Fabrication of carbon-metal oxide nanocomposites as electrode materials for supercapacitors

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2017

Yan, W. (2017). Fabrication of carbon-metal oxide nanocomposites as electrode materials for supercapacitors. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/70353>

<https://doi.org/10.32657/10356/70353>

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**FABRICATION OF CARBON-METAL OXIDE
NANOCOMPOSITES AS ELECTRODE MATERIALS FOR
SUPERCAPACITORS**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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NANOCOMPOSITES AS ELECTRODE MATERIALS FOR
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YAN WEILI

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

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

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Abstract

Supercapacitors (SCs) are deemed as the promising energy storage devices because of their remarkable power density, long cycle life and their special status in terms of power and energy densities that bridges the gap between conventional capacitors and batteries/fuel cells. However, the current SC technique is still confronted with low energy density and high fabrication cost. These issues can be tackled by developing high-performance electrode materials, especially the composites that incorporate high electrically conductive carbon (C) materials with pseudocapacitance-abundant transition metal oxides (TMO). The wet-chemistry approach based solutions/suspensions is an efficient way to prepare TMO-C composites on a large. The performance of the composites made by this method is strongly affected by the starting carbon suspensions. However, the common strategies to prepare homogeneous and stable carbon suspensions suffer from one or more shortcoming, such as tedious processes, high cost, high risk and low efficiency. Thus, in this thesis, I utilized the commercial Chinese ink as a starting material, aiming to develop a cheap, simple and scalable method to fabricate high-performance carbon-based composites as electrode materials for SCs.

To this end, firstly, Chinese ink was incorporated with multiwalled carbon nanotubes (MWCNTs) and vapor-grown carbon nanofibers (VGCNFs), and investigated its effect on the dispersion MWCNTs and VGCNFs under the wet mechanical grinding. I found that, the addition of Chinese ink is beneficial to the dispersion of MWCNTs and VGCNFs in aqueous suspensions, and their distribution in the poly(vinyl alcohol) and the filter paper. Therefore, the resulting conductive composites were ready to be the electrodes for electrical double-layer capacitors or applicable to be the substrate for the electrodeposition of TMOs.

Secondly, Chinese ink was applied to synthesis of birnessite-type MnO_2 through the redox reaction between KMnO_4 and the carbon black from Chinese ink. The results showed that these carbon black particles served as the reducing agent for KMnO_4 , and provided anchoring sites for the resulting MnO_2 . The in-situ deposition of MnO_2 on carbon black particles led to well-defined nanostructures, which could be adjusted by changing the

addition amount of Chinese ink or the reaction temperature. Benefiting from the good dispersion of the carbon black, the obtained MnO_2 -ink composites showed high specific surface area and improved electrochemical performance.

Thirdly, Chinese ink was employed as an inert additive during the synthesis of nickel cobaltite (NiCo_2O_4) via chemical co-precipitation and calcination. I found that during the chemical co-precipitation process, the carbon black particles from Chinese ink served as the nanoscale spacers to alleviate the agglomeration of the precipitated NiCo_2O_4 precursors. Thus, NiCo_2O_4 nanoflakes with a high specific surface area were obtained after calcination at a low temperature (less than 300 °C), which showed much better specific capacitance than pure NiCo_2O_4 .

Therefore, Chinese ink can be used as a building block to prepare high-performance electrode materials for SCs, due to its advantages of ready-made suspension system and the well-dispersed carbon black particles. It is believed that the preparation methods developed in this thesis can be also extended to other TMO-C composites. Furthermore, the methods hold promise for large-scale applications, due to their unique merits, such as low cost, low risk and easy processing.

Acknowledgements

First and foremost, I would like to express my sincere gratitude to my supervisor, Associate Professor Kong Ling Bing, for his continuous support, patient guidance and enthusiastic encouragement throughout my four-year PhD study. I would also like to express my great appreciation to my co-supervisor, Dr. Huang Hui from SIMTech, for his constructive suggestions on my research. It is my fortune to work with them.

Besides my supervisors, I would like to thank the rest of my thesis committee, Associate Professor Dong Zhili, and Assistant Professor Aravind Dasari, for their valuable comments and advice on this thesis.

I would like to extend my thanks to the administrative and technical staff at MSE, for their patient and friendly assistance. Besides, my sincere thanks also go to my labmates and the fellows in HW1 Labs.

Last but not the least, I wish to give special thanks to my beloved family for all their love, encouragement and understanding.

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Abbreviations

AC	Activated carbon
BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda
CB	Carbon black
CNF	Carbon nanofiber
CNT	Carbon nanotube
CV	Cyclic voltammetry
EDLC	Electrical double-layer capacitor
EIS	Electrochemical impedance spectroscopy
GCD	Galvanostatic charge-discharge
GO	Graphene oxide
MI	MnO ₂ -ink composite
MWCNT	Multi-walled carbon nanotubes
NCO	Nickel cobaltite (NiCo ₂ O ₄)
PVA	Poly(vinyl alcohol)
PVP	Poly(vinylpyrrolidone)
RGO	Reduce graphene oxide
RS	Raman spectroscopy
SC	Supercapacitor
FESEM	Field emission scanning electron microscopy
TEM	Transmission Electron Microscope
TGA	Thermogravimetric analysis
TMO	Transition metal oxide
VGCNF	Vapor-grown carbon nanofiber
XPS	X-ray photoelectron spectroscopy
XRD	X-Ray Diffraction

Chapter 1

Introduction

This chapter starts with the background of the research on supercapacitors (SCs). SCs, characterized by their high power density, long cycle life and rapid charging/discharging rates, are deemed as a promising kind of energy storage devices to meet the ever-growing demand for energy and power. However, the current SC technique is still confronted with some major problems, especially low energy density and high cost. Developing cheap and high-performance electrode materials is a key way to tackle the problems. Therefore, this thesis applies the commercial Chinese ink as a starting material, aiming to develop a simple and low-cost solution/suspension-based approach to synthesizing carbon-metal oxide composites. The primary hypothesis is that the Chinese ink can contribute a ready-made carbon black suspension to facilitate the synthesis of well-dispersed carbon-metal oxide composites. The detailed hypotheses are presented in Section 1.2. The scope of thesis as well as the corresponding objectives are elaborated in Section 1.3. Then, the key outcomes and the originality of the thesis are listed in Section 1.4. This chapter ends with the organization structure of the thesis, which provide a glimpse of each chapter.

1.1 Background

The attainability of low-cost and pollution-free energy has become a determining factor for a modern economy. At present, fossil fuels remain to be the primary energy sources for the world. However, the speedy depletion of fossil fuels and the ever-worsening ecological/environmental deterioration have forced people to seek clean, cheap and sustainable energy sources (such as solar, wind and tidal energy) as well as new strategies for energy storage. Energy sources in the form electricity generated from these renewable sources are of great significance. The generation of electricity and its applications in our daily lives and industry provide great potential to reduce our dependence on fossil fuels and relieve the global warming caused by CO₂ emission. The widespread implementation of electrical energy is guaranteed by the efficient electrical energy storage system, ranging from portable electric power to stationary electric power.¹ However, the electrical energy storage technologies at present, especially chemical energy storage (batteries) and electrochemical capacitors (or called supercapacitors) are still fall far short of meeting future energy storage requirement.²

Supercapacitors (SCs) are a type of energy storage devices, capable of achieving high power uptake/delivery in a short time. According to the charge storing mechanism, SCs can be divided into two basic types: electrical double-layer capacitors (EDLCs) and pseudocapacitors. SCs possess many advantages over lithium-ion batteries, such as high power density, fast charging/discharging speed, high rate capability, long cycling life, simple configuration, and safe operation.³ Notwithstanding these tempting merits, at present, SCs still suffers from low energy density and high energy/power costs currently, which are the key challenge for translating current lab-scale SC techniques into practical applications.

Developing new materials is the key to deal with the problem about low energy density. The theoretical energy density (E) of an SC is given by $E = CV^2/2$, where C is the capacitance of the SC and V is the operating voltage. The operating voltage is usually decided by the used electrolyte, while the capacitance is mainly dependent on the electrode materials. So far, intensive research efforts have been made on developing new electrode

materials in order to improve the capacitance of SCs. The materials used in SCs can be divided into three main categories, including carbon materials, transition metal oxides and conducting polymers. Carbon materials, characterized by high electrical conductivity, large surface area and good electrochemical stability, are widely used in EDLCs, but they normally demonstrate limited capacitance.⁴ Pseudocapacitive materials like transition metal oxides and conducting polymers can offer high capacitance from the redox reactions, but they do not possess electrical conductivity and electrochemical stability comparable to those of carbon materials.⁴

Incorporating electrically conductive carbon materials with pseudocapacitance-abundant materials has been proven an efficient strategy to make high-performance electrodes for SCs. There have been numerous carbon materials with multiple dimensions used for fabricating composite electrodes, such as 0D carbon black⁵, 1D carbon nanotubes⁶/nanofibers^{7, 8}, 2-D graphene⁹, 3D mesoporous carbon.^{10, 11} Among various processing methods, wet-chemistry based on solutions/suspensions is most commonly applied since it is simple and easily scalable. A prerequisite for wet-chemistry is to obtain stable solutions/suspensions. However, pristine carbon materials are normally not easy to be dispersed in either aqueous or organic solvent due to their inert surfaces. Different pre-treatments that modify the surface of carbon are usually performed to tackle the problem. These pre-treatments, however, suffer from one or more shortcomings, such as complicated operation, high risk and low efficiency and will cause additional costs. In addition, currently, the power cost and energy cost of SCs are still higher than those of lithium ion batteries. Accordingly, it is always desirable to develop a cheap and effective method to make stable carbon suspensions, dependent on which different wet-chemistry processing can be readily carried out.

1.2 Hypothesis

The primary hypothesis of this thesis is that the well-dispersed carbon black particles from commercially available Chinese ink can be used to disperse other carbon materials and transition metal oxides, and to reinforce the electrical conductivity of the resulting composites, because of which the resulting composites can demonstrate good

electrochemical performance. In details, the hypotheses are specified as follows.

Firstly, multi-wall carbon nanotubes (MWCNTs) and vapor-grown carbon nanofibers (VGCNFs) are good building blocks for high-performance electrode materials. However, pristine MWCNTs and VGCNFs are usually confronted with inevitable entanglement and poor interaction with surrounding matrices. Some reports have proven that wet ball milling (i.e., mechanical grinding) is effective in disentangling and dispersing MWCNTs in suspensions.¹²⁻¹⁵ Besides, inspired by the high stability of carbon black in Chinese ink, I consider applying Chinese ink as an additive for dispersing MWCNTs/VGCNFs. Therefore, it is hypothesized that raw MWCNTs and VGCNFs can be disentangled and dispersed in aqueous solutions by low-energy wet ball milling with the aid of Chinese ink, forming homogeneous suspensions that are stable enough for different applications.

Secondly, manganese dioxide (MnO_2), especially 2D birnessite-type MnO_2 is considered as a promising electrode material for SCs¹⁶. However, self-assembled bulky MnO_2 can only demonstrate limited specific capacitance due to sluggish Faradaic reaction kinetics caused by poor electrical and ionic conductivity, and have unsatisfactory cycling stability due to bad structural stability.¹⁷ Developing nanostructured MnO_2 supported by porous and electrically conductive materials is an effective way to improve the specific capacitance of MnO_2 . Nanoscale MnO_2 can have shortened ion diffusion paths and enlarged surface areas; meanwhile, the conductive supports can facilitate the electron collection and enhance the structure stability.¹⁶ Nanostructured birnessite-type MnO_2 can be synthesized and in-situ deposited onto carbon from the redox reaction between carbon and MnO_4^- ions. In view of the good dispersion and high stability of carbon black particles in Chinese ink, it is hypothesized that Chinese ink can be directly used as the carbon source to react with KMnO_4 to produce birnessite-type MnO_2 . Besides, benefiting from the good dispersion of carbon black particles, the in-situ grown MnO_2 should possess high surface area and decent electrical conductivity. As such, the MnO_2 -ink composites should be able to demonstrate high electrochemical performance.

Thirdly, chemical co-precipitation is a simple, cheap and easily scalable way to prepare transition metal oxides for pseudocapacitors. However, as mentioned above, self-

assembled transition metal oxides will undergo more or less agglomeration during synthesis, which is detrimental to the electrochemical performance. Apart from growing/depositing transition metal oxides onto high-surface-area and conductive substrates, introducing some inert nanoparticles (or called nanopacers) during synthesis is another effective approach to preventing the aggregation of transition metal oxides. 0D carbon black particles can be good choices because they possess fairly good electrical conductivity and they are easier to be dispersed than the other dimensional carbon nanomaterials. Chinese ink is able to provide a ready-made carbon black suspension. Therefore, it is hypothesized that the presence of Chinese ink in the precursor solutions can efficiently alleviate the agglomeration of transition metal oxides during synthesis; hence, the obtained transition metal oxide-ink composites can demonstrate enlarged specific surface area, better pore structures and improved specific capacitance.

1.3 Objectives and Scope

The goal of this thesis is to develop a cheap, simple and scalable method to fabricate high-performance carbon-based composites as electrode materials for SCs, as well as to probe into the mechanisms by which Chinese ink affects the dispersion and the electrochemical behavior of MWCNTs, VGCNFs and transition metal oxides. The objectives and the scope are elaborated below:

First, developing a simple and scalable method to disperse raw MWCNTs and VGCNFs into suspensions and apply the suspensions to fabricate electrodes for SCs.

In this part, a commercial Chinese ink will be utilized to disentangle and disperse raw MWCNTs/VGCNFs into the water by wet manual/mechanical grinding. Then, the resulting carbon suspensions will be used for different post-processing, including wet-casting to form freestanding composite sheets and filter-coating on filter paper to form paper-based composites. The morphology and the electrical conductivity of these composites will be characterized, based on which the influence of Chinese ink will be addressed. Lastly, these composites will be used directly as electrodes for symmetric SCs or as the substrate for electrodeposition of other active materials, and evaluate the electrochemical performance

of these SCs.

Second, synthesizing high-performance birnessite-type MnO_2 -ink composites from the redox reaction between KMnO_4 and Chinese ink

In this part, the commercial Chinese ink will be as the carbon source to react with KMnO_4 to produce birnessite-type MnO_2 -ink via stirring-driven hydrothermal reactions. XRD, XPS, Raman spectroscopy, SEM, TEM and nitrogen isothermal adsorption/desorption will be applied to characterize the properties of the resulting MnO_2 -ink composites, including crystal structures, morphology, surface and pore information. The formation mechanism of MnO_2 and the effect of Chinese ink on the properties of MnO_2 will be explored. Finally, the intrinsic electrochemical behavior of the MnO_2 -ink composites will be investigated in the three-electrode cell, and their practical performance will be assessed in the asymmetric SC configured with the MnO_2 -ink composite as the positive electrode and activated carbon as the negative electrode.

Third, synthesizing high-surface-area transition metal oxides through chemical co-precipitation with carbon black particles from Chinese ink as the nanopacers

In this part, NiCo_2O_4 will be taken as the example transition metal oxide to test this idea. The Chinese ink will be first mixed with the precursor solution during the co-precipitation process. The usage of Chinese ink is intended for providing well-dispersed carbon black particles as the inert nanoscale spacers, whose presence is expected to prevent the NiCo_2O_4 from massive agglomeration. XRD, XPS and Raman will be applied to confirm the formation of NiCo_2O_4 , while SEM, TEM and nitrogen isothermal adsorption/desorption will be applied to analyze the morphology and the surface and pore structures. Based on the analysis results, the influence of Chinese ink will be illustrated. Lastly, the electrochemical performance of the obtain NiCo_2O_4 -ink composites will be evaluated in a three-electrode cell.

1.4 Findings and Outcomes/Originality

This research leads to several novel outcomes:

First, the versatility of Chinese ink as a starting material or an additive in preparing electrode materials for SCs has been well demonstrated.

Second, a simple and cheap method has been developed to disperse raw MWNCTs and VGCNFs by making use of wet mechanical grinding and the assistance of Chinese ink. The obtained suspensions were post-processed by wet-casting on flat substrates or filter-coating on porous substrates to form conductive composites, which were ready to be the electrodes for SCs.

Third, high-surface-area birnessite-type MnO_2 -ink composites with well-defined nanostructures have been synthesized from the redox reaction between KMnO_4 and the carbon black from Chinese ink. The carbon black particles not only served as the reducing agents for KMnO_4 , but also provided the sites for in-situ deposition of MnO_2 . The good dispersity of carbon black particles ensured the high dispersity and homogeneity of the MnO_2 -ink composites. Accordingly, the prepared composites showed high electrochemical performance comparable to that of CNT- or graphene-based composites.

Fourth, well-dispersed NiCo_2O_4 -ink composites have been synthesized by chemical co-precipitation and a subsequent thermal treatment. Chinese ink was mixed with the precursor solution during the chemical co-precipitation process. The well-dispersed carbon black particles provided by Chinese ink functioned as the inert nanopacers to alleviate the agglomeration of NiCo_2O_4 , leading to enlarged specific surface and improved electrochemical performance.

1.5 Dissertation Overview

This thesis contains seven chapters. It focuses on developing simple and low-cost approaches to fabricate high-performance transition metal oxide-carbon composites as electrode materials for SCs. Meanwhile, this thesis demonstrates the electrochemical

performance of the composites as electrode materials for supercapacitors. In detail, the layout of the thesis is list below:

Chapter 1 briefs the background of the research, presents the hypotheses outlines the objectives and scope of this thesis.

Chapter 2 reviews the literature concerning the transition metal oxide-carbon composites as electrode materials for SCs. It starts with the history and basic concepts of SCs. Then it emphasizes on the current research progress on metal oxide-carbon composites for SCs. It ends with the statement of the research gap the thesis is addressing.

Chapter 3 provides the rationales for the selection of materials, synthesis methods and characterization techniques, and discusses the principles underlying the employed techniques.

Chapter 4 elaborates the dispersion of raw MWCNTs and VGCNFs by wet manual/mechanical grinding with the aid of Chinese ink, and the applications of the resulting suspensions in fabricating composites as electrodes for SCs.

Chapter 5 elaborates the synthesis of birnessite-type MnO_2 from the redox reaction between KMnO_4 and Chinese ink, discusses the effect of Chinese ink, and presents the evaluation of the electrochemical performance of the MnO_2 -ink composites as electrodes for SCs.

Chapter 6 elaborates the synthesis of high-surface-area NiCo_2O_4 through chemical co-precipitation with carbon black from Chinese ink as nanopacers, explores the role of Chinese ink in dispersing NiCo_2O_4 , and assesses the electrochemical performance of the NiCo_2O_4 -ink composites as electrodes for SCs.

Chapter 7 summarizes the thesis. It starts with a general discussion on the thesis, which explains how the outcomes are reflected in the original hypotheses. Then it demonstrates some reconnaissance studies that are not included in the main chapters, and provides some recommendations for future work.

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Chapter 2

Literature Review

This chapter reviews the history and the recent progress of supercapacitors (SCs). Section 2.1 begins with a short historical review on SCs, and then introduces the working principles and some key concepts about SCs. Section 2.2 elaborates the progress in carbon-transition metal oxide (TMO) binary composites as electrode materials for SCs, which is divided into four parts according to the dimensions of carbon. It lays emphasis on the fabrication methods and the electrochemical performance of these carbon-TMO composites. This section ends with a general discussion on the pros and cons of each dimensional carbon for fabricating electrode composite materials. The review in this section suggests that the current wet chemistry-based approaches to synthesizing carbon-TMO composites still suffer from high cost and/or complicated operations. Following this, Section 2.3 elaborates the issues to be addressed by this thesis. At last, Section 2.4 explains how the work done in this thesis fill the gap in fabricating well-dispersed carbon-TMO composites.

2.1 Overview

2.1.1 History of supercapacitors

Figure 2.1 The evolution of capacitor technology.¹

Figure 2.1 summarizes the development history of capacitors. The concept dates back to the late 1800s that electrical energy can be stored in the electrical double layers formed at the electrode-electrolyte interface. H. I. Becker from General Electric Company pioneered the first electrical device based on the double-layer charge storage mechanism.² This can be viewed as the prototype of SC, but it was not commercialized. In 1966, Standard Oil Company of Ohio (SOHIO) invented the electrical devices in the format now commonly used.³ This earthshaking invention evoked widespread research attention in both laboratories and industries, resulting in plenty of journal papers, patents and several annual special conferences.⁴ Thereafter, SC technology had rapidly grown into a new industry to meet the higher need for power quality. Since Nippon Electric Company (NEC) brought in the commercial SCs under the license from SOHIO in 1978, SC technology has evolved through several generations.⁵ SCs were initially applied as back-up power supply devices for fluctuant clock chips and complementary metal-oxide-semiconductor computer memories. Since the 1980s, SCs have undergone great progress in design, with continuous improvement in energy and power densities, safety, cost and manufacturing techniques. As

power suppliers or energy backups, they have also been used in many other new fields such as portable electronics, power grid, hybrid electric vehicles and so on.

2.1.2 Comparison of supercapacitors with other energy storage techniques

Figure 2.2 Ragone plot for different energy storage systems.⁶

Electrical energy can be stored in chemical (batteries) and capacitive (capacitors) ways. Batteries and capacitors are two important types of energy storage devices. As seen from Ragone plot (Figure 2.2), which depicts the power density against energy density, SCs bridge the gap of power and energy density between conventional capacitors (or called electrostatic capacitors) and batteries. Table 2.1 lists some important features of the general electrostatic capacitors, SCs and batteries. Compared to lithium ion batteries (LIBs), SCs have an enduring cycling life, and can be charged and discharged in a short time to offer higher power density. These features make them the ideal power supplies for certain applications where a power burst rather than large energy is needed, such as heavy hybrid vehicles,⁷ and power tools.⁴ It should be noticed that currently the cost of SCs (both power and energy cost) is much higher than that of lithium-ion batteries. The high cost of SCs has been the main obstacle to wider commercialization. The best way to solve the problem is to invent cheap but efficient electrode materials.

Table 2.1 Comparison of some important characteristics of electrostatic capacitors, supercapacitors and batteries^{1, 4}

Parameters	Electrostatic Capacitor	Supercapacitor	Battery
Charge Time	10^{-6} – 10^{-3} s	1–30 s	0.3–3 h
Discharge Time	10^{-6} – 10^{-3} s	1–30 s	1–5 h
Energy Density ($\text{Wh}\cdot\text{kg}^{-1}$)	<0.1	1–10	20–100
Power Density ($\text{W}\cdot\text{kg}^{-1}$)	>10000	1000–2000	50–200
Cycle Life	>500000	>100000	500–2000
Coulombic Efficiency	~1.0	0.90–0.95	0.7–0.85
Cost/Wh	-	\$10–20/Wh	\$1–2/Wh*
Cost/kW	-	\$75–150/kW	\$25–50/kW*

* For lithium ion batteries

2.1.3 Working principles of supercapacitors

Figure 2.3 Classification of supercapacitors and the corresponding electrode materials.

Figure 2.3 shows the classification of SC. According to the charge storage mechanisms, SCs can be classified into two basic types: electrical double-layer capacitors (EDLCs) and pseudocapacitors. In addition, studies have been carried out on SCs in a hybrid

(asymmetric) configuration combining one pseudocapacitive electrode and one non-faradaic electrode. By taking advantage of the merits of both types of electrodes, hybrid SCs are designed to optimize the overall performance, including a long cycle life, a high power density, a high energy density, etc.

Figure 2.4 Schematic drawing of a single-cell EDLC and illustration of the potential drop at the electrode-electrolyte interface.⁸

EDLCs

Similar to conventional capacitors, EDLCs store charge in a purely physical way; no electrochemical reaction occurs during the charging/discharging process. In contrast to conventional capacitors, EDLCs store the charges electrostatically through reversible adsorption of electrolyte ions onto high-surface-area and electrochemically stable electrode materials (usually carbon materials such as activated carbon as shown in Figure 2.4).

Figure 2.5 Models of the electrical double layer: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model.

The concept of the electrical double layer was first proposed by von Helmholtz in the 19th century, modified by Gouy and Chapman, and lastly optimized by Stern.⁹ Figure 2.5 shows these three models of the electrical double layer at a positively charged surface: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model which shows the inner Helmholtz plane and outer Helmholtz plane. Hence, the capacitance of the electrical double layer (C_{dl}) can be viewed as the contribution from two regions: the Helmholtz type compact double layer (C_H) and the diffuse layer (C_{diff}). Their relation can be expressed as:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (2.1)$$

In a real EDLCs, the electrical double layer behavior in the interface between porous electrode and electrolyte is much more complex than that at an infinite planar interface since there are many factors that can strongly influence the ion transportation in the confined system. To put it simply, the EDLC is usually treated as a parallel-plate capacitor and its capacitance is estimated by the equation.:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (2.2)$$

Where, ϵ_r is the dielectric constant of electrolyte, ϵ_0 is the permittivity of the vacuum, A is the area of electrode accessible to electrolyte ions, and d is the effective thickness of the electrical double layer. However, in reality, the simple linear relationship is not always followed when multiple pore sizes present.¹⁰ More in-depth understanding of charge storage in nanoscale spaces is still needed.

Carbon materials, such as activated carbon, carbon aerogels and other porous carbon, are the primary electrode materials for EDCLs as they possess sufficient surface areas for ion adsorption and remain inert to electrolytes during the charge/discharge process. Table 2.2 summarizes the properties and capacitance of different carbon materials widely used in EDLCs. From this table, it can be seen that the general capacitance of carbon materials is only around several hundred F g⁻¹, which is smaller than that of most transition metal oxides.

Table 2.2 Properties and capacitance of different carbon materials as electrodes for SCs.⁹

Materials	Surface area/m ² g ⁻¹	Density /m ² g ⁻¹	Aqueous electrolyte		Organic electrolyte	
			/F g ⁻¹	/F cm ⁻³	/F g ⁻¹	/F cm ⁻³
Commercial activated carbon	1000–3500	0.4–0.7	< 200	< 80	< 100	< 50
Particulate carbon from SiC/TiC	1000–2000	0.5–0.7	170–220	< 120	100–120	< 70
Functionalized porous carbon	300–2200	0.5–0.9	150–300	< 180	100–150	< 90
Carbon nanotubes	120–500	0.6	50–100	< 60	< 60	< 30
Templated porous carbon	500–3000	0.5–1	120–350	< 200	60–140	< 100
Activated carbon fibers	1000–3000	0.3–0.8	120–370	< 150	80–200	< 120
Carbon cloth	2500	0.4	100–200	40–80	60–100	24–40
Carbon aerogels	400–1000	0.5–0.7	100–125	< 80	< 80	< 40

Pseudocapacitors

The second type of SCs is the pseudocapacitor or called Faradaic supercapacitors. Beside the charge stored in the double layer, the capacitance of pseudocapacitors mainly origins from the fast and reversible redox reaction between the electrodes and electrolytes

occurring on the electrode surface. When a potential is applied to a pseudocapacitor, the redox reaction takes place, resulting in the transportation of valence electrons (Faradaic current) through the cell, which is similar to the charging/discharging process of a battery. The capacitance is characterized by an approximate linear relationship between the accepted charge (ΔQ) and the change in potential (ΔV), as follows:

$$C = \frac{\Delta Q}{\Delta V} \quad (2.3)$$

The Faradaic processes occurring in a pseudocapacitor are subject to a thermodynamic response of potential over the accumulation of charges, which are different from those in a battery and thus have better reversibility. The Faradaic processes in a pseudocapacitor electrodes include (1) surface reversible adsorption-desorption of proton or cations; (2) electrolyte ions involved redox reactions; and (3) doping-dedoping or intercalation-deintercalation without phase change.^{11, 12} These Faradaic processes contribute a considerable amount of capacitance to the pseudocapacitors. Thus, overall, pseudocapacitors have larger capacitance than EDLCs, but meanwhile, they suffer from a lower power density (due to poor electrical conductivity) and a shorter cycle life.

Materials that have been extensively applied as the electrodes for pseudocapacitors include transition metal oxides¹¹/hydroxides¹²/nitrides¹³/sulfides¹⁴, and conducting polymers¹⁵. The capacitance contributed from the redox reactions. Here in this thesis, the discussion will be focused on the metal oxides for pseudocapacitors.

2.1.4 Key parameters

The electrochemical performance of an SC is evaluated by different parameters, including specific capacitance, energy density, power density, rate capability, Coulombic efficiency and cycling stability.

2.1.4.1 Specific capacitance

By definition, the capacitance of a certain material can be determined by Equation 2.4. For pseudocapacitive materials, the theoretical pseudocapacitance can be calculated by:

$$C = \frac{nF}{MV} \quad (2.4)$$

where n is the mean number of electrons involved in the redox reaction, F is the Faraday constant, M is the molar mass of the material and V is the operating potential.

However, in practice, the capacitance is usually measured by cyclic voltammetry in a three-electrode system according to the following equations:

$$C = \frac{1}{2v(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV \quad (2.5)$$

where I is the response current, v is the voltage sweeping rate, V_c and V_a refer to the high and the low potential limit, and $(V_c - V_a)$ is the operating voltage window. The factor “2” is required since a full CV cycle is composed of a charging process and a discharging process. Alternative, the capacitance can be also determined by galvanostatic charge-discharge according to the equation. below:

$$C = \frac{I\Delta t}{\Delta V} \quad (2.6)$$

where I is the applied current, Δt is the discharging time and ΔV is the operating voltage window. Then, the specific capacitance (C_s) of a certain material can be expressed based on mass (m), area (A) or volume (S) as:

$$C_s = \frac{C}{m, A \text{ or } S} \quad (2.7)$$

2.1.4.2 Energy density and power density

Energy density and power density are two key parameters used to evaluate the performance of an SC. The maximum energy density (E , in Wh kg⁻¹) and power density (P , in W kg⁻¹) of an SC can be calculated by the following equations:

$$E = \frac{C_T V^2}{2} \quad (2.8)$$

$$P = \frac{V^2}{4R_s} \quad (2.9)$$

where C_T is the total capacitance of the cell (in F), V is the operating voltage of the cell and R_s is the equivalent series resistance (ESR, in Ω). For a two-electrode SC cell, the total capacitance can be calculated as follows:

$$\frac{1}{C_T} = \frac{1}{C_p} + \frac{1}{C_n} \quad (2.10)$$

where C_p and C_n are respectively the capacitance of positive and negative electrode, calculated from a three-electrode test.

C_T . If the positive and negative electrode are identical, then $C_p = C_n$, and the total capacitance will be half of either electrode. The corresponding SC is called symmetric SC. Otherwise, an asymmetric SC contains two different electrodes, and its capacitance relies on the smaller between C_p and C_n .

V . The cell voltage mainly depends on the thermodynamic stability of the used electrolyte. Generally, the cell voltage can be 0.9 V, 2.5–3.0 V or up to 4.0 V, if an aqueous electrolyte, an organic electrolyte or an ionic liquid is used, respectively.¹⁶ It is noteworthy that in an asymmetric SC composed of a carbon-based negative electrode, a TMO-based positive electrode and a mild aqueous electrolyte, the cell voltage can be up to 1.9 V.¹⁷

R_s . The ESR mainly comprises (1) the intrinsic resistance of the electrodes and the electrolyte, (2) the contact resistance between the electrodes and the current collects, and (3) diffusion resistance of ions in the electrodes and through the separator.

It is known from Equation 2.8 that, the improvement in energy density of an SC can be achieved by increasing its specific capacitance or/and its operating voltage. The common approaches to this end are summarized in Figure 2.6.

Figure 2.6 Approaches to improve the energy density of SCs.¹⁸

2.1.4.3 Cycling stability

SCs have a long cycling life of more than one millions cycles. It is impractical to directly measure the cycle number in a lab study. Instead, cycling stability is usually indirectly estimated by comparing the capacitance change before and after thousands of cycles of galvanostatic charging/discharging or constant-rate CV sweeping. Cycling stability predicts the service life of an SC in practical use. Normally, EDLCs have better cycling stability than pseudocapacitors.

2.1.4.4 Coulombic efficiency

By definition, Coulombic efficiency (or called Faradaic efficiency) is the ratio of the output of charge (electrons) by an SC during the charge cycle to the input of charge during the discharge cycle. It evaluates the efficiency with which charge is transferred to facilitate electrochemical reactions.

2.1.4.5 Rate capability

The concept “rate capability” can be used to describe the extent to which an SC can retain the capacitance at a higher sweep rate or higher current densities. The rate capability is largely determined by the electron transportation in the solid electrodes and the ion

diffusion in the electrolyte.

2.2 Metal Oxide-Carbon Composites for Supercapacitors

As seen in Figure 2.3, the materials used for SC electrodes can be divided into three basic types: carbon materials, metal oxides/hydroxides/nitrides/sulfides and conducting polymers. Transition metal oxides are deemed the next generation of electrode materials for SCs. Nevertheless, despite the satisfactorily high theoretic capacitance, TMOs currently still suffer from low utilization ratio and poor rate performance. The main reasons for this are the intrinsic low electrical conductivity of TMOs that compromises fast Faradaic reactions, as well as the inevitable agglomeration of nanoscale TMOs that can lead to a dense structure unfavorable for ion diffusion. Consequently, incorporating TMOs with highly conductive materials has been proven an efficient way to augment the effective utilization. Carbon materials, characterized by their multifarious existing forms, large specific surface area, high electrochemical stability and decent electrical conductivity, have been extensively used as electrodes for EDLCs, or the non-Faradaic electrodes (usually the negative electrodes) for hybrid SCs.⁹ Incorporation TMOs with carbon materials has been proven to be a good strategy to fabricate high-performance electrodes for SCs. In such a configuration, TMOs contribute the main capacitance resulting from their reversible redox reactions with the electrolyte, while the carbon materials function as the electroconductive additives or substrates to expedite the charge transfer.

Herein, we narrow down the literature review on the composites comprising transition metal oxides and carbon materials. The discussion will be organized according to the carbon types based on their nanostructures.

2.2.1 Zero-dimensional carbon-metal oxide composites

Here in this work, we simply classify the spherical carbon materials (such as carbon black, and carbon nanospheres) or the ones without well-defined geometrical shapes in nanoscale (such as activated carbon and mesoporous carbon) as the zero-dimensional (0D) carbon materials.

2.2.1.1 Carbon black.

Carbon black, especially acetylene black, is the most widely used electrically conductive additive in SCs, because of its high electrical conductivity. The common usage of carbon black is to physically mix it with the electroactive material and the binder (according to a certain ratio) to fabricate the electrode. Apart from the electrically conductive additive, carbon black can be directly used the starting material to prepare electrode materials. A good example is reported by Ma et. al., in which Birnessite-type MnO_2 was synthesized and deposited onto acetylene black by simply immersing acetylene black into a KMnO_4 aqueous solution.¹⁹ They found acetylene black acted as the reducing agent and the substrate for the heterogeneous nucleation of MnO_2 . On this basis, Huang et. al. further investigated this reaction mechanism and proposed the reaction equation as:²⁰

The remaining carbon black improved the electrical conductivity of the composite. However, the resulting composites do not demonstrate satisfactory electrochemical performance. Similarly, Chu et. al. applied this redox reaction and prepared the MnO_2 /acetylene black composite.²¹ The composite only demonstrated limited capacitance of $127.2 \text{ F}\cdot\text{g}^{-1}$ and retained 61.7% of the initial capacitance after 1200 cycles. The low capacitance may be due to the non-uniform deposition of MnO_2 on acetylene black as acetylene black is not well dispersed.

