Hierarchical metal-oxide nanostructures for high-performance supercapacitor electrodes

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2013

Guan, C. (2013). Hierarchical metal-oxide nanostructures for high-performance supercapacitor electrodes. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/54763>

<https://doi.org/10.32657/10356/54763>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**HIERARCHICAL METAL-OXIDE NANOSTRUCTURES
FOR HIGH-PERFORMANCE SUPERCAPACITOR
ELECTRODES**

GUAN CAO

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2013

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ELECTRODES**

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A thesis submitted to the Nanyang Technological University

in fulfillment of the requirement for the degree of

Doctor of Philosophy

2013

Acknowledgements

At this stage, I am very grateful for what I have loosed and achieved in the last three years, which, to someone may be negligible or even miserable, but to me is constructive and fruitful. It not reasonable to image that I could be here when I first came to Singapore as an innocent big boy, so what I want to say most here is THANKS, to all the people and things I met in these years.

First and foremost, I would like to express my sincere appreciation and deepest respect to my supervisor Prof. Fan Hongjin and co-supervisor Prof. Zhang Hua for their meaningful guidance, creative educational way and firmly support to me throughout my Ph.D. years --not only on my research project, but even on my own personal problems. From them I could not only learn a lot on science, how to find problems and to solve them, how to try new things from fails, but also I could understand more deeply on life, life is just like experiments, or experiments are just like life.

I also thank my colleagues, Dr. Liu Jinping, Dr. Chen Chuanwei, Dr. Li Hongxin, Dr. Zhou Weiwei, Dr. Xia Xinhui, Dr. Zeng Zhiyuan, Dr. Cao Xiehong, Dr. Zhu Yong, Dr. Pan Guoxiang, Mr. Li Xianglin, Mr. Luo Jingshan, Mr. Jiang Jian, etc. for their useful guidance, fruitful collaborations and helpful suggestions for my experiments and life. I feel so honored and pleased to work and live with them.

I also thank all the students in 2010 batch of PAP, Mr. Chen Renjie, Miss Zhao Yanyuan, Mr. Wu Bo, Miss Dai Xing, Mr. Wang Zilong, Miss Li Fenfang, Miss Malin, Mr. Shen Xiaonan, Mr. Lin Weinan, I really appreciate to be in this big family.

Last, but by no means the least, I thank my family for their love and understanding. Without them I would forget myself and lose my own. I will keep going.

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Summary

With the blooming development of nanoscience and nanotechnology, and the urgent requirement for high performance energy storage devices, huge efforts have been devoted for developing high quality supercapacitor electrodes. Metal oxides with high energy density are regarded as a good candidate for energy storage, and rational construction of materials with different functions into a proper integrated system represents a promising way to create next generation electrodes materials. In this thesis, we took advantage of several proper methods and then designed and constructed several metal oxide based hierarchical nanostructures, which showed great potential for electrochemical energy storage devices.

1 D nanowires and 2D nanowalls have received great research concern, because of their uniform structure with high surface/volume ration, especially if they have porous features. In this thesis, we have designed two hierarchical structures based on CoO and Ni(OH)₂ nanomaterials, both of which are synthesised with easy and controllable methods, and have demonstrated the merits of the hierarchical structure design with good electrochemical properties. The first demonstration is a hybrid nanostructure of porous cobalt monoxide nanowire @ ultrathin nickel hydroxidenitrate nanoflake, the hierarchical core-shell nanostructure demonstrates a specific capacitance of ~798.3 F g⁻¹ and excellent rate performance in electrochemical test. And the cycling ability of the structure is also good, with less than 5% of capacitance loss after 2000 charge–discharge cycles. The second demonstration is a

hierarchical nanostructure with highly porous CoO nanowalls decorated with nickel hydroxide. The compound oxide nanostructures are found to substantially boost up the areal capacitance up to 11.49 F cm^{-2} , which is, to the best of our knowledge, the highest value reported on metal oxides /hydroxides. Besides, the active material's size and morphology can be easily controlled. In all, the fabrication technique is indeed simple and scalable, and the unprecedented high capacitance, thus the “porous and layered” electrode structure will find promising applications in electrochemical charge storage.

Atomic layer deposition (ALD) has been widely developed for energy and environmental applications. In the thesis, we have designed and constructed two novel structures with the assistance of ALD. The first example is a hollowed core-shell nanostructure with a nanogap, as demonstrated by CoO nanorods/NiO nanowalls which served as core and a TiO_2 nanotube shell with a thin gap between them. Both “wire in tube” and “wall in box” structures have shown evident differences between the solid core-shell nanostructure and the bare core when they are tested as supercapacitor electrodes. The enhancement is ascribed to the conformal hollow design which provides enlarged specific surface areas and shorter ion transport path. It is prospected that such positive nanogap effect may also exist in other electrochemical cell electrodes such as lithium ion batteries and fuel cells. The second demonstration is a new method for the generation of carbon nanoflakes on various metal oxide nanostructures by combining ALD and glucose carbonization. With the

method, different metal oxide@nanoflake carbon (MO@*f*-C) core-shell nanostructures are obtained. When tested as electrochemical supercapacitor electrode, the hierarchical MO@*f*-C nanostructure exhibit better performance compared with the pristine metal oxides or the carbon coating without ALD. The enhancement is largely due to the increased specific surface areas and electric conductivity. This peculiar carbon coating method with the unique hierarchical nanostructure may provide a new insight into the preparation of ‘oxides + carbon’ hybrid electrode materials for energy storage applications.

In all, the rational designed hierarchical nanostructures plus the newly ALD method provided several demonstrations for the fabrication of novel and high-performance metal oxide based supercapacitor electrodes. The controlled fabrication and functional combination of different materials on the nanoscale represents a promising way for advanced materials for supercapacitor application in the future.

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Chapter 1

Introduction and Literature Survey

1.1 Introduction to supercapacitors

Energy crisis along with the rapid depletion of fossil fuels, increasing energy consumption and environmental pollution have aroused great demands for effectively production of sustainable and renewable energy. Recent years have witnessed worldwide efforts to produce new and clean energy from Sun and wind. Then additional efforts are urgently needed to develop new and advanced energy storage devices for effectively using and storing the clean energy.^{1, 2}

Up to now, electrochemical energy storage is the promising and most widely used technologies among the various alternative energy storage processes, in terms of their unique advantages such as high efficiency, versatility, and flexibility. Generally, electrochemical energy storage devices store energy (in the format of electricity) in electrochemical processes by charge and discharge electron and ions (such as Li^+ , Na^+ , K^+ , H^+ , OH^- , etc.). A typical electrochemical energy storage device has the following three indispensable components: an anode, a cathode, and an electrolyte. Detailed charge-discharge process, i.e. energy storage-release of an electrochemical energy storage device, is as follows. During discharge, ions desorb/extract at one electrode and transfer to the other one, with generated electron flows pass through an external circuit; reversibly, during charge, under an external potential across the electrodes,

reversed electrochemical reactions (ions adsorption/insertion) occur at the electrodes, resulting in the polarization of the electrochemical device.

Supercapacitors, also named as electrochemical capacitors or ultracapacitors, are one of the most promising electrochemical energy storage devices, because of their high power density, long lifecycle and high-safety. In addition, supercapacitors can effectively bridge the energy/power gap between commercial batteries (which have high energy density) and traditional dielectric capacitors (which have high power density). Owing to these merits, supercapacitors have attracted significant research attention in recent years.

1.1.1 History of Supercapacitors

A brief look of advanced capacitors in the history of 1745-2004 can be found in Figure 1.1. Electrostatic capacitors were widely used as energy storage device before 1960s. Supercapacitors were firstly reported since 1960s by H.I. Becker of General Electric (U.S. Patent 2,800,616), and then commercially introduced by Nippon Electric Company (NEC) and Panasonic in 1980s. At that stage, those supercapacitors were used primarily as uninterruptible back-up power devices to support and replace the unreliable coin cell batteries. And the major differences between the Panasonic and NEC products were the electrolyte: NEC used an aqueous electrolyte, while Panasonic used a nonaqueous electrolyte in the cell construction thus obtained higher working window.

Since 1980s, many big manufactures such as ELIT, ELNA, MAXWELL, ESMA, CAP-XX, NIPPON CHEMI-CON, and NESSCAP have developed different supercapacitor manufacturing technologies with improvements in power density, energy density, safety, cost and manufacturing techniques. For example, in 1989, ELIT produced the first asymmetric supercapacitor, which is composed with a nickel oxyhydroxide (positive electrode) and an activated carbon (negative electrode), and potassium hydroxide is used as the electrolyte. The powerful devices were successfully utilized for power wheelchairs and children's cars. Another example is, in 1993 ESMA developed supercapacitors ranging from small 20 kJ, 14 volt cells up to large 30 MJ, 190 volt systems used for buses and trucks. The ESMA cells are also able to offer high power density with long cycling life.

Within these decades' development, supercapacitors have been widely utilised in portable electronics, power generation systems, industrial power sources, electric vehicles (EVs) and hybrid electric vehicles (HEVs). Today, the functionalities of supercapacitors in these areas include power storage/supplying, energy backup and safety maintenance. A good example is reported in 2008 that the Airbus A380 has assembled supercapacitors in its emergency doors and slide management system.³

Figure 1. 1 Development history of advanced capacitors.⁴

1.1.2 Ragone plot

Generally, supercapacitors possess high power density, highly reaction reversibility, low equivalent series resistance (ESR) and long life cycle when compared with batteries. Direct comparison between batteries and supercapacitors is shown in Table 1.1. In addition, from the Ragone plot in Figure 1.2 (power density VS energy density), we can clearly see that supercapacitors exhibit much higher energy density than conventional capacitors and much higher power density than batteries. Thus supercapacitors can effectively shorten the gap between conventional capacitors and batteries.

Parameters	Supercapacitor	Battery
Charge Time	1–30 s	0.3–3 h
Discharge Time	1–30 s	1–5 h
Energy Density (Wh kg ⁻¹)	1–10	20–100
Power Density (W kg ⁻¹)	1000–2000	50–200
Cycle Life	>100 000	500–2000
Charge/Discharge Efficiency	0.90–0.95	0.7–0.85

Table 1.1 A comparison of supercapacitors and battery⁴.

Figure 1.2 A Ragone plot: the energy density VS. the power density for different energy storage devices. (From: <http://www.mpoweruk.com/performance.htm>)

1.1.3 Two types of Supercapacitors

Based on the charge storage mechanism, supercapacitors can be divided into two types: electric double-layer capacitors (EDLCs) and pseudocapacitors.

EDLCs store electrical energy only by physical adsorption/desorption of ions from an electrolyte onto two porous electrodes. In this way, an electric double layer is formed at an electrode/electrolyte interface. An electric double layer (typically has a thickness of 1 nm) is composed of a space charge layer in an electrode, a compact Helmholtz layer, and a diffusive layer in an electrolyte.

Pseudocapacitors store energy by using electrochemically active electrode material, which directly store charges with electrochemical reactions during the charging and discharging processes. So pseudocapacitors are different from EDLCs, which have no electrochemical reaction on the electrode material during charge/discharge.

1.1.3.1 Electric double-layer capacitors (EDLCs).

As defined, EDLCs only involve physical adsorption of ions but without any chemical reactions during charge/discharge process, thus the capacitance of the EDLCs is solely associated with the electrostatic accumulation of charges at the electrode/electrolyte interface. The surface charges can be generated from surface dissociation, ion adsorption from both the electrolyte and surface defects. In an EDLC, charges are accumulated on the electrode surfaces, with electrolyte ions with counterbalancing charge on the electrolyte side to meet electroneutrality, as shown in Figure 1.3a.

Figure 1. 3 The working principle of supercapacitors. (a) Electric double layer, (b) redox reaction on surface.⁵

During charge process, the electrons move from the negative electrode to the positive electrode by an external potential. Within the electrolyte, cations (such as Li^+ , Na^+ , K^+ , H^+ , etc.) travel towards the negative electrode and anions (such as OH^- , Cl^- , etc.) travel towards the positive electrode. During discharge, the processes work reversely. In the charge/discharge process, no electrochemical reaction is produced. In this way, energy is stored in the double-layer interface.

Since the electric energy is stored in charges that are aggregated at the surface of electrode materials, the capacitance of an EDLC is proportional to the electrode surface area. And the electrode materials essentially have a large pore volume and high surface area. The specific capacitance, C (F g^{-1}), of a capacitor is given by:

$$C = \varepsilon_0 \varepsilon_r \frac{S}{D} \quad (1.1)$$

where ε_0 is the electric constant ($8.854 \times 10^{-12} \text{ F m}^{-1}$), ε_r is the relative dielectric constant of the interface, S is the specific surface area of the electrodes ($\text{m}^2 \text{ g}^{-1}$), and $D(\text{m})$ is the effective thickness of the electrical double layer.

The electrode materials for EDLCs are usually carbonaceous materials, such as graphite, active carbon, carbon nanotubes (CNTs) and graphene. In order to have higher capacitance, the EDLCs should have large surface area, so many research efforts have been carried out to fabricate carbon-based materials with high surface area and proper pore size distribution. Detailed discussion of the EDLCs electrode materials will be in the later part.

1.1.3.2 Pseudocapacitors (Faradaic supercapacitors)

Another type of supercapacitors is pseudocapacitors (faradaic supercapacitors), which are based on reversible faradaic reactions (redox reactions) on the electrode materials to store energy. The main feature that made pseudocapacitors different from EDLCs is that, during charge/discharge chemical reactions take place on the electrode and charges pass through the double layer between electrode/electrolyte. Thus the process in pseudocapacitors is similar to the charge/discharge process in batteries.

Because the electrochemical processes of the pseudocapacitors occur both on the surface and in the bulk near the surface of the electrode, and much electrochemical reaction is involved, a pseudocapacitor usually exhibits much larger capacitance value and energy density than an EDLC (Figure 1.3b). However, compared with an EDLC, a pseudocapacitor usually suffers from relatively lower power density and cycling stability due to the limited active surface area and relatively slow redox reactions. Electrode materials involves redox reactions can be divided into conducting polymers (such as polypyrrole and polyaniline) and metal oxides/hydroxides (such as RuO_2 ,

MnO_2 , Co_3O_4 , and $\text{Ni}(\text{OH})_2$). Generally, the electrode materials should have large surface area, appropriate pore-size distribution, and high electrochemical conductivity. Detailed discussion of the electrode materials for pseudocapacitors will be in the later part.

1.1.4 Component of Supercapacitors

As shown in Figure 1.4, a supercapacitor consists of two electrodes, an electrolyte, and a separator that electrically isolates the two electrodes.

Figure 1. 4. Component of a supercapacitor.

Some key parameters that determine the performance of a supercapacitor are discussed as follows.

When a supercapacitor is charged with a voltage (V) through the two electrodes and obtains a capacitance (C), the energy (E) and power densities (P) of the supercapacitor can be expressed as follows:

$$E = \frac{1}{2} CV^2 = \frac{QV}{2} \quad (1.2)$$

$$P = \frac{1}{4R_s} V^2 \quad (1.3)$$

where Q is the charges stored in the supercapacitor and R_s is the equivalent inner resistance of the supercapacitor.

From the above two equations, the performance of a supercapacitor is mainly determined by its working potential window, capacitance and equivalent inner resistance. In order to have high energy density, efforts should be made to increase the values of both working potential window and capacitance. And to obtain high power density, besides a large working window, a small equivalent inner resistance is also required.

In a supercapacitor, the value of the working potential window is related to the electrode material and electrolyte. A typical example is that the working window of carbonaceous materials in aqueous electrolyte is about 1 V, and in organic electrolytes it can be in the range of 2.5–3.5 V. Besides the intrinsic nature of electrode material and electrolyte, optimized electrode structures can also help to obtain high working window.

Another key parameter influencing the performance of a supercapacitor is equivalent inner resistance, which is composed with resistance for ion diffusion in electrolyte, resistance for charge transfer at electrode/electrolyte interface, and bulk resistance of the electrochemical system.

In the last, increasing the capacitance of electrode material is also an important way to achieve high performance supercapacitor. And in fact, developing advanced electrode materials is the key approach to improve the electrochemical properties of supercapacitors.

All in all, the electrochemical performance of supercapacitors mainly depends on property of the electrode materials and electrolyte.

1.1.4.1 Electrode materials

As discussed above, the electrochemical performance of supercapacitors is highly related to the property of the electrode materials. Therefore, developing advanced electrode materials with high capacitance and improved electrochemical performance is the most important strategy to achieve better supercapacitors.

In general, the electrode materials of supercapacitors can be categorized into three types: (1) carbon materials with high specific surface area, (2) conducting polymers, and (3) metal oxides/hydroxides, such as RuO_2 , MnO_2 , Co_3O_4 , and Ni(OH)_2 .

Carbon materials based electrodes store energy mainly by using EDLC mechanism, thus high surface area and rational porous structures is highly required for carbonaceous materials. Considerable efforts have been carried out to fabricate carbon electrodes with high specific surface area, suitable pore size distribution, and moderate surface modification to optimize the overall supercapacitor performance.

While the other two types of materials store charges not only in the double layer, but also using fast and reversible surface redox reactions (faradaic reactions). The electrochemical conductivity, reaction reversibility and stability of these materials are essential for the supercapacitor performance. Therefore, developing electrode materials with proper structures and better properties plays an important role for the improvement of pseudocapacitors.

All in all, electrode materials are the most important component of a supercapacitor, and detailed discussion of the materials will be in the later part.

1.1.4.2 Electrolyte

As shown in Figure 1.4, the electrolyte fills in the separator and the electrode materials, serving as another important supercapacitor component. From the discussion above, the electrolyte influence the working potential window, equivalent inner resistance thus determining the performance (power density and energy density) of supercapacitor. Generally speaking, a proper electrolyte in supercapacitors should have the following merits: wide cell voltage window, high electrochemical stability, low resistivity, and low toxicity as well as low cost.

Three types of electrolyte can be used for supercapacitors: (1) aqueous electrolyte, (2) organic electrolyte, and (3) ionic liquids (ILs).⁶

1.1.4.2.1 Aqueous electrolyte.

Generally speaking, aqueous electrolytes (such as Na_2SO_4 , NaOH , H_2SO_4 and NH_4Cl aqueous solution) can provide higher ionic concentration and lower electrochemical resistance, when compared with organic electrolytes. In this way, the capacitance and power density obtained by adopting aqueous electrolyte can be higher than those by using organic electrolyte. Another advantage of aqueous electrolytes is that the preparation and utilization processes and conditions of aqueous electrolytes is easier to control, while organic electrolyte require strict preparation and control conditions to be ultra-pure for usage. However, the working potential window of aqueous electrolytes is very small (~ 1.2 V), which is much lower than those of organic electrolytes (2.5-3.5 V). As been discussed previously, the working window plays an important role in determining both energy and power densities of supercapacitors, so the disadvantage of using aqueous electrolyte is obvious.

1.1.4.2.2 Organic electrolyte.

As discussed, organic electrolytes can hold a working voltage window up to 3.5 V, which is much higher when compared with aqueous electrolytes. This is a primary advantage of organic electrolytes.

Two typical organic solvents that are widely used for supercapacitor electrolytes are acetonitrile and propylene carbonate (PC). Acetonitrile can be used for dissolving

large quantity of salt for supercapacitor application. However, its environmental toxicity prohibits it from extensive commercialization. PC solvents can not only provide a large working window with good conductivity, but also is environmental friendly. Organic salts usually used in electrolytes are $R_4N^+, Li^+, Me_4N^+, Et_4N^+, Bu_4N^+, Me_3EtN^+$ (used as cations) and $ClO_4^-, BF_4^-, PF_6^-, AsF_6^-$ (used as anions).

Although organic electrolyte are electrochemical stable and can provide a wide working potential window with high energy and power densities, its shortcoming are also significant. The electrochemical resistance of organic electrolyte is high and the preparation/usage condition of the organic electrolyte should be strictly prevented from water.

1.1.4.2.3 Ionic liquids (ILs)

An ionic liquid (IL) is a salt in the liquid state, or molten salts which have melting point below some arbitrary temperature, such as 100 °C (212 °F), which means the ILs can exist in liquid form at the desired temperature.⁶ In addition, ILs have many other advantages, such as low vapour pressure, high thermal and chemical stability, low flammability, and wide electrochemical stable working potential window (2-6 V, typically ~ 4.5 V), which is promising for supercapacitor electrolytes. Besides, the conductivity of ILs is relatively high, and the ion size of the ILs can be well adjusted as no solvation shell exists in ILs. Several supercapacitor devices have been reported by using ILs with different salts. For instance, aliphatic quaternary ammonium and pyrrolidinium salts can have a wide working potential window which

exceeds 5 V, and 1-ethyl-3- methylimidazolium-based ILs can achieve a high conductivity at room temperature.⁶ To construct ILs with both wide working potential window and high conductivity in a wide temperature range for application remains a challenge.⁷

1.1.5 Advantages and challenges of Supercapacitors.

1.1.5.1 Advantages of Supercapacitors.

Batteries and supercapacitors are two typical and most widely used electrochemical energy storage devices. Compared to batteries, supercapacitors have the following advantages:

(1) High power density.

