Metal oxide/sulfide-based nanostructured materials for supercapacitors

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**Metal Oxide/Sulfide-Based Nanostructured Materials for
Supercapacitors**

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Abstract

Batteries have been the technology of choice for energy storage in many applications, because of their high energy density with sustainable power supply. However, in recent times the expanding power markets are calling for alternative pulse batteries with high power density and longer cycle life. Inspired by these urgent and increasing demands, research scientists have been paying more attentions to the electrochemical capacitors, which are also known as supercapacitors, due to their much higher power density and longer cycle life than those of the batteries.

The research work presented in this project is concentrated on the exploration of novel nanostructured transition metal oxide/sulfide (Co_3O_4 , NiO and $\text{CuS/NiS/Ni}_3\text{S}_2$) based active materials with porous texture for high-performance supercapacitors. First, various cobalt based precursors (CBP) with one to three dimensional microparticles have been synthesized by a facile solvothermal method, and the as-prepared CBP are converted into corresponding porous Co_3O_4 nanostructures by calcinations in air. When evaluated as supercapacitive electrodes, capacitances of $44\text{-}254.2\text{ F g}^{-1}$ can be obtained from these Co_3O_4 products, demonstrating their promising application in supercapacitors. The similar synthetic protocol is also applied to prepare porous nickel oxide (NiO) hierarchical nanospheres for supercapacitive application.

Secondly, hierarchical nickel sulfide (NiS) hollow spheres are constructed using silica nanocolloids as hard templates. In this strategy, silica@nickel silicate ($\text{SiO}_2\text{@NiSilicate}$) core/shell nanostructures are readily prepared, which can be hydrothermally converted into hierarchical nickel NiS hollow spheres assembled from

ultrathin nanosheets with effect of Na_2S . When served as electrode materials in supercapacitors, the as-derived NiS hollow spheres exhibited high specific capacitance with good cycling stability.

Lastly, in order to further improve the cyclic performance of the supercapacitors, carbon nanotubes (CNTs) are introduced as backbones for preparation of CNTs based inorganic nanocomposites because the CNTs can increase the electrical conductivity as well as serving as the cushion structure to alleviate the volume change during the charge-discharge process. Based on this synthetic strategy, CNTs supported copper sulfide (CuS) ultralong nanoneedles and nickel sulfide (Ni_3S_2) ultrathin nanosheets are constructed by the sulfidation of the corresponding metal silicate precursors. As a result, the as-formed CNTs supported metal sulfide nanocomposites have exhibited excellent stability upon the cycling when tested as supercapacitive electrodes.

In brief, this research has tried to explore the great potential of novel metal oxide/sulfide with porous textures as electrodes for high-performance electrochemical capacitors. The electrochemical performance is considered to be affected significantly by the morphology and porous texture of the electrode materials, hence, design and construction of novel and unique nanomaterials with high specific surface areas is essential to develop high-performance supercapacitors.

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List of Abbreviations

Co_3O_4 : tricobalt tetraoxide

CoS , CoS_2 , Co_9S_8 : cobalt sulfide

Co^{2+} : cobalt ion

CoCO_3 : cobalt carbonate

$\text{Co}(\text{OH})_2$: cobalt hydroxide

ZnO : zinc oxide

RuO_2 : ruthenium oxide

CBP: cobalt based precursors

Ni: nickel metal

$\text{Ni}(\text{OH})_2$: nickel hydroxide

NiO : nickel oxide

Na_2S : sodium sulfide

NiSilicate: nickel silicate

Ni_3S_2 , NiS , NiS_2 : nickel sulfide

CNTs: carbon nanotubes

CuO : copper oxide

CuS : copper sulfide

CuSilicate: copper silicate

S: sulfur

CS_2 : carbon disulfide

PMMA: poly-(methyl methacrylate)

PET: polyethylene-terephthalate

CNTs: carbon nanotubes

SiO₂: silica

Co(Ac)₂: cobalt acetate

NaAc: sodium acetate

EtOH: ethanol

EG: ethylene glycol

PEG: polyethylene glycol

MnO₂: manganese oxide

CS₂: carbon disulfide

Co(NH₂)₂: urea

CH₄N₂S: thiourea

TETA: triethylenetetramine

PVP: polyvinyl-pyrrolidone

TEOS: tetraethyl orthosilicate

CVD: chemical vapor deposition

EPD: electrophoretic deposition

LIB: lithium-ion batteries

EDL: electric double layer

Cs: specific capacitance

CV: cyclic voltammogram

Pt: platinum

FESEM: field-emission scanning electron microscope

TEM: transmission electron microscope

HR: high-resolution

SAED: selected-area electron diffract

XRD: X-ray diffraction

BET: Brunauer–Emmett–Teller

BJH: Barrett–Joyner–Halenda

TGA: thermogravimetric analysis

EDX: energy-dispersive X-ray spectroscopy

PVDF: poly(vinylidene difluoride)

HCl: hydrochloric acid

KOH: potassium hydroxide

SCE: standard calomel electrode

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Chapter 1. Introduction

1.1. Background

Supercapacitors are raising intensive consideration as potential power source for electric devices, such as mobile phones, laptops, and electric vehicles for their excellent electrochemical characteristics, such as very high power density, long cycle life and high energy efficiency.¹ The exploration of new materials for supercapacitive electrodes has attracted great attentions in the research community. So far, much focus has been directed to the porous species such as carbon materials and conducting polymers because of their good electric conductivity and large specific surface area which may offer significant contact area for the charge storage.² However, the capacitance of electrodes fabricated from these porous materials is relatively low, which may be largely limited by the physical ion adsorption occurred between the electrode material and the electrolyte. In recent years, transition metal oxide/sulfide based electrode materials including cobalt oxide (Co_3O_4), nickel oxide (NiO), ruthenium oxide (RuO_2), manganese oxide (MnO_2), and cobalt sulfides (CoS_x) are raising popularity in the supercapacitive applications for their much higher theoretical capacitance and redox activity compared to the traditionally used carbon materials.³⁻⁵

It is widely reported that the electrochemical performance of the electrode materials is significantly affected by their morphologies and porous texture. Hence, careful design of nanostructured metal oxide/sulfide materials with porous texture is of great interest and importance to develop high-performance supercapacitors.⁶

1.2. Motivation

Lithium ion batteries have attracted most of the attentions when they come to the energy storage for mobile phones, laptops and hybrid vehicles. However, other well-known electrochemical devices such as supercapacitors are raising their importance as alternative power sources that can provide quick bursts of energy. It was suggested that supercapacitors may not have an energy density as high as lithium ion batteries, but the latest development of this device is closing the gap, and their storage capabilities may create another landmark in the power industry.

As an important component of supercapacitors, the electrode active material has always been one of the research focuses by the electrochemists. So far transition metal oxides/sulfides have been widely studied as electrode materials for their high theoretical capacitance and redox activity, therefore, exploration of transition metal oxide/sulfide materials with high capacitance and good cycle capability is very demanding for the next generation high-performance supercapacitors.

1.3. Objectives of research

This PhD project mainly aims to find suitable metal oxides and sulfides with unique structures and porous textures for high-performance supercapacitors. During the programme, intensive research efforts have been paid to explore transition metal oxides/sulfides such as Co_3O_4 , NiO , CuS and NiS_x by using solvothermal/hydrothermal approaches, generating hierarchical nanostructures composed of interesting nanobuilding blocks with high specific surface areas for supercapacitors.

Specifically, the objectives of this study can be divided into the following three categories.

1.3.1. Synthesis of Co_3O_4 and NiO nanostructures with porous textures for supercapacitors

In order to find inexpensive and non-toxic metal oxides to replace the traditional supercapacitive materials RuO_2 , Co_3O_4 and NiO with unique nanostructures have been developed using one-pot syntheses in aqueous/solvothermal systems. The BET tests characterize their porous textural characters, and the as-prepared metal oxides materials have exhibited enhanced capacitance with good cycling stability.

1.3.2. Construction of NiS hollow spheres with high specific surface area for the supercapacitor application

To overcome the low conductivity and slow ion diffusion rate of solid materials, research work has been extended to prepare hollow structures to improve the electrochemical performance of supercapacitors, since compared to the solid counterparts, the hollow structures hold a number of advantages, such as lower mass density, much larger surface area and faster electrolyte ion diffusion rate. In the subsequent work, nickel sulfide hollow nanostructures were successfully prepared by employing silica nanocolloids as hard template using hydrothermal conditions. Well-defined hierarchical NiS hollow spheres assembled from ultrathin nanosheets have been achieved by hydrothermally treating uniform Silica@Nickel silicate ($\text{SiO}_2\text{@NiSilicate}$) nanospheres with effect of sodium sulfide (Na_2S), and their

electrochemical properties have shown high specific capacitance with good cycling capability.

1.3.3. Synthesis of CNTs supported copper/nickel sulfides with hierarchical and porous one-dimensional nanostructures for high-performance supercapacitors

It has been reported that high conductivity, short electron transfer distance can be achieved by construct one-dimensional nanostructures, which may lead to better cycling performance in electrochemical devices. Based on this inspiration, carbon nanotubes have been introduced as supporting backbones to grow copper sulfide (CuS) and nickel sulfide (Ni_3S_2) to form hierarchical 1D nanostructures with high surface areas for supercapacitors. By employing a conversion route, CNTs supported CuS nanoneedles/ Ni_3S_2 nanosheets are prepared for electrode materials for supercapacitors, where high specific capacitances and excellent cycling stability have been demonstrated.

1.4. Organization

In Chapter 1, a brief introduction of the background of supercapacitors is presented, followed by the motivation and objectives of this PhD research. The Chapter 2 reviews the representative types of metal oxides/sulfides with various structures, and the supercapacitive properties of some of the structures are also demonstrated. Some common methods for material characterization and electrochemical evaluation are summarized in Chapter 3. In Chapter 4, a facile solvothermal method is employed to synthesize porous Co_3O_4 nanostructures, and their supercapacitive properties are also

investigated. By a similar solvothermal approach, Ni-EG nanospheric complexes are prepared and corresponding NiO nanospheres with porous texture are obtained by a subsequent calcination process. The supercapacitive properties of the as-obtained NiO nanospheres are evaluated, which has been presented in Chapter 5. The Chapter 6 demonstrates the development of well-defined NiS hollow nanospheres assembled from ultrathin nanosheets via conversion from uniform silica@nickel silicate nanospheres, and the capacitive property of the as-prepared NiS hollow spheres is also investigated. For Chapter 7 and 8, CNTs are introduced as the supporting backbone to prepare CNTs supported CuS nanoneedles and Ni₃S₂ nanosheets, and their supercapacitive properties are also studied. The last chapter is the conclusion of this thesis, and some continuous works have been proposed for the future work.

Chapter 2. Literature Review

2.1. Overview of supercapacitors

Lithium ion batteries (LIBs) have been considered to be the main power sources for many applications in the past decades, because of their high energy density and long-lasting power supply.⁷ However, with the emergence of new electrical and electronic devices, such as mobile phones, laptops, and electric vehicles, it becomes harder for the standard-designed batteries to meet the rising power markets, and hence it is essential and stringent to develop alternative energy storage devices with higher power density and longer cycle life.⁸ Electrochemical capacitors, which are also known as supercapacitors, have recently been paid great research attentions by both the industry and scientific community, because much higher power density and much longer cycle life can be delivered for supercapacitors compared to the battery technology. In supercapacitors, the charge can be stored and released in a very short time, which usually leads to relatively lower energy densities than batteries, but a supercapacitor is able to deliver a much higher power density. Consequently, they are showing the rising importance in the complementary or back-up power supply systems. A recent exciting report for the application of supercapacitors demonstrated that the appropriately designed supercapacitors have been in use in the emergency doors in an Airbus A380, exhibiting their safety and reliability.⁹

The principle of supercapacitors was described for the first time in 1957.⁶ After that, the Japanese company NEC successfully explored aqueous-electrolyte capacitors, which is a landmark for the commercial use of supercapacitors.¹⁰ Later the

popularization of the new technologies such as electronic devices and transportations has fostered the capacitors largely, showing the increasing interest of this technology by the research community and general public. Since 1990, supercapacitors have developed quickly, thanks to the advances of the material science. In the recent decades, they are finding expanding applications in diverse industrial fields.⁹

The conventional capacitors are able to store the energy by charge separation, where the charges are stored by physically forming static electric double layer by using two metal plates. The charge Q captured in such device is given by CV , where V is the potential drop across the two plates, and C is the capacitance of the device. Hence, the energy stored can be described as $\frac{1}{2} CV^2$, which also indicates the capability of the charge storage for a capacitor.¹ The capacitance delivered by these conventional capacitors is usually less than 1 F.

Figure 2.1 Schematic representation of supercapacitors.

Different from the conventional capacitors, a supercapacitor is composed of a positive electrode, a negative electrode, and electrolyte (Figure 2.1).¹¹ In these devices,

the charged ions are stored by the formation of electrochemical double layer (EDL) at the interface between the electrodes and electrolyte. In the charge process, the positively charged ions are transferred to negative electrode, while the negatively charged ions travel to the positive electrode. By this way, charge can be stored and a potential difference is created across the two electrodes. The inverse movements take place in the subsequent discharge process. Based on the mechanisms, supercapacitors can be divided into EDL supercapacitors and pseudocapacitors.¹²

For an EDL supercapacitor that is based on the adsorption of electrolyte ions, the charge is stored physically into the double layers and hence there are no Faradaic reactions involved between the electrode material and the electrolyte, where the capacitance is mainly dependent on the textual properties and surface area of the electrode materials. The typical electrode materials include porous carbon, carbon nanotubes, conducting polymers and so on. The specific capacitance delivered from these electrochemical capacitors are usually several to tens of Farads per gram. While in Faradaic mechanism based pseudocapacitors, most of the charge is transferred to the interface of electrode and electrolyte for the occurrence of redox reactions, which usually leads to much higher capacitance.¹³ As a result, the capacitance generated in a Faradaic capacitor is voltage-dependent, which can be calculated conveniently using the specific capacitance (C_s) from

$$C_s = Q_{\text{tot}} / V_{\text{tot}}$$

where Q and V indicate the total charge transferred and the potential change for a charge or discharge process of an electrode.¹¹

Compared to the EDL supercapacitors, the electrode materials of pseudocapacitors are also expected to hold specific characteristics, such as large surface area, good electronic conductivity, and high theoretical capacitance.⁹ Therefore the development of electrode materials with high surface area is considered to be potentially significant for the improved electrochemical performance. One of the strategies to obtain high surface area is to endow the porous structures with mesoporous or microporous textures.^{2, 14} It has been reported that the smaller pore size in a material, the larger surface area it holds, but it is still important for the nanotechnology to reach a compromise between the pore size distribution and the surface area of electrode materials since it is critical to make the pores accessible for electrolyte ions to form the charged double layers.¹⁵ So far the widely studied electrode materials for double-layer capacitors are high-surface-area carbon materials because of their high electronic conductivity, electrochemical stability, and open porosity.⁷ In many previous studies, intensive research interests have been paid to the surface area and pore sizes of carbon materials. Unfortunately, the enhanced capacitance is not linear with the increase of surface area based on the trials with different material pore sizes and electrolyte.¹⁶⁻¹⁸ Some reports indicate that it is difficult for the charged ions to access the small pores less than 0.5 nm, especially for the organic electrolyte whose ions are larger than 1 nm.¹⁹ Thus, a balance of high surface and small pore size should be considered when designing a porous material for good electrochemical performance. However, based on the physical absorption mechanism, capacitance reported from these carbon materials is still very limited, usually from several to tens

of Farads per gram, which is a restriction for practical use.²

Recently, metal oxides/sulfides are showing their superiority to improve the capacitance and power density because of their high theoretical specific capacitance and redox activity.²⁰⁻²² For example, Co_3O_4 is able to generate a very high theoretical capacitance of 3560 F g^{-1} based on the Faradaic character, which has attracted tremendous interests by the electrochemical community.²³ But it should also be noted that redox reactions are involved in these Faradaic-based capacitors, therefore, just like batteries, supercapacitors are facing the same problem of lack of stability over the prolonged cycles.⁹

Among all the metal based materials, ruthenium dioxide (RuO_2) is a conventionally studied capacitive material for its good electronic conductivity and Faradaic property. The reversible redox reaction can be described as follows:

where the proton performs the insertion and de-insertion process with a potential higher than 1.2 V, thus limits their application in some electronic devices even though high capacitance has been reported.^{9, 24} Furthermore, RuO_2 is expensive and toxic in nature, which will increase the cost and bring about the environmental problems after use. Hence more and more research interests have been given to other inexpensive and nontoxic transition metal oxides to replace RuO_2 for the next generation supercapacitors. In addition, as the high surface area is crucial for the good capacitive property, it would be reasonable and promising to design inexpensive metal oxides with high surface area to improve the interfacial exchange between the electrode

material and electrolyte ions, so that high capacitance and better cycling performance can be obtained.