2.2.1.2 Activated carbon

Activated carbon (AC) is the most widely used carbon material in SCs. It is commonly used for fabricating the electrodes for symmetric EDLCs, or the negative electrode for asymmetric SCs. AC is distinguished by the remarkable specific surface area (up to $3000 \text{ m}^2\cdot\text{g}^{-1}$) and a broad pore size distribution consisting of micropores ($< 2 \text{ nm}$), mesopores ($2\text{--}50 \text{ nm}$) and macropores ($> 50 \text{ nm}$).⁹ Notwithstanding the high specific capacitance, AC merely demonstrates moderate capacitance. The reason is that some pores contributing to the total surface area do not necessarily contribute to total capacitance; only the pores with a diameter close to the ion size are the most efficient for charge accumulation.²²

Incorporating AC with TMOs is a good strategy to make the best of its high surface area since AC can enlarge the effective surface area of TMOs. An example is the NiO/AC composite electrode, which was prepared by the precipitation of nickel hydroxide onto activated carbon and the follow-up calcination in air.²³ The addition of dramatically improved the specific surface area of NiO from $150 \text{ m}^2\cdot\text{g}^{-1}$ to up to $702 \text{ m}^2\cdot\text{g}^{-1}$. The composite with 7 wt% of NiO demonstrated a capacitance of $107 \text{ F}\cdot\text{g}^{-1}$, measured in a three-electrode system by CV at a scan rate of $5 \text{ mV}\cdot\text{s}^{-1}$. A second example is the nickel hydroxide/activated carbon composite reported by Yuan et. al.²⁴ The composite was obtained by depositing nickel hydroxide onto activated carbon via chemical precipitation. Without heat treatment, the obtained composite containing 4.3 wt% of nickel had a specific capacitance of $1232.4 \text{ m}^2\cdot\text{g}^{-1}$ and a specific capacitance of $194 \text{ F}\cdot\text{g}^{-1}$. Huang et. al. also reported a similar result with an improved specific capacitance.²⁵ A third example is the ruthenium oxide/sol-gel derived carbon.²⁶ To prepare the composite, a sol-gel derived carbon-Ru xerogel was first prepared from $\text{RuO}_2\cdot x\text{H}_2\text{O}$ -contained resorcinol-formaldehyde resins, and the xerogel was further converted to Ru/carbon by carbonization at 750°C in N_2 . The metallic Ru was subsequently oxidized to electrochemically active ruthenium oxide by a charge-discharge cycle. The composite containing 14 wt% Ru had a specific capacitance of $256 \text{ F}\cdot\text{g}^{-1}$ at $0.1 \text{ A}\cdot\text{g}^{-1}$ and showed no decline in capacitance after 2000 cycles.

It should be pointed out that, activated carbon is the main component in these composites while the TMOs are just the pseudocapacitive additives. The high specific surface area makes AC a suitable electrode material for SCs. Meanwhile, when incorporated with TMOs, AC suffers from a low utilization rate of the high surface area, because of the wide pore size distribution and the irregular geometrical shape. This is a possible reason why only a small amount of TMOs is added to prepare the composites.

2.2.2 One-dimensional carbon-metal oxide composites

One-dimensional (1D) carbon refers to the fiber/tube-shaped carbon materials with a large length-diameter ratio. Carbon nanotubes and carbon nanofibers are two popular 1D carbon materials. Due to their good electrical conductivity, they are expected to boost the charge

transfer in electrochemical reactions.

2.2.2.1 Carbon nanotubes

Carbon nanotubes (CNTs) have attracted special research attention in the field of energy storage because of their unique physical and chemical properties. The high electrical conductivity, good mechanical resilience and unique pore structures make them the suitable supporters for pseudocapacitive materials.⁹ When incorporated with TMOs, their superb conductivity can improve the overall conductivity of the composites. Their mesoporous character stemming from the open tubular network will induce more porosity that can provide more channels for electrolyte ions and shorten the diffusion distance. Besides, the functional groups on the surface also facilitate the interaction between the electrode and the electrolyte at the interface.²⁷ There have been many reports about the composites composed of CNTs and the oxides of various metals such as manganese,^{28,29} ruthenium,³⁰ iron,³¹ vanadium,³² nickel³³ and cobalt.³⁴

Bi et al. reported the direct growth of RuO₂ nanoparticles on the CNT surface by a simple solution-based method.³⁰ The composite with a RuO₂: CNT mass ratio of 6: 7 showed a specific capacitance of 953 F g⁻¹, and a capacitance retention of 98% after 2000 cycles. They ascribed the improvement in capacitance and cycling life to the multiple functions of CNTs. That is to say, CNTs provided the anchoring sites for the RuO₂ nanoparticles, facilitated the dispersion of RuO₂ and improved the electrical conductivity of the composite. Similarly, the CNT/Fe₃O₄ composite was prepared by directly growing the Fe₃O₄ nanoparticles in the CNT aqueous suspension in a hydrothermal reaction.³⁵ The resulting composite composed of Fe₃O₄ cubic nanoparticles inlaid on the surface of CNTs, showed an improved specific capacitance of 117.2 F g⁻¹ at 10 mA cm⁻², three times higher than that of pure Fe₃O₄. The improvement in the specific capacitance is also observed in the V₂O₅/CNT composite, which was composed of interweaved CNTs and V₂O₅ nanowires and prepared by a hydrothermal process. The composite with 33 wt% of CNTs exhibited a surface area of 125 m² g⁻¹ and an average pore size of 15.2 nm. It delivered a specific capacitance of 313 F g⁻¹ at 1 A g⁻¹, much higher than that of CNTs (75 F g⁻¹) and pure V₂O₅ nanowires (146 F g⁻¹). In these cases, CNTs mainly serve as the chemically inert and

conductive supports for TMOs. They were first mixed with the TMO precursors in solutions, then converted into desired TMO/CNT composites by subsequent hydrothermal reactions or calcination. The presence of CNTs has been proven to be efficient in preventing the agglomeration of TMOs and creating some effective spaces for ion diffusion.

In addition to direct blending with TMOs or their precursors, CNTs can be also used the substrate for the electrochemical or electrophoretic deposition of TMOs, because of their good electrical conductivity. Li et al. applied the electrophoretic deposition method to simultaneously deposit MWCNTs and chemical precipitation-made MnO_2 nanofibers onto stainless steel foils and graphite substrates.³⁶ The thickness and the pore size of the composite films were tuned by changing the voltage and the deposition time. Lee et al. first deposited CNTs onto the Ni substrate by electrophoretic deposition and then deposited $\text{MnO}_x \cdot \text{H}_2\text{O}$ onto the obtained CNT/Ni substrate by anodic deposition.³⁷ The $\text{MnO}_x/\text{CNTs}/\text{Ni}$ composite demonstrated a specific capacitance of 415 F g^{-1} measured by CV at 5 mV s^{-1} , higher than that of MnO_x/Ni (233 F g^{-1}). The improvement in capacitance is due to the presence of CNTs that increase the surface roughness and creates a better interaction between MnO_x and the current collector. Similarly, Hu et. al. conformally electrodeposited MnO_2 nanoflowers onto a CNT/textile substrate.³⁸ By taking advantage of the porous structure of the textile and the good conductivity and flexibility of CNTs, the obtained $\text{MnO}_2/\text{CNT}/\text{textile}$ composite showed a high specific capacitance of 410 F g^{-1} and a high areal capacitance of 2.8 F cm^{-2} .

Besides serving as the chemically inert and conductive supports for TMOs, CNTs can also react with the TMO precursors. A good example is the MnO_2/CNT composites prepared from the redox reaction between CNTs and KMnO_4 .^{28, 39-41} In these redox reactions, CNTs acts as the reducing agent to convert KMnO_4 into MnO_2 . The resulting MnO_2 in situ covers on the surface of the CNTs, forming an intimate contact with CNTs that can effectively boost the charge transfer. The morphology of MnO_2 can be altered by changing the solution composition, pH, reaction temperature and reaction time.³⁹ As reported by Xie et. al., the CNT with a 6.2 nm-thick MnO_2 coating could exhibit a specific capacitance of up to 250.5 F g^{-1} .

2.2.2.2 Carbon nanofibers

Carbon nanofibers share many similar characteristics with CNTs. But compared with CNTs, carbon nanofibers (CNFs) have a lower price and thus are feasible for large-scale applications. Basically, according to the preparation method, CNFs can be classified into template-grown carbon nanofibers,⁴² activated electrospun CNFs (ECNFs) and vapor-grown carbon nanofibers (VGCNFs), etc.

Zhang et. al. synthesized carbon nanofibers by the hydrothermal reaction with Te nanowire as the template.⁴² In the reaction, glucose was converted into carbon and grown on the Te nanowires. After the Te nanowires were etched away, pure carbon nanofibers were obtained, which were further used as the substrates to synthesize NiCo_2O_4 nanosheets and nanorods through chemical co-precipitation and calcination. These carbon nanofibers provided a robust support for the NiCo_2O_4 and promoted the charge transfer during the electrochemical process. Thus, the $\text{CNF@NiCo}_2\text{O}_4$ nanosheets showed a capacitance of 902 F g^{-1} at 2 A g^{-1} , and retained 96.4% of initial capacitance after 2400 cycles.

ECNFs are made by the electrospinning of a polymer precursor and the follow-up carbonization. ECNFs are deemed as the promising conductive supports for metal oxide due to their high specific surface area, tunable fiber and pore size, good mechanical properties and low manufacturing cost. One way to incorporate TMOs into ECNFs is to directly mix the TMOs/TMO precursors with an appropriate ECNF precursor to form a homogeneous mixture and convert the mixture into TMO/ECNF composite via electrospinning and activation. For example, Kim et. al. directly blended V_2O_5 with polyacrylonitrile (PAN) in dimethylformamide (DMF), and converted the resulting mixture into $\text{V}_2\text{O}_5/\text{ECNF}$ composites by electrospinning and follow-up carbonization.⁴³ They found morphology and the pore structure were largely influenced by the content of V_2O_5 . The composite with a higher content of V_2O_5 exhibited higher specific surface area and better electrical conductivity. The composite with 20 wt% of V_2O_5 showed a specific capacitance of 150 F g^{-1} at 1 mA cm^{-2} , and enhanced energy density ($18.8\text{--}13.8 \text{ Wh kg}^{-1}$) and power density ($0.4\text{--}20 \text{ kW kg}^{-1}$). For another example, Kim et. al. introduced phenylsilane (PS) into the PAN/DMF solution to produce porous silica/ECNFs composites by electrospinning

and physical activation.⁴⁴ The PS was converted into silica via a steam-facilitated sol-gel process during carbonization. The composite combined the high electrical conductivity and large surface area of ECNFs and the hydrophilicity nature of silica, and thus demonstrated improved electrochemical performance. The composite made from 5 wt% PS showed the highest energy density of 88 Wh kg⁻¹ at the power density of 1 kW kg⁻¹, and retained 87% of the initial capacitance after 1000 cycles. In this cases, TMOs can be easily inlaid into ECNFs by uniformly mixing their precursors. However, this method suffers from low utilization rate of TMOs as the embedded TMO particles may not be accessible to electrolyte ions. Besides, if the precursor solution is not homogeneously mixed, it will lead to uneven distribution of the TMO particles in the ECNFs. What's worse, once there are some large-size TMO clusters, it is very likely that the ECNFs will break during electrospinning or carbonization.

Alternatively, pure ECNF mats can be first fabricated and activated before doped with TMOs. Zhi et. al. fabricated freestanding iron acetylacetonate (AAI)-incorporated ECNF sheets from PAN by electrospinning and carbonization.⁴⁵ The AAI was converted into Fe₃O₄ phased during carbonization. Birnessite-type MnO₂ was coated onto the AAI-ECNF sheet by a simple redox deposition as mentioned above. They found the addition of AAI improved the electrical conductivity of ECNFs and facilitated the charge transfer between MnO₂ and ECNFs, especially in the composite with a high content of MnO₂. The obtained MnO₂/AAI-ECNF composite with 13.9 wt% of MnO₂ loading demonstrated a specific capacitance of 311 F g⁻¹ for the whole electrode (900 F g⁻¹ for MnO₂ only) at a scan rate of 2 mV s⁻¹. Similarly, Ma et. al. reported an analogous MnO₂/ECNFs composite, composed of lignin/PVA derived ECNFs and redox-deposited MnO₂ nanowhiskers.⁴⁶ The composite exhibited the highest capacitance of 83.8 F g⁻¹, energy density of 84.3 Wh kg⁻¹ and power density of 5.72 kW kg⁻¹. With the same strategy, different kinds of TMOs can be also decorated onto the as-prepared freestanding ECNFs sheets (or mats), such as V₂O₅,⁴⁷ TiO₂,⁴⁸ and Fe₃O₄.⁴⁹

2.2.3 Two-dimensional carbon-metal oxide composites

Graphene, a 2D carbon allotrope, is expected to be an outstanding electrode material for

SC because of its strong mechanical strength,⁵⁰ high specific surface area,⁵¹ superb electronic conductivity⁵² and good electrochemical stability.⁵³ In addition to graphene, graphene oxide (GO) and chemically reduced graphene oxide (RGO) made from graphite are also appealing electrode materials for SCs. Compared with graphene, GO and RGO have more structure defects, i.e. more electroactive sites. The function group-rich surface makes it easy to integrate GO or RGO with TMOs. GO/RGO has potential to be a powerful reinforce for TMOs. So far, numerous research works have been reported on the preparation of TMO-graphene composites and their application in SCs.

Many methods have been developed to obtain graphene- or RGO-TMO composites, such as chemical precipitation,⁵⁴⁻⁵⁶ sol-gel synthesis,⁵⁷ chemical bath deposition,^{58, 59} microwave-assisted synthesis,^{60, 61}, hydrothermal synthesis,^{58, 61-63} and electrodeposition.^{64, 65} The combination of graphene/GO/RGO with TMOs can lead to a synergistic improvement in the electrochemical performance as it mutually mitigates the agglomeration of each component. Here, we use some examples to illustrate the synergistic effect brought by graphene/GO/RGO.

Chemical precipitation synthesis and hydrothermal synthesis are most widely applied for synthesizing powder samples since they are easy to operate. They both require the metal ions of the desired species and the precipitants, and a subsequent thermal treatment process to convert the precursor to desired oxides. The chemical precipitation synthesis is usually carried out at a temperature less than 100 °C, and the process can be accomplished in a short time, which sometimes make it difficult to precisely control the size and morphology of the products.^{63, 66} By contrast, hydrothermal (or solvothermal) synthesis can be applied to synthesize metal oxides with tuned morphology and particle sizes, but it requires a higher reaction temperature and a longer reaction time. A simple strategy to incorporate graphene with metal oxides is to mix the well-dispersed GO suspension with the precursor solution during chemical precipitation/hydrothermal process.⁶⁷⁻⁶⁹ Such a treatment can result in the random mixing of graphene and metal oxides. The metal oxides reduce the stacking of graphene, in return, the graphene boosts the electrochemical activity of the metal oxides.

Chemical bath deposition is commonly applied to conformally deposit a layer of active

materials on the substrate. It also involves the chemical precipitation of the desired oxides/hydroxides from the precursor solution. Graphene/graphene oxides can be first coated on the substrate, then through chemical bath deposition, TMOs are randomly anchored on the graphene nanosheets. For instance, Wu et. al. reported a 3D NiO/ultrathin derived graphene hybrid on Ni foam.⁵⁹ They firstly applied nanocasting to prepare the 3D ultrathin derived graphene on Ni foam, and used the obtained graphene/Ni foam as the scaffold to grow NiO by the chemical bath deposition and calcination. The highly conductive graphene/Ni foam scaffold engendered a thin active material layer that shortened the diffusion path for ions and boosted the electron transport for NiO. Hence, the composite showed a specific capacitance of 425 F g^{-1} at 2 A g^{-1} , higher than 235 F g^{-1} of NiO/pure Ni foam, but it retained only 79% of the initial capacitance after 2000 cycles of charging-discharging at 10 A g^{-1} . For another instance, Xia et al. first coated the Ni foam with GO by electrophoretic deposition and reduced the GO with hydrazine monohydrate.⁵⁸ Then, they grew a thin film of NiO flakes on the RGO-Ni foam by chemical bath deposition. They found that the introduction of RGO enhanced the electrochemical activity of the reversible reaction between Ni (II) and Ni (III). Consequently, the NiO/RGO-Ni foam showed an improved specific capacitance of 400 F g^{-1} at 2 A g^{-1} , and maintained 94% of capacitance after 2000 cycles.

The sol-gel process is also widely applied to combine graphene with TMOs. Similar to the chemical precipitation process, a follow-up thermal treatment is usually required to convert the precursors to the desired TMOs. Normally, graphene oxides made by chemical exfoliation of natural graphite flakes are used since they can be easily dispersed in aqueous solutions. Wu et al. applied the sol-gel and low-temperature annealing to anchor RuO_2 nanoparticles onto the RGO.⁵⁷ Such an integration reduced the aggregation of RGO and RuO_2 and constructed a conductive network. As a result, they observed a synergistic effect on the specific surface area and electrochemical performance. The composite showed a specific capacitance of 570 F g^{-1} and around 97.9% capacitance retention after 1000 cycles.

Electrodeposition is also used to prepare TMO-graphene composites. In this case, graphene (or RGO) merely serves as the conductive substrate for electrodeposited TMOs. The presence of graphene (or RGO) leads to a rough surface that can create more active sites

for the electrodeposition of TMOs. Thus, the electrodeposited TMOs on a graphene-coated substrate can show improved electrochemical performance than the one on a bare substrate. Commonly, well-dispersed GO will be first deposited onto a conductive substrate (such as nickel foam, graphite paper, etc.) by electrophoresis or simple drop-deposition, reduced to RGO, and used as the substrate. For example, Hassan et al. reported a $\text{MnO}_2/\text{RGO}/\text{nickel}$ foam electrode, which was made in two steps: the electrophoresis of GO onto nickel foam and the anodic deposition of MnO_2 on the RGO/nickel foam.⁶⁴ The composite electrode showed a high specific capacitance of 822 F g^{-1} at 1 mA cm^{-2} .

2.2.4 Three-dimensional carbon-metal oxide composites

An SC with high power and energy density is always desirable. The high power and energy density require a high loading density of active materials. However, due to the dimensional limitation, 0D, 1D and 2D carbon materials are not able to load a large amount of TMOs without undermining their performance. By contrast, 3D porous carbon materials are capable of providing enough room for TMOs, and creating a continuous charge transfer network and shortened ion diffusion paths for the loaded TMOs. Many types of 3D carbon materials have been developed, such as polymer-derived carbon aerogels (or mesoporous carbon),^{70, 71} biomass-derived carbon hydrogels and aerogels,⁷² CNT-assembled carbon aerogels,⁷³⁻⁷⁷ and graphene-assembled carbon hydrogels/aerogels.⁷⁸⁻⁸¹

2.2.4.1 Polymer-derived carbon aerogels (or mesoporous carbon),

Polymer-derived carbon aerogels are commonly obtained by carbonizing (i.e. pyrolyzing in an inert atmosphere) polymers made by a sol-gel process. The obtained carbon aerogels are ideal electrode materials for EDLCs because of their high electrical conductivity, high porosity and large specific surface area.⁸² For instance, Wei et al. used soluble resol the carbon source, dicyandiamide as the nitrogen source and the co-polymer F127 as the soft template to synthesize order mesoporous carbon in three steps.⁸³ They first used the starting materials to make mesostructures by an evaporation-induced self-assembly process, then converted the mesostructured mixture into rigid phenolic resin by thermosetting, and lastly converted the phenolic resin into mesoporous carbon by pyrolysis at 600°C in N_2 .

Besides as the electrode materials for EDLCs, polymer-derived carbon aerogels are also the ideal buttress for 0D and 1D TMOs. For instance, Dong et al. synthesized and embedded the MnO_2 into the wall of mesoporous carbon by the redox reaction of the host mesoporous carbon and KMnO_4 .⁸⁴ The MnO_2 -mesoporous carbon showed a specific capacitance of over 200 F g^{-1} for the whole composite and 600 F g^{-1} for the MnO_2 . Lin et al. integrated phenol-functionalized iron oxide nanoparticles into block copolymers by cooperative self-assembling.⁸⁵ After carbonization, the block copolymers were converted into mesoporous carbon, with Fe_2O_3 nanoparticles dispersed in the framework. The addition of Fe_2O_3 nanoparticles improved the specific capacitance from 153 F g^{-1} to 235 F g^{-1} . Another example is reported by Chien et al.⁷⁴ They first prepared the carbon aerogel from resorcinol and formaldehyde by condensation polymerization and subsequent carbonization, and then deposited NiCo_2O_4 on the carbon aerogel. Benefiting from the mesoporous structure of carbon aerogel, the thin nanostructured NiCo_2O_4 exposed more to the electrolyte, which facilitated the ion and charge transportation. Thus, the resulting NiCo_2O_4 -carbon aerogel composite showed a specific capacitance of about 1700 F g^{-1} at a scan rate of 25 mV , and retained 97.6% of the initial capacitance after 2000 cycles.

2.2.4.2 Biomass-derived carbon aerogels

Compared with the other carbon aerogels, carbon aerogels derived from biomass (carbohydrates or crude plants) are cheaper and easier to be processed. Besides, they possess an open 3D porous structure, which is beneficial to rapid ion transportation. Thus, they are viewed as the competitive materials for SCs. Similarly, carbonization is the prerequisite step to obtain biomass-derived carbon aerogels. Many kinds of biomass have been applied as the carbon source for aerogels, such as bacterial cellulose,^{86, 87} lignin cellulose,^{73, 88, 89} gelatin,⁹⁰ humic acid⁹¹, etc. An interesting example is reported by Wu et al.⁷² They used watermelon to prepare the carbon aerogel by hydrothermal carbonization, and then used the carbon aerogel as the backbone to incorporate Fe_3O_4 nanoparticles through chemical precipitation. The obtained Fe_3O_4 -carbon aerogel composite showed a specific capacitance of 333.1 F g^{-1} at a current density of 1 A g^{-1} , and retained 96 % of initial capacitance after 1000 cycles.

2.2.4.3 CNT-assembled carbon aerogels carbon aerogels

CNTs are good building blocks for 3D aerogels because of their high aspect ratio and outstanding mechanical properties. The freestanding 3D CNT aerogels can be constructed by chemical vapor deposition (CVD).^{92, 93} CVD is a direct technique to randomly or orderly grow CNTs on a metallic substrate. However, the CNT aerogel made by CVD usually can only have limited dimensions. Thus, this technique is not suitable for large-scale application.

Alternatively, pristine CNTs can be first functionalized and dispersed into a polymer matrix to form a hydrogel, where the CNTs are immobilized. Then, the hydrogel is converted to CNT-dominated aerogels by freeze-drying/supercritical drying and subsequent carbonization. Zhang et al. embedded MWCNTs and acid-treated MWCNTs in a poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT–PSS) matrix with the aid of a small amount of PVA. The hydrogels were converted to an ultralight CNT/PEDOT–PSS composite aerogel by supercritical CO₂ drying, which showed specific surface areas of 280–400 m² g⁻¹, and electrical conductivities of 1.6–6.9×10⁻² S cm⁻¹.⁹⁴ Zou et al. used poly(3-(trimethoxysilyl) propyl methacrylate) (PTMSPMA) to disperse and functionalize MWCNTs. The hydrolysis and condensation of PTMSPMA brought about the strong and permanent chemical bonding among MWCNTs. The as-prepared MWCNT aerogel showed a specific surface area of 580 m² g⁻¹, and an electrical conductivity of 3.2×10⁻² S cm⁻¹.⁹⁵ CNTs are also widely incorporated with the polymer scaffold made by the condensation polymerization of resorcinol and formaldehyde.^{96, 97} For the CNT-polymer aerogel made by this method, there is always a tradeoff between the electrical conductivity/specific surface area and the mechanical strength, which can be adjusted by changing the weight ratio of CNTs to polymers. When the aerogels are used as the electrode materials for SCs, more weight should be given in the electrical conductivity and specific surface area.

2.2.4.4 Graphene-assembled carbon hydrogels/aerogels

2D graphene is another ideal building block to construct 3D carbon aerogels because of their high specific surface area and the unique 2D structure. The most direct way to

construct freestanding 3D graphene aerogels is the template-directed CVD. Commonly, the graphene made CVD is deposited on a porous metallic substrate (such as nickel foam). The nickel foam serves not only as the porous template, but also as the catalyst. After the CVD process, the Ni foam is etched away, then a freestanding aerogel can be obtained.⁸¹ The obtained 3D graphene aerogels are good electrode materials for EDLCs. More importantly, they are also the good substrates for TMOs. For example, Dong et al. used the hydrothermal processing to deposit Co_3O_4 in situ on the 3D graphene foam made by CVD.⁹⁸ With the same idea, they grew ZnO on the graphene foam.⁹⁹ Zhou et al. also reported a similar example. They implanted Ni_3S_2 nanorod@ $\text{Ni}(\text{OH})_2$ nanosheet core-shell on the graphene foam.¹⁰⁰

However, CVD is not suitable to massively produce graphene aerogels because of its low efficiency and high cost. In comparison to the directly grown graphene, GO made from natural graphite flakes by the Hummer's method is a more practical starting material for 3D aerogels. The hydrothermal treatment is a simple method, widely applied to make self-assembled 3D graphene hydrogels from the GO aqueous suspensions.^{80, 101-103} For example, Zhang et al. applied the hydrothermal reaction to prepare a graphene-dominated hydrogel from the suspension containing sucrose and GO. After the second-step activation by KOH, the aerogel showed a high specific surface area of $3523 \text{ m}^2 \text{ g}^{-1}$ and a bulk conductivity of 303 S cm^{-1} . Benefiting from these properties, the hydrogel displayed a specific capacitance of 231 F g^{-1} and an energy density of 98 Wh kg^{-1} .⁸⁰ Similarly, Chen et al. reported a nitrogen-doped graphene hydrogel prepared by hydrothermally reacting GO with organic amine, which showed a high specific power density of 205 kW kg^{-1} .¹⁰³ The graphene hydrogels made by the hydrothermal treatment are also the good supports for TMOs. Yuan et al. applied the hydrothermal reaction to incorporate Co_3O_4 with the graphene hydrogel. During the gelation of GO, $\text{Co}(\text{CH}_3\text{COO})_2$ was converted to Co_3O_4 and anchored onto the graphene nanosheets. The composite showed a specific capacitance of 757.5 F g^{-1} at 0.5 A g^{-1} .¹⁰⁴ With the same strategy, Xu et al. integrated $\text{Ni}(\text{OH})_2$ nanoplates into the graphene hydrogel. The resulting composite showed a specific capacitance of 1352 F g^{-1} at 5 mV s^{-1} .¹⁰⁵

Self-assembled graphene hydrogels usually suffer from low mechanical strength. Thus,

some measures have been taken to strengthen the inter-sheet binding/crosslinking, such as introducing gelating agents (e.g. polyethylene oxide and polyvinyl pyrrolidone) or crosslinking agents (e.g. polyethylenimine) by form hydrogen bonds with the GO network,¹⁰⁶ or integrating GO with a polymer matrix.¹⁰⁷ The graphene hydrogels can be converted to aerogels by freeze-drying or supercritical drying. The obtain aerogels can be further reduced by thermal reduction,¹⁰⁸ and H_2 ,¹⁰⁹ in order to improve their electrical conductivity. Besides, the graphene aerogels can be further decorated with other electrode active materials to improve the overall energy storage ability, such as MWCNTs,⁷⁸ Fe_3O_4 ,¹¹⁰ TiO_2 ,¹¹¹ etc.

2.2.5 Summary

In this section, we have review the fabrication of the composites composed of multiple dimensional carbon materials and TMOs, as well as their performance as the electrodes for SCs. The structural diversity of carbon materials provides great flexibility to design the multifarious types of composites. The characteristics of each dimensional carbon materials can be summarized in this way.

0D carbon nanoparticles have high specific surface area and are easy to be dispersed in either solvents or polymer matrices. They can be the important additives or reinforcers for higher dimensional carbon materials and TMOs.

1D carbon nanotubes/nanofibers have high electrical conductivity and high aspect ratio. Thus, they can be easily used to construct a conductive network within a polymer matrix or a graphene gels to boost the overall electrical conductivity and the charge transfer during the electrochemical process.

2D graphene naonsheets have high specific surface area and the unique nanostructure. Thus, they are promising to be the hosts for thin-film and flexible composites. Besides, they are also the also the important building block for 3D hybrid-structured composites.

3D carbon materials have large pore volume and surface, and thus are able to provide enough supports for the lower dimensional carbon and TMOs. They can integrate the merits

of each component.

Despite these merits, the high cost and/or tedious processing usually hinder these multiple-dimensional carbon materials (especially CNT- and graphene-based carbon materials) from large-scale applications. As for the fabrication methods, the wet-chemistry approach stands out among rest because it is simple, low-cost, and thus easy for scaling up. However, the prerequisite for the wet-chemistry-based fabrication is to disperse the carbon materials in appropriate solvents fully. Thus, it is imperative to develop simple wet-chemistry-based methods to process these high-performance carbon materials, and/or to find some cheap substitutes, so as to bring the SC technique closer to practical use.

2.3 Questions to Answer Based on Literature

As discussed in the foregoing section, great progress has been made in fabricating carbon-TMO composites and in exploring their roles as electrode materials for SCs. Different dimensional carbon materials with multifarious properties have been widely adopted as the supports for TMOs. Despite these achievements, some questions remain to be answered.

Firstly, the wet-chemistry approach based on solutions/suspensions has been widely applied to synthesize carbon-TMO composites. A prerequisite for the wet-chemistry approach is to disperse the carbon materials completely into aqueous/organic solvents. However, pristine carbon materials are not easy to be dispersed since they have a bad interaction with these solvents. The issue is usually tackled by surface functionalization by strong acids (the chemical approach) or surfactant-mediated sonication (the physical approach). The chemical approach involves high-risk and time-consuming reactions, and causes structural defects that are detrimental to electrical conductivity. The physical approach, which takes advantage of ultrasonication and the amphipathicity of surfactants to disperse carbon, suffers from two problems. A long period of sonication may damage the structures of carbon materials, and the presence of insulating surfactants sets up barriers to electron transfer. Therefore, one question raised is whether there is an alternative way to achieve the dispersion of carbon materials in solvents, which can be carried out in a mild condition and does less harm to the carbon materials. Besides, provided a stable carbon

(especially 1D and 2D carbon) suspension can be made by the improved method, the suspension is expected to be easily deposited onto a porous substrate by different post-processing methods, such as filter-coating, spray-coating, etc. In that case, questions raised are how these carbon materials will distribute on the substrate, and whether the resulting carbon-based composites are suitable to be the electrodes for SCs.

Secondly, TMOs made from chemical precipitation tend to agglomerate severely, leading to bulky structures that go against rapid electron transfer and ion diffusion. Thus, in many reports, 1D carbon nanotubes/nanofibers and 2D graphene nanosheets have been extensively added as the inert spacers to mitigate the agglomeration of TMOs. Likewise, when used as the nanospacers, these carbon materials should be well dispersed prior to incorporation with TMO precursors. A poor dispersion of carbon materials may weaken their role as the spacers, and cause the inconsistency in the properties of composites. By contrast, so far, there are only a few studies using carbon black for this purpose. This is mainly because carbon black cannot construct an interwoven conductive network for TMOs, and it only shows inferior properties. However, compared with 1D and 2D carbon materials, 0D carbon black is cheaper and easier to be dispersed even at a high concentration.

Hence, in terms of the role of nanosized spacers, questions that can be raised are whether carbon black particles are capable of replacing the 1D and 2D carbon materials, and the extent how the higher loading ratio and better dispersion of carbon black can compensate for its shortage in the intrinsic properties and its dimensional limitation. Another question is what electrochemical performance the TMO-carbon black will achieve.

Thirdly, there have been many reports applying the carbon-involved reactions to grow the TMO in situ on the host carbon. In these self-limiting reactions, carbon materials act as not only the starting reagents, but also the substrates for the depositing products. The most common example is the in-situ deposition of MnO_2 on carbon, which is synthesized from the redox reaction between MnO_4^- ions and the host carbon. 1D, 2D and 3D carbon materials with various nanostructures have been widely applied to make the MnO_2 -carbon composites, while 0D carbon black is seldom studied for this purpose. The reason may also

lie in the mediocre properties and dimensional limitation of carbon black. However, from another perspective, these dispersive carbon black nanospheres may provide a special opportunity to synthesize well-dispersed and well-defined nanostructured composites. Thus, questions that can be raised are whether the carbon black particles can provide enough room for the deposition of the resulting MnO_2 , and what the nanostructures will be formed in the MnO_2 -carbon black composites. Besides, another question is whether the MnO_2 -carbon black composites can show better electrochemical performance than MnO_2 -1D (or 2D or 3D) carbon composites.

Lastly, regarding the carbon black, the one that has been most commonly used for electrical/electrochemical purposes is acetylene black, because of its high electrical conductivity and high purity. However, it is noteworthy that Chinese ink is actually a ready-made carbon black suspension. The low cost, ease of processing, and stability of Chinese ink make it an attractive material for research. Thus, one may wonder whether Chinese ink can be directly used as a building block for electrode composites.

2.4 Thesis in the Context of the Literature

From the viewpoint of materials, the composites with large specific capacitance, high power and energy density, and long cycle life are always desirable. However, from the viewpoint of fabrication costs, composites that can be prepared by simple and cheap methods are more likely to be accepted and put in practical use. Unfortunately, in reality, the performance of a material often conflicts with its fabrication cost. Thus, consideration should be given to the performance and the fabrication cost in order to bring the SC technique closer to reality. In this context, this thesis aims to develop a simple and cheap approach to fabricate carbon-TMO composites. To this end, the ready-made carbon black suspension provided by a commercial Chinese ink is used as the starting material. The correlation between the thesis and the literature can be summarized as below:

Firstly, wet mechanical grinding has been proven to be an effective method to disentangle MWCNTs and VGCNFs by previous reports. Besides, compared to chemical functionalization and sonication, wet mechanical grinding causes less detrimental effect on

the MWCNTs and VGCNFs. On this basis, this thesis takes advantage of commercial Chinese ink to disperse raw MWCNTs and VGCNFs into water via wet mechanical grinding. It is noteworthy that, this is the first example applying Chinese ink to facilitate the preparation of MWCNT/VGCNF suspensions. It is proved that the addition of Chinese ink improves the distribution of MWCNTs/VGCNFs on the PVA matrix and on the filter paper. The improvement is ascribed to influence of the glue (as the surfactant and stabilizer) and the carbon black particles (as the spacers and electrical conductivity reinforcers) contributed by Chinese ink. It is also demonstrated that the resulting composites composed of MWCNTs/VGCNFs and Chinese ink are ready to the electrode for SCs.

Second, the redox reaction between MnO_4^- ions and carbon offers a direct way to deposit MnO_2 onto carbon in situ. In view of this, in this thesis, Chinese ink is directly reacted with MnO_4^- ions to synthesize MnO_2 . This may be the first example using Chinese ink as a starting material for synthesizing MnO_2 . It is demonstrated that the good dispersion of carbon black facilitates the formation of well-defined nanostructures, and ensures the homogeneity of the MnO_2 -ink composites. Benefitting with the structures, the MnO_2 -ink composites show high electrochemical performance, which is comparable to that of the composites made with graphene or CNTs. These results suggest well-dispersed carbon black is a good carbon source for the in-situ growth of MnO_2 , regardless of its mediocre intrinsic properties. Moreover, the manner in which MnO_2 and carbon black are integrated may outweigh the intrinsic properties of each component to some extent.

