemistry).

On the other hand, D.P. Dubal et al. highlighted the effect of morphology on the electrochemical behavior [70]. Different nanostructures of $\beta\text{-Ni(OH)}_2$ (shown in Figure 1.11) controlled by choice of nickel salts have been successfully developed using simple chemical bath deposition (CBD) method. Nanoflakes, nanosheets and honeycomb-like nanoarchitectures were successfully fabricated. The maximum specific capacitance was determined to be 462 F g^{-1} in 2 M KOH in the case of Ni(OH)_2 nanosheets, suggesting its potential application in electrochemical supercapacitors.

Figure 1.11. Scanning electron micrographs of $\text{Ni}(\text{OH})_2$ with different morphologies (Reprinted from reference [70] with permission from Elsevier).

The first attempt to potentiostatically electrodeposit $\text{Ni}(\text{OH})_2$ at -0.75 V was reported in [71].

Wide application of $\text{Ni}(\text{OH})_2$ is also hindered by its high electrical resistivity. As such, composite materials of nickel hydroxide and highly conductive materials seem to be a better option. Graphene is a suitable candidate to provide a flexible two-dimensional support for the dispersion of $\text{Ni}(\text{OH})_2$ network. Since its discovery in 2004, graphene and its derivatives have been regarded as two-dimensional unrolled carbon nanotubes

with bright future [72-74]. The integration of graphene into composite structure not only enlarges surface area but also enhance overall conductivity [75, 76]. These two main objectives were fully achieved by J.W. Lee and his colleagues [77]. They also reported a very high capacitance of 1215 F g^{-1} at scan rate of 5 mV s^{-1} , which is substantially far better than that of pure Ni(OH)_2 prepared by similar procedure. On the other hand, mesoporous carbon was also successfully introduced nickel hydroxide network to generate composite material, which reduced charge-transfer resistance [78]. As a result, the authors achieved a very high capacitance of 2570 F g^{-1} at charge/discharge current of 5 mA cm^{-2} .

Mesoporous structures are usually highly preferred since they can result in higher active surface area and larger capacitance. With that in mind, J.-W. Lang et al. demonstrated the preparation of mesoporous loose-packed Ni(OH)_2 nanoflake with specific capacitance of 2055 F g^{-1} at 0.625 A g^{-1} [79].

1.4.3. MnO_2

In recent years, manganese dioxide has arisen as potential energy-storage material. Its natural abundance allows wide commercialization if specific capacitance is sufficiently high.

Aqueous Na_2SO_4 solution is a common electrolyte for manganese dioxide electrode. The pseudocapacitance of MnO_2 can be elaborated by two mechanisms proposed for the charge storage in MnO_2 -based electrode. In both charge storage mechanisms, a oxidation/reduction reaction between the Mn^{3+} and Mn^{4+} oxidation states occurs.

In the first proposed mechanism, the alkali metal cation is intercalated in electrode during reduction and deintercalated in oxidation as follows:

The second one is associated with adsorption of Na^+ cation in electrolyte on electrode surface as follows:

It is commonly believed that the electrochemical properties of MnO_2 largely depend on synthesis route [80, 81]. A large variety of studies have been actively performed to understand the effect of particle size, morphology and crystal structure on electrochemical behavior [82-84]. Various MnO_2 nanostructures have been synthesized owing to its superior performance as compared to its bulk counterpart [85-87]. On top of that, the presence of diffusion channels present in nanostructure also facilitate ion and electrolyte transport. W. Xiao et al. attempted to synthesize single-crystal α - MnO_2 nanotubes by hydrothermal method [88]. This nanotubular structure possesses inner tunnel as large as of 0.46 nm, capacitance as high as 220 F g^{-1} and excellent cycle life (Figure 1.12).

Figure 1.12. (a) TEM, (b) HRTEM images and (c) SAED pattern of prepared MnO₂ nanotubes (Reprinted from reference [88] with permission from Elsevier).

α -MnO₂ nanorods were prepared by chemical precipitation with CTAB as the surfactant as the structure-directing agent followed by calcination at 800 °C [89]. This structure was capable of delivering a maximum capacitance of 166.2 F g⁻¹ and possessed good cycling stabilities, indicating its promising application as electrode material.

Unlike cobalt and nickel oxides, MnO₂ can be obtained through reduction of KMnO₄ by reducing agents such as ethanol, ethylene glycol and MnSO₄. In a recent study, EO₂₀PO₇₀EO₂₀ triblock copolymer Pluronic P123 with weight of 5800 was used as structure-directing agent to prepare MnO₂ nanowires (8–20 nm in diameter and 200–400 nm in length) [90]. Anodic aluminum oxide (AAO) templates was also employed to synthesize α -MnO₂ nanowire arrays with capacitance of 165 F g⁻¹ [91]. Even though

above studies achieved promising and fruitful result, it is essential to develop a simpler and more cost-effective technique for commercialization of manganese oxide.

As an attempt to improve supercapacitive performance of MnO_2 , carbonaceous materials such as graphite, graphene and carbon nanotube have been introduced to form composite materials [91-94]. The integration of carbon-based material can help in improving conductivity and extending potential window. Therefore, the specific capacitance of composite material is generally larger than those of its individual counterparts. For instance, this concept was vividly demonstrated in the study done by J. Yan and his group [95]. Graphene/ MnO_2 composite (graphene : MnO_2 = 22 wt% : 78 wt%) synthesized through self-limiting deposition of nanoscale MnO_2 on the surface of graphene under microwave irradiation exhibited a specific capacitance of 310 F g^{-1} at 2 mV s^{-1} . Its electrochemical performance was certainly higher than those of pure graphene (104 F g^{-1}) and birnessite-typed MnO_2 (103 F g^{-1}). The authors also highlighted the effect of addition of graphene into composite structure on improved electrode conductivity and enlarged interfacial area (Figure 1.13).

Figure 1.13. Schematic illustration for the synthesis and electrochemical performance of graphene-MnO₂ composite (Reprinted from reference [95] with permission from Elsevier).

On the other hand, one promising method to compensate for the poor electrical conductivity of MnO₂ is to deposit a MnO₂ layer on the surface of a high surface area and excellent conductivity. Carbon microfiber was utilized as conductive substrate for the growth of Zn₂SnO₄ nanowires followed by coating of MnO₂ film [96]. This hierarchical heterostructure shown in Figure 1.14 was capable of delivering maximum specific capacitance of 642.4 F g⁻¹ at discharge current of 1 A g⁻¹, energy density of 36.8 W h kg⁻¹ and power density of 32 kW kg⁻¹ at 40 A g⁻¹ in Na₂SO₄ electrolyte. As

elaborated by the authors, highly conductive Zn_2SnO_4 nanowires on substrate of carbon microfibers served as a platform to provide diffusion channels and pathway facilitating electron transport to and from ultrathin MnO_2 shell.

Figure 1.14. Structural characterization of $\text{MnO}_2/\text{ZTO}/\text{CMF}$ hybrid composite. (a-d) SEM images of ZTO nanowires grown radially on the woven CMFs. (e) TEM image of MnO_2 -coated ZTO nanowire and (f) corresponding SAED pattern. (g) HRTEM image of an individual ZTO/ MnO_2 nanocable, showing that the rough and thin amorphous layer on the surface of the nanowire is amorphous MnO_2 shell, inset is the corresponding FFT pattern. (h) Lattice-resolved HRTEM image of the ZTO/ MnO_2 core/shell nanocable, showing the detailed interface of crystalline ZTO core and amorphous MnO_2 shell. (i,j) TEM image and line-scan profiles (indicated by a line in panel i) of the ZTO/ MnO_2 core/shell nanocable, showing Zn, Sn, O, and Mn elemental profiles. (k) A representative EDS spectrum taken on the nanocable. (Reprinted with permission from reference [96]. Copyright 2014 American Chemical Society).

Carbon nanotube, an interesting material with various applications, can also be integrated into composite nanostructure. Despite the complicated synthesis, aligned CNT structures have drawn tremendous attention from scientific society, with respect to their applications in energy storage devices. This is largely due to its advantageous properties such as high electrical conductivity, low contact resistance and large specific surface area [97, 98]. In his paper, R. Amade et al. employ plasma enhanced chemical vapour deposition (PECVD) technique to fabricate dense and vertically aligned CNTs followed by electrodeposition of a thinner layer of MnO_2 [99]. Introduction of uniformly aligned CNT increase capacitance of electrode to 642 F g^{-1} which is much higher than that of activated carbon/ MnO_2 (110 F g^{-1}) electrodes reported in [100]. However, additional work must be carried out to vary carbon content in the composite material to determine optimal ratio and further improve specific capacitance [101].

In summary, several problems associated with common electrode design must be addressed such as low surface area, high internal resistance and limited electrolyte diffusion. With that in mind, the main goal of this thesis is to implement a new electrode design or binder-free electrode fabrication technique in order to overcome as-mentioned issues. This objective can be achieved by introduction of highly conductive indium-tin oxide nanowires and mesopores into the system by chemical vapor deposition followed by potentiostatic electrodeposition through a hexagonal liquid crystalline phase of a nonionic surfactant. The subsequent chapters will discuss in detail about how new electrode fabrication technique can be applied to various transition metal oxide/hydroxide systems (i.e. Co(OH)_2 , NiO and MnO_2) and enhance their electrochemical performance.

Chapter 2: Fabrication of Co(OH)₂/ITO nanowire composite electrode and its application in supercapacitors

Reprinted from RSC Advances, Issue 28, Duc Tai Dam, Xin Wang and Jong-Min Lee*, Fabrication of a mesoporous Co(OH)₂/ITO nanowire composite electrode and its application in supercapacitors, 10512-10518, Copyright (2012), with permission from The Royal Society of Chemistry.

In this chapter, a novel mesoporous α -Co(OH)₂/ITO NWs heterostructure has been successfully synthesized via a new method of combining chemical vapor deposition (CVD) on titanium substrate and electrodeposition through hexagonal lyotropic liquid crystalline (LLC) phase for electrochemical energy storage application. Electrochemical measurements demonstrate the improved ionic conductivity of an electrode and enhanced supercapacitive behavior, as compared to mesoporous cobalt hydroxide film on titanium current collector without indium tin oxide (ITO) NWs as “electron highways”. Galvanostatic charge–discharge measurements in 1 M KOH solution prove that the electrode of as-prepared heterostructure possesses excellent electrochemical capacitance, in the potential range from -0.1 V to 0.5 V with maximum specific capacitance of 1128 F g⁻¹ at discharge current density of 1 A g⁻¹. The unique mesoporous α -Co(OH)₂/ITO NWs heterostructure provides high capacitance retention ratio at high discharge current densities and long-term electrochemical stability.

2.1. Background

In recent years, electrochemical supercapacitors (ECs) have been extensively studied as attractive energy storage devices. They have potential applications in portable electronics and electric vehicles because of their high power energy densities and long cyclic life [8, 102, 103]. Based on the nature of the charge-storage mechanism and active materials, electrochemical capacitors can be classified into two types: electrochemical double layer capacitors (EDLCs) and redox supercapacitors (pseudocapacitors). EDLCs utilizing carbon-based active materials, such as activated carbon (AC) and carbon nanotubes (CNTs) with charge stored at electrode-electrolyte interface, are currently the most commonly used devices [2]. On the other hand, pseudocapacitors or redox capacitors use fast and reversible faradaic surface reactions for charge storage. Conducting polymers [104, 105] and transition metal oxides and hydroxides [82, 106, 107] have been investigated as possible electrode materials for redox capacitors. Redox capacitors have drawn much more attention than EDLCs due to their high theoretical specific capacitance (SC) values, which are determined by specific surface area and the faradaic redox characteristics of materials [108].