In the following sections, several transitional metal oxides/sulfides based materials serving as the electrodes for supercapacitors will be compared and discussed, and their supercapacitive properties have also been reviewed.

2.2. Cobalt oxide/sulfide ($\text{Co}_3\text{O}_4/\text{CoS}_x$)

As mentioned above, the utilization of ruthenium oxide (RuO_x) for electrochemical capacitors has been popularized for a long time due to its high specific capacitance, reversible charge-discharge features, and good electric conductivity.^{9, 25-28} However, Ru is still not attractive for commercial use so far because of its high cost and toxic nature. Hence, it is desirable to develop inexpensive and nontoxic alternative materials for capacitive electrodes.

As an important p-type semiconductor with direct optical band gaps at 1.48 and 2.19 eV,²⁹ Co_3O_4 has been widely used in many applications such as lithium-ion batteries,³⁰⁻³³ catalysis,³⁴ solid state sensors,³⁵⁻³⁶ supercapacitors,³⁷⁻⁴⁰ and magnetic materials.⁴¹ In recent years, tremendous efforts have been made to prepare Co_3O_4 semiconductor nanostructures with different morphologies using various methods,⁴²⁻⁴⁶ among which some exciting results have been reported. For example, Lou et al. have successfully synthesized needlelike Co_3O_4 nanotubes using a facile one-step self-supported topotactic transformation approach (Figure 2.2), and the obtained

Figure 2.2 SEM images of Co_3O_4 nanotubes prepared by topotactic transformation approach. Reprinted with permission from ref. 47. Copyright 2008 Wiley.

products exhibited ultrahigh capacity with nearly 100% retention for 30 cycles when served as anode materials in LIBs.⁴⁷ After that, the same group reported the formation of single-crystal Co_3O_4 nano-needles at different calcination temperatures in a similar synthesis condition, and the results have showed enhanced electrochemical properties.⁴⁸

Figure 2.3 Low magnification TEM images of porous Co_3O_4 nanorod. Reprinted with permission from ref. 49. Copyright 2009 ACS.

An earlier fabrication of Co_3O_4 films for supercapacitors is reported by Yoon et al. using a sputtering method and their results show that the capacitive behavior of Co_3O_4 -based electrode materials is dependent on the ratio of sputtering gas.⁴⁰ In addition to the sputtering approach, hydrothermal synthesis is another effective way to synthesize Co_3O_4 with unique structures and porous texture. Wang et al. presented a facile hydrothermal route to prepare porous Co_3O_4 nanorods (Figure 2.3), demonstrating a capacitance of 280 F g^{-1} which is much higher than that of the commercial Co_3O_4 microcrystalline powders (maximum capacitance is 43 F g^{-1}).⁴⁹

Figure 2.4 SEM images of Co_3O_4 nanowire arrays grown on silicon wafer (a), polystyrene substrate (b), and silicon wafer with Au patterned (c and d). Reprinted with permission from ref. 51. Copyright 2006 ACS.

Recently, deposition of Co_3O_4 on a substrate for supercapacitive electrodes has received intensive research interests for the straightforward formation of capacitive electrodes. The electrodes developed by this way have a better adhesion of active

materials onto the conducting substrate, and hence are free from the utilization of conducting agents and binders which are commonly used in the conventional electrode fabrication.⁵⁰ A typical example is that freestanding hollow Co_3O_4 nanowire arrays were successfully fabricated by Wu et al. on various conducting substrates, including transparent conducting glass, silicon wafer, and polystyrene substrate (Figure 2.4).⁵¹

Figure 2.5 SEM (a), TEM (b) images, the first and second charge-discharge curves (c), and cyclic performance (d) of the Co_3O_4 nanowire on Ni foam substrate. Reprinted with permission from ref. 23. Copyright 2010 Elsevier.

Another example of substrate supported fabrication is reported by Cao et al, where Ni foam is served as a substrate for Co_3O_4 nanowires deposition using a template-free growth method.²³ In their work, the Ni foam not only worked as a three-dimensional

network for supporting the Co_3O_4 active material, but also as a current collector for the electrode. As a result, the Co_3O_4 nanowires developed therein have displayed a specific capacitance of 746 F g^{-1} at a current density of 5 mA cm^{-2} , demonstrating the high capacitance and good cycling performance (Figure 2.5).

Figure 2.6 TEM images of the Co nanocrystals (a and c), and cobalt sulfide products obtained from a reaction time of 1 minute at different temperatures: room temperature (b), and 182°C (d). Reprinted with permission from ref. 59. Copyright 2006 Wiley.

As promising industrial materials in catalysis,⁵² semiconductor,⁵³ magnetic materials,⁵⁴⁻⁵⁵ lithium-ion batteries,⁵⁶⁻⁵⁷ and supercapacitors,^{5, 58} cobalt sulfides have drawn increasing attentions in recent years. Similar to other transition metals, cobalt can form a large family of sulfide materials such as CoS , Co_2S_3 , Co_3S_4 , CoS_2 , and Co_9S_8 . Among all these sulfides, Co_9S_8 hollow nanocrystals have been formed through a Kirkendall-like mechanism in a recent work developed by Yin et al.⁵⁹ In their work, temperature is intensively investigated during the formation of cobalt sulfide. The results show that higher temperatures lead to the fast formation of single void inside each shell, while room temperature leads to multiple voids (Figure 2.6). Similarly, based on the nanoscale Kirkendall effect, Wang et al. have successfully

prepared Co_9S_8 nanotubes via a hydrothermal synthesis using $\text{Co}(\text{CO}_3)_{0.35}\text{Cl}_{0.2}(\text{OH})_{1.1}$ nanorod bunches as sacrificial templates.⁶⁰

Another contribution for Co_9S_8 is from Zhou et al, where hollow microspheres with hierarchical structures are synthesized in a binary solution of triethylenetetramine (TETA) and deionized water (Figure 2.7).

Figure 2.7 SEM images of Co_9S_8 hollow microspheres (a and b: low magnification; c and d: high magnification) prepared by a solvothermal synthesis in a mixed solvent with volume ration $V_{\text{TETA}} : V_{\text{water}}=1:1$. Reprinted with permission from ref. 61. Copyright 2010 Wiley.

The hollow microspheres prepared in their work showed promising lithium storage properties with discharge capacities of $910.4 \text{ mA h g}^{-1}$, $762.3 \text{ mA h g}^{-1}$, and $692.8 \text{ mA h g}^{-1}$ for the first three charge-discharge cycles, respectively.⁶¹

A recent work by Yang et al has shown the synthesis of hexagonal CoS nanosheets using thioacetamide as the sulfur source in the presence of PVP (Figure 2.8). The supercapacitor electrode fabricated from these CoS nanosheets exhibits a capacitance

of 138 F g^{-1} with excellent cycling life (over 10000 cycles).⁶² Another work developed by Dong et al. presents the formation of hierarchical CoS nanostructures in a simple hydrothermal system, in which various structures such as flower-like, ball-like, cube-like and surface hollowed-out morphologies are reported.⁶³ Therein an interesting shape evolution process was also investigated to demonstrate the formation of CoS flower-like nanostructures, and the as-prepared flower-like CoS showed a high specific capacitance of 389 F g^{-1} at a relatively high current density..

Figure 2.8 TEM image (a) and cyclic performance (b) of supercapacitors performed in 1M of KOH of the CoS hexagonal nanosheets. Reprinted with permission from ref. 62. Copyright 2011 Elsevier.

In another report for the synthesis of cobalt sulfide by Liu et al., unusual worm-like $\text{Co}_{0.75}\text{S}$ microtubes assembled from hexagonal nanoplates were prepared through a one-pot hydrothermal synthesis assisted by the self-assembly of the surfactant used. The $\text{Co}_{0.75}\text{S}$ microtubes formed in their synthesis were fabricated into capacitive electrodes, and the charge-discharge results showed that a capacitance of 201 F g^{-1} can be calculated at a relatively high current density (Figure 2.9).⁶⁴

Figure 2.9 A SEM image of the worm-like $\text{Co}_{0.75}\text{S}$ microtubes (a) and the charge-discharge curve of these microtubes at a current density of in 6 M KOH aqueous solution (b). Reprinted with permission from ref. 64. Copyright 2010 Wiley.

2.3. Nickel oxide/sulfides (NiO/NiS_x)

With promising electrochemical performance and low cost, nickel oxide (NiO) has been of particular interests in electrochemical devices.⁶⁵⁻⁶⁶ It was reported that the electrochemical properties are greatly dependent on the morphology and structures of NiO crystals, and hence many research attentions have been paid to prepare NiO nanocrystals with different structures for electrode material candidates.^{21-22, 67} Among all the preparations, synthesis of nickel hydroxides with novel structures is a facile and straightforward approach to obtain nanostructured NiO particles since NiO materials can be readily acquired by calcining the hydroxide products at elevated temperatures in air. Qian et al. have prepared NiO nanoplatelets with porous structures by thermally treating the hydroxide nanoplatelets at 400 °C in air for 2 h, and the as-prepared oxide products exhibit improved electrochemical performance.⁶⁸ Hierarchical $\beta\text{-Ni}(\text{OH})_2$ and corresponding NiO microspheres are successfully fabricated by Kuang et al via a hydrothermal process (Figure 2.10).⁶⁹

Figure 2.10 SEM images of the as-prepared β -Ni(OH)₂ samples in the presence of (a, b and c), and absence of PENS (d); and NiO microspheres (e) obtained from the calcination of β -Ni(OH)₂ sample shown in (a). (Scale bars in a, b and c are 200 nm, d is 2 μ m, and e is 10 μ m.). Reprinted with permission from ref. 69. Copyright 2009 ACS.

In their synthesis, the surfactant PENS was found to play an important role in the formation of nanoplate-constructed microspheres, and their protocol was also extended to preparation of CuO microspheres.

So far, many reports have presented the NiO/Ni(OH)₂ nanosheets or nanoplates via one-pot synthesis methods in the presence of surfactants, while NiO/Ni(OH)₂ hollow structures are attracting more attentions due to their unique structures and shapes. Yuan et al. reported a templating method to prepare non-spherical hollow NiO crystals with well-defined octahedral structure (Figure 2.11). In their synthesis, carbon spheres have been employed as hard templates for the precipitation of nickel ions, and it is interesting to find that the octahedral hollow structure is formed after the

carbothermal process.⁷⁰

Figure 2.11 SEM (a and b) and TEM (c) images of NiO octahedral hollow structures. Reprinted with permission from ref. 70. Copyright 2007 ACS.

In another report, polystyrene monolayer is used as a template for preparation of interconnected NiO nanoflakes by an electrophoretic deposition (Figure 2.12). Their results show that the as-obtained NiO hold high specific surface area with open macroporous texture, which exhibits higher specific capacitance (351 F g^{-1}) than common bare NiO film (140 F g^{-1}).⁷¹

Figure 2.12 SEM image (a) and cycling performance (b) of NiO film with open macropores as electrode materials in supercapacitors. Reprinted with permission from ref. 71. Copyright 2010 Elsevier.

Recently, Lee et al. have reported a template-free synthesis of $\alpha\text{-Ni(OH)}_2$ microstructures, and corresponding NiO microstructures with morphologies well

retained can be readily obtained by the subsequent calcinations process.⁷² The NiO sample acquired by the heat treatment at 300 °C (N300) shows the highest specific surface area of 258 m² g⁻¹ among all the samples. In virtue of the high surface and porous structure, the sample N300 has delivered a high specific capacitance of 403 F g⁻¹ at scan rate of 20 mV s⁻¹ with good retention after 1000 cycling test (Figure 2.13).

Figure 2.13 SEM image (a), and cycling performance (b) of the NiO sample obtained from calcinations at 300 °C. Reprinted with permission from ref. 72. Copyright 2011 Elsevier.

As we know, supercapacitors can deliver very high power density but much lower energy density compared to batteries, which has limited their practical use. However, a recent exciting work has reported a three-dimensional nanoporous NiO film through an electrochemical route. These obtained NiO film is proven to hold high specific surface area (264 m² g⁻¹) with porous character. When evaluated as electrode materials for supercapacitors, a very high capacitance of 1776 F g⁻¹ with a considerable energy density (16.5 kW kg⁻¹) have been delivered for this material, which shows a potential use in electric vehicles.⁷³

Nickel sulfides are a class of semiconductors that are widely used in many applications, such as industrial tougheners, hydrogenation catalysts, electrodes and lithium ion batteries.⁷⁴⁻⁷⁷ In some reported systems, sulfur sources such as elemental sulfur (S), thiourea ($\text{CH}_4\text{N}_2\text{S}$) and carbon disulfide (CS_2) are usually employed to prepare nickel sulfides.

Figure 2.14 SEM images of the β -NiS products prepared at different temperatures: 120 °C (a) and 180 °C, respectively. Reprinted with permission from ref. 79. Copyright 2007 ACS.