From the Ragone plot in Figure 1.2, which compares power versus energy of different storage devices, supercapacitors present a much higher power delivery (1–10 kW kg⁻¹) than lithium ion batteries (~150Wkg⁻¹). The power density is revealed by charge/discharge time. As an example, a supercapacitor can be fastly charged within seconds (60 s), while to charge a batteries, several hours is usually needed. This is because supercapacitors store charges both at the electrode surface and in the bulk near the solid electrode interface, so the electrochemical reaction will not be limited by conductivity of the bulk electrode. In this way, the charging and discharging reactions of supercapacitors will be much faster than the reactions inside batteries, thus lead to high power density in supercapacitors.

(2) Long cycling life.

Generally, the electrochemical reactions at supercapacitors electrodes are reversible, rather than those in batteries, which usually lead to irreversible interconversion of the electrode materials and irreversible phase changes. In this way, supercapacitors can achieve long-time cycling ability (little electrochemical properties change even after many charge–discharge cycles of up to 1 000 000). Although pseudocapacitors also using fast redox reactions, their cycling stability is still much better than that of batteries.

(3) High efficiency.

The efficiency of supercapacitors can be as high as ~95% after long-time cycling and the energy loss to heat is negligible.

(4) Wide temperature range for operation.

Supercapacitors can be used effectively in extremely environment with high/low temperatures. This makes supercapacitors suitable for military and aerospace applications with reliable energy for electronic devices usage. And the typical temperature range for supercapacitors is -40 to 70°C.

(5) Environmental friendly.

The components of supercapacitors are generally nontoxic with no environmental hazardous, while some components of batteries can be dangerous when they become wasted.

(6) Safety.

Supercapacitors are safer than batteries in normal usage. For example, lithium-ion batteries may lead to combustion under shortcut or high temperature (e.g. can be caused by overcharge) conditions.⁸

In summary, supercapacitors show many advantages over batteries in terms of power density, long-time cycling ability, efficiency, operating temperature, environmental friendly, and safety.

1.1.5.2 Challenges for Supercapacitors.

Although supercapacitors show many merits which are better than those of batteries, some challenges still exist for present supercapacitor technology. For instance, the energy density of supercapacitors is low and the cost for supercapacitors is high, which block the wider commercialization of supercapacitors.

(1) Low energy density.

From Figure 1.2, supercapacitors have lower energy density ($\sim 5 \text{ Wh kg}^{-1}$) than those of batteries ($>50 \text{ Wh kg}^{-1}$), yet current commercialized supercapacitors only can achieve energy densities of $\sim 3\text{--}4 \text{ Wh kg}^{-1}$. Low energy density means a larger-scale supercapacitor device is required for application, which not only need huge space (or huge mass for use), but also cost much. Low energy density is the major barrier for the commercialization of supercapacitors in present stage.

(2) High cost.

To realize wide commercialization of supercapacitors, the costs of materials and manufacturing processes should also be carefully considered. For electrode materials, carbon materials with high surface areas are generally expensive (US\$50–100 per kg)⁹, not to mention the cost of metal oxide (such as RuO₂). The electrolyte may also cost much especially when organic ones are adopted for supercapacitors. Currently the cost for supercapacitors (US\$10–20 Wh⁻¹ and US\$25–50 kW⁻¹) is much higher than those (US\$1–2 Wh⁻¹ and US\$75–150 kW⁻¹) for batteries.⁴ Thus to reduce the cost of supercapacitors is also an urgent challenge.

1.2 Supercapacitor Electrode Materials

As mentioned previously, electrode materials act as the most important role in supercapacitors and the materials for electrodes are divided into three parts: carbonaceous materials, which usually using EDLC mechanism; conducting polymers and metal oxides/hydroxides, which store energy based on Faradic reactions.

1.2.1 Carbonaceous Materials

Generally, carbon materials can provide high surface area with interconnected pores, high electrical conductivity and good electrochemical stability. In addition, carbon materials are abundant in nature and lower cost. All the above merits make carbon materials promising for energy storage. The most common used carbon materials include activated carbon, carbon nanotubes (CNTs), graphene, templated porous carbons, carbon aerogels, and carbon nanofibres.

1.2.1.1 Activated carbon

Activated carbons are usually generated by physical (thermal treatment) and/or chemical activation of different carbonaceous materials (e.g. coal, graphite, nutshell.). Physical activation of carbon materials is usually carried out by heating the carbon precursors at a high temperature (from 700 to 1200 °C) with oxidizing gases such as CO₂ and air. Chemical activation is to treat carbon precursors with activating agents (such as potassium hydroxide and phosphoric acid) at lower temperatures (from 400 to 700 °C).

The electrochemical properties of activated carbons are mainly determined by the porous structure and the surface functionalities on the carbon materials. The most favoured pore structures should have a proper pore size distribution with most pore sizes matches the size of the electrolyte. That means the pores in the activated carbon should not be so big to reduce the surface area, either so small to ineffectively accumulate charges on the surface. The surface functionalities of activated carbon will influence its wettability with the electrolyte ions and possibly contribute additional pseudo-capacitance. In general, the capacitance of activated carbons is in the range from 100 F g⁻¹ to 300 F g⁻¹ when aqueous electrolytes are used.

1.2.1.2 Carbon nanotubes (CNTs)

CNTs have attracted a plenty of research attentions for supercapacitor electrode applications since its discovery, because of their excellent electrical conductivity, pore structure, good mechanical and thermal stability. CNTs can be categorized into three types based on their wall numbers: single-walled nanotubes (SWNTs) with a single

graphite sheet seamlessly wrapped into a cylindrical tube; double-walled nanotubes (DWNTs) and multiwalled nanotubes (MWNTs) which consist of two or more such nanotubes. Research efforts have found that CNTs can reveal high power density for supercapacitor application. For example, a MWNTs-based supercapacitor with a power density of 8 kW kg^{-1} has been reported, where the CNTs can obtain a high specific capacitance of 102 F g^{-1} with a surface area of $430 \text{ m}^2 \text{ g}^{-1}$.¹⁰ However, the limited surface area of CNTs, together with a high cost for the production of purified CNTs still restricts CNTs for application as the practical high performance supercapacitor electrodes.

1.2.1.3 Graphene

Graphene is a novel 2D one-atom-thick sheet of honeycomb carbon lattice. Due to the unique single atomic layer crystal structure, graphene has a high theoretical specific surface area of $2620 \text{ m}^2 \text{ g}^{-1}$. In addition, graphene also exhibits excellent electrical conductivity, flexibility, and wide electrochemical window. A detailed comparison of graphene and other carbon materials are listed as follows (Table 1.2). From which we can see graphene is promising for high performance supercapacitors electrodes.

For supercapacitor application, graphene is usually produced by (1) the historical method of thermal decomposition of graphite oxide and the following reduction of graphene oxide to graphene¹¹, (2) CVD growth by adopting a metal catalyst¹² and (3) electrochemical exfoliation of graphite.¹³ Graphene is a promising supercapacitor

material, and it shows specific capacitances of 135 in aqueous electrolyte and 99 F g⁻¹ in organic electrolyte, respectively.¹⁴ In addition, the graphene material illustrates very good rate capability with its excellent conductivity. In supercapacitor application, graphene is also combined with other materials to obtain even better performance. This point will be discussed later.

Carbon allotropes	Graphite	Diamond	Fullerene (C ₆₀)	Carbon nanotube	Graphene
Hybridized form	sp ²	sp ³	Mainly sp ²	Mainly sp ²	sp ²
Crystal system	Hexagonal	Octahedral	Tetragonal	Icosahedral	Hexagonal
Dimension	Three	Three	Zero	One	Two
Experimental specific surface area (m ² g ⁻¹)	~10-20	20-160	80-90	~1300	~1500
Density (g cm ⁻³)	2.09-2.23	3.5-3.53	1.72	> 1	> 1
Optical properties	Uniaxial	Isotropic	Non-linear optical response	Structure-dependent properties	97.7% of optical transmittance
Thermal conductivity (W m ⁻¹ K ⁻¹)	1500-2000 ^a , 5-10 ^c	900-2320	0.4	3500	4840-5300
Hardness	High	Ultrahigh	High	High	Highest (single layer)
Tenacity	Flexible non-elastic	-	Elastic	Flexible elastic	Flexible elastic
Electronic properties	Electrical conductor	Insulator, semi-conductor	Insulator	Metallic and semiconducting	Semimetal, zero-gap semiconductor
Electrical conductivity (S cm ⁻¹)	Anisotropic, 2-3 × 10 ^{4a} , 6 ^b	-	10 ⁻¹⁰	Structure-dependent	2000

^aa-direction.
^bc-direction.

Table 1. 2 The comparison of properties of graphene and the carbon materials.¹⁵

1.2.2 Conducting Polymers

Both conducting polymers and metal oxides store energy by redox reaction of the material, therefore their energy densities are higher than those of carbonaceous materials. Compared with the relatively expensive metal oxides, conducting polymers are generally low cost. A conducting polymer supercapacitor can achieve double the energy density (10 Wh kg⁻¹) than carbonaceous based ones with a slightly lower power density. However, swelling and shrinking of conducting polymers during the intercalating/deintercalating process will lead to mechanical degradation of the

conducting polymer materials, thus the cycling stability of conducting polymers is not as good as that of carbonaceous materials and metal oxides. In supercapacitors application, the major used conducting polymer materials are polypyrrole, polyaniline, polythiophene and derivatives of polythiophene.

Polyaniline has been extensively studied as supercapacitor electrode material, due to its high electroactivity, excellent stability, and high specific capacitance (typically 400–500 F g⁻¹ in an acidic electrolyte). The structure of polyaniline is shown in Figure 7a.

polyaniline

polypyrrole

Figure 1. 5 Structure of polyaniline and polypyrrole.

Polypyrrole (structure showing in Figure 1.5) has a high capacitance per unit volume (400–500 F cm⁻³), but its disadvantage is also obvious. The dense growth nature of polypyrrole will prevent the dopant ions accessing to the interior material, thus reducing the capacitance. The capacitance loss is more significant especially when very thick coating of polypyrrole is carried out.¹⁶

1.2.3 Metal Oxides/Hydroxides

Transition metal oxides/hydroxides can provide a variety of oxidation states for redox reaction, thus their energy density is high. Metal oxides based electrodes have become a hot research topic recently, and the most studied materials are: RuO₂, IrO₂, MnO₂, NiO, Co₃O₄ and Ni(OH)₂, Co(OH)₂.

1.2.3.1 Ruthenium oxide

Ruthenium oxide (RuO₂) is one of the promising materials for supercapacitor application, because of its ultrahigh theoretical capacitance of ~2000 F g⁻¹, high electrical conductivity and a wide potential window of 1.4 V. The energy storage mechanism in RuO₂ is as follows¹⁷:

On the other hand, the cost of RuO₂ is high, and its toxic nature generally prohibits it from wider commercialization.

1.2.3.2 Manganese oxide

As another promising candidate, Manganese oxide (MnO₂) may provide a replacement for ruthenium oxide because of its lower cost, environmental friendly and also a high theoretical capacitance of ~1370 F g⁻¹. The redox reaction of MnO₂ materials is based on its surface adsorption and insertion/extraction of metal alkali cations (Li⁺, Na⁺, K⁺, H⁺). Because the electrochemical conductivity of MnO₂ is relatively low, so in electrochemical tests the capacitance of MnO₂ (e.g. 400 F g⁻¹) is usually far from its theoretical capacitance. To improve the electrochemical

performance, efforts have been made to fabricate nanostructured MnO_2 and construct high conductive substrate for MnO_2 .⁴

1.2.3.3 Cobalt oxides

Cobalt oxides/hydroxides (CoO , Co_3O_4 and $\text{Co}(\text{OH})_2$) are other widely studied materials for supercapacitor electrodes. Co_3O_4 have excellent reversible redox behaviour, relatively high conductivity, and good corrosion stability. The redox reaction of Co_3O_4 is mainly from the following reaction:

And Co_3O_4 can be synthesized into different micro/nanostructures (microspheres, nanosheets, nanowires, nanorods, nanotubes). For example, Co_3O_4 nanowires by hydrothermal growth have been reported, and it shows a capacitance of 754 F g^{-1} .¹⁸ $\text{Co}(\text{OH})_2$ -based materials are also attractive for supercapacitor electrodes, due to their layered structure with high surface area which is favoured for fast redox reaction. The energy storage mechanism of $\text{Co}(\text{OH})_2$ is as follows:

$\text{Co}(\text{OH})_2$ -based materials show much higher specific capacitances than Co_3O_4 -based materials, which may because in alkaline electrolyte $\text{Co}(\text{OH})_2$ has better wettability. For example, $\text{Co}(\text{OH})_2$ nanoflakes¹⁹ show a capacitance of 1128 F g^{-1} in 1M KOH solution. However, the electrochemical working window for cobalt oxides

is narrow, usually from 0-0.45 V, which is much less than carbonaceous materials and RuO₂.

1.2.3.4 Nickel oxide

Nickel oxide (NiO) is another alternative electrode material in alkaline electrolytes. In addition, NiO has high specific capacitance (theoretical specific capacitance of 3750 F g⁻¹), and is environment friendly with low cost. The redox reaction of nickel oxide in an alkaline electrolyte is as follows:

Generally, NiO with porous structures can show better electrochemical performance because the high surface area will create more sites for reaction and the pores can ease the transportation of electrolyte ions. For example, a Hierarchically porous NiO film show a specific capacitance of 309 F g⁻¹.²⁰

Ni(OH)₂ is also a good candidate for supercapacitor application, and the capacitance of Ni(OH)₂ can be usually much higher than NiO. As reported, Ni(OH)₂ nanowalls shows a capacitance of (2675 F g⁻¹) and good cycling performance.²¹

Nickel oxide also suffered from narrow working window and its cycling ability is also not good enough for application at this moment.

1.3 Synthesis methods of nanostructured metal oxides for supercapacitor electrodes

Fabrication of nanomaterial electrode is a key route for better supercapacitors, as the fabrication processes and parameters will largely determine the electrochemical performance of the electrode. In order to rational fabricate ordered metal oxides electrodes with good properties, the methods should be easily controllable and adjustable. Another requirement of the methods is low cost and easy for large-scale industrial production. In the following part, several typical methods (electrodeposition, sol-gel coating, hydrothermal, CVD, and ALD) that could fulfil these requirements will be discussed and some other useful processes will also be mentioned.

1.3.1 Electrodeposition

Electrochemical deposition is a very useful method for controlled growth of nanomaterials directly on conductive substrate (usually graphite, stainless steel, titanium foil and metal foam). Generally, electrochemical deposition technique has many advantages over the other methods because by simply adjusting the current, deposition time, bath solution components and temperature, the physical properties (mass, thickness, and morphology) of the metal oxide/hydroxides nanostructures may be easily controlled, thus the electrochemical performance can be accordingly tuned.

There are two major categories of electrodeposition for metal oxides/hydroxides: anodic and cathodic.

In anodic electrodeposition, charged metal ions (M^{n+}) will firstly diffused to the anode once an external electric field is applied, then oxidation of the metal ions would

occurred on the surface of the electrode.²²⁻²⁵ For example, MnO_2 can be deposited with the following reaction:

Cathodic deposition of metal oxide/hydroxide is usually by increasing the PH with reduction reaction, then metal ions can deposit in the form of metal hydroxides. Generally, the reaction here is: $\text{Mn}^{+} + \text{n}(\text{OH})^- \rightarrow \text{M}(\text{OH})_n$. By the following annealing process, the metal oxides can be obtained. One thing to notice is that the metal ion could be reduced in cathodic electrodeposition, so sometimes the potential for deposition and ion density in the solution should be carefully chosen that reduction reaction in the solution (consumption of H^+ ions or production of OH^- ions) will override the reduction reaction of metal.²⁶

Another type of cathodic electrodeposition is by reducing high valence metal ions at the cathode surface.²⁷ For example, nanostructured MnO_2 can be obtained by electrodeposition from KMnO_4 solutions with the reaction as the following:

In application, electrodeposition can be divided into templated and untemplated ways.

Templated method usually use anodic aluminium oxide (AAO), silica, polystyrene (PS) sphere and so on, as a guidance to direct uniformly growth of the materials, after removing the template, ordered porous structures could be formed. A

mesoporous RuO_2 nanotube array was prepared by template (AAO) electrodeposition, as shown in Figure 1.6a. With a deposition time of 10-30 min at 1.0 V in a solution of $\text{RuCl}_3 + \text{CH}_3\text{COONa}$, ordered $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ nanotubular arrays can be obtained followed by removing the template. The porous structure with crystalline thin walls (~ 40 nm) is believed to reduce the diffusion resistance of electrolytes as well as enhance the ion transportation (Figure 1.6b), as a result, a high specific capacitance of 1300 F g^{-1} is achieved. Besides, at extremely rapid charge/discharge rate, the structure could still maintain an effective electron pathways for the smooth reaction, as there was only a 40 % loss of capacitance when the scan rate increased from 10 to 1000 mV s^{-1} .

Figure 1. 6 (a) SEM image of mesoporous RuO_2 nanotube array. (b) Schematic of the nanotubes in electrochemical reaction¹⁷. (c) $\text{Ni}(\text{OH})_2$ nanostructure by electrodeposition. (d) Cycling performance of the $\text{Ni}(\text{OH})_2$ nanostructure.²⁸

Untemplated electrodeposition is simpler, but the feature cannot be so controllable compared with templated methods. Many conductive substrate (Pt foil, nickel foil, Cu plate, graphite, F-doped SnO₂ coated glass (FTO), etc.) can be chose for electrodeposition of many metal oxides/hydroxides and conducting polymers, for example, ordered nanostructures of Co₃O₄, Ni(OH)₂, Fe₃O₄, MnO₂, ZnO and PANI with 1D or 2D morphology and good electrochemical properties have been reported^{22, 29-36}. A porous and 3D nanostructure of Ni(OH)₂ was fabricated on nickel foam by galvanostatic deposition at -0.7 V in a Ni(NO₃)₂ solution,²⁸ as shown in Figure 1.6c. The loosely dispersed porous material with a thickness of ~200 nm could fully contact with the electrolyte and a very high specific capacitance of 3152 F g⁻¹ has been achieved (at 4 A g⁻¹). While due to its loose packing nature, the rate stability(3152 F g⁻¹ at 4 A g⁻¹, and 280 F g⁻¹ at 16 A g⁻¹, only 9 % capacitance retention) and cycling ability (48% capacitance loss in 300 cycles) of the structure is not satisfied, which leaves much space for further improvement (Figure 1.6d).

As the electrodeposition parameter can be easily adjusted, it is a useful and simple way to fabricate ordered nanomaterials with different morphology and properties.

1.3.2 Sol-gel coating

Sol-gel process is another efficient way to obtain the desired nanostructures, typically with highly specific surface areas and porosities.³⁷⁻⁴⁰ The general process for

sol-gel coating is very simple, first a solution-based sol-gel precursor was prepared and then the material was annealed at certain temperature.⁴¹

Although the sol-gel progress is not so complex, the morphology of the final products is a little difficult to control, as many complex parameters (such as reaction temperature, concentration of starting materials, evaporation rate and heat treatment condition) would influence the final product.

The heat treatment temperature (to evaporate the adsorbed water, solvent, or organic molecules) was found to have a significant influence on the high porosity and pore size distribution of sol-gel derived materials, thus surface morphology, specific surface area, and specific capacitance of the materials are largely related to calcination temperature. A mesoporous nickel cobaltite aerogels⁴², as shown in Figure 1.7, was obtained by sol-gel method with a starting Co/Ni ratio of 0.5 with propylene oxide in ethanol. The best calcination temperature was found to be 200 °C to obtain optimized crystal grain and pore sizes (most pores of the structure were falling in the range of 2–5 nm, which is believed good for supercapacitor applications). In the following electrochemical test, the highest specific capacitance of the material is 1400 F g⁻¹ and the capacitance decay is 9% after 2000-cycles.

Generally, the sol-gel method can provide high specific surface area electrodes⁴³⁻⁴⁹ and ensure rapid mass transfer through the mesopores, thus lead to high performance in electrochemical test. The sol-gel method shows high potential to fabricate ordered metal oxides with good properties for supercapacitors.

1.3.3. Hydrothermal growth

Figure 1. 7 (a) and (c) SEM and TEM of the oxide with sol–gel method. (b) Pore size distribution of the metal oxide. (d) Cycling ability of the metal oxide in electrochemical test.¹⁷ Hydrothermal synthesis of metal oxides/hydroxides is generally simple, facile, low cost and suitable for large-scale of nanostructures.^{50, 51}

With hydrothermal method, many ordered arrays of nanostructures (nanorods, nanowires, nanoflowers, nanourchins, nanotubes and hollow nanospheres) could be created just by properly choosing the solvent, temperature and time for the reaction.^{21,}

52-63

One thing interesting is that many porous structures of metal oxides can be easily obtained by annealing the as-prepared precursors produced by hydrothermal process.^{59, 64, 65} For example, porous NiO nanoflake and CoO nanowire can be

fabricated by annealing the precursor of $\text{Ni}_2(\text{OH})_2\text{CO}_3$ and $\text{Co}_2(\text{OH})_2\text{CO}_3$ (Figure 1.8ab).