Third, in this thesis, Chinese ink is added to the precursor solution of NiCo_2O_4 during the chemical precipitation process to provide the dispersive carbon black particles, which acts as the spacers to reduce the aggregation of the NiCo_2O_4 precursor. The intention to mitigate the agglomeration of TMOs by inserting inert spacers is in accordance with that in previous reports. However, unlike the other dimensional carbon materials, carbon black particles are too small to provide enough room for the anchoring of NiCo_2O_4 . Thus, a well-defined core-shell or an urchin-like structure that is usually formed on large-size carbon is not obtained in this thesis. Instead, the carbon black particles are found to be inserted into the NiCo_2O_4 nanosheets. The results of surface analysis and electrochemical measurement indicate that such a structure is as favorable for rapid electron transfer and ion diffusion as the other

structures. Hence, these observations suggest that 0D carbon black can be also utilized as spacers for TMOs, and the fabrication method can be extended to other TMOs.

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Chapter 3

Experimental Methodology

This chapter summarizes the experimental methodology employed in this thesis. Section 3.1 first explains the reason for the usage of the commercial Chinese ink, and then elucidates rationales behind the selection of synthesis methods, including the wet grinding to prepare MWCNT/VGCF suspensions, the stirring-driven hydrothermal reaction to synthesize MnO_2 -ink composites and the chemical co-precipitation to synthesize NiCo_2O_4 -ink composites. Section 3.2 details the synthesis procedures of the composites. Lastly, Section 3.3 lists the characterization techniques applied in this thesis. In these characterization techniques, XRD, XPS and Raman spectroscopy identify the phases present in the composite. SEM and TEM examine the appearance and morphology of the composites. BET tests provide information about the surface area and pore size distribution. Four-point-probe resistivity measurement determines the sheet resistance. TGA studies the thermal stability of the composites and decides their composition. Lastly, the electrochemical tests (including cyclic voltammetry, galvanostatic charge/discharge and electrochemical impedance spectroscopy) evaluate the electrochemical performance of the composites.

3.1 Rationales for Selection

3.1.1 Reason for the usage of Chinese ink

Commercially available Chinese ink was used throughout the thesis. The original intention of using Chinese ink was to take advantage of its ready-made carbon black suspension to open a simple and cheap approach to preparing electrode materials for supercapacitors (SCs). As discussed in Chapter 2, carbon materials play an irreplaceable role in fabricating high-performance electrodes for SCs. Various nanostructured carbon materials have been extensively used as the starting materials or the reinforcers for electrode composites. In comparison, carbon black only possesses mediocre properties and thus attracts less research attention. Nonetheless, it still has advantages over these carbon materials in its low cost and easy processing. Especially, the usage of Chinese ink can save the trouble of tedious pre-processing that is usually required in order to get a carbon suspension. In essence, Chinese ink is a kind of carbon black suspension, mainly composed of water, carbon black and glue, in which the carbon black particles are dispersed and stabilized by glue. In view of the high dispersion and stability of carbon black in Chinese ink, in this thesis, commercial Chinese ink was directly applied to fabricate composites. The basic assumption was that, when incorporated with metal oxides, these well-dispersed carbon black particles could exert effects on metal oxides similar to those by the other carbon materials.

3.1.2 Rationales for the selection of synthesis methods

In Chapter 4, the assumption is tested that Chinese ink can facilitate the dispersion of the other carbon nanomaterials in different media. The 1D carbon nanomaterials – multi-walled carbon nanotubes (MWCNTs) and vapor-grown carbon nanofibers (VGCNFs) were selected as the starting materials, because raw MWCNTs and VGCNFs usually suffer from severe entanglement and poor dispersion in solvents. As for the preparation method, wet manual or mechanical grinding (milling) was applied to ensure a full contact between MWCNTs/VGCNFs and Chinese ink. Wet grinding has been proved to be effective in dispersing MWCNTs by some previous reports.^{1, 2} In comparison to sonication and

chemical functionalization that are commonly applied to pretreat raw CNTs, wet grinding is simple, safe and low-cost, and causes less detrimental effects on CNTs.

The obtained MWCNT-ink and VGCNF-ink aqueous suspensions were stable enough for different post-treatments. First, the suspensions were incorporated with PVA and then wet-cast onto flat substrates to form freestanding sheets, aiming to investigate the distribution of MWCNTs/VGCNFs surrounded by carbon black particles within the polymer matrix. Second, the suspensions were directly coated onto filter paper by filter coating, aiming to examine the distribution of MWCNTs/VGCNFs surrounded by carbon black particles in a porous substrate. Third, the obtained composites were applied as the electrodes to fabricate all-solid-state EDLCs, aiming to evaluate their electrochemical performance.

In Chapter 5, the hypothesis is tested that the carbon black in Chinese ink can be directly used as a starting material to produce metal oxides from carbon-involved reactions. Thus, birnessite-type MnO_2 was selected as the target subject as it could be synthesized from the redox reaction between MnO_4^- ions and carbon.³ The synthesis was conducted in a hydrothermal reactor heated by an oil bath, where magnetic stirring was applied to ensure the homogeneity of the reacting mixture. The carbon black from Chinese ink acted as the reducing agent and provided the anchoring sites for resulting MnO_2 . It was assumed that, after the Chinese ink mixed with KMnO_4 , the outer surface of carbon black particles would react with MnO_4^- ions. The resulting MnO_2 would in-situ grow on the carbon black particles and cease the redox reaction. Thus, a nanostructure was expected to be obtained, in which the carbon black particles were wrapped by MnO_2 . Finally, the intrinsic electrochemical behavior of the MnO_2 -ink composites was tested in three-electrode cells. Besides, their performance in practical use was tested in asymmetric SCs configured with the composites as the positive electrode and activated carbon as the negative electrode.

In Chapter 6, the hypothesis is examined that Chinese ink provides well-dispersed carbon black particles as the inert nanopacers for transition metal oxides to enlarge their specific surface area. To this end, the binary metal oxide NiCo_2O_4 was selected as the target subject, which can be easily synthesized from low-temperature chemical co-precipitation and subsequent calcination.^{4, 5} It was supposed carbon black particles did not involve in the

reaction during the chemical co-precipitation process, but only functioned as spacers to prevent the stacking of precipitates. However, in the subsequent calcination process, these carbon black could be oxidized into CO/CO₂ at a high temperature. Thus, the calcination temperature was carefully controlled so as to preserve these carbon black particles. Finally, the electrochemical performance of the NiCo₂O₄-ink composites was measured in three-electrode cells.

3.2 Sample Preparation

The detailed sample preparation methods are described in the second section of each Chapter.

3.3 Characterization Techniques

Different characterization techniques were utilized to probe into the properties of the prepared composites, including the morphology, the composition, the crystal structures, the surface area and pore structures, the electrical conductivity, and the electrochemical behavior, etc. Each characterization technique has its specialized functions and limitations, so it is of great importance to combine different characterization techniques in order to obtain comprehensive and accurate information about the samples. In the following section, present the selection of applied techniques and brief their working principles will be presented.

3.3.1 Powder X-ray diffraction (XRD)

XRD is a tool used for identifying the crystallographic nature of materials; it can be used to analyze a wide range of materials from powder samples and thin films to nanomaterials and bulk solid matters. Powder XRD technique analyzes powdery materials consisting of fine grains of single crystalline materials, as well as polycrystalline solids like thin film or bulk matters. The term “powder” here refers to that crystals in tested samples have random orientation.

XRD is based on the constructive interference between the crystalline samples and the incident monochromatic X-rays. X-rays are applied to generate diffraction patterns because their wavelengths are in the same order of magnitude (0.1 to 10 nm) as the interplanar spacing in crystals. Crystals are regular arrays of atoms while the X-rays can be viewed as waves of electromagnetic radiation. In principle, any waves can produce diffraction when impinging on a regular array of scattering points. Therefore, the incident X-ray beam can diffract into some specific directions when interacting with the crystalline atoms. The diffraction orients from the elastic scattering of X-ray photons when they collide with electrons in atoms.

Figure 3.1 X-ray diffraction on crystal lattices.

The interaction of the incident X-ray beam with the atomic planes of samples will produce constructive interference when Bragg's Law is satisfied.

$$2d \sin \theta = n\lambda \quad (3.1)$$

Here, d is the inter-plane spacing between lattice planes ("d-spacing"), θ is the angle between the incident X-ray beam and the lattice plane, n is any integer representing the order of diffraction peak, and λ is the wavelength of the incident X-ray. According to the law, the interplanar spacing d can be determined provided that the wavelength of X-ray and the diffraction angle is known. It should be pointed out that, this law could be also applied to polymers and colloids as they include molecules or collections of molecules with a periodic distribution of electron density that can act as a scattering point.

In practice, an X-ray diffractometer is used to detect X-ray diffraction and record the diffraction intensity over a range of diffraction angle. A diffractometer is mainly comprised of five basic parts: an X-ray tube, the primary optics, a sample holder, the secondary optics and a detector. The X-ray tube generates continuous X-rays with a range of wavelengths, which are further filtered by a monochromator to produce a single wavelength (monochromatic) X-ray radiation needed for diffraction. The X-rays are converged and directed onto samples. As the test begins, the sample stage and/or the detector rotate. The X-ray signals are recorded and converted by the detector into count rates. When the Bragg's Law is satisfied, constructive interference occurs and an intensity peak appears. Consequently, at the end of a test, an XRD diffractogram recording the diffraction intensity with diffraction angle (2θ) is obtained.

The characteristic diffraction patterns obtained from an XRD analysis reveal the unique “fingerprints” of crystalline presented in the tested samples. The diffractogram can be basically interpreted in the following ways.⁶ (1) The diffraction peaks indicate the presence of crystalline structures. The angular position and the intensity of peaks are the key parameters used to identify the present phases. The crystal phase identification is done by comparing against a database of powder diffraction files. (2) The peak positions are also used to determine and refine unit cell parameters. (3) The angular width of diffraction peaks can be used for peak analysis, by which the information about the crystalline size (by the Scherrer formula), microstrain and crystal defect can be extracted. (4) The peak areas can be used for quantitative analysis and determine a preferential orientation for a specific matter. (5) The presence of a broad diffraction pattern indicates the presence of amorphous materials.

In this thesis, X-ray powder diffraction analysis was carried out on a Shimadzu 6000 X-ray diffractometer with Cu K α radiation operated at 40 kV and 30 mA ($\lambda = 1.54178 \text{ \AA}$). The XRD analysis was done to study the crystalline quality of composites, to identify crystalline phases present, to estimate crystalline size, and to determine interplanar spacing. It should be pointed out that, the presence of a high weight percentage of amorphous carbon black (coming from the used Chinese ink) broadens the diffraction patterns and even masks some diffraction peaks to some extent. In addition, since the as-prepared materials usually

had a nanoscale particle size, the short range of ordered atom arrays also weakens the diffraction peaks. Thus, in this case, it is difficult to get a diffractogram with sharp peaks and low noise.

3.3.2 Scanning electron microscopy (SEM)

SEM is a tool for observing otherwise invisible microscale and nanoscale worlds. By using a converged beam of high-energy electrons as the probe, the SEM can visualize the topographic details of solid specimens with high resolution and great depth of field, which are inaccessible to optical microscopy. SEM is also applied to obtain elemental maps and to discriminate different phases in multiphase specimens.⁷⁻⁹

Figure 3.2 Schematic representation of the interaction between the high-energy electrons (the primary electron beam) with the specimen.¹⁰

As schematized in Figure 3.1, when a focused beam of highly energetic electrons strikes the specimen surface, the carried energy is dissipated into various signals, such as secondary electrons, backscattered electrons, Auger electrons, cathodoluminescence,

characteristic X-rays and continuum X-rays. The electron-specimen interaction occurs within a certain depth (nm to several μm) under the surface, and the interaction zone is unusually depicted as a pear shape. As such, SEM analysis is considered as non-destructive since it does not cause much volume loss for specimens.

Secondary electrons (SE, arising from inelastic scattering) and backscattered electrons (BSE, arising from elastic scattering) are mainly applied as the signals for imaging specimens. Secondary electrons are used to show the morphology/topography of samples. When a SEM is operated in the SE mode, the variation in geometric features on the sample surface can generate topographic contrast, from which the microstructure of the sample can be seen. Alternatively, backscattered electrons are used to obtain the compositional maps of multiphase samples and to quickly distinguish different phases. When a SEM is operated in the BSE mode, the variation in chemical composition (based on different atomic numbers) can produce compositional contrast.

The key operation parameters of a SEM include the working distance, aperture size, acceleration voltage and probe current. The working distance and the aperture size are adjusted to obtain the appropriate depth of field, while the acceleration voltage and the probe current are adjusted to achieve high resolution. It should be pointed out that there is a tradeoff between resolution and depth of field. For example, a small aperture size and a long working distance are favorable for a high depth of field. However, the small aperture size reduces the probe current and decrease the signal to noise ratio, and the long working distance intensifies the spherical aberration, both of which will worsen the resolution.

In addition to imaging morphology and phase composition, SEM is can be used for microanalysis when incorporated with an Energy-Dispersive X-Ray Spectroscopy (EDS) system. After the primary electron beam interacts with the sample, the generated characteristic X-rays are separated and processed by an EDS detector (typically a lithium-drift silicon). EDS is applied to identify the chemical composition of specimens and generate element composition maps over a certain raster area.

In this work, SEM was used mainly to study the morphology of the prepared samples, to estimate the particle size of nanoparticles (or the diameter of nanorods), and to roughly determine the composition of composites. Two different field emission scanning electron microscopes (JEOL JSM-6340F and JEOL JSM-7600F) were used for SEM analysis, which are equipped with a cold cathode field emission gun (FEG) and a thermal FEG as the electron source, respectively. It is worth mentioning that, due to the low electrical conductivity of the metal oxides, surface charging becomes an inevitable problem as it will cause distortion and produce artifacts in SEM images. To solve the problem, the samples were coated with a thin layer of Au (or Pt) prior to analysis.

3.3.3 Transmission electron microscopy (TEM)

Table 3.1 A comparison between an optical microscope and a transmission electron microscope.⁷

	Optical microscope	TEM
Sample	Polished surface and thin section	Thin section (< 200 nm)
Resolution	~ 0.2 μm	~ 0.2 nm
Magnification	2 to 2000 $\times$	500 to 1000000 $\times$
Illumination source	Visible light	High-energy electrons
Lens	Glass	Electromagnetic lens
Operation environment	Air or liquid	High vacuum
Image formation for view	By eyes	On fluorescent screens or photographic films

In a TEM analysis, a focused beam of high-energy electrons is transmitted through a very thin sample; the interaction between the energetic electrons and the atoms in the samples can be used to reveal the details about micro-structure. A transmission electron microscope works on many principles as an optical microscope. It has this main component along its optical path: a light source, condenser lenses, sample stage, objective lens and projector lens; but unlike a light microscope, a high-energy electron beam is used as the illumination source, and electromagnetic lenses are used to converge the electron beam. Besides, the electrons can be easily deflected by gas molecules, so the transmission electron microscope has to be operated in a high vacuum environment. Table 3.1 compares the differences between an optical microscope and a transmission electron microscope. Since the

wavelength of high-speed electrons is much smaller than that of visible light, the optimal resolution of a TEM image can be many orders of magnitude better than that of an optical microscopy. Thus, TEMs can disclose the fine structure details even at the atomic level. A TEM analysis can be operated in either image mode or selected area electron diffraction (SAED) mode.

Image mode. An observable image must show adequate contrast. The contrast in TEM depends on the deflection of electrons from their primary transmission direction; it is caused by the difference in the number of electrons scattered away from the primary. The images created by electron scattering are based on mass-density contrast and diffraction contrast. Mass-density contrast can be found in all types of materials; it is the primary mechanism on which the images are formed for non-crystalline materials. The difference in thickness and density in a sample will cause the variation in electron intensity received by an image screen that leads to the contrast. Diffraction contrast is the main mechanism for TEM image formation for crystalline specimens. Similar to x-rays, when the Bragg conditions are satisfied, electrons can generate constructive diffraction that results in strong electron deflection in samples. Thus, the diffraction contrast is very sensitive to the angle to which the sample tilts. The diffraction contrast can produce bright-field and dark-field images. When only the transmitted beam is allowed to pass the objective aperture, a bright-field image is generated; otherwise, if the diffraction beam is allowed to pass the objective aperture, a dark-field image is obtained. In addition to mass-density contrast and diffraction contrast, contrast can be generated by the phase difference in electron waves. The phase contrast is often named as high-resolution transmission electron microscopy (HRTEM). HRTEM is very useful for analyzing crystalline defects and interfaces and observing different phases.

SAED mode. When an electron beam transmits through a crystalline sample, a diffraction pattern is generated in the back-focal plane of the objective lens, which can be magnified on the screen or record by a camera. Similar to X-ray diffraction, SAED can be used to identify the crystallinity, study the crystal structures and measure the lattice parameters.

In this work, TEM was applied mainly to examine the morphology of prepared composite, to distinguish the synthesized materials from the substrates, and to identify the phases present in the composites. TEM analysis was performed with JEOL 2010 UHR transmission electron microscope, which is equipped with a thermionic emission gun (lanthanum hexaboride, LaB6) and operated at 200 kV.

3.3.4 X-ray photoelectron spectroscopy (XPS)

Figure 3.3 Schematics of (a) the photoemission process and (b) an X-ray photoelectron spectrometer.^{11, 12}

XPS is a surface-sensitive spectroscopic technique that analyses the surface chemistry of a material. It can measure the elemental composition in the ppt range, and determine the chemical and electronic states of the elements present in the outer surface layer of a material. XPS is a large-area analysis with a probing depth of several nanometers. Figure 3.3a illustrates the photoemission process. In detail, when the x-ray photons (with the energy of $h\nu$) irradiate the tested sample, they will be absorbed by the atoms, resulting in the ionization and the emission of the inner-shell electrons or valence electrons. The ejected electrons are called photoelectrons. By measuring the kinetic energy of the emitted photoelectrons, the binding energy of electrons can be thus determined based on the conservation of energy equation as shown below:

$$E_b = h\nu - E_{kin} \quad (3.1)$$

where, $h\nu$ is the energy of the X-ray photons, E_b is the electron binding energy, and E_{kin} is the kinetic energy of the ejected photoelectron measured by the spectrometer. In practice, the binding energy is measured with respect to the Fermi-level, rather than the vacuum level. As a result, the above equation should be corrected as:

$$E_b = h\nu - E_{kin} - W_f \quad (3.2)$$

where, W_f is the working function that is dependent on the spectrometer and the tested sample. It accounts for a few eV of kinetic energy absorbed by the instrument detector, but usually, it can be treated as a constant.

The binding energy relies on many factors, including the chemical element, the level where photoemission occurs, and the oxidation state and the local physical/chemical environment of the atoms. Every element has its characteristic binding energy related to each core atomic orbital. In other words, every element has a set of characteristic peaks in the photoelectron spectrum. Thus, in XPS, element identification can be done by indexing the peaks at particular binding energies, and the composition determination can be done by measuring the intensities of the peaks. In addition, XPS can provide information about the chemical states.

In this thesis, XPS was applied mainly for element identification and chemical state analysis. A broad survey scan was performed to identify the present elements and their relative content by indexing their characteristic peak. Meanwhile, a high-resolution scan was performed to reveal the chemical states of the target elements. The XPS was recorded on a Thermo Scientific ESCALab 250Xi, which is equipped with a monochromatic Al K α (1486.7 eV) x-ray source. All spectra were calibrated by using C 1s peak (284.5 eV) as the reference. The peak fitting was done on the software XPSPEAK41.

3.3.5 Raman spectroscopy (RS)

RS is an important spectroscopic technique used for studying the information about the vibrational and rotational motion of molecules, based on which structure identification and sample quantitation can be achieved. RS depends on the inelastic Raman scattering of

incident radiation by its interaction with vibrating molecules. When a monochromatic radiation impinges on the molecules of the sample, it generates three types of scattering (as seen in Figure 3.4): Rayleigh scattering, Stokes scattering and anti-Stokes scattering. Rayleigh scattering is elastic in which no energy exchange occurs. It makes up the majority of the scattered light. Stokes scattering and anti-Stokes, collectively called Raman scattering, are inelastic and result in energy shift (or called Raman effect). Stokes scattering occurs when the molecules absorb energy from the incident light, whereas anti-Stokes happens when the molecules reemit energy to the incident light. As a result, the Stokes scattering causes a red shift, while the anti-Stokes scattering causes a blue shift.

Figure 3.4 Schematic presenting light scattering after a laser radiates onto a sample surface.¹³

In essence, the Raman effect is due to the molecular deformations in electric field E , and determined by the molecular polarizability α . The electric dipole moment P can be thus defined as $P = \alpha E$, which deforms molecules. When the laser, the oscillating electromagnetic wave with a frequency ν_0 , radiates on the sample, it periodically deforms the molecules and transforms them into oscillating dipoles with a characteristic frequency ν_m . Such oscillating dipoles will reemit light of three different frequency (ν):

$\nu = \nu_0$ (non-Raman-active, Rayleigh scattering.)

$\nu = \nu_0 - \nu_m$, Stokes frequency.

$\nu = \nu_0 + \nu_m$, anti-Stokes frequency.

Therefore, the incident laser can generate Raman signals with a frequency of $\nu_0 \pm \nu_m$. However, compared to Rayleigh scattering, Raman scattering is a small probability event; roughly 1 in every 30 million photons is Raman scattered. In order to increase the photon density, a laser with a frequency in the range of visible light is used as the light source. The scattered light is further filtered to remove the Rayleigh scattering before collected by the detector.

In practice, by plotting the intensity of the “shifted” light against the frequency, a Raman spectrum can be obtained, from which the information about the vibrational, rotational and other low-frequency modes in molecules can be extracted. In a Raman spectrum, the Raman bands (or call peaks) is attributed to an oscillating induced dipole, caused by the interaction between the laser and the polarized ellipsoid of a vibrating molecule. Hence, symmetric stretches and vibration involving heavier atoms or multiple bonds can produce the strong band, while asymmetric molecules will show some bands at the same frequency as IR but with different intensities. By indexing the bands to the standard database, one can identify the composition of samples.

In this thesis, RS was used mainly to confirm the presence of the target metal oxides. This was achieved by studying the molecular vibrations that reveals the local crystal structure. The M=O and M-O vibrations can be readily detected by RS below 1000 cm^{-1} . Besides, RS was also applied to monitor the change in the content of carbon, which was done by observing the change in the relative intensity of D band and G band—the characteristic bands of carbon black. The Raman spectra were recorded on Renishaw InVia Raman Microscope, equipped with Argon ion laser source (514 nm).

3.3.6 Analysis on surface area and pore size

In this thesis, the specific surface area (expressed in the unit of $\text{m}^2 \cdot \text{g}^{-1}$) of the samples was determined by nitrogen multilayered adsorption at 77 K over a wide range of relative

pressures, on the basis of the Brunauer–Emmett–Teller (BET) theory. An automatic analyzer was used to record the amount of adsorbed gas against the relative pressure, i.e., the adsorption/desorption isotherm. The isotherm can be classified into six types (as seen in Figure 3.5). Normally, Type II, IV and VI of isotherm can be decided by the BET method. The powder sample with pores in the range of 1.5 to 100 nm usually has a capillary condensation occurring in these mesopores, and thus displays an adsorption hysteresis loop in the isotherm, corresponding to the Type IV or Type V isotherm.

Figure 3.5 Different types of adsorption isotherms classified by the IUPAC.¹⁴

The porosity, pore sizes and pore size distribution were measured by the Barrett-Joyner-Halenda (BJH) method. The pores are classified into three types according to their sizes: micropores (< 2 nm), mesopores (2–50 nm) and macropores (> 50 nm). The BJH method is accurate in determine. The BJH theory assumes all pores in the isotherm are rigid and of regular shapes; it is suitable for determining mesopores and macropores. Typically, in a BJH pore size distribution plot, the dV/dr pore volume ($\text{cm}^3 \cdot \text{g}^{-1} \cdot \text{nm}^{-1}$) is plotted against the pore diameter (nm).

In this thesis, the BET specific surface area and the BJH pore size distribution were measured with TriStar II 3020 surface area analyzer from Micromeritics.

3.3.7 Analysis on sheet resistance

Figure 3.6 Configuration of four-point-probe sheet resistance tester.

The sheet resistance of the composite sheets was measured by the four-point-probe method. Figure 3.5 shows the configuration of the four-point-probe sheet resistance tester. In the tester, the outer two probes are used to supply the sourcing current, while the inner two probes are used to measure the voltage across the sample surface. The sheet resistance $\rho_{\square}$ ($\Omega \square^{-1}$) is calculated by the equation.:

$$\rho_{\square} = \frac{\pi}{\ln(2)} \frac{V}{I} \quad (3.3)$$

The volume resistivity (or called bulk resistivity) ρ ($\Omega \text{ cm}$) is calculated by

$$\rho = \rho_{\square} \cdot t \quad (3.4)$$

where t is the thickness of the composite. The reciprocal of the volume resistivity is the electrical conductivity ε ($\text{S} \cdot \text{cm}^{-1}$) of the composite.

3.3.8 Thermogravimetric analysis (TGA)

TGA is a branch of thermal analysis which measures the change in weight (gain or loss) as a function of temperature or time when the sample is subjected to a controlled temperature program under a certain atmosphere. Some physical phenomena (such as vaporization, sublimation, physical absorption/desorption) and some chemical phenomena (such as

pyrolysis, dehydration, oxidation/reduction, chemical adsorption/desorption) can undergo drastic weight change with increasing temperature. The results are shown in TG curves, in which normally the mass change in percentage is plotted on the y-axis and the temperature or time is plotted on the x-axis. Besides TG curves, the first derivative TG (DTG) curves which are plotted curve with the rate of mass loss versus temperature, are also widely used to determine certain features in depth. TGA can be used to study the degradation mechanism and reaction kinetics, to determine the content of certain organic/inorganic matters in composites, and to characterize materials by analyzing the decomposition profiles.¹⁵

Basically, TGA can be divided into two type: dynamic TGA, in which the sample is heated at a constant ramping rate, and isothermal or static TGA, in which the sample is kept at a constant temperature and the weight change against time is recorded. The recording of the change in weight is influenced by (1) sample properties (such as the loading mass, volume, structure); (2) the nature and the flow rate of the atmosphere; (3) the temperature scanning rate and (4) the nature of the sample holder.

In this work, the prepared composites were mainly composed of metal oxides and the carbon black from Chinese ink. TGA was applied mainly to determine the content of the transition metal oxides. The basic assumption is that, in these thermal events, the metal oxides do not experience remarkable weight change, whereas the adsorbed water evaporates, the volatile matters from Chinese ink decomposes and the carbon is oxidized into CO₂/CO. TGA was performed on TA Instruments Q500. To estimate the content of metal oxides, the composites were heated at 20 °C·min⁻¹ to 600 °C (or 800 °C) under the air atmosphere. The residual ratio at the final temperature can be regarded as the content of the metal oxides. In addition, TGA was applied to help explain the change in composition by comparing the TG/DTG profiles of the composites calcinated at different temperatures.

3.3.9 Electrochemical measurement

The electrochemical performance of the prepared composites was evaluated in two-electrode cells (solid-state) or in three-electrode cells (liquid state). The three-electrode-cell test is aimed to investigate the intrinsic electrochemical behavior of the sample, while the two--electrode-cell test is aimed to inspect the performance of the sample in practical use. Different Electrochemical measurement techniques were applied for these purposes, including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS).

CV is one kind of potentiodynamic electrochemical measurement. In a CV measurement, a constant rate of scanning is applied, so the potential is ramped linearly versus time within a potential window. The scanning can be repeated for as many times as needed. CV curves that record the response current of the working electrode against the applied voltage are plotted during the measurement. CV can be used to study the redox processes occurring in the working electrode and the reversibility of the redox reactions. An ideal EDLC is expected to show a rectangle CV curve, but a practical EDLCs usually shows a distorted quasi-rectangle shaped CV curve due to electrode polarization. Pseudocapacitors usually display several pairs of peaks in the CV curve, indicating the presence of redox reactions.

GCD is fulfilled by applying a constant current on the working electrode to ramp the potential practical to the upper potential limit and then negatively to the lower potential limit. For SCs, GCD is usually applied to measure the specific capacitance and to assess the rate capability at different current densities. It is also applied to study the cycling life of the SC.

EIS is a perturbative characterization of the dynamics of an electrochemical process. It measures the impedance of a system over a range of frequencies, and reveals the information about an electrochemical process, such as charge transferring, ion diffusion, capacitive behavior, etc. EIS is fulfilled by applying a small sinusoidal potential or current perturbation on the system over a range of frequency, measuring the response and computing the impedance at each frequency. The obtained results are usually depicted in a

Bode plot or a Nyquist plot. The EIS data can be further interpreted into equivalent circuits, from which the details about the electrochemical process can be extracted.

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Chapter 4

Chinese Ink-facilitated Fabrication of MWCNT- and VGCNF-Based Composites for Supercapacitors

This chapter tests the hypothesis that commercial Chinese ink can facilitate the dispersion of pristine multi-walled carbon nanotubes (MWCNTs) and vapor-grown carbon nanofibers (VGCNFs) and explores the electrochemical behavior of the resulting composites. To this end, Chinese ink was first mixed with MWCNTs (or VGCNFs) in water through manual milling or ball milling. Then the obtained suspensions were wet-cast on flat substrates to form freestanding composite sheets, or filter-coated on the filter paper to form conductive paper-based composites. The morphology and electrical conductivity of the freestanding composite sheets and paper-based composites were examined. Based on the observations, the role of Chinese ink in the dispersion of MWCNTs (or VGCNFs) and their distribution within the polymer matrix or paper was illustrated. Lastly, the electrochemical performance of the prepared carbon-based composites was evaluated. Through the work done in this chapter, the conclusions that can be drawn are: (1) Chinese ink facilitates the dispersion of raw MWCNTs and VGCNFs in water under the action of wet grinding; (2) Chinese ink also improves their distribution in a polymer matrix or a porous substrate; and (3) the resulting carbon-dominated composites are ready to be electrodes for supercapacitors.

4.1 Introduction

Chinese ink is rarely applied as a material for scientific research, though it has a long history of being a black pigment for calligraphy and drawing. Technically speaking, Chinese ink is one kind of colloidal suspension (i.e., sol), with water as the continuous phase and glue-coated carbon black particles as the dispersed phase. Chinese ink can be regarded as a ready-made suspension of carbon nanomaterials owing to the contained carbon black. The homogeneity of Chinese ink inspires me to apply it as a starting material for research.

By contrast, carbon nanotubes (CNTs) have aroused great interest among researchers in various research fields since their discovery by Iijima in 1991.¹ CNTs are considered as promising electrode materials for high-performance supercapacitors (SCs) because of super electrical conductivity,² high mesoporosity, high electrolyte accessibility and good electrochemical stability.³ They can be directly used as the electrodes for SCs (usually the electrical-double layer capacitors, EDLCs),⁴ or as the conductive supports/additives for other electrochemically active materials.^{5, 6} Vapor-grown carbon nanofibers (VGCNFs) is another type of one-dimension carbon nanomaterials. VGCNFs shows some similarities with CNTs, such as the high aspect ratio, high electrical conductivity and good electrochemical stability. However, compared with CNTs, VGCNFs have more microstructure defects, larger fiber sizes and lower bulk density.⁷ Wet chemistry on the basis of CNT/VGCNF suspensions is a simple and efficient approach to preparing electrode materials for SCs. Nevertheless, both pristine CNTs and VGCNFs suffer from low dispersity due to their high aspect ratio and poor interfacial interaction with aqueous or organic solvents, which drastically reduces their performance. To tackle this problem, these pristine CNTs and VGCNFs are commonly subjected to surface functionalization by strong acids or surfactants in prior to use.⁸⁻¹⁰ Nonetheless, these pre-treatments have one or more shortcomings like tedious processes, high cost, high risk and low efficiency. Thus, it is always desirable to find alternative methods to develop high performance electrode materials.

In view of the good stability of carbon black particles in Chinese ink, it was assumed that Chinese ink could be used to facilitate the dispersion of multiwalled CNTs (MWCNTs) and VGCNFs by taking advantage of its colloidal suspension system as well as the dispersive carbon black particles. To test this idea, the commercial Chinese ink was first mixed with raw MWCNTs (or VGCNFs) through manual milling or ball milling. The resulting suspensions were post-processed in two different ways, i.e., wet-casting on flat substrates to form freestanding composite sheets and filter-coating on paper to form conductive paper. The morphology and the electrical conductivity of the composites were investigated. Based on the observations, the mechanism is proposed, by which Chinese ink facilitates the dispersion of MWCNTs/VGCNFs and improves their distribution in a polymer matrix or a porous substrate. These results confirm that Chinese ink is effective in improving the dispersion of raw MWCNTs/VGCNFs in suspensions. This work may open up a new path for the large-scale application of MWCNTs/VGCNFs.

Besides, considering the good electrical conductivity and the even distribution of MWCNTs/VGCNFs, the freestanding sheets and the composite paper were applied as the electrodes for symmetric EDLCs. These EDLCs show decent electrochemical performance. The VGCNF-ink/paper composites were also used as the substrate for the electrodeposition of MnO_2 . Benefiting from the porous structure of filter paper and the good electrochemical properties of VGCNFs, the electrodeposition of MnO_2 was achieved efficiently on the paper-based substrate. The resulting MnO_2 /VGCNF-ink/paper electrode display good electrochemical performance. These tentative results of electrochemical measurement show promise in using these carbon-based composites as building blocks for electrodes of SCs.

4.2 Materials and Experimental Methods

4.2.1 Materials

MWCNTs

The MWCNTs used in this report were supplied by CheapTubes.com (USA), which were synthesized by catalytic chemical vapor deposition and purified by acid treatment. Their specifications are listed in Table 4.1.

VGCNFs

The used VGCNFs were Pyrograf-III carbon nanofibers (PR-24-XT-HHT), purchased from Pyrograf Products, Inc (USA). The specifications of the VGCNFs are listed in Table 4.1. According to the manufacturer, these VGCNFs, produced by a vapor-grown carbon fiber (VGCF) process, have a minimal chemically vapor deposited (CVD) layer of carbon on the surface of the fiber over a graphitic tubular core. A subsequent heat-treatment at 3000 °C was applied to convert the fibers to fully graphitized forms and make them highly conductive; moreover, it also reduced the iron content to a very low level.

Table 4.1 Specifications of the used MWCNTs and VGCNFs.

