Functional nanocarbon based hybrid materials for high performance supercapacitors

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**FUNCTIONAL NANOCARBON BASED HYBRID
MATERIALS FOR HIGH PERFORMANCE
SUPERCAPACITORS**

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Functional Nanocarbon Based Hybrid Materials For High Performance Supercapacitors

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Abstract

The electrochemical capacitors, or supercapacitors, have been widely considered as promising alternatives to conventional batteries, due to their high power and long cycle life. They can be applied in different applications according to their specific characteristics. For example, for large scale energy storage, the key challenges are to increase the energy density, rate capability and cycle life of supercapacitors. For portable flexible electronics, research efforts have been focused on developing flexible supercapacitors with both high energy density and excellent mechanical flexibility. For microscale energy storage, increasing the volumetric energy density of micro-supercapacitors is a key task. My thesis targeted these key challenges in supercapacitor research by designing novel functional nanocarbon based hybrid materials as supercapacitor electrodes.

Nickel hydroxide (Ni(OH)_2) is a promising pseudocapacitive material to increase the energy storage capacity of supercapacitors. In the first part of this thesis, three nanocomposites with thin layers of amorphous, α -, and β - Ni(OH)_2 deposited on conductive multi-walled carbon nanotubes (MWCNTs) were synthesized, and then fabricated into supercapacitor electrodes. My results showed that the electrochemical performances of MWCNT/ Ni(OH)_2 nanocomposites depend on the crystallinity of Ni(OH)_2 . Amorphous- Ni(OH)_2 has superior performances, however, they change upon the crystalline structure

transformation of Ni(OH)_2 under repeated redox reactions.

In order to utilize amorphous- Ni(OH)_2 for high performance supercapacitors, in the second part of this thesis, a coaxial ternary hybrid material was prepared by wrapping MWCNT/ Ni(OH)_2 nanocomposites with a conducting polymer, poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS). The polymer layer prevents the degradation of amorphous- Ni(OH)_2 . The assembled asymmetric supercapacitors using this ternary hybrid material exhibit high energy density of 58.5 W h kg^{-1} at the power density of 780 W kg^{-1} as well as long cycle life (86% capacitance retention after 30 000 cycles).

Next, a cellulose paper based hybrid ternary composites were synthesized for potential portable and flexible supercapacitor applications. The hydroxyl chemistry of cellulose fibers in rice paper was explored to synthesize hybrid ternary nanocomposites, comprised of rice paper, single-walled carbon nanotubes (SWCNTs) and manganese oxide (MnO_2) nanoparticles. Using this hybrid ternary composite as electrodes, the assembled two-electrode supercapacitors achieved not only high performances in capacitance, energy, power, and cycle stability, but also good mechanical strength and excellent mechanical flexibility with negligible changes after bending more than 100 times.

Last, fiber based micro-supercapacitors are promising candidates as microscale energy storage devices. A versatile and scalable space-confined hydrothermal

assembly approach was demonstrated to synthesize hybrid all-carbon fibers. They are comprised of nitrogen doped reduced graphene oxide and multiple walled carbon nanotubes. The diameter of hybrid carbon fibers can be easily tuned across a wide range from 30 to 240 μm , while maintaining their good electrical conductivity, high ion-accessible surface area and mechanical strength. Using the space-confined hydrothermal assembly approach, hybrid carbon fibers of different diameters and lengths were created to build highly customized micro-supercapacitors. They can cover a broad range of energy and power capacities, realizing the built-to-order concept without compromising their excellent charge/discharge stability and mechanical flexibility.

Overall, this thesis shows that the rational architecture design of functional nanocarbon based hybrid materials can address several key challenges in developing high performance supercapacitors for various potential applications. The fundamental understanding on the structure-property correlation of capacitive materials will pave the way for releasing the great potentials of supercapacitors.

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List of Abbreviation

AgCl	Silver Chloride
BET	Brunauer-Emmett-Teller
BJH	Barret-Joyner-Halenda
CFs	Carbon Fibers
CNTs	Carbon Nanotubes
Cu ₂ O	Copper (I) Oxide
CV	Cyclic Voltammogram
DI	Deionized
EC	Electrochemical Capacitor
EDLC	Electric Double Layer Capacitor
EDX	Energy-dispersive X-ray Spectroscopy
ESR	Equivalent Series Resistance
eV	Electron Voltage
FESEM	Field Emission Scanning Electron Microscopy
GO	Graphene Oxide
MnO ₂	Manganese Oxide
Ni(OH) ₂	Nickel Hydroxide

NiO	Nickel Oxide
PANI	Polyaniline
PEDOT	Poly (3,4-ethylenedioxythiophene)
PPy	Polypyrrole
PSS	Polystyrenesulfonate
RGO	Reduced Graphene Oxide
SC	Supercapacitor
SCE	Saturated Calomel Electrode
TGA	Thermogravimetric Analysis
TEM	Transmission Electron Microscopy
UV-Vis-NIR	ultraviolet–visible–near-infrared spectrometer
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray Diffraction

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Chapter I Bibliographic Summary

1.1 Overview of Energy Storage Systems

Energy has always been one of the most important issues in human history since the very first use of the crude fire. However, in dealing with today's huge and increasing global energy consumption, we have to concern more about the environmental issues brought by the massive burning of the fossil fuel and even face the threat of possible depletion of traditional fossil fuel in the near future.¹ Thus, a revolutionary ways to produce energy has been put on a very conspicuous place. Alternative renewable energy sources have been attracting a lot of recognitions, research interests, policy support, investments and application developments, especially in the field of wind power, photovoltaic and hydroelectricity technology. However, these types of renewable energy sources often rely on weather, climate or terrain, which are erratic and intermittent in nature and usually come as distributed generation.² Thus, the renewable energy sources are often problematic in directly uploading to the grids and even not capable of satisfying the continuous variations of the load.^{3,4} Energy storage is thus one of the important intermediate link between new energy discovery and reliable and efficient use of energy. Since electricity is the most important primary form of consumed energy with highly diversified consumption manners, the electrical energy storage takes the majority of the world energy storage

capacity. Typically, the electrical energy storage process involves conversion from the electricity into another form of storable energy and inverse conversion to electricity when needed without severe energy loss. There are many possible techniques for energy storage, mainly coming as mechanical, thermal and chemical forms.⁵ Figure 1.1 shows the current techniques for the electrical energy storage with their characteristic power rating and duration of discharge, including pumped hydro solution which is one of most mature technology for electrical energy storage and also takes over 99 % of worldwide installed storage capacity of 127,000 MW and compressed air storage which takes the second but quite distance place of 440 MW (data at the year of 2010).⁶ Both of the techniques can reach extremely high power (hundreds of MW or even GW). The technology of pumped hydro storage is mature and readily available. However, both of their response time is too long for potential grid applications that need peak shaving and loading shifting for frequency regulation and load management.¹ On the other hand, the huge sizes bring them high cost both in operation and maintenance and even not to mention the unfeasibility of their applications in daily domestic energy storage.

Figure 1.1 Comparison of power rating and their discharge time for different types of electrical energy storage technologies.⁶ (Courtesy of Electric Power Research Institute, Inc.)

In Figure 1.1, there are several types of energy storage techniques based on batteries and supercapacitors (SCs) that can offer flexible power and energy characteristics with shorter discharge time. They are also the two most important energy storage media in meeting the great demands for portable electronic devices and electrical vehicles especially in this twenty-first century.⁷ Both batteries and supercapacitors belong to the electrochemical energy storage which undergoes electrochemical process by electron and ion charge and discharge between the device electrodes and electrolyte. Generally, electrochemical energy storage possesses advantages in several features including pollution-free operation, high round-trip efficiency, long life time, low maintenance cost, easily

tunable energy and power to meet many different kinds of grid and loading functions.¹ Rechargeable batteries have many types according to their components, such as lead-acid, nickel-hydrogen, nickel-cadmium, zinc-air, sodium-sulfur, sodium-nickel-chloride, flow batteries, lithium-ion batteries (LIBs) and so on. Among them, LIBs are the most widely-used and effective rechargeable batteries.^{7,8} However, as shown in Figure 1.2, although the LIBs can achieve energy densities as high as hundreds of Wh kg⁻¹, they are unable to meet fast power delivery or uptake.⁹ As a consequence, the LIBs are limited to be widely applied in energy storage systems where fast and higher-power storage devices are highly required.¹⁰ In contrast, the conventional electrostatic capacitors, regardless of the ability to offer very high power densities, are too poor in storing energy that can hardly satisfy majority of the electronic devices as powering sources. As a combination and balance of high power and high energy, supercapacitors, also known as electrochemical capacitors or ultracapacitors, have attracted a lot of attention in research and application from both the academia and industry.

