Carbon based nanostructures for electrochemical energy storage

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**CARBON BASED NANOSTRUCTURES FOR
ELECTROCHEMICAL ENERGY STORAGE**

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SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

2014

**Carbon Based Nanostructures for Electrochemical Energy
Storage**

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School of Electrical & Electronic Engineering

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Dedicated to my family

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Abstract

Nowadays, the decreasing availability of fossil fuels has made the demand for efficient storage and usage of energy urgent than ever. Recently, two types of electrochemical energy storage devices have caught extensive attention, namely lithium ion batteries (LIBs) and electrochemical capacitors (ECs).

LIBs are now serving as the most important power sources for mobile electronics, while ECs are rising rapidly as an important complement to LIBs, because of their capability to deliver much higher power density as well as longer life time. However, almost all of the advanced materials for anodes in LIBs or electrodes in ECs face the problems of structural failure and hence severe energy density fading, which have dramatically hindered the further development of these systems.

In this project, fabricating these materials into nanostructures and combining them with advanced carbon materials, such as carbon nanotubes (CNTs) and ultrathin graphite (UG), are employed as an effective solution. The obtained carbon based nanostructures have been successfully demonstrated as promising candidates for high performance anode materials in LIBs and/or electrode materials for ECs.

The work starts with the growth of CNT network on stainless steel (SS) substrate by chemical vapor deposition (CVD). Molybdenum disulfide (MoS_2), a typical type of TMDs, is then decorated onto the CNT network through hydrothermal reaction and annealing treatment. The rationally designed MoS_2 /CNT composite can be directly tested

as an anode material in LIBs, without the necessity for any binders. Encouragingly, a high and reversible capacity over $1300 \text{ mAh}\cdot\text{g}^{-1}$ is retained for 50 cycles at the current density of $200 \text{ mA}\cdot\text{g}^{-1}$, while excellent rate performance is also delivered because of the enhanced structural stability and reaction kinetics in the material.

Secondly, vertical aligned arrays of CNTs are fabricated through plasma enhanced CVD (PECVD). The CNT array can be a good template for Si, which is of the highest theoretical capacity among alloy-type anodes in LIBs. By introducing rough Ni layers in between the CNT cores and the Si shells, enhanced adherence, accelerated charge transport and more effective strain relaxation can be achieved. The core-shell Si/Ni/CNT anode manages to provide a high capacity of over $2500 \text{ mAh}\cdot\text{g}^{-1}$ with a low fading rate of merely 0.2% per cycle over 110 cycles.

The CNT arrays are also used to support NiCo_2O_4 , a novel type of TMOs, with advantages in electrical conductivity and ionic reactivity. The coating of NiCo_2O_4 is realized by a facile electrochemical deposition method followed by subsequent annealing in air. The $\text{NiCo}_2\text{O}_4/\text{CNT}$ arrays obtained demonstrate outstanding performances as anodes in LIBs, including a high capacity ($1147.6 \text{ mAh}\cdot\text{g}^{-1}$ at $100 \text{ mA}\cdot\text{g}^{-1}$), excellent cycling retention (no capacity fading over 200 cycles) and outstanding rate capability ($712.9 \text{ mAh}\cdot\text{g}^{-1}$ at $1000 \text{ mA}\cdot\text{g}^{-1}$). The applications of $\text{NiCo}_2\text{O}_4/\text{CNT}$ core-shell structures are not limited to LIBs but also suitable for ECs. When tested in a three-electrode configuration, the as-prepared $\text{NiCo}_2\text{O}_4/\text{CNT}$ structures exhibit a specific capacitance of $695 \text{ F}\cdot\text{g}^{-1}$ at the current density of $1 \text{ A}\cdot\text{g}^{-1}$ and $576 \text{ F}\cdot\text{g}^{-1}$ at $20 \text{ A}\cdot\text{g}^{-1}$. Hence, the capacitance of the $\text{NiCo}_2\text{O}_4/\text{CNT}$ electrode remains 91% of its initial value after 1500 cycles at the current density of $4 \text{ A}\cdot\text{g}^{-1}$.

Furthermore, this structure is enhanced by using the substrate of 3D UG-coated Ni foams, resulting in the architecture of NiCo₂O₄/CNT/UG on Ni foams. The fabrication processes consist of sequential CVD growth of 3D UG on Ni foam and CNT network on the surface of UG, respectively and hydrothermal and annealing preparation of NiCo₂O₄ nanorods. This architecture brings advantages including huge surface area, enhanced active material loading and facile electrolyte access. A high capacitance of 973.0 F·g⁻¹ at the current density of 1 A·g⁻¹, outstanding rate performance (capacitance of 715.9 F·g⁻¹ at 15 A·g⁻¹) and also stable cycling at 5 A·g⁻¹ have been successfully demonstrated.

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List of Abbreviations

LIB: lithium ion battery

EC: electrochemical capacitor

TMD: transition metal dichalcogenide

TMO: transition metal oxide

EDLC: electrochemical double layer capacitor

CNT: carbon nanotube

CVD: chemical vapor deposition

MoS₂: molybdenum disulfide

UG: ultrathin graphite

EV: electric vehicle

PECVD: plasma enhanced chemical vapor deposition

SiONW: silicon oxide nanowire

EC/DEC: ethylene carbonate/diethyl carbonate

IPA: isopropyl alcohol

DI: de-ionized

List of Abbreviations

SS: stainless steel

SEM: scanning electron microscopy

TEM: transmission electron microscopy

HRTEM: high resolution TEM

MWCNT: multi-walled CNT

SWCNT: single-walled CNT

EDX: energy-dispersive X-ray spectroscopy

XPS: X-ray photoelectron spectroscopy

XRD: X-ray diffraction

CV: cyclic voltammetry

EIS: electrochemical impedance spectroscopy

SEI: solid electrolyte interface

RF: radio frequency

SCE: standard calomel electrode

Chapter 1 Introduction

1.1 Motivations

Since the industrial revolution, fossil fuels, such as coal, petroleum and natural gas, have been serving as the most important energy sources for the human society for centuries. They were burnt to propel steam engines in 1800s and nowadays still power vehicles worldwide. Meanwhile, electricity produced by burning fossil fuels takes the largest share in the electricity generation, as shown by Figure 1-1. [1]

Figure 1-1 Energy sources for electricity generation in United States of America in 2013.

However, limited feedstock and decreasing availability of the fossil fuels have become a potential crisis for this development strategy. More importantly, despite the

great merits brought to the society and convenience to the human being, serious side effects have been created at the same time. Serious air pollution by the waste threatens the health of people while numerous amount of CO₂ emission causes climate warming and detriments the ecological systems.

As such, fast rising demands for the alternatives to fossil fuels spread globally and green energy such as solar, wind and tidal powers have caught significant attention. As compared to traditional fuels, they come with advantages including renewability, cleanness and environment-friendliness. However, most of them are limited by time and/or regions. For example, the sun does not shine in the night while wind does not blow everywhere. Therefore, suitable devices are required to store the renewable energy and release it when necessary. [2] In the meantime, electric vehicles (EVs) have been identified the effective solution to reduce petroleum consumption and the CO₂ emission produced. Clearly, electric power supplies with sufficient energy and acceptable weight and volume are the foundation for a successful EV.

Lithium ion batteries (LIBs) are the most successful electrochemical energy storage devices in market till date. [3] As shown in Figure 1-2, over the long history of rechargeable batteries, LIBs possess a balance of high energy density and relatively low weight and volume. [4-7] They have become the dominating power source for consumer electronics. Driven by the Moore's law, consumer electronics have been developing exponentially over the years. Users' experiences have been continuously improved while more efficient energy supplies are required at the same time.

Figure 1-2 Energy density (Wh/L) and specific energy (Wh/kg) for the major rechargeable battery systems. [5]

What is more, the development of EVs is also raising the requirements for the energy densities of LIBs significantly, in order to achieve longer distance and exclude the inconvenience of frequent charging. However, conventional LIBs can hardly keep pace with these uprising requirements. Graphite is the mainstream anode material for conventional LIBs. Despite the stable cycling performance, limited capacity of $372 \text{ mAh}\cdot\text{g}^{-1}$ and safety concerns of the graphite have become the bottlenecks. [3] In this regard, alloys, transition metal oxides (TMOs) and transition metal dichalcogenides (TMDs) have been investigated as possible alternatives, because of their potential for much higher energy densities and also enhanced safety. However, during

charge/discharge processes, these materials are prone to structural failures, due to huge stress caused by volume changes upon intercalation/extraction of the lithium ions.

Meanwhile, LIBs fall short in power density which limits their applications where large energy is required to deliver in very short duration. It triggers the development of electrochemical capacitors (ECs), also named as supercapacitors, which could serve as an important complement to LIBs because of their much higher power density as well as longer life time, as shown in Figure 1-3.

Figure 1-3 Specific power against specific energy for various electrical energy storage systems. [2]

ECs can be categorized into three types based on the energy storage mechanisms, namely electrochemical double layer capacitors (EDLCs), pseudo capacitors and hybrid capacitors, which combine the mechanisms of the former two. EDLCs depend on the electrostatic ion adsorption by carbon materials. Nevertheless, owing to this mechanism, the capacitances are limited (below $400 \text{ F}\cdot\text{g}^{-1}$) and progress in the improvement is rather slow. Unlike EDLCs, pseudo capacitors utilize the fast surface redox reactions of TMOs or polymers. Therefore, they are of potential for much higher capacitances and hence energy densities. However, because of the redox reactions, structural deteriorations tend to occur in the electrodes as the side effect. As a consequence, pseudo capacitors are more prone to poor cycling performance.

Under this situation, it is increasingly urgent for the innovations of science and technologies in electrochemical energy storage, in terms of mechanisms, devices and especially materials. Materials lie in the heart of advancements in energy storage. [2, 8] For the further development of electrochemical energy storage technologies, rational design and modification of the materials are essential. In the past few decades, nanostructured materials have demonstrated much better performances over their bulk form counterparts. At confined dimensions, nanosized materials have exhibited much higher surface area/volume ratio and also electrochemical reactivity. More importantly, nanostructures are more favourable for strain relaxation, which can help to retain the structural integrity during cycling. Therefore, making active materials into nanostructures can be one of the routes to improve their electrochemical performances. On the other hand, advanced carbon materials such as carbon nanotubes (CNTs) and ultrathin graphite (UG) are catching more and more research interest because of their superior mechanical,

electrical and structural properties. They can serve as excellent templates for active materials, providing them the mechanical support and electrical conducting pathways.

As such, carbon supported nanostructured active materials can be an effective solution to realize the potential of these materials for electrochemical energy storage.

1.2 Objectives

The main objectives of this Ph. D study are to develop nanostructured active materials supported by advanced carbon materials for LIB anodes and EC electrodes with improved performances and extended life span.

- To fabricate advanced carbon materials including CNTs and UG as templates for active materials.
- To explore the technology aspects to combine the carbon templates with active materials, including MoS_2 , Si and NiCo_2O_4 , with controllable configurations including morphologies, structures and dimensions.
- To study the electrochemical behaviors of the synthesized carbon supported MoS_2 , Si and NiCo_2O_4 nanostructures as anodes for LIBs.
- To investigate the performances and mechanisms of carbon supported NiCo_2O_4 as electrodes of ECs.

1.3 Major contributions of the thesis

The major contributions of this thesis can be summarized as below:

- Network of CNTs are successfully grown on stainless steel (SS) substrate by CVD method. MoS₂ is decorated onto the CNTs network through hydrothermal method. The MoS₂/CNT composite can be directly tested as an anode material in LIBs, without the necessity for any binders. Enhanced structural stability and reaction kinetics enable its high capacity over 1300 mAh·g⁻¹ for 50 cycles at the current density of 200 mA·g⁻¹, as well as superior rate capability.
- Vertical aligned array of CNTs are obtained through PECVD and employed as a multifunctional template. On the one hand, vertically aligned CNT array is possible to support Ni catalysts to promote the growth of Si oxide nanowires (SiONWs) using Si substrate as the solid sources. More importantly, the Ni/CNT array produced on SS substrate are able to support the Si materials for LIB anode application. The obtained Si/Ni/CNT array demonstrates a high capacity over 2500 mAh·g⁻¹ over 110 cycles.
- The CNT array is also a possible support for NiCo₂O₄, through a facile electrochemical deposition method followed by subsequent annealing in air. When tested as LIB anodes, the stubborn support of CNTs and fast ion/electron transport at the electrode interface enable a high capacity (1147.6 mAh·g⁻¹ at 100 mA·g⁻¹), excellent cycling retention (no capacity fading over 200 cycles) and outstanding rate capability (712.9 mAh·g⁻¹ at 1000 mA·g⁻¹).
- The unique core-shell structure of the NiCo₂O₄/CNT enable it as a promising electrode material for pseudo capacitor type of ECs. An initial specific capacitance of 695 A·g⁻¹ is obtained at the current density of 1 A·g⁻¹ while a value of 576 F·g⁻¹ is kept at 20 A·g⁻¹. Hence, capacitance of the NiCo₂O₄/CNT electrode remains 91% of its original value after 1500 cycles at the current density of 4 A·g⁻¹.

- By using the substrate of 3D UG, the $\text{NiCo}_2\text{O}_4/\text{CNT}$ nanostructures can be further enhanced for EC applications. This $\text{NiCo}_2\text{O}_4/\text{CNT}/\text{UG}/\text{Ni}$ foam architecture brings advantages including huge surface area and significantly increased active material loading without compromising the electrochemical performances.

In conclusion, this Ph. D work provides proofs for the potential of advanced carbon materials in the field of electrochemical energy storage. With the support of these carbon materials, a variety of nanostructured materials have exhibited promising performance in LIBs and/or ECs.

1.4 Organization of the thesis

The thesis is organized into the following chapters:

- Chapter 1 introduces the motivations, objectives and major contributions of the thesis.
- Chapter 2 covers the literature review on LIB and EC technologies including and fundamental working mechanisms and state-of-the-art components. The opportunities and challenges in the alternative materials for LIB anodes and EC electrodes are also discussed. In addition, the electrochemical characterization techniques are introduced.
- Chapter 3 is dedicated to the design and fabrication of the binder-free MoS_2/CNT composite as a high-performance anode material for LIBs. The experimental design, fabrication processes, structural and Electrochemical characterization and results are addressed in detail.

- Chapter 4 shows the possibility to obtain a vertically aligned array of CNTs by PECVD. The CNT array can be easily coated by Ni using magnetron sputtering. The Ni/CNT array obtained is possible to promote the growth of SiONWs using solid source. Furthermore, after coating of Si, the Si/Ni/CNT is capable to provide improved performance as compared to Si/CNT as an anode material for LIBs.
- Chapter 5 & 6 reports coating of NiCo_2O_4 onto the CNT array by a facile electro-deposition processes. The multi-functional core-shell $\text{NiCo}_2\text{O}_4/\text{CNT}$ structures demonstrate excellent performances as both anode materials for LIBs and electrode materials in pseudo capacitor type of ECs.
- Chapter 7 provides a further improved structure of $\text{NiCo}_2\text{O}_4/\text{CNT}/\text{UG}/\text{Ni}$ foams. The huge surface area, facile electrolyte access and numerous active sites of this structure enable its promising performance as an electrode material for ECs.
- Chapter 8 concludes the work and recommends some possible directions based on the findings of this Ph. D study.

Chapter 2 Lithium ion batteries and electrochemical capacitors

2.1 Working mechanisms of lithium ion batteries

2.1.1 Historical Development

In general, batteries store energy in chemical form and convert it back into electricity to power devices in the circuits. [3] Rechargeable batteries belong to the subcategory that can be charged and discharged for many times. Lithium based batteries started with the configurations using lithium metal as the anodes. [7] Dated back to 1970s, the concept of electrochemical intercalation was already raised and preliminary work on Li metal (anode)/TaS₂ (cathode) with lithium perchlorate in dioxolane as the electrolyte was also carried out in laboratories. [9] The idea comes from the fact that lithium metal possesses one of the most electropositive potentials (-3.04 V versus standard hydrogen electrode). It is also the lightest metal. [6] Therefore, these lithium metal based batteries were expected to provide high energy density. Unfortunately, it was soon found the problem of dendritic lithium growth from the anodes in each discharge-charge cycle due to replating of the metal. In detail, in the charging process, lithium ions are supposed to be moved back to the lithium metal anodes and reduced to the metal state. However, as illustrated in Figure 2-1, the lithium metal particles obtained may not be completely restored to the original locations on the anodes but form dendrites on their surface. After many cycles, short circuit, inflammation and even explosion could be the serious outcome.

Many efforts have been made to develop suitable alternative architectures, but it was not until the rise of lithium-ion technology that this problem could be perfectly solved. Lithium ion batteries (LIBs) utilize lithium in its ionic state rather than metallic state. Therefore, they are inherently safer by reducing the possibility of lithium dendrites. [10, 11] The later discovery of highly reversible lithium intercalation/extraction in carbon materials triggers breakthroughs and commercialization of LIBs based on C (anode)/lithium cobalt oxide, LiCoO_2 (cathode). [12, 13] Today, this architecture still lies as the heart for most LIBs in the market and powers most of the mobile electronics.

Figure 2-1 Schematics of dendritic lithium growth in lithium metal batteries. [3, 6]

2.1.2 Principle and Components

Batteries are typically composed of three main components, namely positive (cathodes), negative (anodes) electrodes and suitable electrolytes in between. The anodes

usually possess lower potential which could act as electron donors while the cathodes are good oxidizing agents to accept electrons. [3] Difference in the electrochemical potentials between the two electrodes determines the output voltage of the batteries. The electrolyte serves as the ionic conductor providing environment for ion transfer. In addition, a porous electrically insulating separator is often applied to avoid direct contact of the electrodes which would short-circuit the batteries. Figure 2.2 represents the most popular structures and material selections of LIBs in the market where graphite, LiCoO_2 and LiPF_6 dissolved in ethylene carbonate/diethyl carbonate (EC/DEC) are used as the anode, cathode and electrolyte, respectively. Chemical energy is stored in the electrodes during charging when a reversed bias higher than the output voltage is applied. Inside the battery cell, the lithium ions are forced to leave the cathode, cross the electrolyte and intercalate into the matrix of the graphite anode. Meanwhile in the external circuit, electrons are extracted from the cathode and injected into the anode. Herein, the LiCoO_2 cathode is oxidized to be $\text{Li}_{1-x}\text{CoO}_2$, while the graphite anode is reduced to Li_xC as shown in following equations, respectively.

Upon discharge, the stored energy is transformed back into electrical energy and released into the circuit. As the anode possesses a lower potential than the cathode, the above reactions will take place spontaneously in the reverse directions where anode releases the stored lithium ions and electrons at the same time. Lithium ions move from the anode towards the cathode while electrons flow in the external circuit and drive the

loads. After full discharge, the anode is oxidized to graphite while the cathodes are restored to be LiCoO_2 .

Figure 2-2 Components and operation principles of LIBs. [5]

2.1.3 Problems of current anodes

The graphite anodes provide energy storage capabilities based on the intercalation mechanisms. Because of its unique structure of stacked graphene layers, the volume expansion upon intercalation in graphite is less than 10%. [14-16] Therefore, graphite anodes are possible to provide stable cycling and good life span. Meanwhile, graphite comes with benefits including controllable morphologies, electrochemical stability and

relatively good electrical conductivity. Thus, it is little wonder that graphite is now the market choice for anodes. However, there are still many challenges for graphite anodes, of which the two major ones are described as follows.

Firstly, in graphite, every six carbon atoms can only host one lithium ions at full lithiation, resulting in a limited capacity of $372 \text{ mAh}\cdot\text{g}^{-1}$. With the efforts of industry, the performances of commercial graphite anodes are approaching the theoretical limits. Although research work has been carried out to further enhance the capacity of graphite anodes, the margin for improvement is limited and the progress is rather slow. Instead, increasing research attention has been paid to the alternative materials with substantially higher theoretical capacities.