MWCNT¹¹		VGCNF¹²	
Item	value	Item	value
Outer Diameter	30–50 nm	Fiber diameter	100 nm
Inner Diameter	5–10 nm	Fiber length	50–200 μm
Length	10–20 μm	Specific surface area	41 $\text{m}^2\cdot\text{g}^{-1}$
Ash	< 1.5 wt%	Dispersive surface energy	135 $\text{mJ}\cdot\text{m}^{-2}$
Purity	> 95 wt%	Moisture	< 5 wt%
Bulk density	0.28 $\text{g}\cdot\text{cm}^{-3}$	Iron	< 100 ppm
True density	$\sim 2.1 \text{ g}\cdot\text{cm}^{-3}$	PAH*	< 1 mg PAH $\cdot\text{g}^{-1}$
Specific Surface Area	60 $\text{m}^2\cdot\text{g}^{-1}$	CVD carbon overcoat	No
Electrical Conductivity	> 100 $\text{S}\cdot\text{cm}^{-1}$	present on fiber	

* PAH refers to polycyclic aromatic hydrocarbon.

Chinese ink

The used Chinese ink was Kaimei SU3005, supplied by Kaimei & Co., Ltd (Japan). This kind of Chinese ink uses commercial carbon black particles as the carbon source, and synthetic resin as the surfactant/dispersant. The Chinese ink was used without any pretreatment since it was very homogeneous and stable.

4.2.2 Material preparation

4.2.2.1 Preparation of freestanding ternary composite sheets

Freestanding MWCNT-ink/PVA and VGCNF-ink/PVA composite sheets were prepared in two steps including suspension preparation and wet casting. In a typical procedure, 2.0 g of Chinese ink and up to 0.1 g of MWCNTs (or up to 0.1 g of VGCNFs) were first mixed through by pestle milling in an agate. Then, up to 5.0 g of PVA aqueous solution (2.5 wt%) were added. The mixture was kept milling until no lump was seen. The resulting smooth and viscous suspension was cast on a plastic petri dish and allowed for air-drying at room temperature. The time needed for air-drying varied from 24 to 72 h, depending on the volume of the suspensions. When dry, the freestanding composite sheet was peeled off from the petri dish and ready for subsequent characterization and applications.

4.2.2.2 Preparation paper-based composite sheets

MWCNT-ink/paper and VGCNF-ink/paper were prepared in two steps: including suspension preparation and filter deposition. The MWCNT-ink and VGCNF-ink suspensions were made through horizontal ball milling. In a typical procedure, Chinese ink and VGCNFs (or MWCNTs) were first mixed in a plastic bottle and subjected to horizontal ball milling at a speed of 250 rpm for different periods. Deionized water was added at twice to dilute the suspension, in order to make it suitable for filtering. After ball milling, the diluted VGCNF-ink (or MWCNT-ink) suspension was transferred onto a piece of filter paper through vacuum filtration. After filtration, the VGCNF-ink/paper (or MWCNT-ink/paper) was taken out from the Buchner funnel, dried in an oven at 60 °C for 12 h. The dried paper-based composite was thus ready for characterization and applications.

The addition amount of Chinese ink, VGCNFs and MWCNTs were calculated based on the area of the filter paper. For example, for the used round filter paper with an area of 36.30 cm², 91 mg of VGCNFs were added in order to obtain a calculated loading density of 2.5 mg cm⁻². For simplicity, the loading density of VGCNFs was treated as 2.5 mg cm⁻², without regard to the portions that penetrated the filter paper.

4.2.2.3 Electrodeposition of MnO₂ on VGCNF-ink/paper composites and the electrochemical measurement

The VGCNF-ink/paper with 2.0 mg cm⁻² of VGCNFs and 50 mg cm⁻² of Chinese ink was used as the substrate for the Electrodeposition of MnO₂. The VGCNF-ink/paper was cut into a rectangle shape with dimensions of 1.0 × 1.4 cm², on which 1.0 cm² was used as the working area, while the rest part was used as the current collector.

The electrodeposition was carried out in a three-electrode cell, equipped with a platinum counter electrode and an Ag/AgCl reference electrode. The electrolyte was an aqueous solution of 0.1 mol L⁻¹ Mn(OAc)₂ and 0.1 mol L⁻¹ Na₂SO₄. The MnO₂ was deposited onto the VGCNF-ink/paper by galvanostatic electrodeposition (GED) and potentiostatic electrodeposition (PED). For GED, 5.0 mA of current was applied on the working electrode, while for PED, 1.0 V (vs. Ag/AgCl) of potential was applied on the working electrode. After electrodeposition, the surface of the VGCNF-ink/paper turned from black to brownish. The MnO₂/VGCNF-ink/paper was taken out from the electrolyte bath, rinsed with deionized water and dried in an oven at 60 °C. The mass of electrodeposited was determined by comparing the mass of the paper before and after electrodeposition.

4.2.2 Material Characterization

Morphology and microstructures. The morphology and microstructures of the composites were examined by FESEM (JEOL, JSM-7600F and -6340F, operated at 5 kV).

Crystallographic structures. The crystallographic structures of the composites were characterized by XRD (Shimazu, XRD-6000) operated at 40 kV and 30 mA, and equipped with Cu Kα radiation ($\lambda = 0.15406$ nm).

Thermal properties and component content. The thermal properties of Chinese ink and the component content of the prepared composites were investigated by TGA (TA Instruments, Model Q500). The samples were loaded on a platinum pan, heated from room temperature to 600 °C at a ramping rate of 10 °C·min⁻¹ under the nitrogen/air atmosphere.

Electrical conductivity. The electrical conductivity of the prepared composite sheets was characterized by the four-probe method, which was performed on an automatic-mapping four-point-probe system (Materials Development Corporation, Model CMT-SR2000N) at room temperature. The tested samples were placed onto a glass slide as the probes may penetrate the sheets and give false results. For each sample, nine even-distributed points were tested to get an average value.

Mechanical properties. A computer-controlled tension tester (Instron, Model 5567) was used to measure the mechanical properties of the prepared composite sheets, including Young's modulus, tensile strength and elongation at break. Before tested, all the samples were cut by a standard dumbbell-shape cutter with dimensions in line with ASTM D638-Type V. A lab micrometer (Mitutoyo) was used to measure the thickness of the samples in triplicate. The test method for these thin sheets-which usually had a thickness of around 0.1 to 0.5 mm-followed the standards in ASTM D882 (as shown in Table 4.2). The initial distance between grips was set at 25.4 mm. An initial strain rate of 10.0 mm (mm·min)⁻¹ was applied since the elongation at break of both pure PVA and PVA-contained composites was larger than 100%. For each type of the composite sheet, 8 to 10 specimens were tested to obtain an average value.

Table 4.2 Standards for mechanical testing.

Standards	Items	Values
ASTM D638 (Type V)	Width of narrow section	3.18 ± 0.03 mm
	Gage length	7.62 ± 0.02 mm
	Length of narrow section	9.53 ± 0.08 mm
	Length overall	63.5 mm
ASTM D882	Initial strain rate	10.0 mm (mm·min) ⁻¹
	Initial distance between grips	25.4 mm
	Rate of grip separation (extension rate)	254 mm min ⁻¹

4.2.4 Electrochemical measurement

4.2.4.1 Solid-state symmetric EDLCs with freestanding composites sheets as electrodes

The prepared MWCNT-ink/PVA and VGCNF-ink/PVA freestanding composites sheets were directly used as the electrodes and current collectors to assembly symmetric EDLCs. Figure 4.1 displays the configuration of the symmetric EDLCs. The composite sheets were cut into a rectangle shape with dimensions of $1.0 \times 2.0 \text{ cm}^2$ and stacked face-to-face with an overlapping area of 1.0 cm^2 . A piece of qualitative filter paper with dimensions of $1 \times 1 \text{ cm}^2$ was inserted between these two electrodes and used as a separator, which was saturated with 1: 2 H_3PO_4 : PVA (10 wt% in water) solution at 60°C in advance. The assembly was tightly pressed by tweezers and dried at 50°C overnight.

Figure 4.1 Configuration of the EDLCs with the freestanding MWCNT-ink/PVA or VGCNF-ink/PVA sheets as the working electrodes and filter paper as the separator.

The electrochemical performance of the solid-state symmetric EDLCs was evaluated by CV and GCD, performed on PGSTAT302N galvanostat/potentiostat Autolab (Metrohm-Autolab, Netherlands). The CV tests were conducted within an operating voltage window of -1.0 to 1.0 V at scanning rates of 25, 50, 100 and 200 mV s^{-1} . The GCD was carried out in a potential window of 0 to 0.8 V at current densities of 0.5, 1.0, 2.5, 5.0 and 10 mA cm^{-2} . The specific capacitance was calculated from GCD by the equation:

$$C_s = 2 \frac{I \Delta t}{S \Delta V} \quad (4.1)$$

where I is the applied current, Δt is the discharging time, ΔV is the operating voltage window excluding IR drop and S is the area of one electrode (i.e., 1.0 cm²).

4.2.4.2 Solid-state symmetric EDLCs with paper-based electrodes

The prepared MWCNT-ink/paper and VGCNF-ink/paper were also directly used as the electrodes and current collectors to assembly symmetric EDLCs. The configuration of these EDLCs is shown in Figure 4.2, which is distinct from the one in Figure 4.1 in the used gel electrolyte.

Figure 4.2 Configuration of the EDLCs with VGCNF-ink/paper or MWCNT-ink/paper as the working electrodes and the cross-linked PVA-H₂SO₄ gel electrolyte.

Figure 4.3 shows the process for producing the cross-linked H₂SO₄-PVA gel electrolyte. In a typical procedure, 1.6 g of poly(vinyl alcohol) (PVA, 87–89% hydrolyzed, Mw = 31000–50000) and 0.4 g of Poly(vinyl pyrrolidone) (PVP, K30, Mw ~ 40000) were firstly added into 24 ml of deionized water and heated at 80 °C until the solution became clear. After the solution cooled down to room temperature, the cross-linking agent (glutaraldehyde, 2.0 wt% of PVA) and the catalyst (2 M H₂SO₄, 200 μL) were added. The resulting mixture was

stirred for 30 min, allowed for degassing and then cast onto a plastic petri dish (polystyrene, Dia.90 mm $\times$ 15mm), where it was cured at 50 °C for 5 h to form PVA-PVP hydrogel. The hydrogel was freeze-dried to remove water. The obtained dry and porous PVA-PVP sheet was soaked into a 1: 10 H₂SO₄: H₂O electrolyte solution under vacuum. After the sheet was saturated with electrolyte, it was removed from the electrolyte bath and placed on a glass plate, where it was air-dried for 24 h to remove the free water on the surface. Finally, the resulting translucent and flexible PVA-H₂SO₄ gel electrolyte was ready for use.

Figure 4.3 Fabrication process of cross-linked H₂SO₄-PVA gel electrolyte.

The electrochemical performance of the solid-state symmetric EDLCs was evaluated by CV, GCD and EIS on an electrochemical workstation (BioLogic, VSP). The CV tests were conducted within an operating voltage window of 0 to 0.9 V at scanning rates of 25, 50, 100 and 200 mV s⁻¹. The GCD was carried out in a potential window of 0 to 0.9 V at current densities of 0.5, 1.0, 2.5, 5.0 and 10 mA cm⁻². The specific capacitance was calculated from GCD by Equation 4.1. EIS was done at open circuit potential over a frequency range from 100 kHz to 10 mHz, with an AC amplitude of 5 mV. The obtained data were fitted into equivalent circuits by the built-in function in the testing software. For cycling stability test, the electrode was charged and discharged at a current density of 5 mA cm⁻² for 10000 cycles.

4.2.4.3 Electrodeposited MnO₂/VGCNF-ink/paper

The electrochemical performance of the electrodeposited MnO₂ on the VGCNF-ink/paper were evaluated by CV, GCD and EIS on an electrochemical workstation (BioLogic, VSP). These tests were carried out in a three-electrode cell, with a platinum counter electrode, an SCE reference electrode and 1.0 M Na₂SO₄ as the electrolyte. The CV tests were conducted within an operating voltage window of -0.2 to 0.9 V (vs. SCE) at varied scanning rates. The GCD was carried out in a potential window of -0.2 to 0.9 V (vs. SCE) at different current densities. The specific capacitance was calculated from GCD by following equation:

$$C_s = \frac{I\Delta t}{S\Delta V} \quad (4.2)$$

EIS was done at open circuit potential over a frequency range from 100 kHz to 10 mHz, with an AC amplitude of 5 mV. The obtained data were fitted into equivalent circuits by the built-in function in the testing software. For cycling stability test, the electrode was charged and discharged at a current density of 5 mA cm⁻² for 2000 cycles.

4.3 Results and Discussion

4.3.1 A short discussion about Chinese ink

Liquid-state Chinese ink is the intimate mixture of carbon particles, glue, miscellaneous additives and water. Technically speaking, Chinese ink is one kind of colloidal suspension, composed of water as the continuous phase and the surface-modified carbon nanoparticles as the dispersed phase.

The carbon used in traditional Chinese ink is either soot or lampblack, which are respectively the products of incomplete combustion of wood (especially pinewood) and oil lamp (such as tung oil, rapeseed oil, lard, *etc.*)¹³⁻¹⁵. In some brands of modern Chinese ink, soot and lampblack are replaced with commercial carbon black, which is produced under well-controlled conditions and thus has smaller particle sizes, a narrower size distribution and fewer impurities than soot and lampblack. In this work, the carbon in the used Chinese ink is commercial carbon black, whose SEM image is shown in Figure 4.4a. Strictly

speaking, the basic unit of carbon black is an aciniform-shape cluster composed of several individual particles (or called primary particles), rather than the individual particles as seen in the SEM image.¹⁶ The particle size of these constituent primary particles ranges from 50 to 100 nm, estimated from the SEM image. From the TEM image (Figure 4.4b), it can be seen that the constituent primary particles are actually composed of numerous imperfect graphite layers oriented around the center. The graphite layers endow carbon black with quasi-crystal features that can be detected by XRD or Raman spectroscopy. The content of water and carbon black in this Chinese ink were determined by TGA as 92.3% and 5.2%, respectively.

Figure 4.4 (a) SEM image of dried Chinese ink (carbon black); the inset is the schematic diagram of carbon black particles in Chinese ink. (b) TEM image of carbon black in Chinese ink.

The glue is used as the surfactant and stabilizer for modifying the surface chemistry of carbon black particles and stabilizing them in the aqueous solution. Animal glue (such as hide glue and egg white) and/or plant gum (such as Arabic gum and starch) are widely used in traditional Chinese ink, while the synthetic resin is commonly used in the modern Chinese ink as it can disperse and stabilize carbon black in a more efficient way. Beside glue, some other additives, normally perfumes and herb extract may also be added to improve the physical properties of Chinese ink, such as odor, tint and appearance. In this work, synthetic resin is used in this Chinese ink. The total content of the synthetic resin and miscellaneous additives is only 2.5%.

The starting point for using commercial Chinese ink in fabricating carbon-based composites is to apply its ready-made colloidal system and the glue-stabilized carbon black particles as spacers and electricity enhancers. The Chinese ink used in this work is delicately selected from many brands of Chinese ink. The reason for the selection because it contains high-quality carbon black and an appropriate content of glue.

4.3.2 Freestanding MWCNT-ink/PVA ternary composites

Figure 4.5 Representative photographs of (a) the freestanding MWCNT-ink/PVA composite sheets, (b) the MWCNT-ink composite, and (c) the MWCNT /PVA composite. In these samples, the amounts of MWCNTs, Chinese ink, and PVA (2.5 wt%) are 0.1 g, and 2.0 g and 5.0 g, respectively.

4.3.2.1 Morphology study

A freestanding MWCNT-ink/PVA composite sheet can be easily fabricated by wet-casting and air-drying the MWCNT-ink-PVA aqueous suspension on a plastic petri dish. The suspension was simply made by manual milling in an agate mortar. Figure 4.5 displays the

typical appearance of the prepared MWCNT-ink/PVA composite sheet, and the composites without PVA or ink. The ternary composite shows high flexibility; it can be easily rolled into a cylinder shape. By changing the amount of the suspension and the dimensions of the substrate, the ternary composite can be made in any size and thickness. By contrast, the composite without PVA has many cracks and cannot form a complete sheet, while the one without Chinese ink forms a dense cake.

FESEM was applied to unveil the microstructure of the MWCNT-ink/PVA ternary composite. The representative SEM images are shown in Figure 4.6a–d. The images of MWCNT/PVA (Figure 4.6e,f) and ink/PVA (Figure 4.6g,h) binary composites are also presented for comparison. As seen in the low-magnification image (Figure 4.6a,c), MWCNTs, surrounded by the carbon black particles (CBPs) from the Chinese ink, are well dispersed within the composite. The high-magnification images (Figure 4.6b,d) provide an insight into the arrangement of MWCNTs and carbon black particles. These spherical particles, with a diameter close to the outer diameter of the MWCNTs, are found to be inserted into the space between adjacent MWCNTs, leading to the separation of MWCNTs. It is seen from the cross-sectional view that, the MWCNTs form a framework for the “bricks”—the dispersive carbon black particles, which in return support the framework. Meanwhile, PVA functions as a binder to hold these MWCNTs and carbon black particles together to form a cohesive composite sheet. It is thus can be concluded that, the high flexibility of the ternary composite is because of the well-constructed “framework (MWCNT)-brick (CBP)-binder (PVA)” structure. By contrast, in the MWCNT/PVA composite, MWCNTs are found to be highly entangled and non-uniformly distributed within the PVA matrix; whereas in the ink/PVA composite, the carbon black particles are tightly bound together by PVA due to their small size and spherical shape, forming a void-free structure.

Figure 4.6 Representative SEM images of (a-d) the MWCNT-ink/PVA composite; (e, f) the MWCNT/PVA composite; and (g, h) the ink/PVA composite. (c) and (d) are cross-sectional images. In these samples, the amounts of MWCNTs, Chinese ink, and PVA (2.5 wt%) are 0.1 g, and 2.0 g and 5.0 g, respectively.

Based on the observations above, the role of Chinese ink in dispersing MWCNTs in the

composite can be summarized in this way. On the one hand, as the surfactant and stabilizer, the nomadic glue from the Chinese ink may exert the same influence on MWCNTs as on carbon black. Hence, as schematized in Figure 4.7, the glue attaches to the surface of MWCNTs upon contacting with MWCNTs. The coating of glue induces steric repulsion that can counterbalance the Van der Waals attraction between adjacent MWCNTs.^{17, 18} During manual milling, the local shear force delivered by milling will tear the MWCNT bundles apart and create more exposed surface for the adsorption of glue, whilst carbon black particles infill the space among the MWCNTs. As manual milling goes on, more glue adsorbs onto MWCNTs and more carbon black particles infill the void among MWCNTs, resulting in the separation of entangled MWCNTs. Besides, the introduction of PVA increases the viscosity of the suspension, limiting the movement of MWCNTs and carbon black particles, and further preventing them from the rapid settlement. As a result, after thorough milling, a smooth MWCNT-ink-PVA suspension is obtained, which is stable enough for follow-up air-drying.

Figure 4.7 (a) Schematic diagram of the disentanglement of pristine MWCNT bundles with the aid of Chinese ink. SEM images of (b) the MWCNT-ink/PVA composite and (c) the MWCNT/PVA composite. The insets schematize the distribution of MWCNTs and carbon black particles in the PVA matrix.

On the other hand, carbon black particles can also act as nanosized spacers to prevent the MWCNTs from severe secondary agglomerating during the air-drying process. The evaporation of water causes a decrease in the volume of suspension, diminishing the motion space for MWCNTs and carbon black particles. When the volume decreases to a certain level, these dispersive carbon black particles and MWCNTs will begin to settle down in synchrony. The synchronous sedimentation makes the carbon black particles and MWCNTs inter-lapped, preventing MWCNTs from secondary agglomerating. Therefore, both the carbon black particles and MWCNTs are evenly distributed within the PVA matrix, as shown in the FESEM image (Figure 4.7b). By contrast, the composite prepared in the same condition without the addition of Chinese ink shows large MWCNT lumps unevenly distributed in the PVA matrix (Figure 4.7c).

4.3.2.2 Mechanical properties

As shown earlier in Figure 4.8a, the MWCNT-ink-PVA composite sheet possesses high flexibility; it can be easily rolled or folded at a large angle and rapidly return to their origin shapes without any cracks. The good mechanical properties are mainly attributed to the presence of PVA and good interaction between MWCNTs and Chinese ink. By contrast, although the composite sheets can be fabricated without PVA, they usually have a loose structure, consisting of many visible pores or cracks.

Table 4.3 Results of mechanical testing of different samples*.

Samples**	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
Pure PVA sheet	35.3±9.2	41.6±3.2	902±36
Ink/PVA sheet	34.7±3.9	19.3±1.4	524±27
MWCNT-ink/PVA sheet	66.7±8.6	16.8±1.4	205±14

* Data are mean ± standard derivation

** The amounts of MWCNTs, Chinese ink, and PVA (2.5 wt%) are 0.1 g, and 4.0 g and 10.0g respectively.

In general, the flexibility of the as-prepared composite sheets mainly depends on (i) the weight ratio of PVA to the sum of MWCNTs and carbon black, (ii) the moisture content in

the composite, and (iii) the degree of uniformity of the milled suspension. It is well expected that the flexibility of the composite sheet will be enhanced with increased amounts of PVA and moisture. A thorough milling ensures a high degree of uniformity, which facilitates the interaction between the PVA matrix and the dispersed MWCNTs and carbon black and minimizes the number of possible weak points.

Figure 4.8 (a) Typical stress-strain curves of the pure PVA sheet, the ink/PVA composite sheet and the MWCNT-ink/PVA composite sheet. (b) Evolution of sheet resistance and conductivity of the MWCNT-ink/PVA composites with 4.0 g of 2.5 wt% PVA solution but varied mass ratios of MWCNTs to Chinese ink.

The mechanical properties of the ternary composite sheet were quantitatively measured by a tension tester. For comparison, the pure PVA sheets and the ink/PVA composite sheets were also tested. Compared to pure PVA and ink/PVA composite sheets, the MWCNT-ink/PVA composite sheets demonstrates lower tension strength and lower elongation at break, but higher Young's modulus. CNTs, especially SWCNTs, are deemed as ideal reinforcements for polymers because of their excellent mechanical properties and high aspect ratio, but normally they only make up a small weight of volume ratio.¹⁹⁻²¹ However, in my case, the weight ratio of MWCNTs, carbon black (assuming that the dry matters in Chinese ink are all treated as lampblack particles) and PVA are about 16.9%, 40.7% and 42.4%, respectively. Such a large addition amount of MWCNTs and carbon black is unfavorable for transfer within the composite sheet because of the deficiency of a polymer matrix.²⁰ Even so, the presence of MWCNTs improves the crystallinity of PVA, so that the Young's

modulus of the composite sheet increases.²² It is noteworthy that such mechanical properties should be acceptable if the composite sheet is applied as a functional material that lays more emphasis on the other properties, such as electrical and thermal conductivity.

4.3.2.3 Electrical conductivity

The electrical conductivity of a composite sheet is essentially dependent on the conducting network within the polymer matrix. The high aspect ratio and high electrical conductivity make CNTs ideal reinforcements for conductive composites. In addition to CNTs, carbon black particles are also proved to be good conductive fillers for conductive composites; they can construct a conducting pathway in the polymer matrix like CNTs.^{23, 24} In my case, the usage of Chinese ink introduces carbon black particles into the composites. Besides the conductive fillers, the electrical conductivity of a composite sheet is also significantly influenced by its moisture content. Since water-soluble PVA and the materials in the Chinese ink (such as glue and carbon black particles) can easily absorb water from the air, the as-prepared composite sheets always contain a certain amount of moisture that has a positive effect on flexibility but a negative effect on electrical conductivity. Thus, secondary drying is necessary in order to remove the moisture. The conditions of secondary drying should be well controlled to reach a compromise between mechanical strength and electrical conductivity. In this work, the secondary drying was conducted at 50 °C for 8 h.

Table 4.4 Electrical conductivity of MWCNT-ink/PVA ternary composite and the binary composite without either MWCNTs, ink or PVA.

No.	MWCNTs (g)	Chinese ink(g)	2.5 wt%-PVA (g)	Conductivity (S·cm ⁻¹)
1	—	2.0	5.0	0.80
2 ^b	0.10	—	5.0	0.61
3 ^b	0.10	2.0	—	3.40
4	0.10	2.0	5.0	5.07

Table 4.4 compares the electrical conductivity of the MWCNT-ink/PVA ternary composite and three binary composites without MWCNTs, ink or PVA. The ternary composite shows higher electrical conductivity than any binary composites. The value is comparable to the ones reported previously.^{4, 25} It is noteworthy that the MWCNT/ink binary composite

without an insulating polymer has a lower conductivity than the ternary composite. This can be attributed to its loose structure that is unfavorable for constructing a robust conducting network. As such, a certain amount of PVA is necessary to maintain a conductive network. It should be also noted that, even though the MWCNT/PVA composite contains highly conductive MWCNTs, it shows lower electrical conductivity than the ink/PVA composite with the almost the same content of carbon. This suggests that, apart from the content of the conductive fillers (MWCNTs or carbon black), the way whereby a conducting pathway is built in the composite also largely affects the electrical conductivity. As shown in Figure 4.7b,c, compared with the MWCNT/PVA composite, the ink/PVA composite contains a smoother conducting network within the PVA matrix, because the quasi-spherical CBPs are easier to be dispersed in PVA than the entangled MWCNTs.

The observed synergistic improvement in the electrical conductivity of the MWCNT-in/PVA ternary composites can be attributed to the good interaction between MWCNTs/CBPs and PVA. The entangle MWCNTs are separated by milling with the aid of Chinese ink. During the air-drying process, as the MWCNTs and the CBPs settle down simultaneously without any disturbance, a conducting network is gradually formed. As discussed earlier, the MWCNTs construct the main framework, whilst the conductive CBPs infill the space between MWCNTs and support the MWCNT framework. These CBPs increase the connecting points of the conducting network with the PVA matrix, forming a good interaction that guarantees high electrical conductivity.

This will be particularly useful when the sheet is subjected to mechanical deformation. I found that, the electrical conductivity of the ternary composite remained unchanged after it was bent or folded. As seen in Figure 4.8b, with the fixed carbon content, the sheet resistance of the composite is in inverse proportion to the mass ratio of MWCNTs to Chinese ink (only carbon black is counted) and reaches the lowest value when the ratio is 0.15. After this, the sheet resistance increases with increasing content of MWCNT. This phenomenon can be ascribed to the relative shortage of Chinese ink. When there are not sufficient Chinese ink, the pristine MWCNTs cannot be well disentangled and dispersed into PVA. Poor dispersion of the MWCNTs lowers their effective utilization as electrical conductivity enhancers. Besides, the presence of excessive MWCNTs in the composite

makes the structure loose, which is unfavorable to electrical conductivity.

These observations confirm the assumption that pristine MWCNTs can be dispersed by mechanical force with the aid of Chinese ink. The high electrical conductivity makes the composites possible for various applications, such as electrode materials of energy storage devices and electromagnetic shielding. Since the electrical conductivity of the composites is mainly contributed by the conductive components, further enhancement in conductivity is possible by using high-quality CNTs or graphene nanosheets.

4.3.2.4 Electrochemical performance

Figure 4.9 Electrochemical behavior of the EDLC with MWCNT-ink/PVA composite electrodes. (a) CV curves at different scanning rates within a potential window of -1.0 to 1.0 V. (b) GCD curves at 0.5 mA cm^{-2} within a potential window of 0 to 0.8 V. (c) Cycling performance at a current density of 5 mA cm^{-2} .

In view of the high electrical conductivity and flexibility of the composite, I believe these composites should possess decent electrochemical performance. Thus, I directly applied these composite sheets as the electrodes for solid-state symmetric EDLC-type SCs. The configuration of the EDLCs is shown in Figure 4.1 Here, the EDLC made with the composite sheets composed of 2.0 g of Chinese ink, 0.10 g of MWCNTs and 1.0 g of PVA solution (2.5 wt%) is taken as the example. As expected, the EDLC shows characteristic quasi-rectangle shaped CV curves, and linear charging/discharging curves (Figure 4.9a,b). The observed large IR drop indicates high equivalent series resistance in the EDLC. The composite sheets are used without post-treatment. Thus, the presence of the insulating glue and additives from Chinese ink is unfavorable for electron transport, especially when the composite sheets are also used as the current collectors. The calculated specific capacitance at a current density of 0.5 mA cm^{-2} is 213.2 mF cm^{-2} , or 42.6 F g^{-1} . The EDLC retains 86.9% of the initial capacitance after charging and discharging for 1000 cycles at 5 mA cm^{-2} .

4.3.3 Freestanding VGCNF-ink/PVA ternary composites

Figure 4.10 Comparison of the microstructures of MWCNTs and VGCNFs.^{12, 26}

In view of the good performance of VGCNF-ink/PVA ternary composites, I applied the same fabrication method to prepare freestanding VGCNF-ink/PVA ternary composites. VGCNFs and MWCNTs are similar in some ways as they are both produced by metal-catalyzed chemical vapor deposition, and are hollow and nanometer in scale. However, VGCNFs are distinct from MWCNTs in their fiber diameters, microstructure, price and ease of processing. As schematized in Figure 4.10 VGCNFs are composed of cup-shape

graphene planes stacking along the fiber axis, while MWCNTs are composed of concentric cylinders of graphene. Compared to MWCNTs, due to their larger fiber sizes and length, VGCNFs are less influenced by Van der Waals force and thus easier to be dispersed. Besides, in my case, the VGCNFs have a smaller bulk density than MWCNTs, so they have a larger volume than the MWCNTs of the same weight.

Figure 4.11 SEM images of VGCNF-ink/PVA composites: (a) top view and (b) cross-sectional view. (c) Evolution of sheet resistance and conductivity of the VGCNF-ink/PVA composites with varied mass ratios of MWCNTs to Chinese ink. (d) Comparison of sheet resistance between VGCNF-ink/PVA and MWCNT-ink/PVA composites.

The appearance and the microstructure of the prepared VGCNF-ink/PVA composites are similar to those of MWCNT-ink/PVA composites. As seen in Figure 4.11a,b the VGCNFs are dispersed and carbon black particles are filled in the space among VGCNFs, forming a “framework (VGCNF)-brick (CBP)-binder (PVA)” structure similar to that of the MWCNT-ink/PVA composite. Compared with MWCNTs, the larger tube diameter and

long length make VGCNFs better dispersed in the composite. The effect of Chinese ink and the manual milling on the dispersion of the VGCNFs in the PVA matrix, as well as the formation process of the VGCNF-ink/PVA composite can be explained in the same way as those for the MWCNT-ink/PVA composite.

Figure 4.11c shows the sheet resistance and electrical conductivity of the VGCNF-ink/PVA composites. The sheet resistance decreases with increasing content of VGCNFs and shows the minimum at $3.1 \Omega \cdot \text{sq}^{-1}$ when the mass ratio of VGCNFs to ink is 0.23. After this, the sheet resistance increases instead of decreasing with more VGCNFs. This can be ascribed to the relative shortage of Chinese ink. Insufficient Chinese ink cannot well disperse VGCNFs, lowering their effective utilization as electrical conductivity enhancers. By comparing Figure 4.8b and Figure 4.11c, it can be seen that the VGCNF-ink/PVA composite shows lower sheet resistance than the MWCNT-ink/PVA counterpart at the same mass ratio. Besides the higher intrinsic electrical conductivity of VGCNFs, the observed better electrical conductivity of VGCNF-ink/PVA composites can be also ascribed to a better distribution of VGCNFs in the PVA matrix that forms a smooth conducting network favorable to electrical conductivity.

Figure 4.12 Electrochemical behavior of the EDLC with VGCNF-ink/PVA composite electrodes. (a) CV curves at different scanning rates within a potential window of -1.0 to 1.0 V. (b) GCD curves at 0.5 mA cm^{-2} within a potential window of 0 to 0.8 V.

The prepared VGCNF-ink/PVA composites were also applied as the electrodes for EDLCs,

whose fabrication methods and configuration are similar to those of MWCNT-ink/PVA composites. Here, the EDLC made with the composite sheets composed of 2.0 g of Chinese ink, 0.10 g of VGCNFs and 1.0 g of PVA solution (2.5 wt%) is taken as the example. As expected, the EDLC displays characteristic quasi-rectangle shaped CV curves, and linear charging/discharging curves. Like the one made with MWCNTs, this EDLC shows evident IR drop that suggests high equivalent series resistance (Figure 4.12a,b). The calculated specific capacitance at a current density of 0.5 mA cm^{-2} is 98.9 mF cm^{-2} .

4.3.4 Fabrication of VGCNF-ink/paper as electrodes for supercapacitors

4.3.4.1 Appearance and morphology

The foregoing paragraphs have proven that Chinese ink is effective in dispersing the pristine MWCNTs and VGCNFs into PVA under the action of the mechanical force. In light of this, it was assumed that an aqueous suspension composed of MWCNTs (or VGCNFs) and Chinese ink could be directly made by ball milling these raw materials, and the obtained suspension would be stable enough for the subsequent operation. To verify these assumptions, the Chinese ink was mixed with MWCNTs/VGCNFs by horizontal ball milling, and the resulting suspensions were filter-coated onto filter paper to fabricate MWCNT-ink/paper (or VGCNF-ink/paper) composites.

Figure 4.13a displays the appearance of the VGCNF-ink/paper composite, which has a uniform coating layer of VGCNFs and carbon black particles from the Chinese ink. The glue from Chinese ink functions as the binder to fix the VGCNFs and carbon black particles firmly on the surface of the filter paper. It is noteworthy that carbon black particles can easily penetrate the filter paper, but VGCNFs not due to their long fiber length. The VGCNFs thus form a mesh that can hold up most of the carbon black particles. By contrast, in the sample fabricated without adding Chinese ink (Figure 4.13b), VGCNFs tend to pile up around the pores in the Buchner funnel due to the large suction force there, but they are easy to drop out from the filter paper after drying. Figure 4.13c,d compare the morphology of the filter paper before and after depositing the VGCNF-ink suspension. It is clearly seen that, after filtration, the raw paper is uniformly covered by the VGCNF-ink layer. Figure

4.13e,f provide insights into the microstructure of the coating layer, which is composed of well-dispersed VGCNFs and carbon black particles inserted into the space among the VGCNFs.

Figure 4.13 Appearance of (a) VGCNF-ink/paper and (b) VGCNF/paper. SEM images of (c) raw filter paper and (d–f) VGCNF-ink/paper.

With the same loading mass of VGCNFs, the appearance and the morphology of the VGCNF-ink/paper composites are strongly affected by the amount of Chinese ink added

and the time of ball milling. Figure 4.14 shows the tape test results of the composites containing different amount of Chinese ink. The adhesion of the VGCNFs/carbon black to the filter paper is drastically improved with increasing content of Chinese ink, because of the increasing amount of glue. It should be pointed out that, however, as more Chinese ink is added, the coating layer thickens and becomes brittle after drying. Therefore, the addition amount of Chinese ink should be well controlled to obtain flexible VGCNF-ink/paper with a robust coating layer.

On the other hand, ball milling is effective in disentangling the pristine VGCNFs. However, an excessive time of ball milling can cut off the VGCNFs. The resulting broken VGCNF fragments cannot form a robust network due to their short fiber length. Thus, the obtained coating layer tends to crack after drying.

Figure 4.14 Tape test of the VGCNF-ink/paper with different calculated loading densities of Chinese ink. The adhesion of VGCNFs and ink on the filter paper increases from I_0 to I_{400} . In the sample name “ I_x ”, “I” stands for Chinese ink, and the subscript number “ x ” signifies that the loading density of Chinese ink in this sample is $x \text{ mg cm}^{-2}$.