In an early report by Hu et al., a γ -irradiation assisted method was developed to prepare submicrometer-sized NiS hollow spheres by a PMMA- CS_2 -ethanol aqueous reaction solution.⁷⁸ In a later work by Li et al., β -NiS with 3D flowerlike architectures are hydrothermally synthesized in the presence of ammonia and trisodium citrate using thiourea as the sulfur source (Figure 2.14).⁷⁹ Recently, a facile Ni substrate supported growth method is designed for oriented crystallization of trinickel disulfide (Ni_3S_2) nanowire array in large scale with assistance of elemental sulfur. The as-fabricated Ni supported Ni_3S_2 nanowire array has exhibited high reversible

capacity and good cyclic performance for lithium storage.⁸⁰

By using Ni nanochains as precursors, NiS with chain-like tubular and echinus-like nanostructures were achieved by a solution chemical route.⁸¹ In a similar work, Ni/Ni₃S₂ peapod nanochains were prepared using Ni nanochains as sacrificial templates in a thiourea contained EG system (Figure 2.15).⁸²

Figure 2.15 TEM images of the peapod nanochains of Ni/Ni₃S₂. Reprinted with permission from ref. 82. Copyright 2010 Wiley.

2.4 Carbon nanotubes (CNTs) based inorganic nanocomposites

Carbon nanotubes have been have been popularized greatly in the material family with diverse applications in electronics, gas storage, electrochemistry, and biomedical areas,⁸³⁻⁸⁵ because of their large specific surface areas, good mechanical property and excellent electric conductivity. In recent years, the CNTs based inorganic nanocomposites materials are raising extensive research attentions, in which CNTs are employed as supporting backbone to improve the property for a variety of applications.⁸⁶⁻⁸⁹

Figure 2.16 SEM image of the deposited single walled CNTs network and (a) of the CNTs, and thin film supercapacitor using single walled CNTs films on PET as electrodes. Reprinted with permission from ref. 93. Copyright 2009 ACS.

Carbon nanotubes have been introduced as electrode materials for electrochemical capacitors due to their excellent characteristics.⁹⁰⁻⁹¹ A later report by Lee et al has investigated the supercapacitive performance for single-walled CNT electrodes comprehensively.⁹² Therein they found that a high temperature of heat treatment is a key factor to increase the specific surface and enrich the pore structures, which are essential for enhancing the capacitance while minimizing the resistance of the CNT-electrode. As a result, a maximum specific capacitance of 180 F g^{-1} is obtained for their CNT-electrode, and a power density of 20 kW kg^{-1} is delivered with an energy density of 6.5 Wh kg^{-1} .

Recently, thin film supercapacitors have been fabricated from sprayed networks of single walled CNTs by Kaempgen et al. By using printable aqueous gel electrolyte and organic liquid electrolyte, the devices have delivered high energy and power

density (Figure 2.16).⁹³

Figure 2.17 SEM images of CNT (a), CNT-ZnO nanocomposites with ZnO deposited in (b) 2 min, (c) 5 min, (d) 10 min, and (e) 20 min; and the corresponding cyclic performance of the electrodes (f). Reprinted with permission from ref. 94. Copyright 2009 Elsevier.

With the development of hybrid materials, some important inorganic species are grown and incorporated into the CNTs matrix to increase the capacitance of the electrode materials. Pan et al. have prepared a CNT-ZnO nanocomposite for capacitive electrodes (Figure 2.17). By depositing the ZnO nanodots onto the CNT film using ultrasonic spray pyrolysis, an enhanced specific capacitance of 323.9 F g^{-1} can be obtained compared to the pure CNT electrode (less than 150 F g^{-1}).⁹⁴

Manganese oxide is another promising electrode material for electrochemical capacitors, which has attracted great research interests recently.⁹⁵⁻⁹⁸ However, these reported results showed relatively low specific capacitance with poor cycle retention due to the low conductivity and surface area. The concept of introducing the CNTs as supporting structure to fabricate CNTs-metal oxides/sulfides has been proposed recently to improve the mechanical and electrical property of the composite materials. It is expected that the electrochemical performance of the CNTs based composite materials can be significantly improved compared to the pure metal oxide/sulfide electrodes. By using the electrophoretic deposition (EPD) method, Zhitomirsky et al. have developed a composite film of manganese dioxide-multiwalled carbon nanotubes (MnO₂-MWCNT) for capacitive electrodes. The electrochemical results showed a high specific capacitance of 650 F g⁻¹ at a scan rate of 2 mV s⁻¹ in a 0.5 M Na₂SO₄ solution.⁹⁹ A recent report by Cao et al has presented a manganese oxide nanoflower-carbon nanotube array (CNTA) composite for capacitive electrodes (Figure 2.18).⁸⁸ The composite materials prepared therein possesses hierarchical structure, large surface area with porosity, and good electric conductivity, and the electrochemical results show a specific capacitance of 199 F g⁻¹ with a very long cycle life (3% capacitance loss after 20000 charge-discharge cycles).

Figure 2.18 TEM images (a) and cyclic performance of the manganese-CNTA composite electrode (b). Reprinted with permission from ref. 88. Copyright 2008 ACS.

In summary, this literature review has provided a brief introduction of supercapacitors in fundamentals, including developing history, device fabrication, mechanism, and the typical electrode materials. As the most important components of supercapacitors, various metal oxide/sulfide based electrode materials have been reviewed and their electrochemical performances are also presented. The recently developed carbon nanotube based hybrid materials are also introduced as they are promising candidates for the next generation high-performance supercapacitors. In this thesis, we have been focused on the fabrication of unique and hierarchical metal oxide/sulfide nanostructures for high-performance supercapacitors, because it has been widely reported that the electrochemical performance of nanostructured materials are highly dependent on the composition, structure, subunits, and porous texture.

Chapter 3. Material Characterizations and Electrochemical Measurements

3.1. Material characterizations

3.1.1. X-ray diffraction

X-ray diffraction (XRD) is a non-destructive material analytical technique used to examine the chemical compositions and crystal phases of materials. An X-ray diffractometer is composed of X-ray generator, angular instrument, detector, and computing system. During the operation process, X-ray beam is generated by the generator, and then strikes the sample that is waiting for analysis. Particular diffraction patterns will be produced during this process due to the specific arrangement of atomic layers. These obtained XRD patterns with strong and weak peaks are used to determine the chemical composition, crystal structure, and particle size of the samples. The X-ray diffractometer (Shimadzu XRD-6000, Cu K_{α} , $\lambda = 1.5406 \text{ \AA}$) is employed in this project to examine all the products.

3.1.2. Field-emission scanning electron microscopy

The field-emission scanning electron microscopy (FESEM) is an analytical instrument that can provide basic information about the sample including the surface morphology and structure, and chemical composition (EDX attached). Usually, a SEM is made up of electron source, electron lenses, sample stage, signal detector,

output attachment and so on. During the operation, incident electrons generated by the electron source are accelerated and hit the surface of the sample. The secondary electrons and backscattered electrons activated in this process will be collected and magnified to generate image signals. The field-emission scanning electron microscopy (JOEL, JSM-6700F) equipped with EDX will be used to examine the morphologies of all the samples.

3.1.3. Transmission electron microscopy

Transmission electron microscopy (TEM) is a microscopy instrument used to examine the morphology of a sample with significant high resolution. The device usually consists of components, including electron source, thermionic gun, electron beam, electromagnetic lenses, vacuum chamber, condensers, sample stage, and computing system. For the operation principle, a TEM is quite similar with an optical microscope, but the TEM makes it possible to provide much higher resolution due to the small de Broglie wavelength of electrons. Electrons generated by the electron source can be transmitted through the thin sample and interact with the sample, forming the image of the sample. After magnified and focused onto an imaging system, the image can be detected and output by a CCD camera. Transmission electron microscopy (JEM-2010, 200 kV) with selected area electron diffraction (SAED) has been used to examine all the products throughout this research project.

3.1.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is an analytic method that used to measure the mass changes of a sample with the temperature increase at a constant heating rate. This technique reflects the mass change real time as the temperature increase, from which a weight loss of the sample can be identified after the heating process. The heating process can be performed in air or inert gas according to the different requirements of the test. In this project, thermal behaviors will be characterized by thermogravimetric analysis (Shimadzu TGA-60) in a flow of air at a heating rate of 5 °C min⁻¹ using α -alumina crucibles.

3.1.5. Brunauer-Emmett-Teller

Brunauer-Emmett-Teller (BET) is an analytical method used to evaluate the specific surface area, pore size distribution, and pore volume of a material by nitrogen multilayer adsorption at different relative pressures. The measurement of specific surface area and analysis of porosity in this research are carried out through measuring N₂ adsorption-desorption isotherms at 77 K with a Quantachrome NOVA-3000 system.

3.2. Electrochemical measurements

3.2.1. Electrode fabrication

The slurry of working electrode is prepared by mixing 80 wt% of the electroactive material, 10 wt% of carbon black (super-P-Li), and 10 wt% of polyvinylidene

difluoride (PVDF, Aldrich). A piece of nickel foam is used as the current collector for the three-electrode testing system. The nickel foam is immersed into a 0.1 M of HCl for 2 hours to remove any NiO impurities before the slurry was pressed onto Ni foam and dried at 60 °C in vacuum for 24 h.

3.2.2. Electrochemical testing

The electrochemical tests are conducted using a three-electrode configuration in a KOH aqueous solution with a Pt foil serving as the counter electrode and a standard calomel electrode (SCE) as the reference electrode.

The capacitive performances are evaluated using a CHI 660D electrochemical workstation (Shanghai Chenchua, China). The relationship between current and voltage of the working electrode is measured by Cyclic Voltammetry (CV) at different scan rates. CV is usually used to examine the electrochemical activity of a material and the redox character can be determined by the pairs of peaks in relation to the reduction and oxidation occurred on the electrode.

Chronopotentiometry tests are also performed in this project using the same three-electrode test system. For this measurement, a constant current will be applied to the testing cell to examine the voltage response as a function of time.

Chapter 4. Solvothermal Synthesis of Co_3O_4 Porous Nanostructures for Supercapacitors[†]

4.1. Introduction

In the past decades, transition metal oxides have been widely used in gas sensors,¹⁰⁰ optical and magnetic materials,¹⁰¹⁻¹⁰² heterogeneous catalysts,¹⁰³ and electrochemical applications.^{36, 47, 104} As a result, developing metal oxides with new morphologies and structures for enhanced properties has attracted great research interests. Cobalt oxide (Co_3O_4)–based porous structures have been one of the subjects as they have been broadly employed in the above-mentioned applications. Many efforts have been devoted to develop effective approaches to synthesize Co_3O_4 mesostructures with different morphologies.¹⁰⁵⁻¹¹² At the same time, cobalt based intermediate compounds, such as cobalt carbonates (CoCO_3), beta-cobalt hydroxide ($\beta\text{-Co(OH)}_2$), are equally important, because inorganic salts such as metal nitrates and carbonates have long been used as solid intermediates to obtain functional metal oxides and advanced ceramic materials by thermal decomposition.¹¹³ For example, we have previously demonstrated that Co_3O_4 nanotubes and mesoporous nanoneedles can be obtained through appropriate thermal treatments of $\beta\text{-Co(OH)}_2$ precursor in nanoneedle shape.⁴⁷⁻⁴⁸ More recently, Zeng and coworkers have obtained porous

[†] Reproduced from [T. Zhu, et al., J. Mater. Chem., 20, 7015 - 7020 (2010)] by permission from *The Royal Society of Chemistry*. Copyright 2010.

Co₃O₄ from CoCO₃ submicrometer particles, which demonstrates good performance in gas-sensor application.¹¹³

Herein we carried out the solvothermal synthesis for preparation of Co-based intermediates in a mixed solution of polyethylene glycol (PEG) and water. Based on this technique, products with a wide range of morphologies have been successfully synthesized, including 2D leaf-like nanosheets (designated as sample I), 3D oval-shaped micro-particles (designated as sample II), and 1D needle-like nanorods (designated as sample III). By annealing at 300 °C in air, these three products were converted into phase-pure spinel porous Co₃O₄ with no substantial alterations in morphology. In view of their porous structure and relatively high specific surface areas, the capacitive properties of derived porous Co₃O₄ materials have also been evaluated and the needle-like Co₃O₄ nanorods exhibit the best performance among the three samples.

4.2. Material synthesis

All chemicals were of analytical grade and used as received without further purification. In a typical synthesis, cobalt acetate tetrahydrate (Co(Ac)₂·Co(CH₃COO)₂·4H₂O, Aldrich) and 0.5 g of polyvinyl-pyrrolidone (PVP; MW = 58000, Reagent Chemicals) were first dissolved in a mixed solution of polyethylene glycol (PEG; MW = 400, Aldrich) and de-ionized water at room temperature (the total volume is 20 mL), followed by the addition of 0.25 g of urea (CO(NH₂)₂, Aldrich) under vigorous stirring. After stirring for 15 minutes, the mixture was transferred into

a 60 ml Teflon-lined stainless steel autoclave and placed in an electric oven at 220 °C for 18 h. After that, the product was harvested, and washed with de-ionized water and ethanol several times by a centrifugation-redispersion process. Then the final products were dried in an oven at 60 °C for 24 h. The as-prepared powder was converted to Co₃O₄ via thermal decomposition at 300 °C for 2 h in air with a ramping rate of 1 °C /min. In the experiments (detailed conditions are given in Table 1), only the concentration of Co(Ac)₂ and volume ratio of PEG/water were adjusted while keeping all other conditions unaltered.

4.3. Results and discussion

4.3.1. Characterization of the morphology and composition

Table 4.1 shows the experimental conditions for materials synthesis. Morphologies of all intermediate products were examined with FESEM (images of sample 1, 3, 5 and 7 not shown here).

Exp. No.	[Co ²⁺]/M	PEG/ml	Morphology
1	0.1	0	Overgrowth rhombus
2	0.1	10	Leaf
3	0.01	20	Dumbbell
4	0.02	20	Oval
5	0.05	20	Oval with smooth facet
6	0.1	20	Rod
7	0.2	20	Thick rod

Table 4.1 Experimental conditions and morphologies of the products. Samples I, II and III correspond to experiments 2, 4, and 6, respectively.

Figure 4.1 a and b show the morphology of sample I. It is observed that sample I consists of uniform leaf-like structures with about 1 μm in length and 300 nm in width.

To the best of our knowledge, this type of Co-based nanostructure has not been reported before, as the 2D architectures demonstrated previously are generally hexagonal nanodiscs.^{45, 114-117} It can be clearly identified from the magnified image (Figure 4.1 b) that these “nano-leaves” have relative smooth surface, and a thickness of about tens of nanometers. Figure 4.1 c illustrates the oval-shaped CoCO_3 microparticles in sample II prepared in the absence of PEG with a $\text{Co}(\text{Ac})_2$ concentration of 0.02 M. These oval-shaped particles are of relatively uniform size distribution, with approximately 2 μm in length and 1 μm in width.

Figure 4.1 Field-emission scanning electron microscopy (FESEM) images of as-prepared sample I (a and b), sample II (c and d), and sample III (e and f).