Figure 1.2 A ragone plot of specific energy and power comparisons of electrochemical energy storage devices as well as conventional electrostatic capacitors.¹¹ Copyright 2011, Materials Research Society.

1.2 Introduction to Supercapacitors

Capacitor is a passive two-terminal electrical component, which contains at least two conductive electrodes and a dielectric to separate the electrodes. Conventional physical capacitors usually consist of two metal foils as electrodes separated by an insulating film and store electric charge electrostatically as shown in schematic symbol in figure 1-3a. In this electrostatic capacitor, the electric field keeps constant and the electric potential decreases linearly between two electrodes if the dielectric is uniform. The capacitance(C) has the equation:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (1.1)$$

where ϵ_r is dielectric constant and ϵ_0 is the permittivity of the vacuum,

respectively; A and d stand for the overlapping area and distance of two counter charged electrodes, respectively. Next level of capacitors is called electrolytic capacitors. Unlike the conventional electrostatic capacitors, it uses electrolyte, liquid or ceramic electrolyte, as one electrode plate and a dielectric material as the other electrode which is a layer of metallic oxide, usually Ta, and Al, generated on the anode metal surface as illustrated schematically in figure 1-3b. Though anodically formed metallic oxide layer is very thin and uniform and can largely promote the capacitance per volume, it suffers higher leakage current, lower capacitance stability and shorter working life than other types of capacitors. Supercapacitors (SCs) provide relatively the highest capacitance per volume and per weight among all types of currently available capacitors, which is the reason why they can obtain the title of “super”. The capacitance of the SC is achieved through electrochemical process. Typically, a SC has very similar structures as conventional capacitors. It is formed from two polarized porous electrodes, arranged in a parallel manner, enfolding a porous dielectric separator immersed in an electrolyte instead of the dielectric materials, as schematically illustrated in Figure 1-3c. Unlike conventional capacitors which hold the charges on the two electrodes, the SCs have polarization at the very thin interfacial layers called Helmholtz layers between the electrode surface and the electrolyte.^{12,13} The name, electrochemical capacitor, is actually more accurate in describing the working principles of the SC. Detailed introduction of the principles and mechanism of

energy storage on SCs will be given in the following parts.

The SC was first introduced as a concept and reported in a patent by Becker in 1957, in which he coated high surface area carbon on a metal collector and immersed into sulfuric acid.¹⁴ Only until after more than ten years later in 1969, that a prototype of standard SC using activated carbon as electrode material and a thin porous insulator as separator was designed by researchers from Standard Oil of Ohio (SOHIO). Then again almost ten years passed by before the first commercial case of the SC was realized by Nippon Electrical Company (NEC) in 1978 who got licensed from SOHIO and developed aqueous-electrolyte SCs for power-saving units in electronics.¹⁵ However, before 1990s, the performance of the SCs, especially energy density, remained poor and so limited the commercial applications. With the up-rise of hybrid electric vehicles in the 1990s, the SCs were given more attention both in research and applications, because the SCs could boost batteries and fuel cells by providing necessary power for vehicle acceleration and recuperating brake energy.¹⁵ Thanks to the advancement on nanomaterials and their application in SCs, more varieties of advanced SC electrode materials with improved performance came along the way. In 2005, SCs were successfully integrated into Airbus 380 planes to power emergency evacuation slides. Nevertheless, there still remain a lot of challenges with the application of the SCs, including improving energy density for more energy storage applications, further enhancing the long term cyclic life, reducing the cost

and adding some special characteristics mechanically, morphologically, geometrically or in other aspects to meet more diversified applications.

Depending on their electrochemical energy accumulating process, SCs can be classified into two types: the electric double layer capacitor (EDLC) and pseudocapacitor. The details of the two types SCs will be introduced later in part 1.2.1 of this thesis.

Figure 1.3 (a-c) Schematic of evolving capacitors

1.2.1 Types of supercapacitors

Depending on their electrochemical energy accumulating process, SCs can be classified into two types: the electric double layer capacitor (EDLC) and pseudocapacitor. The electrode materials of EDLCs are highly conductive and porous, such as activated carbon, but electrochemically inert such that they

cannot react with the electrolyte or decompose themselves during SC charging and discharging process. It only undergoes pure reversible physical charge accumulation and release or charged ions physical adsorption/desorption at the electrode/electrolyte interface during the charging and discharging of the SCs.¹⁶ Pseudocapacitor can also be called faradaic SC, from which it can be seen that the pseudocapacitor involves the faradaic process. In other words, the electrode materials of the pseudocapacitors are electrochemically active, e.g. metal oxides/hydroxides and conducting polymers, that store charges through faradaic reactions when they are charged or discharged.¹⁷ In the following, we will discuss the two type of SCs with their specific energy storage mechanisms separately, though both mechanisms may be occur simultaneously in many supercapacitors.

i. Electric Double Layer Capacitors (EDLCs)

Figure 1.4 Schematic of charge storage mechanisms of (a) electric double layer capacitors and (b) pseudocapacitors.¹⁸ Copyright 2011, Materials Research Society.

The EDLCs are the simplest and most commercially advanced SCs with a basic cell configuration of two symmetric high-surface-area and highly conductive electrodes immersed in electrolyte and separated by a porous separator. Figure 1.4a shows a mechanism model of an EDLC. The charge can be accumulated and released at the interface between the conductive solid particle surface and the electrolyte, e.g. positive charge accumulated on the electrode particle surface and a compact layer of the negative charged solvated ions from the electrolyte distributed in a parallel fashion near the electrode surface, forming a layer of capacitor. Such interfacial capacitors can form on both of the parallel electrodes of an EDLC, equivalent to two layers of capacitors connected in series. This is the origin of the electric double layer (EDL). This capacitive layer is called the Helmholtz layer, which, as well as the concept of EDL, was first modeled and described by von Helmholtz in the 19th century.¹³ During the charge and discharge process of EDLCs, there are no charge transfer or ion exchange happening between the electrode and the electrolyte.¹⁶

This capacitance of EDLC can also be express by equation 1.2, which is similar with equation 1.1 but with some modification:

$$C = \frac{\varepsilon A}{4\pi d} \quad (1.2)$$

ε is the electrolyte dielectric constant. A is attributed to the porous electrode material surface which is accessible to the electrolyte ions and d is the effective

thickness of the EDL (the Debye length), *i.e.* the distance between the adsorbed electrolyte ions and the corresponding charged electrode surface. Both of the parameters make the capacitance of EDLC much larger than the conventional capacitors. As a consequence, it implied several direct and effective routes to improve the energy storage capability of the EDLCs, including increasing the surface areas of electrode materials, applying highly conductive materials for electrodes, improving the wettability of the electrolyte to the electrode surface and looking for new electrolyte or ameliorating current electrolyte to deliver better performance.

ii. Pseudocapacitors

Different with EDLCs, pseudocapacitors execute a faradaic process which involving fast and reversible redox reactions between electroactive species on the electrode surface and the electrolyte, leading to the charge transfer across the electrode/electrolyte interface and faradaic current passing through the SC cells, which is similar to the charge storage mechanism of batteries. The pseudocapacitance originates from thermodynamics reasonings and can be attributed to the change in potential (ΔV) as a function of charge accumulation (Δq). Thus, it can be calculated from the derivative equation (1.3):^{13,19}

$$C = d(\Delta q) / d(\Delta V) \quad (1.3)$$

The pseudocapacitors usually involve three types of faradaic processes: (i)

two-dimensional depositions (underpotential deposition) of atoms on electrode surface (e.g. protons or hydrogen adsorbed on the surface of platinum or gold); (ii) redox reactions where the electrode potential is determined by the ratio of the redox species (such as the redox couple of the transition metal oxides; as shown in figure 1.4, RuO_2 is illustrated as an example, $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}$ is a redox couple that contributes to the Faradaic charge transfer during charging and discharging); (iii) chemisorption of ions at electrode interfaces, leading to electrosorption valency from potential-dependent partial Faradaic transfer.¹⁹⁻²¹ Since the charge transfer process of a pseudocapacitor occurs at the interface between the electrode and the electrolyte, it is usually accompanied with an additional EDL capacitance (usually quite small due to relatively much lower surface area and electrical conductivity of the pseudocapacitor electrodes as compared with EDLC electrodes) from non-Faradaic charge transfer.¹⁹