Initially, J.P. Zheng et al. reported the crystal structure, particle size and prominent electrochemical properties of hydrous ruthenium oxide formed by sol-gel process [109]. In this study, specific capacitance as high as 720 F g^{-1} was measured for RuO_2 powder annealed at 150°C . Further effort was devoted by C.C. Hu and W.C. Chen to obtain the maximum capacitance of 1580 F g^{-1} from $\text{AC-RuO}_x/\text{RuO}_x/\text{Au/SS}$ composite electrode which was very close to the theoretical value [22]. Nonetheless, ruthenium oxide was not widely commercialized due to its high cost. Therefore, it is essential to develop

alternative inexpensive electrode materials with high capacitive performance such as $\text{Co}(\text{OH})_2$ [38, 42], $\text{Ni}(\text{OH})_2$ [110, 111], NiO [112], CoO_x [113], MnO_x [94, 114-117], etc. They are of particular interest as high-performance EC electrode materials because of their abundant resources, low fabrication cost and well-defined oxidation/reduction activities. Tremendous efforts have been devoted to fabricate electrodes utilizing above transition metal – based materials by different experimental approaches. The major synthetic techniques include chemical precipitation [62], sol-gel [64], hydrothermal and electrodeposition.

The precipitation methodology was initially used to synthesize $\text{Co}(\text{OH})_2$ for a supercapacitor [20, 21]. However, cobalt hydroxide prepared by this technique demonstrated very low specific capacitance (SC) of less than 400 F g^{-1} . Since the major limitation of $\text{Co}(\text{OH})_2$ is low conductivity, S. Chen et al. initiated the idea of fabricating graphene- $\text{Co}(\text{OH})_2$ nanocomposites by the use of some reducing agents such as HS^- and H_2S [118]. As a result, this research group managed to achieve specific capacitance of 972.5 F g^{-1} which is much higher than each individual counterpart. However, in above study, uniform distribution of $\text{Co}(\text{OH})_2$ is believed to be the main challenge. On the other hand, most of the reports were more concerned about the enhancement of SC values. Insufficient attention was paid to capacitance degradations of metal oxide/hydroxide materials at high current densities [119]. Our group previously reported the utilization of lyotropic liquid crystal (LLC) template in potentiostatic electrodeposition of $\text{Co}(\text{OH})_2$ which led to significant improvement in electrochemical performance [120]. Indium-tin oxide nanowire is known to possess excellent electrical properties and thermal stability [121, 122] which allows great applications in the field of

electronics. On top of that, titanium was chosen as current collector owing to its well-known excellent mechanical, chemical and thermal stability as well as abundance in the Earth's crust. In this study, we first prepared indium-tin oxide nanowires (ITO NWs) by chemical vapor deposition (CVD) on titanium substrate, and then different mesoporous structures such as $\text{Co}(\text{OH})_2$ nanoflake (NF) were deposited onto the indium-tin oxide nanowires (ITO NWs) by electrodeposition through lyotropic liquid crystal (LLC) template. In addition, mesoporous $\text{Co}(\text{OH})_2$ film, directly deposited on pure Ti substrate, was prepared for comparison.

2.2. Experimental

2.2.1. Fabrication of array of indium-tin oxide nanowires (ITO NWs) on titanium substrate

The array of indium-tin oxide nanowires was generally fabricated using the carbothermal reduction method. The double-quartz tube system which consists of a slender quartz tube (inner diameter 1.5 cm, length 25 cm, one sealed end and one opened end) and a large furnace tube (inner diameter 3.3 cm, length 85 cm) was utilized for the growth of ITO NWs, as illustrated in Figure 2.1. In order to prepare the material source for CVD, In_2O_3 , SnO_2 , and graphite powders with the weight ratio of 9 : 1 : 2 were thoroughly mixed and placed at the closed end of the small quartz tube. Titanium foils were chosen as the substrate for this CVD process. Typically, titanium substrates were firstly polished by SiC abrasive paper, dipped in diluted HCl solution (0.1 M), rinsed with DI water, air-dried and coated with a 5nm gold catalyst before being placed downstream from the powder mixture near the opened end. Subsequently, the

slender quartz tube was loaded into a large quartz tube in such a way that the closed end was located at the central temperature region.

Figure 2.1. Schematic illustration of the experimental setup for synthesis of ITO nanowires by chemical vapor deposition (CVD).

Prior to heating, the large furnace tube was purged with 200 sccm high purity argon gas for 10 minutes to evacuate air and achieve an inert atmosphere. The central temperature was gradually raised to 1000 °C and kept at this temperature for 2 hours under working pressure of 5 – 6 mbar controlled by rotary pump and pressure gauge. Argon gas with the flowrate of 50 sccm was continuously introduced at the inlet during growth. A series of trials was conducted earlier to determine the optimal temperature for the growth of ITO nanowires to be in the range of 400–600 °C where the Au-coated titanium substrates were located. Upon completion of the reaction, the furnace was cooled to room temperature by Ar gas under natural convection. The loading of ITO nanowire array is measured by microbalance and estimated to be in the range of 400-500 mg.cm⁻²

2.2.2. Preparation of cobalt nitrate electrolyte solution and electrodeposition of mesoporous cobalt hydroxide

Brij56 (polyoxyethylene(10) cetyl ether, C₁₆ [EO]₁₀) and Co²⁺ electrolyte (0.9 M Co(NO₃)₂ and 0.075 M NaNO₃) with a weight ratio of 1:1 were mixed thoroughly to prepare lyotropic liquid crystalline (LLC) template. This template was used as electrolyte for electrodeposition. A standard three-electrode cell was used for electrodeposition with ITO NWs/Ti working electrode, a large surface area platinum counter electrode and a standard Ag/AgCl electrode (Figure 2.2). The potentiostatic electrodeposition was performed with a voltage of -0.75 V (vs. Ag/AgCl) at 50 °C using a CHI660d potentiostat and total passed charge was 0.6 C cm⁻² for the same amount of electroactive Co(OH)₂. The mechanism of electrodeposition could include electrochemical reaction and precipitation as follows:

Figure 2.2. Schematic illustration of the electrochemical deposition

After the electrodeposition, the electrode was immersed into ethanol to remove Brij56 and ethanol was replaced every 2 hours for at least 4 times in order to completely remove the surfactant. Subsequently, the electrode was immersed in 2-propanol for another 2 hours, rinsed by DI water and annealed under vacuum at 120 °C for 2 hours. Similar procedure was used to deposit $\text{Co}(\text{OH})_2$ on pure Ti substrate for comparative studies.

2.2.3. Characterization

The crystalline structures of the samples were examined by X-ray diffraction measurements (Bruker D8 Advance X-Ray Diffractometer) with Cu $\text{K}\alpha$ radiation. The phase characterization of electrolyte for electrodeposition was performed by polarized optical microscopy (POM, XJP400T, KOZO) equipped with a KER-3100-08S heating

stage and temperature control unit. Morphologies of the products were characterized by field emission scanning electron microscopy (JEOL-JSM-6700F microscope). The chemical compositions were analyzed using energy-dispersive X-ray spectroscopy (EDX) attached to FESEM. Detailed structure analyses were conducted by transmission electron microscopy (TEM, JEOL 2010) operated at 300 kV and high resolution TEM (HRTEM, 300 kV). Raman measurements were also performed by a Renishaw inVia Raman Microscope using Ar⁺ ion laser with the wavelength of 514nm under ambient conditions. The electrochemical behaviors of all electrodes were examined by CHI660d electrochemical workstation. Electrochemical impedance analysis was performed by Autolab PGSTAT302 potentiostat. All measurements were done at room temperature.

2.3. Results and discussion

2.3.1. Indium–tin oxide nanowire array (ITO NWs) on titanium substrate

Surface morphology and crystal structure of as-grown ITO nanowires were examined by FESEM and TEM as shown in Figure 2.3. Figure 2.3a illustrates a typical cross-sectional FESEM image of the as-grown ITO NWs on Ti substrate. ITO NWs with typical lengths of 50 μm in direct contact with the substrate surface was observed. In addition, the top-view low magnification FESEM images (Figures 2.3b and 2.3c) confirm the growth of uniform and well-separated ITO nanowire on titanium substrate. The array is composed of ordered and well-separated ITO nanowires having the length ranging from 30 – 50 μm . Au catalyst of vapor-liquid-solid (VLS) might have been blown away by the argon carrier as it was cooled down to a lower temperature and solidified. This resulted in clean tip of nanowire observed in Figure 2.3d. A typical ITO nanowire

possesses uniform diameter and smooth surface, as shown in a low-magnification TEM image (Figure 2.3e). High-resolution TEM image (HRTEM, Figure 2.3f) was taken to shows that ITO crystal is mainly composed of (111) plans with interlayer spacing of 0.29 nm.

Figure 2.3 FESEM images (cross-sectional view (a), top view (b, c) and high magnification view (d)) of ITO nanowires on Ti substrate. (e) low magnification TEM image of individual ITO nanowire. (f) high-resolution TEM image of ITO nanowire, showing single crystalline structure.

2.3.2. $\text{Co(OH)}_2/\text{ITO}$ NWs heterostructure

Figure 2.4 illustrates the fabrication procedures of $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs composite electrodes. The electrodes were prepared by a new method of combining CVD and potentiostatic electrodeposition. One side of titanium current collector was used for ITO growth and $\alpha\text{-Co(OH)}_2$ electrodeposition. The loading mass of $\alpha\text{-Co(OH)}_2$ was controlled by varying a total passed charge. For comparison, mesoporous $\alpha\text{-Co(OH)}_2$ film was also directly deposited onto bare Ti substrate.

Figure 2.4. Schematic illustration of the experimental procedure for fabrication of $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs and $\alpha\text{-Co(OH)}_2/\text{Ti}$ electrodes via a new method of combining chemical vapor deposition and potentiostatic electrodeposition.

Mesoporous α -Co(OH)₂, which possesses layered structure, acts as electroactive material in the as-prepared composite electrode. On the other hand, ITO NWs play the role of “electron highways”, facilitating charge transport, which may have great potential for achieving good electrochemical properties.

Figure 2.5a shows the wide-angle XRD pattern of mesoporous α -Co(OH)₂/ITO NWs heterostructure. The eight peaks detected can be indexed as ITO(221), ITO(222), ITO(321), ITO(400), ITO(411), ITO(420), ITO(332) and ITO(422) (JCPDS 06-0416). The other two diffraction peaks at 10.8° and 22.2° can be assigned to (003) and (006) planes of layered α -phase Co(OH)₂ [123], which is usually observed in Co(OH)₂ nanostructures prepared by electrodeposition [124]. The sharp and dominant ITO peak at 30.58° indicates that the majority of ITO nanowires grew along [111] direction while only a small amount of nanowires were oriented in other directions. Moreover, as shown in the low-angle XRD pattern (Figure 2.5b), the heterostructure shows a strong reflection peak of at 2 θ equals to 1.46°. This peak can be attributed to d₁₀₀ plane of the P6mm space group with d-spacing of 60.4 Å [120], indicating that the ordered mesoporous structure of lyotropic liquid crystalline (LLC) template was still retained in α -Co(OH)₂ after the electrodeposition. The pore-to-pore distance for this mesoporous array given by d₁₀₀ / cos 30° is determined to be 69.7 Å.