Figure 4.1 d shows a FESEM image with a higher magnification, which shows that the surface of these oval-shaped particles are quite rough composing of fine nanoparticles. Interestingly, dumbbell-shaped structures (not shown) are produced if the $[\text{Co}^{2+}]$ is decreased to 0.01 M, while oval-shaped particles with smooth surface are acquired when $[\text{Co}^{2+}]$ is increased to 0.05 M. Figure 4.1 e and f depict the

morphology of the needle-like nanorods in sample III, which are around 50 nm in diameter and 400 nm in length. They nanorods, prepared with an increased $[\text{Co}^{2+}]$ of 0.1 M, demonstrate highly anisotropic 1D growth along the long-axis.¹¹⁸ As indicated in Table 1, thicker rods (not shown) can be obtained when $[\text{Co}^{2+}]$ is doubled to 0.2 M.

The crystal phase of all samples was analyzed by powder X-ray diffraction (XRD), with the results shown in Figure 4.2. It is clear from pattern I that the leaf-like structure prepared in a PEG/water mixed solvent system contains mixed phases of CoCO_3 (space group: $R\bar{3}c$, JCPDS file no. 11-0692; $a_0 = 4.659 \text{ \AA}$ and $c_0 = 14.96 \text{ \AA}$) and $\beta\text{-Co(OH)}_2$ (space group: $R\bar{3}c$, JCPDS file no. 30-0443; $a_0 = 3.183 \text{ \AA}$ and $c_0 = 4.652 \text{ \AA}$). The formation of $\beta\text{-Co(OH)}_2$ can be attributed to the participation of the hydroxyl groups from H_2O or more likely the hydrolysis of urea.¹¹⁹

Figure 4.2 X-ray diffraction (XRD) patterns of as-prepared samples I, II and III. The peaks marked by black dots and asterisks are attributed to CoCO_3 and $\beta\text{-Co(OH)}_2$, respectively.

On the other hand, indicated by patterns II and III, the crystal phase of samples II and III is mainly CoCO_3 as the synthetic system does not contain added water (see Table 4.1). All the identified peaks can be indexed to the rhombohedral phase of CoCO_3 (JCPDS file no. 11-0692), and the absence of other diffraction peaks affirms the phase-pure cobalt-based intermediates.

As revealed by the above characterization, Co-based intermediates were formed via an aggregative attachment process during our synthesis. The formation pathway of these intermediate crystals can be explained by a mechanism of precipitate-dissolution-renucleation-growth-aggregation. Initially, a number of primary particles were formed in the solution when supersaturation was reached. The following was that the particles whose sizes were smaller than critical size would be dissolved again, and only those whose sizes are big enough can develop into nuclei for further crystal growth. The resultant crystallites were aggregated and attached one another to form final crystals, as commonly described in mineralization process.^{113, 120} It is also noteworthy that surfactant PVP and urea have been introduced into our system, which may make the crystallization more complicated, and the resultant morphologies we obtained depended on not only the concentration of Co^{2+} , but also the organic additives.

The thermal behavior of the as-prepared Co-based intermediates has been investigated by thermogravimetric analysis (TGA), as presented in Figure 4.3. These three samples demonstrate similar TGA profiles.

Figure 4.3 Thermogravimetric analysis (TGA) curves of samples I, II and III in air with a temperature ramp of $5^{\circ}\text{C min}^{-1}$.

The initial weight loss of all three samples up to 100°C can be mainly attributed to the evaporation of absorbed/trapped water molecules. As the temperature rises, the weight of samples II and III drops gradually until around 200°C where sharp weight loss is observed. Finally, it flattens out at around 400°C . This is consistent with previously reported thermal behavior of CoCO_3 .¹¹³ Compared to samples II and III, the significant weight loss of sample I is only observed at around 240°C , which probably indicates its different chemical composition. The above decomposition process of the samples can be described by the following two reactions:

From the above processes it can be calculated that the theoretical weight loss of CoCO_3 to Co_3O_4 is 32.49 %, while $\text{Co}(\text{OH})_2$ to Co_3O_4 is 13.6 %. Based on the results, the actual weight losses of samples I, II and III were determined to be 28.54 %, 30.79 % and 36.14 %, respectively. Therefore, it can be deduced that the proportion of

CoCO_3 phase in sample I is approximately 79.1 %, implying that CoCO_3 was the preferred phase to form than $\beta\text{-Co(OH)}_2$ in this synthetic system. Because of its relatively large size (see Figure 4.1 c and d), sample II is more robust to complete thermal decomposition, leading to a weight loss that is slightly lower than the theoretical value. On the other hand, needle-like CoCO_3 in sample III shows a slightly higher weight loss, which may be due to the combustion of adsorbed organic species in view of the considerable amount of PVP and PEG used in the synthetic system (see Experimental section).

After being annealed at 300 ° C for 2 h in air, the as-synthesized Co-based intermediates crystals were completely converted to phase-pure spinel Co_3O_4 .

Figure 4.4 FESEM (a) and transmission electron microscopy (TEM) (b) images of sample I. FESEM images of sample II (c and d), and FESEM (e) and TEM (f) images of sample III. The insets in b and f are a selected-area electron diffraction (SAED) pattern and a magnified TEM image of the corresponding sample.

Figure 4.4 shows the morphologies of the products after heat treatment. It can be seen from Figure 4.4 a that sample I shows good thermal stability as the overall structure is largely intact, even though some broken or tips-cutoff “nano-leaves” can be observed. From the TEM image (Figure 4.4 b), it can be observed that the surface of the leaves becomes much rougher, and the surface defects can be clearly revealed as a porous structure resulting from the thermal decomposition.⁴⁸ The selected-area electron diffraction (SAED; Figure 4.4 b, inset) shows a poorly defined hexagonal spot pattern, indicating the relatively poor single-crystallinity of these leaf-like structures, and the topotactic transformation to (111) planes of Co_3O_4 .⁴⁷ The oval-shaped microparticles in sample II are shown to be quite thermally stable (Figure 4.4 c and d) with no collapse of structure. Sample III also exhibits no substantial morphological alteration after the annealing process (Figure 4.4 e and f). From the TEM image (Figure 4.4 f), it can be seen that these needle-like nanorods self-organize to form compact bundles, which is in good agreement with the FESEM analysis. The inset shows the tips of some nanoneedles at a higher magnification. It is clear that the needle-like nanorods appear thinner compared to the counterparts before annealing due to crystal shrinkage during thermal decomposition.

The crystallographic phase of all three samples is again examined by XRD (Figure 4.5). All diffraction peaks can be assigned to the cubic phase of Co_3O_4 (space group $Fd3m$; lattice constant $a_0 = 8.0837 \text{ \AA}$; JCPDS PDF file no. 42-1467).¹²¹⁻¹²²

Figure 4.5 XRD patterns of samples I, II and III after annealing at 300 °C in air.

Brunauer-Emmett-Teller (BET) gas-sorption measurements were performed at 77 K to investigate the textural characteristics of the Co_3O_4 samples. Nitrogen adsorption/desorption isotherms of these samples are shown in Figure 4.6, and the insets show the corresponding Barrett-Joyner-Halenda (BJH) pore size distribution obtained from both branches of the isotherm.

Figure 4.6 N_2 adsorption-desorption isotherms of samples I (a), II (b), and III (c). Inset in each isotherm is the corresponding pore size distributions.

These isotherm profiles can be categorized as type IV with small hysteresis loops observed at a relative pressure of 0.2 - 0.9 for sample I, and 0.5 - 1.0 for sample II,

and no distinct hysteresis is present for sample III. The BET specific surface areas of these three samples are measured to be $86.16 \text{ m}^2 \text{ g}^{-1}$, $110.2 \text{ m}^2 \text{ g}^{-1}$, and $121.5 \text{ m}^2 \text{ g}^{-1}$ for samples I, II and III, respectively, which shows that all of them possess relatively high specific surface areas. It can be concluded from the BJH pore size distribution that both samples I and II have pores with diameter less than 10 nm, while sample III has generally larger pores of about 20 nm. It can also be observed that sample II only shows a monomodal pore size distribution in the range of 4 – 10 nm, which together with the isotherm indicates a well-defined mesoporous structure constructed from crystal re-construction.⁴⁸

4.3.2. Investigation of electrochemical performance

Co_3O_4 has been widely studied as the electrode material for supercapacitors and lithium-ion batteries.^{50, 123-125} Here we analyze the electrochemical capacitance of the three samples. The measurements are conducted using cyclic voltammetry (CV) in a 2 M KOH electrolyte, and the optimized CV curves are presented in Figure 4.7.

The voltage window of sample I (Figure 4.7 a) and II (Figure 4.7 b) is from -0.15 V to 0.45 V with a scanning rate of 0.015 V s^{-1} , while that used for sample III (Figure 3.7 c) is optimized to be from 0 to 0.5 V with the same scanning rate. It can be clearly observed that there is a distinct pair of redox peaks during the anodic and cathodic sweeps, with the presence of a broad redox background. It is thus evident that our samples demonstrate pseudo-capacitive properties that originate from the reversible

and continuous electrochemical reactions of Co_3O_4 involved in the charge-discharge processes.^{50, 126-127}

Figure 4.7 Cyclic voltammograms of samples I (a), II (b), and III (c) in a 2 M KOH aqueous electrolyte at a scan rate of 0.015 V s^{-1} . The voltage window used for samples I and II is $-0.15 \text{ V} - 0.45 \text{ V}$, while that used for sample III is $0 - 0.5 \text{ V}$.

Figure 4.8 presents the dependence of the discharge specific capacitance of the electrodes on the charge-discharge cycle number, and the insets are corresponding voltage profiles of the first 4 charge-discharge cycles.

Figure 4.8 Specific capacitance of samples I (a), II (b), and III (c) in an aqueous KOH (2 M) electrolyte as a function of cycle number. The insets show the voltage profiles of the first 4 charge-discharge cycles.

The measurements are performed with the voltage windows the same as that for the CV analysis. The specific capacitance can be calculated according to the following equation:

$$C_m = I \times \Delta t / (\Delta V \times m)^{37, 128} \quad (1),$$

where C_m (F g⁻¹) is the specific capacitance, I (mA) is the discharge current, Δt (s) is the discharge time, ΔV (V) is the potential change during discharge, and m (mg) is the mass of active material within the electrode. The specific capacitance values of samples I, II, and III can thus be calculated from the discharge curves to be 44 F g⁻¹, 62 F g⁻¹, and 111 F g⁻¹, respectively, at the end of 1000 charge-discharge cycles. This indicates that as much as 86.9 %, 80 %, and 88.2 % of their initial capacitance can be maintained for samples I, II, and III, respectively. These results show that these active Co₃O₄ nanomaterials have relatively good supercapacitive properties with excellent capacitance retention. Among them, sample III possesses the highest capacitance and best retention capability, largely due to its highest specific surface area and largest mesopores granting good accessibility for the electrolyte. It should also be noted that the voltage window used for sample III is 0 - 0.5 V, which is narrower than that of the other two samples, implying that the calculated capacitance based on equation 1 can be further improved if the charge storage can be achieved within a narrow voltage window.

It also should be noted that the voltage windows within which the CVs are performed have been adjusted and optimized before the test, because we expect that the pairs of redox peaks can be included in the cycled voltage window in order to

deliver Faradaic capacitances. From our trial experiments, we found that the oxidative peak voltage of sample III is slightly higher than those of sample I and II, so we increased the cut-off potential of sample III from 0.45 V to 0.5 V. In addition, we also observed that the CV curve (-0.15 to 0 V) of sample III is nearly flat, which means that there is no Faradaic contribution to the capacitance, and hence the bottom potential is increased from -0.15 V to 0 V. In addition, the slight difference of oxidative and reductive peaks of sample I, II and II may be partly due to the different polarization process which may have resulted from their different structures.

In addition, for the cycling performances, it can be concluded from Figure 4.8 that the interface between the electrodes and the electrolyte is not stable, which led to the initial decrease of the capacitance observed in the first 200 cycles. This may have been due to the loss of the active materials, as the active materials on the surface of electrode may not so firmly binded together. However, it should be noted that the particle size of sample II is the largest among all the three samples, which may be the reason for its fastest capacitance decrease, because it is more difficult for the electrolyte to diffuse into the interior of the particles. After the active materials are cycled for some times, the electrodes become more stable and can afford prolonged cycling test.

4.4. Conclusions

In summary, Co-based intermediates with different morphologies were synthesized in a solvothermal system with a mixed solvent of PEG400 and water. Three samples

with distinct morphologies, i.e., 1D needle-like nanorods, 2D leaf-like nanosheets, and 3D oval-shaped microparticles, were discussed in this report. It has been found that both the concentration of cobalt acetate precursor and the volume ratio of PEG400 and H₂O play very important roles in determining the final structure of the products. After converting these three samples into pure spinel Co₃O₄ by thermal annealing, the obtained porous products with high surface areas show no substantial morphological alterations. The electrochemical measurements reveal that these Co₃O₄ products manifest promising pseudo-capacitive properties with high capacitance and good retention. We believe that these active Co₃O₄ materials with distinct nanostructures could serve as promising candidates for other applications, such as catalysis and lithium-ion batteries.

Chapter 5. Solvothermal synthesis of Self-Assembled Ni-EG Complexes and Their Conversion to Porous NiO Nanospheres for Supercapacitors[†]

5.1. Introduction

In recent years, nickel-based materials, such as nickel oxide (NiO) and nickel hydroxide (Ni(OH)₂) have received enormous research interest because of their promising applications in electrochemical devices.¹²⁹⁻¹³⁴ It has now been well accepted that electrochemical performance of an electrode material depends on not only the structure but also the crystallite size and shape of the active material.¹³⁵ Hence, control over the size and morphology of the active materials is widely believed to be an effective way to improve their electrochemical performance.¹³⁶

Nickel oxide is a promising electrode material for supercapacitors compared to the state-of-the-art material, RuO₂, in view of its high theoretical specific capacitance (2573 F g⁻¹),¹³⁷⁻¹³⁸ high chemical and thermal stability, and environmental benignity.¹³⁹⁻¹⁴⁰ So far various types of NiO have been prepared via different approaches,^{69, 141} in which NiO nanomaterials are commonly prepared from their

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hydroxide precursors. However, alkaline precipitator such as sodium hydroxide, ammonia, urea and so on are usually used in the synthesis, which may cause environmental concerns. Therefore, it is practically significant to develop facile and environment-friendly routes to prepare NiO materials with novel structures.