Safety is another concern for LIBs. The intercalation potential of graphite by lithium ions is very close to Li/Li^+ (within 100 mV versus Li/Li^+). [6, 17] At high charging rate, when transport of lithium ions into the graphite anode exceeds what can be inserted into the graphite structure, lithium ions may be deposited as metallic lithium at the surface of the electrode. It is also known as plating of the lithium metal. With the existence of metallic lithium, problems like short circuits may occur as what happened in lithium metal batteries as shown in Figure 2-1. As a consequence, lifetime and durability of batteries can be harmed. Furthermore, as lithium plating has higher tendency at low temperature, this problem also limits the applications of LIBs in harsh environments. [17-19] Therefore, alternative materials with slightly higher intercalation voltage are desired to enhance the safety of LIBs and hence broaden their range of applications.

2.2 Advanced materials for anodes in LIBs

2.2.1 Transition Metal Dichalcogenides

Transition Metal Dichalcogenides (TMDs) have been investigated since the very early stage of LIB development when TiS_2 was used as the counter electrode material to Li metals. Nowadays they are still a topic of vast interest in LIB research.

Figure 2-3 Schematic of the MoS_2 structure. [20]

MoS_2 is a typical type of layered TMDs. Analogous to the structure of graphite, S-Mo-S are bound by strong covalent forces to form two-dimensional layers and these individual layers stack together with relatively weak Van der Waals interaction, as shown

in Figure 2-3. [21] The layered structures provide access and accommodation for a number of guest species such as lithium ions, while much smaller volumetric changes would happen upon lithiation/de-lithiation. Therefore, high capacities over $1000 \text{ mAh}\cdot\text{g}^{-1}$, lower rates of cycling induced degradation and better rate capability are expected in MoS_2 based anodes. [22-31] On the other hand, MoS_2 based anodes possess an intermediate lithiation voltages (0.6-2.0 V vs Li/Li^+). Therefore, they are inherently safer because of the reduction in the driving force for lithium plating. [29]

Unfortunately, attempts to commercialize MoS_2 anodes even since the early stage of lithium metal batteries in 1980s have never been really successful. Those bulk MoS_2 based anodes provided only limited capacity and/or suffered from severe capacity fading. There could be several reasons. Firstly, the intrinsically poor electric and ionic conductivities of MoS_2 impede efficient transfer of the charges. [26] Besides, the typical conversion of MoS_2 to Li_2S and Mo , as shown in Equation 2-3, happening during the reaction with lithium ions (also known as lithiation) [23, 29, 32] is likely to degrade the electrodes, resulting in loss in capacity eventually.

In addition, in bulk forms of MoS_2 , electrolyte is often hindered from entering the internal portion, leading to the difficulty in the complete reaction of active material with lithium ions.

Figure 2-4 MoS₂ nanostructures used as anode materials in LIBs: (a) (c) (e) SEM images of MoS₂ nanoplates, [25] nanorods [33] and nanowalls; [34] (b) (d) (f) are the corresponding higher magnification SEM images.

Recently, by modifying MoS₂ into various nanostructures, improved anode performances have been reported. As shown in Figure 2-4 (a) (b), Hwang *et al.* prepared MoS₂ nanoplates which performed a reversible capacity of 907 mAh·g⁻¹ up to 60 cycles at the current density of 1062 mA·g⁻¹. [25] Liu *et al.* reported highly disordered mesoporous MoS₂ nanorods with a capacity of 876 mAh·g⁻¹ at the current density of 100 mA·g⁻¹. [33] Ulttam *et al.* synthesized 2D MoS₂ nanowalls which demonstrated a high discharge capacity of 880 mAh·g⁻¹ at the same current density. [34]

Figure 2-5 Examples of MoS₂ combined with 1D nanostructures: (a) TEM image of MoS₂/CNT [24]; SEM images of (b) MoS₂/polyaniline nanowires and [35] (c) MoS₂/carbon nanowires; (d) schematics of the preparation method of MoS₂@CMK-3. [36]

On the other hand, MoS₂ are also combined with other types of nanomaterials including 1D nanowires or nanotubes, as shown in Figure 2-5, and 2D graphene, for improved performances. For instance, Wang *et al.* reported a hybrid material with several MoS₂ layers supported on CNTs which demonstrated a reversible capacity near 400 mAh·g⁻¹ for 50 cycles at the current density of 0.6 mA·cm⁻². MoS₂/CNT obtained in different morphologies through a variety of synthesis approaches have also been reported by several other groups. [22, 24, 27, 28, 37] 1D nanostructures used to enhance the performances of MoS₂ are not limited to CNTs. As reported by Zhang *et al.*, MoS₂/carbon nanowire exhibited a reversible and stable discharge capacity of 996 mAh·g⁻¹ for 50 cycles at the current density of 200 mA·g⁻¹. [26] Zhou *et al.* synthesized MoS₂/CMK-3 nanocomposite with an improved cycling performance of 602 mAh·g⁻¹ at 250 mA·g⁻¹ after 100 cycles. [36] Hierarchical MoS₂/polyaniline nanowire exhibited a high charge capacity of 1063.9 mAh·g⁻¹ at the current density of 100 mA·g⁻¹, retaining 90.2% of the initial reversible capacity after 50 cycles, as reported by Ding *et al.*. [32] Meanwhile, 2D materials, especially graphene have also been investigated as a possible compositing material for MoS₂. For instance, Chang *et al.* reported the in situ synthesis of MoS₂/graphene nanosheet composite with extraordinary capacity up to 1300 mAh·g⁻¹ at current density of 100 mA·g⁻¹ for 50 cycles. [30] [23]

2.2.2 Alloys

Dated back to 1970s, a variety of metallic or semi-metallic elements have been demonstrated as electrochemically active towards lithium, such as Si, Ge, Al, Sb, Mg, Bi, In, Zn, Pb, Ag. [4] They are able to alloy with lithium ions even at room temperature and

thus gain attention for applications as anode materials in LIBs. Unlike graphite, where every six carbon atoms can only host one lithium ion at full lithiation, each atom in the anodes made of above-mentioned elements are capable to alloy with many more lithium ions, leading to substantially higher gravimetric and volumetric capacities, as shown in Figure 2-6.

Figure 2-6 Gravimetric and volumetric capacities of several alloying materials. [4]

Among all the alloy materials for anodes, Si has attracted particular interest for the reasons as follows. Firstly, the theoretical capacity of Si ($4200 \text{ mAh}\cdot\text{g}^{-1}$ at fully lithiated state of $\text{Li}_{22}\text{Si}_5$) is the highest among all the alloy candidates. Secondly, Si comes with abundant resources and long fabrication history in microelectronic industries, providing its potential for low cost and mass fabrication capability. More importantly, Si reduces the hazard of lithium plating by a moderate onset potential ($0.3\sim 0.4 \text{ V}$ versus Li/Li^+).

Therefore, Si based anodes can be safer in operation. Besides, Si is non-toxic to human beings and also environmentally friendly.

Figure 2-7 SEM images of (a) crystalline Si nanowires; [38] (b) interconnected Si nanowires; [39] (c) SEM and (d)TEM image of Si nanotubes. [40]

Despite of merits, bulk Si based anodes suffer from very poor capacity retention, especially when subjected to deep discharge. The capacity may fade dramatically in only a few cycles. This problem mainly comes from the side effects of alloying with lithium. Upon the interaction/extraction of lithium ions, huge volume change up to 400% happens at the same time, resulting in significant stress to the Si structure. Therefore, the Si anodes

may suffer from cracks and pulverizations and the capacity will disappear when the Si material lose contact to the current collectors. In addition, poor conductivity of Si hinders efficient charge transport and constrains its rate performance as anode materials.

At present, different types of Si nanostructures were also reported with improved performances. As simple as direct deposition of Si film in the thickness of nanometer onto metal substrate, a reversible capacity of near $3800 \text{ mAh}\cdot\text{g}^{-1}$ at the current density of $4200 \text{ mA}\cdot\text{g}^{-1}$ can be achieved after 200 cycles. Si in 1D nanostructures, including nanowires and nanotubes are of high interest for electrochemical applications, as shown in Figure 2-7. For instance, crystalline Si nanowires synthesized on SS current collectors were demonstrated as a promising anode material with a lithiation capacity of over $4000 \text{ mAh}\cdot\text{g}^{-1}$. [38] Nguyen *et al.* demonstrated improved cycling performance in interconnected Si nanowires. [39] To further alleviate the strain, Song *et al.* fabricated arrays of sealed Si nanotubes which demonstrate capacity retention over 82.2% after 50 cycles at the rate of $840 \text{ mA}\cdot\text{g}^{-1}$. [40]

3D nanostructures are another possible route to reduce the stress endured by Si during cycling. Kim *et al.* prepared 3D porous Si particles, as shown in Figure 2-8 (a) (b) with good capacity retention of 90% over 100 cycles at the current density of $840 \text{ mA}\cdot\text{g}^{-1}$. [41] Later, Esmanski *et al.* demonstrated a similar but more sophisticated 3D macroporous Si film as shown in Figure 2-8 (c) (d), using closely packed multi-layer silica spheres as the template. [42]

Figure 2-8 SEM images of (a) 3D porous Si particles [41] (c) inverse-opal-based macroporous Si structures; [42] (b) and (d) are the corresponding higher magnification SEM images respectively.

Extrinsic nanomaterials are also employed to enhance the performances of Si as anode materials. Many electrochemically inert elements such as Ni, Cu, Mg and Fe have been introduced into Si to form alloys. For instance, NiSi and FeSi alloys were prepared by Wang *et al.* using high-energy ball-milling method. [43, 44] Nanostructured NiSi thin films were also successfully fabricated by pulsed laser deposition method. [45] Mg₂Si was synthesized by mechanically activated annealing. [46] Improved performances reported in these composites can be attributed to the fact that the inactive composition can serve as a buffering matrix for the Si material and prevent it from pulverization.

Electrochemical inactive materials are also used to coat or support Si nanostructures. Yang's group coated Si nanowires with copper towards a better strain management of the Si nanowires in electrochemical cycling. [47] Cao *et al.* fabricated well-organized Si-Cu nanocables directly on a current collector to enhance the cycling stability and high rate capability of Si, as shown in Figure 2-9. The conductive Cu cores act as both current collectors and structural reinforcement for the Si shells. [48]

One type of particular interests in Si composites is Si-C composites. Carbon materials are generally electrochemically active towards lithium ions. Thus, they can also contribute to overall capacities. More importantly, advanced carbon materials, especially carbon nanotubes (CNTs) and ultrathin graphite (UG) come with extraordinary properties, which could enhance the performance of Si materials. The details will be further addressed in Section 2.5.2.

Figure 2-9 (a) TEM image and (b) HRTEM image of a Cu-Si-Al₂O₃ nanocables; (c) TEM image and (d) corresponding EDX elemental mappings of O, Al, Si, and Cu. [48]

2.2.3 Transition Metal Oxides

Unlike the insertion/extraction process in graphite or alloying in Si, transition metal oxides, TMOs (where M can be Co, Ni, Mn, Fe or Cu), exhibit electrochemical reactivity towards lithium ions in a different way. [6] During the first de-lithiation process, these TMOs are reduced electrochemically into metal nanoparticles. In the following cycles, reversible formation and decompositions of Li_2O are enabled for the lithiation and de-lithiation of the anodes, hence the rechargeable behaviours of the batteries. The reversible reactions can be written as follows: [49]

Compared with graphite anodes, TMOs based anodes are able to provide gravimetric capacities over two times higher. [50] Considering their much higher density, the volumetric capacities of TMO anodes can be even larger. Recently, spinel structure NiCo_2O_4 , a type of TMOs, has drawn intensive research attention because of its advantages of low cost, environmental friendliness and more importantly, much better electrical conductivity and electrochemical activeness than monometallic nickel oxides and cobalt oxides. [51-54] These appealing properties make up the potential of NiCo_2O_4 in high-performance anodes of LIBs, as well as electrodes for pseudo capacitor type of ECs.

The performance of TMO based anodes depends largely on the sizes of composing materials. Therefore, confinement of the dimensions is one of the challenges, which will be further addressed in the solutions and strategies section 2.5.1. Moreover, two major problems associated with TMOs are the poor electrical conductivities and severe volume variations in cycling. Low electrical conductivities inhibit fast charge transfer, leading to

reduction of the power densities. [49] On the other hand, large volume change upon charge/discharge renders the damage of structural integrity of the TMO anodes. Therefore, long term stability is lacked because of the pulverizations. These are also the challenges for their applications in pseudo capacitors.

2.3 Electrochemical capacitors

2.3.1 Rise of the ECs

ECs are rapidly-growing technologies in recent years which bridge the gap between batteries and conventional capacitors, as shown in the Ragone plot of Figure 1-3. [2] ECs have caught extensive attention because of their capability to deliver or uptake energy in greatly reduced durations as compared to batteries. Thus, they are possible to complement or replace batteries in many applications where much higher power is desired such as uninterruptible power supplies and starters and brakes of automobiles. ECs have a similar construction structure to batteries, in which two electrodes are separated by the electrolyte, but the energy storage mechanisms are distinctly different. Depending on the mechanism, ECs can be classified into three categories, namely electrochemical double (EDLCs), pseudo capacitors and hybrid capacitors.

2.3.2 EDLCs

EDLCs store the charges and hence electrostatic energy by means of reversible adsorption of ions from the electrolyte onto the surface of the electrodes. Capacitance C originates from charge separation in Helmholtz double layer at the electrode/electrolyte interfaces. When a potential difference exists between the two electrodes, positive and negative ionic charges in the electrolyte accumulate at the electrode surface and compensate for the electronic charge in the electrodes, hence forming the double layer. [55] C can be described by the following equation:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (2 - 5)$$

where ϵ_r , ϵ_0 , d and A are the electrolyte dielectric constant, vacuum dielectric constant, charge separation distance and specific surface area of the electrode, respectively. Surface area plays a vital role in the capacitance and hence the energy stored in the system. Therefore, electrode materials with high surface area are more desirable for EDLCs. Graphitic carbon materials offer possibility for controllable porosities and also morphologies. Meanwhile, other advantages including electrochemical stability and relatively good electrical conductivity provide extra benefits for their applications in EDLCs. Various carbon materials have been demonstrated as good candidates for EDLCs, as shown in Table 2-1.

Although the energy storage mechanism based on electrostatic surface charging enables stable performance over numerous cycles, it results in a limited energy density for EDLCs at the same time. Efforts have been carried out to further improve the performance

mainly by means of increasing the surface area of the electrode, but the improvement is still unsatisfactory. [2]

Table 2-1 Performances of various carbon electrode materials for EDLCs. [56]

Materials	Specific surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Density ($\text{g}\cdot\text{cm}^{-3}$)	Organic electrolyte			
			Aqueous electrolyte		electrolyte	
			$\text{F}\cdot\text{g}^{-1}$	$\text{F}\cdot\text{cm}^{-3}$	$\text{F}\cdot\text{g}^{-1}$	$\text{F}\cdot\text{cm}^{-3}$
CNTs	120-150	0.6	50-100	<60	<60	<30
Graphene	2630	>1	100-205 [57, 58]		80-110	
Activated Carbon	1000-3500	0.4-0.7	<200	<80	<100	<50
Porous carbon	300-3000	0.5-1	120-350	<200	60-150	<100
Carbon aerogels	400-1000	0.5-0.7	100-125	<80	<80	<40

2.3.3 Pseudo capacitors

Unlike EDLCs, pseudo capacitors store electrochemical energy mainly based on reversible faradic redox reactions at the electrodes. [59, 60] This is also the reason for the term “pseudo” since the major part of capacitance does not come from electrostatic charging.

Upon charging, a bias is applied over the two electrodes of the device. Polarized ions or charged atoms will migrate in the electrolyte to the opposite polarized electrode and pervade over the electrolyte/electrode interface, as shown in Figure 2-10. Pseudo capacitance are associated with electron and charge transfer between electrolyte and electrode which originates from a very fast sequence of reversible redox reactions. With

the involvement of redox reactions not only on the surface of electrodes but also the bulk portion closely underneath, much more electrical energy can be transformed and stored in the form of chemical energies. [8] As a consequence, pseudo capacitors can easily outperform EDLCs in terms of specific capacitance and energy density. Typically, the specific capacitance provided by pseudo capacitors can be over ten times higher than EDLCs. To achieve the faradic process, TMOs and conducting polymers are the possible candidates for the electrode materials. One thing to note is that faradic redox process not only provides the potential for much higher energy density, but also renders the risks of structural failure of the electrodes. It results in the limitation in the cycling stability which has become the bottleneck for pseudo capacitors.

Figure 2-10 Mechanism of pseudo capacitance with specifically adsorbed ions. [61]

2.3.4 Hybrid capacitors

Hybrid capacitors combine the mechanisms of EDLC and pseudo capacitance. They are often assembled with asymmetric electrodes, one of which exhibits mostly electrostatic and the other mostly pseudo capacitance. An appropriate electrode combination can bring in improvement in the cell output voltage and energy and power densities. [2]

2.4 Advanced materials for electrodes in pseudo capacitors

In contrast to the electrodes of EDLCs which are dominated by carbon materials, electrodes of pseudo capacitors are of more choices. TMOs and conducting polymers are the current mainstreams under research.

2.4.1 Transition Metal Oxides

With the pseudo capacitance effect, TMOs are capable to provide much higher energy density over EDLCs. In the early state of pseudo capacitor research, conductive RuO_2 exhibited promising performance and promoted the research in this field. However, concerns of high cost and environment pollution have constrained its applications. In response, manganese, [62] nickel and cobalt oxides [63, 64] have been investigated as the possible alternatives. These materials come with vast resources and are less or not hazardous to the environment and thus more favourable for future commercialization.