Figure 2.5. (a and b) Wide-angle and low-angle XRD patterns of α -Co(OH)₂/ITO NWs heterostructure, respectively. (c) Room temperature Raman spectrum of α -Co(OH)₂/ITO NWs heterostructure.

Figure 2.5c demonstrates the Raman spectrum of the mesoporous α -Co(OH)₂/ITO NWs heterostructure. ITO is known to possess cubic structure that belongs to I_a^3 , T_h^7 space group. The spectrum shows vibrational modes at 110, 135, 308, 366, 495 and 631 cm⁻¹, which is certainly the signature of the ITO cubic structure. The highest Raman shift at 631 cm⁻¹ is largely due to the superposition of the In–O vibrational modes with frequency 629 cm⁻¹ and the Sn–O vibrational modes with frequency 633 cm⁻¹ [125, 126]. The Raman spectrum also proves the presence of Co(OH)₂ in the as-prepared heterostructure: three intense bands were detected at 456, 522 and 613 cm⁻¹, which are attributed to OCoO bending mode, CoO (A_g) symmetric stretching mode, and CoO (F_{2g}) mode, respectively [127].

Figure 2.6 shows morphology, structural analysis and chemical composition of the mesoporous Co(OH)₂/ITO NWs heterostructure. A uniform Co(OH)₂ shell with the

thickness of 200 – 300 nm was successfully deposited on the ITO NWs, as shown in FESEM images (Figures 2.6a and 2.6b) and low magnification TEM image (Figure 2.6c). The as-deposited $\text{Co}(\text{OH})_2$ exhibits densely interlaced nanosheets with a high active surface area. - The cobalt hydroxide possesses a layered and mesoporous structure, as revealed by the TEM Figures at higher magnification (Figure 2.6d and 2.6e). The bright dots represent pores formed by removing the surfactant template. The cylindrical pores typically have diameters of 2 – 3 nm with interpore distance of about 7nm, calculated from the low-angle XRD result. This mesoporous structure is expected to have a high surface area which is in turn beneficial to improve electrochemical properties. Chemical compositions of the heterostructure were analyzed using EDX attached to the FESEM system. The major existences of In, Co and O are shown in the EDX spectrum recorded from the entire mesoporous $\text{Co}(\text{OH})_2/\text{ITO}$ NWs heterostructure in Figure 2.6f.

Figure 2.6. (a and b) FESEM images of mesoporous α -Co(OH)₂ coated along ITO nanowires. (c and (c and d) Low magnification TEM images of α -Co(OH)₂/ITO NWs heterostructure, showing uniform distribution and layered structure of Co(OH)₂. (e) High magnification TEM image of Co(OH)₂ coating, indicating mesoporous structure. (f) EDX spectrum of the entire α -Co(OH)₂/ITO NWs heterostructure.

From the results obtained from the physical characterizations, it was proven that mesoporous $\alpha\text{-Co(OH)}_2$ on a uniform ITO NWs were successfully synthesized.

Both cyclic voltammetry (CV) and chronopotential charge–discharge methods were used to investigate capacitor behavior of the as-prepared electrodes. All electrochemical measurements were conducted in a 1 M KOH aqueous solution. Figures 2.7a and 2.7b represent CV response of $\alpha\text{-Co(OH)}_2/\text{Ti}$ and $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrodes of the same passed charges and loading masses within potential ranges from -0.2 to 0.65 V, respectively. It is interesting to note that one pair of redox peaks were observed in CV curves at all scan rates, which is distinct from the shape of CV curves of EDLCs (close to ideal rectangular shape), likely due to the electron transfer process in pseudocapacitive $\alpha\text{-Co(OH)}_2/\text{Ti}$ and $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs. The surface faradic reaction can be given as follows [8]:

It can be observed that the shapes of CV curves change with scan rates and those changes can be attributed to peak current (I_p) and peak potential separation (ΔE_p). In the case of $\alpha\text{-Co(OH)}_2/\text{Ti}$, the anodic peak current increases from 0.00298 A to 0.00813 A, 0.01188 A and 0.01692 A and peak potential separation increases from 0.081 V to 0.156 V, 0.201 V and 0.261 V as potential scan rate increasing from 10 mV s^{-1} to 50 mV s^{-1} , 100 mV s^{-1} and 200 mV s^{-1} . This indicates the kinetics-controlled nature of charge/discharge process of Co(OH)_2 . Similar trends are observed in the CV curves of $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs at scan rates equal to 10 mV s^{-1} to 50 mV s^{-1} , 100 mV s^{-1} . However, no cathodic peak was observed at scan rate of 200 mV s^{-1} due to the quasi-

reversible characteristic of the faradic reaction (equation 2.3) and uncompensated potential drop (IR drop). The anodic peak (above 0.1 V) is due to the oxidation of Co(OH)_2 to produce Co(OOH) and the cathodic peak (below 0.1 V) is due to the reverse process. As compared to the CV curves of $\alpha\text{-Co(OH)}_2/\text{Ti}$, $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs generates much larger cathodic and anodic area at all scan rates, indicating its enhanced capacitive behavior.

Figure 2.7. Electrochemical performance. (a and b) CV plots at different scan rates. (c and d) discharge curves at different current densities in potential range of -0.1 V to 0.5 V (e) Capacitance retained ratio versus current density. (f) complex-plane impedance spectra of the $\alpha\text{-Co(OH)}_2/\text{Ti}$ and $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrodes (Potential (V) is with respect to Ag/AgCl reference electrode).

Figures 2.7c and 2.7d show the chronopotential discharge curves of α -Co(OH)₂/Ti and α -Co(OH)₂/ITO NWs electrodes at different discharge current densities in potential windows of -0.1 to 0.5 V, respectively. Their specific capacitance can be calculated from the discharge curve using following equation:

$$SC = I/m \times \Delta t/\Delta V \quad (\text{eqn. 2.4})$$

where SC is specific capacitance (F g⁻¹), I is charge-discharge current (mA), m is the mass of active material (mg, α -Co(OH)₂), Δt is discharge time (s) and ΔV is the potential drop (V). In order to calculate specific capacitance, the mass of Co(OH)₂ is estimated by Faraday's Law, assuming that current efficiency for the electrodeposition is 100%.

The specific capacitance values of α -Co(OH)₂/Ti electrode were determined to be 688, 591, 543 and 473 F g⁻¹ corresponding to the discharge current densities of 1, 5, 10 and 20 A g⁻¹, respectively. The specific capacitance values of α -Co(OH)₂/ITO NWs electrode were calculated to be 1128, 1033, 945 and 913 F g⁻¹, respectively. As expected, the calculated specific capacitance values of two types of electrodes decrease with increasing discharge current density, which is attributed to IR drop [128, 129]. The IR drop increases at higher current density. Moreover, at a higher discharge current, less time is given for diffusion and reaction, which results in higher ionic diffusion resistance. As a result, active Co(OH)₂ may inefficiently get involved in the faradaic reaction. On the other hand, as compared to α -Co(OH)₂/Ti electrode, α -Co(OH)₂/ITO NWs electrode not only demonstrates a significant improvement in capacitive behavior at all current densities, but its capacitance also is not significantly influenced by increasing current density as shown in Figure 2.7e. Taking a specific

capacitance value at 1 A g^{-1} as 100% retention, $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrode retained 100%, 91.56%, 83.78% and 80.94% of its original capacitance at 1 to 5 A g^{-1} , 10 A g^{-1} and 20 A g^{-1} , respectively. The results can be attributed to the high porosity and uniform dispersion of Co(OH)_2 on the conducting substrate. With maximum capacitance of 1128 F g^{-1} , our newly designed electrode demonstrates superior performance compared with previously reported electrode materials such as novel $\beta\text{-Co(OH)}_2$ asymmetric supercapacitor (170 F g^{-1}) [130], graphene- Co(OH)_2 nanocomposites (972.5 F g^{-1}) [118] and mesoporous Co(OH)_2 nanowire (993 F g^{-1}) [120]. As such, $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs heterostructure can be considered as a promising electrode material that can provide high power density.

Electrochemical impedance spectroscopy was carried out in the frequency range from 30 kHz to 0.1 Hz, with the amplitude of perturbation signal equal to 50 mV in order to verify the conductivity enhancement, as presented in Figure 2.7f. The measurement was performed on two types of electrodes ($\alpha\text{-Co(OH)}_2/\text{Ti}$ and $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrodes) with the same mass of active material. The semicircular loops at high frequencies are attributed to charge-transfer resistances of the electrodes and the straight segments at lower frequencies represent capacitive behaviors of the electrodes. The diameter of the semicircular loop for the $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrode is determined to be $11.74 \text{ } \Omega$, which is much smaller than that of the $\alpha\text{-Co(OH)}_2/\text{Ti}$ electrode ($129.63 \text{ } \Omega$), indicating that the mesoporous nanowire structure can significantly improve electron transfer and reduce interfacial resistance during the reaction.

Ruthenium is known as rare transition metal and as a result, it is unarguably highly expensive material. This is certainly the motivation for searching alternative active materials in many studies in the last decade. In contrast, titanium is the ninth most abundant element and contributes up to 0.56% the mass of Earth's crust [40]. Therefore, titanium is certainly a good choice of substrate material in CVD method due to its excellent conductivity and vast resources. As mentioned in this study, only a thin layer of Au was coated on titanium substrate. Although Au is expensive nowadays, only a trace amount of Au was used to achieve a thickness of 5nm. Therefore, we believe that Au-coated titanium substrate is more cost-efficient than ruthenium oxide.

When particles of Co(OH)_2 are used for the electrode, it is required that particles, carbon black, and binder are uniformly distributed on the electrode; the thickness of composite is thin and uniform; the contact between the composite and the substrate is good, to achieve uniform current distribution on the electrode, which leads to the full capacity of the active material in the system. However, it is often difficult to satisfy all the requirements. To overcome such problems, an electrode of Co(OH)_2 nanowire array was introduced using a template method [120]. However, some drop of capacitance of the nanowire array was reported due to the collapse of the end parts of the nanowires during the synthesis procedure. Thus, this proposed heterostructure for $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrode is quite promising because it is a binder-free structure. Moreover, the proposed structure provides an increased accessibility of electrolyte to the electrode and prevents the aggregation of nanowires as presented in Figure 2.4. Such advantages lead not only to reduce charge transfer resistance in the electrode, but also provide the shortest electron transfer pathway through the nanowires.

Nevertheless, further work is required to optimize the formation of $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrode, which leads to more enhanced electrochemical properties.

The study of electrochemical stability of $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrode was performed in 1 M aqueous KOH electrolyte by charge–discharge cycling. At current density of 10 A g^{-1} , the electrode retained 90.9% of its initial specific capacitance after 500 cycles as shown in Figure 2.8, indicating that the as-prepared electrode has long-term electrochemical stability in alkaline solution.

Figure 2.8. Electrochemical properties of $\alpha\text{-Co(OH)}_2/\text{ITO}$ NWs electrode – cycle life data at a discharge current density of 10 A g^{-1} in the potential range of -0.1 to 0.5 V (Potential (V) is with respect to Ag/AgCl reference electrode).