Metal oxides/hydroxides such as ruthenium oxide (RuO_2), nickel oxide (NiO), nickel hydroxide (Ni(OH)_2), manganese oxide (MnO_2) or iron oxide (Fe_2O_3) and some conducting polymers including polyaniline (PANI), polypyrrole (PPy) or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) have been widely studied as promising electrode materials for pseudocapacitors in the past decades.⁹ Oxygen- or nitrogen- containing surface functional groups recently have also been considered effective contributors in adding extra pseudocapacitance to some carbonaceous SC electrodes.^{13,22,23}

1.2.2 Evaluation of supercapacitors

The performance of the SCs is mainly evaluated on the basis of the specific capacitance of the electrode materials, total capacitance of the assembled cell, energy and power density, and their long-term cyclic life time. Cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS) test are the most commonly used techniques for the electrochemical performance characterization of SCs. Both the CV and GCD tests can be used to measure the capacitance and rate capability (capacitance retention ability with the increase of CV scan rates or GCD currents) of SCs either in the three-electrode configuration which includes a working electrode of electrode material, a counter electrode of inert conductive materials (usually Pt or graphite) for collecting and measuring the current between the working electrode and itself and a reference electrode used to control the potential loaded on the working electrode, or in the two-electrode systems which both electrodes are made of electrode materials of SCs. CV testing is considered as the most suitable approach in examining the storage mechanisms of SC materials and determining the proper operating voltage or potential window for the electrode materials in the three-electrode system.^{19,24,25} GCD testing is more versatile and accurate in characterizing the capacitive performance of two-electrode SC devices.²⁵

As mentioned above, the entire SC cell can be treated as two capacitors in series. Thus, the overall capacitance of a SC cell, C_{cell} , can be expressed in equation 1.4:

$$\frac{1}{C_{cell}} = \frac{1}{C_{ED1}} + \frac{1}{C_{ED2}} \quad (1.4)$$

where C_{ED1} and C_{ED2} are the capacitance of each electrode, respectively. In symmetric SCs, of which the two electrodes are the same, $C_{ED1} = C_{ED2}$, the total capacitance of the cell is only half of each electrode capacitance. While in the case of asymmetric SCs, whose two electrodes are usually fabricated from different materials, the cell capacitance is mainly dominated by the smaller value of the electrode capacitance.

The energy density and power density of the cell can be theoretically estimated by equation 1.5 and 1.6:^{13,16,26}

$$E = \frac{1}{2} C_{cell} V^2 = \frac{QV}{2} \quad (1.5)$$

$$P = \frac{V^2}{4R_s} \quad (1.6)$$

Q here is the total stored charges in a SC cell and R_s represents the equivalent inner resistance of the SC. Judging from equation 1.5 and 1.6, the performance of the SCs is mainly determined by C , V , R_s . Higher C and V , and lower R_s contribute to larger energy and power density. Meanwhile, in many literatures, the power can also be calculated from the galvanostatic charge/discharge as

following:²⁷⁻³⁰

$$P = \frac{E}{\Delta t} \quad (1.7)$$

where the Δt is the discharge time. The capacitance depends on electrode materials. The voltage applied on the cell is limited by the thermodynamic stability of the electrode and electrolyte materials, especially the latter. The voltage window is about 1 V in aqueous electrolyte,³¹⁻³³ and can reach higher in organic electrolyte³⁴⁻³⁶ and ionic liquid^{37,38} where it can even exceed 3 V. Using polymer electrolyte^{39,40} and asymmetry of the two electrodes⁴¹⁻⁴³ in SCs are alternative ways to effectively extend the voltage window in aqueous electrolyte. Since R_s come from various origins, there are a lot of factors that can affect this value. Hence, to optimize the performance of SCs, developing novel electrode materials and electrolytes is the priority.

Since capacitors are widely used in low-frequency electrical filtering and for other uses in electronics, SCs are also utilized for such purposes. Alternating current (ac) impedance spectroscopy, or called EIS, is one of the important characterization methods for SCs, which can give information on the impedance and resistance of the systems, charge transfer, mass transport and charge storage mechanisms. The electrical behavior of the electrode interphase can be represented by equivalent circuits. An ideal capacitor can be represented in Figure 1-5a. However, an electrochemical double-layer capacitor not only

contains capacitive double-layer capacitance (C_{dl}), is also in series with an equivalent series resistance, R_s , contributed from ohmic resistance of the electrolyte and separator, any internal resistance of the electrode materials, as illustrated in Figure 1-5b. There is no charge leakage pathway, so that such an interphase is referred to as an “ideally polarizable electrode”. In practice, this is rarely the case. In real systems, series resistance is not enough, they would also have some Faradaic leakage resistance due to overcharge or to Faradaic redox reactions caused by impurities, which can be represented by R_F in circuit Figure 1-5c, in parallel across capacitance.¹⁹ For those electrochemical capacitors with low concentration of reaction species in electrolyte and/or large electrochemical reaction rate, local concentrations of reacting ions in the interphasial boundary region (Nernst diffusion layer, ca. 0.1-0.01 mm in thickness) are kinetically controlled by diffusion. This diffusion control leads to another modulation of impedance in the equivalent circuit, the “Warburg impedance element”, represented by W . For simple charge transfer reaction under diffusion control, which is common in electrochemical capacitors, the equivalent circuit in Figure 1-5d with Faradaic charge transfer resistance, R_F , and Warburg impedance element, W , in parallel with the double-layer capacitance is called the “Randles circuit”.⁴⁴ As to pseudocapacitor, we need to involve a pseudocapacitance, C_P , in the circuit as well. Similarly, R_F' , representing desorption equivalent resistance of an electroactive species, is in parallel with the C_P in the circuit in Figure 1-

The electrodes of SCs have transient response when applied on an alternating current. This ac response behavior is frequency depended and can be present in a function of frequency, ω . A sinusoidal ac potential $E_{ac}(t) = E_m \sin \omega t$ (E_m is the amplitude) is applied to the electrode, there is a corresponding current, $I_{ac}(t)$. If the $E(t)$ is applied to a resistor R , the response current I is $E_{ac}(t)/R = (E_m/R) \sin \omega t$. Thus, the $I_{ac}(t) = I_m \sin \omega t$ ($I_m = E_m/R$, amplitude of current). However, in the case of a capacitance, the instantaneous charge q on the capacitor is $q = CE_{ac}(t) = CE_m \sin \omega t$, the corresponding changing current is $I(t) = dq/dt = \omega CE_m \cos \omega t$. Thus, the current $I(t)$ is out of phase with the voltage or potential $E(t)$ by -90° . However, the real electrode with a resistive part besides capacitive component cannot get this behavior. The current and potential always have a phase difference of α . The impedance of a capacitor can be expressed as its equivalent resistance, since $I_m = \omega CE_m = E_m/(1/\omega C)$, and define an impedance Z_c as $1/\omega C$. Since current is out of phase with voltage, the Z_c can be expressed as $Z_c = -j/\omega C = 1/j\omega C$, where $j = \sqrt{-1}$, which is an imaginary quantity and represents the capacitive part. The impedance of a resistor is simply $Z_R = R$, a real quantity, representing the resistive part. Combining these two impedance components of the circuit with parallel forms the overall impedance Z of the electrode:

$$\frac{1}{Z} = \frac{1}{Z_c} + \frac{1}{Z_R} = j\omega C + \frac{1}{R} = \frac{j\omega RC + 1}{R} = -\frac{\omega^2 R^2 C^2 + 1}{R(j\omega RC - 1)} \quad (1.8)$$