Because of its advantages in electrical conductivity and electrochemical activeness among these materials, NiCo_2O_4 is of high potential to provide better electrochemical performance. It has become a popular material in pseudo capacitor research. [65-68] Various nanostructures of NiCo_2O_4 , as shown in Figure 2-11 have been developed to fulfill the potential of NiCo_2O_4 for EC applications. Pu *et al.* synthesized porous hexagonal NiCo_2O_4 nanoplates as electrode materials for ECs, which demonstrated a specific capacitance of $294 \text{ F}\cdot\text{g}^{-1}$ at the current density of $1 \text{ A}\cdot\text{g}^{-1}$ and good retention of 89.8% of the highest capacitance after 3000 cycles. [69] Lu *et al.* synthesized vertically aligned NiCo_2O_4 nanosheets with porous structures, of which the specific capacitance was $506 \text{ F}\cdot\text{g}^{-1}$ at the current density of $1 \text{ A}\cdot\text{g}^{-1}$. [70] Yuan *et al.* demonstrated a template-engaged synthesis of uniform mesoporous hollow NiCo_2O_4 sub-microspheres with a specific capacitance of $678 \text{ F}\cdot\text{g}^{-1}$ at the current density of $1 \text{ A}\cdot\text{g}^{-1}$, and cycling stability of only 13% degradation over 3500 continuous cycles at the current density of $10 \text{ A}\cdot\text{g}^{-1}$. [71] [72] Hierarchical $\text{NiCo}_2\text{O}_4/\text{NiCo}_2\text{O}_4$ nanoflake arrays were reported by Liu *et al.* with a capacitance of $2.20 \text{ F}\cdot\text{cm}^{-2}$ at the current density of $5 \text{ mA}\cdot\text{cm}^{-2}$ and 98.6% retention after 4000 cycles. [73]

Figure 2-11 Examples of NiCo_2O_4 nanostructures used as electrode materials for ECs: (a) porous hexagonal NiCo_2O_4 nanoplates; [69] (b) vertically aligned NiCo_2O_4 nanosheets; [70] (c) mesoporous hollow NiCo_2O_4 sub-microspheres [71] and (d) hierarchical $\text{NiCo}_2\text{O}_4/\text{NiCo}_2\text{O}_4$ nanoflake arrays. [73]

The challenges for TMOs in pseudo capacitors are similar to the problems of their applications in LIBs, as a result of the redox reactions on the electrodes. Nevertheless, in contrast to LIBs where the entire anodes may participate in the redox reaction, in pseudo capacitors, the redox reactions mainly take place at the electrode surface or closely beneath. [2, 8] Therefore, they tend to be more resistant to the deterioration during electrochemical cycles in principle. However, with the accumulation of cracks after a number of cycles, loss of capacitances and energy densities will still occur as the serious

impacts. Meanwhile, the conductivities of these alternative materials, including NiCo_2O_4 are not comparable with the RuO_2 . As a consequence, charge and electron transfer may not be as efficient, which also has negative effects over the performance. [51, 65-68, 74, 75]

2.4.2 Conducting polymers

Many types of conducting polymers have been demonstrated of pseudo-capacitance effects. Their conductivity comes from their molecular structures with backbones of contiguous sp^2 hybridized carbon centers, which could give the high mobility of valence electrons on these centers. These materials include polyaniline (PANI), [76, 77] polypyrrole (PPY), [78] polythiophene (PTH) [79] and their derivatives, as shown in Figure 2-12. [80]

Figure 2-12 Structure formulae of some conductive polymers: (a) polyacetylene; (b) polyphenylene vinylene; (c) polypyrrole (X=NH) and polythiophene (X=S) and polyaniline (X=NH/N) and polyphenylene sulfide.[81]

The advantages are low cost, controllable morphologies and redox activities by chemical modifications. Capacitance is provided by the redox process. When oxidation/reduction occurs upon charging, ions are inserted into the polymer matrix, while in reduction/oxidation the ions are released into the electrolyte in discharge. The positively-charged polymers, generated by oxidation on the polymer chains, are also termed as ‘p-doped’, while negatively-charged polymers because of reduction are termed as ‘n-doped’. [8]

However, when used as in bulk form for pseudo capacitor electrodes, conducting polymers can hardly sustain long term cycling stability. With repeated cycles, accumulated damages caused by doping/de-doping will harm the electrical conductivity as well as the mechanical robustness of the polymer electrodes. Therefore, sharp reductions in the specific capacitances and energy densities may occur. [82]

2.5 Solutions and Strategies

A variety of approaches have been adopted to circumvent the problems associated with the emerging materials for electrochemical energy storage. They can be roughly categorized into nanostructuring and nanocompositing, which are explained as follows.

2.5.1 Nanostructuring

In recent years, nanostructuring emerges as a promising strategy for a variety of technologies, especially electrochemical energy storage. [83-87] Nanostructured active materials have demonstrated significant advantages over their bulk-form counterparts.

Advantages of the nanostructures may include the following aspects. Firstly, their huge surface area/volume ratio brings in numerous electrochemical active sites and facile access to the electrolyte. Thus, exchange of ions and charges can be facilitated and the electrochemical reactions can be promoted.

On the other hand, nanosized materials prevent excessive accumulation of strain and enable facile relaxation of stress.[38] There have been a number of theoretical calculations and modelling work dedicated to the strain induced fractures during electrochemical cycling. For instance, Huggins and Nix applied Griffith-Irwin relation to predict the critical particle size below which fracture will not occur. [88] Aifantis *et al.* estimated the sizes of active sites that prevent the fracture of the electrodes. [89] Deshpande *et al.* developed a mathematical model clearly indicating that below a certain wire diameter, the surface effect plays an important role in the stress engineering. [90] All of these modelling work predicated that nanostructures are more resistive to fractures induced by stress during electrochemical cycling over their bulk counterparts. These predictions are ascertained by recent *in situ* TEM studies. Liu *et al.* observed a strong particle-size-dependent fracture behaviour of Si nanoparticles upon lithiation. [91] Ghassemi and co-workers' study showed that stress during lithiation did not cause cracking in Si nanorods as small in diameter as 26 nm, larger than which cracks tended to occur. [92]

Figure 2-13 Examples of nanostructures: (a) nanosheets; [93] (b) nanoparticles; [94] (c) nanowires and (d) nanotubes. [95]

Through engineering of active material into forms of nanofilms, [45, 96-98] nanosheets, [51, 66, 67] nanoparticles [99-101], nanowires and nanotubes, [65, 74, 75] as depicted in Figure 2-13, enhanced performance has been reported in LIBs as well as ECs.

Among various nanostructures, core-shell structures with nanosized active materials supported on the cores are of high importance. Firstly, one key advantage of nanostructured core materials, such as nanospheres, nanowires, nanotubes is their huge surface area/volume ratio. Due to significantly increased surface area, relative large quantities of active material can be accommodated, even if the coating thickness on

individual nanostructures is maintained at sub-micrometer. As such, the potential towards high energy density for practical application is provided. Furthermore, due to their advantages in electrical, thermal or mechanical characteristics, core materials are possible to make benefits to the electrochemical performances. In addition, core-shell structures rooted on the current collectors are able to provide direct charge transport pathways during charging and discharging. [102] Among all the core materials under research, CNTs have been considered as one of the most promising choices, because of their superior electrical, thermal and mechanical properties. [87, 103-111]

2.5.2 Compositing with advanced carbon materials

Advanced carbon materials, including CNTs and UG have been considered as important compositing materials to improve the performances of active materials. There have been reports on the enhanced electrochemical behaviours of MoS_2 , Si and NiCo_2O_4 , after incorporation of these advanced carbon materials.

Figure 2-14 TEM image and schematic drawing of MoS_x/CNT. [28]

In 2007, Wang *et al.* observed facilitated lithium storage in MoS₂ overlayers supported on coaxial CNTs. [22] Lou's group developed a facile glucose-assisted hydrothermal method to directly grow ultrathin MoS₂ nanosheets on CNTs. [24, 26] Shi and co-workers synthesized hierarchical core-shell MoS_x/CNT nanocomposites (Figure 2-14), as an anode material for LIBs which demonstrated specific capacity over 1000 mAh·g⁻¹ for 45 cycles at the current density of 50 mA·g⁻¹. [28]

Figure 2-15 Examples of core-shell Si/CNT nanostructures: (a) TEM image of Si/vertical CNT heterostructure; [87, 112] (b) SEM image of Si/3D porous CNT sponge, (c) SEM image of the array of large diameter CNTs; (d) TEM image of a single Si/large diameter CNT nanowire. [106]

CNTs in different morphologies were also employed to support Si shells, as shown in Figure 2-15. For instance, vertical aligned CNTs were hybrid with nanostructured Si which exhibited high reversible capacity of $2000 \text{ mAh}\cdot\text{g}^{-1}$ over 25 cycles at the current density of $100 \text{ mA}\cdot\text{g}^{-1}$. [87, 112] Hu *et al.* designed a Si/CNT coaxial sponge structure as anode materials. [103] Fan and co-workers synthesized vertically aligned CNTs with

relatively large diameters and large inter-wire spacing as core wires for Si shells. [106] The rationally structured Si/CNT heteronanowires enable a high capacity over 2500 mAh·g⁻¹ and excellent retention of 91% after 80 cycles at the rate of 840 mA·g⁻¹. The superior electrochemical performance in these composites can be attributed to the unique properties of CNTs, which are introduced as follows.

2.5.2.1 Carbon nanotubes

Since the discovery in 1991 by Iijima, [113] CNT has attracted tremendous research interest. CNT belongs to the carbon family with sp² hybridization and can be categorized into single walled (SW) and multi walled (MW) CNTs. A SWCNT can be conceptualized by wrapping a graphene nano ribbon into the structure of a seamless cylinder. The rolling up direction of the graphene nano ribbon is termed as the chirality of a SWCNT which lays influences its properties, such as conductivities and mechanical strength. As depicted in Figure 2-16, chirality is defined by a chiral vector, [114] $\vec{C}_h = n\vec{a}_1 + m\vec{a}_2$, where $|\vec{a}_1| = |\vec{a}_2| = a = 0.246 \text{ nm}$, which is the lattice constant. SWCNTs can be in three different types of chirality. For zigzag SWCNTs, $m = 0$. If $n = m$, they are armchair SWCNTs. The remaining are chiral SWCNTs.

Figure 2-16 Definition of chirality of a SWCNT. $\vec{a}_1, \vec{a}_2$ are the unit lattice vectors. Insets illustrate armchair and zig-zag SWCNTs. [114]

As depicted in Figure 2-17, MWCNT consists of multiple concentric shells of the carbon cylinders. The distance between adjacent shells is approximately 0.34 nm, which is also the distance between adjacent graphene layers in graphite. The unique sp^2 bonds and honeycomb crystal lattice, along with cylinder structures result in superior properties of the CNTs.

Figure 2-17 Structure of MWCNTs. (a) Schematic illustration of a triple-layer MWCNT. (b) TEM image of a MWNT containing nine concentric layers. [115]

2.5.2.1.1 Electrical properties

SWCNTs may be either metallic or semiconducting, depending on their chirality. [115] All armchair SWNTs ($n = m$) are metallic. SWCNTs with $n - m = 3k$, where k is a non-zero integer, are semi-conducting with a small band gap; and all others are semiconductors with a relatively larger band gap that inversely depends on the nanotube diameter. [115] MWCNTs are generally metallic, as a result of statistical probability of the individual constructing tube. Because of the large electronic mean free path in the systems, electronic transport occurs ballistically in metallic SWCNTs and MWCNTs with perfect structures. Therefore, defectless metallic SWCNTs and MWCNTs are able to carry large current density without energy dissipated. [116]

2.5.2.1.2 Mechanical properties

CNTs are one of the strongest and stiffest materials. Both experimental work and theoretical investigations have shown the remarkable mechanical properties of CNTs, such as exceptionally high Young's modulus [114, 117, 118] and large elastic strain sustaining capability. [119, 120] The Young's modulus of individual CNT was estimated in the terapascal (TPa) range. [117] Wong *et al.* obtained an average bending strength of 14 GPa. [118] In agreement with their results, Yu *et al.* [121] managed to measure the strength of CNT in the range of 10–63 GPa. These superior mechanical properties come from the covalent sp^2 bonds between carbon atoms in the honeycomb lattices and the seamless cylinder structure.

2.5.2.1.3 Thermal properties

Heat transfer in crystalline carbon is dominated by phonons. [122] Both theoretical [123-125] and experimental [126-129] work shows that similar to graphene and graphite, SWCNTs and MWCNTs possess high thermal conductivities. Berber *et al.* demonstrated that the thermal conductivity of an isolated (10, 10) nanotube could reach up to 6600 W/m·K at room temperature. Due to additional intertube scattering, the thermal conductivity of MWCNTs, is relatively lower as compared to SWCNTs. [130] Nevertheless, Kim *et al.* demonstrated that the thermal conductivity of an individual MWCNT can be more than 3000 W/m·K at room temperature, using a MEMS measurement technique. [126]

As CNTs have superior properties such as excellent electrical, [131] thermal conductivities [123] and structural stability, [117] they have been considered as promising candidate to support active materials for electrochemical energy storage. For CNTs based composites, highly conductive CNT content facilitates charge transfer during cycling. Besides, owing to their hollowed structure and mechanical strength, CNTs are able to act as volume buffer for active materials. In addition, their high thermal conductivity is able to promote thermal dissipation, which is beneficial for the safety. Because of the absence of semiconducting types in SWCNTs and feasibility in fabrication, MWCNTs are chosen for this project.

2.5.2.2 Graphene

Graphene is another crystalline allotrope of carbon. A layer of graphene is one-atom-thick planar sheet of sp^2 bonded carbon atoms organized in a honeycomb crystal lattice. Graphite is composed by stacks of graphene with Van der Waals interaction. The unique structures of the graphene results in excellent properties, for instance, huge specific surface area of over $2630 \text{ m}^2\cdot\text{g}^{-1}$, high thermal conductivity of around $5000 \text{ W/m}\cdot\text{K}$, high carrier mobility over $2\times 10^5 \text{ cm}^2/\text{V}\cdot\text{s}$ and Young's modulus of 1100 GPa . [132, 133] These properties enable their promising applications in various fields, such as electronics, sensors, strong and lightweight compositing materials etc. In particular, 3D ultrathin graphite (UG) also termed as 3D graphene have been considered of great importance in electrochemistry. [134-141] 3D UG provides the platform to assemble various nanostructures into macro frameworks, as shown in Figure 2-18. [31, 137, 138, 142] Merits of this unique macroporous frame include facile access for the electrolyte and

possibility for binder-free construction. Improved performance was reported in MoS₂-coated 3D UG on Ni foam as an anode material for LIBs. After 50 cycles at current density of 100 mA·g⁻¹, a reversible capacity of 877 mAh·g⁻¹ could be retained. [31] He *et al.* showed 3D UG networks supported MnO₂ permitted a high area capacitance of 1.42 F·cm⁻² as the electrode material for pseudo capacitor at a scan rate of 2 mV·s⁻¹. [137]

Figure 2-18 SEM images of (a) MoS₂/3D UG [31] and (b) MnO₂/3D UG. [137]

2.6 Electrochemical characterization techniques

2.6.1 Cyclic voltammetry

Cyclic Voltammetry (CV) is a powerful electroanalytical technique in electrochemistry. In a typical measurement, potential of the working electrode is ramped linearly versus time at a predefined rate and swept reversely when it reaches the set potential. This sweep may be repeated several times in the set potential range while the

current at the working electrode is recorded and plotted against the potential to draw the CV curves. CV test can be used to investigate the kinetics and reversibility of redox reactions in the measured potential range. Peaks on the CV curves may be attributed to redox reactions in the following way. Redox reactions occurred at certain potentials will induce large quantities of charges and hence sharp increase of the current. Current then decay fast when the reaction species at electrode/electrolyte interface are depleted. In addition, specific capacitance C of the electrode material in ECs can be estimated by the CV tests, according to the following equation: [82, 143]

$$C = \frac{\int_{E_1}^{E_2} i(E) dE}{(E_2 - E_1) \cdot v} \quad (2 - 6)$$

where E_2 , E_1 , v , $i(E)$ are the upper, lower cut-off potentials, potential scan rate and instantaneous current density with respect to potential E , respectively. Obviously, under the same scan rate and potential window, the capacitance is propotional to $\int_{E_1}^{E_2} i(E) dE$, which is integral area of the CV curve.

2.6.2 Galvanostatic charge/discharge

Galvanostatic charge/discharge is a useful tool to determine the performance and cycling stabilities of LIBs and ECs. Charging and discharging are conducted at constant current until a set voltage is reached. A loop of charging and discharging is termed as a cycle. A number of cycles are usually repeated to evaluate the cycling stability of the electrodes while the rate performance can be determined by varying the charge/discharge currents. From the galvanostatic charge/discharge measurement, the capacities Q_c of the

LIBs can be calculated according to the formula of $Q_c = i \cdot t$, where i is the constant current density applied, t is charge/discharge duration. Q_c determines the amount of charges that can be stored in the anode material. Coulombic efficiency is defined as the fraction of the capacity stored in a rechargeable battery during charging that is recoverable by discharging. [144] In the galvanostatic charge/discharge testing of an anode material, the Coulombic efficiency can be obtained according to the equation: Coulombic efficiency = De-lithiation capacity/Lithiation capacity. In addition, capacity vs. potential curve may show characteristic plateaus of a particular electrode material during charging/discharging. For example, as shown in Figure 2-19, a wide plateau can be found in the lithiation part of the capacity vs. potential curve of Si. On the other hand, for ECs, the capacitances can be got according to the equation:

$$C = \frac{i \cdot t}{|\varphi_1 - \varphi_2|} \quad (2 - 7)$$

where C , i , t , $|\varphi_1 - \varphi_2|$ are the capacitance, current density, discharge duration and potential range, respectively.

Figure 2-19 Capacity vs. potential curves of a 40nm thick Si film vacuum-deposited on Ni foil in the initial (solid) and second (dotted) cycles, respectively. [145]

2.6.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is also a standard diagnostic technique in electrochemistry. [8] As shown in Figure 2-20, in EIS measurements, impedance data $Z(\omega)$ is collected at the open-circuit potential by applying a small amplitude (e. g. 5 mV) of alternative potential over a wide range of frequency (e.g. 1 mHz to 1 MHz). Data obtained by EIS is often expressed graphically in Bode or Nyquist plots. Bode plots show variations of the capacitance against frequency. In Nyquist plot, the real

part of the impedance Z' is plotted on the X axis and the imaginary part, $-Z''$ is plotted on the Y axis of a chart.

Figure 2-20 Illustration for the electrochemical impedance spectroscopy.

2.7 Morphology and structure characterizations

Several techniques have been employed to characterize the structures, morphologies and compositions of the materials. Here is a brief introduction of the characterization tools used which will not be redundantly described in the following chapters.

Scanning electron microscopy (SEM): SEM images were taken by LEO 1550 Gemini field-emission scanning electron microscopy.

Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) were carried out in JEOL JEM-2100F (HR).

Energy-dispersive X-ray spectroscopy (EDX): EDX was done by an EDAX detector equipped in the JEOL JEM-2100F HR TEM.

Raman Spectroscopy: Raman spectrum was obtained using a WITec Raman system with a laser wavelength $\lambda=532$ nm.

X-ray photoelectron spectroscopy (XPS): XPS was carried out using a Thermo Scientific Theta Probe XPS. Monochromatic Al K α X-ray ($h\nu=1486.6$ eV) was employed for analysis with an incident angle of 30° with respect to surface normal. Photoelectrons were collected at a take-off angle of 50° with respect to surface normal.

X-ray Diffraction (XRD): XRD signal was collected by powder XRD (Max 18 XCE, Japan) with a Cu K α source ($\lambda=0.154056$ nm).

Chapter 3 MoS₂/CNT as an anode material for LIBs

Composite of CNTs and MoS₂ combining the extraordinary properties of CNTs and high capacity potential of MoS₂ have attracted tremendous attention in the research of anode materials for LIBs. One important feature of MoS₂ is its relatively smaller volumetric changes in the lithiation/de-lithiation processes. [21-31, 146, 147] As such, it could provide the potential for less structural degradation during cycling. However, the performances of anodes made of bulk MoS₂ materials are still far from ideal. Only limited capacities may be exhibited and the capacities may drop rapidly in a few cycles.

Combining MoS₂ with CNTs [24, 26-28, 37] is considered as a promising solution for the problems. CNTs are well known for their superior electrical, [131] thermal conductivities [123] and structural stability.[107, 117] Therefore, it is expected that by combining the merits of CNTs and MoS₂, the MoS₂/CNT composite can be a good candidate for anode material in LIBs.

3.1 Binder-free configurations

There have been a number of reports on the synthesis of MoS₂/CNT composites, as mentioned in Section 2.2.1 and 2.5.2 [22, 24, 28] , which demonstrate the significant roles of the synthesis methods as well as morphology control in the performance. Yet, it may be noteworthy that how such composites are assembled onto the current collector is also of high importance. In particular, direct conductive pathways constructed between

active material and current collectors have proven to be beneficial for the efficient charge transfer. [148, 149] Unfortunately, there have not been such reports on MoS₂/CNT composites so far. Active materials have to be mixed with polymer binders before electrochemical testing, as shown in Figure 3-1. On the one hand, charges have to make way through the less conductive polymer matrix before they can reach the current collectors, laying obstacles for the efficient transfer of charges. On the other hand, these polymers may not be strong enough to withstand the huge stress in the active materials during electrochemical cycling. Therefore, active materials in such configuration tend to suffer from structural failures and the capacities of batteries may fade as a consequence.