L.Q. Mai et.al. reported synthesis of hierarchical $\text{MnMoO}_4/\text{CoMoO}_4$ heterostructured nanowires electrode for supercapacitor application by facile hydrothermal method [106]. Their electrode design resembles our approach when nanowires are the base and further decorated with another active material. Their technique utilized newly found

multicomponent oxide and achieved encouraging result with capacitance of 187.1 F g^{-1} and excellent cyclability. However, their study encountered the common problem of complicated electrode fabrication. Fabrication of a traditional supercapacitor electrode generally requires a great deal of time to mix the active material with the carbon black and the binder [131]. This mixture will be subsequently pressed or drop-casted onto conductive current collectors, such as graphite paper or nickel foam, followed by a time-consuming drying process. The active material needs to be uniformly distributed around conductive agents (i.e. carbon black species) so that the maximum specific capacitance can be obtained. In other words, the capacitive behavior of electrode depends not only on the nature of the active material but also on its preparation technique. Therefore, our electrode engineering design offers an alternative to fabricated supercapacitor electrodes without the need of using carbon black and a binder. More importantly, this binder-free electrode also provides uniform distribution of active material and prevents agglomeration problems commonly encountered in the preparation of electrode mixture paste. In addition, the contact between nanosheets and ITO nanowire provides the express transport path for fast electron transfer. Many studies were conducted to investigate the feasibility and effectiveness of using binder-free electrodes [132, 133]. In those papers, the authors mainly focused on utilizing carbon fibers and carbon nanotubes as orienting agents. However, carbon-based materials are not as chemically and thermally stable as ITO nanowires at elevated temperature and in an oxygen-rich atmosphere. In addition, as mentioned earlier, the micro spacings between nanowires play a crucial role in maximizing actual active surface area and electrolyte diffusion.

However, carbon fibers/nanotubes were split up by huge spacings and hence, high specific capacitance could not be easily achieved.

C. Yan and coworker's work previously reported $\text{Co}(\text{OH})_2/\text{ITO}$ NWs heterostructure composite for supercapacitor application [134]. Based on cyclic voltammetry measurements, they reported specific capacitance of around 622 F g^{-1} . Inspired by their work, in this study, we tried to further improve supercapacitive performance by increasing surface area. Our main approach is to employ mesoporous structure and to perform Ni doping. The highlight of our work is introduction of lyotropic soft template into deposition of coating along ITO nanowires in order to form mesopores. This approach is only commonly utilized in electrodeposition of film onto two-dimensional substrate but not on one-dimensional array. In order to successfully generate mesoporous structure in nanosheet network coating, various parameters (temperature and electrodeposition rate) must be optimized to achieve efficient diffusion of electrodeposition electrolyte into nanowire array. This is to ensure uniform coating of $\text{Co}(\text{OH})_2$. Therefore, proposed uniform deposition of mesoporous $\text{Co}(\text{OH})_2$ on the nanowires leads to improved ionic diffusion, ultrahigh specific capacitance, and excellent cycle life. All of the above characteristics of as-prepared hierarchical electrodes help to promote itself as the next generation of pseudocapacitor.

2.4. Conclusion

In conclusion, we demonstrated a new method of combining of CVD and potentiostatic electrodeposition methods to synthesize a $\alpha\text{-Co}(\text{OH})_2/\text{ITO}$ NWs heterostructure, which possesses an enhanced supercapacitive behavior and an

improved high discharge rate capability. It has been shown that uniform α -Co(OH)₂ along the ITO NWs can be obtained by electrodeposition at -0.75 V. In addition, α -Co(OH)₂ has mesoporous and layered structure with a high surface area, which results in excellent electrochemical properties. Both CV and chronopotential charge–discharge curves showed that the supercapacitive behavior of α -Co(OH)₂/ITO NWs electrode was superior to that of α -Co(OH)₂/Ti electrode at all scan rates and current densities, due to its one-dimensional-like mesoporous structure, which has a high surface area and improved electron transport from the indirect connection of Co(OH)₂ to Ti current collector through ITO NWs. The unique design of nanoscale heterostructure which combines the advantages of highly active Co(OH)₂ and excellent conductivity of ITO NWs can be considered as a new technique to fabricate porous electrodes for ECs and even for Li-ions battery applications.

Chapter 3: Mesoporous ITO/NiO with a core/shell structure for supercapacitors

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In this study, a novel mesoporous NiO/ITO NW with a shell/core structure has been successfully synthesized by combining chemical vapor deposition (CVD) on titanium substrate and electrodeposition of H₁₂E (hexagonal lyotropic) nickel hydroxide through a lyotropic liquid crystalline (LLC) template, followed by calcination in air at 270 °C. The electrode material is characterized by X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Both cyclic voltammetry (CV) and chronopotentiometry demonstrate enhanced electrochemical properties of NiO/ITO NWs composite electrode and improved supercapacitive behaviors as compared to bulk mesoporous nickel oxide film. Maximum specific capacitance of 1025 F g⁻¹ at a discharge current density of 1 A g⁻¹ in the potential ranges from 0 V to 0.5 V is determined by galvanostatic charge–discharge measurement in 1 M KOH solution. The newly synthesized heterostructure also possesses high capacitance retention ratio at high discharge current densities and long-term electrochemical stability in an alkaline solution. Therefore, this study provides a promising electrode engineering technique for various applications.

3.1. Background

Nickel oxide has drawn tremendous attention because of its well-defined electrochemical redox activity, low fabrication cost and possibility of improved capacitive performance, through different preparation methods. The chemical precipitation method was firstly employed to synthesize NiO for a supercapacitor [135]. However, the electrode prepared by this technique demonstrated very low specific capacitance (SC) of about 108 F g^{-1} . On the other hand, electrochemical techniques are known to possess unique principles and allow certain controls over the structure and morphology of active materials [136, 137]. In addition, the surface area of active material can be enhanced by introduction of porous structure. However, one main problem encountered by electrochemical method is lowered conductivity of electrode when deposited layer is thickened. On top of that, most of the reports were more concerned about the enhancement of SC values and insufficient attention was paid to capacitance degradations of metal oxide/hydroxide materials at high current densities.

One major approach to solve this problem is to employ a nanowire/nanotube system as scaffold for electrodeposition. Carbon nanotubes, indium-tin oxide nanowires (ITO NWs), and zinc oxide nanowires (ZnO) are potential candidates. Nonetheless, carbon nanotubes are not suitable for those applications at elevated temperature and can be easily oxidized by oxygen in atmosphere. On the other hand, ITO generally has higher electrical conductivity than ZnO [138, 139]. ITO NWs are known to possess excellent electrical properties and thermal stability [140] which allow great applications in the electronics. ITO NWs array can be easily grown on different substrates [122, 141] by chemical vapor deposition in an oxygen deficient atmosphere and under a vacuum

condition. Therefore, in this study, we decided to utilize chemical vapor deposition (CVD) to develop indium-tin oxide nanowires on a titanium substrate and then deposited mesoporous hydroxide on the nanowires by electrodeposition through a lyotropic liquid crystalline (LLC) template. NiO nanoflake (NF) onto indium-tin oxide nanowires (ITO NWs) was obtained after heat treatment in the air at 270 °C. Titanium was chosen as current collector owing to its well-known excellent mechanical, chemical and thermal stability as well as abundance in the Earth's crust. A mesoporous nickel oxide film on the titanium substrate was also prepared for comparison.

3.2. Experiment

3.2.1. Preparation of nickel nitrate electrolyte solution and electrodeposition of mesoporous nickel oxide

50 wt.% Brij56 (polyoxyethylene(10) cetyl ether, C₁₆ [EO]₁₀) and 50 wt.% Ni²⁺ electrolyte (1.8 M Ni(NO₃)₂ and 0.075 M NaNO₃ as supporting electrolyte) were mixed thoroughly to prepare the lyotropic liquid crystalline (LLC) template. A standard three-electrode cell with an ITO NWs/Ti working electrode, a platinum counter electrode, and a standard Ag/AgCl electrode was used for electrodeposition. Potentiostatic electrodeposition for H₁-e Ni(OH)₂ was performed at 40 °C and with a voltage of -0.7 V (vs. Ag/AgCl) using CHI660d potentiostat. A total charge of 1.2 C cm⁻² was applied to obtain the same amount of electroactive Ni(OH)₂ in all samples. The mechanism of the electrodeposition could include electrochemical reaction and precipitation as follows:

After the electrodeposition, the electrode was immersed into ethanol to remove the surfactant. Ethanol was replaced every 2 hours for 4 times and the electrode was then immersed in 2-propanol for another 2 hours. This was to ensure complete removal of the surfactant. Subsequently, the electrode was rinsed with DI water and annealed in the air at 270 °C for 2 hours. At a temperature of 270 °C, Ni(OH)_2 was converted to NiO as previously reported in [142]. A similar procedure was adopted to deposit NiO on the pure titanium substrate for comparative studies.

3.2.2. Characterization

Morphologies of the products were characterized by using a field emission scanning electron microscopy (JEOL-JSM-6700F microscope) operated at 5 kV. The crystalline structures of the specimens were examined by a X-ray diffraction measurements (Bruker D8 Advance X-Ray Diffractometer) with Cu K α radiation ($\lambda = 0.15406$ nm) in the ranges from 10° to 45°. Detailed structure analyses were carried out by a transmission electron microscopy (TEM, JEOL 2010) at 300 kV. Prior to the TEM analysis, the samples were dispersed in ethanol, sonicated, dropped onto a copper grid, and dried in a vacuum oven. The chemical compositions were investigated using an energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM. Raman measurements were also performed by a Renishaw inVia Raman Microscope equipped with a charge couple device (CCD) detector to analyze chemical bonding states of the surface. An Ar⁺ ion laser with a wavelength of 514nm was used as an excitation source. The electrochemical measurements of all samples were conducted by CHI660d electrochemical workstation. Electrochemical impedance analysis was conducted by an

Autolab PGSTAT302 potentiostat. Their specific capacitance was calculated from the discharge curves using the following equation:

$$SC = I/m \times \Delta t/\Delta V \quad (\text{eqn. 3.2})$$

where SC is the specific capacitance (F g⁻¹), I is the charge-discharge current (mA), m is the mass of active material (mg, NiO in this study), Δt is the discharge time (s) and ΔV is the potential drop (V). In order to calculate a specific capacitance, the mass of NiO was estimated by the Faraday's law, assuming that current efficiency for the electrodeposition is 100%.

3.3. Results and discussion

Figure 3.1 shows the wide-angle XRD pattern of mesoporous ITO NWs, as-prepared Ni(OH)₂/ITO NWs and NiO/ITO NWs heterostructure. The analysis of XRD pattern of ITO NWs confirms the successful synthesis of the cubic phase of the ITO. Six peaks detected can be indexed as ITO(211), ITO(222), ITO(400), ITO(411), ITO(420) and ITO(332) (JCPDS 06-0416). The XRD pattern of Ni(OH)₂/ITO NWs heterostructure shows three additional peaks at 11.6°, 33.6° and 41.1° which can be assigned to (001), (110) and (103) planes of a layered nickel hydroxide hydrate (JCPDS 22-0444). Heat treatment of the Ni(OH)₂/ITO NWs heterostructure at 270 °C led to the removal of water molecules and hydroxyl group residue, resulting in the conversion of Ni(OH)₂ to NiO. This is clearly illustrated in the XRD pattern of NiO/ITO NWs heterostructure by absence of Ni(OH)₂ peaks but by appearance of two sharp NiO peaks at 37.2° (111) and 43.3° (200) (JCPDS 04-0835).