Therefore, we get the Z:

$$Z = -\frac{j\omega R^2 C - R}{\omega^2 R^2 C^2 + 1} = \frac{-j\omega R^2 C}{\omega^2 R^2 C^2 + 1} + \frac{R}{\omega^2 R^2 C^2 + 1} = Z'' + Z' \quad (1.9)$$

Thus,

$$Z'' = \frac{-j\omega R^2 C}{\omega^2 R^2 C^2 + 1} \quad (1.10)$$

$$Z' = \frac{R}{\omega^2 R^2 C^2 + 1} \quad (1.11)$$

We can get:

$$\omega RC = \sqrt{(R - Z')/Z'} \quad (1.12)$$

Rearranging equation (1.10), (1.11) and (1.12), we get:

$$Z'' = \frac{-jR}{R/Z'} \sqrt{(R - Z')/Z'} \quad (1.13)$$

Rearranging equation (1.13), we have:

$$(jZ'')^2 + (Z' - R/2)^2 = (R/2)^2 \quad (1.14)$$

From equation (1.14), we can get an equation of a circle with a radius of R/2 when jZ'' is plotted against Z' . The circle has two intercepts of 0 and R on the Z' axis when value of Z'' is 0. The impedance behavior in this case is represented by a semicircle as shown in figure 1-5f. If R_s is considered in the equivalent circuit, the semicircle becomes displaced along the Z' axis by R_s . Thus, the

intercepts become $Z'=R_s$ and $Z'=R_s+R$ as shown in figure 1-5f. Two limiting cases for Z above are: 1. When $\omega \rightarrow \infty, Z' \rightarrow 0, Z \rightarrow Z''$, herein, Z'' is small and Z is determined by the C , which provide the main ac current pathway. 2. When $\omega \rightarrow 0, Z'' \rightarrow 0, Z \rightarrow Z' = R$, the only current pathway is through R . Therefore, in low-frequency region, the impedance plot has an almost linear behavior (Figure 1-5f). A 45° straight line in the plane plot represents the diffusion behavior, which is called the Warburg impedance, W . In pseudocapacitor cases, two semicircles can be observed in the plane plot as shown in Figure 1-5g, since both species of capacitance, EDLC and pseudocapacitance, have relaxation process coupled with ohmic resistance. Three intercepts herein are $Z'=R_s$, $Z'=R_s+R_F$ and $Z'=R_s+R_F+R_{F'}$. The radii of two semicircles are determined by R_F and $R_{F'}$, respectively.¹²

Figure 1.5 RC equivalent circuits from (a) to (e) representation illustrates the basic operation of a single-cell supercapacitor. The ac responses to the latter two circuits of (d) and (e) are shown in (f) and (g), respectively.^{12,17} Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

1.2.3 Supercapacitor electrode materials

Materials used in supercapacitors include the electrode materials, electrolyte, separator as well as the charge collectors and the packaging materials. There are a lot of factors that can affect supercapacitor performance including electrolyte accessible surface area and conductivity of electrode materials, wettability of the electrolyte to the electrode materials, size of electrolytic ions, physical and chemical stability of both electrode materials and electrolyte, electrochemical potential window limits of the electrolyte solvent, properties of separator, etc. The general goal is to optimize all those factors in order to achieve high energy and power density with long durability. However, it is impossible to simultaneously ameliorate so many parameters in such a complex energy storage system. Electrodes are the main components of a SC and also the key factor that determines the performance of the SC. Thus, developing new materials for the electrodes with improved performance relative to existing electrode materials and/or additional novel characteristics that can fulfill more and more special demands appearing on SCs from practical applications have drawn the majority

of the attention on the extensive research for the SCs.^{16,45-47} Generally, the electrode materials should have large surface area, be electrically conductive and possess of high electrochemical cyclic stability. For pseudocapacitors, the electrode materials should be capable of allowing redox reactions. Carbon materials, especially activated carbons, carbon nanotubes and graphene, metal oxides and conducting polymers are the most commonly used materials as SC electrodes.

i. Carbonaceous Materials

Since Becker firstly applied high-surface-area carbon for the electrochemical capacitor, carbon materials have been mostly considered as the electrode materials for EDLCs due to their excellent electrical conductivity, high surface area, controlled porosity, ease of processability, variety of forms such as particles, powers, sheets, tubes, fibers, monoliths, composites, etc., broad chemical corrosion resistance and wide range of temperature stability, cost effectiveness and environmental friendliness.^{13,48-51}

The energy storage in carbon materials mainly undertake electric double layer across the electrode/electrolyte interface. In the development of novel carbon materials for energy storage, a pursuit of increasing their specific surface area and a proper control over their pore size distribution have always been emphasized in order to achieve both high power density and energy density.

So far, activated carbons (ACs) are the most widely used electrode materials in commercialized SCs because of their large surface area, easy processability, abundant source and low cost.^{50,52} In their 3D structures, the pore distribution of ACs can be well controlled by different activation methods.⁵¹ The porous structures of ACs after activation have a broad pore size distribution ranging from micropores (<2 nm), mesopores (2-50 nm) and macropores (>50 nm). Though ACs can achieve a specific surface area up to 3000 m²/g, their specific capacitance (<10 μF/cm²) is relatively small, indicating that not all surface areas are effectively utilized for charge storage.⁵³

Carbon nanotubes (CNTs) are allotropes of carbon which are formed by atomic carbon sheet (graphene sheet) rolled coaxially into one dimensional (1D) nanostructures. They can be categorized as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). CNTs have many remarkable characters including excellent electronic conductivity, high surface area, low mass density, outstanding chemical and physical stability,¹³ has made them attractive materials applied in energy storage field since 1991.⁵⁴ Both SWCNTs and MWCNTs have been assembled into various patterns, structures and forms,^{32,55-58} as well as forming hybrid composites composed with many other materials including other types of carbon materials,^{38,59-61} metal oxides,^{62,63} conducting polymers⁶⁴⁻⁶⁶ and so on. Using CNT based composites as SC electrodes has showed improved performances.

Graphene is a one atom thick, 2D nano carbon structure.⁶⁷ It has excellent electronic conductivity, good chemical and physical stability and large surface area. It is also a promising candidate for electrochemical energy storage device applications.⁵⁰ The general strategies used for graphene in SCs are similar with those applied for CNTs. A common issue for both CNT and graphene is that they would stack together due to the strong Van der Waals forces among graphitic carbon, which would decrease the surface area and block the access of electrolyte ions. A combination of CNTs and graphene may solve the problem to some extent. Two approaches have been studied to realize the combination of CNTs and graphene. One is to form a porous hybrid composite of reduced graphene oxide and CNTs.^{33,38,68,69} The other is to first grow graphene on metal substrates or fabricate graphene oxide and then in situ grows CNTs on graphene layers by chemical vapor deposition.^{29,70-72} The mixture makes the CNTs separate graphene layers by inserting between two layers of graphene preventing them from stacking together. On the other hand, graphene layers also lower the bundling of CNTs, and also act as good current collectors for CNTs. The novel structure leads to higher accessible surface area of electrodes, also makes it an extreme outstanding conductive network, overcoming the limitation of interlayer conducting of graphene and weak conductivity of point contact between CNTs.

Other carbon materials such as templated carbons,^{73,74} active carbon fibers,⁷⁵⁻⁷⁷ and carbon aerogels^{78,79} have also been investigated for SC applications.

ii. Metal Oxides/Hydroxides

EDL based SCs are favored by their high power density, current rate capability and long cycling lifetime with low maintenance cost.¹³ Nevertheless, their moderate energy density often fail to meet the performance requirements of a lot of power consuming electronics, especially electrical vehicles. In order to answer this challenge, researchers have devoted tremendous efforts to the development of novel performance SCs. Since S. Trasatti and G. Buzzanca discovered the outstanding capacitive property of RuO_2 ,⁸⁰ the metal oxide materials have attracted extensive research interest for the application of pseudocapacitors to achieve higher energy densities. As mentioned before, besides RuO_2 , many other metal oxides/hydroxides such as NiO or Ni(OH)_2 ,^{26,76,81-85} MnO_2 ,⁸⁶⁻⁹⁰ Co_3O_4 or Co(OH)_2 ,⁹¹⁻⁹⁴ Fe_2O_3 ,⁹⁵⁻⁹⁹ V_2O_5 ,¹⁰⁰⁻¹⁰³ etc. have also been discovered as promising candidates as pseudocapacitor electrode materials. Among them, RuO_2 , NiO or Ni(OH)_2 and MnO_2 are most widely and frequently studied and most promising in real applications for commercialization.