Figure 3-1 Schematic of the traditional anode constructions, in which active materials are binded by polymer materials (a) before and (b) after cycling. [150]

If there was a method to exclude these less conductive additives, it could be a step further in the development of MoS₂/CNT anode materials. In this regard, this chapter is devoted to the synthesis of binder-free MoS₂/CNT composite. It is enabled by the growth of CNTs directly on the SS current collectors, followed by hydrothermal and annealing preparation of MoS₂ on surface of the CNTs. The MoS₂/CNT composite obtained can be directly used for LIB testing without any binders. As indicated in Figure 3-2, the

fabrication process mainly involves three steps: substrate preparation, growth of CNT network and synthesis of MoS₂ by hydrothermal reaction and subsequent annealing.

Figure 3-2 Schematic of the fabrication processes of MoS₂/CNT composite as a binder-free anode material: (a) SS substrate preparation; (b) growth of CNTs onto the SS substrate; (c) synthesis of MoS₂ flakes onto the CNT surface.

3.2 Growth of CNTs by CVD method

Growth of the CNTs on the SS current collectors serves as the foundation for the success of the binder-free MoS₂/CNT composite. It is fulfilled by CVD method. Since the discovery of CNTs in 1991, many technologies have been developed to grow CNTs, such as arc discharge, [113, 151] laser ablation [152] and CVD. The former two processes require extremely high vacuum, high temperature or high power laser. Besides, the CNTs yielded usually need further separation and purification before they can meet the requirements for applications. These disadvantages have limited their applications. CVD is a widely used technique in industries and laboratories with a long history for synthesis of various materials. It was not until 1993 that the CVD method was utilized for the fabrication of CNTs. [153]

Nowadays, CVD has become the dominating technology in the fabrication of CNTs. Compared to the arc-discharge and laser-ablation techniques, CVD comes with many advantages. Firstly, formation of the CNTs in CVD is driven by thermal energy rather than by high power arc or laser. CNTs can be obtained at much lower temperature, typically below 1000 °C, without the need for high vacuum. Meanwhile, the CVD system is usually relatively low-cost and easy to handle. More importantly, in CVD process, CNTs can be directly grown on various substrates, including metals, favouring CNTs' applications in various fields. In addition, the properties of CNTs can be controlled by simply changing the CVD parameters. The advantages of CVD have made it to be a suitable method to grow CNTs for a variety of applications, particularly in the field of electrochemistry and it is therefore chosen in this Ph. D work.

3.2.1 Setup and mechanisms

Setup of the CVD system used in this project is shown in Figure 3-3, which consists of the following three main components: (1) a furnace to heat up the samples and maintain high temperature for reaction; (2) a quartz tube where the samples are placed and (3) flow controllers through which the reaction gases are fed.

Figure 3-3 (a) Photograph and (b) schematic of the CVD furnace.

In a typical process, after sequentially cleaned in acetone, isopropyl alcohol (IPA) and de-ionized (DI) water in an ultrasonic basin, SS chips with the diameter of 1.5 cm are blown by N₂ and then baked in oven to dry. 8 nm Ni films are deposited onto the chips as catalyst by electron beam evaporation (Auto 306, HHV system). The chips are put in the CVD furnace shown in Figure 3-3, in the flow of 180 sccm Ar and 70 sccm H₂. Once temperature has been ramped up to 700 °C, ethanol vapor is introduced into furnace as the carbon source for CNT growth. After 15 minutes of growth, the ethanol vapor is cut off and the furnace is cooled down to room temperature. The SS chips are covered by black layer of CNTs.

It is generally accepted that the formation of CNTs takes place as follows. [154] During the CVD process, the Ni catalyst film on the substrate transforms into nanoparticles (NPs) after annealing. At the growth temperature, reactive carbon atoms are dissociated from the input carbon feedstock with the catalyzation of catalyst nanoparticles. The resulted carbon atoms then dissolve into the catalyst NPs. Catalyst NPs are eventually

saturated owing to continuous supply of the carbon feedstock. At last, carbon atoms precipitate onto the surface of the catalyst NPs, leading to the formation of tubular carbon structures which are in the low energy state. The mechanisms are depicted in Figure 3-4. With respect to the location of catalyst NPs in the eventual CNTs, growth of CNTs can be categorized into tip-growth and base-growth mode. The difference between the two modes derives from the adhesion between the catalysts and the substrate. The tip-growth mode happens if the catalyst-substrate adhesion is relatively weak. Carbon feedstock is fed to the tip of a growing CNT at the interface between CNT and the catalyst NP. As a result, catalyst is lifted up from the substrate, and carried all the way during the growth. In contrast, in the base-growth mode, strong interaction to the substrate anchors the catalyst NPs onto the substrate during the growth. The base part of growing CNTs remains reactive during the growth, where the new tubular structures are formed.

Figure 3-4 CNT growth mechanism. Left: base-growth mode; right: tip-growth mode.

3.2.2 Growth results

Figure 3-5 (a) SEM image of the CNT network prepared by CVD; (b) (c) TEM image of randomly selected CNTs at different magnification; (d) HRTEM image of the rectangle region in (c).

SEM image in Figure 3-5 (a) displays the CNTs successfully grown on the SS substrate by the CVD method, using the set-up and recipe described in Section 3.2.1. Lengths of the CNTs are about several tens of micrometers while the diameters are in the range of 10 to 50 nm. Interestingly, CNTs are self-assembled into a sparse network, leaving notable space inside, which is beneficial for the access of electrolyte and lithium ions during charge/discharge. TEM images of Figure 3-5 (b) and (c) provide direct proof for the multi-walled characteristic of the as-synthesized CNTs. The CNTs are clearly

constituted by tens of walls while cavities can be found in the axis. As indicated in the HRTEM image of Figure 3-6 (d), carbon layers that construct CNTs are separated by ca. 0.34 nm, matching the wall separation in MWCNTs. MWCNTs may be a better choice for this application. Firstly, MWCNTs are possible to exhibit higher electrical conductivity as there are no semiconducting types which exist in SWCNTs. Besides, MWCNTs generally have larger diameters and hence more surface area, enabling the accommodation of more active material on the surface. In addition, the synthesis of MWCNTs is relatively feasible as compared to that of SWCNTs, in which precise control over the catalysts and sophisticated processes are required.

3.3 Hydrothermal preparation of MoS₂

Hydrothermal process is an important wet chemistry synthesis method. It has been employed to prepare various nanomaterials with controllable morphologies. Benefits of the hydrothermal process include low temperature and facile blending of different materials. Schematic diagram of a Teflon-lined SS autoclave for the hydrothermal reaction is shown in Figure 3-6. [155, 156]

Figure 3-6 Schematic of a Teflon-lined SS autoclave.[155, 156]

CVD-prepared CNTs often come with hydrophobic surfaces. Surface properties of the CNTs can be modified by O₂ plasma to ensure their complete wetting by aqueous solution. The O₂ plasma treatment was carried out at RF power of 30 W for 10 seconds. As shown in Figure 3-7, the contact angle turns from 142° to below 10° after O₂ plasma treatment, indicating the change from super hydrophobic to hydrophilic.

Figure 3-7 Contact angle measurement results before (a) and after (b) O₂ plasma treatment.

As CNTs are grown on one side of the SS substrate, before hydrothermal reactions of MoS₂, the other side of the samples without CNTs was covered and protected by Polytetrafluoroethylene (PTFE) tape. Samples were then put in 20 ml Teflon-lined SS autoclaves with 6 mL 2.5 mM ammonium tetrathiomolybdate (purity 99.95%, Sigma Aldrich) solution and kept at 200 °C for 10 hours. After cooling down to room temperature naturally, the protecting PTFE tape was removed and the obtained samples were rinsed several times with de-ionized (DI) water followed by baking at 60 °C for 8 hours in ambient. Finally, the samples were annealed at 500 °C for 2 hours with Ar and H₂ as the protection atmosphere.

3.4 Morphology and structure characterizations

After hydrothermal reaction and the annealing process, the surface of the CNTs is completely covered by MoS₂ nanoflakes, as displayed in Figure 3-8 (a) and (b). The connection of the CNT network to the substrate is so strong that it survives from the harsh conditions during long-duration hydrothermal reaction. This is also advantageous for the stability of anode. Compared to those of bare CNTs, diameters of the composite nanowires increase to be 200 to 300 nm, but the porosity among the CNT network is still maintained to a large extent. Such structure could facilitate the contact of the active material with electrolyte and ensure all of its portions into electrochemical reactions. In TEM image of Figure 3-8 (c), the core-shell structure of the MoS₂/CNT nanowire is clearly presented. As indicated in the HRTEM image of Figure 3-8 (d), the MoS₂ flakes surrounding the CNTs consist of several (<10) layers, in between which the distance is

around 0.64 nm, in line with the interlayer distance of (002) plane orientation in MoS₂. [157]

Figure 3-8 (a) (b) SEM images of the MoS₂/CNT composite on SS substrate at different magnifications; (c) (d) TEM and HRTEM image of MoS₂ flakes on the surface of a CNT, respectively.

As shown in Figure 3-9, the Raman spectrum of as-synthesized CNTs exhibits a G peak at 1581 cm⁻¹ and a D peak at around 1347 cm⁻¹, consistent with previous reports. [158] The G peak is the signature for the graphenic lattice of the CNT walls while D band represents the defects and imperfections in the structure. The I_D/I_G ratio of as-synthesized CNTs is relatively high, probably due to the relatively low growth temperature and high growth rates of the CNTs. Such defects are possible to serve as nuclei centers for MoS₂,

which have already been proven in previous work of nanoparticles on CNTs. [159] After hydrothermal reaction, two characteristic peaks of MoS₂ are found at 379 and 405 cm⁻¹, which belong to the E_{2g}¹ and A_{1g} modes, respectively. [160, 161] In the meantime, both D and G bands of the CNTs diminish significantly, due to the screening effects of the covering MoS₂ flakes. [22]

Figure 3-9 Raman spectra of the CNTs (dotted) and MoS₂/CNT composite (solid).

XPS reveals that the ratio between Mo and S is 1:1.86, close to the stoichiometric ratio in MoS₂. As shown in Figure 3-10 (b), the binding energy profile of Mo 3d shows two strong peaks at 229.3 and 232.4 eV which can be attributed to Mo 3d_{5/2} and Mo 3d_{3/2} while in Figure 3-10 (c), S 2p_{3/2} and S 2p_{1/2} peaks clearly exhibit at 162.1 and 163.3 eV, respectively. [22, 37, 162, 163] Hence, the XPS data further ascertains the successful synthesis of the MoS₂ material.

Figure 3-10 XPS spectra of the MoS₂/CNT composite: (a) survey scan and (b) (c) high resolution scans of Mo 3d and S 2p, respectively.

EDX line scan manifests the element distribution in the nanowires, as shown in Figure 3-11. The difference in element distribution from shell to core parts of the nanowires is clearly displayed. Carbon content increases towards the axis of the nanowire, which is the signal from the CNTs.

Figure 3-11 EDX results: (a) distribution of C, S and Mo elements across the MoS₂/CNT interface (inset indicates the scanning route); (b) element composition of the scanned area. (Copper signal comes from the supporting TEM grid.)

The crystallographic structures of the CNTs and MoS₂ are confirmed by XRD analysis, as shown in Figure 3-12. Although the signal from SS substrate is very strong, yet the phases of CNTs and hexagonal MoS₂ (JCPDS No.: 37-1492) can still be observed.

Figure 3-12 XRD patterns of the CNTs (a) and MoS₂/CNT (b) on SS substrate, respectively.

3.5 Half-cell assembly and electrochemical characterization

3.5.1 Half-cell Assembly

Figure 3-13 (a) Components of a CR 2032 half-cell used in the experiments; [164] (b) schematics for the assembly [112] and (c) an assembled half-cell.

To evaluate its performance as an anode material, MoS₂/CNT composite on SS chips is directly assembled into CR 2032 type half-cells for electrochemical testing without the usage of any binders or additives. In the half-cells, the obtained composite on SS substrates were used as the working electrodes while pure lithium foils were used as the counter electrodes. The assembly was done in a glove box filled with pure Ar (Innovative Technology, Inc. H₂O < 0.1 ppm, O₂ < 0.1 ppm). The electrolyte was LiPF₆ (1.0 M) dissolved in EC/DEC (1:1 by volume). Working electrode, separator, lithium foil, SS spacer and spring were sequentially placed into the positive shells, as shown in Figure 3-13 (a) (b). Negative caps were used to close the cells after introduction of several

droplets of the electrolyte. The cells were then crimped and sealed by a hydraulic crimping machine (MSK-110, MTI Corporation). Assembled half-cells, as shown in Figure 3-13 (c), were aged for 24 hours before subjected to measurement of the LIB performances. The same configuration and assembly method are also used in the following experiments of LIBs.

3.5.2 Electrochemical Characterization

The half-cells were tested in galvanostatic charge and discharge cycling over the potential range of 0.01-3.0 V vs. Li/Li⁺ in a battery tester (NEWARE BTS-5 V, Neware Technology Co., Ltd.). CV test and EIS were carried out using Solartron 1287/1260 Electrochemical Interface. The CNT mass loadings were determined by weighing the samples before and immediately after the CVD growth using an analytical balance (Mettler Toledo XP 26, 0.002 mg) while for MoS₂, weight was measured after the annealing process. The total mass of MoS₂/CNT composite was around 1 to 1.3 mg on each sample, with CNT and MoS₂ mass ratio around 1:3 to 1:2. Current applied and capacities obtained were all calculated based on the mass of the MoS₂/CNT composite.

The representative CV curve for the first three cycles is shown in Figure 3-14. In the first cycle, two distinct peaks are observed on the CV curve at 1.0 and 0.4 V, consistent with previous reports. [23, 30, 33] The cathodic peak at 1.0 V can be assigned to insertion of lithium ions (Li⁺) into the interlayer of MoS₂, transforming its phase from 2H-MoS₂ (Mo in trigonal prismatic coordination) to 1T-Li_xMoS₂ (Mo in octahedral coordination). [23, 27] The subsequent sharp peak located at 0.4 V is associated with the

further reaction between MoS₂ and Li⁺, resulting in LiS₂ and Mo metallic particles, following the reaction of $MoS_2 + 4Li^+ + 4e^- \rightarrow Mo + 2Li_2S$. [27] It should be mentioned that both these two reduction peaks disappear in the following cycles, suggesting irreversibility in the conversion of MoS₂ into Li₂S and Mo.[29] Meanwhile, a remarkable cathodic peak appears at 1.8V, which indicates the lithiation process of S into Li₂S. Therefore, in the following cycles, reactions may take place between lithium and sulfur. In anodic sweeps, a broad peak around 1.5 V can be attributed to the partial oxidation of Mo to MoS₂ [35] and/or de-lithiation of residual lithium intercalates (Li_xMoS₂). [22] The following pronounced peak at 2.3 V corresponds to conversion of Li₂S to S₈²⁻. [24]

Figure 3-14 CV curve of MoS₂/CNT composite for the first 3 cycles measured at a scan rate of 0.1 mV·s⁻¹ between 0.01 V and 3 V.

In the initial lithiation profile tested at $200 \text{ mA}\cdot\text{g}^{-1}$ in Figure 3-15, two voltage plateaus at around 1.1 and 0.6 V can be observed, corresponding to the formation of Li_xMoS_2 and reduction of MoS_2 into Mo particles embedded in Li_2S matrix, respectively. In the de-lithiation plots, well-defined plateaus at 2.2 V can be attributed to extraction of lithium from Li_2S . These plateaus are in line with the aforementioned peaks in the CV curves.

Figure 3-15 Voltage capacity profiles of MoS₂/CNT composite at the current density of $200 \text{ mA}\cdot\text{g}^{-1}$.

From the galvanostatic charge/discharge measurement, the capacities of the LIBs can be obtained according to the formula of $Q_c = i \cdot t$, where i is current density of 200 mA·g⁻¹ applied in the measurement, t is charge/discharge duration. As shown in Figure 3-16, initial lithiation and de-lithiation capacities at 200 mA·g⁻¹ of the MoS₂/CNT composite are 1715 and 1305 mAh·g⁻¹, respectively, corresponding to a Coulombic efficiency of 76.1%. The irreversible capacity loss of 23.9% is probably caused by formation of solid electrolyte interphase (SEI), which is almost inevitable in nanosized anode materials.[165] SEI is a layer formed on the anodes of LIBs as a result of electrolyte decomposition, mainly during the first cycle. [166] Nevertheless, the efficiency keeps at nearly 100% in the following cycles and the composite demonstrates an impressively high de-lithiation capacity of 1456 mAh·g⁻¹ after 50 cycles. This is among the highest capacities as well as best cyclic performances of MoS₂/CNT composites ever reported at the current density of 200 mA·g⁻¹. [21]

Figure 3-16 Specific capacities and Coulombic efficiency of the MoS₂/CNT composite versus cycle number charged/discharged at 200 mA·g⁻¹.

To verify the improvement brought-in by the binder-free configurations and CNTs contents, commercial MoS₂ powder (~6 μm particle size, Sigma Aldrich) was mixed with acetylene black and poly(vinylidene difluoride) (PVDF) binders at the weight ratio of 8:1:1 and tested under the same conditions for comparison. Besides, bare CNTs on SS substrates were also tested to evaluate contribution of the CNTs to the overall capacity. As shown in Figure 3-17, in sharp contrast to the high and stable capacity of binder-free MoS₂/CNT composite, MoS₂ powder with binders exhibits significant different electrochemical performances. A much lower capacity of 663 mAh·g⁻¹ was manifested upon de-lithiation in the initial cycle and it dropped sharply to below 400 mAh·g⁻¹ after

20 cycles. Without the support of CNTs, the electrochemical reactions between lithium ions and MoS₂ powder could cause damage to the MoS₂ material. When MoS₂ loses contact to the SS substrate, capacity drops consequently. These results in this control group confirm the superiority of the binder-free construction and combination with CNTs. On the other hand, bare CNTs on the current collector demonstrate a limited capacity of below 200 mAh·g⁻¹. Thus, the high and reversible capacity demonstrated by the MoS₂/CNT composite probably comes from the MoS₂ content and also the strong synergetic effects of MoS₂ and CNTs. [26]

Figure 3-17 Specific de-lithiation (hollow) and lithiation (solid) capacities of binder-free MoS₂/CNT composite (triangle), commercial MoS₂ particles with binders (square) and bare CNTs (circle) versus cycle number charge/discharged at 200 mA·g⁻¹.

EIS measurements are also carried out to compare the internal impedances of the as-assembled half-cells. The result is presented in the Nyquist plot of Figure 3-18, in which low frequency data are on the right and higher frequency data are on the left and each point represents the impedance at one frequency. The Nyquist plot can be understood according to the equivalent circuit model, as displayed in the inset of Figure 3-18. R_i is the internal resistance of the cell. R_{ct} and CPE represent the charge-transfer resistance and constant phase element (CPE) at the electrode/electrolyte interfaces. Z_w is the Warburg impedance associated with the lithium-diffusion process. The semicircle in the high-medium frequency region corresponds to the charge-transfer resistance while the inclined line at lower frequencies is associated with the lithium-diffusion process in the anode material. [23]

Figure 3-18 Nyquist plots (100 kHz–50 mHz) of MoS₂/CNT composite and MoS₂ powder. Inset is the equivalent circuit model.

Diameter of the semi-circle at high-medium frequencies in Nyquist plot is significantly reduced in the MoS₂/CNT composite as compared to MoS₂ powder with binders. It proves that in the binder-free MoS₂/CNT composite, charge transfer resistance is remarkably reduced owing to the binder-free construction and introduction of CNT content. [35]

Figure 3-19 Specific capacities at different current rates.