Ethylene glycol (EG) is an automotive antifreeze with a relatively high boiling point (ca. 197 °C), and it has been widely employed to synthesize nanomaterials of metal oxides (TiO₂, SnO₂, In₂O₃, and PbO) in large scale by forming glycolate intermediates,¹⁴²⁻¹⁴³ because of its strong chelating ability with the transition metal cations.¹⁴⁴⁻¹⁴⁵ Herein, we employed a glycol-assisted non-aqueous method to synthesize Ni-EG intermediate complex in the presence of additives, sodium chloride (NaCl) and sodium acetate (NaAc). By controlling the concentrations of nickel ions and additives, uniform Ni-EG nanospheres can be easily obtained. Control experiments suggest that NaCl and NaAc play vital roles in the formation of these uniform nanospheres. The corresponding NiO nanospheres with porous texture can be acquired by calcining the as-prepared spherical Ni-EG complex intermediate at 300 °C, and the porous structure after calcination is confirmed by the N₂ sorption measurement. When tested for their potential use in supercapacitors, such porous NiO nanospheres exhibit a high specific capacitance (254.2 F g⁻¹) at a discharge current density of 0.56 A g⁻¹. When the discharge current density is increased to 5.6 A g⁻¹, a relatively high capacitance of 213.4 F g⁻¹ still can be obtained, which is 83.8% of the capacitance at 0.56 A g⁻¹. Moreover, these porous NiO spheres also exhibit excellent cyclic retention of capacitance up to 1000 cycles.^{21, 37, 138}

5.2. Material synthesis

All the chemicals are of analytical grade and used as received without further purification. In a typical synthesis of Ni-EG complex intermediate, 2 mmol of nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Aldrich) and 0.234 g of sodium chloride (NaCl, Aldrich) are sequentially added into a 20 ml of ethylene glycol (EG, Aldrich) to form a clear light green solution, to which then 2.624 g of sodium acetate (NaAc, Aldrich) is added to give a concentration of 2.0 M. After vigorous stirring for 20 minutes, the solution is transferred into a Teflon-lined stainless steel autoclave and heated at 190 °C for 8 h. After the heat treatment, the autoclave is allowed to cool naturally to room temperature, and the green products are collected, rinsed by distilled water and ethanol several times. Then the final products are dried in an oven at 60 °C for 24 h. To obtain the nickel oxide product, the dried green powder is calcined in air at 300 °C for 2 h with a ramping rate of 1 °C min⁻¹.

5.3. Results and discussion

5.3.1. Characterization of morphology and composition

The morphology and hierarchical structure of a typical Ni-EG complex product are presented in Figure. 5.1. Clearly the as-synthesized Ni-EG particles are all spherical with a mean diameter of ca. 600 nm (Figure 5.1 a). The high-magnification FESEM image (Figure 5.1 b) reveals that the hierarchical nanospheres are comprised of many densely packed well-defined flake-like structures. This suggests that the

Ni-EG nanospheres are self-assembled from these fine flakes, which may further give rise to a porous structure of the Ni-EG spheres due to the congregation of the building blocks. The crystal phase of the Ni-EG complex spheres is revealed by the XRD pattern (Figure 5.1 c). As can be seen, a strong diffraction peak appears at around 10.3° , which is the characteristic of coordination polymers from metal ions and ethylene glycol.¹⁴⁴⁻¹⁴⁵

Figure 5.1 Field-emission scanning electron microscopy (FESEM) images (a and b), X-ray diffraction (XRD) pattern (c), and thermogravimetric analysis (TGA) curve (d) of the typical Nickel-Ethylene glycol (Ni-EG) complex spheres.

The TGA curve in Figure 5.1 d shows a total weight loss of about 51.4 % up to 600 °C in air, which is comparable to a previously reported value (58%) for Ni-EG

complex.¹⁴⁶ For present hierarchical Ni-EG complex spheres, it might be relatively more difficult to completely combust the deeply trapped organic molecules.

In order to study the roles of NaCl and NaAc in the formation of uniform Ni-EG nanospheres, control experiments have been carried out. Figure 5.2 a shows a FESEM image of Ni-EG particles prepared in the absence of NaCl while keeping other conditions unchanged. It can be observed that most Ni-EG particles are composed of flower-like structures with random shapes, which indicates that the presence of NaCl is critical for the formation of well-defined flake-constructed nanospheres. While in the absence of NaAc, largely interconnected Ni-EG complex with spherical subunits is obtained, as shown in Figure 5.2 b.

Figure 5.2 FESEM images of the sample prepared in the absence of NaCl (a), in the absence of NaAc (b), with the concentration of NaAc at 1.09 M (c), and with the concentration of NaAc at 4 M (d), while keep all the other conditions same.

Furthermore, it can be clearly seen that the sample prepared at a lower NaAc concentration of 1.09 M consists of relatively uniform spherical particles with different structures (Figure 5.2 c). When the concentration of NaAc is increased to 4.0 M, aggregates of Ni-EG complex with thickened flake-like building blocks are obtained. Hence, it is apparent that the formation of well-defined spheres is very sensitive to the concentration of NaAc. It seems that the NaAc has favored the formation of uniform Ni-EG particles at a lower concentration.

Figure 5.3 Schematic illustration of the formation of Ni-EG complex: (A) Chelation between nickel ions and ethylene glycol chain-like molecules followed by the formation of Ni-EG complex; (B) The growing process of Ni-EG complex.

Based on the above observations, a plausible formation mechanism has been proposed in Figure 5.3. It has been reported that there is strong chelating interaction between ethylene glycol and metal ions. For example, Yamamoto et al. employed the glycol (primarily ethylene glycol) chelates to control the hydrolysis and polycondensation rates of tin alkoxides.¹⁴⁷ It was also found by Xia et al. that glycols could serve as a ligand to form chain-like coordination complex with many metal ions

(Ti^{4+} , Sn^{2+} , In^{3+} , and Pb^{2+}), and the as-formed chain-like complexes would congregate and self-assemble into bundles when such chains become sufficiently long.¹⁴³

As illustrated in Figure 5.3, initially the nickel ions (Ni^{2+}) would diffuse in the EG solution and then attach onto the EG molecules to form glycolates by the strong chelating interaction. Then the polymerization of nickel glycolates occurs (Figure 5.3, step A), which is an important process that has been discussed in many other reports for the formation of nanostructured metal oxides.¹⁴⁸⁻¹⁵⁰ The nickel glycolates would subsequently grow into a bigger size, and the thermally stable Ni-EG complex can finally be formed (Figure 5.3, step B). It should also be mentioned that the formation of typical well-defined Ni-EG spheres has been assisted by the additives (NaCl and NaAc) present in the system. That is to say, the presence of NaCl and NaAc may have crucial effects on the chelating interaction between nickel ions and EG molecules, which should be responsible for the morphological transformation as discussed above.

Uniform NiO nanospheres can be readily obtained by calcining the Ni-EG complex precursor, with the morphology shown in Figure 5.4 a. The high-magnification FESEM image (Figure 5.4 a, inset) shows that the overall structure is completely intact after the thermal treatment indicating good thermal stability. The TEM image shown in Figure 5.4 b clearly shows the flake-constructed nanospheres of this calcined product. Furthermore, the TEM image of a single nanosphere presented in Figure 5.4 c reveals that the structure is composed of radially oriented ultrathin flake-like nanosheets, consistent with the above SEM observation. The crystallographic phase of NiO is confirmed by XRD analysis (Figure 5.4 d), and all

the diffraction peaks agree well with the standard pattern of NiO (PDF card no 71-1179).

Figure 5.4 FESEM image (a), TEM images (b and c), and XRD pattern (d) of the NiO nanospheres calcined from Ni-EG nanospheres at 300 °C for 2 h.

The textural characteristic of as-prepared NiO nanospheres is investigated by the gas sorption measurement at 77 K. The nitrogen adsorption-desorption isotherm of the NiO sample is shown in Figure 5.5, and the inset shows the Barrett-Joyner-Halenda (BJH) pore size distributions obtained from both branches of the isotherm.

Figure 5.5 N₂ adsorption and-desorption isotherm of the prepared NiO nanospheres, and the inset is the pore size distribution obtained from desorption branch.

This isotherm profile can be categorized as type IV with a small hysteresis loop observed at a relative pressure of 0.5 – 1.0, indicating the presence of a mesoporous structure in the sample. As a result, the sample has a relatively high specific surface area of 221.7 m² g⁻¹. It can be seen from the pore size distributions that the porous NiO nanospheres have pores with diameter in the range of 4 – 10 nm, which are formed by organization of nano-flakes and also crystal re-construction during the calcination.¹⁵¹

5.3.2. Investigation of electrochemical performance

NiO has been widely studied as the electrode materials for supercapacitors and lithium ion batteries,¹⁵²⁻¹⁵⁴ and we have subsequently evaluated the supercapacitive properties of the as-prepared porous NiO hierarchical nanospheres. The

electrochemical capacitance of the sample is analyzed using a three-electrode cell system. Figure 5.6 (a) shows cyclic voltammetry (CV) curves of the NiO nanospheres with a voltage window of 0 – 0.5 V at various scan rates.

Figure 5.6 Cyclic voltammogram (CV) curves of the prepared NiO nanospheres at various scan rates (a); Average specific capacitance of the NiO nanospheres at various scan rates (b); Galvanostatic discharge curves of the NiO nanospheres at various discharge current rates (c); Average specific capacitance of the NiO nanospheres at various discharge current densities (d).

It can be clearly seen from the CV curve that the capacitive characteristic is completely different from that of electric double-layer capacitance in which the CV curve is usually close to a rectangular shape. Typically, a pair of redox peaks is

observed within the potential range of 0.3 – 0.5 V, which is believed to be caused by the following reversible process:¹⁵⁵

Therefore, the capacitance is mainly from the pseudo-capacitive process based on the above redox reaction. The average specific capacitance of this NiO material is calculated to be 276.8 F g⁻¹ at a scan rate of 5 mV s⁻¹ (Figure 5.6 b), and 224.5 F g⁻¹ at a higher scan rate of 20 mV s⁻¹, ca. 81.1% of that at 5 mV s⁻¹. Figure 5.6 c shows the galvanostatic discharge curves of this NiO material at various current densities. The corresponding average specific capacitance is calculated to be as high as 254.2 F g⁻¹ at a charge-discharge current density of 0.56 A g⁻¹ (Figure 5.6 d), and a specific capacitance of 146.8 F g⁻¹ can still be retained at a very high current density of 28.2 A g⁻¹. Herein the phenomenon of decrease in capacitance with the increasing scan rate or current density may be referred to the ion diffusion limitation during the charge-discharge process. At a high scan rate or current density, it will require the rapid intercalation of ions at the interface of electrode/electrolyte. Therefore the efficiency of the whole process is determined by the ion diffusion.¹⁰ Nevertheless, the discharge capacitance (225.6 F g⁻¹) at 2.8 A g⁻¹ is 88.7 % of that at 0.56 A g⁻¹, demonstrating a good rate capability of this porous NiO sample.

Figure 5.7 Average specific capacitance versus cycle number of the NiO nanospheres at a galvanostatic charge and discharge current density of 5.6 A g^{-1} , and the inset is the first 10 charge-discharge cycles at the same current density.

In order to study the cycling performance of this NiO material, the profile of discharge capacitance vs. cycle number is presented in Figure 5.7, and the inset shows the voltage profile of the first 10 charge-discharge cycles. The measurement is performed at a high current density of 5.6 A g^{-1} with the same voltage window as that for the CV analysis. It is interesting to observe that the capacitance starts to increase after 500 cycles, which may be due to the activation of the electroactive material.¹⁵⁶ Afterwards, the capacitance is stabilized at about 225 F g^{-1} from the 700th cycle to 1000th cycle, indicating the excellent capacitance retention of this NiO active material. The relatively high capacitance could be attributed to the high surface area of the porous NiO nanospheres, which provides large contact area between the electrode material and the electrolyte.¹⁵⁷⁻¹⁵⁸ Furthermore, the unique hierarchical structure of the

sample grants better bulk stability during the prolonged cycling, leading to a greatly enhanced cyclic retention of capacitance.¹⁵⁹

It should be noted that the electrode materials is believed to have experienced an activation process, such as higher ratio of the active materials is available for redox reaction with the diffusion of electrolyte into the electrode. The capacitance may reach a stable value when the electrode reaches a balanced condition with a relatively stable electrochemical interface with electrolyte. The slight drop of capacitance observed in the first 300 cycles may be due to the mass loss at the initial reversible cycles.

5.4. Conclusions

In summary, a facile solvothermal method has been developed to synthesize uniform Ni-EG complex nanospheres by forming the glycolate. Uniform NiO nanospheres with a porous hierarchical structure can be obtained after calcination of the Ni-EG nanospheres. The supercapacitive properties of these porous NiO nanospheres are subsequently evaluated. The results show that these porous NiO nanospheres exhibit relatively high supercapacitance at fast scan rates or high current densities with excellent cyclic capacitance retention. This improved supercapacitive performance could be attributed to the unique hierarchical structure and high surface area of the as-synthesized porous NiO nanospheres.

Chapter 6. Construction of NiS Hollow Nanospheres with Porous Texture for Supercapacitors[†]

6.1. Introduction

Hollow micro/nanostructures have attracted tremendous research interests in a myriad of applications such as lithium-ion batteries,¹⁶⁰⁻¹⁶² catalysis,¹⁶³⁻¹⁶⁴ chemical sensors¹⁶⁵⁻¹⁶⁷ and biomedical areas¹⁶⁸⁻¹⁷⁰ due to their unique structural feature including well-defined interior voids, low density, large surface area and surface permeability. Templating against colloidal particles is regarded as the most straightforward and effective route towards hollow structures with narrow size distribution and well-defined shape.¹⁷¹⁻¹⁷³ Generally, templating method involves the growth of a shell of designed materials on various colloidal templates (*e. g.* monodisperse latex and silica spheres) and subsequent removal of the template to generate the interiors with desirable complexity. The use of the templates in principle allows one to manipulate the size and morphology of resultant hollow particles for greater control of the local chemical environment and extraordinary properties. However, the difficulties ranging from material incompatibility to the collapse or

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deform of hollow structure upon template elimination are common in practice. The disadvantages of time-consuming and tedious procedure for the removal of the template also greatly restrict the extensive application of template method.

Nickel sulfides with lots of phases such as NiS, NiS₂, β -Ni₃S₂, α -Ni_{3+x}S₂, Ni₄S_{3+x}, Ni₆S₅, Ni₇S₆, Ni₉S₈ and Ni₃S₄ are cheap and abundant materials with widespread applications in ceramic tougheners, hydrogenation catalysts and electrode materials, etc.^{80, 174-177} Despite of the success in the synthesis of various morphologies, including nanochains,⁸² hollow spheres¹⁷⁸⁻¹⁷⁹ and layer-rolled structures,¹⁸⁰ the preparation of either hierarchical or hollow nanostructures of nickel sulfides still remains a big challenge. Herein, we developed a facile method for controllable synthesis of uniform NiS hollow nanospheres with hierarchical feature by template-engaged precipitation of nickel silicates and subsequent *in-situ* chemical conversion to NiS phase. Remarkably, these hollow nanospheres are entirely assembled from ultrathin NiS nanosheets with a thickness of a few nanometers and can be synthesized at one step by simultaneously etching of silica template in alkaline solution generated from the hydrolysis of sulfurizing agent. When evaluated as electrode material for supercapacitors, the NiS hierarchical hollow nanospheres exhibit excellent electrochemical performance due to their unique structure.