These observations confirm my assumption that entangled VGCNFs can be dispersed by Chinese ink under the action of ball milling. Through filtration, these VGCNFs and carbon black particles are transferred onto filter paper and stick to the paper by the glue from Chinese ink. In these processes, Chinese ink not only helps to disperse the pristine VGCNFs, but also provides the necessary binder that solidifies the contact between the filter paper and the VGCNFs/carbon black.

4.3.4.2 Electrical conductivity

The electrical conductivity of the VGCNF-ink/paper composites were investigated by four-probe resistivity measurement. Figure 4.15a displays the sheet resistance of the VGCNF-ink/paper composites with different compositions. As expected, the sheet resistance decreases with incremental amounts of VGCNFs. As discussed in previous sections that, Chinese ink can improve the distribution of VGCNFs, which is conducive to high electrical conductivity. Accordingly, the sheet resistance also reduces with increasing loading density of Chinese ink. It is worth mentioning that, the VGCNF-ink/paper composite shows lower sheet resistance than the freestanding VGCNF-ink/PVA composite with the same content of VGCNFs and ink.

Figure 4.15 Evolution of sheet resistance of VGCNF-ink/paper with (a) different loading densities of VGCNFs and ink; and (b) different time of ball milling.

4.3.4.3 Electrochemical performance

In consideration of the high electrical conductivity and flexibility of the paper-based composites, I believe they can demonstrate decent electrochemical performance. Thus, the prepared VGCNF-ink/paper composites were applied as the electrodes for solid-state symmetric EDLCs.

Figure 4.16 Electrochemical performance of EDLC with VGCNF (2.5 mg cm^{-2})-ink (200 mg cm^{-2})/paper electrodes: (a) CV curves at 200 mV s^{-1} within different potential windows. (b) Coulombic efficiency against different potential windows. (c) CV curves at different scanning rate within a potential window of 0 to 0.9 V. (d) GCD curves at different current densities within a potential window of 0 to 0.9 V. (e) Capacitance retention rate at a current density of 5.0 mA cm^{-2} for 10000 cycles. (f) Three EDLCs in series to light up a LED.

The configuration of the EDLCs is schematized in Figure 4.2a,b. The overlapping area of the working electrodes was 1.0 cm^2 . A piece of cross-linked PVA- H_2SO_4 gel was used as

the electrolyte and the separator. This cross-linked gel is more suitable for paper-based SCs because unlike the non-cross-linked PVA-H₂SO₄ solution, the immobile gel cannot be absorbed by the paper, but it can still reserve a considerable amount of electrolyte ions.²⁷ The EDLC was simply packed by the scotch tape, in order to seclude it from the air. To achieve a packing without sacrificing electrical conductivity of the composites, two pieces of copper foil were used as the external current collectors. The appearance of the fabricated EDLC is shown in Figure 4.2c.

The electrochemical behavior of the prepared symmetric EDLC was studied by CV and galvanostatic charge-discharge (GCD). Figure 4.16a shows the CV curves at a constant scanning rate of 200 mV s⁻¹ within different potential windows. The CV curves within a potential window less or equal to 1.2 V show a quasi-rectangle shape and nearly symmetric current response on reverse scanning, which suggests fast capacitive response and good reversibility. However, when the potential window exceeds 1.2 V, the CV curve distorts at high potentials due to the electrode polarization and some irreversible reaction.²⁸ Similar electrochemical behavior can be also found in GCD. The inset in Figure 4.16b displays the curves of GCD. When the potential window is less or equal to 1.2 V, both the charge and the discharge curves show a nicely linear profile, indicating good capacitive characteristics.²⁹ However, as the upper potential limit exceeds 1.2 V, the charge curve distorts at high potential due to electrode polarization. Based on the GCD, the Coulombic efficiency was calculated by the equation:

$$\eta = \frac{q_d}{q_c} \times 100\% = \frac{\Delta t_d}{\Delta t_c} \times 100\% \quad (4.3)$$

where, q is the number of involved charges during charging (or discharging), Δt is the time of charging (or discharging), and the subscripts “d” and “c” refer to “discharge” and “charge”, respectively. As seen in Figure 4.14b, the Coulombic efficiency declines with increasing potential windows. An enlarged potential window is advantageous to high specific capacitance, but in this case, it also leads to a decay in Coulombic efficiency. Thus, a trade-off is needed to be made between specific capacitance and Coulombic efficiency by adjusting the potential windows. Here, the potential window was fixed at 0–0.9 V. At

this potential window, the EDLC demonstrates ideal capacitive performance. As shown in Figure 4.16c,d, the corresponding CV curves at different scanning rates have a quasi-rectangle shape, while the GCD curves are nearly linear and symmetric. The EDLC retains 86.4% of the initial capacitance and shows little change in the CV after galvanostatically charged and discharged at 5.0 mA cm^{-2} for 10000 cycles (Figure 4.16e). Figure 4.16f demonstrates that three EDLCs in series can light up a LED after charged by a commercial battery for 10 s.

The effect of Chinese ink on the electrochemical performance of the paper-based electrodes was investigated. The paper-based composites containing different loading density of Chinese ink (50, 100, 200 and 300 mg cm^{-2} , denoted as I_{50} , I_{100} , I_{200} and I_{300} , respectively) were applied to fabricate symmetric EDLCs. Figure 4.17a displays the CV curves of these symmetric EDLCs at a scanning rate of 50 mV s^{-1} . All these CV curves have a quasi-rectangle shape, suggesting a good capacitive performance. The enclosing area of CV curves increases with incremental loading density of Chinese, corresponding to improved specific capacitance. The specific capacitance and the rate capability of these EDLCs were assessed by GCD at different current densities, and the calculated results are depicted in Figure 4.17b. All these EDLCs have similar rate capability; around 72% of the specific capacitance is retained as the current density rises from 0.5 A cm^{-2} to 10 A cm^{-2} . It is found that the specific capacitance has a good linear relation with the loading density of Chinese ink, but the EDLCs prepared with only Chinese ink shows a very low specific capacitance.

Figure 4.17 Evolution in electrochemical performance of EDLCs with VGCNF-ink/paper electrodes containing different loading densities of Chinese ink: (a) CV curves at 50 mV s⁻¹; (b) specific capacitance at different current densities; (c) equivalent series resistance; (d) Nyquist plots; (e) Bode plots and (f) cycling stability measured at a current density of 5.0 mA cm⁻².

The enhancement in specific capacitance by Chinese ink can be explained in this way. For one thing, as discussed above, Chinese ink facilitates the dispersion of pristine VGCNFs and provides the necessary binder that ensures a robust conducting network. Thus, the conductivity of the paper-based composites improves with more Chinese ink. Evidence for

this can be also found from the equivalent series resistance (ESR) of these EDLCs (Figure 4.17c), estimated from IR drop in galvanostatic discharging curves, which reduces by half when the loading density of Chinese ink is raised from 50 mg cm⁻² to 200 mg cm⁻². For another thing, the well-dispersed VGCNFs form a mesh with narrow pore sizes that can retain carbon black particles during filtration. The retained carbon black particles can contribute additional capacitance as they have a large surface area. However, in the absence of VGCNFs, most of the carbon black particles will directly pass through the filter paper due to their small particle sizes. Moreover, these adsorbed carbon black particles on the filter paper cannot form an efficient conducting network that is necessary for fast capacitive response. As a result, the EDLC constructed without VGCNFs only show limited capacitance. These observations confirm the synergistic effect of Chinese ink and VGCNFs on the capacitance of the prepared EDLCs.

Table 4.5 Calculated values of the components in the equivalent circuits of the samples I₅₀, I₁₀₀, I₂₀₀ and I₃₀₀.

	I ₅₀	I ₁₀₀	I ₂₀₀	I ₃₀₀
R_{Ω} (Ω)	11.44	9.90	9.78	7.45
CPE (mF.s ^{α-1})	6.47	13.11	12.96	22.21
α	0.662	0.731	0.772	0.791
R_{ct} (Ω)	2.894	0.810	0.344	1.499
C_p (mF)	17.00	37.99	48.94	56.07

The capacitive behavior of these EDLCs was also studied by EIS. The obtained EIS data are fitted into equivalent electric circuits, and the values of each component are listed in Table 4.5. It is obvious seen from the table that the increasing loading density of Chinese ink has positive effects on the electrical conductivity and the capacitance of the EDLCs, which are indicated by the reduced ESR (R_{Ω}) and the enlarged CPE and C_p , respectively. Besides, the value of the exponent α (related to the frequency dispersion) is more close to 1 as the loading density of Chinese ink increases, suggesting a more ideal capacitor.

Figure 4.17d exhibits the Nyquist plots. In accordance with the previous discussion, the sample with a higher loading density of Chinese ink demonstrates better capacitive performance as indicated by the less deviation from the imaginary axis. The Bode plots in

Figure 4.17e show the evolution of the real part (C') and imaginary part of capacitance (C'') against frequency, which provides insight into the rate capability of these devices. The EDLC can be simplified as a combination of a resistor and a capacitor whose impedance is dependent on the angular frequency ω . The capacitance of the EDLC can be expressed in the form of a complex as:

$$C(\omega) = C'(\omega) - jC''(\omega) \quad (4.4)$$

The real part (C') and the imaginary part (C'') of the capacitance are expressed as:

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (4.5)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \quad (4.6)$$

where $Z'(\omega)$ and $Z''(\omega)$ are the real part and imaginary part of the impedance $Z(\omega)$.³⁰ The real part of the capacitance (C') is effective capacitance delivered by the EDLC, while the imaginary part of the capacitance (C'') corresponds to the energy dissipation by IR drop and irreversible Faradaic reaction that can lead to a hysteresis in the electrochemical process.³¹⁻³³ The real part of the capacitance (C') is highly dependent on the frequency and increases sharply as the frequency goes below 1 Hz. At low frequency, electrolyte ions can permeate into the deep pores of the electrode which can contribute to a considerable amount of capacitance, while at high frequency, the majority of electrolyte ions can only access to the surface of the electrode.³⁰ The frequency at which the C'' peaks is defined as the characteristic frequency (f_0); it marks the point where the resistive and capacitive impedance is equal.³⁴ The reciprocal of the characteristic frequency f_0 is referred as the time constant $\tau_0 = 1/f_0$, representing the minimum time needed to discharge all the energy from the device with an efficiency of $> 50\%$.³⁰ As seen in Figure 4.17e, the characteristic frequency drops from 0.66 to 0.43, 0.29 and 0.19 Hz as the loading density of Chinese ink in the electrodes increases from 50 to 100, 200 and 300 mg cm⁻², corresponding to the increase in the time constant from 1.51 to 2.33, 3.45 and 5.26 s, respectively. According to the equation $\tau = RC$, the observed positive correlation between the time constant and the

loading density of Chinese ink in the electrode can be attributed to the enlarged capacitance by increasing addition amount of Chinese ink.

To evaluate the cycling stability, these devices were continuously charged and discharged at a constant current of 5 mA for 10000 cycles. Figure 4.17f plots the capacitance retention rate against cycling number. From the plots and their derivatives, it can be seen that these devices (especially Ink₃₀₀) undergo remarkable degradation in the first 1400 cycles, and stabilize afterward. The capacitance retention rates after 10000 cycles for Ink₅₀, Ink₁₀₀, Ink₂₀₀ and Ink₃₀₀ are 81.7%, 85.1%, 86.4% and 74.1%, respectively. Although the sample made with more Chinese ink tends to have better cycling stability, excessive Chinese ink can lead to a counterproductive result. The reason for this may lie in the negative side of the glue as its presence erects barriers to ion diffusion. Even so, such cycling stability is still acceptable.

Figure 4.18 (a) specific capacitance and (b) characteristic frequency of EDLC with VGCNF (2.5 mg cm⁻²)-ink (200 mg cm⁻²)/paper electrodes made with different time of ball milling.

It should be pointed out that, besides the addition amount of Chinese ink, the ball milling also plays an important role in capacitance of the prepared EDLCs. As shown in Figure 4.18a, the areal specific capacitance of the device has a positive correlation with the time used for ball milling the VGCNFs with Chinese ink. The improvement can be attributed to a better dispersion of VGCNFs by Chinese ink under prolonged ball milling, which may create more accessible pores and surface for ion adsorption. Likewise, as seen from the Bode phase plots (Figure 4.18b) that, as the capacitance is improved, the characteristic

frequency at the phase of -45° decreases and the phase at low frequency has a larger deviation from the ideal capacitor -90° .

VGCNF-ink/paper as the substrate for electrodeposition of metal oxides

The high electrical conductivity and the porous structure make it possible to directly apply these the VGCNF-ink/paper composites as the substrates for the electrochemical deposition (or electrodeposition, ED) of metal oxides. Compared to nickel foam or carbon cloth, these paper-based substrates can provide more surface for the electrodeposition. Thus, it was assumed the prepared composites could demonstrate good electrochemical performance. To test this idea, the composite made with 2.0 mg cm^{-2} of VGCNFs and 50 mg cm^{-2} of Chinese ink was used as the substrate for electrodepositing MnO_2 .

Commonly, the techniques used for electrodepositing MnO_2 include (1) potentiostatic ED (PED), achieved by applying a constant voltage on the working electrode;³⁵⁻³⁷ (2) galvanostatic ED (GED), achieved by applying a constant current on the working electrode;³⁸ and (3) potentiodynamic-ED (i.e., CV), achieved by applying a constant sweeping rate on the working electrode within a certain potential window.³⁹⁻⁴⁴ These ED techniques can be classified into anodic electrodeposition and cathodic electrodeposition. Anodic electrodeposition occurs at the positive electrode (anode); it involves the directional migration of Mn^{2+} from the electrolyte to the anode where the Mn^{2+} is electrochemically oxidized into MnO_2 according to the proposed reaction equation.⁴⁵

On the contrary, cathodic electrodeposition occurs at the negative electrode (cathode); it normally performed with MnO_4^- -contained electrolytes. In cathodic electrodeposition, the applied electric field directs MnO_4^- ions to the cathode, where these ions are electrochemically reduced by the equation:

Figure 4.19 (a) Current response during potentiostatic electrodeposition of MnO₂ at 1.0 V vs. SCE. (b) Potential response during galvanostatic electrodeposition of MnO₂ at 5 mA. (c, d) XRD patterns of electrodeposited MnO₂/VGCNF-ink/paper and pure starting materials. SEM images of pristine VGCNF-ink/paper, and electrodeposited MnO₂/VGCNF-ink/paper: (f) 5 mA_1 min, (g) 5 mA_5 min and (h) 5 mA_10 min.

Besides MnO_4^- , cathodic electrodeposition can be also achieved with Mn^{2+} -contained electrolytes, which involves more processes, including the decomposition of H_2O that gives rise to OH^- ions, the reaction between OH^- and Mn^{2+} that produces $\text{Mn}(\text{OH})_2$, and finally the oxidation of $\text{Mn}(\text{OH})_2$ into MnO_2 .⁴⁵ Here in this thesis, as a demonstration, the VGCNF-ink/paper was applied as the anode to electrodepositing MnO_2 from $\text{Mn}(\text{CH}_3\text{COO})_2$ by PED and GED.

Figure 4.19a,b record the evolution in the current and the potential of working electrode during PED and GED, respectively. In the case of PED, the current of the working electrode undergoes a sharp decrease in the first 80 s and a steady decline afterward. The derivative curve gives a better insight into the change in the current response, which stabilizes after 80 s. Likewise, in the case of GED, the potential of the working electrode rises quickly in the first 150 s and increases steadily afterward. The high electrical conductivity of the substrate guarantees an efficient electron transportation. Thus, MnO_2 is produced rapidly cover the substrate after applying the current on the working electrode. Due to the low electrical conductivity of MnO_2 , the deposition of MnO_2 will dramatically raise the resistance of the working electrode, which reduces the electron transfer efficiency and slows down the formation of MnO_2 .

The formation of MnO_2 was confirmed by XRD. Figure 4.19c compares the XRD pattern of the working electrode with those of the raw materials, and Figure 4.19d gives a clear view of the XRD patterns of the working electrode. The electrodeposited MnO_2 can be indexed to $\gamma\text{-MnO}_2$.^{41,44} Figure 4.19e–h show the morphology of the raw substrate, as well as the electrodeposited MnO_2 obtained in different time. As the time of ED is prolonged, the MnO_2 crystals grow and evolve into well-defined nanostructures, covering the surface of the substrate. However, it should be pointed out that, the adhesion between the ED layer and the substrate weakens with the thickened ED layer. As a result, the thick ED layer tends to fall off during testing, which will cause a remarkable degradation in the capacitance and cycling stability.

Figure 4.20 Electrochemical performance of electrodeposited $\text{MnO}_2/\text{VGCNF-ink/paper}$ tested in a three-electrode cell. (a) CV curves at varied scanning rates, (b) GCD curves at different current densities, and (c) cycling stability of (5 mA_5 min)-electrodeposited $\text{MnO}_2/\text{VGCNF-ink/paper}$. Comparison in (d) specific capacitance, (e) Nyquist plots, (f) characteristic frequency, and (g, h) Bode plots of pristine VGCNF-ink/paper and electrodeposited $\text{MnO}_2/\text{VGCNF-ink/paper}$ obtained in different ED conditions.

The electrochemical performance of the (5 mA_5 min)-electrodeposited MnO₂/VGCNF-ink/paper was evaluated by CV, GCD and EIS in a three-electrode system with SCE as the reference electrode and 1M Na₂SO₄ as the electrolyte. Here, the sample prepared by GED (5 mA_5 min) is used as the example to illustrate the typical electrochemical behavior of the electrodeposited MnO₂. Figure 4.20a,b present the typical testing curves for CV and GCD. The quasi-rectangle shape of CV curves and linear charge/discharge curves confirm the good capacitive behavior.^{44, 46} The small IR drop suggests good electrical conductivity of the electrode resulting from the intimate contact between ED-MnO₂ and the substrate. The areal specific capacitance is calculated from the GCD. The (5 mA_5 min)-electrodeposited MnO₂/VGCNF-ink/paper shows a specific capacitance of 317 mF cm⁻² at the current of 1 mA, much higher than 16 mF cm⁻² of the substrate. Besides, this sample retains 81.94% of the initial capacitance after continuously charged and discharged at a current of 2 mA for 2000 cycles.

The samples prepared by GED and PED with different parameters show similar curves of CV and GCD, but different calculated capacitance. The areal specific capacitance of the working electrode is proportional to the amount of electrodeposited MnO₂, which is mainly determined by the applied current (or potential) and the time for ED, regardless of whether the ED is carried out in a galvanostatic mode or in a potentiostatic mode. As seen in Figure 4.20d, the specific capacitance of these samples is in the sequence of PED (1 V_2 min) < GED (5 mA_5 min) < GED (5 mA_10 min) < PED (1 V_10 min).

EIS analysis was applied to probe into the impedance behavior of the prepared composites. Basically, a Nyquist plot for an SC can be resolved into three regions. In the high-frequency region, the intercept of the curve with the real Z axis represents the ESR of the electrode. In the high-to-medium frequency region, usually a semicircle is observed, associated with the charge transfer resistance. In the medium-to-low frequency region, a linear with a finite slope is observed, representing the diffusion resistance of electrolyte ions in the pores of the electrode.^{43, 47} From the Nyquist plots (Figure 4.20e), it is observed that the electrode with a thicker ED layer shows larger ESR, charge transfer resistance and diffusion resistance. It is understandable that with prolonged time for ED, the ED layer gets thicker and its inner structure becomes denser, which increases the resistance between the active

material and the current collector, and poses obstacles to ion diffusion. The Bode plots (Figure 4.20f–h) also proves the deviation of the electrode from the ideal capacitor. The electrode with a thicker depositing layer has a phase at the low frequency deviating more from -90° of the ideal capacitor; it also shows a reduced characteristic frequency, i.e., an enlarged time constant.

In summary, in this section, the feasibility of applying filtration-made VGCNF-ink/paper composites as the substrate for electrodeposition of MnO_2 is demonstrated. The high electrical conductivity and large surface area of the paper-based composite ensure a good electrodeposition. The thin layer of electrodeposited MnO_2 drastically boosts the areal specific capacitance of the composites. It is believed that the fabrication method can be also extended to other transition metal oxides made from electrodeposition.

4.3.5 Fabrication of MWCNT-ink/paper as electrodes for supercapacitors

The method use for fabricating VGCNF-ink/paper composites can be also applied to prepare MWCNT-ink/paper composites. However, unlike VGCNF-ink/paper composites, the obtained MWCNT-ink/paper composites have an uneven surface and tend to crack after drying (Figure 4.21a–d), especially when the loading density of Chinese ink is high. From the SEM images, it is known that the MWCNTs are not completely dispersed during ball milling, and thus not uniformly distributed on the filter paper. The undispersed MWCNT clusters form a rough surface (Figure 4.21e); while the dispersed MWCNTs are mixed well with carbon black particles, forming a smooth surface (Figure 4.21f). Compared with VGCNFs, MWCNTs have smaller tube sizes and shorter tube lengths, but larger bulk density, which make them more strongly affected by Van der Waals' force. As a result, more shear force is needed in order to separate the entangled pristine MWCNTs. However, in such a ball milling process, the presence of Chinese ink and water dilute the concentration of MWCNTs, and reduces the impact of balls on the MWCNTs. After filtration, these MWCNTs cannot form a well-connected network on the filter paper, and the local agglomeration of MWCNTs with carbon black particles and glue brings about cracks. The uneven distribution of MWCNTs causes the significant difference in the sheet resistance

within the same composite. Besides, the cracked surface makes it difficult to correctly determine the sheet resistance by the four-probe resistivity tester.

Figure 4.21 Appearance of MWCNT-ink/paper composed of 2.5 mg cm^{-2} of MWCNTs and (a) 50, (b) 100, (c) 200 and (d) 300 mg cm^{-2} of Chinese ink. (e, f) SEM images of Sample (b) at different parts.

Likewise, the MWCNT-ink/paper composites were used as the electrodes for symmetric EDLCs, whose configuration and preparation are analogous to those of VGCNF-ink/paper composites. Figure 4.22a,b show the typical results of CV and GCD for the EDLCs with MWCNT (2.5 mg cm^{-2})-ink (50 mg cm^{-2})/paper electrodes. The evident IR drop represents high ESR of the devices, because of which the CV curve distorts severely at a high scanning rate. The specific capacitances are listed in Figure 4.22c. The MWCNT-based EDLC show smaller specific capacitance and lower rate capability than the VGCNF-based counterpart, which can be also ascribed to the high ESR. Unlike the VGCNF-based composites, however, these MWCNT-based composites are not suitable to be used as the substrate for electrodeposition, because of their high sheet resistance and the uneven distribution of MWCNTs.

Figure 4.22 (a) CV curves at different scanning rate and (b) GCD curves at different current densities of EDLCs with MWCNT (2.5 mg cm⁻²)-ink (50 mg cm⁻²)/paper electrodes. (c) Comparison of the specific capacitance of EDLCs with different electrodes.

4.4 Conclusions

In this chapter, it is proved the commercial Chinese ink is effective in dispersing raw MWCNTs and VGCNFs via wet manual or mechanical grinding. The role of Chinese ink in this process is explored, which can be summarized into two aspects. For one thing, the glue of other surfactants from Chinese ink can have the same effect on MWCNTs and VGCNFs as that on carbon black. When manual or mechanical milling is applied, the delivered local shear force can easily tear apart these MWCNTs and VGCNFs with a glue-attached surface. For another thing, Chinese ink provides a large number of carbon black particles, which act as the spacers to separate the adjacent MWCNTs and VGCNFs.

The obtained suspensions were applied for fabricating electrodes for SCs by two methods. First, the suspensions was incorporated with PVA and the resulting mixture was cast on flat substrates to form freestanding composites sheets. The presence of Chinese ink improves the distribution of MWCNTs and VGCNFs in the PVA, and enhances the interaction between MWCNTs/VGCNFs and the PVA matrix. As a result, these composite sheets show high mechanical properties and electrical conductivity. In addition, the flexible and conductive composite sheets were directly used as the electrodes to fabricate all-solid-state EDLCs, which however, only showed mediocre electrochemical performance. Hence, more research work is needed to optimize the electrochemical performance of the freestanding composite sheets without sacrificing its flexibility.

Second, the suspensions were filter-coated on the filter paper to fabricate paper-based composites. The presence of Chinese ink not only improves the distribution of MWCNTs and VGCNFs on the paper, but also reinforces the adhesion of MWCNTs and VGCNFs to the paper after drying. The VGCNF-ink/paper composites have a crack-free surface and show high electrical conductivity, while the MWCNT-ink/paper tends to crack and thus are not suitable for subsequent applications. Accordingly, the VGCNF-ink/paper composite was used as the electrodes for EDLCs. A positive correlation is observed between the areal specific capacitance of the EDLCs and the addition amount of Chinese ink, which is attributed to the improved dispersion of VGCNFs and the capacitance contribution from carbon black. Besides, the VGCNF-ink/paper composite was used as the substrate for the electrodeposition of MnO_2 . Benefiting from the high electrical conductivity and the porous surface of the paper-based composite, $\gamma\text{-MnO}_2$ was firmly electrodeposited onto the composite. The resulting MnO_2 /VGCNF-ink/paper composite show much higher specific capacitance than pristine VGCNF-ink/paper.

The method to prepare MWCNT/VGCNF suspensions is simple, safe and low-cost. Therefore, it holds promises for large-scale applications. Apart from wet-casting and filter-coating, the suspensions can be also used in other ways, such as spray-coating, inkjet printing, through which the fabrication cost of electrodes for SCs can be reduced. Besides, the electrochemical performance of the obtained carbon-based composites can be also improved by incorporating other pseudocapacitive materials.

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Chapter 5

Nanostructured MnO₂-Ink Composites for Supercapacitors

This chapter aims to explore the role of Chinese ink as a starting material to prepare electroactive materials for supercapacitors. This chapter reports the synthesis of MnO₂-ink composites from the redox reaction between potassium permanganate and Chinese ink, which was conducted in a hydrothermal reactor under magnetic stirring. The properties of the prepared MnO₂-ink composites were first examined, including the morphology, the crystal structure, the specific surface area and the pore size distribution. Then, the intrinsic electrochemical behavior of the MnO₂-ink composites was investigated in three-electrode cells. Lastly, the electrochemical performance of the MnO₂-ink composites in practical use was assessed in asymmetric supercapacitors, which were configured with the composites as the positive electrode and activated carbon as the negative electrode. This chapter ends up with conclusions that: (1) carbon black particles from Chinese ink is a good carbon source to react with MnO₄⁻ to synthesize birnessite-type MnO₂; (2) the good dispersion of carbon black particles from Chinese ink ensures high specific surface area and homogeneity of the MnO₂-ink composites, which are favorable for high electrochemical performance; and (3) the nanostructures of the MnO₂-ink composites can be easily adjusted by changing the addition amount of Chinese ink.

5.1 Introduction

Unlike electrical double layer capacitors (EDLCs), the capacitance of pseudocapacitors is mainly contributed by the fast and reversible faradaic redox reactions occurring on the surface of electroactive materials, such as transition metal oxides and conducting polymers. Among numerous transition metal oxides as electrode materials for supercapacitors, manganese dioxide (MnO₂) always attracts special research attention in scientists for two reasons. For one thing, MnO₂ demonstrates good electrochemical performance including high theoretical specific capacitance (up to 1370 F g⁻¹),¹ wide potential window (around 1.0 V) and the capability to use mild electrolytes. For another thing, it also has many remarkable merits such as low cost, natural abundance and eco-friendliness.²

The charge storage of MnO₂ has been well studied, which is mainly ascribed to three aspects: (i) adsorption/desorption of protons (H⁺) and alkali metal cations (C⁺) at the surface of MnO₂ (as seen in Equation 5.1):

(ii) intercalation/deintercalation of protons (H⁺) and alkali metal cations (C⁺) into the bulk (subsurface) of MnO₂ (as seen in Equation 5.2):

and (iii) pseudocapacitive (Faradic) redox reactions occurring at the surface and in the bulk of MnO₂ according to Equation 5.3):

Where, C⁺ = Li⁺, Na⁺, K⁺.³

Figure 5.1 shows a typical cyclic voltammetry (CV) curve of a single MnO₂ electrode in a neutral aqueous electrolyte, which has a quasi-rectangle shape analogous to that of EDLCs. The quasi-rectangle shaped CV curve can be resolved into multiple anodic peaks and cathodic peaks; each pair of peaks represents a pair of reversible redox reactions. The fast

and reversible successive redox reaction between Mn(IV) and Mn(III) oxides makes the MnO₂ behave like an EDLC.

Figure 5.1 Schematic of cyclic voltammetry for a MnO₂ electrode in a mild aqueous electrolyte.³ The inset shows the schematic representation of the crystal structure of Birnessite-type MnO₂.⁴

The capacitance of MnO₂ is mainly dependent on its physical properties (such as microstructure and surface morphology) and chemical properties (such as crystal structure, crystallinity, the hydrous state and valence).⁵ Regarding the crystal structure, MnO₂ has many different crystallographic forms made with edge-shared [MnO₆] octahedra in different configuration, such as α -, β -, γ -, δ -, ϵ - and λ -type.^{4, 6} Among these, δ -MnO₂ (Birnessite-type) attracts special research interest in its 2D tunnel structure (as shown in the inset of Figure 5.1). Compared with other types of MnO₂, birnessite-type MnO₂ shows relatively high specific capacitance despite its moderate specific surface area.⁷

Birnessite-type MnO₂ can be synthesized by many methods, such as electrodeposition,⁸ the chemical co-precipitation of KMnO₄ and MnSO₄,⁹ and the redox reaction between KMnO₄ and carbon.¹⁰ Self-assemble birnessite-type MnO₂ tends to aggregate due to the fast and

uncontrolled growth, leading to the limited surface area and poor electrical conductivity.¹¹ Alternatively, birnessite-type MnO₂ can be grown on conductive substrates. As reported in previous articles that, the in-situ redox reaction between the MnO₄⁻ ions and carbon dispersed in a suspension is a simple and effective approach to synthesize well-dispersed and high-performance MnO₂-inkarbon composites. The carbon materials that have been used for the synthesis include acetylene black,¹² carbon nanotubes,¹³ and graphene,¹⁴ etc. In this synthesis, carbon not only acts as the reductant for MnO₄⁻ ions, but also provides the substrate for the produced MnO₂. Accordingly, the dispersion status of the carbon largely affects the homogeneity of the resulting composites.

In light of the good dispersion and high stability of carbon black in Chinese ink, it was hypothesized that these carbon black particles could be used as the carbon source to react with MnO₄⁻ ions to produce homogenous MnO₂-ink black composites. To this end, commercial Chinese ink was directly reacted with KMnO₄ in a stirring-driven hydrothermal reactor to synthesize MnO₂. The characterization results from SEM, TEM, and XRD confirm the uniform in-situ deposition of MnO₂ on the carbon black particles. Benefiting from the high disparity of carbon black, these composites demonstrate high specific surface area and good electrochemical performance, which are comparable to those of the composites made with high-performance carbon nanomaterials, such as carbon nanotubes or graphene. These results indicate commercial Chinese ink can be directly used as a carbon source for synthesizing high-performance electrode materials by taking advantage of its ready-made stable suspension system. The low cost and easy processing of Chinese ink make it possible to scale up the preparation and cut down the overall cost of supercapacitors.

5.2 Experimental Methods

5.2.1 Synthesis of MnO₂-ink composites

Nanostructured MnO₂-ink composites were synthesized by means of a magnetic stirring-driven hydrothermal reaction. The experiment flow chart is shown in Figure 5.1 In a typical procedure, 0.316 g (i.e., 2 mmol) of potassium permanganate (KMnO₄) powder was first

dissolved in 35 g of deionized water in a screw-cap reagent bottle. Then, different amount of Chinese ink was dispersed into the KMnO₄ solution. The resulting mixture was kept at 60 °C with stirring for 30 min (for pre-reaction). Afterward, the mixture was transferred to a 45 mL Teflon-lined stainless-steel autoclave and heated at 120 °C in an oil bath (set on a hotplate) with varied stirring rates for different periods of time. The oil-bath hydrothermal reaction setup is shown in Figure 5.2. After the reaction, the autoclave naturally cooled down to room temperature. Then the precipitate was collected by filtration, and purified by deionized water (three times) and ethanol (one time). The obtain dark brown or black product was dried at 60 °C for 12 h in a vacuum oven before further characterization. Samples were labeled as “MI_x”, where “M” stands for MnO₂, “I” stands for Chinese ink, and “x” denotes the addition amount of Chinese ink.

Figure 5.2 Experiment flowchart for the synthesis of MnO₂-ink composites.

5.2.2 Material Characterization

The morphology and microstructure of the composites were examined by FESEM (JEOL, JSM-7600F, operated at 5 kV) and TEM (JEOL, JEM-2010 UHR). The crystallographic structures of the composites were characterized by XRD (Shimazu, XRD-6000) operated at 40 kV and 30 mA, and equipped with Cu K α radiation ($\lambda = 0.15406$ nm). The elemental composition and chemical states of the elements were studied by XPS (Thermo Scientific ESCALab 250Xi), equipped with a monochromatic Al K α (1486.7 eV) x-ray source. All spectra were calibrated by using C 1s peak (284.5 eV) as the reference. The peak fitting was done on the software XPSPEAK41. The Raman spectra were recorded on Renishaw InVia Raman Microscope, equipped with Argon ion laser source (514 nm). The content of MnO₂ was determined by TGA, where the samples were heated at a ramping rate of 20 °C min⁻¹ to 800 °C in air. The specific surface area and pore structure were analyzed by physical adsorption of nitrogen at 77 K, performed on TriStar II 3020 surface area analyzer from Micromeritics. The specific surface area was obtained by the Brunauer–Emmett–Teller (BET) method and the pore size and distribution were analyzed by Barrett-Joyner-Halenda (BJH) method

5.2.3 Electrochemical Measurement

5.2.3.1 Fabrication of three-electrode cells

The basic electrochemical performance of the prepared composites was performed in a three-electrode cell, composed of a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrolyte was a 1M Na₂SO₄ aqueous solution. To prepare the working electrodes, the as-prepared sample was first mixed with acetylene black and polyvinylidene fluoride (PVDF) in a mass ratio of 80:10:10. For convenience, the PVDF was dissolved in 1-methyl-2-pyrrolidone (NMP) with a ratio of 5% in advance. The resulting mixture was kept stirring for 8 h to form a smooth slurry. If necessary, ethanol was added to adjust the viscosity of the slurry. The slurry was then spread onto a nickel foam current collector (about 1 cm²) by a flat spatula, and dried in a vacuum oven at 60 °C for 12 h. The loading density of the electrode materials was around

5.0 mg cm⁻². The resulting electrode was pressed by a hydraulic press with a pressure of 6 MPa for 10 s to ensure a good contact between the active materials and the current collector, and then immersed in the electrolyte for 15 min before the test to ensure a full wetting of the electrode.

5.2.3.2 Electrochemical Measurement of three-electrode cells

The electrochemical behaviors of the composites were measure by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). These tests were done with an electrochemical workstation (BioLogic, VSP). The CV was conducted within a potential window of -0.2 to 0.9 V (vs. SCE), with different scanning rate. The GCD was performed in a potential window of 0 to 0.9 V (vs. SCE) at different current densities. The specific capacitance of the composites can be calculated by CV according to the equation:

$$C_s = \frac{1}{2mv(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV \quad (5.4)$$

where I is the response current, m is the mass of the electrode material, v is the voltage sweeping rate, V_c and V_a refer to the high and the low potential limit, and $(V_c - V_a)$ is the operating voltage window. The factor “2” is required since a full CV cycle is composed of a charging process and a discharging process.