Figure 3.1.(a) Wide-angle XRD patterns of ITO NWs, $\text{Ni}(\text{OH})_2/\text{ITO}$ NWs and NiO/ITO NWs heterostructures.

On the other hand, in the low-angle XRD pattern of the NiO/ITO NWs heterostructure (Figure 3.2), a strong and broad reflection peak at 2θ equal to 1.48° was observed, indicating the presence of mesopores in the NiO . This peak can be attributed to the d_{100} plane of the $P6mm$ space group (hexagonal structure) with d-spacing of $59.6 \text{ \AA}$, implying that the ordered mesophase structure of nickel oxide still remains after the electrodeposition through the hexagonal structure of lyotropic liquid crystalline (LLC) template, followed by the heat treatment. The pore-to-pore distance for this mesopore array given by $d_{100} / \cos 30$ is determined to be $68.8 \text{ \AA}$.

Figure 3.2. (b) Low-angle XRD pattern of NiO/ITO NWs heterostructure system.

Figure 3.3 demonstrates the Raman spectrum of the mesoporous Ni(OH)₂/ITO NWs and NiO/ITO NWs heterostructures in different ranges of the Raman shift. The Ni(OH)₂/ITO NWs spectrum in the ranges of 100 – 700 cm⁻¹ (Figure 3.3a) shows the vibrational modes at 109, 133, 307, 367, 496 and 631 cm⁻¹ of the as-grown ITO cubic structure that belongs to I_a^3 , T_h^7 space group [125, 143]. There is no peak associated with the nickel hydroxide detected. A similar spectrum is identified in the NiO/ITO NWs except for a low intensity peak at 367 cm⁻¹. The disappearance of this mode in the NiO/ITO NWs spectrum is likely due to the presence of an additional strong peak at around 518 cm⁻¹, representing the Ni–O stretching vibration of Ni²⁺ species associated with O²⁻ which is not linked to a proton [144]. This transformation was attributed to the removal of the hydroxide group due to the heat treatment. Figure 3.3b presents the spectra of the heterostructures in the range of 700 – 1300 cm⁻¹. The conversion of nickel hydroxide to nickel oxide is clearly observed. The bands at 1002 cm⁻¹ and 1046

cm^{-1} imply the existence of some absorbed nitrate species [126, 145]. At a high temperature, those species were removed and two-phonon 2LO mode of black nickel oxide as assigned in [146] as observed. The spectrum of $\text{Ni}(\text{OH})_2/\text{ITO}$ exhibits a broad peak located at 3641 cm^{-1} which is attributed to the symmetric stretch of surface OH^- groups [144, 147] in the high frequency region in Figure 3.3c. However, after the heat treatment at $270\text{ }^\circ\text{C}$, the peak disappeared, indicating that hydroxide groups were entirely removed in the nickel oxide.

Figure 3.3. Room temperature Raman spectrum of $\text{Ni}(\text{OH})_2/\text{ITO}$ NWs and NiO/ITO NWs heterostructure electrodes in different range of Raman shift (a) $100 - 700\text{ cm}^{-1}$. (b) $700 - 1300\text{ cm}^{-1}$. (c) $3500 - 4000\text{ cm}^{-1}$.

The SEM and TEM images of ITO NWs/ $\text{Ni}(\text{OH})_2$ were also presented in Figures 3.4 and 3.5, respectively.

Figure 3.4. FESEM image of $\text{Ni}(\text{OH})_2$ coated along ITO nanowires.

Figure 3.5. TEM images of $\text{Ni}(\text{OH})_2$ coated along ITO nanowire. Scale bar – 20 nm.

In addition to the crystallinity identified by XRD and the bonding structure determined by Raman measurement, surface morphology was also investigated by FESEM. Figure 3.6 represents the morphology and structure of the mesoporous NiO/ITO NWs heterostructure. In the FESEM images (Figures 3.6a and 3.6b) and low magnification

TEM image (Figure 3.6c), densely interlaced nickel oxide nanoflakes were observed. A uniform NiO shell with the thickness of 50 – 100 nm was deposited along the ITO NWs by the potentiostatic electrodeposition. The shell is composed of ultrathin nanosheets that aggregate with one another. There was no noticeable changes in morphology of NiO as compared to that of $\text{Ni}(\text{OH})_2$ due to heat treatment. However, the existence of the mesopores in NiO matrix appeared more obviously. As-deposited nickel oxide possesses a mesoporous structure with a cylindrical pore of 2 – 3 nm in diameter, as revealed by the TEM image at the high magnification (Figure 3.6d).

Figure 3.6. (a) FESEM image of NiO coated along ITO nanowires. (b) FESEM image of the tip of NiO/ITO NWs heterostructure. (c) Low magnification TEM images of NiO/ITO NWs heterostructure, showing

uniform distribution of NiO nanoflakes. (d) High magnification TEM image of NiO coating, indicating mesoporous structure.

The bright dots in the inset represent the pores formed from the removal of the surfactant by alcohol and calcination in air. Additionally, extra pores may be also generated due to release of H₂O molecules evolved from decomposition of Ni(OH)₂ at high temperature. Average interpore distance calculated from the low-angle XRD result is determined to be about 6.8 nm. This mesoporous structure is expected to have a high surface area which is beneficial for improving the pseudocapacitive behavior.

Chemical composition analysis was also conducted by EDX attached to the FESEM. The major existence of In, Ni and O in the mesoporous NiO/ITO NWs heterostructure is shown in Figure 3.7. Sn was not detected by EDX likely due to its low content in the ITO NWs array.

Figure 3.7. EDX spectrum of the entire NiO/ITO NWs heterostructure.

From the physical characterizations, it is clear that the mesoporous NiO nanoflakes were successfully deposited on the highly uniform ITO NWs. The capacitive behavior of a composite electrode in an alkaline solution arises from the charge storage in an electrical double layer at the electrode/electrolyte interface and redox reactions on the surface of electroactive nickel oxide. The surface faradic reaction in an alkaline solution is as follows [148]:

Both cyclic voltammetry (CV) and chronopotential charge–discharge measurements were used to examine its capacitor behavior and quantify its specific capacitance. All electrochemical measurements were performed in a 1 M KOH aqueous solution. Figures 3.8a and 3.8b represent the CV of the NiO/Ti and NiO/ITO NWs electrodes of the same charges and loading masses within potential ranges from -0.2 to 0.85 V. One pair of redox peaks was observed in the CV curves at all scan rates. The shape of the CV curves of the electrodes is clearly distinguished from those of the EDLCs, which are close to a rectangular shape, due to the faradaic reactions (in equation 3.3) in pseudocapacitive NiO/Ti and NiO/ITO NWs. The shapes of CV curves change with different scan rates because diffusion in the solution and resistance in the electrode affect the current response at the switching potential [39, 149, 150]. Those changes can be represented by a peak current and peak potential separation. In the NiO/Ti (Figure 3.8a), the anodic peak current increases from 0.00409 A to 0.00979 A and 0.01589 A and peak potential separation increases from 0.132 V to 0.229 V and 0.304 V as a potential scan rate increases from 10 mV s⁻¹ to 50 mV s⁻¹ and 100 mV s⁻¹. A similar trend was observed in CV curves of NiO/ITO NWs (Figure 3.8b) when the scan rate

increases from 10 mV s^{-1} to 50 mV s^{-1} and 100 mV s^{-1} . The anodic peak (above potential of 0.35 V) is caused by the oxidation of nickel oxide to nickel hydroxide. The cathodic peak (below potential of 0.35 V) is caused by the reverse process.

Figure 3.8. Electrochemical performance (a and b) CV plots at different scan rates. (c and d) discharge curves at different current densities in potential range of 0 V to 0.5 V of the NiO/Ti and NiO/ITO NWs

electrodes. (e) typical charge-discharge cycle of both electrode at 1 A g^{-1} (Potential (V) is with respect to Ag/AgCl reference electrode).

It is interesting to note that CV curves generated by NiO/ITO NWs electrode has a much larger area than that of NiO/Ti at all scan rates, indicating an enhanced capacitive behavior of the composite electrode.

Figures 3.8c and 3.8d show the chronopotential discharge curves of the NiO/Ti and NiO/ITO NWs electrodes at different discharge current densities in potential window ranges from 0 to 0.5 V. For the NiO/Ti electrode, the specific capacitance values were determined to be 416, 357, 333 and 260 F g^{-1} corresponding to the discharge current densities of 1, 5, 10 and 20 A g^{-1} , respectively according to equation 3.2. For the NiO/ITO NWs composite electrode, the specific capacitance values were calculated to be 1025, 942, 885 and 856 F g^{-1} , respectively. It is worth noting that actual specific capacitances might be higher than reported values in this study due to the fact that electrodeposition current efficiency rarely reaches 100%. The calculated specific capacitance values of both electrodes decrease with increasing discharge current density due to the IR drop [128], which is generated at a large discharge current and results in a low capacitance. Moreover, diffusion in the electrolyte and reaction at the interface is limited at a high discharge current, leading to a large ionic diffusion resistance. Consequently, an insufficient amount of nickel oxide contributes to the faradic reaction and specific capacitance. Nevertheless, the newly synthesized mesoporous heterostructure clearly demonstrates a considerable enhancement in the specific capacitance values of the nickel oxide at all the current densities. Figure 3.8e shows typical galvanostatic charge-discharge cycles of two electrodes at 1 A g^{-1} . Both

electrodes are quickly charged to around 0.35 V and gradually to 0.5 V. The shapes of these two curves are generally identical. There are sudden potential drops at the beginning of discharge, followed by slow decays of potential.

Moreover, the NiO/ITO NWs composite electrode demonstrates much smaller capacitance degradation caused by the increment of voltage (IR drop) at larger current densities than the NiO film on the titanium substrate. For example, taking a specific capacitance value at 1 A g⁻¹ as 100% retention when current density increased from 1 to 5 A g⁻¹, 10 A g⁻¹ and 20 A g⁻¹, the NiO/ITO NWs electrode retained 100%, 91.9%, 86.34% and 83.51% of its original capacitance, respectively. For the NiO/Ti, the capacitance retained ratio was 100%, 85.81%, 80.04% and 62.5% at a discharge current of 1 A g⁻¹, 5 A g⁻¹, 10 A g⁻¹ and 20 A g⁻¹, respectively (Figure 3.9a). The results can be attributed to both the mesoporous structure and the highly uniform dispersion of nickel oxide on the nanowires. Even though capacitance degradation was minimized, the capacitance of the heterostructure at 20 A g⁻¹ was equal to only 83.51% of that at 1 A g⁻¹. Such deterioration in the pseudocapacitive performance comes from the nature of active NiO.

Figure 3.9. Capacitance retained ratio at different current densities.