6.2. Material synthesis

6.2.1. Synthesis of core-shell structures of SiO₂@nickel silicate

The SiO₂@nickel silicate nanospheres were firstly prepared by reported method with slight modification.¹⁸¹ In a typical synthesis, 0.2 g of silica nanospheres were dispersed in 40 ml of DI water in a capped bottle, followed by adding 1 g of urea and 0.18 g Ni(NO₃)₂·6H₂O. The thoroughly mixed solution was stored at 105 °C for 12 h. After cooling down naturally, the product was harvested by several rinse-centrifugation cycles and was fully dried at 60 °C for next-step usage.

6.2.2. Synthesis of NiS hierarchical hollow nanospheres

0.1 g of SiO₂@nickel silicate nanospheres was dispersed in 40 ml of DI water in Teflon container, followed by adding of 0.1 g of Na₂S. After thoroughly mixed, the mixture solution was heated at 160 °C for 12 h. After cooling down naturally, the black precipitates were collected by several rinse-centrifugation cycles before fully drying at 60 °C in vacuum for the characterization.

6.3. Results and discussion

6.3.1. Schematic illustration of synthetic strategy

The scheme in Figure 6.1 illustrates our concept for the synthesis of NiS hollow nanospheres. Firstly, monodisperse silica nanospheres are functionalized with silicate anions in alkaline solution generated by the hydrolysis of urea. Driven by the

interfacial reaction between aqueous solution of nickel nitrate and activated silica nanospheres, uniform coating of nickel silicate simultaneously occurs around the scaffold of silica template to form an intermediate layer.¹⁸²⁻¹⁸³ Such SiO₂@nickel silicate core-shell structures are readily converted into hollow nanospheres at an elevated temperature by reacting with sodium sulfide (Na₂S), where the silica cores are etched simultaneously by OH⁻ released from the hydrolysis of S²⁻. Herein Na₂S not only serves as sulfurizing agent for the phase transition from nickel silicate to thermodynamically favored nickel sulfide, but also grants the as-formed hollow spheres with structural integrity by providing a mild alkaline environment to gradually remove the silica template. As the result of favorable kinetic control over this process, delicate nanosheets are formed as the subunits of the hollow nanospheres to build a hierarchical structure.

Figure 6.1 Schematically illustration for the formation of NiS hollow nanospheres by templating against silica nanospheres: (I) uniform precipitation of nickel silicate layers on silica nanospheres; (II) chemical conversion to NiS hollow nanospheres with simultaneous template elimination in the presence of Na₂S.

6.3.2. Characterization of morphology and composition

The crystallographic phase of SiO₂@nickel silicate was investigated by X-ray diffraction (XRD, Figure 6.2). All peaks can be assigned to Ni₃Si₂O₅(OH)₄ phase¹⁸¹ without noticeable signals from possible impurities such as nickel hydroxides.

A panoramic view of SiO₂@nickel silicate products reveals that the sample consists entirely of uniform nanospheres without impurity particles or aggregates, as depicted in field-emission scanning electron microscopy (FESEM) images (Figure 6.3 a and b). These nanospheres well duplicate the original spherical shape of silica template with a diameter of around 400 nm, and the uniform coating of nickel silicate on the entire surface of silica nanospheres is evidenced by the void space between the silica core and the shell materials with very thin thickness of ca. 10 nm, as shown in transmission electron microscopy (TEM) images (Figure 6.3 c and d).

Figure 6.2 XRD pattern of the core-shell structure of silica@nickel silicate.

Figure 6.3 FESEM images (a, b) and TEM images (c, d) of core-shell structure of SiO₂@nickel silicate.

After simple reacting with Na₂S in solution, uniform NiS hollow nanospheres assembled from ultrathin nanosheets can be produced without losing the spherical morphology, as shown in Figure 6.4 a. The complete phase conversion is confirmed by XRD analysis (Figure 6.4 b), where all the identified peaks can be ascribed to hexagonal NiS phase (JCPDS No. 12-0041) without nickel silicate and silica residues.¹⁸⁰ The hollow interior and geometrical structure of as-synthesized NiS nanospheres were further elucidated by TEM, as displayed in Figure 6.4 c and d. In good agreement with the SEM finding, a high uniformity of hollow nanospheres can be seen from the image, and the inner cavity is clearly revealed by the contrast between NiS shell and hollow interior. No collapse of the shell can be observed owing

to good structural stability and integrity of the hollow spheres. Further TEM observation evidences the presence of ultrathin nanosheets around the shell, of which the thickness is as thin as only a few nanometers (Figure 6.4 e and f).

Figure 6.4 FESEM image (a), XRD pattern (b) and TEM images (c-f) of NiS hierarchical hollow spheres (f is taken from the rectangle area in e).

N₂ adsorption/desorption measurement shows that these hollow nanospheres possess a large Brunauer-Emmett-Teller (BET) specific surface area of ca. 211 m² g⁻¹ with uniform 4 nm mesopores (Figure 6.5). Apparently, such a hierarchical hollow structure holds the great promise in offering sufficient surface area to facilitate electrochemical reactions with respect to their bulk or solid counterparts.

Figure 6.5 N_2 adsorption-desorption isotherm of NiS hollow nanospheres. The corresponding pore size distribution is shown as the inset.

Figure 6.6 TEM images of NiS hollow nanospheres prepared by templating against 200 nm (a and b) and 400 nm (c-f) silica nanospheres in water/ethanol mixture with ethanol volume ratios of 0 % (a), 37.5% (b-d), and 75% (e and f) at 160 °C for 12 h.

Furthermore, the use of pre-grown silica templates allows the structural feature of resultant NiS hollow nanospheres to be rationally controlled in different structural level. For example, analogous hollow colloids with smaller dimension and interior volume (*e. g.* 200 nm) can be prepared through the same protocol by templating against silica nanospheres with corresponding size (Figure 6.6 a and b). By introducing non-ionic solvent such as ethanol into the conversion system, the surface feature of these hollow nanospheres can be further tailored into thicker shells assembled from larger nanosheets with denser packing (Figure 6.6 c-f).

6.3.3. Investigation of electrochemical performance

As a good metallic conductor with low resistivity at room temperature, NiS is a very appealing candidate as the electrode materials in supercapacitor. Generally, its capacitance is mainly derived from the pseudo-capacitive properties based on the following reversible redox reaction:

In the present work, such reversible reaction was detected as a pair of redox peaks in the potential range of -0.15-0.55 V by cyclic voltammetry (CV) analysis at various scan rates (Figure 6.7 a).¹³² The profile of CV curves also suggest a distinctly different capacitance characteristics from that of electric double-layer capacitance with rectangular CV shape.¹³⁴

Figure 6.7 CV curve (a) of NiS hollow nanospheres between -0.15 V-0.55 V at various scan rates; galvanostatic charge-discharge curves (b); average specific capacitance of NiS hollow nanospheres at various current rates (c); and cycling performance of NiS hollow nanospheres at a current rate of 4.2 A g⁻¹ (d).

The galvanostatic discharge tests at various current densities of 4.08 A g⁻¹ and 8.16 A g⁻¹ deliver high average specific capacitances of 927 F g⁻¹ and 618 F g⁻¹, respectively (Figure 6.7 c). At a higher current density of 10.2 A g⁻¹, a specific capacitance of 583 F g⁻¹ can still remain as a value of around 62.8 % of the capacitance at 4.08 A g⁻¹. Figure 6.7 d shows the cycling performance of NiS hollow spheres at a current density of 4.2 A g⁻¹ between -0.15-0.55 V. A capacitance of 587.1 F g⁻¹ can be retained after 1000 cycles with an initial value of 823 F g⁻¹. Such

relatively high initial capacitance may be attributed to the high surface area of hollow structure composed of ultrathin nanosheets, which offers a large interface between the electrode material and the electrolyte and sufficient physical cavities for charging ion storage.¹⁵⁸ After deep cycling of 3000 times, around 74.1% of the capacitance at 1000th cycle can still be recovered, evidently showing very stable cycling ability. The greatly improved capacitance retention may be attributed to the hierarchical structures with enhanced structural integrity and large surface area.¹⁵⁷

6.4. Conclusions

In summary, we have reported a facile templating approach for the preparation of hierarchical NiS hollow nanospheres assembled from ultrathin nanosheets under hydrothermal conditions. The as-prepared NiS hollow spheres are shown to be very uniform in size, mesoporous in textual property and with good structural stability due to mild and one-pot template elimination. In virtue of the unique structural feature, these NiS hollow nanospheres exhibit high specific capacitances of 583-927 F g⁻¹ at various current densities of 4.08-10.2 A g⁻¹. Over 70% of the initial capacitances can be retained even after deep cycling of 1000-3000 times. This justifies their promising application as electrode material for high-performance supercapacitors.

Chapter 7. CNTs Supported CuS Nanoneedles Porous Composite Materials for Supercapacitors[†]

7.1. Introduction

As demonstrated in the above sections, electrochemical capacitors (or supercapacitors) have attracted intensive research interests for their prominent characteristics of high power density, long cycle life, and great safety.^{10, 184} However, the lack of advanced electrode materials has hindered their development. Compared with the widely studied metal oxides such as NiO and Co₃O₄ described previously, some metal sulfides (eg., CoS_x and CuS_x) are receiving increasing attentions as electrode materials for supercapacitors in view of their interesting intrinsic properties and good performance.^{58, 185}

Copper sulfides are a class of functional semiconductors with many different phases available such as chalcocite (Cu₂S), villamaninite (CuS₂), djurleite (Cu_{1.95}S), anilite (Cu_{1.75}S) and covellite (CuS).¹⁸⁶ Different approaches have been developed to prepare copper sulfides, including solvothermal,¹⁸⁷ microemulsions,¹⁸⁸ and surfactant templating.¹⁸⁹ Among these chalcogenides, CuS is widely used in gas sensors,¹⁹⁰⁻¹⁹¹ lithium-ion batteries,¹⁹² solar cells,¹⁹³ and photocatalysts.¹⁹⁴ Recently, CuS

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nanostructures with different morphologies including nanoparticles,¹⁹⁵ nanoplatelets,¹⁹⁶ nanorods,¹⁹⁷ and hollow spheres¹⁹⁸⁻¹⁹⁹ have been reported. However, complex nanostructures such as arrays of CuS nanoneedles supported on the CNT backbone are rarely reported. In previous reports about copper sulfide/CNT nanocomposites, the copper sulfide components are generally in the form of nanocrystals randomly deposited on the CNTs.²⁰⁰⁻²⁰¹

As an important one-dimensional (1D) tubular structure, CNTs have been one of the hot materials for many years in both fundamental studies and practical applications because of their good conductivity, thermal and chemical stability, and excellent mechanical properties.^{85, 202-204} In most of these applications, CNTs are introduced as the support to form hybrids with other functional materials such as metals, oxides/chalcogenides to improve the property of the nanocomposites.^{203, 205-206} Some early works attempt to fill the tubular structure with metal oxides and metals to make CNT-inorganic hybrids.²⁰⁷⁻²⁰⁹ Also various strategies have been developed to attach inorganic species to the outer surface of CNTs to generate novel hybrid functional materials.⁸⁴ Some recent works have demonstrated the attachment of various metal oxides (such as MnO₂, MgO and TiO₂) onto CNTs without any linking agent. However, only weak interaction between the oxides and the acid-terminated CNTs is observed, resulting in the nonuniform distribution of the nanoparticles on the outer surface of CNTs.²¹⁰⁻²¹² Hence, it is still desirable to develop new routes to integrate functional materials with CNTs to form novel hybrid nanomaterials.

By applying a similar synthetic strategy for the previous NiS hollow spheres, herein

we used such template-engaged method to grow ultrafine CuS nanoneedles on the CNT backbone to form complex CNT@CuS 1D hierarchical structures, which exhibit interesting properties for supercapacitors. First, CNT@SiO₂ core-shell nanowires are introduced as the substrate for the uniform growth of CuSilicate nanoneedles. Then the as-formed CuSilicate is converted into CuS phase without sacrificing the pristine shape of nanoneedles. Simultaneously, the intermediate silica layer is also eliminated by the alkaline dissolution during the sulfidation, thus creating the CNT@CuS 1D hierarchical nanostructures. When tested as the electrode for supercapacitors, the as-prepared CNT@CuS 1D structures exhibit high capacitance and excellent cycling stability.

7.2. Material synthesis

7.2.1. Synthesis of CNT@ SiO₂ and CNT@SiO₂@CuSilicate

The CNT@SiO₂ is prepared by a previously reported method.²¹³ In a typical synthesis, 0.16 g of cetyltrimethyl ammonium bromide (CTAB) is dissolved into a mixture solution containing 30 mL of DI water, 120 mL of ethanol and 1.5 mL of ammonia (28 wt%) at room temperature (RT). Under vigorous stirring, 0.1 g of functionalized CNTs (diameter~50 nm) is dispersed into the above mixture followed by ultrasonication for 40 min. Then 1 mL of tetraethyl orthosilicate (TEOS) is added into the mixture, which is further stirred at RT for 6 h. The obtained product is centrifuged and washed with ethanol and DI water before drying at 60 °C for 12 h. The dried product is ground mildly in a mortar for further use. For preparation of

CNT@SiO₂@CuSilicate, 10 mg of CNT@SiO₂ is dispersed in a blue-cap glass bottle containing 36 mL of DI water by ultrasonication for 40 min, followed by addition of 2 mL of ammonia under mild stirring. After 5 min, 1.2 mL of Cu(NO₃)₂ (0.1M) is added dropwise, and the mixture is stirred for another 5 min before the glass bottle is heated at 120 °C in an electric oven for 12 h. After cooling down naturally, the product is harvested by several rinse-centrifugation cycles and fully dried at 60 °C for 12 h for further use.

7.2.2. Synthesis of CNT@CuS

20 mg of CNT@SiO₂@CuSilicate is dispersed into 40 mL of DI water by ultrasonication for 40 min. After adding another 20 mg of Na₂S, the mixture is transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 140 °C for 12 h. The product is collected and washed with several rinse-centrifugation cycles and dried in vacuum at 60 °C for 24 h.

7.3. Results and discussion

7.3.1. Schematic illustration of synthetic strategy

The Figure 7.1 illustrates the procedure for the fabrication of CNT@CuS 1D hierarchical nanostructures. First, the functionalized CNTs are coated uniformly with a layer of mesoporous silica as shown by step I. Driven by the interfacial reaction between copper nitrate and the silica, the CuSilicate nanoneedles are grown readily around the silica surface to form the CNT@SiO₂@CuSilicate core-shell 1D

nanostucture (step II). Finally the CuSilicate nanoneedles are transformed into CuS nanoneedles by a chemical conversion route in the presence of sodium sulfide (Na_2S). Interestingly, the silica layer is etched simultaneously by OH^- ions released from the hydrolysis of sulfide ions (step III). In this sulfidation process, Na_2S not only serves as the sulfur source for the transformation of CuSilicate to CuS, but also grants the as-formed complex structures with structural integrity by providing a mild alkaline environment to remove the silica gradually. As a result of this facile chemical transformation, arrays of CuS ultrafine nanoneedles are generated as the subunits of the 1D hierarchical complex structures.