Figure 1. 8 (a) and (b) TEM images of porous NiO nanoflake and CoO nanowire^{64, 65}.
(c-e) SEM images of Cobalt Oxide grown on carbon fiber.⁵⁵

Recently L. Yang and coworkers reported a Cobalt Oxide Nanonet grown on commercial carbon fiber paper with hydrothermal method⁵⁵, as shown in Figure 1.8c-e. Cobalt nitrate and urea were used for the growth, and the reaction is carried out at 90 °C for 10 h. The Cobalt Oxide / carbon fiber paper electrode with the hierarchical network structures shows ideal rectangular shape in cyclic voltammograms (CV) test and illustrates high specific capacitance (1124 F g^{-1}) at high charge/discharge current (25.34 A g^{-1}), high rate capability (94% capacitance retain from 0.25 A g^{-1} to 25.34 A g^{-1}) and excellent cycling stability (even a slightly

increase after 5000 cycles). The improved electrochemical performance is mainly due to the unique hierarchical network architecture (nano active material grown on micro 3D substrate), which could improve electron/ion transport, enhance the kinetics of redox reactions, and facilitates facile stress relaxation during cycling.

Many metal oxides/hydroxides with different morphologies have been reported through hydrothermal methods, and the good electrochemical properties reveal their promising applications for supercapacitors electrodes. Despite the long-time reaction and the pollution of the rest solution, hydrothermal is still a very useful method.

1.3.4. Chemical Vapor Deposition

Chemical Vapor Deposition (CVD) refers to the formation of a solid material on a substrate from the chemical reaction of vapor phased reactants in an activated (heat, light, plasma) environment, and it is a common method to produce highly pure and uniform materials with good reproducibility.

In a CVD process, the characteristics of the products (crystal structure, surface morphology and orientation, and deposition rate) can be well controlled by parameters such as temperature, pressure, reactant gas concentration and total gas flow.^{66, 67}

By CVD process with resources of Zn and SnO powders at 900 °C, highly electrical conductive Zn_2SnO_4 (ZTO) nanowires were fabricated on carbon microfibers⁶⁰, as shown in Figure 1.9. The ZTO nanowires are fully covered the carbon fiber and grown radially. After an ultrathin coating of nanostructured MnO_2 , novel core/shell nanostructure of ZTO/ MnO_2 has fully covered the carbon fiber. In

electrochemical test, the hierarchical structure expressed a much better electrochemical performance (621.6 F g^{-1}) than its single component (ZTO and MnO_2 , with 46.6 and 5.6 F g^{-1} , respectively), and high energy and power density (36.8 Wh kg^{-1} & 32 kW kg^{-1}) have been achieved. Although the ZTO nanowire alone is not a promising material for supercapacitor, in the work, its conductive nature with high specific area could provide smooth channels for effectively transport of the electrolyte, thus contribute much to the improved performance. On the other hand, to fully utilize the property of MnO_2 , the design of thin coating is essential so to enable fast and reversible faradic reaction with short ion diffusion path, in this way, the low weight loading of MnO_2 can achieve high specific capacitance.

Figure 1. 9 (a) and (b) SEM, (C) and (d) TEM images of the core/shell nanostructure of ZTO/ MnO_2 on carbon fiber.⁶⁰

CVD is also a good method to prepare many carbonaceous materials⁶⁸⁻⁷⁰. X. H.

Figure 1. 10 (a) Photographs of Nickel foam before and after the fabrication of graphene. (b) Large quantity of 3D graphene networks obtained by a single CVD process. (c) SEM image of 3D graphene with Nickel foam and (d) after removal of Nickel foam¹².

Cao and coworkers reported a 3D graphene networks by CVD method with ethanol as carbon source and Ni foam as a sacrificial template¹², as shown in Figure 1.10. Graphene was firstly synthesised directly on Ni foam, after removing the template, high-quality 3D graphene network with large specific surface area can be produced. In addition, the grapheme network can be further loaded with metal oxides to enhance the energy density for supercapacitor electrode. By growing NiO with electrodeposition, the unique structure of NiO/3D graphene shows a specific

capacitance of 816 F g^{-1} with excellent electrochemical stability (no capacitance drop for 2000 cycles). The 3D grapheme foam shows great potential as an excellent substrate for supercapacitor application.

As the parameters for CVD growth is generally easy to control, it is widely used for fabricating ordered metal oxides, CNT and grapheme with high quality.

1.3.5. Atomic Layer Deposition (ALD)

Atomic layer deposition (ALD) is a useful thin film technology that rapidly bloomed in the past few decades. ALD is a unique and useful deposition method to fabricate conformal and homogenous thin films—the thickness of the film can be precisely and simply controlled by the number of cycles.⁷¹ ALD has been reported as a useful method in the application of energy and environmental areas, such as catalysis and fuel cells. For supercapacitor application, ALD is also helpful. For example, by ALD coating of V_2O_5 , the electrochemical performance (especially the energy density) of porous CNTs can be significantly increased.⁷²

1.3.6 Others

Besides the previous methods, many other processes are also used for the assistance to fabricate ordered nanostructures.

By simply dip and dry textile fibers into graphene ink followed by electrodeposition of nanostructured MnO_2 ⁷³, hybrid graphene/ MnO_2 -based textile is successfully fabricated and promising supercapacitor characteristics have been demonstrated with the unique structure.

Another work by electrochemically anodizing of alloyed metal foil⁷⁴, oriented NiO-TiO₂ nanotube has been obtained and shows higher electrochemical properties than the randomly packed nanoparticle-based electrodes.

Graphene paper was obtained by vacuum filtration of aqueous solution of graphene sheets⁷⁵, and its great potential for high-performance supercapacitor is demonstrated.

Last but not least, chemical bath deposition (CBD)²⁰ is also a useful way to directly synthesis order metal oxides and good supercapacitor properties have been also achieved.

1.4 Recent Advances in Metal Oxide Based Hierarchical Nanostructures for Supercapacitor Electrode

As mentioned previously, consumer and industrial demand is constantly driving further improvements on supercapacitors with better performance, such as higher power and energy density, better rate property and cycling capability, less physical size, lower weight, lower cost and so on. Among the electrode materials studied so far, metal oxides can provide higher energy density than carbonaceous materials and better electrochemical stability than conductive polymers, thus metal oxides based electrodes have drawn much attention for next generation supercapacitors^{76, 77}.

Generally, compared to bulk materials, nanostructured metal oxides can provide many merits, including enlarged electrode/electrolyte contact area for reaction, short ion diffusion distance and better charge transfer kinetics^{4, 52}. Recent efforts on

nanoscale electrodes have shown promising direction to improve the properties of metal oxides-based supercapacitors^{16, 78-86}. In the design of metal oxides-based electrode materials, the favored properties of the metal oxides include: (1) high specific surface area for more active reaction sites, (2) low internal electrical resistance to facilitate the charge transport in the electrode, (3) porous structure with proper pore-size distribution for effective ion diffusion even at a high current rate, (4) mechanical and electrochemical stability for long-time cycling, and (5) cheap, flexibility and environment friendly for large-scale commercialization.

To fulfil the above aims, several useful strategies have been carried in recent research efforts, such as constructing porous metal oxides with high surface area structures, loading metal oxides with highly conductive 3D substrate, and rational designing all-solid-state flexible supercapacitors.

1.4.1 Rational Designed Metal Oxide Nanostructured Materials

For pure metal oxides-based supercapacitor electrodes, an effective way to improve the electrochemical properties is to construct nanostructured active material with high-surface area, which is often revealed with porous and hollow feature, so to create more reaction sites with the electrolyte and short the electron pathway. Another useful way is to rational construct two or more metal oxides structures together, so to obtain the possible better electrochemical properties than the single component. Besides, directly fabrication of metal oxides on conductive substrate also offers many merits for improved properties in electrochemical measurement.

1.4.1.1 Porous

Rational designed metal oxides electrode with proper pore structure is highly desirable for supercapacitors. Generally, with porous electrode materials, not only more electric double-layer capacitances will be involved with the increased specific surface area, but also larger area of active sites will be effectively utilized for faradaic redox reactions between the electrolyte and the active material. In addition, suitable pore sizes can ease the mass transfer of electrolytes within the pores during fast charging/discharging⁸⁷⁻⁸⁹.

Many methods have been carried out to fabricate porous electrode materials for high performance electrodes. Generally, a large amount of porous structures of metal oxides can be easily obtained by annealing the as-prepared precursors, which can be metal hydroxides, metal-inorganic compound, and metal-organic compound^{12, 42-51, 59, 64, 65, 90-93}. For example, electrochemical deposition^{12, 90} is an effective way to produce metal hydroxides and porous metal oxides (by decomposition of the metal hydroxides). In the fabrication of metal oxides, electrochemical deposition has many advantages because by simply adjusting the current, deposition time, bath solution components and temperature, the physical properties (mass, thickness, and morphology) of the metal oxide/hydroxides nanostructures may be easily controlled, thus the electrochemical performance can be accordingly tuned. In addition, various kinds of porous metal oxides can be also obtained with hydrothermal method^{59, 91, 92}. For example, porous CoO nanowire and NiO nanoflake can be fabricated by annealing the precursor of $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowire and $\text{Ni}_2(\text{OH})_2\text{CO}_3$ nanoflake,

respectively, both of which are synthesised with hydrothermal route (see Figure 1.8a-b). Hydrothermal method is generally simple, facile, low cost and suitable for large-scale of nanostructures^{50, 51, 59, 64, 65}. One thing to notice is that, with hydrothermal method, many ordered arrays of nanostructures (nanorods, nanowires, nanoflowers, nanourchins, nanotubes and hollow nanospheres) could be created just by properly choosing the solvent, temperature and time for the reaction. Besides, sol-gel coating⁴²⁻⁴⁹ and electrospinning⁹³⁻⁹⁶ are also useful methods to prepare porous metal oxides with proper pore size distribution and good electrochemical properties.

Figure 1. 11 (a) and (b) SEM images of $\text{Ni}(\text{OH})_2$ nanowalls. (c) Schematic image of the nanostructures that is suitable for electrochemical energy storage.²¹

Porous electrode is favored for supercapacitor application. For example, with hydrothermal growth and poster annealing, a highly porous NiO nanowalls was

fabricated on 3D macroporous nickel foam, which has a cross-linked structure (see Figure 1.11a-c). The porous walls expressed a high areal pseudocapacitance (7.85 F cm^{-2}), mainly due to the high surface area rendered by its unique hierarchically porous structure.

Several other porous metal oxides also revealed the merits of porous structure^{55, 97-99}. As the kinetics of electron and ion transport in electrodes and at the electrode/electrolyte interface are key issues to enhance rate property of supercapacitors, and the reaction sites of the electrode is largely determined by its surface area, fabricating porous oxides plays an important role in improving electrochemical performance for supercapacitors.

1.4.1.2 Hollow

Hollow centers in metal oxide electrodes can provide easier electrolyte penetration and increase surface-to-bulk ratio thus produce more contact area between the active material and the electrolyte, leading to more efficient ion transport. Furthermore, improved rate capability and cycling performance can also be achieved because these void spaces could effectively buffer the strain generated during the fast charge/discharge process. As a result, hollowed metal oxides nanostructures usually show much better properties than those of bulk solid structures^{54, 61, 100-105}. Generally, hollow structured metal oxides can be fabricated with either templated methods, using solid carbonaceous microspheres, polystyrene colloid spheres and ordered metal-oxides as template^{58, 106, 107}, or untemplated methods, which may involving

Ostwald ripening process^{61, 108, 109}, Kirkendall-effect¹¹⁰⁻¹¹², and self-assembly process¹¹³.

Figure 1. 12 Hollow nanostructured metal oxides. (a) MnO₂/Mn/MnO₂ nanotube structure with high conductivity can provide ion and electron “superhighways”. (b) Illustration of the fabrication process of the nanostructure.¹¹⁴

A unique sandwich like nanotubes of MnO₂/Mn/MnO₂¹¹⁴ is fabricated by electrodeposition of metal Mn on ZnO nanowire template followed by controlled oxidation (see Figure 1.12a-b). The hollow structure with double MnO₂ shells has a large reaction area with electrolyte and can ease the transport of ions, while crystalline metal Mn layers can serve as highly conductive cores to provide electron “superhighways” to improve electrical conductivity of the electrode. The specific capacitance of the hollow structure is 955 F g⁻¹ at a current density of 1.5 A g⁻¹ in 1.0 M Na₂SO₄, which is very high in reported MnO₂ based supercapacitors. Besides, high specific energy (45 Wh kg⁻¹), specific power (23 kW kg⁻¹) and excellent cycling

stability (less 5% loss of capacitance in 3000 cycles) have also been demonstrated with the electrode. Other hollow structures of metal oxides^{105, 115-117} (which are often nanotubes) have also illustrated the merits of hollow.

1.4.1.3 Hybrid metal oxide with metal oxide

Another effective research direction on metal oxides electrodes is to construct hybrid electrode with two or more metal oxides components. The most popular hybrid structures of metal oxides are core/shell, stem-branch, and multi segmented heterojunction^{118, 119}, in either case, multiple metal oxides are linked together in a programmed way. For metal oxides based electrodes of supercapacitors, rational design of hybrid nanostructures of metal oxides aims to construct certain structures that the good combination of the physical and chemical properties could be realized, and the possible synergy effect between the metal oxides could be achieved. As many metal oxides based materials are suffered from low electric conductivity, so efforts have been made to build a relatively conductive core of metal oxide for loading of active shell material. Y. B. He et al. reported a core/shell electrode of single-crystal ZnO nanorod/amorphous and nanoporous metal oxide of MnO₂, as shown in Figure 1.13a-b. The single-crystal ZnO nanorods serve as good mechanical and electrochemical support for MnO₂, while the nanoporous MnO₂ shell could increase the reaction area. The ZnO/ MnO₂ shows a high specific capacitance of 405 F g⁻¹ and better cycling ability than MnO₂ nanotubes alone (see Figure 1.13c-d). Other works with ZnO nanorods as cores also showed similar improvement over its single component^{120, 121}, mainly due to the conductive nature of ZnO and its unique 1D

structure which is easier for charge transfer. However, the ZnO core is not a good active material for supercapacitor application, which means these structures have a ZnO dead-mass, and the ZnO may suffer from collapse during long time cycling. Thus efforts have been made to substitute the core with other materials.

Figure 1. 13 Hybrid core-shell metal oxides. (a-b) ZnO nanowire and ZnO/MnO₂ core/shell structure. (c-d) CV curve and cycling ability of ZnO and ZnO/MnO₂.¹²⁴ (e) Co₃O₄@MnO₂ structure. (f) CV curves of Co₃O₄ and Co₃O₄@MnO₂.¹²²

A novel core@shell structure of Co₃O₄@MnO₂ with a two-step hydrothermal method was reported¹²²(see Figure 1.13e-f). MnO₂ nanosheets are extensively

distributed on the highly ordered porous Co_3O_4 nanowire so to have large active sites for reaction with Li^+ ; the Co_3O_4 core nanowires can also reacted with OH^- and contribute to the capacitance. With the structure design, the synergic effort of the core@shell structure is obvious that the electrode demonstrated a high capacitance with good cycle performance (2.7% capacitance loss after 5000 cycles) and high rate capability. Another core/shell electrode with two active materials aligned on a 3D nickel foam was fabricated with a two-step hydrothermal process¹²³(see Figure 1.14a). Both core (porous Co_3O_4 nanowire) and shell (NiO nanoflake) react with the electrolyte ion (OH^-). Furthermore, Co_3O_4 nanowires serve as both the backbone and conductive connection for NiO nanoflakes, and ultrathin nanoflake-like NiO can enlarge the contact area with electrolyte. In electrochemical measurement, the hybrid structure shows a good combination of the properties between the core and shell materials (see Figure 1.14b), and a high performance with a specific capacitance of 853 F g^{-1} and excellent rate capability have been demonstrated. The improved performance can be largely resulted from the unique porous core/shell nanoarchitecture and possible synergic efforts generated from the two electrochemically active materials.

Figure 1. 14 Hybrid core-shell metal oxides. (a) $\text{Co}_3\text{O}_4@\text{NiO}$ structure. (b) Rate properties of Co_3O_4 , NiO and $\text{Co}_3\text{O}_4@\text{NiO}$.¹²⁴

Many other electrodes based on two or more metal oxides materials have also been reported and showed good performance when tested as supercapacitor electrodes. For example, core-shell structure of $\text{WO}_{3-x}@\text{Au}@\text{MnO}_2$ and $\text{Ni}(\text{OH})_2@\text{MnO}_2$, mixed composites of $\text{Co}_3\text{O}_4/\text{Ni}(\text{OH})_2$ and $\text{V}_2\text{O}_5/\text{TiO}_2$ and so on^{74, 99, 115, 125-128}. To some extent, any two metal oxides could be combined together with some properties better than one of its single parts, so in real application, how to efficiently utilize the best properties of each material in a cheap way is a key challenge¹²⁹.

1.4.1.4 Grow on substrate

Conventional electrode materials are often mixed with polymer binder (polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), etc.) and conductive additives (usually acetylene black or carbon black), then under high pressure (~10MPa) the mixture are pressed on some conductive substrate (nickel foil, Pt-Rh mesh, etc.) before electrochemical tests. The fabrication process has some drawbacks as the active materials could hardly be uniformly dispersed on the current

collector so to have fine connection with it. Furthermore, much unconnected/unused mass is wasted, and sometimes the materials may be damaged by the high pressure. In contrast, directly fabricating ordered nanomaterials on conductive substrate and subsequently using it as working electrode can provide a new direction for better performance supercapacitor electrodes as it shows the following merits over the traditional way^{52, 130}:

(1) The active material has direct connection with the substrate, so the conductivity and good mechanical adhesion to the current collector can be ensured, which is favored for ion transport.

(2) Without further resistance and mass caused by carbon black and conductive polymer, the electrode can substantially reduce the “dead volume”.

(3) The surface area can be maintained and the testing result can be trusted without the influence of carbon black and polymer binder.

1.4.2 Further Improvement of the Conductivity and Surface Area of Metal Oxide

Electrodes Materials

The rational construction of metal oxides with porous/hollow feature and hybrid structures is efficient to improve the electrochemical properties. However, many other useful ways are available for the further enhancement of metal oxides-based electrodes, among which, the most popular way is introducing other conductive materials as conductive supporting or conductive coating for the metal oxides.

1.4.2.1 3D hierarchical conductive network for metal oxides

By designing porous 3D current collectors/substrates for the loading of nanoactive metal oxides, electrolyte would become more easily penetrated into the electrode thus all active materials are fully enclosed by electrolyte with the interconnected porosity, and the transportation distance of ions into the nanoactive materials would also be shortened which leads to fast ion diffusion^{97, 131-137}. The porous 3D architectures could be carbon nanofoams, templated mesoporous carbon/conductive metal, nanographite, nanotube assemblies and polymer networks. By construction of a uniform nanoporous gold as a 3D porous electrode followed by electrodepositing nanocrystalline MnO₂ to form hybrid structure(see Figure 1.15a-c), a high specific capacitance($\sim 1145 \text{ F g}^{-1}$) of the MnO₂ has been reported¹³¹, which is close to its theoretical value (1370 F g^{-1}). The nanoporous gold with a size around 40 nm serves as a conductive path for electron transfer and fast ion diffusion between the MnO₂ and the electrolyte. In addition, the nanogold can also contribute a double-layer capacitance. Even the mass of gold is considered, the hybrid electrode still expressed a high specific capacitance of 601 F g^{-1} , which is higher than the values of many other MnO₂ and carbonaceous (or conductive polymer) composites. Another electrode containing metal-based 3D current collector (Ni) (see Figure 1.15d) and a thin layer of nano NiO on the surface also showed a high specific capacitance (900 F g^{-1})¹³². High-energy (60 Wh kg^{-1}) and high-power (10 kWkg^{-1}) densities is achieved from the Ni-NiO structure, mainly due to the highly conductive Ni metal network and the high surface area of the NiO. Other templated methods are also useful to construct 3D

current collectors, among them a bicontinuous electrode fabricated using multi-layered polystyrene as template shows promising potential in electrochemical energy storage^{136, 137}. The general way to create such inverse opal based electrodes is as follows (see Figure 1.15e): Ordered polystyrene colloid spheres were deposited onto fluorine-doped tin oxide (FTO) substrates; Conductive backbones (such as Ni metal) were then electrodeposited within the pore space; After dissolving the PS template, active material (such as NiO, MnO₂) were electrodeposited on the surface of Ni. The resulted 3D current collector is believed to provide efficient and rapid pathways for ion and electron transport and short the solid-state diffusion length.

Figure 1. 15 3D current collectors. (a-c) Nanoporous gold substrate. (d) 3D nickel substrate. (e-i) Fabrication process of 3D inverse opal based electrodes.^{131, 137}

1.4.2.2 Constructing metal oxides with carbonaceous materials

Although metal oxides electrodes have higher energy densities than carbonaceous materials, they usually suffered from low specific surface area, low

electric conductivity and poor rate property^{4, 78}. Thus fabrication of metal oxides/carbonaceous materials composites by using carbon as a support will not only result in better utilization of the active materials, but also improve the electrical conductivity, and mechanical strength of the composite materials^{85, 119}. It has been demonstrated that composites with metal oxides and carbonaceous materials will result in high capacitance, good rate capability, and improved cycling stability^{15, 138}.