Rate capability is another important criterion to evaluate the performance of an anode material. Good rate performance is highly desired for the systems that require high output currents and fast charging, such as EVs. As shown in Figure 3-19, a de-lithiation capacity of 1450 mAh·g⁻¹ is obtained after 10 cycles at the charge/discharge current of 200 mA·g⁻¹, consistent with the value in Figure 3-15. When the current densities are raised to 400, 600, 800 and 1000 mA·g⁻¹, the corresponding de-lithiation capacities after 10 cycles are 1431, 1367, 1302 and 1224 mAh·g⁻¹, respectively, demonstrating high

capacities and plausible cycling behaviour even at high current density. Eventually, when the current is set back to 200 mA·g⁻¹, the de-lithiation capacity recovers to 1535 mAh·g⁻¹, indicating excellent rate capability of the composite.

The outstanding performances including high capacity, excellent cycling retention and rate capability of the binder-free MoS₂/CNT composite are enabled by the rational selection, composition and also construction of materials. Improved structural stability as well as efficient reaction kinetics is realized in this hierarchical assembly of CNT network and MoS₂ flakes. Firstly, the network of CNTs provide a strong skeleton for the composite, avoiding aggregation of the active material, retaining its inter-space and also large surface area to a considerable extent. Secondly, the internal cavity and flexibility of the CNTs can help to absorb or buffer the mechanical stress induced by volume variation of MoS₂ upon repetitive lithium insertion/extraction. Meanwhile, voids inside the composite not only provide space to accommodate volume change but also shorten the diffusion pathways, enabling fast lithium ion transport and hence good rate capability. Furthermore, highly conductive CNTs are widely known as good pathways for charge transfer in nanocomposite. In this MoS₂/CNT composite, charge transfer can be further enhanced because of the direct rooting of CNT network onto the SS current collector as well as the binder-free construction.

3.6 Conclusions

In summary, an approach to fabricate binder-free MoS₂/CNT composite anode material has been successfully developed. It consists of CVD growth of CNTs on SS

substrate and hydrothermal and annealing preparation of MoS₂ nanoflakes. Because of reinforced structural stability and also enhanced reaction kinetics, the MoS₂/CNT composite obtained demonstrates impressive electrochemical performances. Importantly, a high and reversible capacity over 1300 mAh·g⁻¹ is retained for 50 cycles at the current density of 200 mA g⁻¹, while excellent rate performance is also delivered. This method offers a new idea to optimize the MoS₂/CNT composites which are under intensive research. Moreover, the binder-free construction and usage of CVD-grown CNTs on SS substrate instead of dispersed CNTs may not be limited to MoS₂/CNT composite but also of potential for the improvement of other CNTs based composite anode materials.

Chapter 4 Si/Ni/CNT as an anode material for LIBs

In Chapter 3, CNT network demonstrates its promising application to improve the performance of MoS₂ as anode materials. However, the network configuration of CNTs is not suitable for all occasions. It may not be feasible to coat the CNTs uniformly with active materials using deposition approaches other than hydrothermal method. For instance, in physical vapour deposition (PVD) methods, such as magnetron sputtering, nano particles of active materials arrive in preferable directions from the target. As such, considering the high density of the CNTs, it is unlikely for all the CNTs in the network, especially those underneath the surface, to get uniformly coated by the active materials. In addition, for deposition methods with high rates, such as electrodeposition, the materials deposited in the earlier stage tends to fill the spaces in the network. Further access of the deposition precursor to the CNTs underneath may be blocked. Therefore, it may be necessary to modify the CVD method to achieve more controllable organizations of the CNTs for extended range of applications.

Plasma Enhanced CVD (PECVD) is improved deposition technology from CVD, as shown in the following schematic, Figure 4-1. In PECVD, an extra plasma generator is installed in the growth chamber. The dissociation of the carbon source can be facilitated with the help of the plasma energy, which makes possible the fabrication of CNTs with relatively large diameters. Meanwhile, an electrical field is also applied at the vertical direction which enables the alignment of CNTs at the vertical direction into arrays.

Figure 4-1 Schematic of the PECVD system.

4.1 Growth of CNTs array by PECVD method

In a typical process, the substrate such as Si wafers and SS foils were coated with TiN barrier layer in an Elite sputtering system, followed by electron beam deposition of thin Ni layer as catalyst in an Auto 306, HHV system. CNTs growth was carried out in a Nano Instrument PECVD system. 60 sccm C_2H_2 was the carbon source and 240 sccm NH_3 was used to decompose C_2H_2 and also etch away byproducts. Chamber pressure was kept at 9.0 mbar. Temperature was ramped up and kept at 800 °C during growth. An electric field was applied between the top disc and bottom plate and biased at 700 V in the chamber and the plasma power was controlled at 120 W.

Figure 4-2 Growth results of the PECVD method: (a) (b) cross-section and top view SEM images of the vertical CNT array, respectively; (c) TEM image of the fabricated CNTs; (d) HRTEM image presenting the lattice structure.

The SEM images of the CNTs fabricated are shown in Figure 4-2 (a) (b). Owing to the electrical field applied during PECVD growth, the CNTs obtained are well aligned vertically, forming an array. The plasma helps the dissociation of the carbon precursor and therefore facilitates the formation of CNTs. The CNTs exhibit lengths in the range of 7 to 10 μm, and a rather large and uniform diameter around 100 nm. It may be noteworthy that

the density of CNTs is not very high, around ca. $3.45 \times 10^8 \text{ cm}^{-2}$, leaving plenty of space between neighboring CNTs. This is beneficial for the complete coating of CNTs by materials in PVD processes. [106, 167] The relatively large diameter brings in more surface areas which also help the accommodation of coating material.

TEM images of the CNTs are shown in Figure 4-2 (c) (d), clearly manifesting their MWCNT characteristics. The diameters of the MWCNTs are around 100 nm, in line with the SEM observations in Figure 4-2 (a) (b). Walls of the MWCNTs are constructed by several tens of carbon layers which surround cavities with diameter around 30 nm in the axis. Wedge-shape catalyst particles can be found in the tips, indicating the CNT follows a tip-growth mode and the bottom part of catalyst is the front end for formation of graphene sheets. Therefore, the sidewalls of the CNT are constituted by stacked cone-segment shaped graphene sheets which follow the bottom profile of the catalyst particle. [168, 169] The constructing sheets are separated by ca. 0.34 nm, consistent with the theoretical value. [113]

In the Raman spectrum, Figure 4-3, there are two characteristic peaks of CNTs at around 1582 cm^{-1} and 1350 cm^{-1} , which belongs to the G and D bands, respectively. The relatively high I_D/I_G ratio could come from the MWCNT nature and also the plasma utilized during growth which may increase the possibility of vacancy and disordering of the constructing carbon atoms in the structure.

Figure 4-3 Raman spectrum of the CNT array.

4.2 Ni/CNT and application for SiONW growth

As a proof of concept for the advantages of the CNT array, CNTs grown on the Si substrate were coated by the Ni using a typical PVD process, magnetron sputtering. The Ni/CNT array on Si substrate is then utilized as catalyst for the growth of Si oxide nanowires (SiONWs). With confined dimensions, 1D nanomaterials have exhibited unique properties. Recently intensive research has been carried out on 1D nanomaterials, [115, 170-173] including SiONWs which are considered as a promising material in a wide

range of potential applications such as low-dimensional waveguides, blue light emitters, sacrificial templates and anode material in LIBs. [174-177]

The controllable fabrication of 1D nanomaterials remains a topic of great importance and also challenges. For the growth of silicon-based nanowires, several methods have been developed and the representative mechanisms are understood as vapor-liquid-solid (VLS) [178, 179] and solid-liquid-solid (SLS) growth. [177, 180-186] In a VLS growth process, catalysts like Au nanoparticles are employed as active sites to absorb Si atoms from vapor phase source, typically gaseous silane (SiH_4). On the other hand, in SLS mechanism, Si solids such as wafers and particles are utilized as the source for the nanowire growth. The SLS mechanism is of potential for low cost and abundant resources. More importantly, it completely excludes the need for SiH_4 which is extremely toxic. [187] Therefore, this method is more favorable for the fabrication of SiONWs and has caught a lot of research interest. [177, 180-185, 188]

In this section, a method is developed to further promote the growth of SiONWs within the frame of SLS mechanism. Owing to their exceptional mechanical robustness and structural stability, CNTs have been demonstrated as excellent templates for catalyst in chemical reaction. [189, 190] By using the Ni/CNT array where Ni serves as the catalyst, rapid growth of SiONWs can be achieved using bulk substrate as the Si source.

4.2.1 Experimental procedures

The growth process is shown in Figure 4-4, which mainly involves PECVD fabrication of CNTs and solid source growth of SiONWs.

Figure 4-4 Schematic of the fabrication process: (a) PECVD growth of CNT array; (b) magnetron sputtering of Ni; (c) solid source growth of SiONWs.

After PECVD growth of CNTs, the samples with CNTs were coated by 100 nm nickel which served as the catalyst for SiONW growth. Growth was carried out in the tube furnace. Flow rates of 500 sccm Ar and 200 sccm H_2 were used as the process gases. The furnace pressure was maintained at atmospheric pressure during the entire growth process. Temperature was kept at 1000 °C for 15 min, followed by cooling down.

4.2.2 Results and discussions

CNT array after magnetron sputtering of Ni is shown in Figure 4-5 (a). The unique vertical array arrangement of the CNTs enables feasible coating of the Ni shell onto the CNTs. Diameters of the core-shell Ni/CNT heterogeneous nanowires are around 200 nm, relative larger than those of CNTs in Figure 4-2. Figure 4-5 (b), (c) and (d) display the SiONWs after growth in the tube furnace. Clearly, SiONWs completely fill the space among the CNT array. Density of the SiONWs is so high that the hybrid networks of SiONWs and CNTs become a densely packed layer on the substrate, as shown in Figure

4-5 (b). It is also consistent with top angle view SEM, Figure 4-5 (c), in which entire surface of the sample is covered by the dense network of SiONWs.

Figure 4-5 (a) Top view SEM image of the Ni/CNT array on Si substrate; (b) (c) (d) cross-section, top and higher magnification top views SEM images of the SiONW and CNT hybrid film, respectively.

Distinctly different from CNTs, SiONWs display diameters below 40 nm, as shown in Figure 4-5 (d), which are much smaller than those of the CNTs. Besides, there are particles on the tip parts of the SiONWs, which are possibly the Ni catalysts. The growth is likely to follow a tip growth mode, which typically happened in solid source growth of SiONWs. [191, 192] Here, the lengths of the SiONWs could reach several tens of micrometers, forming a densely packed layer with thickness of over 30 μm. Given the growth time of 15 minutes, the growth rate can be considered as very fast as compared to

previous reports on solid source growth of SiONWs catalyzed by Ni. [177, 180, 182-184] On the contrary, without the CNTs, growth of SiONWs is dramatically impeded as displayed in the Figure 4-6 (a) and (b). SiONWs are merely formed in limited areas on the surface. The difference probably comes from the enhancement role of the CNT array, which will be analyzed in details later.

Figure 4-6 (a) (b) Top and cross-section view SEM images of the growth results without CNTs.

Figure 4-7 (a) gives the TEM image of a randomly selected SiONW. The diameter is around 25 nm. There is not any obvious crystalline lattice that can be observed in wide range. Hence, fast Fourier transform (FFT) pattern in the inset ascertains that the SiONWs obtained are amorphous. EDX spectrum in Figure 4-7 (b) reveals that the film is mainly composed of Si, O and C elements, in accordance with its composition of SiONWs and CNTs. The properties of the SiONWs are further characterized by XPS, by which the stoichiometric ratio of O to Si is determined to be 1.66. Moreover, as shown in Figure 4-7 (d), Si 2p peak located at 103.3 eV clearly evidences the Si^{4+} state in the Si oxide while

signal from the unoxidized state of Si^0 at 99.4 eV could hardly be detected in the binding energy. Meanwhile, O 1s peak can be observed at 532.6 eV, as indicated in Figure 4-7 (e). Therefore, the XPS data confirms the successful synthesis of the Si oxide compound in the nanowires. [193-196]

Figure 4-7 (a) HRTEM image of a randomly selected SiONW; inset is the corresponding FFT diffraction pattern. (b) EDX spectrum of the hybrid film fabricated. XPS spectra of SiONWs: (c) Survey scan; high resolution scan of the Si 2p (d) and O 1s (e), respectively.

Growth of SiONWs using solid source in our method follows a typical solid-liquid-solid mechanism. In this mechanism, Ni catalyst reacts with the Si at the solid interfaces between them and form liquid droplets of Ni-Si alloys at a relatively low

temperature. [180] With further increase of the temperature, vast amount of the Si atoms start to transfer from the Si substrate and diffuse into the Ni-Si droplets through the solid and liquid interfaces. When these droplets are saturated, Si atoms precipitate into the solid form of whiskers or nanowires. [177, 180, 182-184, 186, 188] It should be mentioned that O_2 absorbed on the surface of samples as well as residual O_2 in the growth atmosphere also take part in the reaction. As a consequence, amorphous SiO_x clusters are formed as precursors. Eventually, continuous diffusion of the Si atoms to the Ni-Si/ SiO_x interfaces results in the formation of amorphous nanowires of SiO_x . [177].

Figure 4-8 Cross-section view SEM images of samples obtained after growth at 800°C (a), 900°C (b) and 950°C (c) respectively.

With the introduction of CNT array, growth of $SiONWs$ is promoted significantly, but the underlying mechanism is yet to be known. To investigate the role of the CNTs, supplementary experiments were carried out, in which CNTs on Si substrate samples were heated to lower temperatures with other conditions unchanged. The growth results at temperature of 800 °C, 900 °C and 950 °C are shown in Figure 4-8. As evidenced by the SEM images, $SiONW$ formation starts at around 950 °C. Despite slight bending, the structures of the CNTs are well maintained in the entire ramping-up process and they are still organized in vertical aligned array. More importantly, the Ni catalysts are well

dispersed on the CNTs. It is widely known that CNTs are able to serve as excellent support for metal catalysts, because of their stubborn mechanical strength and structural stability. [189] The CNTs fabricated by our PECVD method come with large diameters which further benefit accommodation of the catalysts. Hence, the distribution of the SiONWs obtained can be improved, resulting in a densely packed film. On the contrary, if not for the CNTs, Ni catalysts are agglomerated into large particles, as shown in Figure 4-6. Large particles come with greatly reduced surface area-volume ratio, which is not favorable for diffusion, saturation and precipitation of the Si atoms. This probably accounts for the greatly deteriorated growth results without the CNTs. Nevertheless, with the introduction of the CNT array, the catalysts are prevented from agglomeration and they can be kept at small dimensions which enhance their reactivity. In this manner, the growth of SiONWs can be accelerated. In addition, it is noteworthy that the CNT array is also a good scaffold with a lot of space left inside for the process gases. As H_2 is able to enhance surface diffusion kinetics of Si, [186] with H_2 filled in the space provided by the CNT scaffold, Si transport from the substrate can be promoted dramatically. Hence, enhanced supply of the Si atoms will boost the formation of SiONWs. In summary, the CNT array helps dispersion of the catalysts and also enhances Si diffusion by providing space for H_2 .

In summary, vertical CNT array serves as an excellent template for the Ni catalysts and also enhances Si supply, therefore promoting the growth of SiONWs with Si substrate as the solid source. The findings shed light on the advantages of PECVD method and vertically aligned array organization of CNTs as well as a possible application of the Ni/CNT array.

4.3 Si/Ni/CNT as an anode material for LIBs

CNT array has proven its promising potential in the growth of SiONWs. Nevertheless, the Ni/CNT array may not be limited for this application. Since, there is still plenty of space left among the array of Ni/CNTs, they are possible to accommodate further coating of active materials, such as Si, for LIB applications. Among a number of alloy-type anode materials, Si exhibits the highest theoretical capacity of $4200 \text{ mAh}\cdot\text{g}^{-1}$, corresponding to the $\text{Li}_{22}\text{Si}_5$ phase, [197] as shown in Figure 2-6. Unfortunately, conventional bulk-form Si anodes face many preliminary problems, especially significant volume change and poor electrical conductivity. Among them, the huge volume change up to 400% during insertion/extraction of lithium ions may be the most serious. It may cause cracks in the material, pulverization of the anode, and hence failure of the battery. Moreover, poor conductivity of Si hinders efficient charge transport, and constrains its rate performance.

Recently, core-shell Si/CNT structures have been under extensive research. The main idea is to combine the extraordinary properties of CNTs with the high capacity of the Si for improved performance. However, the performances are still not satisfactory. Revealed by recent in-situ TEM experiments, [102, 198] small cracks are likely to occur on the Si shell after shrinkage and expansion, which may result in fracture and detachment of the shell eventually. This problem is commonly encountered in the core-shell Si anodes. [83, 86, 103] To solve the problem, current work is more focused on the utilizing different kinds of CNTs as the cores, as well as fabricating the Si shells into various morphologies. However, the core-shell interfaces, which could play critical role in such core-shell

nanowires, have rarely been investigated. In fact, the importance of engineering the interfaces has already been demonstrated in traditional thin film Si anodes. In this work, the Ni/CNT array is utilized to support the Si materials. The Si/Ni/CNT obtained is able to demonstrate stable capacity retention and excellent rate performance, as an anode material for LIBs because of engineering of the interface by the rough Ni layer in between the CNT cores and Si shells.

4.3.1 Experimental details

Round SS chips with diameters of 1.5 cm were used as the substrates. CNT growth and Ni coating were prepared following the same procedures described in Section 4.1. Si coating was performed in a Cello PECVD system with 50 sccm SiH_4 mixed with 160 sccm N_2 as the precursor. The process temperature was 200°C and the deposition rate was around 1 nm/s on flat surface. The Ni and Si mass loading were determined by weighing the samples before and immediately after the coating processes using an analytical balance. The mass ratio of Ni and Si was around 1:1 with the Si mass around 0.1 mg to 0.15 mg on each sample.

4.3.2 Structural characterization

Figure 4-9 (a) is the SEM image of the CNT array fabricated on a SS current collector using PECVD. Similar to the results on Si substrates in Figure 4-2, most of the CNTs exhibit diameters of around 100 to 150 nm and have fairly large inter-wire spacing typically around 400 nm. Figure 4-9 (b) is the SEM image of the Si/Ni/CNT

heterogeneous nanowires after magnetron sputtering of Ni and PECVD coating of Si onto the CNTs. Diameters of the nanowires are increased to 300 to 400 nm. Nevertheless, there is still much space between the nanowires, which not only helps to accommodate radial expansion of the Si shells, but also offers efficient access of electrolyte to the entire core-shell nanowire array.

Figure 4-9 Tilted angle SEM images of (a) the CNT array and (b) the Si/Ni/CNT array on SS chips, respectively.

Figure 4-10 (a) is the TEM image of a randomly selected as-fabricated CNT. After coating of the Ni and Si, a tri-layer structure is formed which is clearly displayed in TEM image, Figure 4-10 (b). The dark region with a thickness of about 20 nm is the Ni interfacial layer. The Ni layer shows a “brush-like” rough morphology, which is distinctly different from the smooth surface of the underneath CNT. This unique morphology could be caused by the small coating thickness. Meanwhile, the surface of the CNTs is actually

edges of the constituting graphene planes which may serve as nucleation centers for the Ni atoms, promoting the formation of “Ni brush” during sputtering.

Figure 4-10 (a) TEM image of a CNT; (b) TEM image of a Si/Ni/CNT nanowire; (c) Scanning TEM (STEM) image of a portion of the nanowire and the corresponding EDX mapping data of Si, Ni, O, C, respectively; (d) HRTEM image at the Si/Ni/CNT interface, inset is the corresponding FFT pattern of the Si layer.

The EDX mapping data in Figure 4-10 (c) affirms the tri-layer structure with the element distribution of Si/Ni/C. It is noted that O can be detected on some areas of both

Ni and Si surface, probably due to oxidation from air during sample transfer. However, it is unlikely for O composition to hinder charge transfer and affect the performance significantly. As it is developed at room temperature in limited time, the oxidation is very thin and only happens partially, allowing direct contact between Ni and Si in other areas. The outer Si layer is around 40 to 60 nm thick. Under HRTEM shown in Figure 4-10 (d), no obvious crystalline structures can be found and the corresponding FFT pattern shows that the Si layer is amorphous. Following the roughness of the Ni layer, the Si surface also exhibits a non-continuous morphology with micro valleys and hills spreading all over.