Figure 7.1. Schematic illustration of the formation of CuS nanoneedles array supported on the CNT backbone (CNT@CuS) by a template-engaged conversion route: (I) uniform coating of a silica layer on CNT; (II) growth of copper silicate nanoneedles on the silica layer; and (III) chemical conversion to CNT@CuS with the silica layer simultaneously eliminated.

7.3.2. Characterization of morphology and composition

After silica coating, the morphology of CNT@SiO_2 is examined by transmission electron microscopy (TEM). As shown in Figure 7.2a, the diameter of CNT@SiO_2 is

increased to 80 –100 nm. The uniform growth of needle-like CuSilicate onto the silica layer can be observed distinctly from the field emission scanning electron microscopy (FESEM) image shown in Figure 7.2b, where the CuSilicate appears as the “hairy” structure along the longitudinal axis of the CNTs. Figure 7.2c is a typical TEM image that shows the detailed structure of CNT@SiO₂@CuSilicate. It can be observed that the overall diameter of these worm-like structures is further increased to 270 – 300 nm and the length of the CuSilicate nanoneedles is about 100 - 150 nm. The crystallographic phase of CNT@SiO₂@CuSilicate is determined by X-ray powder diffraction (XRD) shown in Figure 7.2d. Although the diffraction intensity is quite weak, all the indexed peaks (marked by asterisks) except the (002-CNT) at about $2\theta = 26^\circ$ can be assigned to copper silicate (CuSiO₃·H₂O, JCPDS card no. 03-0219).²¹⁴

Figure 7.2. TEM images of CNT@SiO₂ (a) and CNT@SiO₂@CuSilicate (c); FESEM image (b) and XRD pattern (d) of the as-prepared CNT@ SiO₂@CuSilicate.

After the simple chemical conversion with Na_2S under hydrothermal conditions, hierarchical structures composed of ultrafine CuS nanoneedles are produced without losing the topology, as shown in Fig. 7.3a. A magnified FESEM image presented in Fig. 7.3b further reveals clearly that the nanoneedles are densely packed with their structures well retained compared to the $\text{CNT@SiO}_2\text{@CuSilicate}$ structure. As displayed in Fig. 7.3c, the dually walled structure of the as-prepared CNT@CuS is further elucidated by observing the CuS outer shell, the CNT wall and the void space in between. The naked wall of the CNT backbone is marked by the black arrow, while the white arrow indicates the as-formed CuS nanoneedles array. In addition, the dissolution of the intermediate silica layer results in some void space between the outer CuS shell and the inner CNT backbone.

Figure 7.3. FESEM (a, b) and TEM (c, d) images of the as-prepared CNT@CuS 1D hierarchical structures.

The high-resolution TEM image shown in Fig. 7.3d reveals the details of the CuS nanoneedles with an average length of around 100 – 150 nm and a diameter of 5 – 10 nm. As expected, the dimensions of these formed CuS nanoneedles are largely determined by that of the CuSilicate precursor nanoneedles, although they vary slightly sample by sample.

The complete phase conversion is confirmed by XRD analysis (Figure 7.4a), where all the identified peaks except the (002-CNT) peak can be ascribed to hexagonal CuS phase (JCPDS card No. 78-876).¹⁹⁸ The N₂ adsorption/desorption measurement (Figure 7.4b) shows that the as-prepared CNT@CuS hybrid nanocomposite exhibits a relatively large Brunauer–Emmett–Teller (BET) specific surface area of 98 m² g⁻¹ with mesoporous texture (Figure 7.4b inset).

Figure 7.4. XRD pattern (a) and N₂ adsorption-desorption isotherm (b) of CNT@CuS 1D hierarchical structures. The inset in (b) shows the corresponding pore size distribution obtained from the desorption branch.

7.3.3. Investigation of electrochemical performance

It has been suggested that hierarchical 1D nanostructures are promising in the application of electrochemical devices,²¹⁵⁻²¹⁷ because they possess low dimensional structures that will facilitate the charge transport.²¹⁸⁻²¹⁹ The as-prepared CNT@CuS hybrid structure is then evaluated as a supercapacitor electrode in view of their relatively large surface area and unique structural features. Figure 7.5a shows the cyclic voltammetry (CV) analysis at various scan rates in a potential range of 0 – 0.5

Figure 7.5. Electrochemical characterization of CNT@CuS hierarchical structures. (a) CV curves at different scan rates, and the corresponding specific capacitance (b), specific capacitance calculated from various charge-discharge current densities (c), and (d) cycling performance at a current density of 2.9 A g⁻¹. The inset in (d) shows the charge-discharge voltage profiles for the first 5 cycles at the same current density.

V (vs. SCE). This CV profile clearly reveals pseudo-capacitive characteristics different from the nearly rectangular CV shapes for conventional electric double-layer capacitor.¹¹ Based on the various scan rates of 2 – 50 mV s⁻¹, specific capacitance ranged from 114 to 97 F g⁻¹ can be delivered, as shown in Figure 7.5b. For the CNT@CuS electrode, the galvanostatic charge-discharge tests are also conducted at various charge-discharge current densities. It is found that a capacitance in the range of 122 – 89 F g⁻¹ can be obtained with the current density varied from 1.2 to 7.4 A g⁻¹ (Figure 7.5c).

In a supercapacitor, cycling stability is also a very important parameter. Therefore, galvanostatic charge-discharge measurements for 1000 cycles are further conducted at a constant current density of 2.9 A g⁻¹ with a potential window of 0 – 0.5 V (Figure 7.5d). Remarkably, the initial capacitance of 110 F g⁻¹ is nearly 100% retained after 1000 cycles, indicating excellent cycling stability of these CNT@CuS hybrid nanostructures. This good electrochemical performance with high capacitance and excellent cycling stability may be attributed to multiple factors. Specifically, the unique CNT-supported hierarchical nanostructure composed of 1D subunits is in favor of the electron transport, which might improve the conductivity of the electrode.^{88, 220} The porous hierarchical structure with relatively high specific surface area would have offered large contact area for the fast diffusion of electrolyte ions between the electrode active material and electrolyte.²²¹ In addition, the CNTs that serve as the supporting backbone for the CuS nanoneedles array will enhance the structural integrity and flexibility of this hybrid material. Lastly, it is worth mentioning that

nanostructures directly grown on CNTs generally do not show strong interaction with the CNT backbone. In the present work, an important difference is that the CuS nanoneedles are not grown directly on the CNT backbone. Instead they are chemically converted from CuSilicate nanoneedles which are grown from the conformal silica layer tightly coated on the CNTs backbone. Therefore, arrays of these CuS nanoneedles as a whole are strongly attached to the CNT backbone, thus leading to the good capacitance retention.²²²

7.4. Conclusions

In summary, we have developed a novel and efficient template-engaged conversion route to grow arrays of ultrafine CuS nanoneedles on the CNT backbone with hierarchical nanostructures. The CuS nanoneedles are facilely derived from CuSilicate nanoneedles under hydrothermal conditions. The as-formed CuS nanoneedles are around 100 – 150 nm in length and 5 – 10 nm in diameter. In virtue of the unique structural features, these CNT@CuS hybrid nanocomposites exhibit high capacitance with excellent cycling stability, which suggests their potential application in supercapacitors.

Chapter 8. CNTs Supported Ni₃S₂ Nanosheets Porous Composite Materials for Supercapacitors[†]

8.1. Introduction

It is of great significance to design low-dimensional hierarchical nanostructures because of their fascinating properties and promising applications in a wide range of fields.²²³⁻²²⁸ In particular, numerous works have attempted to construct one-dimensional nanocomposites by depositing functional inorganic nanomaterials on the carbon nanotubes (CNTs) backbone.²²⁹⁻²³³ However, the relatively weak interaction between the inorganic species and CNTs usually leads to the non-uniform deposition of the inorganic component on the outer surface of the CNTs backbone.^{211, 234-235} As a result, it is still highly desirable to design new strategies to construct well-defined hierarchical structures by growing low-dimensional nanostructures of functional materials on the CNTs backbone. In the last section, we have presented the growth of CuS nanoneedles using the silica coated CNTs as substrate as well as the supporting backbone, in this part, similar synthetic strategy will be applied to prepare CNTs supported nickel sulfide nanostructures for supercapacitors.

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Stated in the NiS work, nickel sulfides are a group of semiconductor materials with various compositions such as NiS, NiS₂, β -Ni₃S₂, Ni₆S₅, Ni₇S₆, and Ni₃S₄, which find many important applications as ceramic tougheners, hydrogenation catalysts and electrode materials.^{74-75, 221, 234, 236} Many recent efforts have been made to synthesize diverse nanostructures of nickel sulfides, including hollow spheres,⁷⁸ nanochains,²³⁷ nanowires,⁸⁰ nanorods,²³⁸ and layer-rolled structures²³⁹ for various applications. However, synthesis of heterostructures integrating nickel sulfides with other functional materials such as CNTs still requires further development for different applications. For example, Su and coworkers have used a chemical vapor deposition (CVD) method to synthesize iron/nickel sulfide filled CNTs as microwave absorbing materials.²⁴⁰ In another work, Du and coworkers have successfully functionalized multiwalled CNTs with Ni₃S₂, in which only Ni₃S₂ film and particles are observed on the CNTs with less satisfactory uniformity and distribution.²⁴¹

Following the strategy for preparation of CNTs supported CuS nanoneedles, herein we applied a similar conversion approach to grow Ni₃S₂ nanosheets on the CNT backbone to form CNT@Ni₃S₂ 1D hierarchical structures, which exhibit interesting properties for energy storage and hydrogen production. First, CNT@SiO₂ core-shell 1D structures are formed as the substrate for the uniform growth of NiSilicate nanosheets. Then the as-formed NiSilicate nanosheets are transformed into phase-pure Ni₃S₂ nanosheets by a chemical conversion, while perfectly retaining the nanosheet morphology. Interestingly, the intermediate silica layer is simultaneously dissolved during the sulfidation process, thus forming the CNT@Ni₃S₂ 1D hierarchical structure.

The as-prepared CNT@Ni₃S₂ 1D hierarchical structures are shown to exhibit improved performance as an electrode material, which show their promising use in supercapacitors.

8.2. Material synthesis

8.2.1. Synthesis of CNT@ SiO₂ and CNT@SiO₂@NiSilicate

The CNT@SiO₂ is prepared by a previously reported method.²¹³ In a typical synthesis, 0.16 g of cetyltrimethyl ammonium bromide (CTAB) is dissolved into a mixture solution containing 30 mL of DI water, 120 mL of ethanol and 1.5 mL of ammonia (28 wt%) at room temperature (RT). Under vigorous stirring, 0.1 g of acid treated functionalized CNTs (diameter~50 nm) is dispersed into the above mixture followed by ultrasonication for 40 min. Then 1 mL of tetraethyl orthosilicate (TEOS) is added into the mixture, which is further stirred at RT for 6 h. The obtained product is centrifuged and washed with ethanol and DI water before drying at 60 °C for 12 h. The dried product is ground mildly in a mortar for further use. For preparation of CNT@SiO₂@NiSilicate, 30 mg of CNT@SiO₂ is dispersed in a blue-cap glass bottle containing 40 mL of DI water by ultrasonication for 40 min, followed by addition of 1 g of urea under mild stirring. After 5 min, 1 mL of Ni(NO₃)₂ (0.1 M) is added dropwise, and the mixture is stirred for another 5 min before the glass bottle is heated at 105 °C in an electric oven for 12 h. After cooling down naturally, the product is harvested by several rinse-centrifugation cycles and fully dried at 60 °C for 12 h for further use. For comparison, nickel based precursor is also synthesized with Ni(NO₃)₂

(0.1 M) aqueous solution and urea but in the absence of CNT@SiO₂.

8.2.2. Synthesis of CNT@Ni₃S₂

10 mg of CNT@SiO₂@NiSilicate is dispersed into 40 mL of DI water/ethanol mixture (EtOH v%=25 %) by ultrasonication for 40 min. After adding another 40 mg of Na₂S, the mixture is transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 160 °C for 12 h. The product is collected and washed with several rinse-centrifugation cycles and dried in vacuum at 60 °C for 24 h. NiS nanosheets are also obtained by the same sulfidation process using the nickel based precursor. Control experiment is also performed to prepare CNT/NiS_x without the silica coating, where only CNTs, Na₂S are added into the Ni(NO₃)₂ reaction solution.

8.3. Results and discussion

8.3.1. Schematic illustration of synthetic strategy

Figure 8.1 is a scheme illustrating the procedure for the preparation of CNT@Ni₃S₂ 1D hierarchical structures. First, the functionalized CNTs are coated uniformly with a layer of mesoporous silica as shown by step I. Driven by the strong reaction between nickel ions and silica, NiSilicate nanosheets are grown readily around the silica surface to form the CNT@SiO₂@NiSilicate core-double shell 1D structure (step II). Finally the NiSilicate nanosheets are converted into Ni₃S₂ nanosheets by a chemical conversion route with sodium sulfide (Na₂S). Simultaneously, the intermediate silica layer is eliminated by OH⁻ ions released from the hydrolysis of sulfide ions (step III).

It is interesting to observe that the Na_2S additive plays a dual role in this sulfidation process. It acts as the sulfur source for the conversion of NiSilicate to Ni_3S_2 and at the same time it provides a mild alkaline environment in the hydrothermal system to etch the silica gradually, thus leading to the well retained 1D hierarchical Ni_3S_2 nanosheets with structural stability and integrity.

Figure 8.1 Schematic illustration of the formation of Ni_3S_2 ultrathin nanosheets supported on CNT backbone ($\text{CNT}@\text{Ni}_3\text{S}_2$) by a multi-step conversion route: (I) uniform coating of a silica layer on CNT; (II) in-situ formation of nickel silicate shell on the silica layer; and (III) chemical conversion of nickel silicate into Ni_3S_2 to form $\text{CNT}@\text{Ni}_3\text{S}_2$ with simultaneous elimination of the intermediate silica layer.

8.3.2. Characterization of morphology and composition

The morphology of $\text{CNT}@\text{SiO}_2$ after silica coating is examined by transmission electron microscopy (TEM). As shown in Figure 8.2a, the diameter of $\text{CNT}@\text{SiO}_2$ is increased to 90 –100 nm from about 50 nm (the diameter of CNTs). The uniform growth of NiSilicate around the silica layer can be observed distinctly from the field emission scanning electron microscopy (FESEM) image shown in Figure 8.2b, where

the NiSilicate grows as the shell structure along the longitudinal axis of the CNTs to form coaxial 1D nanocable-like structure. Figure 8.2c is a typical TEM image that shows the detailed structure of CNT@SiO₂@NiSilicate. It can be observed that the overall diameter of these worm-like structures is further increased to around 250 nm with ultrathin nanosheets grown on the surface. The crystallographic phase of CNT@SiO₂@NiSilicate is determined by X-ray powder diffraction (XRD) shown in Figure 8.2d. All the indexed peaks except the (002-CNT) at about $2\theta = 26^\circ$ can be assigned to the Ni₃Si₂O₅(OH)₄ phase.²⁴²

Figure 8.2 (a) TEM image of CNT@SiO₂. FESEM (b) and TEM (c) images, XRD pattern (d) of the as-prepared CNT@ SiO₂@NiSilicate.