Among the carbonaceous materials, CNTs and graphene are the most common materials for the loading of metal oxides. Generally, both CNTs and graphene have high specific surface area, high surface-to-volume ratio, structural flexibility and superior conductivity, so depositing pseudo-capacitive materials on CNTs or graphene electrodes is a promising way for the construction of novel hierarchical electrodes with superior capacitive properties¹³⁹⁻¹⁴⁵. For example, the high theoretical pseudocapacitance of vanadium oxides is rarely realized because of its low electrical conductivity and specific surface area¹⁴⁶. As shown in Figure 1.16a-c, by using MWCNTs as conductive support for uniform deposition of vanadium oxides, the electrochemical properties of the MWCNT–vanadium oxide electrode can be remarkably improved with capacitance up to 1550 F g^{-1} and good long-time cycling ability (8% capacitance loss in 5000 cycles). For the composites of graphene/ metal oxide, different structures can be formed, such as anchored, wrapped, encapsulated and mixed models¹⁵. Porous activated microwave expanded graphite oxide (aMEGO) was used as conductive scaffold for MnO_2 nanoparticles, which is low cost, high theoretical specific capacitance ($\sim 1370 \text{ F g}^{-1}$) material but with poor electrical

conductivity¹⁴⁷. After homogeneous deposition of MnO₂ particles with size in the range of 2-3 nm (see Figure 1.16d-e), the aMEGO/MnO₂ composites still maintains high specific surface area. Furthermore, the specific capacitance of the composite was 850 F g⁻¹, and the energy and power density measured in asymmetric cells are promising for real application. Besides, the cycling ability of the composite is also good with capacitance retention of 87.7% after 1000 cycles. The excellent properties of the composite showed the merits of constructing graphene with metal oxides in supercapacitor application. Other cases of metal oxides/carbonaceous materials composites has also shown significant enhancement in the electrochemical properties, such as high capacity, high rate capability and excellent cycling stability^{54,141, 148, 149}.

Figure 1. 16 Carbonaceous material supported metal oxides. (a-b) Bare MWCNT and MWCNT supported V₂O₅ nanostructure.⁷² (c) Cycling ability of CNT supported V₂O₅. (d-e) aMEGO loaded with MnO₂ nanoparticles¹⁴⁷

1.4.2.3 Surface conductive coating (metal oxides@carbon)

The construction of metal oxides with conductive carbonaceous support can significantly improve the electrochemical properties, while fabricating metal oxide with uniform conductive coating is also a good method to improve the supercapacitor performance¹⁵⁰.

For example, by a simple method of conductive wrapping of single wall carbon nanotubes or conductive polymers on the surface of graphene/MnO₂ (GM) nanostructure, the electrochemical properties of the graphene/MnO₂ can be significantly improved¹⁵¹. The conductive coatings are contributing to the enhancement of electron transport and providing more electric double layer capacitance (EDLC) or pseudocapacitance (see Figure 1.17a-b). Other carbon coating methods on metal oxides using glucose and sucrose as carbon source also showed improved electrochemical reversibility and cycling ability^{107, 152-155}. And in these reports, the thickness of carbon coating is in the range of 2-10 nm.

Figure 1. 17 Conductive coating on the surface of metal oxides. (a-b) Charge-discharge curve and rate property of GM and GM with conductive coating of CNT (GMC) or conductive polymer (GMP).¹⁵¹

1.4.3 For Application of Metal Oxides Electrode

1.4.3.1 Flexible full cell

For the commercialized application of metal-oxides based supercapacitors, such as power back-up, air bags, pacemakers, and different kinds of electrical vehicles, the supercapacitors should not only provide sufficient energy and power densities with high rate property and cycling ability, but also maintains high flexibility and device safety^{14, 75, 127, 142, 143, 156-161}. With these concern, hybrid supercapacitors with asymmetrical electrodes (one electrode consists of electrostatic carbon material to provide high power density, and the other one uses faradaic metal-oxides material to provide high energy density) have been extensively studied as to fully utilize the advantages on both electrode materials and extend the cell potential window thus significantly improve the energy density.¹⁶² For example, as reported by Gao et al., a hybrid supercapacitor (with MnO₂ nanoplates on nickel foam as the positive electrode and graphene hydrogel (GH) with 3D interconnected pores as the negative electrode) extended the operating voltage to 2 V in a 0.5 M Na₂SO₄ aqueous solution¹⁶², while the symmetrical electrodes of MnO₂ //MnO₂ or GH//GH has only an operating voltage window of 1 V. As a result, with the asymmetrical configuration, the energy density is increased ~3 times from 6.7 to 23.2 Wh kg⁻¹. Using non-aqueous electrolyte and Ionic liquids are also good methods to extend the potential window to get higher energy density.

Considering the poor conductivity of metal oxides may result in low power density, efforts have been made to mix metal oxides electrode with materials of good conductivity, like graphene, carbon nanotube and Au nanoparticles. Reduced grapheme oxide sheets (RGO) and its modified ruthenium oxide (RGO– RuO₂) or polyaniline (RGO–PANi) have been used as anode and cathode for supercapacitor¹⁶³. The asymmetrical supercapacitor also exhibited significantly improvement in electrochemical performance than that of the symmetric supercapacitors fabricated with RGO–RuO₂ or RGO–PANi as the electrodes. And high power density of 49.8 kW kg⁻¹ was obtained at a high energy density of 6.8 W h kg⁻¹. The good performance of the RGO– RuO₂//RGO–PANi can be attributed to the broadened voltage window and improved conductivity with RGO.

On account of safety use, low weight and flexibility, all-solid-state capacitive devices with highly flexible substrate are drawing research concern and showing their potential application for portable electronics.^{127, 158, 159, 164}. A highly flexible solid-state supercapacitor was fabricated on carbon fabric substrate using electrode material of carbon nanoparticles/MnO₂ nanorods hybrid structure and electrolyte of polyvinyl alcohol/H₃PO₄. The flexible carbon fabric is a promising lightweight current collector for conformal coating of active materials with easy electrolyte access and charge transfer. In electrochemical test, the solid-state supercapacitor showed an energy density of 4.8 Wh kg⁻¹ at a power density of 14 kW kg⁻¹, and also excellent cycling ability with 97.3% capacitance retention after 10 000 cycles.

1.4.3.2 On Nickel form

As to flexible conductive substrate, nickel foam has aroused many interests for loading of active materials in supercapacitor application, mainly due to its very good conductivity and 3D network structure that would reduce the diffusion resistance of electrolyte and provide ideal electron pathway. Besides, nickel foam can load more active materials per unit area than flat substrate (such as FTO and Ni foil) and it is also a commercialized cheap material.^{28, 36, 56, 57, 90, 161, 165, 166} By XPS and CV measurements, research efforts have found Ni foam surface is mostly metallic in nature, while long-time exposing to moist air will result in passivated and metallic sections on the surface, which make Ni foam stable even under high temperature annealing in an oxidizing environment¹⁶⁷. Chemical etching of nickel foam can remove the native oxide/hydroxide without damaging the structural integrity, and also increase the electrochemically active and specific surface areas of Ni foams. So the chemical etched nickel foam could be successfully employed for rechargeable batteries¹⁶⁷.

While in research work on supercapacitors, nickel foam becomes a controversial substrate as itself can participate in electrochemical tests which may bring about exaggerated capacitance, especially in alkaline electrolyte (the capacitance of nickel foam in 1 NaOH is $\sim 2 \text{ F g}^{-1}$). The substantial error would become more obvious if the active material involved in experiment has a very small amount compared with nickel foam substrate¹⁶⁸. Even worse, in supercapacitor application the contribution of nickel foam is still obvious even after been washed by diluted HCl solution¹⁶⁸. Thus a possible suggestion for this problem is to substitute the nickel foam with Ti foil or Pt

plate to reduce the influence of substrate, but in this way the other merits of nickel foam (like porous 3D structure) is totally excluded.

Herein, we believe nickel foam is still a good substrate for supercapacitor use due to its unique structure and high conductivity for electrochemical application. Also, any substrate would contribute to some extent the possible capacitance in electrochemical test, accurate result can be obtained once we carried out proper methods to deal with it¹²⁴. So for research purpose, we suggest the following methods to get correct and reasonable specific capacitance values of the active materials loaded on nickel foam^{21, 169}.

First, the surface native oxide/hydroxide on nickel foam should be removed by chemically etching or thermally reducing in an H₂ (g) atmosphere, so to prevent their unnecessary influence and to increase the electrochemically active and specific surface areas which would be good for electrochemical test.

Second, in the later fabrication procedure of active materials, it would be praised to prohibit the possible oxidation of nickel foam in air under high temperature.

Third, controlled experiment of bare nickel foam should be carried out, and the possible contribution of nickel foam should be subtracted, leading to reasonable result for the active material on nickel foam.

Last but not least, the active material loaded on nickel foam should not be less than 1 mg, so to increase the result accuracy.

1.5 Motivation, Objectives and Scope of This Thesis

As been discussed previously, many challenges still exist for the developing of high performance energy storage devices to fulfill the ever-increasing requirements of modern portable electronics and to keep pace with the large sustainable and clean energy produced from Sun and wind. On considering that the performance of the supercapacitors (e.g., capacity, power density, rate capability and cycling stability) are largely determined by the intrinsic properties of electrode materials, the proper fabrication and design of electrode materials can be expected to significantly influence the performances of supercapacitors. Metal oxides have great potential for supercapacitor electrode materials, as they have high energy densities than carbonaceous materials, and proper design of metal oxides and/or rational combination metal oxides with other materials would lead to high performance supercapacitor electrodes. We hope our efforts will pave a good way for commercialized metal oxides based supercapacitors with high energy/power density, long-time cycling stability, low-cost, flexibility and safety

The main objectives of this thesis are further specified as follows.

Material synthesised with proper methods and feature. We aim to fabricate different metal oxides based nanostructures with suitable methods which are controllable, cheap and easy for large-scale production. In addition, the nanostructure of the metal oxides should be suitable for supercapacitor application, such as high surface area for larger electrode/electrolyte contact.

Rational construction of hierarchical metal oxides based nanostructures with improved properties for supercapacitor electrodes. Based on the methods and metal oxides materials, we aim to design and construct hierarchical metal oxides based nanostructures, which could utilize the best of each component and have synergetic effects with better physical and chemical properties thus would express improved performance for supercapacitor application. For this purpose, we aim to construct core-shell or stem-branch structures, based on previous successful reports.

With these objectives, several useful methods for the synthesis of nanomaterials have been studied and several metal oxide based hierarchical nanostructures have been designed and tested for efficient supercapacitor electrodes. The main component of this thesis can be divided into two major parts.

1 D nanowires and 2D nanowalls based hierarchical nanostructure. In Chapter 2 and 3, two types of hierarchical core-shell nanostructures comprised of 1 D nanowire/2 D nanowall with branched structures will be presented. In both cases, the core structure is highly porous and has robust connection with the current collector with hydrothermal growth. The branched structure is coated on the core by hydrothermal growth or electrodeposition, both of which are easy to control, cheap and easy to scale-up. Both structures have shown improved electrochemical performance and the synergetic effects will be discussed.

ALD based hierarchical nanostructured electrodes. In Chapter 4 and 5, two hierarchical nanostructures by means of ALD will be presented. One is using ALD to

create a hollowed core-shell structure; the other one is using ALD to fabricate metal oxide@carbon core-shell structure. Both methods are simple, efficient and versatile. The improvement with the ALD leaded structure will be discussed and the advantages of using ALD will be discussed.

The thesis will be ended with an overall conclusion and future suggestions. Although our reports have successfully shown the merits of rational designed hierarchical metal oxides for supercapacitor electrodes, huge space still exists for further improvements not only in fundamental nanoscience but also in technical methods for new advanced materials for supercapacitor application.

Chapter 2

1 D Porous Cobalt Monoxide Nanowire @ Nickel Hydroxidenitrate Nanoflake Electrode

2.1 Introduction

As been discussed previously, supercapacitors are playing an important role in hybrid electric vehicles and industrial equipments^{3, 170}, and many research efforts have been devoted to metal oxides materials, because of their variety of oxidation states for charge transfer and high mass densities to produce high energy density. For example, a report of Ruthenium oxide nanotube has shown a capacitance as high as 1300 F g⁻¹ in aqueous acidic electrolyte¹⁷. However, the expensive nature and toxicity of ruthenium have limited it from extensive commercialization. Research efforts on other cost-effective and nontoxic nanomaterials, e.g. MnO₂¹⁷⁵, Co₃O₄^{176, 177}, and Fe₃O₄¹⁷⁸, have also demonstrated improved performance than bulk materials. In addition, many efforts have been devoted to mix these metal oxides and hydroxides with conductive porous metal structure¹⁷⁹, graphitic materials^{52, 180, 181}, or conducting polymers¹⁸². In this way, better properties can often be achieved, while the reaction was typically at low charge/discharge rate with lower power density, and the content of these active materials for supercapacitors was relatively scarce in some cases, therefore energy and power per unit area were to some extent low. Mixed metal oxides¹⁸³ represents another way to obtain high performance electrode materials, but so far their electrochemical performance was far from satisfactory, thus developing

well-defined micro-/nanostructure of the mixed metal oxides would be helpful. As been discussed, three-dimensional (3D) hybrid nanostructures can provide with short ion diffusion path and enlarged surface area for more efficient contact between electrolyte ion and active materials for Faradaic energy storage¹³⁶, thus construction of 3D hybrid nanostructures is a promising way to obtain better electrochemical materials. For example, several reports on 3D hybrid nanostructures of Zn_2SnO_4 @ MnO_2 ⁶⁰ and ZnO @ MoO_3 ¹²⁰ have shown significantly enhanced supercapacitor performance.

Based on the above consideration, materials with 3D hybrid structures would be favoured for supercapacitor electrodes. Herein, we report a novel 3D hybrid structure of porous cobalt monoxide (CoO) nanowire @ ultrathin nickel hydroxidenitrate (NiHON) nanoflake which are directly grown on nickel foam, and also the structure has robust hierarchical porosity and high specific surface area. One significant feature that make the structure different from the precious mentioned 3D hybrid nanostructures is that, in this structure both CoO and NiHON are employed as active electrode materials and they both have relatively high capacitance based on previous reports^{184, 185}. On one hand, CoO with well-defined single-crystalline nanostructure can serve well as both the robust backbone and conductive connection for NiHON, and its porous feature is suitable for electrochemical reaction. On the other hand, ultrathin nanoflake-like NiHON can not only enlarge the contact area with electrolyte which enable fast redox reaction, but also well protect the inner structure of CoO thus improve the durability. Besides, we choose nickel foam as a cost-effective substrate

CHAPTER 2

Cobalt Monoxide Nanowire @ Nickel Hydroxidenitrate Nanoflake for High-Rate Supercapacitor

on considering that it has high conductivity with a unique 3D network structure, so it can (1) reduce the diffusion resistance of electrolyte into the active material, (2) provide ideal electron pathway even under a very rapid charge/discharge reaction, (3) load more active materials per unit electrode area due to its high surface area compared with planar substrate.

2.2 Experiments

2.2.1 Sample Fabrication

The 3D hierarchical electrode material was prepared with a simple two-step hydrothermal process, which is suitable for large-scale production. Firstly, the CoO nanowires were synthesized on nickel foam by a hydrothermal process as described previously⁶⁴. In detail, 0.582 g $\text{Co}(\text{NO}_3)_2$ and 0.6 g urea were dissolved in 50 mL deionized water, the obtained homogeneous solution was further transferred into Teflon-lined stainless steel autoclave with a piece of clean nickel foam ($10 \times 15 \times 0.1 \text{ mm}^3$, 100 PPI, 330 gm^{-2} , Changsha Lyrun Material Co., Ltd. China) immersed into the reaction solution. After 8 h growth at 95°C , the as-prepared precursors were annealed under a constant flow of argon (50 sccm) at 450°C for 2 h ; Then the nickel foam with CoO nanowires was immersed into a 0.1 M $\text{Ni}(\text{NO}_3)_2$ aqueous solution and maintaining at 85°C for 5 h. After cooling to room temperature, the samples were obtained. For nickel hydroxidenitrate powder synthesis, 0.25 M $\text{Ni}(\text{NO}_3)_2$ ethanol solution was first prepared, and then transferred to a Teflon-lined stainless steel autoclave to react at 130°C for 3 h. After cooling down to room temperature, the

green precipitation was washed with deionized water and dried at 60 °C to obtain the final sample.

2.2.2 Material and Electrochemical Characterizations

All samples have been characterized using scanning electron microscopy (SEM) (JSM-6700F, 10.0 kV), transmission electron microscopy (TEM) (JEM-2010FEF, 200 kV) equipped with an energy dispersive X-ray spectrometry (EDS), powder X-ray diffraction (XRD) (Bruker D-8 Avance). Fourier transform infrared (FTIR) spectrum was recorded on a Bruker Vertex 80V HYPERION 2000 Microscope using MCT detector. The mass was recorded by an AX/MX/UMX Balance (METTLER TOLEDO, maximum=5.1 g; d= 0.001 mg).

Electrochemical measurements (ZAHNER ENNIUM Electrochemical Workstation) were performed in a three-electrode electrochemical cell at room temperature, and a 1 M NaOH solution was used as electrolyte. The nickel foam supported hybrid nanostructure (~1 cm² area; CoO mass: ~2.2 mg; NiHON mass: ~0.8 mg) acted directly as the working electrode. A Pt plate and Ag/AgCl were used as the counter electrode and the reference electrode, respectively. All potentials were referred to the reference electrode. The weight in specific capacitance (F g⁻¹) and current rate (A g⁻¹) was calculated based on the whole mass of the two active materials (CoO and NiHON). Electrochemical impedance spectroscopy (EIS) measurements were carried out by applying an AC voltage with 1 mV amplitude in a frequency range from 0.1 Hz to 100 kHz at open circuit potential.

2.3 Results and Discussion

2.3.1 Structure Characterization

The SEM image of the nickel foam with a 3D porous structure can be seen from Figure 2.1. Figure 2.1b shows the aligned CoO nanowires, which have diameter and length in the range of ~60-100 nm and ~2-3 μm , respectively, and from the magnified image in the inset one can see that the nanowires are highly porous. This result matches well with the previous reported CoO nanowires which were directly grown on titanium foil, and has porous and single-crystalline structure⁶⁴. After the second-step growth, the hybrid structure on the nickel foam is shown in Figure 2.1c, d. From a typical part of nickel foam, as shown in Figure 2.1c, we can see that after growth, the nickel foam is uniformly covered with the hybrid structure. And From enlarged image in Figure 2.1d, we can clearly observed that the CoO “nanostems” are

Figure 2. 1 SEM images of (a) the 3 D structure of nickel foam, (b) the CoO nanowire on the nickel foam. (c,d) low and high magnification images of the hybrid structure on the nickel foam. Insets in Figure 2.1b and 2.1d are the enlarged pictures.

tightly bonded and totally covered with "leaves" of nanoflakes. In this way, after the second-step growth of the nanoflakes, the space between the CoO arrays is abundantly utilized, which would result in increased energy and power per unit area. The mechanism of the nanoflakes is as follows, in the $\text{Ni}(\text{NO}_3)_2$ solution, the Ni^{+} will hydrolysis on the CoO surface, thus leading to the hydrotalcite-like nickel hydroxide structure intercalated with the NO_3^{-} group.¹⁰⁷ In this way, nanoflakes will form on the CoO surface. The hierarchical structure is further studied by TEM, as shown in Figure 2.2. From Figure 2.2a, the surface of CoO nanowire is fully covered with ultrathin nanoflakes, and the nanoflakes has a width up to ~100 nm. In Figure 2.2c, which

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shows the EDS analysis data in two typical areas (A1, A2), we can see the existence of elements of O, N and Ni in the "leaves".

Figure 2. 2 TEM images of an individual hybrid nanostructure. The EDS signals of the areas labeled as A1 and A2 in (b) are shown in (c).

XRD is also carried out to study the two materials (the CoO nanowires and the hybrid nanostructure), as shown in Figure 2.3a. The XRD pattern of the CoO nanowires correspond with the reported pattern of CoO (JCPDS, card no: 48-1719). And from the XRD pattern of the hybrid nanostructure, other two peaks appear after the second step growth, which matches previous report of $\text{Ni}_3(\text{NO}_3)_2(\text{OH})_4$ (JCPDS, card no: 22-0752)¹²¹. From FTIR spectrum in Fig. 3b, we can get further information of the Ni-based hydroxidenitrate. From the FTIR result, a group of peaks in the range of 990 to 1384 cm^{-1} can be well defined to be the nitrate anion¹⁸⁶. Two peaks observed at 657 and 3633 cm^{-1} represent the σ -OH vibrations and ν -OH stretching,

respectively¹⁸⁷. Three peaks at 839, 1641, and 3363 cm^{-1} correspond well with the vibrations of H_2O molecules.

Figure 2. 3 (a) XRD patterns of the CoO nanowire and the hybrid structure on the nickel foam. (b) FTIR spectrum of the hybrid structure.