Alternatively, the specific capacitance can be also calculated from galvanostatic discharging, according to the equation:

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (5.5)$$

where I is the applied current, Δt is the discharging time and ΔV is the operating voltage window excluding IR drop.

EIS was done at open circuit potential over a frequency range from 100 kHz to 10 mHz, with an AC amplitude of 5 mV. The obtained data were fitted into equivalent circuits by

the built-in function in the testing software. For cycling stability test, the electrode was continuously charged and discharged at a constant current for 4500 cycles.

5.2.3.3 Fabrication of asymmetric SCs

The asymmetric SC was fabricated with the prepared MnO₂-ink composites as the positive electrode material and the commercial activated carbon (used without any treatment) as the negative electrode materials. Prior to fabricating the asymmetric SC, it is crucial to determine the mass ratio of the positive electrode material to the negative electrode material, in order to satisfy the charge balance. To this end, both electrodes were measured by CV in the three-electrode cell with the same scanning rate of 20 mV s⁻¹ but within different potential windows. Based on the CV test, the potential window and the specific capacitance of each electrode were thus determined by the method described above.

The charge (q) stored by each electrode depends on the specific capacitance (C_s) and the loading mass (m) of the electrode material, and the potential window ΔE , which is expressed as:

$$q = C_s \times m \times \Delta E \quad (5.6)$$

Therefore, to achieve $q^+ = q^-$, the mass ratio is determined by the equation:

$$\frac{m_+}{m_-} = \frac{C_{s-} \times \Delta E_-}{C_{s+} \times \Delta E_+} \quad (5.7)$$

The fabrication of working electrodes was the same as the aforementioned. The area of the working electrodes was 1.0 cm², and the loading density of the electrode materials was controlled in the range of 3 to 5 mg cm⁻². The asymmetric SC was assembled into a CR2032-type coin cell, with a 1M Na₂SO₄ aqueous solution as the electrolyte and a piece of filter paper as the separator. The assembled cell was placed statically for 12 h before the test to ensure the electrolyte can well wet the electrodes.

5.2.3.4 Electrochemical Measurement of asymmetric SCs

The electrochemical performance of the asymmetric SCs was measured by CV, GCD and EIS, which were recorded on an electrochemical workstation (BioLogic, VSP). The CV was conducted in different potential windows at various scanning rates to explore the optimum operating potential. The GCD was conducted in the potential window of 0 to 1.8 V.

The specific capacitance is calculated from CV, given by:

$$C_s = \frac{4}{2mv(V_c - V_a)} \int_{V_a}^{V_c} I(V) dV \quad (5.8)$$

or from galvanostatic discharging by the following equation:

$$C_s = 4 \times \frac{I\Delta t}{m\Delta V} \quad (5.9)$$

In these two equations, m is the combined mass of positive and negative electrode materials (without excluding the mass of Chinese ink). The multiplier 4 is used to adjust the capacitance and the combined mass of the asymmetric SC with the capacitance and the mass of a single electrode.¹⁵

Based on the specific capacitance calculated from galvanostatic discharging, the energy density (E , in Wh kg⁻¹) and power density (P , in W kg⁻¹) are thus determined by the following equations:

$$E = \frac{C_s V^2}{2 \times 3.6} \quad (5.10)$$

$$P = \frac{E}{\Delta t} \times 3600 \quad (5.11)$$

5.3 Results and Discussion

5.3.1 Formation mechanism

Birnessite-type nanostructured MnO₂ can be in situ deposited in onto the outer surface of different carbon materials, such as carbon nanotubes¹⁶ and amorphous acetylene black^{12, 17}. The in-situ deposition produced an intimate bonding between the resulting MnO₂ and the carbon substrates. In a neutral solution, the self-limiting deposition is based on the redox reaction between permanganate ions (MnO₄⁻) and carbon, according to the following reaction equation^{7, 12}:

The reaction releases CO₂ gas and raises the concentration of OH⁻. When the concentration of OH⁻ reaches a certain degree, the reaction ceases to give off the CO₂ gas. The reaction proceeds in the following way:

In an acidic aqueous solution, the redox reaction can be expressed as:

This reaction can occur even at room temperature as it satisfies the thermodynamic condition.¹⁸

In these three cases, carbon not only serves as the reducing agent to convert MnO₄⁻ into insoluble MnO₂, but also provides a substrate for the resulting MnO₂, whose growth kinetics strongly relies on the carbon structure and initiate favorably on the defect sites on the carbon surface.¹⁸ As a result, the redox reaction is difficult to initiate on defect-free or defect-lacking carbon, such as carbon nanotubes or graphite. In this work, carbon black from Chinese ink was chosen as the carbon source, which has a quasi-crystal structure and

abundant surface defects.¹⁹ The ready-made commercial Chinese ink containing well-dispersed carbon black particles saves the trouble of pretreating and dispersing carbon into water, and ensures the homogeneity of the products.

5.3.1.1 XRD

Figure 5.3 XRD patterns of (a) the MI_{0.606} composites, synthesized at 120 °C with 500-rpm stirring for different periods of time; (b) pristine dried ink and the MnO₂-ink composites with different content of ink, synthesized at 120 °C with 500-rpm stirring for 3 h.

The crystallographic structure of pristine Chinese ink and MnO₂-ink composites was investigated by powder XRD and Raman spectroscopy. Figure 5.3a shows the XRD patterns of the MI_{0.606} composites (MI_{0.606} signifies that the composite was made with 0.606 g of Chinese ink), synthesized at 120 °C with 500-rpm stirring for different periods of time. It is seen that the composite obtained from the pre-reaction displays no distinct peak, while the composites after hydrothermal reaction show two characteristic peaks at $2\theta = 37^\circ$ and 66° , regardless of the difference in reaction time. This suggests that the pre-reaction only gives rise to low-crystallinity manganese oxides, which are further transformed into the desired products during hydrothermal reaction. Figure 5.3b shows the XRD patterns of pristine ink (carbon black) and the MnO₂-ink composites synthesized by a three-hour hydrothermal reaction. The XRD pattern of pristine ink displays a broad peak at around 25° and a weak peak at around 42° , corresponding to the (002) and the (100) plane of quasi-crystal carbon, respectively.²⁰ From the TEM image (Figure 5.7c), it can be seen that the constituent primary particles of carbon black are actually composed of numerous imperfect graphite layers oriented around the center. The graphite layers endow carbon black with

quasi-crystal features that can be detected by XRD or Raman spectroscopy. On the other hand, the XRD patterns of MnO₂-ink composites can be indexed to monoclinic potassium birnessite (PDF #01-080-1098, see Appendix), which comprises 2D edge-shared MnO₆ octahedral layers with K⁺ cations and water molecules (as schematized in Figure 5.1).²¹⁻²³ In the XRD pattern of the less-ink composite (MI_{0.152}), the two strong diffraction peaks at $2\theta = 12^\circ$ and 25° correspond to the (001) and (002) basal reflection, while the other two asymmetric and weak diffraction peaks at $2\theta = 37^\circ$ and 66° can be indexed to the (20//11/) and (02//31/) diffraction bands.²¹ However, with the increasing loading mass of Chinese ink, the peaks $2\theta = 12^\circ$ and 25° are gradually overshadowed by the signals from amorphous carbon black and even turn invisible. It should be pointed out that, all the peaks in the XRD patterns of these composites are relatively weak and dispersive, indicating the low crystallinity of the synthesized MnO₂.

5.3.1.2 Raman spectroscopy

Figure 5.4 Raman spectra of (a) dried ink and the composites with different content of Chinese ink and (b) MI_{0.152}.

Raman spectroscopy has been proven an effective technique to investigate the local structure of manganese dioxides, especially for the ones with low crystallinity that are difficult to be further analyzed by Rietveld refinement of XRD data.²⁴⁻²⁶ Figure 5.4 shows the Raman spectra of pristine Chinese ink and MnO₂-ink composites with different content of Chinese ink. The spectrum of the pristine Chinese ink shows two sharp bands centered at 1360 cm⁻¹ (D band) and 1590 cm⁻¹ (G band). The G band arises from the in-plane bond-stretching motion of the sp²-C atom pairs (the E_{2g} phonons),²⁷ while the D band represents

the presence of disorder in sp^2 -hybridized carbon systems, such as hetero-atoms, vacancies, or grain boundaries that lower the crystalline symmetry of the quasi-infinite lattice.²⁸ The high intensity of D band indicates there are abundant defects present in the carbon black, which are preferable for the reaction with MnO_4^- . On the other hand, the spectra of MnO₂-ink composites spectra show a sharp band (centered at 648 cm^{-1}), and two weak bands (centered at around 358 cm^{-1} and 305 cm^{-1}), which are ascribed to the $\nu_{2(Mn-O)}$ symmetric stretching vibration of (MnO₆) octahedron in MnO₂·nH₂O and the bending modes of Mn-O, respectively.²⁹⁻³¹ These results are in accord with the XRD, confirming the formation of birnessite-type MnO₂. However, neither the D band nor the G band is seen in these spectra. The absence of the D and the G band indicates the carbon black from Chinese ink (as the reductant and substrate) has been reacted with KMnO₄ and coated by the resulting MnO₂.

5.3.1.3 XPS

Figure 5.5 XPS spectra of the composite MI_{0.606}: (a) survey spectrum; (b–d) core-level spectra of Mn 2p, O 1s and Mn 3s.

XPS was applied to investigate the oxidation state of manganese as well as the chemical composition in the MnO₂-ink composite. Here, the sample MI_{0.606} is taken as the example to interpret the XPS test results. Figure 5.5a depicts the XPS full scan spectrum, in which the signals of the elements C, O, K and Mn can be clearly seen. The presence of element K is attributed to the hydrated K⁺ cations inserted in the interlayers of birnessite-type MnO₂.^{32, 33} In the high-resolution Mn 2p spectrum (Figure 5.5b), the two characteristic peaks at 642.1 eV and 653.8 eV correspond to the Mn 2p_{1/2} and Mn 2p_{3/2} spin-orbit peaks of Mn, respectively. The spin-energy separation of 11.7 eV is in agreement with previous reports.³² The average valence of Mn can be estimated from the O 1s and Mn 3s spectra. The O 1s spectrum (Figure 5.5c) can be deconvoluted into three component peaks at 529.5 eV, 531.1 eV and 532.0 eV, corresponding to the Mn-O-Mn in the tetravalent oxide, the Mn-O-H in the hydrated trivalent oxide and the H-O-H, respectively. The average valance can be calculated by:^{1, 33}

$$\text{Average valence} = \frac{\text{IV} \cdot (S_{\text{Mn-O-Mn}} - S_{\text{Mn-O-H}}) + \text{III} \cdot S_{\text{Mn-O-H}}}{S_{\text{Mn-O-Mn}}} \quad (5.15)$$

This equation can be simplified as:

$$\text{Average valence} = 4 - \frac{S_{\text{Mn-O-H}}}{S_{\text{Mn-O-Mn}}} \quad (5.16)$$

where, S stands for the signal in the O 1s spectrum. In this work, the ratio of $S_{\text{Mn-O-H}}$ to $S_{\text{Mn-O-Mn}}$ is 0.13. Thus, the average valance of Mn is determined to be 3.87. In addition, the average valance of Mn can be also estimated from the binding energy width (Δ_{BE}) between the separated Mn 3s doublets, which arise from the parallel spin coupling of the 3s and the 3d electrons.^{1, 34} It is assumed that there is a linear relationship between the Δ_{BE} and the average valance of Mn. By referring to Δ_{BE} of genuine samples of MnO (5.79 eV), Mn₃O₄ (5.50 eV), Mn₂O₃ (5.41 eV) and MnO₂ (4.78 eV), the Δ_{BE} of the MI_{0.606} (4.90 eV) suggests that the average valance of Mn in this composite can be estimated to be 3.81. The value is very close to the one determined from the O 1s spectrum. The relatively high valance of Mn indicates the high purity of MnO₂ in the composite as well as the existence of low-

valence manganese oxides, which may be conducive to the fast and reversible redox reaction

5.3.2 Morphology and specific surface area

This section discusses the morphology of the synthesized MnO₂-ink composites based on which the formation mechanism is proposed.

5.3.2.1 Effect of reaction time

Figure 5.6a displays the morphology of carbon black in the Chinese ink. Accurately speaking, the basic unit of carbon black is an aciniform-shape cluster composed of several individual particles (or called primary particles), rather than the individual particles that are seen in this image. This is because the adjacent primary particles can fuse into a cluster during synthesis. In other words, the carbon black particles seen from the SEM image may join with their neighbors. As seen from the HRTEM image, the primary carbon black particle is composed of multiple graphite layers surrounding a center, similar to human's fingerprints, which endow the carbon black with quasi-crystal features.¹⁹ With respect to the primary particles, due to the well-controlled synthesis conditions, carbon black has smaller particle sizes and a narrower size distribution than the soot or lampblack that are widely used in the traditional Chinese ink. For this reason, in this work, this carbon black-type Chinese ink is selected as a starting material. To put it simply, the carbon black is treated as individually dispersive spherical particles.

Figure 5.6 SEM images of (a) pristine ink and (b-f) the MI_{0.606} composites synthesized under the same conditions (120 °C and stirring at 500 rpm) in different hours: 0, 1.0, 2.0, 3.0, 4.5, 6.0 and 9.0 h, respectively. The top-right insets are the schematics for the morphology and the bottom-right inserts are the corresponding TEM images.

Figure 5.6b–f exhibit morphology of the MI_{0.606} composites, which were synthesized at 120 °C under 500-rpm stirring for different periods of time. Comparing the Figure 5.6a and 5.6b, it is seen that the composite obtained from the pre-reaction (60 °C, stirred at 500 rpm for 30 min) has a morphology similar to that of the pristine carbon black particles, with the only difference in the particles size. The enlargement in particle size is attributed to the deposition of the resulting MnO₂. The first-deposited MnO₂ act as the crystal nuclei for the subsequent growth of MnO₂ in the hydrothermal reaction. Accordingly, once the composite is transferred into the hydrothermal reactor and kept at 120 °C, its morphology gradually evolves with the growth of MnO₂ outside the carbon black. After a one-hour hydrothermal reaction, more MnO₂ emerge in the form of whiskers on the particle surface (Figure 5.6c). These whiskers elongate into long and narrow nanowires ((Figure 5.6d–f) with increasing reaction time as well as the action of magnetic stirring, forming a network that encloses the primary carbon black particles.

The HRTEM image (Figure 5.7b) of MnO₂ demonstrates distinct lattice fringes with a lattice spacing of 0.25 nm, corresponding to the (20/*l*/11/*l*) lattice planes of birnessite-type MnO₂.²¹ However, as observed in Figure 5.6f,g, a prolonged reaction will disorganize the well-defined structure of the composite. This is because the ever-growing MnO₂ nanowires tend to aggregate, and the formation of MnO₂ consumes the carbon black (as the reductant), weakening its second role (as the nanosized spacers) in preventing the aggregation of MnO₂. Consequently, in these composites obtained from the prolonged reactions, thick nanowires and clusters are observed, while the carbon black particles are hardly visible.

Figure 5.7 HRTEM of (a) the primary carbon black particle and (b) the MnO₂ synthesized at 120 °C with 500-rpm stirring for 3 h.

Based on these observations, the formation process of the MnO₂ nanowire-ink composite is proposed and schematized in Figure 5.8. In detail, upon mixing with the KMnO₄ solution at a certain temperature, the outer layer (including glue or surfactants) of carbon black particles will be first eroded by MnO₄⁻ due to the self-limiting redox reaction, forming numerous MnO₂ crystallites in a short time.³⁵ These MnO₂ crystallites nucleate from the solution and adhere to the surface of carbon black particles in order to reduce the surface energy.³⁶ However, due to the rapid nucleation, these first-precipitated MnO₂ crystallites have a low degree of crystallinity, as shown in the XRD pattern, but they act as the crystal nuclei for the follow-up crystal growth. After pre-reaction, the suspension is transferred to a hydrothermal reactor, where an “Ostwald ripening” process takes places.³⁷⁻³⁹ The MnO₂ crystallites grow outwards owing to the 1D growth habit and the assistance of mechanical agitation, forming long and thin nanowires.⁴⁰ As the dwell time is extended, the MnO₂ nanowires thicken and tend to entangle, meanwhile the carbon black particles are consumed and thus dwindle in their particle sizes. Such a self-limited redox reaction ensures a good interaction between MnO₂ and carbon black particles. The structure of the composite is largely decided by the dwell time. An excessive dwell time will lead to a disordered structure in which thick MnO₂ bundles predominate.

Figure 5.8 Schematic of the formation process of the MnO₂ nanowire-ink composite.

5.3.2.2 Effect of the addition amount of Chinese ink

Figure 5.9 compares the morphology of the synthesized MnO₂-ink composites with different content of Chinese ink. Well-defined spherical particles with a flower-shape surface are seen in the composite MI_{0.152} (Figure 5.9a). The flower-shape surface is attributed to the confocal deposition of the MnO₂ produced by the redox reaction between carbon black and KMnO₄. These particles have a uniform particle size of around 200 nm, larger than that of the pristine carbon black particles. From the TEM image, it can be seen that the flower-shape surface is made by numerous nanosheets. The composite MI_{0.303} demonstrates analogous particles but with some whiskers jutting out from the surface. In the composite MI_{0.606}, long and thin nanowires are seen, which form a network enclosing the particles. However, in the composite MI_{0.909}, highly entangled nanowires and some small agglomerates instead of distinct particles are observed. By contrast, the Chinese ink-free sample only shows nanowires with non-uniform diameters, whereas the sample prepared with an equivalent mass of commercial carbon black shows bold and short nanowires as well as some surrounding clusters.

Figure 5.9 SEM images of (a-e) the MnO₂-ink composites synthesized with different content of Chinese ink: (a) 0.152 g, (b) 0.303 g, (c) 0.606 g, (d) 0.909 g and (e) 0 g; (f) the sample synthesized with commercial carbon black.

The reason for the variation of morphology lies in the concentration of carbon black. At a fixed temperature, the kinetics of the redox reaction is largely determined by the concentration of the starting materials. According to the reaction Equation 5.12, it is known that the stoichiometric molar ratio of KMnO₄ to the carbon should be 4: 3. In this work, the amount of KMnO₄ is 1.0 mmol (0.316 g), so the stoichiometric amount of carbon black

is 0.75 mmol (0.009 g), which can be converted into 0.173 g of Chinese ink given that the content of carbon black in this Chinese ink is determined as 5.21%. That is to say, except for the composite MI_{0.152}, all the composites should have sufficient carbon source for the redox reaction, provided all the carbon black can be accessible to MnO₄⁻. However, in reality, since carbon black is not dissolved into ions, only the outer layer of carbon black is accessible to MnO₄⁻. In particular, after the deposition of MnO₂, the inner layer of carbon black is protected by MnO₂ from the erosion by MnO₄⁻. Evidence for this can be found from the TEM images (Insets in Figure 5.9a–c). In other words, within a certain range, the kinetics of the redox reaction is limited by the concentration of available carbon black. By adjusting the addition amount of Chinese ink, the reaction rate can be tuned and thus the morphology of the products can be changed. As a result, when there is only limited Chinese ink, the redox reaction will proceed slowly, allowing more time for the dissolution-recrystallization process that can lead to a highly-ordered structure (Figure 5.9a–c). Otherwise, when there is abundant Chinese ink, the redox reaction will proceed rapidly and the resulting accumulate disorderly (Figure 5.9d). Moreover, more Chinese ink will result in more MnO₂ that tend to aggregate due to Ostwald ripening. In contrast, in the absence of carbon black particles as anchoring sites and effective spaces, the resulting MnO₂ is inclined to agglomerate. Besides, compared with the redox reaction between carbon black and MnO₄⁻ that has an adjustable reaction rate, the reaction between Mn²⁺ and MnO₄⁻ ions is fast and thus give rise to large and uncontrolled MnO₂ nanowires. For the commercial black, its low dispersity in the aqueous solution will inevitably lead to an uneven interaction with MnO₄⁻. Accordingly, both small clusters and bold fibers are seen in the products.

Figure 5.10 (a) Nitrogen adsorption-desorption isotherms of the MI_{0.606} composite and the pure MnO₂ sample; the inset shows the BJH pore size distribution, calculated from the desorption branch; (b) TGA profiles of the MnO₂-ink composites with different content of Chinese ink.

The specific surface area of the composites was determined from the nitrogen adsorption-desorption isotherms at 77 K by the BET method, while the pore size distribution is calculated by the BJH model from the desorption branch of the isothermal. Figure 5.10a presents the nitrogen adsorption and desorption isotherms of the composite MI_{0.606} and pure MnO₂. The MnO₂-ink composite shows a typical Type IV isothermal with a hysteresis loop in the range of 0.4 to 1.0 P/P₀, which suggests the presence mesoporous structure,^{41, 42} whereas the pure MnO₂ sample shows a Type II isothermal without any mesopores. Besides, in the plots of the BJH pore size distribution, it is seen that the MnO₂-ink composite has a narrow pore size distribution centered at 3.8 nm, while no peak is seen for the pure MnO₂ sample. Therefore, the MnO₂-ink composite has a BET specific surface area of 158 m²·g⁻¹, much higher than 30 m²·g⁻¹ of the pure MnO₂ sample. The difference in the mesoporous structure can be also observed from the TGA analysis. Figure 5.11 (b) compares the TGA profiles of the MnO₂-ink composites and the pure MnO₂ sample. All composites show obvious weight loss at around 220 °C, which is mainly attributed to evaporation of the water in the interlayer of MnO₂ and the water absorbed by the hydrophilic synthetic resin in Chinese ink.^{21, 22, 43} However, no similar weight loss is seen in the pure MnO₂ sample, indicating the lack of a porous structure. Based on these observations, it can be thus claimed that, the presence of carbon black particles leads to the formation of a mesoporous structure in the resulting MnO₂ and improve the overall surface area.

5.3.2.3 Effect of magnetic stirring

Figure 5.11 SEM images of the MI_{0.606} composites synthesized at 120 °C for 3 h with a stirring rate of (a, and b) 0 rpm; (c) 250 rpm; (d) 500 rpm; (e) 750 rpm and (f) 1000 rpm. (a) and (b) are collected from the same composite, but (a) is from the bottom part (black in color) while (b) is from the upper part (dark brown in color).

Figure 5.11 compares the morphology of MnO₂-ink composites synthesized under magnetic stirring with different speeds. Except for the composite synthesized without

stirring, all the composites display similar morphology, comprising numerous long and thin nanowires that form a network encircling rough-surface nanoparticles. It appears that with the increasing stirring rate, more nanoparticles are observed while the number of nanowires decreases. As for the composite synthesized in an undisturbed environment, obvious phase separation is observed in this product, which contains a dark brown upper part and a black bottom part. The upper part has a similar morphology to that of the composites prepared under stirring, while the bottom part has a dense cake structure. It is understandable that, in a stirring-free reaction, the carbon black particles will settle down upon being deposited by the MnO₂ due to gravity. However, in the same reaction environment, there still are nanowires produced on the top of the products. This suggests magnetic stirring is not the determining factor the formation of nanowires. Instead, the formation of nanowires largely relies on the 1D growth habit of birnessite-type of MnO₂.^{44, 45} Further evidence for this can be obtained from the analysis on the surface area and the pore size. As seen in Figure 5.12a, all the composites share the similar isothermals and have a peak centered at around 3.8 nm in the plots of the BJH pore size distribution. The BET specific surface area is determined to be 206, 190, 158, 162 and 168 m²·g⁻¹ for the composite synthesized at a stirring rate of 0, 250, 500, 750 and 1000 rpm, respectively. The corresponding average pore diameters are estimated to be 13.4, 13.1, 15.9, 14.8 and 14.1 nm. Based on these observations, it appears that, within a certain range (≤ 500 rpm), the sample synthesized under low-speed stirring has a higher specific surface area than the one synthesized under high-speed stirring. However, beyond this range, the specific surface area has little change regardless of regardless of the variation in stirring speed.

Figure 5.12 (a) Plots of the BJH pore size distribution (calculated from the desorption branch) of MnO₂-ink composites synthesized at different stirring rates; the upper left inset is the enlarged view, and the upper right inset is the corresponding isothermals. (b) The calculated BET specific surface area and the BJH desorption average pore diameter.

Even so, magnetic stirring still plays a positive role in the formation of homogenous MnO₂-ink composites, because it improves the mass transportation, accelerates the dissolution-recrystallization process and prevents the sedimentation of MnO₂-coated carbon black particles so that homogeneous products can be obtained. Indeed, an excessively high stirring rate has its negative side as it reinforces the under-saturation of dissolving regions on the MnO₂ surface.⁴⁶ This may be the reason why less nanowires are seen in the composite prepared under higher stirring.

5.3.3 Electrochemical analysis

The electrochemical properties of the prepared MnO₂-ink composites were analyzed via CV, GCD and EIS. Here, the composite MI_{0.606} is used as an example to illustrate the typical electrochemical behavior of these MnO₂-ink composites. Figure 5.13a shows the typical CV curves of the composite MI_{0.606} at different scanning rates. The quasi-rectangle shape is in accord with the previous reports.^{3, 47} No redox peak is observed, indicating the electrode is charged and discharged at a pseudo-constant rate over the whole cycle, which is the characteristic electrochemical nature of MnO₂.⁴ Due to the good electrical conductivity, the electrode is not badly polarized, therefore the quasi-rectangle shape is still maintained even at a high scanning rate of 200 mV s⁻¹.

Figure 5.13 (a) Typical CV curves of the composite MI_{0.606} at different scanning rates. (b) GCD curves of the composite MI_{0.606} at different current densities. (c) Cycling stability of the composite MI_{0.606}, which was measured by GCD at a current density of 10 A g⁻¹ for 4500 cycles. (d) EIS curves of the composite MI_{0.606} before and after 4500 cycles of GCD.

Figure 5.13b display the GCD curves of the electrode at different current densities. The charge and discharge curves at each current density are linear and symmetric, revealing the rapid I-V response and good electrochemical reversibility.³⁵ Besides, the indistinct IR drop suggests a high electrical conductivity of the electrode material. The specific capacitance of the electrode is calculated from the galvanostatic charge-discharge tests. The capacitance drops from 233 F g⁻¹ to 183 F g⁻¹ (78.5%) as the current density increases from 1 A g⁻¹ to 12 A g⁻¹, suggesting a fairly high rate capability. The good rate capability can be attributed to the unique and well-dispersed structure of the MnO₂-ink composite that shortens the diffusion path for ions, as well as the good interfacial contact between MnO₂ nanowires and the conductive support—carbon black that guarantees a high electrical conductivity.³⁵

The electrode was galvanostatically charged and discharged for 4500 cycles in order to evaluate its cycling stability. The applied current density was 10 A g⁻¹, so that the duration time of each charge/discharge cycle was controlled at around 34 s, as suggested by Stoller and Ruoff.¹⁵ The electrode maintains 96.28% of the initial specific capacitance after 4500 cycles. As seen from the inset in the Figure 5.13c, the CV curve remains in a quasi-rectangle shape, with only a slight diminution in the area. Moreover, during these cycles, the Coulombic efficiency keeps at about 100%. The good electrochemical stability reveals the high reversibility of the redox reaction taking place between the electrode and the electrolyte.

EIS was applied to further understand the change in electrochemical behavior of the electrode, the obtained Nyquist impedance plots are displayed in Figure 5.13d. These experimentally obtained data were fitted into an equivalent circuit by a non-linear least squares fitting algorithm. The equivalent circuit comprises R_{Ω} (equivalent series resistance), R_{ct} (charge transfer resistance), Z_w (Warburg resistance), CPE (constant phase element, representing double-layer capacitance) and C_p (pseudocapacitance). By comparing the Nyquist impedance plots before and after 4500 cycles, it can be seen that, the span of the semicircle in the high and medium-high frequency range enlarges, and the linear portion at low frequency range deviates from the imaginary axis at an enlarged angle, which indicate the charge transfer resistance and the Warburg resistance deteriorate after 4500 cycles. From the fitting results, it is known that the charge-transfer resistance increases from 0.95 Ω to 1.23 Ω , while the Warburg coefficient increases from 0.95 to 1.16 Ω s^{-1/2}. The increased charge transfer resistance may be caused by the divorce of active materials from the nickel foam current collector and the corrosion of nickel foam by dissolved oxygen in the electrolyte.^{35, 48} The increased Warburg resistance can be attributed to some degradation of the nanostructure of MnO₂ that impedes the ion diffusion.

Figure 5.14 (a) Specific capacitance of the composite MI_{0.606} synthesized under different speeds of magnetic stirring. (b) Specific capacitance of the composite MI_{0.606} synthesized in different dwell time. All the specific capacitance is calculated from CV at a scanning rate of 20 mV s⁻¹.

5.3.4 Factors affecting the electrochemical performance.

5.3.4.1 Effect of magnetic stirring.

Figure 5.14a compares the specific capacitance of the composites MI_{0.606} synthesized at 120 °C for 3 h but under different stirring rates. Compared with the composite synthesized statically, the composites synthesized under 250-rpm and 500-rpm stirring show improved specific capacitance, while the ones synthesized under 750-rpm and 1000-rpm stirring show lower specific capacitance. The improved specific capacitance can be attributed to the homogeneous structure and the good interaction between MnO₂ nanowires and carbon black, which are built with the aid of an appropriate stirring. However, as discussed in the previous section, magnetic stirring ensures the homogeneity of the synthesized composites, but meanwhile, it may aggravate the dissolution of the resulting MnO₂ and reduce the crystallinity of MnO₂. Low crystallinity leads to low electrical conductivity. Hence, an excessive rate of speed stirring causes a deteriorated specific capacitance. It should be pointed out that, regarding the statically synthesized composite, although phase separation was observed after synthesis, the inhomogeneity was offset in the follow-up step, where all the obtained products were well mixed by magnetic stirring with acetylene black and binder in order to fabricate the working electrode. As a result, this composite shows decent specific capacitance, even though the result is somewhat deceptive.

5.3.4.2 Effect of the reaction time

Here, the composite MI_{0.606} is taken as the example to illustrate the influence of reaction time on the electrochemical performance. Figure 5.14b shows the change in the specific capacitance with different reaction time. The specific capacitance first increases with the prolonged reaction time, and peaks at 187 F g⁻¹ when the reaction time is 3h. But after this, increased reaction time causes a decline in the specific capacitance. These results suggest the prolonged reaction time does not necessarily have a positive effect on the specific capacitance although it can improve the crystallinity of MnO₂. The phenomenon can be illustrated in this way. As displayed in the previous section that, the reaction time plays a significant role in controlling the morphology the synthesized composites. During pre-reaction, the rapid redox reaction between carbon and MnO₄⁻ gives rise to MnO₂ crystal nuclei, covering on the surface of carbon black particles. In the follow-up hydrothermal reaction process, these nuclei grow into nanofibers due to 1D growth habit. As the reaction time is prolonged, the crystallinity of MnO₂ improves, but which leads to a loss in surface area. Besides, while the MnO₂ nanofibers elongate and thicken, more carbon black is consumed. The relative deficiency of carbon black leads to more entanglement of MnO₂ nanofibers, which pose more barriers to ion diffusion. As a result, the electrochemical performance gets worse.

5.3.4.3 Effect of the content of Chinese ink

Here, the specific capacitance and the EIS response of the composites containing different content of Chinese ink are compared, in order to explore the effect of Chinese ink on the electrochemical performance. It can be seen from Figure 5.15a that, the MnO₂-ink composites show much better specific capacitance than pure MnO₂ and dried Chinese ink. The improved capacitance by Chinese ink can be explained in this way. For one thing, as discussed in the previous section, compared with pure MnO₂, the MnO₂-ink composite has a higher specific surface area and a better porous structure, which provide more adsorption sites for electrolyte ions and shorten their diffusion path. The shortened ion diffusion path is reflected in the lowered Warburg resistance in the EIS fitting results (as shown in Table 5.1). For another, the presence of carbon black enhances the electrical conductivity of the

composites, so the ESR is reduced.

Figure 5.15 (a) Specific capacitance of dried Chinese ink, pure MnO₂, and the ink-MnO₂ composites with different content of Chinese ink. The specific capacitance is calculated from the CV at a scanning rate of 20 mV s⁻¹, in which “ C_s ” denotes the specific capacitance is calculated based on only MnO₂, while “ C'_s ” denotes the specific capacitance is calculated based on both MnO₂ and Chinese ink.

Table 5.1 Calculated values of the components in the equivalent circuit.

Sample	R_Q/Ω	R_{ct}/Ω	$W/\Omega \cdot s^{-1/2}$	C_p/F
Pure MnO ₂	2.27	0.56	2.54	0.09
MI _{0.152}	1.33	0.97	0.73	0.69
MI _{0.303}	1.65	0.87	0.80	0.63
MI _{0.606}	1.68	0.84	0.52	0.68
MI _{0.909}	1.59	0.74	0.60	0.48

Admittedly, the MnO₂-ink composites display higher charge transfer resistance than pure MnO₂. The reason for this may lie in the possible presence of glue from Chinese ink, as well as the morphology of the composites, which evolves from nanoflowers to nanowhiskers to nanofibers, and to nanofiber bundles (as shown in Figure 5.9a–d) with increasing content of Chinese ink. A structure containing high-aspect-ratio fibers can have a close contact with the current collector, creating a good conducting network that facilitates the charge transfer.

5.3.5 MnO₂-ink//activated carbon asymmetric supercapacitors

An asymmetric supercapacitor that incorporate different positive and negative electrode materials promises to have a wider potential window and thus a higher energy density. In this work, the asymmetric SC was fabricated with the prepared MnO₂-ink composite and the commercial activated carbon as the positive and the negative electrode materials, respectively. The asymmetric SCs were denoted as “MI//AC” SCs. Prior to the assembly of the asymmetric SC, it is very important to determine the stable potential windows of the positive and the negative electrode materials and estimate their mass ratio, in order to take full advantage of their electrochemical performance. Thus, the CV test was performed on the prepared composite (MI_{0.606} as the example) and the commercial activated carbon in the 1.0 M Na₂SO₄ aqueous solution using a three-electrode cell. The scanning rate was set at 20 mV s⁻¹, and the potential windows for the composite and the activated carbon were 0 to 1.0 V (vs. SCE) and -1.0 to 0 V (vs. SCE), respectively. As seen in Figure 5.16a, both samples show CV curves with a quasi-rectangle shape, and nearly symmetric response current on reverse scanning, which suggests their ideal capacitive behavior.³⁵ Therefore, the potential window of the asymmetric SC (denoted as MI//AC) can be up to 1.8 V. The specific capacitance of the composite MI_{0.606} and activated carbon is thus calculated from the CV test by Equation. 5.4. Based on the potential windows and corresponding specific capacitance, the mass ratio of the composite MI_{0.606} to activated carbon can be thus determined by Equation 5.7 to fulfill the charge balance between the positive and the negative electrodes. In this case, the optimum mass ratio of m (MI_{0.606}): m (AC) is 1.37: 1.