RuO_2 is used to be recognized as the most promising pseudocapacitor electrode material because of its excellent electrical conductivity, high theoretical specific capacitance estimated to be able to reach 2200 F g^{-1} ,¹⁰⁴ good chemical stability and long life-time.^{10,104,105} However, in practical SC applications, the performance was reported to depend on several aspects including surface areas, degrees of crystallinity, particle sizes and electrode architecture, and usually

smaller than the theoretical values due to the high crystalline and low-surface bulk structures.¹⁰⁶⁻¹⁰⁸ On top of that, the high cost of the noble metal, Ru, and its detrimental environmental impact further limit its commercial potential.^{46,104}

Compared to RuO₂, NiO and Ni(OH)₂ also exhibit theoretical capacitance (2584 and 2082 F g⁻¹, respectively, in potential window of 0.5 V) and high chemical and thermal stability, but are much more attractive given its acceptable cost and environmentally friendliness.¹⁰⁹⁻¹¹¹ NiOOH is the main counter form conversed from both NiO and Ni(OH)₂ in the redox reactions during the electrochemical charge and discharge. Despite the very high theoretical specific capacitance, the practical electrochemical performance of NiO or Ni(OH)₂ are often far below the expected values. The intrinsic shortage in electrical conductivity of the NiO or Ni(OH)₂ hinders the fast ion diffusion and charge transfer, limiting the redox reactions which can only take place on the surface thin layer. Therefore, the major part of the bulk NiO or Ni(OH)₂ cannot be utilized. In dealing with this issue, researchers have dedicated great efforts to coming up with numerous solutions.

One of the most frequently utilized methods is to control the morphology and particle size. The main aim of this strategy is to increase the electrolyte-accessible surface area providing more ion diffusion channels and electrochemical active sites that redox reactions can occur and to reduce the ion diffusion distance within

the bulk of the materials.^{76,85,109,111} Various morphology and sizes of nano-structured NiO or Ni(OH)₂ have been synthesized ranging from one-dimensional such as nanotubes,^{112,113} nanorods^{59,114} and nanowires,^{115,116} two-dimensional nanoribbons¹¹⁷ and nanoplates^{118,119} to three-dimensional including nanoflowers,^{120,121} hollow spheres,^{122,123} mesoporous film^{76,124} and other novel structures.^{85,125} All of these nano-structured NiO or Ni(OH)₂ with different morphologies have been fabricated into SC electrodes and investigated by different electrochemical and physiochemical methods to characterize their performance. Many reported results have demonstrated the advantages in improving the electrode performance by tailoring the morphology of the materials.²⁸

Another important strategy to enhance the capacitive performance of NiO and Ni(OH)₂ by directly addressing on the weak conductivity problem is to form hybrid composites with conductive components. Combining pseudocapacitor materials such as metal oxides and conducting polymers (an introduction of the conducting polymers will be seen below) with carbonaceous materials, metals, better conductive metal oxides or hydroxides, and conducting polymers to get hybrid composites is a promising way to further improve the performance of SCs. By hybridizing different kinds of SC materials, the synergistic effects of each component material can result in composites with increased capacitance, cycling life and rate performance for SCs.^{62,89,126,127} Generally, among numerous

combination approaches been researched to the hybrid systems, there are mainly three different approaches emerged: (i) physical mixing by various techniques, (ii) in situ deposition of pseudocapacitive materials onto carbon materials or conducting polymers, and vice versa, conductive layer is deposited onto metal oxides, and (iii) one-pot synthesis or co-precipitation of binary or more components formed composites. Deposition of metal oxides on highly conductive carbons following the technique (ii) are the most adopted methods to form hybrid composites for the SC electrodes due to the simple, scalable and cost-effective synthesis and fabrication.⁴⁶

As introduced above, CNTs form a large family of one-dimensional nanomaterials with good electrical conductivity, high surface area and excellent mechanical property, making them excellent substrates for holding metal oxides for composite electrodes and apparently promoting the electrochemical performance.¹²⁸⁻¹³⁰ For example, flexible electrodes fabricated from NiO/MWCNTs nanohybrid thin film on stainless steel were reported to achieve a highest specific capacitance of 1727 F g^{-1} at 5 mA cm^{-2} current density and good capacitance retention of 91% after 2000 cycles.¹³¹ The MWCNTs offered a large surface for the deposition of NiO nanospots which yielded microporous structure with reduced charge transfer resistances and enhanced NiO utilization, specific capacitance, good rate capability, power density and electrochemical stability.

Figure 1.6 (a) SEM image of a hybrid composite from Ni(OH)₂ nanostructures deposited on MWCNTs on a nickel foam (NF); (b) CV curves comparison of the Ni(OH)₂/CNT/NF ternary hybrid composite with the CNT/NF and Ni(OH)₂/NF composites.¹³² Copyright 2012, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

As shown in Figure 1.6a, nano-structured Ni(OH)₂ was deposited on the MWCNTs which were initially grown on a nickel foam (NF) by chemical vapor deposition (CVD), forming a ternary hybrid composite.¹³² This hybrid composite was fabricated to electrodes for SC applications and measured electrochemically by CV and charge/discharge techniques. Figure 1.6b shows the CV curves of the ternary composite electrode as well as CNT/NF and Ni(OH)₂/NF electrodes. The superiority in capacitance from the ternary composites could be apparently interpreted from the CV covering area size difference. A remarkably high specific capacitance of 3300 F g⁻¹ at 1 mV s⁻¹ was obtained contributed from the Ni(OH)₂, much higher than the 2820 F g⁻¹ of the Ni(OH)₂ specific capacitance got from Ni(OH)₂/NF electrode without CNT support by direct Ni(OH)₂ deposition on NF

and even with less Ni(OH)_2 mass loading. With the incorporation of CNTs to provide high surface for well-dispersion of Ni(OH)_2 nano-flakes and to guarantee a fast charge transfer, the ternary hybrid composite electrode benefited from the synergistic effect and achieved exceptional properties.¹³² Though the electrochemical capacitance of the NiO or Ni(OH)_2 based materials has reached a very high level by current strategies, there still remain many challenges such as their narrow potential window in aqueous electrolyte that limits the energy density and moderate electrochemical stability that harms the long-term cyclic life. Moreover, in order to prevent the possible limits of current strategies, not only current methods need to be further ameliorated to develop more novel structures, but more strategies need to be discovered to further improve performance of the NiO and Ni(OH)_2 materials fabricated electrodes such as controlling crystallinities of the materials to prepare more amorphous structures like it have been done on RuO_2 based electrodes.^{28,133}

Among the non-noble metal oxides that have been discovered applicable for pseudocapacitors, none has been investigated as much as MnO_2 since the pioneering work published on its pseudocapactive behavior in 1999 by Lee and Goodenough.^{9,134,135} Beside low cost, resource abundance and environmental friendliness, MnO_2 can have a wide potential window of 1 V in aqueous electrolyte, almost twice of that of Ni(OH)_2 , which means only the capacitance of Ni(OH)_2 electrode being four times of that of MnO_2 electrode in a SC can

equal their energy density, judging from equation 1.5 shown above. However, the theoretical specific capacitance of MnO₂, about 1100 F g⁻¹,¹⁰ is moderate as compared with those of RuO₂ and Ni based materials. And practically, the specific capacitances of MnO₂ electrodes are usually measured to be much lower than those of Ni(OH)₂ based electrodes.¹³⁶ The proposed charge storage of the MnO₂ based on the redox reaction between the III and IV oxidation state of Mn includes a surface adsorption of electrolyte cations (A⁺ = H⁺, Li⁺, Na⁺, K⁺, etc.) as:^{86,136}

and bulk electrolyte cations intercalation upon MnO₂ reduction and deintercalation upon oxidation following:⁸⁶