4.3.3 Electrochemical characterization

Figure 4-11 Specific charge/discharge capacities and Coulombic efficiency of the Si/Ni/CNT nanowire anode vs. cycle number.

To evaluate the electrochemical performance, half-cells are assembled with core-shell nanostructures on SS as the working electrodes and lithium foils as the counter

electrodes. The capacity retention performance is presented in Figure 4-11. The testing is carried out over the potential range of 0.01-1.2 V at rate of 0.2 C. Here, C is the normalized charging/discharging rate defined as

$$C = \frac{i}{Q_{c0}} \quad (4 - 1)$$

where i is the current density flowing in the battery, Q_{c0} is the theoretical capacity. For Si, the theoretical capacity is known as $4200 \text{ mAh}\cdot\text{g}^{-1}$, so that at 1 C rate, the current density equals to $4200 \text{ mA}\cdot\text{g}^{-1}$. [199, 200] All the current rates and capacities are calculated based on the mass of Si. The mass ratio of Si:CNT is estimated to be around 3.4:1. Therefore, although CNTs could react with lithium ions, their contribution is not a dominating factor in the overall capacity. During galvanostatic cycling, the de-lithiation capacity exhibits an initial value of $2527 \text{ mAh}\cdot\text{g}^{-1}$ and then increases slightly at the second cycle, after which the capacity remains quite stable. The initial capacity suppression may be caused by activation of the surface against electrochemical reaction. After 110 cycles, there is still a capacity of $1960 \text{ mAh}\cdot\text{g}^{-1}$, which is 78% of the initial capacity, corresponding to a fading rate of only 0.2% per cycle. Coulombic efficiency of the Si/Ni/CNT nanowires during cycling is also presented in Figure 4-11. After surface activation in the first several cycles, the efficiency maintains at almost 100%, demonstrating good structural stability of the electrodes against lithiation and de-lithiation.

Figure 4-12 is a typical voltage profile in a complete charge/discharge cycle. The voltage profile is consistent with previous studies on Si anodes, showing the sloping charge/discharge behaviour. [38]

Figure 4-12 A typical voltage profile in a full galvanostatic charge and discharge cycle at the current density of 0.2 C.

Another important performance of battery is rate capability, as shown in Fig. 3(c). Firstly, a charging/discharging rate of 0.2 C is applied for 10 cycles to activate the Si material. At the 10th cycle, a de-lithiation capacity of 2508 mAh·g⁻¹ is obtained, consistent with the value in Figure 4-11. The current is then raised to 0.5, 1, 2, 4, 8 and 12 C and the corresponding de-lithiation capacities are 2115, 1885, 1569, 1308, 1046 and 585 mAh·g⁻¹, respectively. Eventually, when the rate is set back to 0.2 C, the de-lithiation capacity recovers to 2246 mAh·g⁻¹. This excellent rate performance suggests that the Si/Ni/CNT tri-layer structures enable fast charge transport and also structural stability even at very high rates.

Figure 4-13 Charge/discharge capacities at different current rates.

In order to ascertain the benefits of Ni interlayer, a control experiment is carried out. Si/CNT nanowires are fabricated and tested, without introduction of the Ni layer, as shown in Figure 4-14.

Figure 4-14 (a) TEM image of a Si/CNT nanowire in the control group; (b) comparison of capacity retention between Si/Ni/CNT and Si/CNT nanowire anodes.

In sharp contrast to the Si/Ni/CNT anode which shows excellent capacity retention, the Si/CNT anode only shows stable cycling for 70 cycles, after which the capacity drops very fast, as shown in Figure 4-14 (b).

Figure 4-15 (a) Top view SEM image of the Si/Ni/CNT nanowire anode in de-lithiated state after 50 cycles at 0.2 C. (b) TEM image of a Si/Ni/CNT nanowire after 70 cycles at 0.2 C.

To understand the mechanism for the excellent performance, half-cells were disassembled in the fully de-lithiated state after galvanostatic cycles for post-mortem investigations. The disassembly was carried out in glove box and the working electrodes were immediately soaked in propylene carbonate (PC) for 24 hours to remove the residual electrolyte and then baked in a vacuum oven at 60 °C for 48 hours to completely evaporate the PC. As shown in Figure 4-15 (a), the Si/Ni/CNT nanowires remain well on

the SS substrate without any detachment. In the TEM image, Figure 4-15 (b), the surface of Si becomes rougher and more porous while minimal changes can be observed in the inner portion of Si as well as the Ni layer and CNT core, as compared to the nanowires before cycling. It is apparent that tri-layer structure of the Si/Ni/CNT is well maintained without any interfacial sliding, fractures or detachment of the Si shell.

There could be several factors that contribute to the stability and hence good performances. Firstly, as electrochemical inactive materials, metals such as Ni, Mg and Cu do not suffer from volume change resulted from lithium insertion/extraction. Thus, they have been investigated as important coating or composition materials to buffer the volume change of Si anode. [45, 48, 201, 202] Ni layer in these heterogeneous nanowires serves as a backbone for the attached Si and suppresses it from excessive volume change. Moreover, owing to its special “brush like” structure, the Ni material is able to extend further into the Si shell and make more contact area to enlarge such constraint effect. Therefore, the possibility of pores or fractures is reduced significantly from happening. As evidenced by the TEM characterization, the structure of Si which is adjacent to the Ni is well kept after cycling.

On the other hand, because of such suppression effect, stress was transferred onto the metal site from Si, as reported in previous publications on metal cored or coated Si material as anodes. [48, 201] Bending and fractures of the metal cores or layers tended to happen, rendering loss of the capacity as the consequence. However, such phenomena were not observed in the Si/Ni/CNT nanowires, as shown in Figure 4-15 (b). It can be attributed to the CNT cores, which serve as a stubborn support. The excellent mechanical properties of CNTs enable them to withstand huge stress without any deformation. [107]

Thirdly, adhesion of Si to the substrates can be a serious problem when Si suffers from severe volume change during cycling. [203-205] Detachment of the Si layer would result in loss of the electric contact and hence fading in capacity. It has been proven that modification of the interface or introduction of an interfacial layer could be effective ways to reinforce the adhesion between the active materials and the planar substrates. [206-208] Similarly, such reinforcement is also made in the core-shell nanowires of this work. The rough surface of the Ni layer provides more contact area, which helps to anchor the deposited Si material firmly and prevent capacity loss caused by interfacial sliding.

Furthermore, because of the supporting Ni layer, the surface of Si also exhibits a rough morphology with micro valleys spreading all over its surface. Such non-continuous surface is beneficial for stress relaxation as free space is provided to accommodate volume change. [208] Therefore, after cycling, although the Si surface becomes more porous, it is still anchored on the substrate rather than fallen off.

In core-shell structures, the types of stress include the radial, axial and hoop stress. The axial and radial stress corresponds to in-plane and out-of-plane stress in flat Si films, respectively, while the hoop stress is caused by the curvature of the shell. [103] For a Si shell, the radial stress is less detrimental due to the relatively small shell thickness and sufficient space around the nanowire to accommodate the radial expansion. The axial and hoop stress is mainly responsible for the structural damage of core-shell nanowires. Previous findings have proven that the CNT cores with relatively large diameter could be used to alleviate hoop stress because of reduced curvature. [106] The hoop stress is likely to be further alleviated in this structure, as the core diameter could be increased because of the Ni coating. More importantly, the rough morphology of the Ni layer is able to

effectively accommodate longitudinal stress similar to the effect of the rough surface on in-plane stress in flat film.

In addition, benefits of engineering the interface may not be limited in the structural sense. The CNT cores serve as excellent current collectors with their ballistic electrical transport to boost charge transfer. Hence, the structural stability of the Si/Ni/CNT nanowires ensures good electrical contact even if the Si shells undergo volume changes. Additionally, charge transfer from Si to Ni is probably more efficient, as compared to that from Si directly to CNTs. For interfaces between Si and graphenic carbon materials, such as CNTs and carbon nanowalls, the bonding is usually built through either amorphous carbon [87] or Si carbide, [209] as evidenced by previous reports. Normally, the electrical conductivity of amorphous carbon is relatively low [210, 211] and Si carbide is commonly known as a semiconductor. Therefore, neither of the two could surpass the electrical performance of the Ni-Si interface theoretically. In fact, Ni and Si alloy exhibits the lowest resistivity over all metal-Si alloys. [212, 213] The Ni-Si interface is likely to exhibit a much smaller contact resistance over amorphous carbon or Si carbide and is therefore more advantageous for the effective charge transfer during charging and discharging of the battery.

4.3.4 Conclusions

A novel core-shell Si/Ni/CNT nanostructures array is developed as a high performance anode material. With the introduction of a Ni layer, the interface between CNT cores and Si shells can be effectively improved for enhanced stability and adherence,

well accommodated stress and improved charge transport. Encouragingly, a high capacity over $2500 \text{ mAh}\cdot\text{g}^{-1}$ is realized over 110 cycles while the anode structure can be well maintained after cycling. This work clearly proves the significant role of interface in such core-shell Si/CNT structures. The architecture presented here offers a new idea to optimize the performance of core-shell Si/CNT anodes which are under intense research towards high capacity as well as prolonged life-time LIB applications.

Chapter 5 NiCo₂O₄/CNT as an anode material for LIBs

Transition metal oxides (TMOs) have been considered as possible alternatives to graphite in the anodes. Among TMOs, spinel NiCo₂O₄, a binary metal oxide, has drawn intensive research attention because of its enhanced characteristics, such as better electrical conductivity and electrochemical activity over the corresponding single component oxide. [75, 214-217]

However, the electrical conductivity is not satisfactory enough. What is more, structural pulverization during charge/discharge processes [218] is also a severe problem that hinders its potential applications. [219] To date, many studies have been devoted to improve the electrochemical performances of NiCo₂O₄, for example, by adjusting the morphology (nanorods, nanotube, nanowires, nanoflakes, and nanosheets), [69, 74, 218, 220] pore size [221, 222] and crystallinity (single-crystalline and poly-crystalline). [51, 68] Although improved performances have been reported in these nanostructures, there are still many problems to be addressed, such as the vulnerability to agglomeration.

In Chapter 4, vertical CNT array has been proved as excellent templates for Ni and Si. It may also be a suitable support for NiCo₂O₄ to further enhance its electrochemical performances. Following this idea, NiCo₂O₄/CNT array is prepared using a facile electrochemical deposition process followed by annealing in air. It is expected that by combining the merits of the CNT array and nanostructured NiCo₂O₄, the array of NiCo₂O₄/CNT heterogeneous nanowires are possible to demonstrate excellent performances as an anode material in LIBs.

5.1 Preparation of NiCo₂O₄ on CNTs array

Figure 5-1 Schematics illustrating the three-step preparation of the vertically aligned NiCo₂O₄/CNT heterostructures on SS substrate.

Figure 5-1 displays the three-step synthesis of the NiCo₂O₄/CNT array. The first step is the growth of vertically aligned CNTs on SS substrate by PECVD method, as described in detail in Chapter 4. Secondly, CNTs obtained are treated by O₂ plasma to change the wettability of CNTs, which favours the following electrochemical deposition process. Subsequently, nickel-cobalt hydroxide is electrodeposited on the CNTs in a typical three-electrode system. The CNT sample, a platinum plate and a saturated calomel

electrode (SCE) were used as the working, counter and reference electrodes, respectively. The electrodeposition was performed at -1.0 V (vs. SCE) in a 4 mM Co(NO₃)₂·6H₂O and 2 mM Ni(NO₃)₂·6H₂O mixed electrolyte using a Solartron (1287+1260) electrochemical work station. After electrodeposition for 10 min, the samples were rinsed with DI water, and dried at 60 °C in air. They were then calcined at 300 °C for 2 h with a ramping rate of 1 °C·min⁻¹ to transform the precursor into spinel NiCo₂O₄. The mass of NiCo₂O₄ nanosheets grown on CNT array is 0.6 mg in average, determined by carefully weighing the samples before electrodeposition and immediately after calcination.

Figure 5-2 Photographs of the bare SS substrate, CNTs grown on SS substrate, nickel-cobalt hydroxide deposited on the CNTs before and after annealing in air, respectively (from left to right).

In addition, it can be observed obvious differences in the colors of the as-prepared samples after each step, as shown in Figure 5-2, which provide proof for the successful fabrication of the NiCo₂O₄/CNT array.

5.2 Morphology and structure characterizations

In the electrodeposition process, NO_3^- is reduced at the cathodic surface with the production of OH^- ions. These OH^- ions raise the PH value in the vicinity of the working electrode, resulting in the precipitation of mixed Ni-Co hydroxide on the surface of the CNTs, as described by the following equations:

The annealing treatment in air converts the Ni-Co hydroxide precursor into spinel NiCo₂O₄ according to the equation of:

Figure 5-3 Low (a) and high (b) magnification SEM images of the NiCo₂O₄/CNT structures.

The morphologies and microstructures of the NiCo₂O₄/CNT structures are examined by SEM and the corresponding results are shown in Figure 5-3. It can be clearly seen that the CNT are uniformly decorated with thin NiCo₂O₄ nanosheets and the NiCo₂O₄/CNT structures are well separated from each other in the array, even after the electrodeposition and annealing treatment.

Figure 5-4 XRD patterns of the NiCo₂O₄/CNT structures scratched from SS substrate.

XRD is used to characterize the phase, composition and structure of the NiCo₂O₄/CNT array. In order to preclude the strong signals from the SS substrate, NiCo₂O₄/CNT structures are scratched from the substrates and the XRD patterns are shown in Figure 5-4. The diffraction peaks at 18.8°, 31.2°, 36.6°, 38.3°, 43.1°, 55.4°, 59.1° and 65.0° can be indexed to (111), (220), (311), (222), (400), (422), (511) and (440) plane

reflections of the spinel NiCo₂O₄ (JCPDF file no. 20-0781), [70, 216, 223, 224] and no noise peaks from other crystallized phases are detected, demonstrating the successful deposition of NiCo₂O₄ on the vertically aligned CNTs.

The morphological and structural details of the NiCo₂O₄/CNT structures are further characterized by TEM, HRTEM and EDX. As shown in the Figure 5-5 (a) and (b), CNTs are uniformly wrapped by the NiCo₂O₄ nanosheets with a thickness of around 30 nm. Importantly, compact contact can be observed between the NiCo₂O₄ nanosheets and CNTs, which is beneficial for electron transfer and structural stability when used as an anode material for LIBs. HRTEM image in Figure 5-5 (c), exhibits that the NiCo₂O₄ products are thin sheets with small and dense nanopores, which may result from the gas release and volume loss during the calcination. [225] HRTEM image, Figure 5-5 (d) reveals the nanocrystalline nature of the NiCo₂O₄ obtained. For instance, there are interplane spacing of 0.48 nm and 0.27 nm, corresponding to the (111) and (220) lattice plane separation in spinel NiCo₂O₄, [51, 217] respectively. It is also confirmed by the FFT patterns in the inset of Figure 5-5 (d). Furthermore, the EDX line-scan results in Figure. 5-5 (e), demonstrate the uniform coating of the Ni, Co and O onto the CNTs. In addition, EDX analysis further elucidate the composition of as-prepared sample, as shown in Figure. 5-5 (f). Ni, Co, O and C are detected and the atomic ratio of Ni to Co is approximately 1:2, which agrees well with the stoichiometric ratio in NiCo₂O₄.

Figure 5-5 (a) (b) (c) TEM images, (d) HRTEM image (insets are the higher magnification HRTEM images of the circles 1 and 2 and its corresponding FFT patterns, respectively.), (e) EDX line-scan profiles and (f) EDX spectrum of the $\text{NiCo}_2\text{O}_4/\text{CNT}$ structures.

5.3 Electrochemical characterization

The NiCo₂O₄/CNT structures on SS substrates are assembled as a binder-free anode material to evaluate the electrochemical performances. Figure 5-6 shows the initial three consecutive CV cycles of the NiCo₂O₄/CNT electrode in the voltage range of 0.01–3.0 V (vs. Li/Li⁺) at the scan rate of 0.1 mV·s⁻¹. In the first cycle, the weak and broad cathodic peak at 1.33 V corresponds to the destruction (or amorphization) of the crystal structure, [220] while the subsequent sharp cathodic peak at 0.81 V is attributed to the further reduction of Co³⁺ and Ni²⁺ to metallic Co and Ni, and the formation of amorphous Li₂O and SEI. [220, 226] Meanwhile, two broad oxidation peaks are observed at 1.5 and 2.2 V in the first cycle, corresponding to the oxidation of Ni and Co nanograins to NiO and Co₃O₄, respectively. However, from the second cycle onwards, the weak cathodic peak at 1.33 V disappears and the main cathodic peak shifted to about 1.0 V, probably due to the irreversibility in the conversion of NiCo₂O₄. The reduction and oxidation peaks in the CV tests overlapped substantially, indicating the outstanding cyclability of the NiCo₂O₄/CNT anode.

Figure 5-6 CV curves of the NiCo₂O₄/CNT anode for the first three cycles measured at a scan rate of 0.1 mV·s⁻¹ between 0.01 V and 3 V.

According to the above analysis and previous reports, [220, 226] the lithiation/de-lithiation reactions for the NiCo₂O₄/CNT structures can be described as follows:

Figure 5-7 Voltage capacity profiles of the NiCo₂O₄/CNT anode at the current density of 100 mA·g⁻¹.

Figure 5-7 is the representative discharge/charge profiles of the NiCo₂O₄/CNT structures for the first three cycles at a current density of 100 mA·g⁻¹. Clearly, the voltage plateau at around 1.5 V in the first discharge process disappears in the following cycles and the plateau between 0.9 and 1.0 V in the first discharge curve shifts to higher voltage and becomes less notable in the following cycles. These phenomena are consistent with the CV measurements. The initial lithiation and de-lithiation capacities of the NiCo₂O₄/CNT anode are 1602 and 1273 mAh·g⁻¹ at the current density of 100 mA·g⁻¹, respectively, corresponding to a Coulombic efficiency of 79.4%. The irreversible capacity loss of 20.6% is probably attributed to the formation of SEI film or undecomposed Li₂O,

which are common for most of the TMOs based anode materials. [219, 225, 226] Nevertheless, the Coulombic efficiency keeps nearly 100% in following cycles, when Ni and Co start to dominate the reversible electrochemical process of lithium ion storage.

Figure 5-8 Charge/discharge capacities at different current rates.

To better understand the electrochemical behaviours of the NiCo₂O₄/CNT anode, its rate performance is measured by increasing the charge/discharge current density from 100 to 1000 mA·g⁻¹ step-by-step after 7 cycles at each current density and then restoring it back to 100 mA·g⁻¹. As shown in Figure 5-8, the de-lithiation capacities are 1147.6, 1031.4, 923.1, 793.6 and 712.9 mAh·g⁻¹ at the current densities of 100, 200, 500, 800 and 1000 mA·g⁻¹ after 7 cycles, respectively. Importantly, when the current density recovers to 100 mA·g⁻¹, a de-lithiation capacity as high as 1185.6 mAh·g⁻¹ can be obtained,

indicating a superior rate performance compared to those of NiCo₂O₄ based anodes reported in literature. [217, 226]

Cycling stability is also important for anode materials in LIBs. In this NiCo₂O₄/CNT anode, it is investigated by cycling the half-cells at the current density of 200 mA·g⁻¹ in the voltage range of 0.01–3.0 V. Surprisingly, the capacity retains to 107% of the initial discharge capacity after 200 cycles, as shown in Figure 5-9. Meanwhile, the Coulombic efficiency is close to 100% in almost all the cycles, indicating the excellent structural stability of the NiCo₂O₄/CNT anode. It should be mentioned that an increase followed by decrease happens in the specific capacity from 11th cycle to 80th cycle. The increase from 11th to 57th cycle probably comes from activation of the nanostructured NiCo₂O₄ material which improves the lithium ion diffusion kinetics. As more lithium ions can be removed/uptaken from/into the material, capacities increase with cycling. [227, 228] The half-cell reaches a maximum in capacity when all of the material is activated. Cracks accumulated in the cycling result in fading of the capacity from 57th to 80th cycle. The slow uptrend in the capacity from 90th cycle onwards, could possibly be attributed to the extra lithium ion storage capability from reversible formation/decomposition of the SEI. This mechanism was proved by Maier's group using XPS [229] and HRTEM, [230] respectively. The half-cell eventually reaches a capacity of 1190 mAh·g⁻¹ at the 200th cycle.