Figure 5.16 (a) CV curves of MI_{0.606} and activated carbon at a scanning rate of 20 mV s⁻¹. (b) CV curves of the MI//AC asymmetric SC at a scanning rate of 20 mV s⁻¹ in different potential windows; the corresponding specific capacitance is calculated by CV. (c) CV curves of the MI//AC asymmetric SC within a potential window of 0 to 1.8V at different scanning rates. (d) The specific capacitance of the MI//AC asymmetric SC at different current densities; the inset shows the corresponding GCD curves. (e) Ragone plots for the MI//AC asymmetric SC in this work and the ones reported recently. (f) Cycling stability of the MI//AC asymmetric SC measured at 2 A g⁻¹ for 4000 cycles.

The asymmetric SC was assembled into CR2032-type coin cell with 1.0 M Na₂SO₄ aqueous solution as the electrolyte and a piece of filter paper as the separator. Figure 5.16b displays the CV of the MI//AC asymmetric SC at a scanning rate of 20 mV s⁻¹ within different potential windows. The quasi-rectangle shape of the CV curve indicates that the asymmetric SC has ideal capacitive behavior, even at a large potential window of 1.8 V. Besides, the calculated specific capacitance based on CV increases with enlarged potential windows. As such, the potential window was determined at 0 to 1.8 V. Figure 5.16c shows the CV curves at different scanning rates. The quasi-rectangle shape of the CV curves remains even when the scanning rate is raised to 200 mV·s⁻¹, suggesting fast the charge/discharge property.

The specific capacitance of the asymmetric SC was determined by galvanostatic charge/discharge measurement. The results are shown in Figure 5.16d. The asymmetric SC demonstrates nearly linear and symmetric charge and discharge curves, in agreement with the CV response, indicating ideal capacitive performance and high reversibility. The calculated specific capacitance is 93.4 F g⁻¹ (based on the total mass of positive and negative materials and without excluding the mass of Chinese ink) at 0.5 A g⁻¹, and declines to 38.2 F g⁻¹ when the current density is raised to 10 A g⁻¹. The non-obvious IR drop suggests a small ESR which is conducive to high power delivery in practical use.

The energy density and power density of this asymmetric SC are calculated from the galvanostatic charge/discharge measurement by the Eqs. 5.10 and 5.11, and plotted on the Ragone chart (power density vs. energy density). The calculated energy density is 42.0 Wh kg⁻¹ at the power density of 1815 W kg⁻¹, and remains to be 17.2 Wh kg⁻¹ even at a high power density of 44101 W kg⁻¹. As seen in the Ragone chart in Figure 5.16e that, compared with the MnO₂-based asymmetric SCs reported recently,^{11, 35, 42, 49-53} this MI//AC asymmetric SC exhibits comparable or higher energy density at the same power density level. Even operated at a high level of power density, this asymmetric SC can still demonstrate satisfying energy density.

The cycling life of this asymmetric SC was assessed by galvanostatically charging and discharging this device for 4000 cycles at a current density of 2 A g⁻¹. As seen in Figure

5.16f that, this asymmetric SC retains 94.67% of the initial capacitance after 4000 cycles, and little degradation is observed in the shape of charge/discharge curves, which indicate high electrochemical stability.

5.4 Conclusions

In this chapter, the stirring-driven hydrothermal reaction was applied to synthesize birnessite-type MnO₂ from the redox reaction between KMnO₄ and carbon. The commercial Chinese ink was used to provide well-dispersed carbon black particles as the carbon source. The resulting MnO₂ in-situ deposited onto the surface of the carbon black particles, forming an intimate contact. The morphology of the MnO₂-ink composites evolved from nanospheres to nanoflowers, nanowhiskers and nanofibers as the content of Chinese ink was increased or the reaction time was prolonged. The MnO₂ (0.316 g)-ink (0.606 g) composite synthesized under a stirring of 500 rpm showed a specific surface area of 158 m² g⁻¹, demonstrated a specific capacitance of 233 F g⁻¹ at 1 A g⁻¹, and maintained 96.28% of the initial specific capacitance after charged-discharged at 10 A g⁻¹ for 4500 cycles.

Asymmetric SCs with the MnO₂-ink composites as the positive electrode and activated carbon as the negative electrode were also assembled to study the practical performance. This MnO₂-ink//activated carbon asymmetric had an operation potential of 1.8 V, showed a specific capacitance of 93.4 F g⁻¹ at 0.5 A g⁻¹, and retained 94.67% of the initial capacitance after 4000 cycles of charging/discharging. In addition, this asymmetric SC displayed a high energy density of 42.0 and 17.2 Wh kg⁻¹, at the power density of 1815 and 44101 W kg⁻¹, respectively. The energy density and power density are comparable to those of asymmetric SCs made with the composite of MnO₂ and CNTs/graphene.

In short, this chapter has proven that commercial Chinese ink can be directly used to react with KMnO₄ to produce MnO₂. The usage of ready-made Chinese ink saves the trouble of pretreating the raw carbon source and lowers the fabrication cost. What's more, the high dispersion of carbon black in Chinese ink ensures the homogeneity of the MnO₂-ink composite that is favorable to good electrochemical performance.

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Chapter 6

Nanostructured NiCo₂O₄-Ink Composites for Supercapacitors

This chapter tests the hypothesis that Chinese ink can be used as an inert additive to improve the dispersion of transition metal oxides and enhance their electrochemical performance. For this purpose, nickel cobaltite (NiCo₂O₄) was taken as the example, which was synthesis from chemical co-precipitation and subsequent calcination. The effect of Chinese ink on the properties of the NiCo₂O₄-ink composites was investigated, including the morphology, the crystal structure, the specific surface area and pore size distribution, and the electrochemical behavior. The obtained results confirm the assumption that the presence of Chinese ink can efficient alleviate the agglomeration of NiCo₂O₄, improve the specific surface area and thus boost the electrochemical performance.

6.1 Introduction

Figure 6.1 Crystal structure of spinel NiCo₂O₄.¹

Among numerous transition metal oxides as the electrode materials for pseudocapacitors, the spinel binary metal oxide NiCo₂O₄ (or NCO for short) stands out for its high theoretical capacitance and good electrical conductivity, as well as some other merits such as low cost, environmental friendliness and natural abundance. Figure 6.1 displays the crystallographic structure of NiCo₂O₄, in which the nickel atoms occupy the octahedral sites and the cobalt atoms locate at the octahedral and tetrahedral interstices.² Some research has interpreted the structural formula of NiCo₂O₄ as Co_{1-x}²⁺Co_x³⁺[Co³⁺Ni_x²⁺Ni_{1-x}³⁺]O₄ ($0 \leq x \leq 1$), in which both redox couples of Ni³⁺/Ni²⁺ and Co³⁺/Co²⁺ are present.³⁻⁵ Benefiting from the crystal structure, NiCo₂O₄ shows an electrical conductivity two orders of magnitude higher than that of monometallic NiO or Co₃O₄.⁶ Besides, NiCo₂O₄ has richer oxidation states, and thus possesses high capacitance than NiO and Co₃O₄.

NiCo₂O₄ with nanostructures can exhibit excellent capacitive performance because of the abundant surface area and the shortened ion and charge transportation paths.⁷ Many articles have reported the various nanostructured NiCo₂O₄, such as 0D nanoparticles,⁸ 1D nanoneedles⁹/nanorods/¹⁰nanowires¹¹, 2D nanosheets¹², and 3D porous network¹³. Nanostructured NiCo₂O₄ can be synthesized by many methods, including low-temperature chemical co-precipitation and subsequent calcination,^{9, 10} hydrothermal reactions,^{11, 14, 15} electrodeposition,¹⁶ and sol-gel processing.¹⁷ Among these methods, low-temperature chemical co-precipitation accompanied by subsequent calcination is a simple and scalable approach to synthesizing nanostructured NiCo₂O₄. However, self-assembled NiCo₂O₄ tends to agglomerate during synthesis, which badly impairs the electrochemical performance. In some previous reports, surfactants (such as CTAB¹⁸ or PVP¹⁹) are used to

tune the microstructure and the pore size of NCO.

Considering the ready-made colloidal suspension system of Chinese ink, it was assumed that Chinese ink could be utilized as an additive for synthesizing nanostructured NiCo₂O₄ by taking advantage of its well-dispersed carbon black particles and the existing glue. To test this idea, Chinese ink was added into the nickel and cobalt precursor solution during the chemical co-precipitation process, and applied magnetic stirring to ensure the homogeneity of the mixture. The precipitated powder was subjected to calcination at different temperatures. The products were characterized by XRD, XPS, and Raman spectroscopy to confirm the formation of NiCo₂O₄. The morphology, surface information and electrochemical behavior of the NiCo₂O₄-ink (or NCO-ink for short) composites were also investigated in order to probe into the effect of Chinese ink. The results indicate the addition of Chinese ink can alleviate the aggregation of NiCo₂O₄ nanosheets, enlarge the specific surface area, and boosts the specific capacitance of NiCo₂O₄.

6.2 Experimental Methods

6.2.1 Synthesis of NCO-ink composites

Figure 6.2 Experimental flow diagram for the synthesis of NCO-ink composites.

Figure 6.2 illustrates the synthesis process of NCO-ink composites, which includes two steps: the low low-temperature chemical co-precipitation to form the precursors and the subsequent calcination to convert the precursors into cobalt–nickel bimetallic oxide. Chinese ink was mixed with the starting materials in the first step.

In a typical experimental procedure, three mixtures needed to be prepared in advance, including a diluted Chinese ink suspension (S_1), a solution containing Co^{2+} and Ni^{2+} (S_2) and a precipitant solution (S_3). A certain amount of Chinese ink was added into 20 mL of deionized water. Under magnetic stirring, this surfactant-stabilized carbon black ink was quickly dispersed into water, forming a homogeneous suspension (S_1). 1 mmol of nickel acetate tetrahydrate ($\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) and 2 mmol of cobalt acetate tetrahydrate ($\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) were dissolved in 30 mL of deionized water to form the second solution (S_2). 12 mmol of urea was dissolved in 10 mL of deionized water to form the third solution (S_3). The S_1 and S_2 were first mixed and stirred for 5 min, and then the S_3 was added to the ($S_1 + S_2$) mixture. The resulting ($S_1 + S_2 + S_3$) mixture was transferred into a screw-cap reagent bottle, where the mixture was heated at 90 °C in a water bath, and stirred at 500 rpm for 4 h.

After the reaction was completed, the bottle cooled down naturally. The precipitated products were collected by centrifugation, and washed by deionized water (three times) and ethanol (one time) to remove impurities. The purified products were dried in a vacuum oven at 60 °C for 12 h. Then the dried grayish blue or black (when ink content was high) powder was calcinated at varied temperatures in air for 2 h with a slow ramping rate of 2 °C min⁻¹. The obtained black powder was ready for further characterization. The composites were labeled as NCO-ink_x, where NCO is NiCo₂O₄ and x denotes the addition amount of Chinese ink in grams.

6.2.2 Material characterization

The morphology and microstructure of the composites were examined by FESEM (JEOL, JSM-7600F, operated at 5 kV) and TEM (JEOL, JEM-2010 UHR). The crystallographic structures of the composites were characterized by XRD (Shimazu, XRD-6000) operated

at 40 kV and 30 mA, and equipped with Cu K α radiation ($\lambda = 0.15406$ nm). The elemental composition and chemical states of the elements were studied by XPS (Thermo Scientific ESCALab 250Xi), equipped with a monochromatic Al K α (1486.7 eV) x-ray source. All spectra were calibrated by using C 1s peak (284.5 eV) as the reference. The peak fitting was done on the software XPSPEAK41. The Raman spectra were recorded on Renishaw InVia Raman Microscope, equipped with Argon ion laser source (514 nm). The content of NiCo₂O₄ was determined by TGA, where the samples were heated at a ramping rate of 20 °C min⁻¹ to 800 °C in air. The specific surface area and pore structure were analyzed by physical adsorption of nitrogen at 77 K, performed on TriStar II 3020 surface area analyzer from Micromeritics. The specific surface area was obtained by the Brunauer–Emmett–Teller (BET) method and the pore size and distribution were analyzed by Barrett-Joyner-Halenda (BJH) method.

6.2.3 Electrochemical Measurement

Fabrication of three-electrode cells

The electrochemical performance of the prepared NCO-ink composites was measured in a three-electrode cell, with a platinum plate as the counter electrode, an Hg/HgO electrode as the reference electrode, and a 2 M KOH aqueous solution as the electrolyte. To prepare the working electrode, the as-prepared sample was first mixed with acetylene black and polyvinylidene fluoride (PVDF) in a mass ratio of 80: 10: 10. For convenience, the PVDF was dissolved in 1-methyl-2-pyrrolidone (NMP) with a ratio of 5% in advance. The resulting mixture was kept stirring for 8 h to form a smooth slurry. If necessary, a certain amount of ethanol was added to adjust the viscosity of the slurry. The slurry was then spread onto a nickel foam current collector (about 1 cm²) by a flat spatula and dried in a vacuum oven at 60 °C for 12 h. The loading density of the electrode materials was around 5.0 mg cm⁻². The resulting electrode was pressed by a hydraulic press with a pressure of 6 MPa for 10 s to ensure a good contact between the active materials and the current collector, and then immersed in the electrolyte for 15 min before the test to ensure a full wetting of the electrode.

Electrochemical Measurement of three-electrode cells

The electrochemical behavior of the composites was measured by cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS), which were done on an electrochemical workstation (BioLogic, VSP). The CV was conducted within a potential window of -0.05 to 0.65 V (vs. Hg/HgO), at different scanning rates. The GCD was performed in a potential window of 0.125 to 0.525 V (vs. Hg/HgO) at different current densities. The specific capacitance is calculated from the galvanostatic discharge curve, according to the equation:

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (6.1)$$

where I is the applied current, Δt is the discharging time and ΔV is the operating voltage window excluding IR drop.

EIS was done at the open circuit potential over a frequency range from 100 kHz to 10 mHz, with an AC amplitude of 5 mV. The obtained data were fitted into equivalent circuits by the built-in function in the testing software. For cycling stability test, the electrode was continuously charged and discharged at a constant current density of 10 A g⁻¹ for 3000 cycles.

6.3 Results and Discussion

6.3.1 Formation mechanism of NCO-ink

The NCO-ink composites were prepared in two steps, including a simple chemical co-precipitation process and a subsequent calcination process. In the chemical co-precipitation process, urea was used as the precipitating agents. Once the reaction temperature goes up to 85 °C, HMT will first decompose to release NH₃ and CO₂, which will further hydrolyze to produce OH⁻ and CO₃²⁻, as described in the following equations:^{20, 21}

The OH⁻ and CO₃²⁻ anions will react with metal cations (Ni²⁺ and Co²⁺) to produce the cobalt-nickel bimetallic carbonate hydroxide salt by the following reaction:

The resulting cobalt-nickel bimetallic carbonate hydroxide hydrate will convert into the cobalt–nickel bimetallic oxide (NiCo₂O₄) during the heat treatment in accompanied by the release of CO₂ and H₂O, as described below:

6.3.1.1 XRD analysis

Figure 6.3 XRD patterns of (a) the NCO precursor, dried ink, pure NCO (calcinated at 300 °C), and the NCO-ink_{3.6} composite (calcinated at 300 °C); (b) pure NCO and the NCO-ink_{3.6} composites calcinated at different temperatures.

XRD was conducted to investigate the phase change during the heat treatment and to confirm the formation of NCO. Figure 6.3a shows the XRD patterns of the composite calcinated at 300 °C and its precursor. For comparison, this figure also includes the patterns of pristine dried ink and pure NCO. The precursor can be indexed to the cobalt-nickel bimetallic carbonate hydroxide hydrate phase (PDF #00-033-0429, see Appendix), while

the calcinated composite is indexed to the cubic spinel NiCo₂O₄ phase (PDF #04-013-0797, see Appendix). In the calcinated composite, the peaks at $2\theta = 31.2^\circ$, 36.7° , 65.0° , and 77.0° are respectively indexed as (311), (400) (440), and (533) crystalline planes of spinel NCO, in line with those in the pattern of pure NCO. It is noteworthy that the peaks in these patterns are broad and dispersive, indicating the low crystallinity nature of the NCO synthesized by this method. Moreover, the presence of amorphous carbon black (from Chinese ink) can also attenuate the peak intensity or even overshadow some weak peaks. However, no peak from the precursor is seen in the pattern of the calcinated composite, implying the precursor has completely decomposed during calcination. Figure 6.2b compares the XRD patterns of the composite NCO-ink_{3.6} calcinated at different temperatures. The characteristic diffraction peaks at $2\theta = 31.2^\circ$, 36.7° , 65.0° begin to show up since the composite calcinated at 200 °C. This suggests that the precursor has been successfully converted to NCO after calcinated at 200 °C for 2 h. Based on the XRD results, it seems that higher calcination temperature does not have an evident effect on the crystallinity of the NCO. However, higher calcination temperature has its negative side as the carbon black can be rapidly oxidized by air at high temperature (which will be discussed later).

6.3.1.2 Raman spectroscopy

Figure 6.4 Raman spectra of the NiCo₂O₄, precursor, pure NiCo₂O₄, and NCO-ink_{3.6} calcinated at different temperatures: (a) 100 to 1000 cm⁻¹; (b) 100 to 2200 cm⁻¹.

Raman spectroscopy is commonly applied to provide the vibrational information about

molecules that can be thus used for material deification and quantitation. Herein Raman spectroscopy analysis was conducted to confirm the co-existence of NCO with carbon black (from Chinese ink) in the prepared composites, as well as to observe the change of the involved carbon black under different calcination temperatures. As seen Figure 6.4a, in the spectra of pure NCO and calcinated composites, two evident bands centered at around 654 and 182 cm⁻¹ correspond to the A_{1g} and the E_{2g} modes of NCO, respectively; while the other two weak bands centered at around 458 and 506 cm⁻¹ correspond to the E_g and the F_{2g} mode of NCO, respectively.^{22, 23} In general, five bands are expected to be shown in the Raman spectra of spinel oxides. For, Co₃O₄, it shows three intensive bands at 693, 526 and 485 cm⁻¹.²⁴ The band at 693 cm⁻¹ is assigned to the vibration of Co³⁺, which is a highly symmetric mode and largely decided by the octahedral oxygen ions. This band, however, is very sensitive to the substitution of Ni²⁺ ions, because the Ni²⁺ substitution can not only lower the concentration of Co³⁺/octahedral O²⁻, but also induce lots of disorder in the lattice and disturb the symmetric mode. As a result, this band turns weak and shifts to lower frequency upon being substituted by Ni²⁺ ions. As for the bands at 526 and 485 cm⁻¹, they are attributed to the combined vibration of octahedral and tetrahedral oxygen atoms in the lattice. Similar to the band at 693 cm⁻¹, these two bands broaden with the Ni²⁺ substitution as the Co³⁺/tetrahedral O²⁻ decreases, and Ni²⁺/octahedral O²⁻ forms that is predicted to have a Raman feature in lower frequency than Co³⁺/octahedral O²⁻.^{24, 25} Compared with pure Co₃O₄, the synthesize composites show weaker bands at lower frequency, corresponding to Co-O and Ni-O vibrations. However, such bands are not remarkable in the spectrum of the precursor. The results imply the cobalt-nickel bimetallic carbonate hydroxide hydrate has been successfully converted into NCO after calcination at 200 °C or above for 2 h, which is in accord with the XRD analysis. Nevertheless, these Raman results suggest higher calcination temperature seems not to have an obvious effect on the crystal structure of the resulting NCO.

One the other hand, the Raman was also applied to investigate the evolution of carbon black under different calcination temperatures. As seen in Figure 6.4b, in the spectra of the precursor and the composites calcinated at temperatures of ≤ 300 °C, there are two broad but evident bands concerted at about 1360 cm⁻¹ and 1590 cm⁻¹, corresponding to the D and

the G band of carbon, respectively. The G band—the E_{2g} mode of graphite, represents the bond-stretching motion of sp²-carbon atoms in a 2-D hexagonal lattice; while the D band—the breathing mode of rings of κ -point phonons of A_{1g} symmetry, represents the defects and disorders in the graphitic carbon layers.^{23, 26} These two characteristic bands can be considered as the evidence for the presence of carbon black. The D and G bands turn weak in intensity with the increasing calcination temperature, and eventually become discernible when the calcination temperature is higher than 300 °C. This indicates that high calcination temperature causes the loss of carbon black in the composites, which is due to the intensified oxidation of carbon black by air. The finding is in line with the TGA analysis.

6.3.1.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive spectroscopic technique that has been widely used to examine the elemental composition and the oxidation states of elements existing within the composite. Here, XPS was applied to help confirm the formation of NCO. Three different samples were used as examples: (1) NCO-ink_{3.6} before calcination; (2) NCO-ink_{3.6} calcinated at 200 °C; and (3) NCO-ink_{3.6} calcinated at 300 °C. The obtained XPS spectra are shown in Figure 6.5. The survey spectra (Figure 6.5a) reveal the presence of Ni, Co, O and C, and absence of other impurity elements. As such, it can be claimed that the addition of Chinese ink into the co-precipitation solution did not introduce a considerable amount of impurities might result in unexpected reactions. The high-energy-resolution (core-level) spectra of Ni 2p and Co 2p are deconvoluted by the Gaussian fitting method, performed with the software XPSPEAK 4.1. The Ni 2p spectrum of the precursor shows two major peaks at 857.4 eV and 874.8 eV with a spin-energy separation of 17.4 eV, accompanied by two satellite peaks at 863.0 eV and 880.4 eV. They correspond to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively, which are the characteristic peaks of Ni²⁺. Similarly, the Co 2p spectrum also shows two characteristic peaks at 782.5 eV (Co 2p_{3/2}) and 798.1 eV (Co 2p_{1/2}), with a spin-energy separation of 15.6 eV, indicating the presence of Co²⁺.²⁷

Figure 6.5 (a) XPS survey spectra of the composite NCO-ink_{3.6} before calcination and after calcination at 200 °C and 300 °C; (b) O 1s core-level XPS spectrum of the composite calcinated at 200 °C; (c, e, g) Ni 2p core-level XPS spectra: (d, f, h) Co core-level XPS spectra. (c, d) the NCO precursor, (e, f) NCO-ink_{3.6} calcinated 200 °C, and (g, h) NCO-ink_{3.6} calcinated 300 °C.

It is thus can be known that no redox reaction occurs during the chemical co-precipitation process, and both Ni and Co exist in the precursor with a single valence state. By contrast, in the calcinated composites, both Ni 2p and Co 2p core-level spectra can be best fitted with two spin-orbit doublets and two shakeup satellites at the high binding energy sides (labelled at “Sat.”), meaning that both Ni and Co are present in two valence states. For example, in the Ni 2p spectrum of the 200 °C-calcinated composite, the fitted peaks at 857.2 eV and 875.0 eV are ascribed to Ni²⁺, while the fitted peaks at 858.7 eV and 876.7 eV are ascribed to Ni³⁺.²⁸ In addition, Co in this composite demonstrates the similar XPS spectrum with the only difference in the binding energy. Table 5.1 summarizes the curve fitting results of these three samples, which are in agreement with the previous reports.^{23, 28-32}

Table 6.1 XPS spectral fitting parameters for Ni 2p_{1/2}, Ni 2p_{3/2}, Co 2p_{1/2} and Co 2p_{3/2}: binding energy (eV), and spectral component separation (eV).

Samples		2p _{3/2} Peak position (eV)			2p _{1/2} Peak position (eV)			Δ_{BE} (eV)
		2 ⁺	3 ⁺	Sat.	2 ⁺	3 ⁺	Sat.	
Ni	Precursor	857.4	—	863.0	874.8	—	880.4	17.4
	200 °C	857.2	858.7	863.5	875.0	876.9	881.3	17.5
	300 °C	855.0	856.7	861.7	872.8	874.6	879.8	17.4
Co	Precursor	782.5	—	786.7	798.2	—	802.3	15.6
	200 °C	782.4	783.9	788.0	798.3	799.8	804.4	15.6
	300 °C	780.2	782.2	785.7	795.7	797.7	803.5	15.5

Besides, as seen in Figure 6.5b, the O 1s core-level XPS spectrum of the composite calcinated at 200 °C can be deconvoluted into four components, denoted as O1, O2, O3 and O4. The well-defined component O1 at 529.8 eV is attributed to the typical metal-oxygen bonds.²⁹ The component O2 at 531.4 eV is related to oxygen in OH⁻ groups, whose presence indicates some oxygen atoms are replaced by OH⁻ groups, or the NCO is somewhat hydroxylated.³³ The component O3 is due to defect sites with low oxygen coordination as well as some contaminants.^{29, 33} The component O4 is attributed to the combination of physically/chemically absorbed water at or near surface.²⁹ These XPS analysis results confirm that the calcination process not only converts the cobalt-nickel bimetallic carbonate hydroxide into cobalt-nickel bimetallic oxides, but also partially

oxidize the cobalt and nickel to higher valence. The coexistence of Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺, which is beneficial to the electrochemical performance of composites.

6.3.1.4 Thermogravimetric Analysis (TGA)

To better understand the calcination process, the precursor and the dried Chinese ink powder were analysis by TGA, in which the samples were heated to 800 °C with a ramping rate of 20 °C per minute, under the atmosphere of air. As seen in Figure 6.6, the pristine ink (dried at the same temperature as the precursor before TGA) undergoes two remarkable steps of weight loss at around 320 °C and 480 °C. The weight loss around these two temperatures can be respectively attributed to the thermal decomposition of some matters used in the Chinese ink (i.e., glue and other additives) and the oxidation of carbon black by air that converts carbon black into CO₂ or CO gas. As a result, the precursor also experiences the similar weight loss at these two temperature ranges. Besides, for the precursor, the evident weight loss at 280 °C, which is indicated by a sharp peak in the derivative TGA curve, is due to the decomposition of the precursor that releases H₂O and CO₂ gas, and produces NCO.

Figure 6.6 TGA and DTG curves of the NCO precursor and air-dried pristine ink, which were heated to 800 °C with a ramping rate of 20 °C min⁻¹, under the atmosphere of air.

6.3.2 Morphology study

Figure 6.7 SEM images of (a) pristine Chinese ink calcinated at 300 °C; (b) pure NCO calcinated at 300 °C; (c) the precursor of the NCO-ink_{3,6} composite; and (d) the NCO-ink_{3,6} composite calcinated at 300 °C

6.3.2.1 Effect of Chinese ink

The morphology and microstructure of the synthesized NCO-ink composites were examined by FESEM and TEM. Figure 6.7a shows the SEM image of carbon in pristine Chinese ink. According to the manufacturer, the carbon – as the black pigment – used in this Chinese ink is commercial carbon black. Different from soot or lampblack that is widely used in traditional Chinese ink, commercial carbon black is produced under controlled conditions in order to obtain desired properties to fulfill the requirements of different applications. Therefore, carbon black has smaller particle sizes and a narrower particle size distribution than soot and lampblack.³⁴ As seen in this SEM image, the carbon

black particles are present in an aciniform shape, similar to a bunch of grapes, rather than in an independently dispersed spherical shape as may be expected. The particle size of these constituent primary particles ranges from 50–100 nm, estimated from the SEM image. On the other hand, from the TEM image (Figure 6.8c) it can be seen that the constituent primary particles are actually composed of numerous imperfect graphite layers oriented around the center. The graphite layers endow carbon black with quasi-crystal features that can be detected by XRD or Raman spectroscopy.

Figure 6.7c, d demonstrate the morphology of the composite NCO-ink_{3.6} before and after calcination at 300 °C for 2 h, in which NCO is present in the shape of nanoflakes, while the carbon black particles are inserted into the space between NCO nanoflakes. It is seen that, these two samples share the similar morphology, indicating that no marked change occurs in calcination at this temperature. The presence of carbon black particles dramatically alleviates the aggregation of NCO and create many voids that can benefit the penetration of ions. By contrast, the sample prepared under the same conditions but without the addition of Chinese ink (Figure 6.7b) shows an agglomerated structure. These thick layers will become barriers to the ion diffusion during charging/discharging.

TEM was performed to further explore the microstructure of the synthesized composite. Figure 6.8a,b show the representative TEM images of the NCO-ink_{3.6} composite (NCO-ink_{3.6} signifies that that composite was made with 3.6 g of Chinese ink) calcinated at 300 °C. It is easy to distinguish carbon black particles from the NCO nanoflakes because the carbon black particles are composed of multiple graphite layers surrounding a center, rather than regular lattice fringes as NCO nanoflakes. The HRTEM image of NCO nanoflakes demonstrates two distinct lattice fringes with a lattice spacing of 0.25 nm and 0.21 nm, corresponding to the (311) and (400) lattice planes of spinel NCO, respectively. As seen in these TEM images, the NCO nanoflakes are in close contact with carbon black particles. Such a good contact between NCO and carbon black can be conducive to fast electron transportation.

Figure 6.8 (a, b) TEM images of the NCO-ink_{3.6} composite calcinated at 300 °C; (c) TEM image of pristine carbon black used in the Chinese ink; the inset is a schematic drawing of the structure of carbon black; (d) HRTEM of NCO nanoflakes.

Based on the FESEM and TEM results, the formation of NCO can be thus concluded in this way. On the first step, when the temperature reaches a certain level, urea will gradually hydrolyze to produce OH⁻ and CO₃²⁻ cations (As indicated by Equation 6.2–6.4). These cations cause the co-precipitation of Ni²⁺ and Co²⁺ anions, producing the cobalt-nickel bimetallic carbonate hydroxide hydrate precipitate (As indicated by Equation 6.5). The precipitated precursor can cover or wrap the carbon black particles from Chinese ink. The high dispersity of the carbon black particles as well as the action of vigorous magnetic

stirring ensure a uniform precipitation of the precursor onto the carbon black particles. Otherwise, obvious phase separation will occur at the end of the reaction without the magnetic stirring, where a lower part containing more carbon black particles and an upper part containing more pale blue precipitate were observed. This is because the carbon black particles covered (or wrapped) by the precipitate will first settle down under gravity, but the subsequently resulting precipitate can only cover the top of the carbon black layer. At the end of the co-precipitation reaction, the homogeneous carbon black-NCO precursor can be obtained. On the second step, the precursor gradually converts into the NCO as the temperature rises at a slow rate. It should be pointed out that an expected structure combining carbon as the substrate and epitaxially grown NCO as in not achieved in these NCO-ink composites as reported in other carbon nanomaterials.^{1, 35, 36} The main reason for this is that the carbon black particles are not large enough to provide sufficient anchoring sites for NCO. Conversely, the adjacent NCO nanoflakes may aggregate into larger ones that will wrap the carbon black particles. Even so, the presence of carbon black particles still holds great significance for the structure of the composites as it prevents the agglomeration of NCO and thus improves the overall specific surface area.

6.3.2.2 Effect of calcination temperature

Figure 6.9a–f demonstrates the SEM images of the composites NCO-ink_{3,6} calcinated at different temperatures. As seen, the composites calcinated at 200 °C, 250 °C and 300 °C well preserve the morphology of the precursor, in which carbon black particles are inserted into the NCO nanoflakes, creating many voids. However, with the increasing calcination temperature, the content of carbon black particles reduces obviously because of the oxidation of carbon black by air.

Figure 6.9 SEM images of the composites NCO-ink_{3,6} calcinated at different temperatures: (a) precursor; (b) 200 °C; (c) 250 °C; (d) 300 °C; (e) 350 °C and (f) 400 °C.

Evidence of this can be found from the Raman spectroscopy analysis (Figure 6.4) as well as the TGA analysis (Figure 6.10). In the TGA curves, the low-temperature-calcinated samples (200 °C, 250 °C and 300 °C), which preserve more carbon black during calcination, undergo a sharp weight loss in the temperature range of 300 °C to 500 °C. In contrast, the

high-temperature-calcinated samples (350 °C and 400 °C) only show a little weight loss in this temperature range. Higher calcination temperature leads to a smaller retained amount carbon black in the composite, which is indicated by the higher weight retention at 600 °C. It is noteworthy that in metal oxides can function as the catalyst to lower the oxidation temperature for carbon black. Hence, by comparing the DTG curves in Figure 6.10b and Figure 6.6, it can be seen that the center of the peak that reveals the intensive oxidation of carbon black shifts from around 480 °C to 400 °C. Consequently, the calcination temperature should be well controlled in order to achieve the optimum condition for the growth of NCO nanoflakes without sacrificing carbon black. Otherwise, in the absence of sufficient carbon black, contiguous NCO nanoflakes tend to fuse together into clusters. This will reduce the overall surface area and the pore size. Evidence can be found from the analysis on the BET surface area (discussed below).

Figure 6.10 (a) TG and (b) DTG curves of the composite NCO-ink_{3.6} calcinated at different temperatures.

6.3.3 Study on specific surface area

To further prove the role of Chinese ink in improving the structure of NCO, the analysis on the surface area and the pore size of was performed. The specific surface area was determined from the nitrogen adsorption-desorption isotherms at 77 K by the Brunauer–Emmett–Teller (BET) method, and the pore size was estimated from the Barrett–Joyner–Halenda (BJH) pore size distribution plots. Figure 6.11a depicts the nitrogen adsorption-desorption isotherms (77 K) of different samples calcinated at 300 °C. These isothermals

can be categorized as the Type IV isothermals, characterized by a hysteresis loop, which indicates the presence of mesoporous structure in the samples.^{23, 29} For pure NCO, the hysteresis loop is observed in the range of 0.4 to 1.0 P/P_0 ; whereas for the dried ink, it is observed in the range of 0.8 to 1.0 P/P_0 . For the NCO-ink composites, with the increasing loading mass of ink, the shape of the isothermal gradually changes from “NCO-dominated” to “ink-dominated”. A similar trend is also observed in the BJH pore size distribution plots, where the pure NCO demonstrates a narrow pore size distribution centered at around 4 nm, and dried ink shows a broad pore size distribution ranging from 4 to 50 nm. For low-ink-content composites (NCO-ink_{0.9} and NCO-ink_{1.8}), the presence of Chinese ink shifts the center of the peak to 15 nm; while for high-ink-content composites (NCO-ink_{3.6} and NCO-ink_{7.2}), the presence of Chinese ink not only shifts the center of the peak, but also broadens the pore size distribution.

Figure 6.11 (a) Nitrogen adsorption-desorption isotherms of ink, pure NCO and NCO-ink composites with different content of ink, all the samples were calcinated at 300 °C; (b) the corresponding BJH pore size distribution plots, determined from the adsorption branch of the N₂ isothermals; (c) the calculated BET specific surface area and BJH desorption average pore diameter.

It can be thus concluded that the carbon black particles function well as the spacers to create large voids in the composites. As a result, the NCO-ink composites show higher BET specific surface area (Figure 6.11c) and larger BJH adsorption average pore size than pure NCO. The composite with 1.8 g of Chinese ink has the largest BET specific surface area of $217 \text{ m}^2\cdot\text{g}^{-1}$. Nonetheless, due to the low specific surface area nature of ink (calcinated at this temperature), excessive addition of Chinese ink will decrease the specific surface area.

Figure 6.12 (a) Nitrogen adsorption-desorption isotherms of the NCO-ink_{3.6} composites calcinated at different temperatures; and (b) the corresponding BET specific surface area and BJH desorption average pore diameter.