2.3.2 Electrochemical Performance

With the above experiment, we believe the hybrid structure is suitable for supercapacitor application. The cyclic voltammetry (CV) curves of the hybrid structure on nickel foam at different scan rates of 5, 10, 20, 40, and 80 mV/s are shown in Figure 2.4a. To better understand the reaction, we also obtain the CV property of CoO nanowires on nickel foam (nanostructures obtained after step 1 in experiment section) at 40 mV/s , and compare it with the hybrid structure. As can be seen from the dotted curve in Figure 2.4b, two pairs of redox peaks can be observed:

Figure 2. 4 (a) The CV curves of the hybrid structure on nickel foam at different scan rates of 5, 10, 20, 40 and 80 mV/s, (b) Comparison of the hybrid structure and CoO nanowires on nickel foam at the same scan rate of 40 mV/s. (c) Charge-discharge behavior of the hybrid structure on nickel foam at different current densities, (d) The comparison of the hybrid structure and CoO nanowires on nickel foam with the same areal charge-discharge current of 10 mA/cm². Note that the redox peaks due to the Ni foam are negligible as shown in supporting information (Figure 2.5).

P1 and P3 are due to the reaction¹⁸⁸,

P2 and P4 are due to the reaction:

Figure 2. 5 A nickel foam (330 g m^{-2}) was tested independently (a) at a scan rate of 10 mV/s in a CV testing; (b) at a charge-discharge rate of 5 mA/cm^2 .

After careful comparison the dotted curve with the solid one in Figure 2.4b, which is the CV curve of the hybrid structure on nickel foam at the same scan rate (40 mV/s), the great contribution of ultrathin NiHON nanoflake can be demonstrated. From the comparison, the CV curve of the hybrid structure has not only fully encompassed all the four peaks of the CoO nanowires, but expanded much as shown with increased the integrated area, indicating the hybrid structure has much larger capacitance than the CoO nanowires alone. Because of NiHON nanoflake, the expanded peaks (P5 and P6) can be mainly ascribed to the reaction between $\text{Ni}^{2+}/\text{Ni}^{3+}$ and anions OH^- ¹⁰². From the CV curve, the ultrathin NiHON nanoflake did not restrain the reaction between the inside CoO nanowire and OH^- , but introduces another effective electrochemical redox reaction with enlarged capacitance.

To further confirm the conclusion, charge-discharge testing is also carried out. The charge-discharge behaviour of the hybrid structure between $0.01\text{-}0.52 \text{ V}$ at different current densities is shown in Figure 2.4c. The SC is calculated as follows:

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$$C = It / m \Delta V \quad (2.1)$$

Where I is the discharge current, m is the mass of the hybrid structure, ΔV is the potential window, t is the discharge time, and C is the specific capacitance. One thing to notice is that nickel foam can also contribute to the capacitance. So a nickel foam under the same pretreatment was also tested independently, and it shows a capacitance of only $\sim 2 \text{ F g}^{-1}$ at a current density of 5 mA cm^{-2} , contributing only 2.89% of the total capacitance of the hybrid structure. Calculation details are as follows:

As both nickel foam substrate and active materials contribute to the charge-discharge behavior of the electrode¹⁶⁸, and they are under the same current, charge-discharge time and potential window, formula $C = It / m \Delta V$ can be converted to¹³⁶:

$$It / \Delta V = C_s * m_s + C_a * m_a,$$

Figure 2. 6 Powder sample of NiHON have been tested and showed a capacitance of $\sim 1200 \text{ F/g}$ at 10.5 A/g .

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Figure 2. 7 (a) Cycling performance of the hybrid structure and CoO nanowires. (b) Last 10 charge-discharge curves of the hybrid structure. (c) The current density dependence of the hybrid structure. (d) Impedance Nyquist plots of the hybrid structure and CoO nanowires on nickel foam at open circuit potential.

where C_s , m_s represent the capacitance and the mass of the nickel foam substrate, C_a , m_a is the capacitance and the mass of the active materials.

For a typical charge-discharge process of the hybrid structure on nickel foam (for example, current density is 5 mA cm^{-2}), the contribution of 1 cm^2 nickel foam can be calculated independently from the above curve in Figure 2.5b,

$$C_s \cdot m_s = It / \Delta V = (5 \text{ mA/cm}^2 \cdot 1 \text{ cm}^2) \cdot 6.72 \text{ s} / 0.51 \text{ V}$$

$$= \sim 66 \text{ mF}$$

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And according to Figure 2.4c, under the same current density, the contribution of the hybrid structure on 1 cm² nickel foam is,

$$\begin{aligned} C_a * m_a &= It' / \Delta V - C_s * m_s \\ &= (5 \text{ mA/cm}^2 * 1 \text{ cm}^2) * 251 \text{ s} / 0.51 \text{ V} - 66 \text{ mF} \\ &= 2395 \text{ mF}, \end{aligned}$$

$$(C_s * m_s) / (C_a * m_a) = 66 \text{ mF} / 2395 \text{ mF} = 2.89\%$$

Thus the contribution of nickel foam in this case is 2.89% of the total capacity of the hybrid structure.

In order to illustrate accurately the contribution from the active material, in all of the following results we have subtracted the small contribution of the Ni foam. Based on the charge-discharge curves, the hybrid structure has specific capacitances of 671.3, 749.9, 781.8 and 798.3 F g⁻¹ at different discharge currents of 13.33, 6.67, 3.33 and 1.67 A g⁻¹, respectively. A typical comparison of the hybrid structure and CoO nanowires on nickel foam with the same areal charge-discharge current of 10 mA cm⁻² is shown in Figure 2.4d. From the direct comparison, after the growth of NiHON, the hybrid structure exhibits much higher capacitance when compared with CoO nanowires alone (from calculation, the CoO nanowire has a SC of 307 F g⁻¹ at a current density of 4.55 A g⁻¹). In addition, another comparison is also carried out to show the merits of the hierarchical structure. If the CoO and NiHON could be simply mixed together with the same mass ratio of the hybrid structure, the specific

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capacitance of this mixture would be only $\sim 545 \text{ F g}^{-1}$, which is still rather smaller the capacitance obtained by the hierarchical structure. The calculation details are as follows:

If we could simply add NiHON and CoO (307 F g^{-1} at 4.55 A g^{-1}) with the same mass ratio of the hybrid structure (CoO $\sim 2.2\text{mg}$, NiHON $\sim 0.8\text{mg}$), the capacitance of the mixture (C) would be calculated as,

$$C \cdot m = It / \Delta V = C_c \cdot m_c + C_n \cdot m_n,$$

where $m = m_c + m_n$ (m , m_c and m_n is the mass of the mixture, CoO and NiHON, respectively), and C_c , C_n is the capacitance of CoO and NiHON, respectively.

At the current density of 13.33 A g^{-1} , even if CoO and NiHON could maintain a same capacitance (as at lower current density) of 307 F g^{-1} and 1200 F g^{-1} , then from the above formula,

$$C \cdot 3\text{mg} = 307\text{F/g} \cdot 2.2\text{mg} + 1200\text{F/g} \cdot 0.8\text{mg}$$

$$C = \sim 545 \text{ F g}^{-1}.$$

The result is still poorer than the data we get from the hybrid structure, which shows a capacitance of 671.3 F g^{-1} at the current density of 13.33 A g^{-1} .

This evidence further shows the merits of the uniformly hybrid structure which has conductive backbones and high surface ultrathin nanoflakes.

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The electrochemical stability of CoO nanowires and the hybrid structure under long-time cycling is further examined. As shown in Figure 2.7a, after 2000 cycles of charge and discharge, both materials show negligible loss of capacitance (less than 5%), and the hybrid structure with a 96.7% capacitance retention demonstrates even better durability than the CoO nanowires alone (which has a 95.1% capacitance retention). From Figure 2.7b, which shows the last 10 charge-discharge cycles of the hybrid structure, we can see after long-time cycling, the hybrid structure still maintains a good electrochemical reversibility (with 98.9% Columbic efficiency). We think the good electrochemical stability can be raised from the following two parts: First, the ordered CoO nanowires are tightly grown on nickel foam, which can provide excellent conducting connection with NiHON nanoflake; Second, the NiHON nanoflake have filled in the surface of CoO nanowires, which can prevent the 'stem' from collapsing in the electrolyte (even under long-time harsh reaction).¹²² The current density dependence of the hierarchical structure is shown in Figure 2.7c. We can see, in the first 150 cycles (with a charge-discharge density of 10 A g^{-1}) the hybrid structure shows a stable specific capacitance of $\sim 710 \text{ F g}^{-1}$. And in the following 400 cycles, the hybrid structure always shows stable capacitance with the charge-discharge rate changes successively. Finally, when the current turns back to 10 A g^{-1} , the capacitance is almost fully recovered ($\sim 710 \text{ F g}^{-1}$) with another 150 cycles. The above experiment can well demonstrate the excellent rate capability of the hierarchical nanostructure.

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Electrochemical impedance spectroscopies (EIS) of the two structures are further studied, and the components of the whole impedance is also well-fitted by a equivalent circuit, as shown in Figure 2.7d. From the EIS curve, the slope of the curve (in low frequency area) shows the Warburg impedance (W), indicating the electrolyte diffusion in the porous electrode and proton diffusion in host materials. As can be seen from the curve, CoO @ NiHON has the more ideal straight line along the imaginary axis, which means its diffusion resistance is lower.¹⁸⁹ The lower diffusion resistance can be attributed to the ultrathin NiHON nanoflake, which provides large surface area with enhanced the electrode materials utilization and thus facilitates the supply of OH⁻ to the entrance of CoO nanopores and nickel foam micropores⁶¹. In high frequency area, the intersection of the curve at real part Z' (which is equal to R_b) represents the bulk resistance of the electrochemical system, and the semicircle corresponds to double layer capacitance C_{dl} and charge-transfer resistance R_{ct}, which is related to the charge-transfer process at the working electrode-electrolyte interface.¹⁹⁰ The hybrid structure also displays lower bulk resistance and charge-transfer resistance than CoO nanowires, as shown from the inset picture in Figure 2.7d. In all, the low diffusion and electron-transfer resistances of the hierarchical structure illustrated from EIS are favoured for the excellent electrochemical performance.

2.4 Conclusion

In summary, based on the motivation, we firstly designed a novel hierarchical nanostructure with two active materials (ultrathin NiHON nanoflake and CoO

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nanowire) fabricated on the 3D nickel foam substrate with a two-step hydrothermal methods. The hierarchical structure has successfully combined the merits of the two active components, as demonstrated by detailed electrochemical characterization. In all, the hierarchical structure has an excellent electrochemical stability, excellent rate property and a maximum specific capacitance of 798.3 F g^{-1} has been achieved with the structure design. On account of the cost-effective fabrication and excellent electrochemical performance, we think this type of hierarchical 3D nanostructure can have great potential as the active electrode for supercapacitors.

Chapter 3

2 D Porous Nanowalls @ Layered Nanoflakes With High Areal Pseudocapacitance

3.1 Introduction

In previous chapter, we discussed about a hybrid oxide nanostructure that has a high specific capacitance and also good cycling ability. For real applications, the areal capacitance is another key factor for a supercapacitor. In order to achieve high areal capacitance, herein, we intend to go further to develop highly nanoporous metal oxides as the high areal-capacitance supercapacitor electrode. Specifically, we adopted 2D porous CoO nanowalls which are fabricated by hydrothermal method, and the nanowall surfaces can be utilized by further deposition of new pseudocapacitive nanomaterials. Electrodeposition as used to deposit Ni(OH)₂ nanolayers on the walls, and the core-shell hierarchical structure can achieve a giant enhancement of areal capacitance up to $\sim 11.5 \text{ F cm}^{-2}$. Here we believe that with the rational combination of two types of materials and/or nanostructures, the synergy effect of the hybrid metal oxides is significant with enhanced electrochemical performance compared to their single-component constituents, just as been demonstrated in some other oxide-based systems.^{122, 123, 185} We think the nanoporous metal oxides/layered hydroxide on metal foams would be a promising type of electrodes for supercapacitors.

3.2 Experimental Section

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3.2.1 Material Synthesis

The 3D hybrid electrode material was prepared by a simple two-step process, which can easily scale up. Firstly, the CoO nanowalls were synthesized on nickel foam by a hydrothermal process as reported. In detail, nickel foam ($20 \times 50 \times 0.1$ mm³, 100 PPI, 330 g m⁻², Changsha Lyrin Material Co., Ltd. China) was pretreated with concentrated HCl solution, absolute ethanol and deionized water for 5 min respectively to ensure its surface was well cleaned. Then the nickel foam with a part leaved as supporting electrode for electrodeposition/testing was put in a Teflon-lined stainless steel autoclave with a 50 mL homogeneous solution containing 5 mmol Co(NO₃)₂•6H₂O and 10 mmol HMT (hexamethylene tetramine). After 8 h growth at 95 °C, the as-prepared precursors were annealed under a constant flow of argon (50 sccm) at 450 °C for 2 h. After 2 h growth at 95 °C, the as-prepared precursors were annealed under a constant flow of argon. Secondly, the nickel foam with CoO nanowalls (mass loading: 4.3 mg cm⁻²) was used as working electrode for electrodeposition of Ni(OH)₂, which was carried out by a Chenhua CHI760D model Electrochemical Workstation (Shanghai), with a three-electrode setup consisting of Ag/AgCl and platinum plate as reference and counter electrode, and with an aqueous solution of 0.1 M Ni(NO₃)₂ as the electrolyte. The electrodeposition experiments were carried out at a constant current of 1 mA with different time ranges from 2-30 min to ensure the conformal coating of Ni(OH)₂ nanostructures on CoO nanowalls, and the mass of deposited Ni(OH)₂ could be calculated by Faraday's law. After deposition,

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the as prepared CoO@Ni(OH)_2 electrode was washed with water several times and then placed in vacuum oven at 60 °C for 2 h. The mass of deposited Ni(OH)_2 nanomaterials was again obtained by the weight difference before and after electrodeposition.

3.2.2 Material Characterization

Samples were studied by powder X-ray diffraction (XRD) (Bruker D-8 Avance), scanning electron microscopy (SEM) (JSM-6700F, 10.0 kV), transmission electron microscopy (TEM) (JEM-2010FEF, 200 kV), and fourier transform infrared (FTIR) spectroscopy (Bruker Vertex 80V HYPERION 2000 Microscope with MCT detector). The mass of electrode materials was recorded by an AX/MX/UMX Balance (METTLER TOLEDO, maximum=5.1 g; d= 0.001 mg). Micromeritics TriStar 3000 porosimeter (mesoporous characterization) and Micromeritics ASAP 2020 (microporous characterization) were used for the measurement of Nitrogen adsorption/desorption isotherms at 77 K. Before the measurement, all samples were outgassed at 100 °C for 6 h under vacuum, and the specific surface areas were calculated with the Brunauer-Emmett-Teller (BET) method.

3.2.3 Electrochemical Characterization

Electrochemical measurements (CHI 760D Electrochemical Workstation) were performed in a three-electrode electrochemical cell at room temperature using a 1 M NaOH as electrolyte. The nickel foam supported hybrid nanostructure (~1 cm² area) acted directly as the working electrode. A Pt plate and Ag/AgCl were used as the

counter electrode and the reference electrode, respectively. All potentials were referred to the reference electrode. The weight in specific capacitance (F g^{-1}) and current rate (A g^{-1}) was calculated based on the whole mass of the two active materials, CoO and $\text{Ni}(\text{OH})_2$.

3.3 Result and Discussion

Figure 3. 1 (a) XRD patterns and (b) FTIR spectrum of the Co(OH)_2 and CoO nanowall on the nickel foam.

3.3.1 CoO nanowalls

Standard X-ray diffraction was used to characterize the crystal phase of the sample obtained by the first growth. As shown in Figure 3.1a, the XRD pattern of the as-prepared sample matches well with the reported pattern of $\text{Co}(\text{OH})_2$ (JCPDS, card no:74-1057).³⁰ After the thermal annealing, the $\text{Co}(\text{OH})_2$ changes to CoO phase,

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which can be seen from the lower branch in Figure 3.1a (JCPDS, card no: 48-1719).⁶⁴

FTIR spectra was further carried out to verified the transformation from hydroxide to oxide, as shown in Figure 3.1b. Two peaks can be observed before annealing, which are in the range of 500 to 700 cm^{-1} , representing the $\nu\text{-Co-O}$;¹⁸⁷ In addition, peaks at 1199 and 1384 cm^{-1} are correlated with the NO_3^- ;¹⁹⁹ and two peaks at 1039 and 1486 cm^{-1} are associated with the CO_3^{2-} ; peaks at 2870 and 2934 cm^{-1} can be well assigned to C-H vibrations, and other two peaks at 1620 and 3644 cm^{-1} are associated with the vibrations of H_2O .²⁰⁰ As shown in the dark line below, most of these peaks disappeared after annealing, while the CoO peaks still remain strong, demonstrating the transformation of Co(OH)_2 to CoO.

Figure 3. 2 (a-c) SEM images of the CoO nanowalls grown directly on the nickel foam. (d) TEM image of an individual piece of CoO nanowall.

From the SEM images in Figure 3.2a-c, we can see the aligned CoO nanowalls are directly grown on the nickel foam, and the macroporous nickel foam is fully covered with the CoO nanostructures. Figure 3.3 and 3.4 shows further information of the photographs and large-scale SEM image of the sample. From Figure 3.2b, we can see the nanowalls have a size of 4-5 μm, and all the nanowalls are overall vertical aligned on the nickel foam with a cross-linked feature. This overall alignment is expected to be beneficial to the charge transport and ion diffusion as there is no polymer binder. From the enlarged image of an individual nanowall in Figure 3.2c,

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the highly porous structure can be clearly observed and the pore diameters are around or below 100 nm. TEM was also carried out to obtain further information on the porous structure, as shown in Figure 3.2d. A typical nanowall is composed of many small nanobricks, which are tightly interconnected with each other. Based on the above characterization, the architecture of the nanowalls was well preserved in the annealing step, and $\text{Co}(\text{OH})_2$ was converted to highly porous CoO during the thermal treatment.¹²³

Figure 3. 3 Photographs of the samples exploited in this study.

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Figure 3. 4 SEM images of the porous CoO nanowalls on macroporous nickel foam with different magnifications. (a) Large-scale view. (b) Zoom-in view of the “cluster” area. (c) High-magnification view of (b) showing that these flakes are also highly porous.

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In order to evaluate the suitability of the porous nanowalls for supercapacitor applications, the electrochemical properties are tested. Figure Figure 3.5a shows the redox reaction of CoO in the electrolyte, as revealed from the cyclic voltammetry (CV) curve. And the charge-discharge behavior of the CoO nanowalls between 0-0.55 V at different current densities is shown in Figure 3.6a. The specific capacitance of the material can be calculated as follows

$$C=It/m\Delta V \quad (3.1)$$

and the areal capacitance can be calculated by

$$C_a=I\cdot t/(\Delta V\cdot S) \quad (3.2)$$

Figure 3. 5 (a) Cyclic voltammetry (CV) curve of the CoO nanowalls, (b) SEM image of the CoO nanowalls after 5000 cycles. At a scan rate of 2mV/s, two pairs of redox peaks can be observed, which correspond to the reversible conversion between different cobalt oxidation states.

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where I is the discharge current, t is the discharge time, m is the mass of the active materials, ΔV is the voltage drop upon discharging, and S is the geometrical area of the electrode. From Equation (3.1), the CoO nanowalls exhibit specific capacitances of 364.2, 461.7, 515.6, and 539.8 F g^{-1} at different discharge currents of 9.30, 4.65, 2.33 and 1.17 A g^{-1} , respectively. This result is higher than that (307 F g^{-1} at 4.55 A g^{-1}) of CoO nanowires reported in previous chapter.¹²³ We think the increase can be attributed to the porous structure of the walls which would provide more surface areas of contact with the electrolyte. A higher surface area means more active materials can be effectively utilized for reaction with the electrolyte and contribute to the capacitance. Calculated from Equation (3.2), the areal capacitance of the CoO nanowalls is 2.32 F cm^{-2} . One thing to notice is that the nickel foam itself can influence the final CV curve with a small capacitance contribution, as discussed in

Figure 3. 6 (a) Charge-discharge curves of the CoO nanowalls at different current densities. (b) Cycling performance of the CoO nanowalls. Inset is the XRD patterns before cycling and after 5000 cycles, showing the structural preservation.

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previous chapter. In order to obtain the accurate contribution of the active material, in all of the following results we subtracted the small contribution from the Ni foam.

As shown in Figure 3.6b, the charge/discharge cyclic stability of the CoO nanowalls is further tested. We can see that the structure show only a small loss of capacitance (less than 5%) after 5000 cycles of charge and discharge at a current density of 4.65 A g^{-1} . And the comparison of the XRD patterns of the CoO nanowalls before and after 5000 cycles, as inset in Figure 3.6b, also demonstrated this good long-term electrochemical stability, because after this long-time cycling little change of the CoO peaks has happened from the XRD results and no other apparent impurity has been observed. Besides, SEM was further carried out to check the morphology of the CoO nanowalls after 5000 cycles. As shown in Figure 3.5b, the porous structure was fully maintained with no obvious changes. So with the electrochemical test, the CoO nanowalls have exhibited not only high capacitance but also long cycling stability, we think the good properties are due to its highly porous and crystalline structure and the direct connection with the macroporous nickel foam.