Figure 5-9 Specific capacities and Coulombic efficiency of the NiCo₂O₄/CNT anode versus cycle number cycled at 200 mA·g⁻¹.

The attractive electrochemical performance of the NiCo₂O₄/CNT anode for LIBs come from the following aspects. Firstly, the CNT array has proved its promising properties in Chapter 4. Herein, in the NiCo₂O₄/CNT structures, highly conductive CNTs serve as excellent media for charge transfer during electrochemical reactions. Furthermore, direct growth of CNTs on the SS substrates ensures good adhesion and electrical contact between NiCo₂O₄/CNT structures and SS substrates. Meanwhile, space among the array of NiCo₂O₄/CNT structures accommodates the volume change effectively during the lithiation/de-lithiation process. In addition, the ultrathin and porous NiCo₂O₄ nanosheets not only increase active sites but also shorten the diffusion paths for lithium ions and hence enhance the rate capability.

5.4 Conclusions

In summary, NiCo₂O₄ nanosheets have been successfully fabricated onto array of vertically aligned CNTs by facile electrochemical deposition and subsequent annealing in air. The array of NiCo₂O₄/CNT structures supported on SS substrates demonstrate outstanding performances as an anode material in LIBs, including high capacity (1147.6 mAh·g⁻¹ at the current density of 100 mA·g⁻¹), excellent cycling retention (no capacity fading over 200 cycles at 200 mA·g⁻¹) and outstanding rate capability (712.9 mAh·g⁻¹ at 1000 mA·g⁻¹), which are enabled by the rational selection, composition and construction of materials. The unique array structure not only favours the fast transport of lithium ions but also accommodates the volume variations effectively during charge/discharge processes. [225] The improved electrochemical performance enables the NiCo₂O₄/CNT structures to be a promising anode material for future high-performance LIBs. In addition, the structures developed here may not be limited to LIB electrode but also applicable for other energy storage mechanisms.

Chapter 6 NiCo₂O₄/CNT as an electrode material for pseudo capacitors

TMOs are widely investigated as electrode materials for pseudo capacitors.[231] The NiCo₂O₄/CNT structures can be a possible component in high performance pseudo capacitors, given that their unique properties have enabled excellent electrochemical performances as an anode material for LIBs in Chapter 5.

6.1 Setup for the electrochemical characterization of ECs

Figure 6-1 Setup of the electrochemical testing of pseudo capacitor electrodes.

The testing environment is shown in Figure 6-1. All electrochemical measurements were carried out using a Solartron 1287/1260 electrochemical work station in an open three-electrode cell system at room temperature. The samples of NiCo₂O₄/CNT structures on SS substrates, a Pt plate (2 cm × 2 cm × 0.2 mm) and SCE served as the

working, counter and reference electrodes, respectively. CV, galvanostatic charge/discharge and EIS were employed to investigate the performance of the NiCo₂O₄/CNT structures as electrodes for pseudo capacitors. CV tests were conducted within the potential window from -0.1 to 0.5 V (vs. SCE) at scan rates varied from 5 to 100 mV·s⁻¹. EIS were tested in the frequency range from 100 kHz to 0.05 Hz at open circuit potential with an AC perturbation of 5 mV. Galvanostatic charge/discharge tests were carried out with the constant current density ranging from 1 to 20 A·g⁻¹. All these experiments were performed at room temperature in an aqueous KOH electrolyte (6.0 M).

It may be worth mentioning that although the electrode structures tested here are the same with the anodes in LIBs, the underlying mechanisms are distinctly different. Anodes in LIBs involve the reversible reaction of the lithium ions while in pseudo capacitors, electrochemical energy is store based on the reversible faradic redox reactions at the surface of the electrodes. [59]

6.2 Supercapacitive performances

Figure 6-2 (a) presents the CV curves obtained, in which there are two anodic peaks at 0.32 and 0.41 V (corresponding to cathodic peaks at 0.28 V and 0.37 V) at the scan rate of 5 mV·s⁻¹. These curves prove that the capacitive characteristics are mainly governed by Faradaic reaction. The two redox peaks can be attributed to redox reactions of Ni and Co species in the alkaline electrolyte according to Equation 6-1: [232, 233]

Figure 6-2 (a) CV curves of the NiCo₂O₄/CNT structures on SS substrates at various scan rates; (b) CV curves of the bare CNTs and NiCo₂O₄/CNT structures at the same scan rate of 10 mV·s⁻¹.

The redox current increases with the scan rate from 5 to 100 mV·s⁻¹ and the anodic/cathodic peak shifts towards the positive/negative potential, respectively. This observation reveals the low resistance of the electrode and the super-fast electron transport between the NiCo₂O₄/CNT structures and SS current collectors. Besides, in Figure 6-2, bare CNTs exhibit a very small area surrounded by CV curve compared to that of NiCo₂O₄/CNT structures at the same scan rate, suggesting that the capacitance contribution from the substrate and CNTs is negligible following Equation 6-2:

$$C = \frac{\int_{E_1}^{E_2} i(E) dE}{(E_2 - E_1) \cdot v} \quad (6-2)$$

where C , E_2 , E_1 , $i(E)$, v are the specific capacitance, upper, lower cut-off potentials, instantaneous current with respect to potential E and potential scan rate, respectively and $\int_{E_1}^{E_2} i(E)dE$ represents integral area of the CV curve.

To understand the rate capability of the NiCo₂O₄/CNT electrodes, charge/discharge measurements are performed in the potential window between 0 and 0.41 V at different current densities. As can be seen in Figure 6-3 (a), constant current charge/discharge curves keep similar shapes and demonstrate ideal capacitive behaviours with very sharp responses. In addition, the voltage plateaus match well with the peaks observed in the CV curves (Figure 6-2), which further confirms the typical pseudo capacitive behaviour of the NiCo₂O₄/CNT electrode.

Figure 6-3 (a) Charge/discharge curves at various current densities and (b) calculated specific capacitance as a function of the current density.

The specific capacitance can be calculated from the discharge curves by the formula:

$$C = \frac{i \cdot t}{|\varphi_1 - \varphi_2|} \quad (6 - 3)$$

Here, C is the specific capacitance ($\text{F} \cdot \text{g}^{-1}$), i is the constant discharge current density ($\text{A} \cdot \text{g}^{-1}$), t is the discharge time (s), $|\varphi_1 - \varphi_2|$ is the potential (V) window for the discharge process.

The values are 695, 656, 638, 591, and 576 $\text{F} \cdot \text{g}^{-1}$ corresponding to the discharge current densities of 1, 2, 4, 10, and 20 $\text{A} \cdot \text{g}^{-1}$, respectively, as shown in Figure 6-3 (b). The specific capacitance decreases slightly with the increment in the current density, but the NiCo₂O₄/CNT electrode remains nearly 82% of its initial capacitance even at the high current density of 20 $\text{A} \cdot \text{g}^{-1}$. Such specific capacitance and rate capability of the NiCo₂O₄/CNT electrode can be considered as quite good as compared with those reported in NiCo₂O₄-based electrode materials, including porous hexagonal NiCo₂O₄ nanoplates, Nickel-Cobalt nanosheets, hollow NiCo₂O₄ sub-microspheres, nanostructured NiCo₂O₄ spinel thin-film electrode, NiCo₂O₄ nanowires-loaded graphene, NiCo₂O₄-reduced graphene oxide composite, nickel cobalt oxide-single wall carbon nanotube composite, cobalt nickel oxysulfide (CoNi)O_xS_y and so on (the corresponding results are listed in Table 6-1). [69-73, 215, 216, 234-239]

Table 6-1 Comparison of the electrochemical performances of the NiCo₂O₄/CNT with those in literature.

Material	Specific capacitance (F·g ⁻¹)	Rate performance	Capacity retention	Reference
NiCo ₂ O ₄ nanoplates	294 (1 A·g ⁻¹)	48% (10 A·g ⁻¹)	89.8% (2200 cycle)	[69]
Nickel-Cobalt nanosheets	506 (1 A·g ⁻¹)	40% (10 A·g ⁻¹)	94% (2000 cycle)	[70]
NiCo ₂ O ₄ -RGO	835 (1 A·g ⁻¹)	74% (16A·g ⁻¹)	108% (4000 cycle)	[216]
NiCo ₂ O ₄	662 (1 A·g ⁻¹)	53% (16 A·g ⁻¹)	52% (4000 cycle)	[216]
NiCo ₂ O ₄ sub-microspheres	678 (1 A·g ⁻¹)	80% (20 A·g ⁻¹)	87% (3500 cycle)	[71]
NiCo ₂ O ₄ thin-film	575 (1 A·g ⁻¹)	98% (10 A·g ⁻¹)	99% (1000 cycle)	[234]
NiCo ₂ O ₄ @RGO	737 (1 A·g ⁻¹)	50% (10 A·g ⁻¹)	94% (3000 cycle)	[235]
NiCo ₂ O ₄ framework	587 (2 A·g ⁻¹)	88% (16 A·g ⁻¹)	89% (3500 cycle)	[72]
(CoNi)O _x S _y	592 (2 A·g ⁻¹)	25% (20 A·g ⁻¹)	95% (2000 cycle)	[236]
NiCo ₂ O ₄ @NiCo ₂ O ₄ core-shell	900 (1 A·g ⁻¹)	75% (20 A·g ⁻¹)	98.6% (4000 cycle)	[73]
NiCo ₂ O ₄	660 (1 A·g ⁻¹)	71% (20 A·g ⁻¹)	66.3% (4000 cycle)	[73]
NiCo ₂ O ₄ nanoflakes	490 (15 A·g ⁻¹)	No data	97% (900 cycle)	[237]
NiCo ₂ O ₄ nanorods	330 (15 A·g ⁻¹)	No data	96 % (900 cycle)	[237]
NiCo ₂ O ₄ hexagonal	663 (1 A·g ⁻¹)	88% (8 A·g ⁻¹)	88.4% (5000 cycle)	[238]
Nickel-cobalt hydroxide	456 (20 mV·s ⁻¹)	70% (200 mV·s ⁻¹)	91% (1000 cycle)	[239]
NiCo ₂ O ₄	222 (1 A·g ⁻¹)	84% (3.5 A·g ⁻¹)	96.3% (600 cycle)	[215]
Core-shell NiCo ₂ O ₄ /CNT	694 (1 A·g ⁻¹)	82% (20 A·g ⁻¹)	91% (1500 cycle)	This Work

Energy density and power density are two key factors for the applications of ECs.

A good electrode material is expected to provide high energy density and high capacitance

simultaneously even at high charge/discharge rates. The specific energy density E (Wh/kg) and power density P (W/kg) are defined by:

$$E = \frac{C \cdot (\varphi_1 - \varphi_2)^2}{7.2} \quad (6 - 4)$$

and

$$P = \frac{3600 \times E}{\Delta t} \quad (6 - 5)$$

The relationship between the energy densities and the power densities are plotted into Ragone plot, as presented in Figure 6-4. It can be observed that when power density is increased, energy density sustains very well, supporting the promising application of the NiCo₂O₄/CNT array as an electrode material in pseudo capacitors. The energy density reaches a value of 16.4 Wh/kg at the power density of 118.4 W/kg, and remains 13.4 Wh/kg at the power density of 4086.3 W/kg.

Figure 6-4 Ragone plot of the NiCo₂O₄/CNT electrode.

Cycling stability is another criterion of great importance to evaluate an electrode material in pseudo capacitors. It is examined by repetitive galvanostatic charge/discharge cycles at the current density of $4 \text{ A} \cdot \text{g}^{-1}$. As shown in Figure 6-5 (a), the specific capacitance is almost constant with only minor fluctuations during the long cycling process. Only 9% of the original capacitance is lost after 1500 cycles, indicating the excellent cycling stability of the NiCo₂O₄/CNT electrode. This is also proved by post-mortem SEM image in Figure 6-5 (b). As compared to the pristine electrode before cycling as shown in Figure 5-3, the morphology and structure of the NiCo₂O₄/CNT array are well maintained after 1500 cycles, indicating good charge/discharge stability and long life span of this material.

Figure 6-5 (a) Variation of the specific capacitance of the NiCo₂O₄/CNT electrode as a function of the cycle number measured at a current density of 4 A·g⁻¹ in 6M KOH electrolyte. The inset shows the charge/discharge curves of the 1st, 500th, 1000th and 1500th cycle. (b) SEM image of the NiCo₂O₄/CNT array on SS substrate after 1500 cycles at the current density of 4 A·g⁻¹.

6.3 Discussions and conclusions

The excellent supercapacitive performances of the NiCo₂O₄/CNT electrode, including high specific capacitance, good rate capability and cycling stability, can be attributed to its unique structure. Firstly, the vertically aligned CNTs serve as strong skeletons for the NiCo₂O₄ nanosheets, avoiding their aggregation and retaining their large surface area. Secondly, the ultrathin and nanoporous characteristics of the NiCo₂O₄ nanosheets provide numerous active sites for the redox reaction. Thirdly, the open space between the NiCo₂O₄/CNT core-shell heterogeneous nanowires minimizes the diffusion distance for ions. Therefore, fast ion transport is enabled for accelerated reaction kinetics.

In addition, direct growth of highly conductive CNTs on the SS current collectors not only benefits the fast electron transfer but also avoids the use of polymer binders which would add in extra resistance.

In summary, vertically aligned arrays of core-shell NiCo₂O₄/CNT heterogeneous nanowires have been successfully prepared by facile electrodeposition and subsequent annealing in air. The as-prepared NiCo₂O₄/CNT structures exhibit specific capacitances of 695 A·g⁻¹ at the current density of 1 A·g⁻¹ and 576 F·g⁻¹ at 20 A·g⁻¹ when tested as electrodes for pseudo capacitors. Furthermore, the capacitance of the NiCo₂O₄/CNT electrode remains 91% of its original value after 1500 cycles at the current density of 4 A·g⁻¹. The high specific capacitance, remarkable rate capability and excellent cycling stability come from the unique properties of the NiCo₂O₄/CNT structures, including stubborn support of the CNTs and efficient exchange between NiCo₂O₄ nanosheets and the electrolyte. This study provides an insight for the design and synthesis of TMOs based electrode materials for high-performance ECs.

Chapter 7 3D NiCo₂O₄/CNT/UG/Ni foam as an electrode material for pseudo capacitors

Good supercapacitive performances have been successfully achieved in the SS substrates supported NiCo₂O₄/CNT core-shell nanowires, by combining the merits of CNT array and nanostructured NiCo₂O₄. In this chapter, this architecture is further exploited by using 3D ultrathin graphite (UG) [134-141] coated Ni foams instead of SS as the substrates. 3D UG grown on Ni foams have been proved to be excellent platforms to assemble various nanostructures into macro frameworks. [137, 138] As compared to the planar substrate, this unique macroporous frame enables enhanced loading of active materials and facile access for the electrolyte.

The architecture of NiCo₂O₄/CNT/UG/Ni foam is realized by CVD growth of CNTs onto the 3D UG-coated Ni foam, forming an interconnected 3D carbon network. Mesoporous NiCo₂O₄ nanorods are decorated onto the surface of CNTs by hydrothermal reaction and subsequent annealing in air. Importantly, CNTs provide direct conducting pathways and robust mechanical support for the NiCo₂O₄ while the 3D UG serves as a macro frame for the nanostructures. The NiCo₂O₄ nanorods/CNT/UG/Ni foam obtained is directly measured as binder-free working electrodes in a three-electrode configuration and demonstrate excellent electrochemical performance in 1.0 M NaOH aqueous electrolyte.

Fabrication processes of the NiCo₂O₄ nanorods/CNT/UG/Ni foam are depicted in Figure 7-1. The details of the experiments are explained as follows.

Figure 7-1 Schematics of the fabrication procedures: (a) CVD growth of UG on Ni foam, (b) CVD growth of CNTs on UG/Ni foam and (c) hydrothermal synthesis and annealing treatment of the Ni-Co precursor.

7.1 CVD growth of 3D UG on Ni foams

0.15 cm thick Ni foam was punched into round chips in the diameter of around 1.2 cm. They were sequentially ultrasonic cleaned in acetone, IPA and DI water and dried at 80 °C in vacuum for 1 hour before loaded into a home-made tube furnace. Ar and H₂ were flowed together at the ratio of 200 sccm to 50 sccm (Ar:H₂) into the tube furnace and the furnace pressure is kept at ambient pressure throughout the growth process. The samples were annealed at 1000 °C for 5 minutes under the Ar and H₂ atmosphere to remove the possible native oxide before introduction of ethanol vapor as the carbon source to initialize growth of UG at 1000 °C. After 10 minutes, ethanol was cut off and the samples were cooled down to room temperature naturally under the protection of Ar and H₂.

7.2 CVD growth of CNTs on 3D UG

The UG/Ni foam obtained was submerged into 10 mM Ni(NO₃)₂ solution which was used as the catalyst precursor for CNT growth. The samples were then put in the furnace under the atmosphere of 180 sccm Ar and 70 sccm H₂. At the temperature of 700 °C, ethanol vapor was introduced into furnace as the carbon source for CNT formation. After 15 minutes' growth, ethanol vapor was cut off and the furnace was cooled down to room temperature naturally. The samples obtained were treated by O₂ plasma at RF power of 30 W and pressure of 100 mbar for 10 seconds, in order to improve their wetting in the following hydrothermal processes.

7.3 Fabrication of mesoporous NiCo₂O₄ nanorods

After the O₂ plasma treatment, the samples were put in 30 mL Teflon-lined SS autoclaves and immersed by 25 mL mixed solution of 5mM Ni(NO₃)₂·6H₂O, 10 mM Co(NO₃)₂·6H₂O, 4 mM hexadecyltrimethyl-ammonium bromide (HTAB), 18 mM urea. The autoclaves were kept at 100 °C for 6 hours and cooled down to room temperature naturally. Samples obtained were rinsed thoroughly several times using DI water before baking at 60 °C for 12 hours. Finally, they were annealed at 300 °C for 2 hours in atmosphere (ramping up at 1 °C per minute).

The dimensions of the samples are around 1.1 cm² × 0.15 cm. The average mass loading of the NiCo₂O₄ is 4.15 mg, determined by measuring the samples before hydrothermal reaction and immediately after annealing treatment. The mass loading is significantly enhanced as compared to that of NiCo₂O₄/CNT structures supported by SS substrate in Chapter 6 (0.6 mg), because of the unique 3D CNT/UG/Ni foam substrate.

7.4 Morphology and structure characterizations

Figure 7-2 SEM images at different magnifications of (a) the 3D UG on top of Ni foam; (b) CNT network on UG/Ni foam and (c) mesoporous NiCo₂O₄ nanorods/CNT/UG/Ni foam, respectively; (d) higher resolution SEM image of the core-shell structure of NiCo₂O₄ nanorods/CNT.