After the simple chemical conversion with Na_2S under hydrothermal conditions, hierarchical structures composed of ultrathin Ni_3S_2 nanosheets are produced without losing the topology, as shown in Figure 8.3a. A magnified FESEM image shown in Figure 8.3b further reveals clearly that the nanosheets are densely packed with the structures well preserved compared to the $\text{CNT}@\text{SiO}_2@\text{NiSilicate}$ structure. A TEM image is displayed in Figure 8.3c, in which the CNT backbone densely covered by nanosheets can still be observed. A magnified TEM image shown in Figure 8.3d clearly reveals that this 1D hierarchical structure is composed of flexible ultrathin nanosheets, which might endow the structure with a high surface area. As expected, the dimensions of the as-formed Ni_3S_2 nanosheets are largely determined by that of the NiSilicate precursor nanosheets. In other words, the structure of Ni_3S_2 is inherited perfectly from the NiSilicate morphology.

Figure 8.3 FESEM (a, b) and TEM (c, d) images of the as-prepared $\text{CNT}@\text{Ni}_3\text{S}_2$ hybrid structure.

Figure 8.4 EDX spectrum of the as-prepared CNT@Ni₃S₂.

In addition, the complete dissolution of the intermediate silica layer can be confirmed by the energy dispersive X-ray spectroscopy (EDX) analysis, where the sample is supported on copper foil substrate (Figure 8.4). Furthermore, the complete phase transformation is confirmed by XRD analysis (Figure 8.5a), where all the identified peaks except the (002-CNT) peak can be ascribed to the rhombohedral

Figure 8.5 XRD pattern (a) and N₂ adsorption-desorption isotherm (b) of the as-prepared CNT@Ni₃S₂ hybrid nanocomposites. The inset in (b) shows the corresponding pore size distribution obtained from desorption isotherm.

Ni₃S₂ phase (JCPDS card No. 85-1802). The N₂ adsorption/desorption measurement (Figure 8.5b) shows that the as-prepared CNT@Ni₃S₂ 1D structure possesses a relatively large Brunauer–Emmett–Teller (BET) specific surface area of 64 m² g⁻¹ with mesoporous texture. The control experiment without silica coating shows that only mixture of CNTs and irregular nickel sulfide particles (Figure 8.6) are obtained, which evidences the merit of our multi-step strategy to firmly grow Ni₃S₂ nanosheets on the CNT backbone.

Figure 8.6 FESEM images of the nickel based precursor (a) and NiS nanosheets (b); XRD (c) and CV (d) results of these NiS nanosheets.

8.3.3. Investigation of electrochemical performance

Many previous reports have suggested that the hierarchical 1D structures are promising for applications in electrochemical devices and H₂ production,^{215, 243} because of their large surface area, and porous structure for enhanced kinetics.²¹⁹ The as-prepared CNT@Ni₃S₂ 1D hierarchical structure is first evaluated as an electrode material for supercapacitors. Figure 8.7a shows the cyclic voltammetry (CV) analysis at various scan rates in the potential range of -0.15 – 0.55 V (vs. SCE). These CV profiles clearly reveal pronounced pseudo-capacitive characteristics different from the nearly rectangular CV shapes for conventional electric double-layer capacitors.¹¹ Based on the various scan rates of 1 – 10 mV s⁻¹, specific capacitance ranged from 586 to 425 F g⁻¹ can be delivered, as shown in Figure 8.7b.

For the same CNT@Ni₃S₂ electrode, the galvanostatic constant-current charge-discharge tests are also conducted at various current densities (Figure 8.7c). It is found that a high specific capacitance of 514 F g⁻¹ can be delivered at a current density of 4 A g⁻¹, while a capacitance of 362 F g⁻¹ can still be retained at a very high current density of 13.3 A g⁻¹ (Figure 8.7d). The electrochemical performance of our nanostructured CNT@Ni₃S₂ composite is comparable to that of other reported CNT-based composite supercapacitive materials.²⁴⁴⁻²⁴⁶ For example, a recent work by Jiang et al. has demonstrated the fabrication of CNT/Ni hybrid nanostructured arrays using a CVD method, and a specific capacitance of 514 F g⁻¹ can be delivered at a high current density of 22.3 A g⁻¹.²⁴⁴

Figure 8.7 Electrochemical characterizations of the CNT@Ni₃S₂ hybrid structure. (a) CV curves at different scan rates, and (b) the corresponding specific capacitance. (c) Charge-discharge curves at different current densities, and (d) the corresponding specific capacitance calculated from the discharge curves at different current densities.

In order to evaluate the cycling stability of the electrode, galvanostatic charge-discharge measurements for 1500 cycles are further conducted at a current density of 5.3 A g⁻¹ with a potential window of -0.15 – 0.55 V. As shown in Figure 8.8, it is interesting to note that the initial capacitance of CNT@Ni₃S₂ (480 F g⁻¹) is about twice of that delivered by NiS nanosheets (243 F g⁻¹) prepared without the CNTs backbone (Figure 8.4). More importantly, nearly 88% of the initial capacitance is retained for the CNT@Ni₃S₂ sample (curve I) after 1500 cycles (424 F g⁻¹), compared

to only 65% retention (160 F g^{-1}) for NiS nanosheets (curve II). It is apparent that these CNT@Ni₃S₂ 1D hybrid nanostructures exhibit high capacitance with good cycling stability. The improved supercapacitive property of the CNT@Ni₃S₂ structure may be brought by the structural advantages. Specifically, the unique CNTs-supported hierarchical 1D structure with high surface area would improve the electrical conductivity and diffusion kinetics. Moreover, the ultrathin Ni₃S₂ nanosheets would allow for the improved cycle life with better flexibility by readily accommodating the charged ions.²⁴⁷⁻²⁴⁸ Furthermore, these Ni₃S₂ nanosheets as a whole are strongly attached onto the CNT backbone to form a core-shell structure with good stability and integrity, thus leading to the good electrochemical performance.

Figure 8.8 Cycling performance of the as-prepared CNT@Ni₃S₂ (I) and NiS nanosheets (II) at a current density of 5.3 A g^{-1} .

8.4. Conclusions

In summary, one-dimensional (1D) hierarchical structures composed of Ni_3S_2 nanosheets grown on CNTs backbone ($\text{CNT}@\text{Ni}_3\text{S}_2$) are synthesized by an efficient multi-step conversion route. In view of the unique architecture and intrinsic properties of NiS_x materials, the as-prepared $\text{CNT}@\text{Ni}_3\text{S}_2$ hybrid structure is evaluated as an electrode material for supercapacitors. Remarkably, this hybrid 1D hierarchical structure exhibits high capacitance with good cycling stability. These results demonstrate the promising use of properly designed hierarchical hybrid nanostructures in energy storage, and other areas.

Chapter 9. Conclusions and Outlook

9.1. Conclusions

This report mainly focuses on the development of transition metal oxide/sulfide based materials with different nanostructures for supercapacitive application. One to three dimensional cobalt based intermediates have been synthesized through varying experimental parameters such as precursor (cobalt acetate) concentrations and volume ratio of polyethylene glycol to water, and corresponding Co_3O_4 products without significant morphological alteration were subsequently obtained by annealing the as-prepared cobalt based intermediates. With relatively high specific surface areas of $86.1 - 121.5 \text{ m}^2 \text{ g}^{-1}$, these Co_3O_4 products with distinct nanostructures have exhibited high capacitance and good retentions when served as supercapacitive electrodes, and capacitance as high as 111 F g^{-1} can be acquired for the needle-like Co_3O_4 nanorods after 1000 charge-discharge cycles.

After that, we have investigated another series of promising electrode materials-nickel based materials. Uniform Ni-EG complex spheres with hierarchical nanostructures were successfully prepared via a facile solvothermal synthesis. Then NiO nanospheres with hierarchical structures and high surface area ($221.7 \text{ m}^2 \text{ g}^{-1}$) were obtained by calcining the as-prepared Ni-EG complex spheres. These hierarchical NiO nanospheres have presented improved capacitance at a high charge-discharge current density (28.2 A g^{-1}), and a high and stable capacitance of 225 F g^{-1} can be recovered after 1000 charge-discharge cycles at a current density of 5.6 A

g^{-1} , showing its good reversible capacitance and excellent cyclic capability.

We then prepared nickel sulfide (NiS) to investigate its supercapacitive properties. Uniform and well-defined silica@nickel silicate nanopsheres were synthesized initially in an alkaline hydrothermal condition. Afterwards, hierarchical NiS hollow spheres assembled from ultrathin nanosheets were achieved by reacting these silica@nickel silicate nanopsheres with Na_2S by a hydrothermal reaction. Herein the Na_2S not only served as sulfur agent for the sulfide conversion, but also provided a mild alkaline condition for the silica core removal, assuring the formation of hollow structure with good mechanical stability. The as-prepared NiS hollow spheres have demonstrated high capacitance of $583\text{-}927 \text{ F g}^{-1}$ at various current densities ranging from $4.08\text{-}10.2 \text{ A g}^{-1}$, and 70% of the capacitance can still be retained even after deep cycling from 1000 to 3000 cycle at a current density of 4.2 A g^{-1} .

In order to improve the electric conductivity of the electrode materials and the cycling stability of supercapacitors, carbon nanotubes are introduced as backbone structures to obtain CNTs based inorganic nanocomposites. Before that, silica is uniformly coated onto the CNTs to prepare CNT@SiO_2 1D structures, which are served as substrates for the growth of hierarchical metal silicate ($\text{CNT@SiO}_2\text{@M-Silicate}$, $\text{M}=\text{Cu, Ni}$). Then the M-Silicate shell structures are converted into M-Sulfide through a hydrothermal system with effect of sodium sulfide, simultaneously, the silica layer is removed, leading to CNTs supported metal sulfide hierarchical nanostructures. In this synthetic strategy, CNTs supported ultralong CuS nanoneedles and ultrathin Ni_3S_2 nanosheets have been successfully

prepared, respectively. The as-prepared nanocomposites are evaluated as electrode materials for supercapacitors, where high capacitances are delivered with good cycling stability.

9.2. Outlook

9.2.1. Synthesis of other metal sulfides (such as CoS_x and CuS_x) hollow structures for supercapacitors

Hollow structures are of great interest in the research community because of their large surface area, low density, and well-defined void interior space. Hence, we have successfully constructed NiS hollow nanospheres using silica nanocolloids as hard template in this project. By the similar protocol, the synthesis can be extended to prepare other hollow metal sulfide nanoparticles such as cobalt sulfide, cadmium sulfide, and copper sulfide. However, it should be noted that the hollow spheres are prone to collapse upon the deep cycling because of the delicate shell structures, which would lead to the fast decay of the capacitance.

Figure 9.2.1.1 SEM images of carbon coated silica nanocolloids ($\text{SiO}_2@\text{C}$).

Hence it is crucial to develop hollow spheres with good physical stability and

structural integrity. In order to prepare hollow structures with better physical robustness, carbon layer is coated onto the silica nanocolloids beforehand to form $\text{SiO}_2@\text{C}$ structure (Figure 9.2.1.1), followed by the deposition of various metal silicates. Finally, the formed metal silicates are transformed to metal sulfide in the presence of sodium sulfide, and the silica cores are removed simultaneously. Thus, the carbon supported hollow structures $\text{C}@\text{MS}_x$ ($\text{M}=\text{Co}, \text{Cu}$) would be formed. It is speculated that the as-formed $\text{C}@\text{MS}_x$ could exhibit enhanced electrochemical performance with better cycling capability.

Figure 9.2.1.2 SEM images of $\text{SiO}_2@\text{C}@\text{CoSilicate}$ (a) and $\text{C}@\text{CoS}_x$ (b); TEM of $\text{C}@\text{CoS}_x$ (c and d) product shown in b.

Our preliminary results of cobalt case shows that the cobalt species can be uniformly

deposited onto the surface of $\text{SiO}_2@\text{C}$ (Figure 9.2.1.2a), and the morphology can be well retained after the sulfidation process in hydrothermal solution effected by sodium sulfide (Figure 9.2.1.2b). Further optimizations will be conducted to remove the silica cores completely to obtain non-impurity $\text{C}@\text{CoS}_x$ hollow spheres.

Figure 9.2.1.3 $\text{SiO}_2@\text{C}@\text{CuSilicate}$ products prepared with different volume of ammonia aqueous solution: (a, b) 1 mL; (c, d) 2 mL; (e) 4 mL and (f) 8 mL.

Similar strategy has been applied to prepare carbon supported copper sulfide hollow spheres. For the first step, copper silicate precursors have been grown on the carbon

coated silica nanocolloids. Figure 9.2.1.3 shows the SEM images of copper silicate grown on the $\text{SiO}_2@\text{C}$ with different addition of ammonia aqueous solution. It can be observed that copper silicate nanoneedles can be grown uniformly onto the $\text{SiO}_2@\text{C}$ at lower concentrations of ammonia. The as-prepared $\text{SiO}_2@\text{C}@\text{CuSilicate}$ will be converted into carbon supported copper sulfide by hydrothermal process in the presence of sulfur source.

9.2.2. Fabrication of $\text{NiS}_x@\text{NiS}_x$ 1D hollow nanostructures for supercapacitors

As shown in this project, nickel sulfides are promising electrode materials for supercapacitors, which would find their importance in the electrochemistry. It has also been shown in our work that 1D nanostructures are good candidates for electrode active materials because of their good mechanical stability, good thermal property and shorter electronic transport lengths. Initially, nickel hydroxide nanorods will be used as template for the silica deposition to form $\text{Ni}(\text{OH})_x@\text{SiO}_2$ co-axial nanorods (Figure 9.2.2.1).

Figure 9.2.2.1 $\text{Ni}(\text{OH})_x@\text{SiO}_2$ template used for NiSilicate deposition

After that, the as-formed $\text{Ni}(\text{OH})_x @ \text{SiO}_2$ co-axial nanorods are employed as the substrate for the growth of nickel silicate in the hydrothermal system in the presence of urea (Figure 9.2.2.2). The optimized sample of $\text{Ni}(\text{OH})_x @ \text{SiO}_2 @ \text{NiSilicate}$ will be converted into $\text{NiS}_x @ \text{NiS}_x$ rod-in-tube structures by removal of the silica layer.

Figure 9.2.2.2 $\text{Ni}(\text{OH})_x @ \text{SiO}_2 @ \text{NiSilicate}$ products prepared with addition of different volume of $\text{Ni}(\text{NO}_3)_2$ aqueous solution: (a) 0.4 mL; (b) 0.8 mL; (c) 1.2 mL and (d) 1.6 mL.

Publications

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