3.3.2 CoO@Ni(OH)₂ hybrid nanostructure

As been discussed in 3.3.1, the porous nanowalls demonstrated good properties for the commercial application in high-demand energy storage. And we believe the areal capacitance can be further increased by the hybridization with an additional metal oxide, as we mentioned in Chapter Two. Another reason is that the aligned and cross-linked CoO nanowalls can serve as a robust and conductive scaffold for the

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loading of additional pseudoactive nanomaterial. In order to achieve synergy, several requirements of the newly-introduced material should be fulfilled. For example, the newly material should contribute effective specific capacitance to the whole electrode.

Figure 3. 7 XRD patterns of the Ni(OH)_2 electrodeposited on CoO nanowalls and bare nickel foam.

In addition, the material should enlarge the surface area but not preventing the contact between the CoO nanowalls and ions in the electrolyte, and maintain the structural integrity. With these consideration, electrodeposition, which is a convenient and controllable method, was chosen to coat the surface of CoO with another pseudocapacitive metal oxide. In our study, a few hybrid nanostructures by changing the solution for electrodeposition have been obtained, such as MnO_2 and Ni(OH)_2 . Both of these materials show a flake structure and demonstrate their promising for the supercapacitor application. We think these porous + flake hybrid nanoscale metal

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oxides can be also useful in lithium ion battery and gas sensing. Herein we choose $\text{Ni}(\text{OH})_2$ as a typical demonstration.

The XRD was used to check the sample, as shown in Figure 3.7. After $\text{Ni}(\text{OH})_2$ electrodeposition on the CoO nanowalls, the new peaks appearing in the XRD pattern of the hybrid structure can be well indexed to $\alpha\text{-Ni}(\text{OH})_2$.²⁰¹ A typical morphology of the nanowalls after 15 min electrochemical deposition is shown in Figure 3.8. We can see the surface of the CoO nanowalls was uniformly covered with leaf-like $\text{Ni}(\text{OH})_2$ thin layers. From TEM image, we think it is also possible that the pores of the CoO nanowall are also filled with the thin layers,

Figure 3. 8 (a-b) SEM and (c) TEM images of the hybrid structure of $\text{CoO}@\text{Ni}(\text{OH})_2$ obtained after 15 min electrodeposition.

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Figure 3. 9 SEM images of the $\text{Ni(OH)}_2@\text{CoO}$ hybrid nanostructure obtained with increasing deposition time of 2, 5, 10, 15, 20, 30 min, respectively.

To better understand the evolution of the nanolayers, time-dependent growth experiments were conducted, as shown in Figure 3.9 and 3.10. From the SEM and TEM images of the sample, which are tested with different electrodeposition times, we can clearly see that the size and coverage of the Ni(OH)_2 nanolayers depends on the deposition time: the Ni(OH)_2 nanolayers grow individually first and then percolate until fully coverage of the CoO nanowall surface. We also test the capacitance with the different electrodeposition time, as shown in Figure 3.11. The highest capacitance corresponds to a 15 min deposition of Ni(OH)_2 . These data clearly illustrate the convenience of electrodeposition in tailoring the nanoelectrode surface and enhancing the electrochemical performance.

In order to show the $\text{CoO}@\text{Ni(OH)}_2$ hybrid nanostructure will have improved electrochemical properties than the single CoO nanowalls, further electrochemical

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Figure 3. 10 (a-d) Magnified SEM and (a'-d') corresponding TEM images of the $\text{Ni(OH)}_2\text{@CoO}$ hybrid nanostructure obtained with increasing deposition times. (a, a') 2 min, (b, b') 10 min, (c, c') 20 min, and (d, d') 30 min.

tests were conducted. The CV curves under the same scan rate and the areal capacitances of pure CoO, Ni(OH)_2 , and hybrid CoO@Ni(OH)_2 are depicted in Figure 3.12, from which we can get a direct comparison. As can be seen from Figure 3.12a, the red curve shows the CV behavior of the hybrid electrode with 15 min electrodeposition (at a scan rate of 2 mV s^{-1}). The CV curves of the CoO nanowalls (shown as blue line) and Ni(OH)_2 nanolayers directly deposited on the nickel foam (black curve) were also shown in the same picture, by comparison with the three curves, we can see the enclosed area of the hierarchical structure is largely increased, indicating larger capacitance obtained. And the capacitance of hybrid electrode is even ~ 3 times more than the simple addition of the two components, as can be seen from Figure 4b. For example, at the current density of 5 mA cm^{-2} , the areal capacitance of the hierarchical structure can reach to 11.49 F cm^{-2} , whereas the values

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for the individual CoO and Ni(OH)₂ are 2.3 and 1 F cm⁻², respectively. The value of areal capacitance (11.49 F cm⁻²) obtained from the CoO@Ni(OH)₂ hybrid structure is, to the best of our knowledge, the highest value reported from metal oxides/hydroxides nanostructures with a high mass loading (~5 mg).^{21, 145}

Figure 3. 11 Specific capacitance (in two units) of the CoO @ Ni(OH)₂ hybrid nanostructure as a function of the Ni(OH)₂ electrodeposition time. All the samples have shown very high specific capacitance (>1200 F g⁻¹) and high areal capacitance (>6 F cm⁻²). The purpose of this study is to optimize the electrodeposition condition so that the resulting Ni(OH)₂ nanomembranes will not have detrimental effect by blocking the space between the CoO nanowalls, which may prohibit fast ion transfer.

The charge-discharge curves can also demonstrate the capacitance improvement, as can be seen from Figure 3.13a. When tested at a same current density (10 mA cm⁻²), the capacitance of the hierarchical core-shell structure is increased by ~4.8 times compared to the bare CoO nanowalls, while the mass increase with the Ni(OH)₂ deposited was only 12.6%. From the charge-discharge curves in Figure 3.13b, the

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hierarchical structure has specific capacitances of 1340.9, 1694.2, 2185.9 and 2374.0 F g^{-1} at currents of 8.26, 4.13, 2.07 and 1.03 A g^{-1} , respectively. G. W. Yang etc. reported, to the best of our knowledge, the highest specific capacitance so far, which is 3152 F g^{-1} , but the corresponding areal capacitance is relatively low ($\sim 1.58 \text{ F cm}^{-2}$).

Figure 3. 12 (a) Comparison of the charge-discharge behavior between CoO nanowall electrode and CoO@Ni(OH)₂ hybrid electrode at the same current density. The scan rate is 2 mV s^{-1} . (b) Comparison of the areal capacitance of the three structures: Ni(OH)₂, CoO, CoO@Ni(OH)₂, at various current densities. The percentage number shows the capacitance retention when the current increased from 5 to 40 mA cm^{-2}

As analysed in the previous chapter, we think the large improvement in areal capacitance in the hierarchical structure could be introduced by a synergy between the two oxides. Firstly, the core CoO nanowalls has excellent electrochemical stability and high surface area, as domstrated, could serve as a robust and conductive host for the Ni(OH)₂ layers; While the Ni(OH)₂ nanolayers can not only contribute another

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effective redox reaction to the capacitance (with reaction between $\text{Ni}^{2+}/\text{Ni}^{3+}$ and anions OH^-),²¹ but also it can provide large surface area. As illustrated by BET method, the surface areas of the hierarchical nanostructure electrode (typically with 15 min electrodeposition of $\text{Ni}(\text{OH})_2$) is $9.12 \text{ m}^2 \text{ g}^{-1}$, while the CoO nanowall-covered nickel foam has a surface area of $7.66 \text{ m}^2 \text{ g}^{-1}$.

Based from previously electrodeposit $\text{Ni}(\text{OH})_2$, the capacitances of the $\text{Ni}(\text{OH})_2$ generally drop sharply with increasing the discharge rate. We also tested the rate capacitance in our case, as shown in Figure 3.12b. We can see the electrodes of $\text{Ni}(\text{OH})_2$ nanolayers directly deposited on nickel foam has poor rate capability, as only 2.57% of capacitance is maintained when the discharge current increased eight times from 5 to 40 mA cm^{-2} . In contrast, for the hierarchical structure, 56.5% of the

Figure 3. 13 (a) Comparison of the charge-discharge behavior between the CoO nanowalls and the $\text{CoO@Ni}(\text{OH})_2$ at a same current density. (b) Galvanostatic charge-discharge curves of the $\text{CoO@Ni}(\text{OH})_2$ nanostructure electrode under different constant currents.

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capacitance (6.49 F cm^{-2}) is maintained with the same current change, indicating that a positive role has been played with the core-shell structure.

Another key parameter of supercapacitor is the cycling performance. Based on previously reports^{21, 145} and also shown by our own study, the Ni(OH)_2 nanolayers directly deposited on nickel foam are not electrochemically stable after long-time cycling. However, after hybridized with the CoO nanowalls, it is found that the capacitance of the coupled electrode decays much slower than the pure Ni(OH)_2 , as can be seen in Figure 3.14. When tested at a current density of 30 mA cm^{-2} , the hierarchical electrode holds a 68.9% capacitance retention after 5000 cycles, whereas the Ni(OH)_2 nanolayers alone has only 52.0% capacitance retention after 500 cycles.

Figure 3. 14 Cyclic performance of the three types of nanostructured supercapacitor electrodes

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We think that the highly pseudocapacitive $\text{Ni}(\text{OH})_2$ becomes more stable when coupled with another oxide rather than directly deposited on metallic current collectors. Thus the synergy can also be seen from the cycling stability.

3.4 Summary

To sum up, we developed another hierarchical core-shell nanostructure, based on 2D porous CoO nanowalls and $\text{Ni}(\text{OH})_2$ nanolayers. The porous CoO nanowalls are fabricated with hydrothermal method, and the $\text{Ni}(\text{OH})_2$ nanolayers are coated on the surface of CoO nanowalls by electrodeposition. With the hierarchical core-shell nanostructure design, the areal pseudocapacitance reaches up to $\sim 11.5 \text{ F cm}^{-2}$, which is much larger than the individual part: 2.3 F cm^{-2} for CoO and 1 F cm^{-2} for $\text{Ni}(\text{OH})_2$. Such ultrahigh areal capacitance of the nanohybrid electrode can be well raised from 1) the much increased surface areas, 2) the hierarchically porous structure, and 3) a synergetic effect between the two oxides. The structure provides another useful example for metal oxides to be utilized in supercapacitor electrodes. Also, it shows that this type of hybrid 3D nanostructure with cost-effective fabrication and promising electrochemical performance has great potential for electrochemical supercapacitor applications.

Chapter 4

Design of Core-Shell Nanostructure Electrodes: Hollow versus Solid Interface

4.1 Introduction

In previous two chapter, two kinds of hierarchical nanostructures have been designed and tested as supercapacitor electrode, one is fabricated by a two-step hydrothermal growth, the other is synthesised by hydrothermal and electrodeposition. The two supercapacitor electrode materials showed high specific capacitance, good rate capability and long cycling stability.

In this and next chapter, we will present two novel structures constructed with ALD, which is a newly developed coating method that can fabricate very uniform thin film.

As previously discussed, in the research on metal-oxide nanostructured electrodes for supercapacitors, the following strategies are often utilized and believed to be useful to obtain high electrochemical properties. The first direction is construct materials with high specific surface area, which is usually manifested by a porous/hollow feature^{21, 54, 61, 91, 102, 202-208}. The material with large porosity can provide easier electrolyte penetration, and the hollow center of the material can increase surface-to-bulk ratio, leading to more contact area between the active material and the electrolyte thus result in more efficient ion transport. In addition, the

porous/hollow structure can also lead to improved rate capability and cycling performance, because these void spaces could effectively buffer the strain which are generated during the fast charge/discharge process. The second useful strategy is to directly grow active nanomaterials of the metal oxides on current collectors^{55, 65, 209}. This method has been demonstrated to be a good way to ensure excellent mechanical connection and solid electric link of the active materials with the current collector, and this method can effectively avoid dead mass as zero polymer binders or conductive additives will be adopted. Last but not least, another useful strategy is to hybridize metal oxides with carbon, conductive polymer and other metal oxides thus construct them into core-shell structures. The hybridization has been proved as an effective way to achieve high performance supercapacitors, as it can effectively combine the merits of the individual components^{12, 60, 73, 145}. As been demonstrated, nanostructured $\text{MnO}_2@\text{NiO}$ ¹⁰⁵, $\text{Zn}_2\text{SnO}_4@\text{MnO}_2$ ⁷³ and $\text{CNT}@\text{MnO}_2$ ¹⁴¹ have been successfully fabricated and improved electrochemical performance which is better than the single component have successfully been achieved.

In this chapter, we intend to combine all these strategies into one structure under rational design of nanostructured metal oxides. With the help of ALD, which is a very useful method for surface engineering, we designed and fabricated a novel type of “wire in tube” electrode nanomaterial. We think the structure can fulfill nearly all the above favorable requirements. The achieved “wire in tube” structure have the following three parts: (1) a highly porous 1D metal oxide (CoO nanorod was used in this case) which is directly grown on conductive substrate serves as the core; (2) a

thin and uniform nanotube shell (TiO_2 in this case, but could be also other materials when the respective the ALD precursors are used) which can provide a stabilization protection to the inner structure serves as the tube shell¹⁵¹; and (3) a nanogap between the core and nanotube shell, which acts as “ion reservoir”. Here ALD is employed for surface coating of a sacrificial layer of Al_2O_3 (for the gap) and an outer TiO_2 nanotube shell. As reported, ALD is a very useful tool technique for surface engineering of electrode materials^{146, 210-214}.

In the following test, compared to the bare nanowire and the solid core-shell wires without gap, the “wire in tube” electrode have demonstrated larger surface area for electrochemical reaction, faster ion transportation and improved cyclic retention (mainly because the TiO_2 shell is very stable so to protect the core structure). In addition, the tube shell can also possibly contribute EDLC or pseudocapacitance to the whole capacitance. As a further demonstration, 2D metal oxide based “wall in box” structure with a gap is also tested and proved to be another good example. We think such unique core-shell “wire in tube” nanoarchitecture with a gap could be generalized to many other energy applications by proper choosing the core and hybridizing with different functionalized shell materials. And the data in this chapter can also provide the usefulness of ALD in nanofabrication and surface engineering of nanoscale electrode materials, which will be further discussed in the next chapter.

4.2 Experimental details

4.2.1 Material synthesis

Figure 4.1 Illustration of the fabrication process of the “wire in tube” structure of $\text{CoO}@\text{TiO}_2$.

The 3D hierarchical “wire in tube” electrode material was prepared by a three-step process, as illustrated in Figure 4.1) Firstly, the CoO precursor was synthesized on nickel foam by a hydrothermal process. For this, 2 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 10 mmol urea and 4 mmol NH_4F were dissolved in 50 mL deionized water, then the obtained homogeneous solution was transferred into Teflon-lined stainless steel autoclave with a piece of clean nickel foam ($20 \times 50 \times 0.1 \text{ mm}^3$, with upper side protected by uniform coating of polytetrafluoroethylene tape) immersed into the reaction solution at 120°C for 8 h growth. 2) The nickel foam with the

as-grown CoO nanostructure precursor was coated with Al₂O₃ followed by TiO₂ by ALD of different cycles using a Beneq system (TFS 200) at 120°C. Trimethylaluminum (Al(CH₃)₃), TiCl₄ and water were used as the aluminium, titanium and oxygen source, respectively. During the deposition process, a steady N₂ stream of 200 SCCM (cubic centimeter per minute) was lead into the reaction chamber, and the chamber pressure was maintained at 1.0 mbar. Each ALD cycle consisted of a 300-ms precursor pulse and 1-s purging time with N₂. 3) The substrates were immersed in a 0.1 M KOH solution in order to dissolve the Al₂O₃ sandwich layer. After that, the samples were annealed in Ar at 350 °C for 2 h. In the following, we use “CoO@TiO₂” to denote the hollow core-shell structure, and “CoO@TiO₂” for the solid core-shell structure.

Similar method was used for the preparation of NiO nanowall in TiO₂ nanobox structure. The NiO nanowall precursor was prepared by chemical bath deposition with a solution of nickel sulfate (80mmol), potassium persulfate (15mmol) and aqueous ammonia (25–28%, 20 ml) in a 150 ml beaker at room temperature reacted for 10 min.

4.2.2 Characterization

In order to show clearly the nanogap, before electron microscopy characterization, the top layer of TiO₂ was etched by a reactive ion etching process²¹⁰ for 35 s in a PECVD system (Plasmatherm 790 model). A mixture gas of CF₄–O₂ (55 sccm + 5 sccm) was employed with a RF power of 175 W and chamber pressure of 55 mTorr.

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Samples were characterized by scanning electron microscopy (SEM, JSM-6700F, 10.0 kV), and transmission electron microscopy (TEM) was performed using JEM-2010FEF (200 kV) equipped with an energy dispersive X-ray spectrometer (EDS). An AX/MX/UMX Balance (METTLER TOLEDO, maximum=5.1 g; delta = 0.001 mg) was used for the recording of the mass of electrode materials. Micromeritics TriStar 3000 porosimeter (mesoporous characterization) and Micromeritics ASAP 2020 (microporous characterization) were used for the measurement of Nitrogen adsorption/desorption isotherms (at 77 K). Before measurements, all samples were outgassed at 100 °C for 6 h under vacuum, and the specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) method.

4.2.3 Electrochemical measurement

Electrochemical measurements using a workstation (CHI 760D) were performed in a three-electrode electrochemical cell at room temperature using a 2 M KOH as electrolyte. The nickel foam supported nanostructure ($\sim 2 \text{ cm}^2$ area; CoO mass: $\sim 3.6 \text{ mg cm}^{-2}$; CoO@TiO₂ mass: $\sim 4.5 \text{ mg cm}^{-2}$, NiO mass: $\sim 0.5 \text{ mg cm}^{-2}$, and NiO@TiO₂ mass: $\sim 0.7 \text{ mg cm}^{-2}$) acted directly as the working electrode. A Pt plate and Hg/HgO were used as the counter electrode and the reference electrode, respectively. All potentials were referred to the reference electrode. The weight in specific capacitance (F g^{-1}) and current rate (A g^{-1}) was calculated based on the whole mass of the active materials (CoO, NiO and TiO₂), and the small contribution from the Ni foam was

subtracted. The specific capacitance is calculated by $C=It/m\Delta V$ and the areal capacitance is calculated by: $C_a=I\cdot t/(\Delta V\cdot S)$, where I is the discharge current, t is the discharge time, m is the mass of the active materials, ΔV is the voltage drop upon discharging, and S is the geometrical area of the electrode. Electrochemical impedance spectroscopy (EIS) results were measured by applying an AC voltage with 1 mV amplitude at open circuit potential. And the frequency range is from 0.1 Hz to 100 kHz

4.3 Results and discussion

4.3.1 Nanostructure of wire-in-tube design

SEM was used to examine the morphologies of the core-shell hollow nanorods, as shown in Figure 4.2. Figure 4.2a shows the bare CoO nanorods were covered uniformly on the substrate surface and the enlarged image from the inset of Figure 4.2a shows that the nanorods have porous feature. Figure 4.3a also illustrate large-scale SEM image of the sample. As reported, by solution methods the uniform growth of metal oxides on nickel foam have also been demonstrated in many literatures.^{18, 56, 57, 101, 215} After ALD coating of an Al₂O₃/TiO₂ bilayer (ALD cycles of 80/165 were used for all the following experiments), the naowires become thicker and smoother, as can be seen from Figure 4.3b-c. After removing the Al₂O₃ layer by KOH and annealing, the structure does not collapse (Figure 4.3d) but its hollow nature can be hardly inspected based on SEM images. In order to disclose the hollow structure, a thin top layer was removed by ion milling. One can see clearly the hollow

core-shell structure from Figure 4.2b and c, in which the porous CoO nanorod is enclosed by a thin tube layer but with a small gap.

Figure 4. 2 SEM images of (a) CoO nanorod, (b-c) “wire in tube” structure of CoO@TiO_2 . TEM images of (d) two CoO nanorods, and (e) “wire in tube” structure of CoO@TiO_2 .

TEM was also carried out to reveal the hollow structure more clearly. The porous CoO nanorod are assembled by numerous interconnected nanoparticles¹²², as can be revealed from Figure 4.2d. A typical TEM image the CoO@TiO₂ can be found in Figure 4.2e, which shows clearly that the porous CoO is enclosed by a thin and continuous layer of TiO₂ with a nanogap in between. And one can clearly see that both the tube layer of TiO₂ and the gap layer after removal of the ALD Al₂O₃ sandwich layer are uniform in thickness, which shows the uniformity and conformity of ALD.²¹⁶ However, direct coating of ALD TiO₂ on the CoO nanorods would only

Figure 4. 3 (a) Large-scale SEM image of CoO nanowire on nickel foam. SEM image of CoO nanowire after ALD coating of (b) TiO₂ (165 cycles), (c) Al₂O₃ (80 cycles) and TiO₂ (165 cycles). (d) SEM image of the structure after immersing in KOH.

result in solid $\text{CoO}@TiO_2$ core-shell structure but without nanopgap (TEM images can be found in Figure 4.4).