Different from many other pseudocapacitive transition metal oxides which often have well-defined redox peaks during CV test, the MnO₂ electrodes usually exhibits a rectangular shape of CV curves (see in Figure 1.7) in neutral aqueous electrolyte, just like those of EDLCs, indicating its redox reactions process in a reversible and successive surface behaviors.⁹ Similar with the NiO and Ni(OH)₂, MnO₂ also suffers from the poor electrical conductivity that limits material

utilization in thick MnO_2 electrodes.¹³⁶ The electrochemical performance of MnO_2 has also been found to depend strongly on the material structures and morphology. Therefore, various MnO_2 with different morphologies and porous nano-structures have been prepared, like it was been done on $\text{Ni}(\text{OH})_2$ based materials, exhibiting large specific surface areas, shorter ion diffusion path length, more diffusion channels and sufficient faradaic reactions, all leading to improved pseudocapacitance.¹³⁷⁻¹⁴¹ Hybridization of the MnO_2 with the conductive components has also been extensively carried out.¹⁴²⁻¹⁴⁵ Depositing MnO_2 on nanoporous gold obtained enhanced conductivity and an extremely high specific capacitance ($\sim 1145 \text{ F g}^{-1}$) of the constituent MnO_2 .¹⁴⁶ $\text{MnO}_2/\text{Mn}/\text{MnO}_2$ sandwich-like hybrid nanotube arrays were prepared and exhibited an excellent rate capability, a high energy and power density of 45 Wh kg^{-1} and 23 kW kg^{-1} , respectively.¹⁴⁷ Chemical co-precipitation, thermal decomposition and electrodeposition are the most common methods used for preparation of MnO_2 -CNT composites.¹³⁶ Besides developing novel morphologies and hybridizing with conductive materials, incorporation or doping of other metal elements such as Co, Ni, Al, Au, V, Fe, etc. into the MnO_2 crystal has been considered as effective approaches to ameliorate the electrical conductivity and increase specific surface areas due to forming more charge carriers and defects in the oxide crystal structures.¹⁴⁸⁻¹⁵² Furthermore, the crystallinity of MnO_2 can also affect the electrochemical performance of its electrodes. More amorphous

crystalline structures of MnO₂ were favored to provide higher pseudocapacitance, which may be attributed to the higher density of the grain boundaries with fine grains in low crystallinity resulting to more diffusion channels for electrolyte ions.^{153,154} So far, most of the MnO₂ synthesis methods required harsh conditions including high temperatures (90-180 °C for wet-preparation and 300-800 °C for thermal-decomposition), acid or basic solutions and existence of reducing or oxidizing agents, especially in the preparation of MnO₂-highly conductive carbon hybrids, the oxidative precursor, KMnO₄, may partially damage the conductive surface of the carbon materials. Therefore, more new approaches for preparation of MnO₂ with novel structures are still worth researching in.

Figure 1.7 CV curve of a MnO₂-electrode cell in neutral aqueous electrolyte (0.1 M K₂SO₄). The dash lines indicate the successive multiple surface redox reactions.⁹ Copyright 2008, Macmillan Publishers Limited.

iii. Conducting Polymers

Electrically conducting polymers have also been regarded as good pseudocapacitive materials for SC electrodes. The π -conjugated polymeric chains distinguished the conducting polymers from normal polymers. The pseudocapacitive storage of the conducting polymers is realized through the redox reactions of the π -conjugated groups on polymer backbones during electrochemical charge and discharge: ions transfer to the polymer backbones when being oxidized and vice versa during reduction. The redox processes not only occur on the surface of the polymers but also happen throughout the entire bulk.¹⁶ However, the redox reactions do not change the structures of the polymer, therefore, own good reversibility in the repeated processes.¹⁷ The main advantage of conducting polymers over majority of metal oxides for applications in SCs is their good electrical conductivity. Due to existence of highly π -conjugation structures, electrons can transfer along the polymer backbones through the π -conjugated bonds. While the conductivity is usually low (in a range of $10^{-10} - 10^{-5} \text{ S cm}^{-1}$) in their neutral states, it can be dramatically increased up to 10^4 S cm^{-1} by chemical or electrochemical doping.¹⁵⁵ The doping happens during the oxidation or reduction of the conducting polymers, which makes them positively or negatively charged, also called p-doped or n-doped, and insertion of outer counter ions onto the polymer chains to balance the charges. Those charges can bring delocalized electrons that induce electrical conductivity under potential.

PANI and PPy are among the most commonly used conducting polymers and have been extensively studied as electrode materials for SC applications because of their good electrical conductivity, low cost, ease of preparation, good electrochemical activity, and high specific capacitance.^{66,156,157} However, they suffer from intense volume change with the insertion and de-insertion of ions into the polymer matrix during charge and discharge, especially PANI who has a higher dopant level.¹⁵⁷ This volume swelling and shrinking can cause physical structure degradation and eventually result in poor cycling stability.^{10,158} In addressing the issue, the conducting polymers have been incorporated with porous and rigid materials as support. It has been demonstrated that the conducting polymers hybridized with carbon, metal and metal oxides/hydroxides to form composites can obtain remarkably improved electrochemical performance including synergistic increase in specific capacitance of all hybridizing components, enhanced electrode mechanical and cycling stability.¹⁵⁹⁻

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Another of the main problems for conducting polymers is the poor solubility or even insolubility in many practically interested solvents, which makes it quite difficult in their solution processing for electrode fabrication.¹⁶² PEDOT is a conducting polymer derived from polythiophene (PTh), but has higher conductivity and wider potential range of 1.4 V, and can be either p-doped or n-doped, unlike PANI and PPy who can only be p-doped and used as cathode

materials.¹⁵⁷ Figure 1.8a shows the structure of PEDOT. When doped with a polyanion, polystyrenesulfonate (PSS) as shown in figure 1.8b, the polymer mixture, PEDOT:PSS, can improve compatibility with polar polymers, enhance aqueous wettability and dispersion ability, and thus achieving better performance in aqueous electrolytes.

Figure 1.8 Chemical structures of PEDOT (a) and PSS (b).

1.2.4 Asymmetric supercapacitors

Liquid electrolytes applied for batteries and supercapacitors mainly come in three categories: aqueous, organic and ionic liquid (IC). Many batteries like lithium and lithium-ion batteries and some commercial EDLCs use organic electrolyte. Though the organic electrolytes have voltage windows higher than 3 V, they can often bring many safety challenges which are seriously related to their flammability. ICs can also provide even higher voltage windows and do not face the flammable issues. Nevertheless, the high cost of the ion liquids limits their widely commercialization. Aqueous electrolytes have been favored in SC applications because of their low cost, low hazard, and low sensitivity to oxygen and moisture that it does not ask for very complicated processes and harsh

conditions for the aqueous based SC production. In addition the aqueous electrolytes have advantages over the organic and ionic liquid electrolytes in higher ionic conductivity and higher ionic concentrations. However, the low threshold of electrochemical water splitting, especially with the existence of several metal oxides that commonly interested for electrode materials, severely limits the potential windows of the aqueous based SCs. Hence, the conventional aqueous based symmetric SCs have relatively narrow potential windows usually at 1 V but cannot exceed 1.2 V (the theoretical water electrolysis voltage is 1.23 V), which severely limits their energy density.¹⁶³

Recent years, a new class of SCs, called asymmetric SCs, has been proposed as a promising approach to extend the voltage limitation of the aqueous based SCs. The name “asymmetric” was earned from the character of two different electrodes paired in a SC: a pseudocapacitive positive electrode fabricated from the pseudocapacitive materials and the other EDLC-type electrode such as using high-surface-area highly-conductive carbon. During the charge and discharge of the asymmetric device, the positive electrode takes charge storage process through faradaic redox reactions, while the negative electrode can have fast charge storage due to the EDL mechanism. The operation voltage of an asymmetric SC can cover both the working potential windows of the positive electrode and the negative, taking advantage of high overpotentials of H₂ and O₂ evolution on carbon based negative electrode and pseudocapacitive positive

electrode, respectively, and kinetically suppressing the water splitting at higher voltage even at 1.8 V.¹⁶³ Hence, the asymmetric SCs can usually achieve much higher energy densities than each of the corresponding electrode formed symmetric SCs. Table 1.1 lists several typical examples of asymmetric SCs with their electrode materials, electrolytes, operation voltages, cell capacitance, energy and power densities

Table 1.1 A comparison of voltage window, capacitance, energy and power density of several typical aqueous-electrolyte based asymmetric SCs.