Electrochemical impedance spectroscopy was carried out with a perturbation signal equal to 50 mV, in order to further understand the capacitive behavior of NiO associated with the resistance of the electrodes as presented in Figure 3.10. Two distinct components (i.e. high frequency and low frequency) can be identified for both complex plane plots of two types of electrodes. The semicircular loop at a high frequency associates with the surface properties of mesoporous materials, representing the charge-transfer resistance of the electrodes. On the other hand, the straight segment at a lower frequency represents capacitive behavior of the electrodes. Its slope exhibits diffusive resistance of the electrolyte in the pores of the mesoporous electrode. The diameter of the semicircular loop of the NiO/ITO NWs electrode is determined to be 12.5 Ω , which is much smaller than that of the NiO/Ti electrode (25.3 Ω), indicating that charge transfer is much faster at the interface of the mesoporous nickel oxide on the nanowire than at that of mesoporous nickel oxide on the flat substrate. Moreover, the

slope of the line of the NiO/ITO NWs heterostructure electrode in lower frequency regions is higher than that of the NiO/Ti electrode, indicating that the kinetics of the oxidation process is much less influenced by the diffusion of reactants in the pores on the nanowires than in those on the flat surface. The low frequency responses may be associated with the diffusion of the components in the pores, the transfer process on the electrode, and/or the generation of intermediate species during the oxidation process.

Figure 3.10. Complex-plane impedance spectra of the NiO/Ti and NiO/ ITO NWs electrodes.

The electrochemical stability of the NiO/ITO NWs electrode was investigated in 1 M aqueous KOH electrolyte by charge–discharge cycling in Figure 3.11. The electrode was tested at current density of 1 A g⁻¹ for 500 cycles in the potential window ranges from 0 V to 0.5 V. It is observed that the specific capacitance degrades clearly in the

first 100 cycles due to the slow oxidation of Ni^{2+} to Ni^{3+} , which is more stable in the KOH electrolyte. After 500 cycles, approximately 7.3% of original capacitance is lost. On top of that, coulombic efficiency (i.e. ratio of discharging time to charging time) is around 98-99.5%. This indicates a good cycle life and long-term electrochemical stability of the NiO/ITO NWs composite electrode in the alkaline solution.

Figure 3.11. Cycle life data of NiO/ITO NWs composite electrode at a discharge current density of 1 A g^{-1} in the potential range from 0 to 0.5 V (Potential (V) is with respect to Ag/AgCl reference electrode).

X.D. Li et. al. utilized carbon microfiber (CMFs) as a substrate for the radial growth of Zn_2SnO_4 (ZTO) nanowires which was then coated with MnO_2 [151]. Their electrode design shares the same approach as ours. This novel nanoarchitecture demonstrated a

very high specific capacitance of 622 F g^{-1} at a scan rate of 2 mV s^{-1} in an aqueous Na_2SO_4 solution. The electrode also possesses excellent cycle life. Similar fruitful results were achieved with our electrode fabrication. X.H. Lu and his coauthors also demonstrated the idea of using carbon fabric as current collector for the growth of titanium nitride (TiN) nanowires [152]. Although TiN possesses superior electrical conductivity ($4000\text{--}55500 \text{ S/cm}$), its application as supercapacitor is hindered by irreversible redox reaction. In order to overcome this problem, the authors propose the use of poly(vinyl alcohol) (PVA)/KOH gel as the electrolyte which is usually not easily handled. Although carbon-based substrate is cheaper and potentially offer a higher surface area than the titanium substrate, it may not be suitable for application at high temperatures and oxygen rich atmospheres. On the other hand, as compared to their study, our ordered mesoporous structure was generated by a simple electrodeposition method through a surfactant, in the deposition of the active layer, which increases its surface area and facilitates the diffusion of electrolyte species. On top of that, due to high activity nature and good reversibility of redox reaction of NiO, we can also avoid the usage of solid-state polymer electrolyte.

One dimensional nanostructure has been known to have unique chemical and physical properties as compared to the bulk materials. In a microscopic point of view, the proposed mesoporous nanowire-like nickel oxide is a new type of one dimensional nanostructure which can have various applications. This nanostructure can provide not only firm transporters (ITO NWs) but also large interfacial areas for the charge transport process and the faradaic reaction. In fact, an electrolyte can access not only the micron spacings between the ITO nanowires but also the mesopores in the nickel oxide,

enhancing the charge transport rates and the faradaic redox process compared to the bulk material. Thus, NiO/ITO NWs heterostructure can be considered a promising candidate for electrode material for various applications.

3.4. Conclusion

In this paper, we combined CVD and potentiostatic electrodeposition methods to fabricate the mesoporous NiO/ITO NW with a shell/core structure. Uniform nickel oxide deposition along the ITO NWs was achieved by electrodeposition at -0.7 V. NiO nanoflakes with mesoporous structure and high surface area were obtained through the lyotropic liquid crystalline (LLC) template, resulting in excellent electrochemical properties. The supercapacitive behavior of mesoporous NiO/ITO NWs electrode was superior to that of the NiO/Ti electrode at all scan rates and discharge current densities. The specific capacitance of 1025 F g^{-1} was obtained from the mesoporous NiO/ITO NWs heterostructure at a discharge current density of 1 A g^{-1} in the potential ranges from 0 V to 0.5 V in 1 M KOH solution. The newly synthesized heterostructure also possesses a high capacitance retention ratio at high discharge current densities and long-term electrochemical stability in an alkaline solution. This unique design of nanoscale heterostructure can be potentially considered as a new technique to fabricate mesoporous nanowire-like composite electrodes for various applications.

Chapter 4: Capacitive behavior of mesoporous manganese dioxide on indium–tin oxide nanowires

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In this chapter, a novel mesoporous MnO_2/ITO NWs nanocomposite is successfully fabricated by using a chemical vapor deposition on a titanium substrate, followed by electrodeposition through a lyotropic liquid crystalline with hexagonal phase and calcination in air. The heterostructure is characterized by low-angle XRD, wide-angle XRD, raman spectroscopy, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Electrochemical measurements are carried out by cyclic voltammetry (CV) and chronopotentiometry in a 0.5 M Na_2SO_4 aqueous solution. The nanocomposite exhibits a significantly enhanced electrochemical performance and higher capacitance retention ratio, as compared to mesoporous manganese oxide (MnO_2) film. From charge-discharge measurements, a specific capacitance of 821 F g^{-1} for the nanocomposite is achieved at a discharge current density of 1 A g^{-1} in potential ranges from -0.1 to 0.8 V. These characteristics allow the newly fabricated hybrid electrode to be widely used for various applications.

4.1. Background

In the last decade, substantial attention is gradually shifted toward manganese oxide because it is more cost-efficient and more environmentally friendly than other transition metal oxides. More importantly, MnO_2 can be operated in a wide potential window and can be easily fabricated using various methods, such as hydrothermal technique [153, 154], sol-gel process [83, 155, 156] and electrodeposition [84, 149, 157]. Among the methods, electrodeposition is the most promising technique because it has unique principles that offer control over the morphology and structure of manganese oxide. Moreover, the capacitive behavior of electrochemically deposited mesoporous MnO_2 film has been extensively investigated in recent studies [158, 159] as a potential electrode for pseudocapacitors. However, the specific capacitance of the mesoporous MnO_2 film in the papers was relatively low ($\sim 460 \text{ F g}^{-1}$), which is likely due to the notoriously low conductivity nature of MnO_2 and the limited access of electrolyte to the basal layers of MnO_2 . In addition, little effort was made to minimize the capacitance degradation at higher discharge current densities.

In this paper, we synthesized a unique nanocomposite to overcome such problems. ITO nanowires have excellent electrical properties and thermal stability. Individual ITO nanowire possesses resistivity of $2.4 \text{ } \Omega \text{ cm}$ and electron density up to $2.6 \times 10^{20} \text{ cm}^{-3}$ [160]. For the synthesis of such MnO_2/ITO NWs nanocomposite, chemical vapor deposition (CVD) was used to develop indium-tin oxide nanowires (ITO NWs), and electrodeposition of MnO_2 was then conducted through a lyotropic liquid crystalline with hexagonal phase.

4.2. Experiment

4.2.1. Preparation of manganese acetate electrolyte solution and electrodeposition of mesoporous manganese (IV) oxide (MnO₂)

Lyotropic liquid crystalline (LLC) template was a binary system of 60 wt% Brij56 (polyoxyethylene(10) cetyl ether, C₁₆ [122]₁₀) and 40 wt% Mn²⁺ electrolyte (0.5 M (CH₃COO)₂Mn and 0.51 M (CH₃COO)K). In order to prepare this electrolyte, the surfactant was first melted at 60 °C and the aqueous salt solution was then added dropwise according to pre-determined ratio. The mixture was stored in a sealed vial and placed in a thermostat oven at 60 °C, followed by vigorous shaking until a homogenous mixture was achieved.

Electrodeposition of manganese dioxide was carried out in a standard three-electrode cell equipped with an ITO NWs/Ti working electrode, a platinum counter electrode, and a standard Ag/AgCl reference electrode. The electrodeposition was performed at 40 °C with a voltage of 1 V (vs. Ag/AgCl) by CHI660d potentiostat. The mechanism is based on the electrochemical reaction and precipitation:

Upon the completion of the electrodeposition, the working electrode was immersed into ethanol (which was replaced every 2 hours for at least 4 times), followed by immersion in 2-propanol for another 2 hours to remove the surfactant completely. The electrode was then rinsed by DI water, air-dried and annealed at 200 °C for 2 hours. Manganese dioxide film on titanium substrate was also prepared for comparison.

4.2.2. Characterization

The crystalline structures of the samples were characterized by using X-ray diffraction measurements (Bruker D8 Advance X-Ray Diffractometer) with Cu K α radiation ($\lambda = 0.15406$ nm) in the range from 10° to 45° . The phase behavior of the electrolyte was investigated by polarized optical microscopy (POM, XJP400T, KOZO) equipped with a KER-3100-08S heating stage and a temperature control unit. Morphologies of the products were examined using field emission scanning electron microscopy (JEOL-JSM-6700F microscope). The chemical compositions were analyzed using energy-dispersive X-ray spectroscopy (EDX) attached to the FESEM. Detailed structure analyses were conducted by transmission electron microscopy (TEM, JEOL 2010) operated at 300 kV. Raman measurements were also performed by a Renishaw inVia Raman Microscope using an Ar $^+$ ion laser with the wavelength of 514 nm under ambient conditions. A CHI660d electrochemical workstation was used to characterize the samples. Electrochemical impedance analysis was performed by Autolab PGSTAT302 potentiostat.

4.3. Results and discussion

Figure 4.1 shows the structures of two types of electrodes ((a) mesoporous MnO $_2$ film and (b) mesoporous MnO $_2$ /ITO NWs). As shown in Figure 4.1a, only the top layer of MnO $_2$ can be exposed to the electrolyte and as a result, a limited amount of active material is involved in the redox reaction. Electrons are required to pass through multilayers of MnO $_2$ to reach the current collector and external circuit. This long electron transport path has negative impact on the supercapacitive performance of the electrode

due to the low conductivity of MnO_2 . These two major problems are commonly encountered in the mesoporous film. Thus, in this study, a novel composite electrode, (with the presence of highly conductive ITO nanowires acting as an electron bridge which connects the active material and the current collector), is introduced to enhance the accessibility of electrolytes and shorten the electron transport path in order to improve its performance. Figure 4.1b shows a proposed design of electrode architecture to solve the problems.

Figure 4.1. Structure of (a) mesoporous MnO_2 film on titanium current collector and (b) mesoporous MnO_2 /ITO NWs composite electrode.