Figure 4. 4 TEM images of CoO nanowire after ALD coating of Al_2O_3 and TiO_2 with cycles of: (a) 80/55, (b) 50/110, (c) 20/110, (d) 0/110, (e) 0/165, and (f) 50/0. (g) Areal capacitance of the 9 structures with different cycles of ALD coating. We think 20 ALD cycles of Al_2O_3 will lead to the optimized gap thickness for supercapacitor (which is ~ 3 nm).

High-resolution TEM (HRTEM) was further used to investigate the atomic structure of the $\text{CoO}@TiO_2$ structure, as shown in Figure 4.5. Figure 4.5b-d are recorded from three different areas as marked in Figure 4.5a, from which we can see clearly the crystalline property of the structure. The core CoO has a cubic lattice distance of 0.21 nm corresponding to the (200) d-spacing. The lattice fringes of the outer shell shows a distance of about 0.35 nm, which matches the (101) planes of anatase TiO_2 . These values matches well with previous reported ones for hydrothermal grown CoO nanorods⁶⁴ and the TiO_2 tubes by

ALD.²¹⁷ One thing to notice is that in our experiment no solid state reactions between the three materials (towards the alloy formation) has happened at the relatively low deposition temperature (120°C in the case).^{217, 218}

Figure 4. 5 HRTEM characterization of a typical CoO@TiO_2 “wire in tube” structure.

By BET measurement, the hollow core-shell structure shows higher surface areas than the bare nanowire and solid core-shell nanostructure. As calculated, the surface area of the bare CoO nanowires on nickel foam is $7.28 \text{ m}^2 \text{ g}^{-1}$. After the hollow design, the hollow core-shell structure has an increased surface area of $11.63 \text{ m}^2 \text{ g}^{-1}$.

Figure 4. 6 (a) CV curves of CoO, CoO@TiO₂ and CoO@TiO₂. (b) Charge-discharge curves of CoO and CoO@TiO₂ at different current densities.

In contrast, if we directly coat of TiO₂ on the porous CoO nanowire, the surface area will be reduced to 5.63 m² g⁻¹. Based on BET result, the CoO@TiO₂ would be able to have a larger surface in contact with electrolyte, which would be beneficial to its electrochemical properties.

4.3.2 Electrochemical property of the wire-in-tube electrode

In order to test whether the gap would contribute improved properties, in the following the electrochemical properties of the “wire in tube” structure were investigated. In Figure 4.6a, the CV curves of the three structures are illustrated: CoO, CoO@TiO₂ and CoO@TiO₂. The CoO has two pairs of redox peaks in the CV curve:

$\text{CoO} + \text{OH}^- \leftrightarrow \text{CoOOH} + \text{e}^-$ and $\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^-$, which is consistent to the previous report¹²³. From the CV curve of the CoO@TiO₂, we can see that after direct coating of TiO₂, the enclosed area of the CV curve is decreased, this may due to the close coating where less active materials would react with the electrolyte. In contrast, for the CV curve of the hollow core-shell CoO@TiO₂, the enclosed area is larger than the bare CoO nanorod one, which indicates its areal

Figure 4. 7 (a) Charge-discharge curve of the three structures (CoO, CoO@TiO₂ and CoO@TiO₂) at the same current density of 10 mA cm⁻². (b) Rate capability of the CoO and CoO@TiO₂. The percentage numbers denote the capacitance retention when the current is increased from 5 to 40 mA cm⁻². (c) Electrochemical impedance spectroscopy of the three structures. (d) Cycling stability of the CoO and CoO@TiO₂. The percentage numbers denote the capacitance retention after 5000 cycles of charge-discharge.

capacitance is increased. In addition, from the CV curve, the current densities of the CoO@TiO₂ hollow core-shell wires are higher than those of bare CoO and CoO@TiO₂, implying it has better electrochemical reactivity with the electrolyte. Although from previous reports that TiO₂ has a low pseudocapacitance in electrochemical test^{116, 219,}

²²⁰, the structure of CoO@TiO₂ still shows an areal capacitance which is 52.4 %

higher than bare CoO sample, and the specific capacitance calculated based on mass is also increased from 518.9 F g⁻¹ to 633.3 F g⁻¹.

Charge-discharge tests in Figure 4.7a also show similar results. As can be seen from Figure 4.7a, at the same areal current density of 10 mA cm⁻², the areal specific capacitance of the solid core-shell CoO@TiO₂ is calculated to be only 0.745 F cm⁻², which is only 39.8 % of that of bare CoO (1.87 F cm⁻²). In contrast, the hollow “wire in tube” structure achieves a higher specific capacitance of 2.85 F cm⁻², which is 3.83 times of that for the CoO@TiO₂. In addition, the specific capacitance shows the same trend. Calculated based on the mass of the three electrodes, the specific capacitance of the hollow structure is the largest, and the specific capacitance of CoO, CoO@TiO₂ and CoO@TiO₂ is 518.9, 187.7 and 633.3 Fg⁻¹, respectively. Figure 4.6b-c illustrated the charge-discharge curves of the CoO and CoO@TiO₂.

Figure 4.7b shows the rate capability, from which we can see the rate capability of the CoO@TiO₂ is also improved. As indicated from Figure 4.7b, the CoO@TiO₂ has a 63.3 % capacitance retention when the current density increased from 5 to 40 mA cm⁻², and for bare CoO, the capacitance retention is only 53.9 % with the same increase. This data demonstrate the structure of CoO@TiO₂ can better maintain the reaction with electrolyte even in fast charge-discharge processes.

Electrochemical Impedence Spectroscopy (EIS) is also carried out as a useful method to evaluate the electrochemical property of the three structures. Figure 4.7c shows the results of EIS of the three materials. In the high frequency region, the

charge-transfer resistance at the electrode/electrolyte interface is revealed by the diameter of the semicircle. As the structure of CoO@TiO₂ shows the smallest radius, it is reasonable to say that the hollow structure is most suitable for charge transport in the electrolyte. While the structure of CoO@TiO₂ shows the largest charge-transfer resistance, which may be because the solid TiO₂ shell would retard the charge transfer to the inner material. In addition, in the low frequency regime, the hollow structure of CoO@TiO₂ also displays a more ideal straight line along the imaginary axis, which means its diffusion resistance is the lowest. In all, EIS measurement illustrates the low diffusion and electron-transfer resistances of the CoO@TiO₂, which are in good accordance with its electrochemical properties previously.

Finally, the cycling stability has been tested as one of key issues for the evaluation of the supercapacitor electrode materials. As shown in Figure 4.7d, the bare CoO itself has a very good stability with 89.7 % capacitance retention after 5000 cycles at 10 mA cm⁻². However, the hollow structure shows even better performance, at a higher current density of 20 mA cm⁻², the CoO@TiO₂ shows slightly better capacitance retention of 95.1 % after 5000 cycles.

With the above electrochemical data of the hollow structure, we believe the enhancement in pseudocapacitive performance of the “wire in tube” structure can be aroused from the following three possible directions.

Firstly, the nanogap can effectively provide a spatial confinement to the electrolyte between the CoO core and ALD shell. The gap structure can ensure a close

contact between CoO and the electrolyte, which is beneficial to rapid ion transport. In this situation, the gap serves well as an “ion reservoir” enabling a relatively stable supply of OH^- even at high current densities. This point can well explain the improved rate capability of CoO@TiO_2 , as shown in Figure 4.7b. With this explanation, for the solid core-shell wires, the dense ALD TiO_2 layer would create a diffusion barrier (but not block) for the OH^- ions to reach the inner CoO core, so the CoO@TiO_2 sample has the largest charge-transfer resistance in EIS test.

Secondly, due to the construction of the thin nanotube wall, the specific surface area is also increased. As reported, a conformal coating of shell material can increase the surface area several times²²¹. Also, if the TiO_2 nanotube shell could be connected to the CoO core at any point, it can effectively contribute to pseudocapacitance in a similar way to the AC-based EDLCs²²⁰.

Finally, as reported, TiO_2 is a quite stable electrochemical material (Note the recent increasing interests in nano TiO_2 in Li-ion battery^{222, 223}). We think in the hollow structure, the thin and conformal ALD TiO_2 shell can effectively protect the core materials from structural deterioration during long-time charge/discharge process. This point can be demonstrated by the improved capacity retention of the hollow core-shell CoO@TiO_2 nanowires compared to the bare CoO nanorods (shown in Figure 4.7d).

As a further demonstration of the usefulness of ALD, several similar “wire in tube” structures with different thickness of the hollow layer and the tube layer can be

easily obtained (with typical TEM images shown in Figure 4.4a-f) just by changing the ALD cycles of Al_2O_3 and TiO_2 . In electrochemical test, all of these “wire in tube” structures prove improved performance in charge-discharge tests than the bare CoO nanorods, indicating the improvement with the gap design. And the structure with 20/110 ALD cycles of $\text{Al}_2\text{O}_3/\text{TiO}_2$ obtains the largest areal capacitance (shown in Figure 4.4g).

4.3.3 Wall-in-box nanostructured electrode

In order to test the generality of the nanogap design, another hollow core-shell structure of “wall in box” was fabricated based on NiO nanowalls. From the SEM image in Figure 4.8a, we can see the NiO nanowalls are vertical aligned on the current collector and have an interconnected feature. With a similar gap construction procedure to the above hollow $\text{CoO} @ \text{TiO}_2$ (i.e., ALD coatings of Al_2O_3 and TiO_2 followed by removal of Al_2O_3), the NiO nanowalls become thicker, as can be seen from Figure 4.8b. Inset of Figure 4.8b shows clearly the nanogap after ion milling. The hollow “wall in box” of $\text{NiO} @ \text{TiO}_2$ has also been tested as supercapacitor electrode. Figure 4.8c-d shows the CV and CD curves of NiO, $\text{NiO} @ \text{TiO}_2$, and $\text{NiO} @ \text{TiO}_2$. We can see that the hollow structure also demonstrate an increased areal capacitance compared to the solid core-shell one and bare NiO. Furthermore, as shown in Figure 4.9a, the rate capability of $\text{NiO} @ \text{TiO}_2$ has also increased (with a 64.3% capacitance retention when the current increased 10 times) compared to the bare NiO nanowall (with only 58.4% capacitance retention). Finally, better cycling stability is

also demonstrated, which can be seen from Figure 4.9b. In all, the improved electrochemical performance is in consistent with that of the porous nanowires, which serves as another demonstration of the advantages of the hollow core-shell structure design.

Figure 4. 8 SEM images of (a) NiO nanowall, and (b) “wall in box” structure of NiO@TiO₂. (c) CV and (d) Charge-discharge curve of the three structures (NiO, NiO@TiO₂ and NiO@TiO₂). (e-f) Schematics of the NiO nanowall and NiO@TiO₂ wall-in-wall structure.

Figure 4. 9 (a) rate and (b) cycling behavior of NiO, and NiO@TiO₂

Finally, we think the hollow electrode design can be better improved with further action, as the materials for the gap layer and outer shell are not limited to Al₂O₃ and TiO₂, respectively. For example, the TiO₂ shell could be replaced with carbon, or more electrochemical active oxides such as NiO and Co₃O₄. We believe better performance can be achieved if such pseudocapacitive shell can be also coated by ALD.

4.4 Conclusion

To conclude, in this chapter we have designed a novel hierarchical hollowed core-shell structure utilizing ALD, and successfully demonstrated its usefulness for electrochemical energy storage application. Two structures of “wire in tube” and “wall in box” have been fabricated and tested as typical examples. As been demonstrated, the hollow core-shell electrode with nanogap has evidently higher areal capacitance than the solid core-shell nanorods without gap or the bare core. And improved rate capability and cycling ability have also been achieved. These improvement is due to the the nanogap structure, which can provide increased

reaction area and facilitates the electrolyte contact with the active material, and the outlayer tube layer, which can effectively preserve the structure integrity after long-time cycling. We think such hollow core-shell nanostructure represents an effective way to improve the electrochemical of metal oxide-based supercapacitors. And we also think further improvement in the supercapacitor properties can be expected by carefully choosing more electrochemical active shell material (such as NiO) and fine adjustment of the gap thickness.

Chapter 5

ALD-Assisted Carbon Nanoflakes and Their Role in Electrochemical Energy Storage

5.1 Introduction

Following the research work in Chapter 4, here we show another example of fabricating core-shell structures with ALD. In this work, nanostructured carbon flakes have been obtained directly on metal oxides surface, which has not been reported before. As mentioned in the Introduction part, nanostructured carbon materials, including activated carbons (ACs), carbon nanotubes (CNTs) and graphene, are being widely studied in energy-related areas (such as solar cells, fuel cells, lithium-ion batteries, and supercapacitors) because of their favored properties including low cost, large specific surface area, high electric conductivity, and environment benignity.^{138, 224} Therefore, fabrication of advanced carbon-based materials with good electrical conductivity and tunable nanostructuring (e.g., porous, thin membranes) has become highly desirable for the application in energy conversion and storage devices. Supercapacitors represent an emerging and promising energy storage device that can combine the advantages of the high specific energy of rechargeable batteries and the high power density of electrostatic capacitors.^{6, 15, 225} Carbonaceous materials are the most widely studied electrode materials for high-performance supercapacitors. Previously, The Ruoff group obtained highly porous carbon by chemical activation of exfoliated graphite oxide with KOH,¹⁹⁸ which exhibited a continuous

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three-dimensional network feature and an ultrahigh surface area of up to 3100 m²/g.

In the supercapacitor test, the porous carbon electrodes showed a high power density of ~250 kW/kg while maintaining an energy density of above 20 Wh/kg at the same time.

Two main strategies have been reported for programmed construction of different carbon-metal oxide hybrids^{141, 228-231}: carbon loaded with metal oxides, and carbon coating on metal oxides. In the first strategy, 1D CNTs and 2D graphene have been extensively studied as ideal conductive connections to load metal oxides. For example, porous CNTs with high conductivity and high surface area was coated with V₂O₅ by ALD.⁷² As a result, significantly increased electrochemical performance was achieved with the hybrid structure. Activated expanded 2D graphene oxide has also been used as a conductive matrix to incorporate MnO₂ nanoparticles to achieve increased energy density.²³² In the second strategy, fabricating metal oxides with uniform conductive carbon coating is also a good method to achieve combined properties. For example, the electrochemical properties of Graphene/MnO₂ nanostructure could be tremendously improved by wrapping of single wall carbon nanotubes or conductive polymers.^{151, 233} The conductive materials are believed to enhance electron transport and contribute more electric double layer capacitance (EDLC) or pseudocapacitance. Uniform amorphous carbon coating (thickness below 10 nm) by carbonization of glucose and sucrose absorbed on the surface of metal oxides has been reported for Li-ion battery electrodes.^{107, 152}

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Herein, we developed a general method to prepare unique carbon nanoflakes directly on the surface of various metal oxides by combining ALD Al_2O_3 and carbonization of glucose. The carbon nanoflakes are uniform grown on the substrate surface with width (up to 200 nm) depending on the ALD Al_2O_3 thickness. In electrochemical application, the coating of carbon nanoflakes contribute to increased conductivity of the electrode, more surface areas, and also new capacitance via EDLC, resulting in drastically improved electrochemical properties. This discovery opens a new way of carbon hybridization in various electrochemical energy conversion devices, as well as new energy application of ALD.

5.2 Experimental Section

5.2.1 Material Synthesis.

The hierarchical electrode material was prepared by a three-step process. Take 1D CoO nanowire based structure as an example. *First*, the precursor of $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires was synthesized on nickel foam by a hydrothermal process. For this, 2 mmol $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 10 mmol urea and 4 mmol NH_4F were dissolved in 50 mL deionized water, then the obtained homogeneous solution was transferred into Teflon-lined stainless steel autoclave with a piece of clean nickel foam ($20 \times 50 \times 0.1 \text{ mm}^3$, with upper side protected by uniform coating of polytetrafluoroethylene tape) immersed into the reaction solution at 120°C for 8 h growth. *Second*, the nickel foam with the starting material of $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires was coated with Al_2O_3 of different cycles by ALD (Beneq, TFS 200) at 120°C . Trimethylaluminum $\text{Al}(\text{CH}_3)_3$

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and water were used as the aluminum and oxygen source, respectively. *Finally*, the Al_2O_3 coated structures were immersed in 0.04 M glucose for 24 h and annealed in Ar at 450 °C for 2 h. The Al_2O_3 was removed before the electrochemical test in 1M KOH.

ZnO nanowire was grown on nickel foam by suspending clean nickel foam in a 200 mL aqueous solution containing 0.035 M $\text{Zn}(\text{NO}_3)_2$ and 0.65 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ at a constant heating temperature of 70 °C for 24 h.²³⁴

SnO_2 nanowires were obtained by CVD growth using equal amount of SnO_2 powder and graphite powder as source and Au sputter-coated Si as substrates. The growth was conducted with temperature ramped to 1050 °C at a rate of 50 °C /min and kept for 1 h under a constant argon flow (50 sccm) and pressure (15 mbar).²³⁵

To grow the NiO nanoflakes, 5 mmol of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 25 mmol urea and 10mmol NH_4F were dissolved in 100ml distilled water, then the obtained homogeneous solution was transferred into Teflon-lined stainless steel autoclave with a clean nickel foam immersed into the reaction solution at 120 °C for 5 h growth. After that, the sample was annealed in Ar at 450 °C for 2 h.⁶⁵

5.2.2 Material Characterization.

Samples were characterized by scanning electron microscopy (SEM, JSM-6700F, 10.0 kV), and transmission electron microscopy (TEM) was performed using JEM-2010FEF (200 kV) equipped with an energy dispersive X-ray spectrometer (EDS). An AX/MX/UMX Balance (METTLER TOLEDO, maximum=5.1 g; delta =

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0.001 mg) was used for the recording of the mass of electrode materials. Micromeritics TriStar 3000 porosimeter (mesoporous characterization) and Micromeritics ASAP 2020 (microporous characterization) were used for the measurement of Nitrogen adsorption/desorption isotherms (at 77 K). Before measurements, all samples were outgassed at 100 °C for 6 h under vacuum, and the specific surface areas of the samples were calculated using the Brunauer-Emmett-Teller (BET) method.

5.2.3 Electrochemical Characterization.

Electrochemical measurements using a workstation (CHI 760D) were performed in a three-electrode electrochemical cell at room temperature using 2 M KOH as the electrolyte. The nickel foam supported nanostructures (~2 cm² area; CoO mass: ~3.6 mg cm⁻²; CoO@*f*-C mass with 80 cycles of Al₂O₃: ~4.0 mg cm⁻², CoO@C mass: ~3.7 mg cm⁻²) were used directly as the working electrode. A Pt plate and Hg/HgO were used as the counter electrode and reference electrode, respectively. All potentials were referred to the reference electrode. The weight in specific capacitance (F/g) and current rate (A/g) was calculated based on the whole mass of the active materials (CoO and carbon), and the small contribution from the Ni foam was subtracted. The specific capacitance was calculated by $C = It/m\Delta V$ and the areal capacitance is calculated by: $C_a = I \cdot t / (\Delta V \cdot S)$, where I is the discharge current, t is the discharge time, m is the mass of the active materials, ΔV is the voltage drop upon discharging, and S is the geometrical area of the electrode.

5.3 Results and Discussion

Figure 5. 1 SEM images of (a) CoO and (b) CoO@f-C nanowires. (c-d) TEM images corresponding to top row. (a) and (b), (c) and (d) share the same scale bar.

5.3.1 Generic growth of carbon nanoflakes.

Figure 5. 2 SEM images of (a) CoO nanowires and (b) CoO@ f-C nanostructures. (a) and (b) share the same scale bar.

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We first use 1D CoO nanowires as the example for discussion. Typical electron micrographs of the CoO nanowires and the nanowires coated with ALD Al₂O₃ induced carbon flakes (labelled as CoO@*f*-C) are shown in Figure 5.1. The SEM image clearly shows that the CoO nanowires (derived from annealing Co₂(OH)₂CO₃ pre-form nanowire in Ar) are highly porous, with diameters of ~60–100 nm and length of ~1 μm, consistent with our previous report.¹²³ Note that these nanowire arrays grow directly on conductive substrates, which is regarded as beneficial to improving the conductive connection between the active material and current collector, and reducing the “dead volume” and resistance possibly caused by the polymer binder.^{52, 124, 130, 236} Figure 5.1b shows the CoO nanoarray coated with carbon nanoflakes, for which the starting material is also Co₂(OH)₂CO₃, but has been subjected to ALD of Al₂O₃, immersing in glucose solution and post annealing in Ar. The carbon coating does not change the morphology and alignment of the nanoarray, which can also be seen from the large scale SEM view in Figure 5.2. TEM image in Figure 5.1c shows the pure CoO nanowire has a porous structure containing interconnected nanocrystallites. For the CoO@*f*-C hybrid sample (Figure 5.1d), the surface of CoO is uniformly covered with thin flakes extending to a width up to 100 nm, forming a core-branch nanostructure. Note that the alumina after the annealing process has been removed by etching in basic solution. The remaining carbon flakes maintain a robust connection with the CoO core, which would otherwise peel off easily during TEM sample preparation.