Positive electrode	Negative electrode	Electrolyte (aqueous)	Operation voltage (V)	Cell capacitance (F g ⁻¹)	Maximum energy density (Wh kg ⁻¹)	Maximum power density (kW kg ⁻¹)	Reference
PANI/CNTs	Carbon black	1 M HCl	1.4	20.5	11.3	0.63	164
MnO ₂	Activated carbon (AC)	0.5 M K ₂ SO ₄	1.8	31	17	2	165
MnO ₂ /nickel foam (NF)	Graphene hydrogel	0.5 M Na ₂ SO ₄	2.0	41.7	23.2	10.0	41
Reduced graphene oxide (RGO)/MnO ₂	Activated carbon nanofiber	1 M Na ₂ SO ₄	1.8	113.5	51.1	16.5	166
Graphene foam/CNTs/MnO ₂	Graphene foam/CNTs/PPy	0.5 M Na ₂ SO ₄	1.6	64.1	22.8	2.7	167
Carbon nanofiber/MnO ₂	Nitrogen-doped carbon nanofiber	1 M Na ₂ SO ₄	2.0	59.2	32.91	284.63	168
Ni(OH) ₂ /RGO	Porous graphene	6 M KOH	1.6	218.4	77.8	15.2	29
Co ₃ O ₄ @Ni(OH) ₂ /NF	RGO	6 M KOH	1.7	110.8	41.9	1.87	169
NiO/3D graphene	AC	1 M NaOH	1.5	440	138	15	170
Ni(OH) ₂ /CNTs	AC	6 M KOH	1.5	96	40	1.5	171
Ni-Co layered double hydroxides (LDH)/RGO	AC	6 M KOH	1.75	87	35.5	8.75	172
RGO/RuO ₂	RGO/PANI	2 M H ₂ SO ₄	1.4	96.6	26.3	49.8	173
RuO ₂ /TiO ₂	AC	1 M KOH	1.4	46	12.5	1.2	174
RGO/V ₂ O ₅	RGO	1 KCl	1.6	195	75.9	0.9	175
Ni-Co LDH/Zn ₂ SnO ₄	AC	2 M KOH	1.22	125.2	23.7	5.82	176

1.2.5 Flexible supercapacitors

Modern portable and flexible electronic devices place a strong demand for flexible, light-weight and environmentally friendly energy storage devices.^{47,177-180} However, the rigid nature of most batteries and the severe safety issues accompanied with potential short circuit risk during bending bring too many challenges to accomplish good flexibility for the batteries. On the contrary, SCs do not possess such problems faced by the batteries and can thus be potential candidates for such applications. To realize such flexibility in SCs with high electrochemical and mechanical performance, researchers have made tremendous effort in developing novel flexible electrodes. Generally, feasible approaches have come into two directions. One is to directly fabricate free-standing flexible electrodes with flexible materials. Typical representatives of such flexible electrodes are CNT paper,^{64,181,182} graphene paper,¹⁸³⁻¹⁸⁵ and their hybrid composites based electrodes^{186,187} for regular-sized SCs and fiber-based flexible electrodes for micro-SCs.¹⁸⁸⁻¹⁹⁰ The fiber-based micro-SCs will be further discussed in later part of 1.2.6. The other major direction is using intrinsically flexible materials as substrates from the electrode active materials, such as carbon cloth,¹⁹¹⁻¹⁹³ metal mesh,^{194,195} paper,^{56,196,197} textile^{198,199} and plastic films.^{200,201} For the free-standing flexible electrodes, they have to be made a little thick to obtain enough mechanical strength to be free-standing. While controversially, too much thickness will dramatically reduce the flexible property

of those nanocarbon based electrodes, increasing the thickness can also negatively affect the electrochemical performance of the electrodes because of electron and ion transfer limitations. Using an intrinsically flexible substrate for electrode fabrication will not face aforementioned contradictions and preparation troubles.²⁰² Among all the flexible substrates, paper, especially cellulosic paper, attracted special interest from researchers.

Cellulosic paper is a sheet material made of a network of natural cellulose fibers.²⁰³ It is by far the cheapest and most widely used flexible substrate in daily life. The paper substrates have many good properties including surface roughness, dimensional stability, thermal stability, flexibility, mechanical strength. The abundance of the resource for paper makes the price substantially lower than that of plastic substrates such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polyimide and polycarbonate.²⁰⁴ In addition, paper is a green material, since it is recyclable and made of naturally renewable materials. Previously, plastic substrates are usually chosen to be “printed” on electronics such as transistors, diode structures like solar cells, organic light-emitting diodes and rectifying diodes, electronic memories, actuators, for displays, RFID tags and sensors applications. Paper can also be used in printing electronics.²⁰⁴ The rough surface of the paper is preferred in energy storage devices like batteries and SCs, since the roughness leads to large surface area and also improves electrolyte absorption.^{204,205} Since the cellulose fibers which make up the paper are

insulating and electrochemically inactive, electronically conductive materials such as carbon nanotube,^{56,202,206-209} graphene,²¹⁰ graphite,²¹¹ metal nanowires,²⁰⁹ conductive metal oxide,²¹² and conducting polymers²¹³⁻²¹⁵ have been integrated to make paper conductive.

In paper-based energy storage applications, there are mainly two approaches for composites preparation. One approach is initiated from dissociative cellulose fibers or nanofibrils. The cellulose fibers are first deposited with electronically conductive and electrochemically active materials such as CNTs^{207,208} and conducting polymers^{213,216}, and then fabricated into composite papers by filtration for SC electrode applications. For the second approach, commercially available paper sheets are directly coated with conducting materials like CNTs^{40,56,202,206,217,218}, graphene,²¹⁰ metal nanowire²¹⁷ and even pencil-drawn graphite²¹¹ to form the conductive electrode materials. However, for the first approach, the separated cellulose fabricated paper sheets need extra processes which are usually more complicated. What's more, the mechanical properties of the paper sheets prepared by post fabrication cannot compare with those of industrial produced paper. Hence, directly utilization of pristine commercial papers may be a better choice for flexible energy storage devices.

Hu *et al.* reported the first study using conventional cellulose paper in 2009, applying SWCNT or silver nanowires (Ag NWs) ink onto Xerox paper using a

Meyer rod coating method to form conductive paper, which was then used as active electrodes and current collectors in ECs, which is illustrated in Figure 1.9a.²¹⁷ A relative uniform coating of CNTs or Ag NWs on the rough paper surface was achieved seen from the SEM images in Figure 1.9c-e and also turned out a good conductivity shown in Figure 1.9f. The results shows that a specific capacitance of 200 F/g in aqueous electrolyte with voltage window of 1 V, specific energy density of 30-47 Wh/kg and specific power density of up to 200 kW/kg in organic electrolyte with voltage window of 3 V can be achieved when only considering the mass of CNTs. Different from the above used roll-to roll printing technique, Hu *et al.* used dip-dry method of cotton paper in acid treated SWCNT water solution⁴⁰ and Kang *et al.* used drop-dry method to coat the CNTs onto an office paper.²⁰² They both utilized solid electrolyte to fabricate all solid-state paper based SCs. Hu *et al.* utilized the H₃PO₄/PVA gel as solid-state electrolyte, charged the device to over 3 V (up to 5.5 V) and got specific capacitance and energy density to be 115.8 F/g and 48.8 Wh/kg carbon, respectively.

Figure 1.9 (a) Coating of CNT or Ag NW ink on commercial Xerox paper. (b) CNT coated Xerox paper. SEM images of (c) surface morphology of Xerox paper, (d) CNT coating along fibers in Xerox paper, and (e) Ag NW coating on Xerox paper. (f) Sheet resistances of conductive paper based on CNTs and Ag NWs with various thicknesses.²¹⁷

There are several unsolved issues which limit the applications of the paper-based flexible SCs. Similar to regular SCs, the energy density of flexible SCs is still low. Energy density of SCs has always been one of the key factors that limit the commercialization potential of SCs.⁹ Among published studies, most work on flexible SCs based on cellulose papers and textiles simply used carbon materials to achieve EDL capacitance. Though EDLC can bring high powder density, it usually cannot provide high energy density. One way to improve the

energy density is to incorporate pseudocapacitive materials such as metal oxides and ECPs. However, the incorporation of pseudocapacitive materials brings other issues. First, the processing of cellulose to form composites with other materials remains complicated. The low solubility of cellulose in water or organic solvents and the difficulty in its chemical functionalization have led to limited success in forming composites with other materials. Moreover, cellulose can easily decompose in acid or alkaline or even high temperature aqueous solvents, especially forming structure controlled metal oxides and/or conducting polymers on cellulose fibers. In a previous reported work on MnO₂ deposited textile based SCs, authors observed cracks of the MnO₂ deposited CNT/fabric fibers in the electrodes after 50000 cycles.⁹⁰ Such crack would further develop and have a negative effect on the electrodes. On the other hand, metal oxides may also be deficient in mechanical flexibility and strength. Thus, further investigations need to be carried out to improve the energy density of the flexible SCs and simultaneously having a good retention of the mechanical properties.