On the other hand, the effect of calcination temperature on the surface area and the pore structure was also examined. As seen in Figure 6.12a, the composites calcinated at different temperatures share the similar Type IV isothermals, indicating the mesoporous structure is still preserved at higher calcination temperatures. The increasing calcination temperature

tends to increase the specific surface and the average pore size, but meanwhile, it also broadens the pore size distribution (Figure 6.12b,c). One possible reason for this is because the removal of glue on the carbon black surface at a high temperature breaks the carbon black cluster and improves the dispersion of carbon black particles in the composite. However, an excessive calcination temperature will cause counterproductive result as it can burn the majority of carbon black. The enlarged average pore size can be ascribed to the voids created by the removal of carbon black particles.

In conclusion, with an appropriate addition amount of Chinese ink, as well as a proper calcination temperature, the composite can be equipped with a large specific surface area and a decent mesoporous structure, which are the desired features for an electrode candidate of SCs.

6.3.4 Electrochemical studies.

The pseudocapacitive behaviors of the synthesized NCO-ink composites were investigated by CV, GCD and EIS, which were performed in a three-electrode cell with a platinum plate as the counter electrode, a Hg/HgO electrode as the reference electrode and a 2 M KOH aqueous solution as the electrolyte.

Here, the composite NCO-ink_{1.8} (calcinated at 200 °C) is taken as the example to illustrate the typical electrochemical behavior of these composites. Figure 13a displays the representative CV curves in a potential window of -0.05 to 0.65 V (vs. Hg/HgO) at different sweeping rates ranging from 5 to 60 mV·s⁻¹. In each CV curve, there is a pair of well-defined peaks, the pseudocapacitive feature of the electrode. The pair of peaks is mainly ascribed to the Faradaic redox reactions between OH⁻ anions and Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺ transitions. Since the redox potentials of Co²⁺/Co³⁺ and Ni²⁺/Ni³⁺ are very close, the two peaks overlap and integrates into a pair of peaks. The redox reactions can be expressed as below:^{32, 37}

Figure 6.13 (a) CV curves of the composite NCO-ink_{1.8} at different scanning rates ranging from 5 to 60 mV s⁻¹; the inset depicts the plot of anodic and cathodic peak current density against scanning rate $v^{1/2}$. (b) GCD curves of the composite NCO-ink_{1.8} at different current densities ranging from 1 to 20 A g⁻¹ within a potential window of 0.125 V to 0.525 V (vs. Hg/HgO). (c) The specific capacitance of dried ink and the composite NCO-ink_{1.8} at different current densities. (d) Nyquist plot of the composite NCO-ink_{1.8} and its corresponding fitting curve and equivalent circuit.

As the scanning rate increases, the anodic and cathodic currents increase, with slight positive/negative shifts in the anodic/cathodic peaks that are due to the strengthened electric polarization. This indicates the electrochemical process is controlled by the diffusion of ions, since the ions can diffuse faster and give rise to a higher current response at a higher scanning rate. Besides, from the inset in Figure 13a, it is seen that there is a good linear relationship between the anodic/cathodic peak currents and the square root of the scanning rate, which also reveals the redox reaction is diffusion-controlled.²⁹ In comparison, the CV curve of pristine dried Chinese ink (at a scanning rate of 60 mV s⁻¹) shows a very small area, indicating its low capacitance. It should be pointed out that the

pair of weak peaks seen in the CV of dried ink is owing to some redox reactions between the nickel foam and the electrolyte. In view of this, the capacitance contribution from the ink and the current collector is simply ignored.

To quantify the specific capacitance of the composite, GCD measurement was carried out in a potential window of 0.125 to 0.525 V vs HgO/Hg, at different current densities. As seen in Figure 13b, the charge and discharge curves are non-linear, with a plateau in the range of 0.25–0.32 V and 0.30–0.23V (at 1 A g⁻¹), respectively, which are corresponding to the redox reactions. Only a very small IR drop is observed, suggesting the low equivalent series resistance of this electrode. The calculated specific capacitance is displayed in Figure 13c. However, for this sample, only 60% of the initial specific capacitance (based on 1 A g⁻¹) is retained when the current density is increased by 20 times.

Electrochemical impedance spectroscopy (EIS) analysis was performed to probe into the detailed electrochemical behavior of the working electrode. Figure 13d shows the experimentally obtained and the fitted Nyquist plots, as well as the corresponding equivalent circuit. As observed, the curve has an intercept of 0.5 Ω at the real axis, which is known as the equivalent series resistance (ESR), a combination of (1) the intrinsic electrical resistance of the electrode and the current collector; (2) the ionic resistance of the electrolyte; and (3) the contact resistance between the electrode and the current collector.³⁸ Besides, the curve shows distinct deviation from the vertical line in the low-frequency range, which means the electrochemical process is limited by ion diffusion at low frequencies. It should be pointed out, a semicircle that represents the Faradaic resistance (charge transfer resistance) is not evident in this case. More information can be extracted from the equivalent circuit, which is composed of five components: R_{Ω} , R_{ct} , CPE , Z_w and C_p . R_{Ω} can be simply equated with the ESR. R_{ct} reflects the charge transfer resistance, i.e., the kinetic resistance in the ion transfer at the electrode-electrolyte interface, and/or the intrinsic charge transfer resistance of the electrode.³⁸ CPE , a constant phase element, represents the electrical double-layer capacitor (imperfect capacitor).²⁹ Z_w is a diffusion-controlled element, denoting the Warburg impedance that is attributed to the diffusion resistance of the electrolyte ions within the porous electrode.²⁹ C_p is a Faradaic

pseudocapacitor, denoting the reversible redox reactions between the electrode and electrolyte.

6.3.4.1 Effect of Chinese ink in electrochemical performance of NCO

In the previous discussion, it has been illustrated that the addition of Chinese ink prevents the agglomeration of NCO, which improves the pore structure and enlarges the surface area for NCO. Thus, it is foreseeable that the addition of Chinese ink will have a positive effect on the electrochemical performance of NCO. Figure 6.14a compares the CV curves of the NCO-ink composites with different loading mass of Chinese ink. Obviously, the enclosing area of the CV curve enlarges with increased loading mass of Chinese ink, suggesting improved specific capacitance. Besides, as the loading mass of Chinese ink increases, the anodic peak shifts to a lower potential, while the cathodic peak shifts to a higher potential.

Figure 6.14 (a) CV curves of dried ink and the NCO-ink composites with different content of Chinese ink: 0, 0.9, 1.8, 3.6 and 7.2 g. (b) The specific capacitance of dried ink and the NCO-ink composites with different content of Chinese ink at 2, 5 and 10 A g⁻¹. (c) Nyquist plots of dried ink and the NCO-ink composites with different content of Chinese ink. (d) Cycling stability of the NCO-ink composites with different content of Chinese ink.

It is understandable that the sample with a high content of Chinese ink will have a relatively low content of NCO since all the electrodes contain almost the same weight of NCO-ink composites. This sample with a lower content of NCO is less polarized and thus the anodic peak locates at less positive potential.³⁹ The specific capacitance of these NCO-ink composites was estimated from GCD at current densities of 2, 5 and 10 A g⁻¹ within a potential window of 0.125 to 0.525 V (vs. Hg/HgO). In accordance with the CV, the gravimetric specific capacitance of NCO is evidently boosted by the addition of Chinese ink. The sample NCO-ink_{7.2} shows a specific capacitance of 2733 F g⁻¹ at a current density 2 A g⁻¹. This value is higher than the previous reports that were tested under the similar conditions.^{33, 40, 41} Figure 6.13c shows the Nyquist plots for these composites. As expected, the introduction of Chinese ink reduces the diffusion resistance for NCO, because the presence of carbon black particles efficiently mitigates the aggregation of NCO and create voids within NCO that are favorable for ion transportation. Meanwhile, Chinese ink also increases the charge transfer resistance. This may be caused by the glue that sets up a barrier between the active materials and the current collector. It is worth mentioning that the EIS measurement is susceptible to many factors, especially the surface conditions of the electrode. Accordingly, distinct testing results may be obtained on the same sample. In this case, gas emission resulting from the decomposition of water tends to occur when the potential rises up. The gas emission gas can cause the divorce of active materials from the nickel foam, and the presence of gas in the electrode changes the surface condition of the electrode. Measures have been taken to ensure a similar testing condition for each sample, but there still are some uncertain factors causing the differences in the results. Therefore, the EIS results do not show a nice correlation with the addition amount of Chinese ink.

The cycling stability of these NCO-ink composites was evaluated by continuous charging and discharging at a high current density of 10 A g⁻¹ for 3000 cycles. Figure 6.14d shows the evolution of capacitance retention with cycle numbers. These NCO-ink composites have a shorter cycling life than the pure NCO, and the one containing more Chinese ink has a worse cycling life. The deteriorated cycling life with incremental loading mass of Chinese ink can be attributed to the dropping of active materials caused by gas emission

when the potential is raised up. It is observed that the sample with more Chinese ink has a more intensive gas emission when charged to a high potential.

6.3.4.2 Effect of different calcination temperature

The effect of calcination temperature on the electrochemical performance was also investigated. Figure 6.15a compares the CV curves (at a scanning rate of 20 mV s⁻¹) of the NCO-ink_{3.6} composites calcinated at different temperatures, and Figure 6.15b lists the specific capacitance calculated from GCD at a current density of 5 A g⁻¹ within a potential from 0.125 to 0.525 V. The CV curves of all the samples have a similar shape but different enclosing area, indicating the increasing calcination temperature does not change the electrochemical behavior, but shrinks the specific capacitance. The sample calcinated at 250 °C shows the highest specific capacitance. Nonetheless, as the calcination temperature goes up above 250 °C, the specific capacitance tends to decrease with increasing calcination temperature.

Figure 6.15 (a) CV curves of the NCO-ink composites calcinated at different temperatures. (b) The specific capacitance of the NCO-ink composites calcinated at different temperatures at 5 A g⁻¹, based on the mass of the active material or the whole electrode.

Calcination plays an important role in the crystallization of NCO. During calcination, the cobalt-nickel bimetallic carbonate hydroxide hydrate gradually converts into NCO, but meanwhile, the glue from Chinese ink decomposes and the carbon black is oxidized and gasified by air. The XRD results verify that the NCO precursor converts into NCO when

the calcination temperature is greater than or equal to 200 °C. In addition, the results of Raman spectroscopy and TGA indicate that most of the carbon black will be removed due to the oxidation-gasification, when the calcination temperature is over 300 °C. It can be known from the BET surface analysis results that a high calcination temperature apparently enlarges the specific surface area and the average pore size. However, there is an inconsistency between the specific capacitance and specific surface area as the calcination temperature is raised above 300 °C. This phenomenon can be explained as follows. For one thing, the removal of glue and carbon black at a high calcination temperature creates some empty space within the NCO nanoflakes, enlarging the specific surface area and broadening the pore size distribution. Nevertheless, as indicated by the EIS analysis (Table 6.2), the broadened pore size does not accelerate the ion diffusion. For another, the high-temperature calcination burns away the majority of the carbon black, resulting in reduced electrical conductivity. As a result, the specific capacitance shrinks with raised calcination temperature.

Table 6.2 Calculated values of the components in the equivalent circuit.

	200 °C	300 °C	400 °C	500 °C
R_{Ω} (Ω)	0.466	0.564	0.51	0.45
CPE ($mF.s^{\alpha-1}$)	15.7	4.28	3.52	3.463
α	0.608	0.738	0.761	0.785
R_{ct} (Ω)	2.102	0.643	0.919	0.523
Z_w ($\Omega.s^{-0.5}$)	2.468	2.056	2.471	2.596
C_p (F)	10.09	8.17	4.658	1.236

EIS gives an insight into the electrochemical behavior. The obtained data are fitted into equivalent electric circuits which are identical to Figure 6.13 (d). The values of components are listed in Table 6.2. It is noticeable that the Warburg diffusion resistance reduces from 200 °C to 300 °C, which can be attributed to the removal of glue that eliminates the barrier to ion diffusion. However, after 300 °C, the Warburg diffusion resistance increases with increasing calcination temperature. One reasonable explanation for this is that the removal of carbon black at 400 °C (or 500 °C) causes the stacking of NCO nanoflakes that reduces the accessible paths for ions. This is in accordance with the FESEM observations. As such,

the pseudocapacitance keeps dropping as the calcination temperature rises up.

6.4 Conclusions

In this chapter, high-surface-area NiCo₂O₄ nanoflakes were synthesized by chemical co-precipitation and subsequent calcination. Commercial Chinese ink was added into the precursor solution to provide well-dispersed carbon black particles. The presence of carbon black particles effectively alleviated the stacking of the precipitated NiCo₂O₄ precursor, and contributed additional electrical conductivity. Thus, the BET specific surface area was increased from 134 m² g⁻¹ of the pure NiCo₂O₄ to the maximum 217 m² g⁻¹ when 1.8 g of Chinese ink was added. The addition of Chinese ink had a positive effect on the specific capacitance, but a negative effect on the cycling stability of the NiCo₂O₄-ink composites. The composite with 7.2 g of Chinese ink showed the maximum specific capacitance of 2733 F g⁻¹ at 2 A g⁻¹, but only retained 29.6% of the initial capacitance after 3000 cycles of charging/discharging.

Besides, the calcination temperature also played a significant role in the electrochemical performance of the NiCo₂O₄-ink composites. The specific capacitance tended to decline as the calcination temperature rose up, especially above 300 °C. The reason for this lied in the depletion of carbon black caused by oxidation-gasification that led to the aggregation of NiCo₂O₄.

In short, it has been proven that commercial Chinese ink can be directly used to provide well-dispersed carbon black particles as the spacer and electrical reinforcers for NiCo₂O₄ synthesized from chemical co-precipitation. Admittedly, the performance, especially the cycling stability remains to be improved. More research work is needed to minimize the negative effect of Chinese ink on the electrochemical performance.

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Chapter 7

Discussion and Future Work

This chapter provides the summary of the work done in this thesis, and the outlook for the future research on supercapacitors (SCs) involving carbon-based electrodes. This thesis has proven the feasibility of using the commercial Chinese ink as a building block to construct well-dispersed metal oxide-carbon composites as electrodes for SCs. Chinese ink is mainly used to provide a ready-made suspension system, and dispersive carbon black particles as inert spacers or a carbon source for synthesizing metal oxides. These Chinese ink-assisted fabrication methods developed by this thesis are simple, cheap and thus promising for scaling up. In the last section of this chapter, some reconnaissance work is also demonstrated, based on which the future work is recommended. In these reconnaissance studies, the Chinese ink-assisted fabrication methods are extended to the composites containing graphene, NiMn_2O_4 and NiMn_2O_4 . The fabrication methods are also incorporated with microwave-assisted hydrothermal synthesis in order to rapidly prepare high-surface-area metal oxide-carbon composites. Besides, two strategies to improve the overall performance of asymmetric SCs are also recommended, i.e. developing reduced graphene oxide nanomeshes as the negative electrode materials and developing the freestanding gel electrolyte.

7.1 General Discussion

In this thesis, the versatility of Chinese ink as an additive or a starting material in preparing electrode materials for supercapacitors (SCs) has been systematically demonstrated. In essence, Chinese ink can be regarded as a colloidal suspension (i.e., sol) of well-dispersed carbon black particles in water. The fundamental starting point of using commercially available Chinese ink is to take advantage of its ready-made colloidal suspension system, which can efficiently save the trouble of pretreating the raw carbon materials.

The roles played by this ready-made carbon black suspension can be summarized into two basic aspects. On the one hand, it functions as an inert additive, providing well-dispersed carbon black particles as the nanospacers and facilitating the dispersion of nanosized metal oxides and other carbon nanomaterials. It has been demonstrated that raw MWCNTs and VGCNFs were disentangled and dispersed into aqueous suspensions through a simple wet manual/mechanical milling process with the aid of Chinese ink. After wet-casting or filter-coating, the presence of Chinese ink also improved the distribution of MWCNTs and VGCNFs in a polymer matrix or a porous substrate, which ensured a good electrical conductivity for the composites. Accordingly, the composites can be directly used as the electrodes for EDLCs or the conductive substrates for the electrodeposition of other electroactive materials. Compared with the other pretreatment methods in previous reports, Chinese ink-involved wet grinding is simpler, safer and cheaper, and has less damage on MWCNTs and VGCNFs. It can be a promising method to wet-process MWCNTs and VGCNFs on a large scale.

Along the same line, Chinese ink was further as an inert additive for synthesizing NiCo_2O_4 from chemical co-precipitation. Chinese ink exerted analogous influence on metal oxides. The presence of carbon black particles effectively reduced the agglomeration of NiCo_2O_4 and created voids therein. Consequently, the NiCo_2O_4 -ink composites showed larger specific surface area and better specific capacitance than pure NiCo_2O_4 . Admittedly, due to the dimensional limitation, carbon black particles cannot provide enough room for the anchoring of nanostructured NiCo_2O_4 . Thus, an anticipated well-defined core-shell-like or sea urchin-like structure were not achieved in this study.

On the other hand, carbon black from Chinese ink can also act as a starting material for synthesizing metal oxides from the carbon involved reactions. In this thesis, it has been demonstrated the preparation of birnessite-type MnO_2 through the redox reaction between the carbon black particles and KMnO_4 . The resulting MnO_2 in-situ grew onto the carbon black particles, leading to an intimate contact shortened the electron transport paths. The structures of the MnO_2 -ink composites can be easily tuned by adjusting the feeding ratio of Chinese ink to KMnO_4 . Compared with CNTs, CNFs and acetylene black that have been widely used as the carbon sources for the redox reaction to prepare MnO_2 , the carbon black particles from Chinese ink have an obvious advantage in their good dispersity, which greatly boosts the effective utilization of carbon and ensures the homogeneity of the products. The obtained MnO_2 -ink composites show high electrochemical performance, comparable to that of CNT/CNF/graphene-based composites.

Carbon nanomaterials, such as CNTs, CNFs and graphene, have been widely used as electrical conductivity enhancers, nanospacers or substrates for metal oxides, owing to their high electrical conductivity and electrochemical stability. By contrast, carbon black is rarely used for these purposes because of the inferior electrical conductivity and the dimensional limitation. However, quasi-spherical carbon black still makes its mark as a building block for composites since it is easier to be dispersed than other carbon nanomaterials. The good dispersion of carbon black can ensure the homogeneity of composites, and may compensate for its shortage of electrical conductivity to some extent. Besides, carbon black is cheaper and easier to be processed than CNTs, CNFs and graphene. These unique features make carbon black outweigh the other carbon nanomaterials. In particular, as shown in this thesis, commercially available Chinese ink can directly provide the ready-made carbon black suspension.

In summary, these outcomes prove the fundamental hypothesis that commercially available Chinese ink can be utilized in fabricating high-performance electrode materials for SCs via wet-chemistry approaches because of its ready-made colloidal suspension system as well as the included carbon black.

7.2 Originality and Scientific Contributions

Through the research work, several novel outcomes have been achieved. First, for the first time, commercially Chinese ink was directly used as a building block for fabricating electrode materials for SCs. Second, with Chinese ink, a simple and cheap method has been developed to obtain MWCNT or VGCNF suspensions by wet mechanical grinding, which were further converted into freestanding composite sheets or paper-based composites. The obtained conductive composites were ready to be the electrodes for SCs. Third, the well-dispersed carbon black particles from Chinese ink was used as the carbon source to synthesize birnessite-type MnO_2 via stirring-driven hydrothermal reactions. The obtained MnO_2 with well-defined nanostructures possessed high surface area and demonstrated high electrochemical performance. Fourth, a new solution has been contributed to solve the problem about the agglomeration of self-assembled NiCo_2O_4 by introducing Chinese ink into the precursor solution during the chemical co-precipitation process. Owing to the presence of Chinese ink, well-dispersed NiCo_2O_4 nanoflakes was obtained, which showed enlarged specific surface area and improved electrochemical performance. These processing methods hold promise for large-scale applications because they are simple, low-risk and low-cost.

7.3 Reconnaissance Work and Recommendations for Future Work

In this thesis, some interesting work has been demonstrated concerning the utilization of commercial Chinese ink in fabricating electrode materials for SCs. However, there is still much room for improvement. Here, some reconnaissance work will be presented, which may point the way to the future research in this field.

1. Incorporating Chinese ink with graphene

It has proven that the commercial Chinese ink is effective in dispersing carbon nanotubes and carbon nanofibers under the action of ball milling. The obtained carbon-based suspensions are stable enough for different post-processing. Besides, CNTs and CNFs, Chinese ink can be directly incorporated with the reduced graphene oxide (RGO)

suspension, which can be converted into a freestanding sheet through filtering (Figure 7.1a). As pointed out by many reports, the introduction of nanoparticles can effectively prevent the stacking of RGO nanosheets, increasing the surface accessible to electrolyte ions during electrochemical processes. However, the mechanical strength of the freestanding RGO-ink sheets still cannot meet the requirement of practical usage (Figure 7.1b).

Figure 7.1 Appearance of the freestanding reduce graphene oxide-Chinese ink composite sheet made through filtration: (a) before drying, and (b) after air-drying.

2. Post-processing carbon-based suspensions by different methods

Regarding the post-processing methods, apart from wet-casting and filter-coating which have been demonstrated in Chapter 4, these carbon-based suspensions can be also transferred onto porous substrates (such as paper or fabric) by various coating or printing techniques, such as dip-coating, spray-coating, slot-die coating, inkjet printing, etc. These techniques make it possible to achieve large-scale fabrication of the carbon-based conductive and porous composites and to lower the overall fabricating cost. Owing to their conductive and porous nature, the carbon-based composites can be used as the direct electrodes for SCs or the substrates for the deposition of other electroactive materials (such as transition metal oxides/nitrides/sulfides). The electroactive materials and the current collector are integrated into these composites. Such a simple but effective configuration makes them the ideal electrodes for all-solid-state SCs.

3. Applying Chinese ink to synthesize well-dispersed nanoscale metal oxides

In the same line of thought, the fabrication method was extended to other binary metal oxides. Here, NiMn_2O_4 and NiMoO_4 are taken as the examples, which were synthesized by stirring-driven hydrothermal reactions. In these synthesis reactions, Chinese ink acted as only an inert additive in these synthesis reactions, providing the carbon black particles as spacers for metal oxides.

Figure 7.2 SEM images of (a, b) pure NiMn_2O_4 and (c,d) the NiMn_2O_4 -ink composite.

Figure 7.2a–d show the SEM images of the NiMn_2O_4 synthesized without/with the addition of Chinese ink. In the absence of Chinese ink, the NiMn_2O_4 nanosheets agglomerate into large cakes. However, with the presence of Chinese ink, the NiMn_2O_4 nanosheets were deposited onto the surface of carbon black particles and were divorced from one another. It is believed that well-defined nanostructures can be achieved by carefully adjusting the feeding ratio of precursors to Chinese ink. It can be also anticipated that the sample with

Chinese ink will demonstrate higher specific surface area and capacitance than the one without Chinese ink.

Figure 7.3 SEM images of (a, b) pure NiMoO_4 and (c,d) the NiMoO_4 -ink composite.

For NiMoO_4 (Figure 7.3a–d), the addition of Chinese ink does not cause an evident change in the morphology, but it enhances the overall electrical conductivity due to the presence of carbon black. The specific capacitance of the NiMoO_4 -ink is 1073 F g^{-1} (based on the mass of the whole composite), higher than 925 F g^{-1} of pure NiMoO_4 .

Based on these preliminary results, this fabrication method is believed to be suitable for the other metal oxides. Chinese ink holds special significance for the materials which tend to grow into 2D nanosheets since it effectively alleviates the stacking of nanosheets. Thus, more future work can be done to utilize Chinese ink to fabricate high-surface-area metal oxides through wet-chemistry routes.

4. Applying Chinese ink into microwave-assisted synthesis of metal oxides

Among these synthesis methods, microwave-assisted hydrothermal synthesis (MAHS) has attracted considerable attention in recent years. MAHS combines the merits of both microwave heating and hydrothermal synthesis, including rapid volumetric heating, high purity and homogeneity, and a narrowed particle size distribution. In conventional hydrothermal reactions, the long initial heating period may cause uneven temperature profiles within the autoclave, and further poor nucleation and non-uniform size of products. By contrast, in MAHS, the temperature can be raised speedily and synchronously, which can ensure the homogeneity of the products.

Figure 7.4 SEM images of MnO_2 synthesized by MAHS: (a–c) 2 mmol of KMnO_4 with 0.35, 0.70 and 1.40 g of Chinese ink, reacted at 120 °C for 1 h; (d–f) 2 mmol of KMnO_4 with 0.35 g of Chinese ink, reacted at 120 °C, 150 °C and 180 °C for 2 h.

Figure 7.4a–f show the SEM images of MnO_2 synthesized by MAHS, which are very similar to those shown in Chapter 5. As discussed in Chapter 5, carbon black from Chinese ink acts as the carbon source and the substrate for MnO_2 . The morphology of MnO_2 can be easily tuned by the addition amount of Chinese ink as well as the reaction temperatures. Although synthesized in a shortened period, these samples demonstrate a specific

capacitance comparable to that of the MnO_2 synthesized by conventional hydrothermal reactions.

Figure 7.5 SEM images of NiCo_2O_4 synthesized by MAHS: (a–d) 1 mmol of NiCo_2O_4 with 0, 0.5, 1.0 and 2.0 g of Chinese ink, reacted at 120 °C for 2 h; (e, f) 1 mmol of NiCo_2O_4 with 0.5 g of Chinese ink, reacted at 150 °C and 180 °C for 2 h.

For NiCo_2O_4 synthesized by MAHS, the morphology has a remarkable change after the introduction of Chinese ink. As seen Figure 7.5, the sample without Chinese ink is present in bulky flakes, while the one with Chinese ink is present in the form of long nanofibers. Besides the addition amount of Chinese ink, the reaction temperature also has a significant effect on the morphology of NiCo_2O_4 . The fiber thickens with the increased reaction temperature. In accordance with this, the specific capacitance of the NiCo_2O_4 drops as the synthesis temperature rises.

Unlike conventional hydrothermal synthesis, MAHS is accomplished in a short time, which does not allow enough time for the precipitates to undergo the dissolution-recrystallization process. As a result, the obtained products are usually of low crystallinity and low conductivity, and may agglomerate into bulky and dense clusters. The addition of Chinese ink in MAHS is a wise strategy because the well-dispersed carbon black particles

not only mitigate the agglomeration, but only facilitate the electrical conductivity. Therefore, more research work can be conducted to explore the role of Chinese ink in MAHS and to rapidly synthesize high-performance materials by taking advantage of MAHS and Chinese ink.

5. Developing high-performance negative electrode materials

Activated carbon has been extensively applied as the negative electrode material for asymmetric SC, but it only shows mediocre specific capacitance. Chemically reduced graphene oxides (RGO) is a promising alternative to activated carbon as the negative electrode material. In particular, recently, graphene nanomeshes have attracted much attention since they have a pore-abundant surface that facilitates the ion transportation. Some attempt has been made to prepare RGO nanomeshes by SnO_2 -catalyzed gasification and rapid thermal expansion. The obtained products showed satisfactory electrochemical performance. Especially, when a certain amount of Chinese ink was added, the presence of carbon black created voids among adjacent RGO nanomeshes, so the composites showed improved specific capacitance. Admittedly, the cycling stability of the RGO nanomeshes-ink composites remains to be improved. Thus, more future work can be carried out to adjust the weight ratio of RGO to ink in order to optimize their electrochemical performance.

6. Developing freestanding gel electrolytes

In addition to the electrode materials, the electrolyte also determines the performance of SCs, especially the all-solid-state ones. Conventional liquid or non-crosslinked polymer electrolytes are not suitable for all-solid-state SCs, because electrolyte may be adsorbed by porous electrode materials, leading to the decay in electrochemical performance of SCs and even some safety issues. By contrast, crosslinked hydrogel electrolytes are the ideal electrolytes for all-solid-state SCs. They are immobile as the solid electrolytes, but store electrolyte ions much higher than solid electrolytes. In Chapter 4, the fabrication and the properties of H_2SO_4 -crosslinked PVA gel electrolyte have been presented. This gel electrolyte is composed of the glutaraldehyde-cross-linked PVA-PVP polymer network as the dispersion medium, and water and H_2SO_4 as the dispersed phases. The gel electrolyte

“locks” a large amount of water and H_2SO_4 within the polymer network, because of which, the gel electrolyte shows high ionic conductivity and high stability. It is also able to be used in a large temperature range.

Although this kind of gel electrolyte shows impressive performance, it suffers from complicated fabrication processes. More research work is needed to simplify the fabrication method. Besides, the thickness and the mechanical strength remain to be improved in order to meet the requirement of practice usage, especially when it is used for flexible SCs.

Appendix

PDF #01-080-1098

Status Primary

QM: Indexed

Pressure/Temperature: Ambient

Chemical Formula: $\text{K}_{0.46}\text{Mn}_{1.54}\text{Mn}_{0.46}\text{O}_4(\text{H}_2\text{O})_{1.6}$

Empirical Formula: $\text{H}_{3.2}\text{K}_{0.46}\text{Mn}_2\text{O}_{5.6}$

Weight %: H1.46 K8.15 Mn49.79 O40.60

Atomic %: H28.42 K4.09 Mn17.76 O49.73

Compound Name: Potassium Manganese Oxide Hydrate

Entry Date: 09/01/1998

Last Modification Date: 09/01/2016

Last Modifications: Quality

Radiation: CuK α 1: 1.5406 Å

d-Spacing: Calculated

Intensity: Calculated - Peak

I/Ic: 5.9

I/Ic - CW ND: 0.34

SYS: Monoclinic

SPGR: C2/m (12)

Author's Cell [**AuthCell a:** 5.149(2) Å **AuthCell b:** 2.843(1) Å **AuthCell c:** 7.176(3) Å **AuthCell:** 100.76(3)°

AuthCell Vol: 103.20 Å³ **AuthCell Z:** 1.00 **AuthCell MolVol:** 103.20]

Author's Cell Axial Ratio [**c/a:** 1.394 **a/b:** 1.811 **c/b:** 2.524]

Density [**Dcalc:** 3.551 g/cm³ **Dstruc:** 3.5 g/cm³]

SS/FOM: F (30) = 637.8(0.0015, 32)

Temp: 298.0 K (Ambient temperature assigned by ICDD editor)

R-factor: 0.091

Space Group: A2/m (12)

Molecular Weight: 220.68 g/mol

Crystal Data [**XtlCell a:** 7.176 Å **XtlCell b:** 2.843 Å **XtlCell c:** 5.149 Å **XtlCell:** 90.00° **XtlCell:** 100.76° **XtlCell:** 90.00° **XtlCell Vol:** 103.20 Å³ **XtlCell Z:** 1.00]

Crystal Data Axial Ratio [**c/a:** 0.718 **a/b:** 2.524 **c/b:** 1.811]

Reduced Cell [**RedCell a:** 2.843 Å **RedCell b:** 2.941 Å **RedCell c:** 7.176 Å **RedCell:** 99.41° **RedCell:** 90.00° **RedCell:** 118.91° **RedCell Vol:** 51.60 Å³]

Subfile(s): Inorganic

Pearson Symbol: mC11.26

Pearson Symbol w/o H: mC8.06

ANX: AB4X12

PDF #00-033-0429

Status Primary**QM:** Indexed**Pressure/Temperature:** Ambient**Chemical Formula:** (Ni_{6.10} Co_{2.90}) (OH)_{18.27} (CO₃)_{1.315} · 6.7H₂O**Empirical Formula:** C_{1.315} Co_{2.9} H_{31.67} Ni_{6.1} O_{28.915}**Weight %:** C1.52 Co16.45 H3.07 Ni34.45 O44.51**Atomic %:** C1.85 Co4.09 H44.67 Ni8.60 O40.78**Compound Name:** Cobalt Nickel Carbonate Hydroxide Hydrate**Mineral Name:** Comblainite**Entry Date:** 09/01/1983

Radiation: CuK α : 1.5418 Å**Filter:** Ni Beta**d-Spacing:** D.S.**Intensity:** Visual**Camera Diameter:** 114.60

SYS: Rhombohedral**Aspect:** R** (166)**Author's Cell [AuthCell a:** 3.038 Å **AuthCell c:** 22.79 Å **AuthCell Vol:** 182.16 Å³ **AuthCell Z:** 0.33**AuthCell MolVol:** 552.00]**Author's Cell Axial Ratio [c/a:** 7.502]**Density [Dcalc:** 3.16 g/cm³ **Dmeas:** 3.05 g/cm³]**SS/FOM:** F (13) = 16.7(0.046, 17)**Temp:** 298.0 K (Ambient temperature assigned by ICDD editor)**Color:** Greenish blue

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Space Group: R****Molecular Weight:** 1039.31 g/mol**Crystal Data [XtlCell a:** 3.038 Å **XtlCell b:** 3.038 Å **XtlCell c:** 22.790 Å **XtlCell :90.00°****XtlCell :90.00° XtlCell:** 120.00° **XtlCell Vol:** 182.16 Å³ **XtlCell Z:** 0.33]**Crystal Data Axial Ratio [c/a:** 7.502 **a/b:** 1.000 **c/b:** 7.502]**Reduced Cell [RedCell a:** 3.038 **RedCell b:** 3.038 Å **RedCell c:** 7.796 Å **RedCell:** 78.77° **RedCell:** 78.76° **RedCell :** 60.00° **RedCell Vol:** 60.72 Å³]

Subfile(s): Inorganic, Mineral Related (Mineral, Natural)**Mineral Classification:** Hydrotalcite (Family), 7R (Supergroup)**Pearson Symbol:** hR7.80**Pearson Symbol w/o H:** hR4.3163

PDF #04-013-0797

Status Primary**QM:** Indexed**Pressure/Temperature:** Ambient**Chemical Formula:** Co₂NiO₄**Empirical Formula:** Co₂NiO₄**Weight %:** Co49.00 Ni24.40 O26.60**Atomic %:** Co28.57 Ni14.29 O57.14**Compound Name:** Cobalt Nickel Oxide**Entry Date:** 09/01/2010**Last Modification Date:** 09/01/2011**Last Modifications:** Reflections

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Radiation: CuK α 1: 1.5406 Å**d-Spacing:** Calculated**Intensity:** Calculated - Peak**I/Ic:** 4.58**I/Ic - CW ND:** 0.75

SYS: Cubic**SPGR:** Fd-3m (227)**Author's Cell** [AuthCell a: 8.114(14) Å AuthCell Vol: 534.20 Å³ AuthCell Z: 8.00 AuthCell MolVol: 66.78]**Density** [Dcalc: 5.982 g/cm³Dstruc: 5.98 g/cm³]**SS/FOM:** F (30) = 999.9(0.0003, 30)**Temp:** 298.0 K (Ambient temperature assigned by ICDD editor)

Space Group: Fd-3m (227)**Molecular Weight:** 240.56 g/mol**Crystal Data** [XtlCell a: 8.114 Å XtlCell b: 8.114 Å XtlCell c: 8.114 Å XtlCell: 90.00° XtlCell :90.00° XtlCell: 90.00° XtlCell Vol: 534.20 Å³ XtlCell Z: 8.00]**Crystal Data Axial Ratio** [a/b: 1.000 c/b: 1.000]**Reduced Cell** [RedCell a: 5.737 Å RedCell b: 5.737 Å RedCell c: 5.737 Å RedCell:60.00° RedCell: 60.00° RedCell: 60.00° RedCell Vol: 133.55 Å³]**Origin:** O2Crystal (Symmetry Allowed): Centrosymmetric

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Subfile(s): Inorganic**Pearson Symbol:** cF56.00