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Figure 5. 3 (a) TEM image and (b-e) element mapping results of two typical $\text{CoO}@f\text{-C}$ hybrid nanowires. (f) Corresponding EDX results recorded from selected area in (a). The dashed lines indicate the outline of CoO core. (g) TEM and EDS mapping after removing the Al_2O_3 .

Elemental mapping result of the $\text{CoO}@f\text{-C}$ prior to removal of the alumina is shown in Figure 5.3. After the ALD Al_2O_3 and glucose carbonization process, the elements of Al and C are uniformly distributed around the Co, which confirms the existence and homogeneous coating of carbon on the CoO surface. Interestingly, the

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Al_2O_3 is also expanded outwards during the annealing process, in contrast to its initial smooth coverage directly on the surface of $\text{Co}_2(\text{OH})_2\text{CO}_3$ (see TEM in Figure S2c). From the EDX result in Figure 5.3f, the molar ratio of O, Al, and Co is determined to be 5.44 : 2.97 : 1. Considering that the O and Co has a ratio of 1:1, the molar ratio of Al and O is 1.49.

In order to further understand the change in the morphology and the formation mechanism of the core-branch heteronanostructure, control experiments were conducted by using different starting materials and ALD Al_2O_3 thicknesses. The corresponding results are summarized in Figure 5.4. The start precursors in (a) and (b) are CoO, whereas for the rest experiments are $\text{Co}_2(\text{OH})_2\text{CO}_3$. The ALD cycle is proportional to the thickness of resulting Al_2O_3 layer. By careful inspection of Figure 5.4, one can deduce the following three results:

First, the ALD Al_2O_3 layer plays the decisive role to the formation of flake carbon. As seen from Figure 5.4 (a) and (c), without the Al_2O_3 , the carbon layer obtained by glucose carbonization is not flake-like but has a thickness of only ~2–10 nm,^{122, 152} independent of the starting material. This implies a strong interaction between Al_2O_3 and the glucose layer. **Second**, the decomposition of $\text{Co}_2(\text{OH})_2\text{CO}_3 \rightarrow \text{CoO} + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$ also contributes to the expansion of Al_2O_3 and carbon by releasing $\text{H}_2\text{O}(\text{g})$ and $\text{CO}_2(\text{g})$ during the annealing process.^{18, 64} When the precursor is changed to CoO with the same ALD Al_2O_3 cycle, carbon nanoflakes

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Figure 5. 4 Summary of the carbon coating results from different starting materials and ALD Al_2O_3 coating cycles. (b-f) share the same scale bar.

can also be observed but with a smaller width (see Figure 5.4b). **Third**, the overall width of the nanoflake carbon branches is evidently dependent on the ALD Al_2O_3

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thickness. As shown in Figure 5.4 (d-f) where the Al_2O_3 coating cycles are 40, 80 and 120, the resulting carbon nanoflake branches have thickness of ~ 50 , ~ 100 , and up to ~ 200 nm, respectively. Furthermore, it is noted that the expansion of Al_2O_3 is induced by its reaction with glucose. Without glucose immersing, the annealing of $\text{Co}_2(\text{OH})_2\text{CO}_3@ \text{Al}_2\text{O}_3$ core-shell nanowires under the same condition caused the formation of hollow pores within the Al_2O_3 layer, but without the occurrence of interface reaction or expansion of Al_2O_3 (see TEM images in Figure 5.5).

On the basis of above results, the formation process for the $\text{CoO}@f\text{-C}$ nanostructure can be proposed as follows (see also the schematics in Figure 5.6). First, the $\text{Co}_2(\text{OH})_2\text{CO}_3$ is uniformly covered with amorphous Al_2O_3 by ALD, and after immersing it in glucose, the glucose can penetrate into the Al_2O_3 layer, forming a composite shell. The composite shell was further confirmed by EDX line scan across a $\text{Co}_2(\text{OH})_2\text{CO}_3@ \text{Al}_2\text{O}_3$ core/shell nanowire after immersing in glucose (Figure 5.7). Further supporting evidence is that, if the ALD and glucose processes were inversed, only a three-layer nanowire was formed but no such alumina-glucose composite shell. In this case, after annealing, a nanogap was produced within the $\text{Co}_3\text{O}_4@ \text{Al}_2\text{O}_3$ core/shell nanowires (see Figure 5.7). In the following annealing process, the glucose carbonizes and also interacts with the Al_2O_3 , causing a simultaneous expansion of the Al_2O_3 . During this process, the carbon deposits on the expanding Al_2O_3 skeleton. In the meantime, the decomposition of $\text{Co}_2(\text{OH})_2\text{CO}_3$ to CoO will also accelerate the expansion of the composite shell by releasing gas molecules outward. The detailed

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reaction between glucose and Al_2O_3 is unclear at this stage. The interaction of Al_2O_3 with carbon is a known nuisance in many catalyst reactions with coke formation

Figure 5. 5 (a-b) TEM images of $\text{CoO@Al}_2\text{O}_3$ from annealing with $\text{Co}_2(\text{OH})_2(\text{CO}_3)_2\text{@Al}_2\text{O}_3$. The pores demonstrate the release of $\text{H}_2\text{O}(\text{g})$ and $\text{CO}_2(\text{g})$ during the decomposition of $\text{Co}_2(\text{OH})_2(\text{CO}_3)_2$, while the Al_2O_3 is not expanded. (c-d) TEM images of $\text{Co}_2(\text{OH})_2(\text{CO}_3)_2\text{@Al}_2\text{O}_3$ with glucose immersing time of 0 h and 24 h without annealing, showing the structure is not expanded before glucose carbonization.

(non-removable carbonaceous deposits on catalyst surface that reduces the catalytic activity).²³⁷ Annealing time-dependent experiments were also conducted in order to reveal the expansion more clearly (see results in Figure 5.8). After removing the Al_2O_3 by KOH, the porous carbon nanoflakes are formed. We believe the expansion of Al_2O_3 here is quite unique, as it creates more space for carbon to load which resulted in higher mass loading of carbon (~4 times with 80 ALD cycles) compared

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with the carbon coating with no ALD Al_2O_3 . In addition, the carbon nanoflakes are also in contact with each other and with the CoO core, which explains why the hierarchical structure of $\text{CoO}@f\text{-C}$ is fully maintained after removing the Al_2O_3 .

Figure 5. 6 Schematics of the formation process of the $\text{CoO}@f\text{-C}$ hybrid nanostructures in a comparison to $\text{CoO}@\text{C}$. (a) ALD coating of Al_2O_3 . (b) Immersion in glucose solution for 24 h. (c) Annealing at 450°C in argon atmosphere for 2 h. (d) Removal of alumina in KOH solution (can be also done just before the electrochemical measurement with KOH electrolyte).

Figure 5. 7 (a) SEM image of one typical $\text{Co}_2(\text{OH})_2\text{CO}_3@\text{Al}_2\text{O}_3$ core/shell nanowire. (b) The EDX line-scan across the nanowire. In order to reveal clearly the composite layer of Al_2O_3 with glucose, the ALD Al_2O_3 is intentionally thick (50 nm) and the immersing time in glucose is 24 h. (c) TEM image of the a core/shell nanowire obtained after immersing the $\text{Co}_2(\text{OH})_2\text{CO}_3$ nanowires in glucose, followed by ALD Al_2O_3 and annealing. In this case, the glucose does not form a composite layer with alumina. After annealing, a nanogap is produced within the $\text{Co}_3\text{O}_4@\text{Al}_2\text{O}_3$ core/shell nanowires.

The XRD results of the three structures, viz., CoO, $\text{CoO}@f\text{-C}$, and CoO with thin-film carbon coating (labelled as $\text{CoO}@\text{C}$), are shown in Figure 5.9a. The XRD pattern of the bare CoO nanowires obtained from annealing in Ar atmosphere corresponds to CoO (JCPDS, card no: 48-1719).²³⁸ After carbon coating, no apparent new peak appeared for both $\text{CoO}@\text{C}$ and $\text{CoO}@f\text{-C}$, implying that the coated carbon are amorphous. Figure 5.9b shows the Raman spectra of the three samples in the 400–2000 cm^{-1} region. CoO, $\text{CoO}@f\text{-C}$ and $\text{CoO}@\text{C}$ spectra exhibit the same pattern

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in the range of 400–1000 cm^{-1} , corresponding to the CoO core. In the region of 1000–2000 cm^{-1} , CoO@f-C and CoO@C showed two strong carbon-related peaks at $\sim 1598 \text{ cm}^{-1}$ (G band) and 1366 cm^{-1} (D band). BET measurement was also carried out to determine the surface areas of the samples. The surface area of bare CoO nanowires on nickel foam is $6.68 \text{ m}^2/\text{g}$. For the CoO@f-C sample, the surface area increases to $13.05 \text{ m}^2/\text{g}$. The increased surface area by the nanoflake carbon branches is expected to increase the effective contact with the electrolyte and provide more EDLC in the supercapacitor application.

Figure 5. 8 Annealing time-dependent morphology change. TEM images of the $\text{Co}_2(\text{OH})_2\text{CO}_3$ @composite layer after annealing at the peak temperature of 450°C for (a) 0, (b) 10, and (c) 20 min, respectively. Note that it takes about 20 min to ramp from room temperature to 450°C , and in fact the decomposition of glucose can occur below 450°C .

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The ALD Al_2O_3 assisted formation of nanoflake carbon coating can be also performed on a wide range of substrates. For their potential applications in optoelectronics and energy storage, ZnO , SnO_2 and Si nanowires were used as the starting materials and the obtained hybrid structures are shown in Figure 5.10. After the same ALD Al_2O_3 induced carbonization process, both ZnO and SnO_2 nanowires have their surface uniform coated by carbon nanoflakes, similar to the case of CoO nanowires shown in Figure 5.4b. As for the Si nanowires, the obtained carbon layer is somewhat different, which is thinner and more porous than the one for oxide nanowires.

Figure 5. 9 (a) XRD and (b) Raman results of the three structure: CoO , CoO@C , and CoO@f-C .

As another example, wide sheets of porous NiO obtained from annealing $\text{Ni}_2(\text{OH})_2\text{CO}_3$ nanosheets was used as the starting material. The same ALD-assisted carbonization process lead to uniform coverage with carbon nanoflakes, forming NiO@f-C hybrid nanosheets (see Figure 5.10d). Such wide nanosheets should be of interest for supercapacitor application. Finally, commercial white sugar was used as a

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different source of carbon for the same experiment. Similar carbon shell is obtained except for a different morphology of the porous carbon layer (see Figure 5.11). In all, the demonstrated formation of carbon nanoflakes on 1D and 2D templates illustrate the versatility of our new nanocarbon coating method.

Figure 5. 10 Growth of carbon nanoflakes on other starting nanostructures. (a) ZnO nanowire, (b) SnO₂ nanowire, (c) Si nanowires, and (d) NiO two-dimensional flakes.

Inset: enlarged view.

5.3.2 Supercapacitor application.

As the carbon nanoflake layer introduces substantial amount of new surface areas for EDLC and improves electrical conductivity, it is interesting to study the electrochemical properties of the MO@f-C hybrid nanoarrays. In the following we

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take 1D CoO nanowire array as the supercapacitor anode for a demonstration study.

The CoO@*f*-C was obtained from 80 cycle ALD Al₂O₃. Figure 5.12a shows the CV curves of the three electrodes: bare CoO, CoO@C, and CoO@*f*-C. After the normal glucose carbonization without ALD Al₂O₃, the enclosed area of the CV curve is only slightly increased compared to that of the bare CoO. This indicates that such thin (<10 nm) layer has a negligible EDLC contribution. As for the sample with nanoflake carbon coating, the CV curve is evidently expanded, indicative of an increase in capacitance.

Figure 5. 11 Nanoporous carbon layer formation using white sugar as carbon source instead of glucose. The starting material is Co₂(OH)₂CO₃ nanowire.

The galvanostatic charge/discharge behavior also shows a similar trend. As shown in Figure 5.12b, at the same scan rate of 10 mA/cm², the CoO@C exhibits a mass specific capacitance of 476.5 F/g, which is just slightly higher than CoO (452.8 F/g). In contrast, the CoO@*f*-C sample demonstrates a specific capacitance of about

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930.9 F/g, nearly double that of bare CoO. In terms of areal capacitance, the value increases from 1.63 F/cm² for the CoO to 3.72 F/cm² for the CoO@f-C. From the plot of capacitance versus ALD Al₂O₃ cycle (Figure 5.13), one can see the capacitance

Figure 5.12 Application of the hybrid CoO@f-C nanowires as the supercapacitor electrode. (a) CV curves of three types of samples at a scan rate of 10 mV/s. CoO: pristine porous CoO nanowires; CoO@C: CoO nanowires coated with <10 nm carbon layers by conventional glucose carbonization; CoO@f-C: CoO nanowires coated with carbon nanoflakes with 80 ALD cycles of Al₂O₃. (b) Charge-discharge curves at a current rate of 10 mA/cm². (c) Rate capability of CoO and CoO@f-C. (d) Cyclic test results.

increases almost linearly with ALD cycle (i.e., Al₂O₃ thickness), which is a result of continuous increase of the surface areas of the carbon flakes.

Figure 5. 13 (a) Charge-discharge curves and (b) Specific capacitance and areal capacitance of CoO@f-C with different Al_2O_3 cycles of 0, 40, 80 and 120.

In order to understand the rate capability, the charge-discharge current was varied from 5 to 40 mA/cm² and data were shown in Figure 5.12c. The bare CoO keeps 60% of its capacitance when the current is increased 8 times, while the capacitance retention of CoO@f-C is nearly 70%.

Figure 5. 14 Charge-discharge curves at different current densities of (a) CoO and (b) CoO@f-C with 80 cycles of ALD Al_2O_3 coating.

Figure 5. 15 Electrochemical impedance spectroscopy of the three structures. *CoO@f-C* shows the least charge-transfer resistance (the smallest radius) which accounts for its good conductivity.

This suggests that the CoO@f-C hybrid structure is more capable to maintain stable reactions with the electrolyte at high charge-discharge currents. As a consequence, when the current density is 40 mA/cm^2 , the CoO@f-C demonstrates an areal capacitance 149% of that of bare CoO nanowires, which is higher than that (129%) at 10 mA/cm^2 . The charge-discharge curves of CoO and CoO@f-C at various current densities can be seen from Figure 5.14.

The cycling ability is also enhanced by the flake carbon coating. As shown in Figure 5.12d, for bare CoO nanowires, at a lower current (10 mA/cm^2) of charge-discharge, the capacitance retention after 5000 cycles is 87.1%. In contrast, the CoO@f-C has only less than 2% loss of capacitance after even at a higher current density of 20 mA/cm^2 . This demonstrates its excellent cycling stability as enabled by the carbon coating. In addition, electrochemical impedance spectroscopy (EIS) data

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also revealed the improved charge conductivity of the electrode due to the carbon coating (see Figure 5.15).

The above demonstrated enhancement of electrochemical performance of the CoO@f-C core-shell nanostructure electrode could be understood as follows. Due to its thin membrane structure, the carbon nanoflake shell increases the total surface area and consequently the contribution of EDLC. Also, its good electrical conductivity and robust connection with CoO core lead to full contact of both the CoO core and carbon shell with the electrolyte, realizing an efficient utilization of the electrode materials. Finally, the rigid core-shell structure (which does not collapse after sonication during TEM sample preparation) accounts for its increased reaction reversibility and rate capability.

5.4 Conclusion

A new carbonization method has been discovered for the generation of carbon nanoflakes on metal oxides as a new type of hybrid nanostructures for energy storage applications. This method starts with the formation of an ALD Al₂O₃ and glucose composite layer. Thermal-induced decomposition glucose will cause expansion of the ALD Al₂O₃, and deposition of carbon on the expanding Al₂O₃. The nanoflakes width is controllable by the ALD thickness. Importantly, the process can be realized nearly on any solid substrate, so long as it can survive in a mild Al₂O₃ etching solution. Furthermore, a metal carbonate starting material has an accelerating effect to the formation of carbon nanoflakes due to gas release. The demonstrated unique ALD

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Al_2O_3 -assisted method can be effectively used for flake carbon coating on pseudocapacitive oxides for their promising application in electrochemical cells. For example, the obtained porous $\text{CoO}@f\text{-C}$ hybrid nanowire arrays show large increased capacitance, good rate ability and cycling stability. It is envisaged that this nanoflake carbon coating can be also useful in other electrochemical applications, such as lithium-ion batteries and catalysts for fuel cells.

Chapter 6

Conclusions and Future Work

6.1 Conclusion of the thesis

Considering that metal oxides can provide large energy density in supercapacitors application, and construction of integrated system may result in better physical and chemical performance than the single component thus is suitable for supercapacitor application, in this thesis, we mainly focus on rational designed hierarchical metal oxides nanostructures for high performance supercapacitor electrodes. The major accomplishments of this thesis can be summarized into the following two points:

(1) *Facile synthesis of two novel core-shell hierarchical nanostructures for electrode performance enhancement.* One is 1D porous CoO nanowire@NiHON nanoflake, the other one is 2D porous CoO nanowall@Ni(OH)₂ nanoflake. Both structures have been synthesised with cheap and simple methods which are easy to scale up. In addition, the two structures have demonstrated high capacitances among common metal oxides, which is promising for commercialization. For example, the core-shell structure of CoO nanowall@Ni(OH)₂ nanoflake showed an areal capacitance up of 11.49 F cm⁻². Also for both two-oxide hybrid electrode materials, the improved electrochemical properties can be ascribed to synergetic effects.

(2) *Utilizing ALD to construct novel hierarchical nanostructures for supercapacitor electrodes.* We have successfully constructed two novel metal oxides

based nanostructures by using ALD, and demonstrated their applicability for supercapacitor electrodes. One is a hollowed core-shell nanostructure which shows the merits of the gap in supercapacitor electrodes; the other one is a metal oxide@carbon core-shell structure which successfully combined the advantage of metal oxide and carbon and provided a new and general way for the fabrication of metal oxides@carbon nanostructures. This part also illustrates the great potential for ALD in energy-related area.

The main contribution of the thesis work can be summarized as follows: we have successfully designed two core-shell metal oxides for supercapacitor electrodes. A high areal capacitance is obtained due to the nanoporous structure of the oxides. In addition, by applying ALD, we firstly demonstrated that a hollow core-shell oxide nanostructure has evidently improved electrochemical properties (higher capacitance and better cyclic stability) than solid ones. Finally, we discovered a novel and generic way to synthesis carbon nanoflakes directly on arbitrary metal oxides for better supercapacitor electrodes.

6.2 Suggestion for Future Work

Following this thesis, some future work can be suggested as follows.

(1)*Developing novel metal oxides based nanostructures with easier and more environmental methods.* As mentioned previously, one of the challenges for metal oxides based supercapacitors is its high cost, albeit the low temperature solution-based synthesis methods utilized in this thesis work. Therefore, developing a

cheaper and more environmental method for the fabrication of desirable metal oxide nanostructure is a prerequisite for large-scale applications. One possibility is electrospinning. Electrospinning is a solution based cheap method to fabricate 1D fiber-like structure in a high large quantity. The as-spun fibers are generally a composite with polymer and metal oxide precursors. After thermal annealing to burn off the polymer, porous or tube-like metal-oxide structures can be obtained. The 1D porous/hollow materials could be directly used for supercapacitor electrode, or can be used as the core/backbone for the further loading of other active oxides/hydroxide/nitride materials to form core-shell structures. Nevertheless, the main challenge for electrospun fibers is the electrical conductivity, which might still need surface coating of nano carbon or polymer binders.

(2)Construction of metal oxides with different carbonaceous materials to achieve high power density. As mentioned previously, carbonaceous materials can provide high conductivity thus high power density. Hence, a judicious combination of metal oxides with carbon materials (e.g. CNTs and graphene) will result in enhanced electrochemical performance. The ALD-obtained amorphous carbon flake coating would be useful when combined with 2D porous nanowalls, because the conductivity and surface area of the structure will be both increased. Another direction is to hybridize metal oxides electrode with carbon materials based electrode so to construct asymmetric supercapacitors, with one electrode supplying high energy density and the other high power density. Graphene gel¹⁶² and 3D graphene¹² would be promising to serve as the electrodes, as they have illustrated excellent behaviour in supercapacitor

application. While there are already quite an amount of publications in this direction, it is still a challenge to achieve high loading of the metal oxides on the carbon to meet commercial application requirements. When simple physical mixing fails to work, one would need solutions for homogeneous grafting of metal oxides on these carbon supports with good control of the hetero-interface and mass loading.

(3) *Theoretical simulation and in-situ observation of the metal oxides in electrochemical test.* The metal oxides in electrochemical energy storage have been widely explored dominantly by experimentalists, but there are relatively less work on theoretical understanding. Further, while there exist wide-spread assumptions of the pros and cons of nanostructured metal oxides, there are little direct evidence. One example is the electrical conductivity; at what length an oxide nanowire is better or worse than a carbon nanotube in terms of conductivity? Evidence to many of these nominal claims will need in-depth systematic investigations.

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