X-ray diffraction measurements were firstly performed to study the crystal structure of final products. Figure 4.2a presents the wide-angle XRD patterns of the as-prepared amorphous MnO_2 /ITO NWs heterostructure annealed at 200 °C and α - MnO_2 /ITO NWs

heterostructure annealed at 450 – 500 °C. The XRD results confirm the successful synthesis of the cubic phase of ITO with six observable peaks indexed as ITO(211), ITO(222), ITO(400), ITO(411), ITO(420) and ITO(332) (JCPDS 06-0416). The ITO(222) peak at $2\theta = 30.6^\circ$ is the sharpest and the most dominant peak, indicating that the majority of ITO NWs were oriented along the [111] direction and only a small amount of nanowires were grown in other directions. On the other hand, as expected, no clear peak associated to MnO_2 can be identified in the XRD pattern of MnO_2/ITO NWs heterostructure annealed at 200 °C in air due to the amorphous nature and the small grain crystal size of MnO_2 [161, 162]. However, when annealing temperature is raised to 450 – 500 °C, the amorphous MnO_2 starts to be converted to $\alpha\text{-MnO}_2$. This leads to the appearance of two additional peaks at 28.8° and 37.5° which can be assigned to (310) and (211) planes of $\alpha\text{-MnO}_2$ (JCPDS 44-0141), respectively. This reveals the presence of MnO_2 in nanowire network. The LLC phase structure of the electrolyte was confirmed by polarized optical microscopy as shown in Figure 4.2b. The POM image shows a focal conic fan texture which is a hexagonal liquid crystalline phase. This plays an important role in the formation of mesopores manganese dioxide. The low-angle XRD pattern of MnO_2/ITO NWs heterostructure is shown in Figure 4.2c. The diffraction pattern depicts a strong and broad reflection peak at 2θ equal to 1.45° , which indicates the presence of mesopores in the MnO_2 . This broad peak can be assigned to d_{100} plane of the P6mm space group with d-spacing of 60.9 Å. The mesopores were formed by the removal of the surfactant present in product of electrodeposition by immersion in alcohol followed by calcination in air. The interpore distance for this hexagonal array given by $d_{100} / \cos 30$ is calculated to be 70.3 Å.

Figure 4.2. (a) Wide-angle XRD patterns of amorphous MnO₂/ITO NWs heterostructure and α -MnO₂/ITO NWs heterostructures annealed at different temperatures. (b) POM image of (CH₃COO)₂Mn electrolyte for electrodeposition with hexagonal structure (c) Low-angle XRD pattern of MnO₂/ITO NWs system.

Figure 4.3 represents the Raman spectrum of MnO₂/ITO NWs heterostructure. ITO was reported to have a cubic structure which belongs to I_a^3 , T_h^7 space group. As such, the presented spectrum of MnO₂/ITO NWs in the range of 100 – 850 cm⁻¹ demonstrates vibrational modes at 110, 134, 307, 366, 498 and 631 cm⁻¹. Those are characteristic modes of as-grown single crystalline ITO nanowires. On the other hand, there are two

additional prominent peaks at 569 and 650 cm^{-1} , which can be attributed to Mn–O lattice vibrations of MnO_2 [163, 164].

Figure 4.3. Raman spectrum of MnO_2 /ITO NW heterostructure electrode.

In addition to the studies of crystallinity and surface bonding structure, surface morphology of the heterostructure was characterized by FESEM. Figure 4.4a shows the cross-sectional view of as-grown ITO NWs with lengths in the range of 30-50 μm . The ITO NWs are uniform and well separated as shown in the high magnification FESEM image (Figure 4.4b). This allows us to confirm the achievement of sufficient spacing between nanowires as stated earlier. More importantly, this design potentially leads to enhanced conductivity and improved capacitance performance, which will be discussed in the latter part of this paper. It is interesting to note that there is no catalyst droplet observed at the tip of the nanowire (Figure 4.4c) even though a thin layer of Au catalyst coating is required for vapor-liquid-solid (VLS) growth in oxygen deficient environment [165]. TEM characterization was also carried out to examine in detail the crystal

structure of the ITO NWs. A smooth surface of a representative ITO nanowire was observed from the low-magnification TEM image (Figure 4.4d). In addition, the high-resolution TEM image (Figure 4.4e) shows that the ITO nanowire is a single crystalline, grown in [111] direction with an interlayer spacing of 0.29 nm corresponding to the dominant ITO peak at 30.6° in the wide-angle XRD pattern. Both high-magnification FESEM and TEM images show that the ITO growth was initiated by the hexagonal (111) crystal face.

Figure 4.4. FESEM images of ITO nanowires (a) cross-sectional view, (b) top view and (c) high magnification view. (d) low-magnification TEM image of single ITO nanowire. (e) high-resolution TEM image of ITO nanowire, indicating single crystalline structure.

FESEM and TEM characterizations were also carried out to ensure the achievement of mesoporous MnO_2 /ITO NWs heterostructure. Highly uniform MnO_2 coating with a thickness of 100–200 nm along the ITO nanowire was observed from the FESEM and TEM images (Figure 4.5a, 4.5b and 4.5d).

Figure 4.5. (a) FESEM image of MnO_2 -coated-ITO nanowires. (b) FESEM image of the tip of MnO_2 /ITO NWs heterostructure showing the thickness of the MnO_2 coating. (c) High magnification FESEM image of MnO_2 coating consisting of nanofibers. (d) Low magnification TEM images of MnO_2 /ITO NWs heterostructure, representing uniform coating of MnO_2 nanofibers. (e) High magnification TEM image of MnO_2 coating with mesoporous structure.

Potentiostatic electrodeposition is proven to be a facile technique to produce such ordered hybrid structure of densely interlaced MnO_2 nanofibers, as presented in high-magnification FESEM image (Figure 4.5c). Additionally, the TEM image at the high magnification (Figure 4.5e) clearly depicts the mesoporous structure of the MnO_2 shell with mesopores of 2 – 3 nm in diameter (bright dots) marked by red arrows. The generation of cylindrical pores was resulted from removal of the LLC template by alcohol and heat treatment. This is also in good agreement with the low-angle XRD result shown above.

Surface chemical composition analysis was also performed by EDX attached to the FESEM. The EDX spectrum presents the main components of the mesoporous MnO_2/ITO NWs as shown in Figure 4.6. Sn was not clearly detected by EDX, which is likely due to its low content as dopant.

Figure 4.6. EDX spectrum of the entire MnO_2/ITO NWs heterostructure.

After typical characterizations, the pseudocapacitive performance of MnO₂/ITO NWs heterostructure was then studied and compared with that of MnO₂ film. The capacitive behavior both types of electrodes was examined in a 0.5 M aqueous Na₂SO₄ electrolyte. The pseudocapacitance of MnO₂ can be elaborated by two mechanisms proposed for the charge storage in MnO₂-based electrode. In the first proposed mechanism, the alkali metal cation (i.e. Na⁺ in this paper) is intercalated in electrode during reduction and deintercalated in oxidation [166] as follows:

The second one is associated with adsorption of Na⁺ cation in electrolyte on electrode surface [167] as follows:

In our present study, the redox process is mainly governed by intercalation and deintercalation of Na⁺ ions into a mesoporous MnO₂ matrix. Scan rate has significant impact on the diffusion of cations. For instance, at slower scan rates, Na⁺ ions have sufficient time to be inserted in all available channels on surface and in the core of the MnO₂ matrix. Nevertheless, at higher scan rates, Na⁺ ions can only reach the outer electrode surface and the interior pores are not accessible, which certainly leads to reduced capacitance. In other words, supercapacitive behavior of MnO₂ depends on the electroactive area of active material, electrolyte diffusion and electron transfer. Inspired by this idea, tremendous effort was devoted to determine the optimal condition for the nanowire synthesis in terms of adequate spacing between nanowires through a series of CVD experiments. Those micro-spacings are of paramount importance since they

allow better diffusion of electrolytes, which is in turn beneficial to interaction between the surface of the active material and electrolyte solution. In addition, great electrical conductivity of ITO nanowires allows them to play the role of electron transport paths facilitating charge transport. These two factors are expected to lead to significantly enhanced electrochemical capacitance.

Figure 4.7. Electrochemical performance (a and b) CV plots at different scan rates. (c and d) discharge curves at different current densities in potential range of -0.1 V to 0.8 V of the MnO₂/Ti and MnO₂/ITO NWs electrodes (Potential (V) is with respect to Ag/AgCl reference electrode).

Both cyclic voltammetry (CV) and chronopotential charge–discharge measurements are reliable techniques that can be used to examine capacitor behavior and quantify specific capacitance of as-prepared electrodes. Figures 4.7a and 4.7b represent CV curves of MnO₂ and MnO₂/ITO NWs electrodes with a same loading mass within potential ranges from -0.1 to 0.8 V in Na₂SO₄ solution. There is no clear oxidation/reduction peak in the CV curves at all scan rates, implying that the redox process is mainly governed by the intercalation and deintercalation of the cations into the mesoporous MnO₂ matrix. On the other hand, CV curves resemble mirror images with respect to zero-current line, which means that the redox process is highly reversible over the potential range. A close comparison shows that the area under the CV curves of MnO₂/ITO NWs electrode is larger than that of MnO₂/Ti electrode, representing its better capacitive behavior.

Charge-discharge measurements at different current densities were performed in potential windows from -0.1 to 0.8 V, as presented in Figures 4.7c and 4.7d. For the estimation of the mass of MnO₂, Faraday's law was used with the assumption that current efficiency for electrodeposition equals 100% as follows

$$m = \frac{Q}{F} \times \frac{M}{z} \quad (\text{eqn. 4.4})$$

where m is mass of MnO₂ (g), F is Faraday constant, M is molecular weight of MnO₂ and z is electrons transferred per ion. The mass of MnO₂ coating is estimated to be around 0.045 mg cm⁻².

For MnO_2/Ti electrode, the calculated specific capacitance at discharge current densities of 1, 5, 10 and 20 A g^{-1} are 439, 302, 242 and 202 F g^{-1} , respectively. In the case of MnO_2/ITO NWs composite electrode, the specific capacitance values at the same discharge current densities are estimated to be 821, 775, 719 and 630 F g^{-1} . It is worth noting that the capacitances of the MnO_2/ITO NWs nanocomposite are about two times higher than those of the mesoporous manganese dioxide film on Ti current collector (MnO_2/Ti) at all the current densities. On the other hand, with increasing charge-discharge currents, the capacitances of both types of electrodes decrease. Since pseudocapacitive behavior arises from electrochemical redox reaction of MnO_2 , it is a common phenomenon when specific capacitance values of both types of electrodes decrease with increasing discharge current density. This can be attributed to kinetic limitation and internal potential loss as commonly reported in many studies [15, 36]. For instance, diffusion limitation of cations at electrode/electrolyte interface at higher discharge current certainly lowers specific capacitance. In other words, limited amount of active MnO_2 on the electrode surface get involved in faradic reaction and hence, specific capacitance decreases. Nonetheless, the MnO_2/ITO NWs nanocomposite was observed to be less current dependent than MnO_2/Ti , indicating more efficient cation diffusion within a mesoporous manganese dioxide matrix at high current densities. This also clearly provides enhanced superior pseudocapacitive performance of a newly designed nanocomposite as compared to that of a traditional MnO_2 in direct contact with the substrate.

Figure 4.8. Capacitance retained ratio.