3D UG grown by CVD is shown in Figure 7-2 (a). Clearly, the Ni foam is completely covered by the UG. Despite some wrinkles, the UG displays a continuous and smooth morphology. In the growth process, 3D Ni foam serves as not only the template

but also the catalyst which helps the decomposition of carbon source at high temperature of 1000 °C and graphene layers are then precipitated on the surface of the Ni foam. As such, 3D UG is formed. [139] After the second CVD growth process, numerous CNTs are formed on the surface of UG as shown in Figure 7-2 (b). The diameters of CNTs are mainly in the range of 10 to 50 nm, while the length can reach tens of micrometers. It is noteworthy that CNTs entangle with each other into networks. More importantly, there is considerable space among the CNT networks, which is beneficial for the decoration of material onto the CNTs in the hydrothermal reaction. Figure 7-2 (c) and (d) present morphologies of the NiCo₂O₄ nanorods synthesized by hydrothermal reaction and the subsequent annealing process. They display length of several hundreds of nanometers and diameter of below 50 nm. Clearly, the NiCo₂O₄ nanorods are self-assembled radially on the CNTs and completely wrap them, forming a core-shell structure of NiCo₂O₄ nanorods/CNT. It may be important that although the nanorods are densely anchored on the CNTs, there is still plenty of room between neighboring nanorods, which facilitates the access of electrolyte and ions during electrochemical testing.

Figure 7-3 TEM images of (a) edge of the UG, (b) a randomly-selected CNT and (c) dispersed NiCo_2O_4 nanorods, respectively; (d) HRTEM of a part of the NiCo_2O_4 nanorod. (The insets indicate some of the crystalline directions observed in the nanorod.)

TEM image taken at the edge of the UG, Figure 7-3 (a), provides direct evidence for its ultrathin characteristic, while Figure 7-3 (b) proves that the CNTs are multi-walled, which are constructed by several tens of carbon walls with a cavity left in the axis. The constructing carbon walls are separated by c.a. 0.35 nm which matches reported wall separation. [113] As shown in Figure 7-3 (c), the NiCo_2O_4 nanorods are actually built up by numerous nanoparticles, giving the nanorods mesoporous characteristic. The nanoparticles are in the size of 5 to 15 nm, with space of several nanometers among them.

Such space is advantageous for the access of electrolyte, hence utilization of the active material. [240] The HRTEM in Figure 7-3 (d) indicates that the nanoparticles are highly crystalline in a variety of typical crystalline phases of spinel NiCo₂O₄. For instance, lattice spacing of 0.47 nm and 0.24 nm are observed in some nanoparticles which correspond to the theoretical interplanar spacing of the spinel NiCo₂O₄ (311) and (111) planes, respectively. [70, 216, 223, 224]

The successful synthesis of the materials is also confirmed by Raman spectroscopy and XRD. Typical Raman spectra of the UG and CNT/UG on Ni foams are shown in Figure 7-4 (a). The high intensity G band at 1582 cm⁻¹ and asymmetric 2D band at 2720 cm⁻¹ are the signatures for UG, consistent with previous reports. [134, 135] After the growth of CNTs, a distinct D peak emerges at 1349 cm⁻¹, probably because the relatively low growth temperature and high growth rates of CNTs increase the possibility of disordering in the structures. [190] XRD characterizes the phase, crystallinity and purity of the as-prepared NiCo₂O₄ nanorods. In order to avoid strong influences from the Ni foam, NiCo₂O₄ nanorods are scratched from the substrates to do the XRD test. As shown in Figure 7-4 (b), the diffraction patterns can be well indexed as crystalline structure of the spinel NiCo₂O₄ (JCPDS: 20-0781). [70, 216, 223, 224] The absence of excrescent peaks manifests high purity of the spinel NiCo₂O₄ synthesized through this method. Furthermore, from the XRD characterization, the particle size can be inferred according to the Scherrer equation based on the strongest peak:

$$D_c = \frac{0.89\lambda}{B \cdot \cos\theta} \quad (7-1)$$

where D_c is the average size of particle, λ is the X-ray wavelength (0.154 nm), B is the full width at half maximum height of a diffraction peak (0.98), θ is the diffraction angle (22°). [241] The average size of the particle is about 8.64 nm, which is consistent with the particle sizes ranging from 5 to 15 nm observed in TEM.

Figure 7-4 (a) Raman spectra of UG (below) and CNT/UG (above) on Ni foams; (b) XRD patterns of the NiCo₂O₄ nanorods.

7.5 Electrochemical characterization

The NiCo₂O₄/CNT/UG/Ni foam samples are directly used as working electrodes for electrochemical testing in 1.0 M NaOH aqueous solution without introduction of any polymer binders. The testing arrangement is similar to that in Chapter 6, where the sample, a Pt plate and SCE were used as the working, counter and reference electrodes in an open three-electrode system, respectively.

Figure 7-5 (a) CV curves of the NiCo₂O₄/CNT/UG/Ni foam at scan rates ranging from 5 to 20 mV·s⁻¹ measured in 1 M NaOH electrolyte; (b) comparison of the CV curves of NiCo₂O₄/CNT/UG/Ni foam and CNT/UG/Ni foam at the same scan rate of 5 mV·s⁻¹.

Figure 7-5 (a) is the representative CV curves at a series of scan rates from 5 to 20 mV·s⁻¹ over the range of 0 to 0.5 V (vs. SCE). The shapes of the CV curves clearly manifest the pseudocapacitive energy storage mechanism. For instance, at the scan rate of 5 mV·s⁻¹, a pair of distinct peaks appear at 0.16 V and 0.33 V, which come from the faradic redox reactions of M-O/MO-O-OH, where M refers to Ni or Co. [51] It may be noteworthy that CNT/UG/Ni foam may also carry capacitances. However, their contribution to the over capacitance is not significant, as evidenced by results of the control group of the CNT/UG/Ni foam without decoration of NiCo₂O₄. As shown in Figure 7-5 (b), the integral area of CV curve of the CNT/UG/Ni foam is much smaller than that of NiCo₂O₄/CNT/UG/Ni foam, indicating that the capacitance contribution from CNT/UG/Ni foam is negligible according to Equation 6-2. Therefore, introduction of the NiCo₂O₄ content enables greatly enhanced performance in terms of capacitance.

Figure 7-6 (a) Charge/discharge profiles of the NiCo₂O₄/CNT/UG/Ni foam at various current densities from 1 to 15 A·g⁻¹ and (b) the corresponding plot of the specific capacitance as a function of the current density.

The supercapacitive mechanism is confirmed by galvanostatic charge-discharge measurements in the potential window of 0 to 0.4 V at different current densities, as shown in Figure 7-6 (a). The plateaus in the charge/discharge curves match with the peaks in CV sweeping. Specific capacitances can be derived from the discharge parts of the curves, according to Equation 6-3. [2, 8] Specific capacitances C of 973.0, 920.3, 885.5, 870.1, 837.1, 776.4, 715.9 F·g⁻¹ are obtained at the current densities of 1, 2, 3, 4, 5, 8, 15 A·g⁻¹, respectively, as indicated in Figure 7-6 (b). Encouragingly, about 74% of the capacitance is retained even if the charge/discharge current is increased 15 fold from 1 to 15 A·g⁻¹, demonstrating superior supercapacitive performance of the material. The high porosity of the NiCo₂O₄ nanorods as well as the vast space provided by the 3D

CNT/UG/Ni foam skeleton enables numerous active sites and also rapid diffusion of the electrolyte, which is beneficial for the excellent rate performance.

Figure 7-7 Cycling performance at a current density of 5 A·g⁻¹ for 1200 cycles.

In addition, long-term capacitance retention is also of high importance. It is evaluated by the repetitive charge/discharge cycling at a constant current density of 5 A·g⁻¹ in this work as shown in Figure 7-7. The sample demonstrates a capacitance of 933.2 F·g⁻¹ in the first cycle and 762.5 F·g⁻¹ after 1200 cycles, corresponding to 82% retention of the initial capacitance. The supercapacitive performances are comparable to those good results in previous reports on NiCo₂O₄ based electrode materials, [69, 216, 223, 242] as well as the NiCo₂O₄/CNT structures in Chapter 6, especially when the dramatically enhanced active material loading is considered.

The excellent performances come from the rational assembly of the UG, CNTs and NiCo₂O₄ nanorods. Firstly, the good electrical conductivity of the UG, [134, 135] as well as its direct contact to the CNTs, [62, 243, 244] is likely to reduce the resistance significantly. Furthermore, highly conductive nature of the CNTs enable them as direct conducting pathways between active material and the UG/Ni foam current collector, facilitating the charge transfer during electrochemical testing. In addition, less conductive polymer binders can be completely avoided in this architecture, which is another advantage.

Secondly, this architecture brings merits by not only its electrical conductivity but also its unique structure. The 3D macroporous frame of UG/Ni foam as well as the space among the CNT network allows facile access for the electrolyte. UG grown on Ni foam provides a solid foundation for the whole system, owing to its excellent mechanical strength and chemical stability. Importantly, the entangled network of the CNTs make them to be strong skeletons, which help to keep the space among active materials. [245] Otherwise, the active material would be more prone to agglomeration, which would hinder the ionic diffusion and also reduce active sites for electrochemical reactions. In addition, with their hollowed structure and mechanical robustness, CNTs are able to serve as volume buffer for the active materials during the cycling and alleviate the stress. [26]

Last but not least, the structure of the active material, mesoporous NiCo₂O₄ nanorods also plays an important role in the excellent electrochemical performance. The open space between neighboring NiCo₂O₄ nanorods on the CNTs and also the mesopores inside individual nanorods are possible to provide facile access for the electrolyte and dramatically shortened diffusion paths for the ions. [240]

7.6 Conclusions

In summary, an interconnected 3D carbon network is successfully built on Ni foam through CVD growth of 3D UG on Ni foam and CNT network on the surface of UG, sequentially. It can be employed as a substrate for mesoporous NiCo₂O₄ nanorods which are prepared by hydrothermal reaction and subsequent annealing. The obtained NiCo₂O₄ nanorods/CNT/UG/Ni foam can be used as binder-free electrodes for ECs. The unique architectures, structures and morphologies, bring in advantages such as numerous active reaction sites, significantly reinforced mechanical strength and also greatly reduced electrical resistance, enabling their promising performance in ECs. Encouragingly, a high capacitance of 973.0 F·g⁻¹ at the current density of 1A·g⁻¹, outstanding rate performance (capacitance of 715.9 F·g⁻¹ at 15 A·g⁻¹) and also stable cycling at 5 A·g⁻¹ have been demonstrated.

Chapter 8 Summary and recommendations for future work

8.1 Summary

The major findings and contributions of this Ph. D study are summarized as follows:

- An approach to fabricate a binder-free MoS₂/CNT composite anode material of LIBs has been successfully developed. This work starts with growth of CNT network on SS substrates by CVD method, followed by hydrothermal and annealing preparation of MoS₂ nanoflakes onto the CNT network. The obtained MoS₂/CNT composite can be directly tested as an anode material in LIBs, without the necessity for any binders. The rational design, selection, composition and also architecture of the materials enhance structural stability and reaction kinetics. Firstly, the network of CNTs provide a strong skeleton for the composite and avoid aggregation of the active materials. Secondly, flexibility of the CNTs helps to absorb and buffer mechanical stress in MoS₂ upon repetitive lithium insertion/extraction. Meanwhile, voids inside the composite not only accommodate volume changes but also shorten the diffusion pathways, enabling fast lithium ion transport for improved rate capability. Furthermore, highly conductive CNTs can serve as good pathways in the nanocomposite. In this MoS₂/CNT composite, charge transfer can be further facilitated because of the direct rooting of CNT network onto the metal current collector as well as binder-free construction. Encouragingly, a high and reversible capacity over 1300 mAh·g⁻¹ is maintained for 50

cycles at the current density of $200 \text{ mA}\cdot\text{g}^{-1}$ over the potential range of 0.01 to 3 V, while excellent rate performance is also delivered.

- PECVD is improved deposition technology from CVD. With an electric field in the PECVD chamber, the CNTs can be well aligned into a vertical array, with considerable space between neighboring CNTs, which is beneficial for the coating of materials. Owing to the unique array organization of CNTs, Ni can be easily and uniformly coated onto the CNTs. The obtained Ni/CNT array on Si substrates is able to produce SiONWs rapidly with Si substrate as the solid source. More importantly, Ni/CNT array on SS substrate is employed as an excellent template for Si. Hence, a novel core-shell Si/Ni/CNT nanostructure array is developed as a high performance anode material of LIBs. CNTs help to alleviate the stress while the relatively large inter tube space accommodates volume variation of the Si. Furthermore, with the interfacial Ni layers, the interface between CNT cores and Si shells can be effectively improved for enhanced stability and adherence, well accommodated stress and improved charge transport. Encouragingly, a high capacity over $2500 \text{ mAh}\cdot\text{g}^{-1}$ at the rate of 0.2 C ($840 \text{ mA}\cdot\text{g}^{-1}$) in the potential range of 0.01 to 1.2 V are achieved over 110 cycles, while the anode structure is well maintained after cycling. This work clearly proves the significant role of interface in such core-shell Si/CNT structures. The architecture presented here offers a new idea to optimize the performance of core-shell Si/CNT anodes which are under intense research towards high capacity as well as prolonged life-time LIB applications.
- The CNT array is also employed to support NiCo_2O_4 , a novel type of TMOs, through a facile electrochemical deposition process followed by subsequent annealing in air.

The unique architecture brings in the following advantages for its electrochemical applications. Firstly, the vertically aligned CNTs serve as strong skeletons for the NiCo_2O_4 nanosheets, avoiding their aggregation and retaining their large surface area. Secondly, the ultrathin and nanoporous characteristics of the NiCo_2O_4 nanosheets provide numerous active sites for the redox reaction. Thirdly, the space between the core-shell $\text{NiCo}_2\text{O}_4/\text{CNT}$ nanowires minimizes the diffusion distance for ions. Therefore, fast ion transport is enabled for accelerated reaction kinetics, hence favoring the high rate performance. Furthermore, the unique array organization accommodates the volume expansion/contraction during charging/discharging process effectively. Because of these intriguing advantages, the $\text{NiCo}_2\text{O}_4/\text{CNT}$ nanostructures are possible to provide excellent electrochemical performances. When tested as an anode material for LIBs, $\text{NiCo}_2\text{O}_4/\text{CNT}$ structures demonstrate high capacity ($1147.6 \text{ mAh}\cdot\text{g}^{-1}$ at $100 \text{ mA}\cdot\text{g}^{-1}$), excellent cycling retention (no capacity fading over 200 cycles at $200 \text{ mA}\cdot\text{g}^{-1}$) and outstanding rate capability ($712.9 \text{ mAh}\cdot\text{g}^{-1}$ at $1000 \text{ mA}\cdot\text{g}^{-1}$) over the potential range of 0.01–3.0 V, which enable their promising applications in LIBs. On the other hand, the $\text{NiCo}_2\text{O}_4/\text{CNT}$ structures developed are also suitable for ECs. When tested as an electrode material for ECs, the $\text{NiCo}_2\text{O}_4/\text{CNT}$ structures exhibit high capacitances of $695 \text{ A}\cdot\text{g}^{-1}$ at the current density of $1 \text{ A}\cdot\text{g}^{-1}$ and $576 \text{ F}\cdot\text{g}^{-1}$ at $20 \text{ A}\cdot\text{g}^{-1}$ and remain 91% of the original capacitance after 1500 cycles at the current density of $4 \text{ A}\cdot\text{g}^{-1}$, demonstrating the high potential of this material in future EC applications.

- An interconnected 3D carbon network is successfully built on Ni foam through sequential CVD growth of 3D UG on Ni foam and CNT network on the surface of UG.

It is employed as a substrate for mesoporous NiCo_2O_4 nanorods which are prepared by hydrothermal reaction and subsequent annealing. The obtained NiCo_2O_4 nanorods/CNT/UG/Ni foam is a further improvement of the NiCo_2O_4 /CNT structure. As compared to the planar SS substrates, this unique 3D macroporous frame of UG/Ni foam enables significant enhancement in the loading of active materials (over 5 times higher) without compromising the supercapacitive performances. Encouragingly, a high capacitance of $973.0 \text{ F}\cdot\text{g}^{-1}$ at the current density of $1 \text{ A}\cdot\text{g}^{-1}$, outstanding rate performance (capacitance of $715.9 \text{ F}\cdot\text{g}^{-1}$ at $15 \text{ A}\cdot\text{g}^{-1}$) and also stable cycling at $5 \text{ A}\cdot\text{g}^{-1}$ for 1200 cycles have been successfully demonstrated.

8.2 Recommendations for future work

Based on the findings in my Ph. D project. A few suggestions are raised here which might be possible directions to further explore this research topic.

- Chapter 3, 4 and 5 include the investigations of MoS_2 , Si and NiCo_2O_4 supported by CNTs for anode applications. Among these three candidates, highest capacity which is over $2500 \text{ mAh}\cdot\text{g}^{-1}$ has been achieved in the Si/Ni/CNT anode at the rate of 0.2 C in the potential range of 0.01-1.2 V, while NiCo_2O_4 /CNT demonstrates the best cycling performance that no capacity fading occurs after 200 cycles at $200 \text{ mA}\cdot\text{g}^{-1}$ over the voltage range of 0.01–3.0 V. Recommended future work towards practical applications may include the following aspects: further enhancement in the mass loading of active materials, further improvement in the lifetime and investigation on suitable cathode materials.

- In Chapter 3, the MoS₂/CNT on SS substrates have exhibited appealing electrochemical performances as an anode material for LIBs. Possible future work may be using 3D UG coated Ni foam instead of the planar SS substrate. In Chapter 7, 3D UG has been proved to be an promising platform to assemble nanostructures of NiCo₂O₄/CNT in relatively much larger quantity. Therefore, it is expected that by using the 3D UG/Ni foam as substrates, the mass loading of MoS₂/CNT could be significantly enhanced which is more favorable for practical applications.
- In Chapter 4, the Si/Ni/CNT heterogenerous nanowires have proven to be an effective architecture to further optimize the core-shell Si/CNT structures. It might be noteworthy that capacity fading, especially after long-time cycling, is almost inevitable in Si based anode materials, including this work. It is suggested that further investigations could be carried out to figure out the detailed fading mechanisms. For instance, *in situ* TEM characterization could be utilized to shed light on this problem. Another suggestion may be an annealing treatment to possibly reinforce the contact between Si/Ni and Ni/CNT interfaces. The extra benefit of the annealing treatment may be the diffusion of Ni atoms into Si shell, driven by the thermal energy. If Ni silicide alloy was formed, the electrical conductivity and mechanical strength of the Si shells could be further enhanced.
- The 3D CNT/UG/Ni foam has proven to be an excellent platform to support NiCo₂O₄ as electrode material of ECs. This unique 3D NiCo₂O₄/UG/CNT/Ni foam may also be a possible anode material for LIBs. In addition, removing the Ni skeloton to obtain a free standing 3D carbon network before deposition of active material is another

suggestion. For practical applications especially in mobile electronics or EVs, it is favorable to reduce the overall weight of the battery or EC cell.

- Chapter 6 and 7 cover the work on ECs. To fulfill the potential of 3D $\text{NiCo}_2\text{O}_4/\text{UG}/\text{CNT}/\text{Ni}$ foam in EC application, future work on the further extension of the lifetime is suggested.

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2. Wen-wen Liu[¶], **Congxiang Lu**[¶], Kun Liang and Beng Kang Tay, ([¶] **equal contribution**), Three dimensional vertically aligned multiwall carbon nanotubes/NiCo₂O₄ core-shell structure for novel high-performance supercapacitors, *Journal of Materials Chemistry A*, 2014, 2, 5100.
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2. **Congxiang Lu**, Wen-wen Liu, Chong Wei Tan, Beng Kang Tay, Edwin Teo and Philippe Coquet, Core-Shell Carbon Nanotube-Nickel Silicide Nanowires as High Performance Anode Material in Lithium Ion Battery, Presented on *Material Research Society 2014 Spring Meeting*, San Francisco, United States of America, Apr. 2014.

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