The improved performance of the nanocomposite at a higher discharge current was further illustrated in Figure 4.8a. When the current density increases from 1 to 5 A g^{-1} , 10 A g^{-1} and 20 A g^{-1} , MnO₂/Ti retains 100%, 68.8%, 55.1% and 46% of its original capacitance (i.e. specific capacitance value at 1 A g^{-1}), respectively, while, in the case of MnO₂/ITO NWs electrode, its capacitance retained ratio is 100%, 94.3%, 87.5% and 76.7%. The poor rate performance of MnO₂/Ti is likely due to low conductivity nature of MnO₂ and inefficient electrolyte diffusion. In electrodeposition process, manganese dioxide is deposited onto titanium substrate layer by layer. At higher current density, electrolyte transport to bottommost layers in direct contact with titanium current collector is inefficient. In other words, the intercalation of cations into those distant layers is limited. As such, MnO₂ coating is underutilized, resulting in poor rate performance at increasing current density.

In order to understand in details the enhanced capacitance performance observed in MnO_2/ITO nanocomposite, electrochemical impedance spectroscopy (EIS) was also carried out with the amplitude of perturbation signal equal to 50 mV. The measurement was performed on MnO_2/Ti and MnO_2/ITO NWs electrodes with the same mass of the active material. In the EIS spectra (Figure 4.9), two distinct components (i.e. semicircular loop at high frequency and straight segment at low frequency) were observed for the two types of electrodes. As compared with the semicircles with a loop at high frequencies, which are influenced by the mesoporous manganese dioxide matrices, the diameter of the semicircular loop of the MnO_2/ITO NWs electrode was determined to be 89.6 Ω , which is much smaller than that of the MnO_2/Ti electrode (196.6 Ω), implying that our new electrode architecture with introduction of a highly conductive ITO array can significantly improve its charge transfer resistance. Moreover, compared with the straight segments at low frequencies, which are associated with the charge-transfer resistance of the materials, the slope of the straight segment of MnO_2/ITO NWs heterostructure electrode in lower frequency region is higher than that of MnO_2/Ti electrode, indicating an enhanced ionic diffusion in the nanowire network resulted from the addition of the well-separated ITO nanowires.

Figure 4.9. Complex-plane impedance spectra of the MnO_2/Ti and $\text{MnO}_2/\text{ITO NWs}$ electrodes.

In order to investigate the stability of $\text{MnO}_2/\text{ITO NWs}$ composite electrode in neutral aqueous electrolyte, charge–discharge cycling was also performed at density of 1 A g^{-1} for 1500 cycles in the potential windows from -0.1 V to 0.8 V (Figure 4.10). The inset represents the first 10 symmetric charge-discharge cycles. 1500 charge/discharge cycles reduce its specific capacitance to 90.3% of the original value, revealing that the MnO_2 shell has good supercapacitive properties and excellent long-term stability in the aqueous Na_2SO_4 electrolyte solution.

Figure 4.10. Cycle life of MnO₂/ITO NWs hybrid electrode at a charge-discharge current density of 1 A g⁻¹ in the potential window of -0.1 to 0.8 V (Potential (V) is with respect to Ag/AgCl reference electrode).

Traditional supercapacitor electrodes require the mixing of active material, carbon black and binder followed by a time-consuming drying process. In order to achieve maximum capacitance, tremendous effort must be devoted to ensure uniform distribution of active material around the carbon species. Therefore, nowadays, research groups are gradually shifting their attention to the development of binder-free electrodes. In our proposed heterostructure electrode, active material is in direct contact with ITO nanowires and the titanium current collector. As such, neither carbon black nor binder is needed, and hence, the supercapacitor electrode can be immediately used after synthesis. This facile technique also prevents a potential agglomeration problem of MnO₂ primary nanoparticles.

On the other hand, mesoporous materials have shown great potential for wide application in advanced supercapacitors due to their high surface area. For instance, a mesoporous MnO_2 film prepared by potentiostatic electrodeposition exhibits enhanced electrocapacitive behavior as compared to nonporous films [37]. However, manganese dioxide is known to possess low electrical conductivity, which often results in its low specific capacitance. This negative effect can be minimized by the addition of ITO nanonetwork as base for electrodeposition. More importantly, ITO nanowires are more thermally stable for those applications at elevated temperatures and an oxygen-rich atmosphere as compared with carbon-based material (e.g. carbon fiber [38]). In this study, we tried to fully make use of the high conductivity of ITO nanowires and the high surface area of mesoporous MnO_2 in the design of a novel composite electrode material. This combination of advantages of counterparts in hybrid MnO_2/ITO NWs/Ti electrode demonstrates not only faster charge transfer at the interface but also improved diffusion of the cations in the manganese dioxide network, as shown in impedance analysis. Therefore, the proposed one-dimensional nanowire network shows superior electrochemical performance as compared to two dimensional mesoporous film structure in terms of higher specific capacitance, minimized capacitance degradation at higher current density and excellent cycle life. All of above characteristics of the as-fabricated MnO_2/ITO NWs hybrid structure promote itself to be the new generation of supercapacitor electrode material.

4.4. Conclusion

In the present work, a MnO_2/ITO NWs composite electrode was successfully synthesized by chemical vapor deposition, followed by potentiostatic electrodeposition.

Highly uniform MnO_2 with a thickness of 100–200 nm along the ITO nanowires was observed from the FESEM and TEM images. Densely interlaced MnO_2 nanofibers on the nanowires have mesopores of 2 – 3 nm in diameter. The specific capacitances of MnO_2 /ITO NWs are estimated to be 821, 775, 719 and 630 F g^{-1} at discharge current densities of 1, 5, 10 and 20 A g^{-1} . As compared with the mesoporous MnO_2 film electrode deposited onto the substrate, the MnO_2 /ITO NWs/Ti composite electrode has a two times higher absolute specific capacitance and lower capacitance deterioration at higher current densities. This is because of the incorporation of ITO NWs into the hybrid electrode which definitely increases the surface area of active material and is beneficial to the electrolyte diffusion. Therefore, this unique design of nanoscale heterostructure can be considered as a potential electrode fabricating technique to prepare a wide range of mesoporous composite electrodes for ECs and even for Li-ions batteries.

Chapter 5: Conclusion and future work

5.1. Conclusion

In this thesis, the syntheses of various heterostructure of ITO nanowires and metal (Co, Ni, Mn) oxides/hydroxides and their application as supercapacitor electrode materials were presented. The incorporation of ITO NWs into the hybrid electrode and the void space between them enlarge the surface area of active material and is beneficial to the electrolyte diffusion. On top of that, the high conductivity of ITO nanowires certainly enhances electron/charge transport within the network, which lowers internal resistance of electrode.

In chapter 2, a novel mesoporous α -Co(OH)₂/ITO NWs heterostructure has been successfully synthesized by combination of CVD and electrodeposition through hexagonal lyotropic liquid crystalline (LLC) phase, as mentioned above. Galvanostatic charge–discharge measurements in 1 M KOH solution prove that the electrode of as-prepared heterostructure possesses excellent electrochemical capacitance, in the potential range from -0.1 V to 0.5 V with maximum specific capacitance of 1128 F g⁻¹ at discharge current density of 1 A g⁻¹. The identical approach was applied on NiO/ITO NW with a shell/core structure in chapter 3. Both cyclic voltammetry (CV) and chronopotentiometry demonstrate enhanced electrochemical properties of NiO/ITO NWs composite electrode and improved supercapacitive behaviors as compared to bulk mesoporous nickel oxide film. Maximum specific capacitance of 1025 F g⁻¹ at a discharge current density of 1 A g⁻¹ in the potential ranges from 0 V to 0.5 V is determined by galvanostatic charge–discharge measurement in 1 M KOH solution. In

chapter 4, mesoporous MnO_2/ITO NWs nanocomposite was successfully fabricated. Electrochemical measurements are carried out by cyclic voltammetry (CV) and chronopotentiometry in a 0.5 M Na_2SO_4 aqueous solution. The nanocomposite exhibits a significantly enhanced electrochemical performance and higher capacitance retention ratio, as compared to mesoporous manganese oxide (MnO_2) film. From charge-discharge measurements, a specific capacitance of 821 F g^{-1} for the nanocomposite is achieved at a discharge current density of 1 A g^{-1} in potential ranges from -0.1 to 0.8 V.

In this thesis, as-elaborated electrode engineering technique was successfully applied to three different metal oxides/hydroxides and demonstrated substantial enhancement in pseudocapacitive behavior. Therefore, we believe that this electrode fabrication technique can be potentially employed to fabricate various mesoporous nanowire-like composite electrodes for other applications.

One main issue associated with electrodeposition is that only limited amount of active materials can be coated and utilized. This is largely due to low conductivity nature of metal oxides/hydroxides. The electrodeposition process is time-consuming and hence, deposition rate substantially decreases with increasing mass loading. As a result, electrode prepared by this fabrication technique is not widely implemented in supercapacitor. The use of ITO nanowire array as base for electrodeposition further enhances effectiveness of electrodeposition and increases mass loading.

Surface area is a crucial parameter that needs to be maximized for better electrochemical behavior. This thesis also highlights the merit of addition of mesopores into the heterostructures of ITO nanowires and transition metal oxides/hydroxides by the

employment of LLC template. As experimentally and scientifically proven in previous chapters, mesoporous structure is beneficial in term of increasing surface area and facilitating mass transport.

5.2. Future work

Rising demand for a new source of sustainable energy requires us to design more advantageous supercapacitor with higher power and energy densities. With this in mind, the key focus of our group is to develop new electrode materials which are capable of delivering high specific capacitance in wider potential window. The desire characteristics of a supercapacitor electrode include large number of electrochemically active sites, porous structure with high surface area, low internal electrode resistance and presence of diffusion channel for access of electrolyte species.

It is commonly believed that nanosized materials/structures usually possess higher electrochemical activity and larger surface area. Nonetheless, from our point of view, most of the reports were more concerned about the initial capacitance and inadequate attention was paid to electrochemical stability during charge/discharge cycles. On the other hand, stable three-dimensional (3D) microstructures of nano-building blocks are highly desirable to achieve enhanced electron transport, improved ionic diffusion, excellent rate capability and great stability. Therefore, it is imperative to develop systematic and rational techniques to fabricate electrode materials with well-defined microstructures with above advantageous properties. In future study, we might want to consider to explore different synthetic techniques for fabrication of ITO nanowire array and to study the effect of fabrication route on electronic properties and chemical

stability. On top of that, this intriguing approach can be potentially adopted to widely synthesize supercapacitor electrode materials with better electrochemical performance to meet rising energy demand in near future. It is also interesting to perform fundamental study to understand the interaction between ITO nanowire and active materials

As mentioned earlier, carbon-based material and conductive polymers (i.e. polyaniline and polypyrrole) can be employed in binary or ternary composites structures. One main intention is to take advantage of highly desirable properties of above materials such as high surface area and excellent conductivity. Those characteristics will certainly be beneficial to charge transport and ionic diffusion, which minimizes capacitance fading and lengthen capacitor's lifetime. This is also known as synergistic effect which leads to more enhanced specific capacitance higher mechanical strength, better cycling stability than individual components. However, we also want to highlight that even though this phenomenon has been reported in many studies, it is still not fully understood and universally proven. Therefore, it provides us with an opportunity to thoroughly investigate this synergistic effect.

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