A brief summary of several flexible supercapacitors based on commercial cellulose papers as substrate are list in table 1.2.

Table 1.2 A brief summary of paper based flexible hybrid electrodes for supercapacitors.

Hybrid electrode materials	Fabrication methods	Electrochemical performance	Reference
SWCNT-printing paper	SWCNT ink coated by Meyer rod	200 F/g in aqueous electrolyte; 30-47 Wh/kg and up to 200 kW/kg in organic electrolyte	209
SWCNT-PVDF-printing paper	PVDF coated by Meyer rod; SWCNT ink coated by Meyer rod or ink-jet printing	About 37 F/g at 0.2 A/g charge-discharge in 1 M LiPF ₆ EC/DEC organic electrolyte	56
DWCNT-bacterial nanocellulose paper	Filtration of DWCNT ink	50.5 F/g, energy density 15.5 Wh/kg, power density 1.5 kW/kg in ionic liquid-based polymer electrolyte	219
rGO-filter paper	Filtration of rGO dispersed solution	120 F/g at 1 mV/s CV in 1 M H ₂ SO ₄ aqueous electrolyte	220
SWCNT-cotton paper	Dip-dry	13.15 F/g, energy density 5.54 Wh/kg	221
Graphite-printing paper	Graphite pencil drawing	12 F/g, 2.3 mF/cm ² in 1 M H ₂ SO ₄ aqueous electrolyte	222
MnO ₂ -SWCNT-printing paper	Drop SWCNT solution onto the paper and dry; electrochemical deposition of MnO ₂	540 F/g, energy density 20 Wh/kg, power density 1.5 kW/kg	223

1.2.6 Micro-supercapacitors

In above part, we have discussed about the development of flexible SCs in order to meet the increasing demand of flexible electronics. Besides, with the higher integration of electronics toward miniaturization, there is a growing demand of small-scale storage units or devices.²²⁴ Future developments of a large diversity in portable and wearable electronics, permanent implantable biosensors, remote and mobile environmental sensors, microelectromechanical systems (MEMS) and nanorobotics are expanding the energy and power requirements for the micropower systems.^{45,225} Currently, the micro self-power devices usually need batteries, especially thin-film batteries, to provide their power and energy. However, the batteries suffer from low power that limits their applications in some fast energy-release fields. Another disadvantage of the batteries is their poor lifetime, which requires a regular maintenance or replacement. Not to mention the extra work and cost for maintenance or change, to change the batteries of some implanted medical devices or devices in some remote or hazardous area may bring potential danger to the implant patients or the site operators. In addition, the non-flexibility and safety issues to the health and the environment are all hindering the batteries based powering systems from broad application in the micro devices.⁴⁵ Micro-supercapacitors (micro-SCs) have been studied and recognized as promising and reliable energy storage solutions for the miniaturized devices, contributing to their capability of small sizes controllability,

higher power densities and longer cyclic life.²²⁶⁻²²⁸ Moreover, the materials for the micro-SCs are generally less hazardous than those from batteries and also do not have safety issues like explosion and fire caused by short circuiting. Recent developed micro-SCs can be mainly categorized into two general configurations: (i) planar-type micro-SCs and (ii) fiber-based micro-SCs.

The unique features of the micro-SCs compared with conventional SCs are much smaller, thinner and flexible. Initially, micro-SCs have quite similar stack configurations like the regular-sized SCs with a planer 2D architecture but thinner film electrodes that stacked parallel on a flat substrate as illustrated in Figure 1.10a. However, the stack configurations have to be at least double in thickness than the single electrodes. If there is a need to achieve higher energy, the thickness will have to increase even more, which limits the effectively percolation and transport of the solid electrolyte and lead to lower power efficiency.²²⁹ As a variation, a new type of planar micro-SCs has been designed with in-plane interdigital configurations. In Figure 1.10b, different from the parallel stack of electrodes, the two opposite electrodes after variation have two-comb-like interdigital patterns that aligned in parallel manner and alternatively with small gaps in the same plane. This in-plane structures can decrease the complexity in device fabrications and gain more feasibility in integration with other planar microelectronics.²³⁰ Moreover, in-plane interdigital configurations do not have high risk of inter-electrode short circuiting compared with the

conventional stack configurations, which, otherwise, need thick enough solid electrolyte to guarantee the sufficient separation of the opposite electrodes. Another merit of the interdigital electrode patterns is the increased surface for the accessibility of the electrolyte. Especially, for graphene or other similar 2D materials formed layered electrodes, the in-plane geometry is more favored for the electrons and ions to transfer fast between layers along the layer directions instead of transferring through the layers along cross layer directions in the stack geometry with much lower efficiency.²³¹ However, the shared drawback of the planar micro-SCs is the low areal capacitance or energy due to their very thin electrodes.⁴⁵

Figure 1.10 Schematic diagrams of (a) a conventional 2D architecture planar micro-supercapacitor and (b) an interdigital planar micro-supercapacitor.⁴⁵

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Catering to the recent emerging and fast developing in smart wearable electronics and smart textiles, higher requirements such as wearability are coming for the development of flexible energy storage systems. Such new challenges are also faced by the development of the micro-SCs. A new family of SCs, fiber SCs with 1D fibers as electrodes, has attracted a lot of attention. The fiber electrodes generally have diameters from micrometers to millimeters, small in size and light in mass. The flexible wired-shaped fibers can further be woven or knitted into fabrics and textiles with excellent wearability. Particularly, it is of great potential to fabricate fiber-based micro-SCs from the fiber electrodes whose diameters are in micro-scale into various desired shapes and capable to fit in different integration space and locations.^{232,233} While compared with the conventional SCs, even the aforementioned planar-type micro-SCs, fiber-based micro-SCs are only researched recently and still in the infancy stage of development. The first prototype of fiber-based micro-SC was invented by Bae *et al.* in 2011, in which they fabricated the wire-shaped electrode utilizing a gold-coated flexible plastic wire as the substrate to support ZnO nanowire arrays as electroactive material.²³⁴ Since then, many more new fibers have been developed and applied as electrodes for the fiber-based micro-SCs. Although plenty of studies have been carried out for fabrication of those fiber electrodes from different materials and various fabrication methods, with diverse technical requirements, they all shared a common research goal of developing flexible

energy storage devices with higher electrochemical performance to satisfy the growing demands of the power-consuming microelectronics and micro-devices. As summarized by our group, so far, the fiber electrodes can be mainly divided into three types: (1) fiber electrodes with metal wires as current collectors, (2) all-carbon fiber electrodes without metal wires, and (3) pseudocapacitive material-carbon composite fiber electrodes without metal wires.¹⁹⁰ Among them, the carbon-based fiber electrodes have been most extensively researched in recent two years because of their superiority in low densities, excellent conductivity and good mechanical properties. The carbon-based fiber electrodes have been fabricated from a wide range of carbonaceous precursors and various fabrication approaches including conventional carbon fibers as cores for active material deposition,^{189,235,236} wet-spinning or dry-spinning of CNTs,²³⁷⁻²³⁹ wet-spinning graphene oxides followed by chemical or thermal reduction,^{111,240-242} tube-confined hydrothermal treatment of graphene oxides.^{30,243,244} The performance of macro-SCs are usually evaluated by their gravimetric performance including capacitance, energy and power densities. However, for micro-SCs, the weight of the electrode materials is often very low. While the limited space on micro-devices for the energy storage systems is the most concerned factor. Therefore, the micro-SCs are usually evaluated based on the volumetric or areal performance, which is more meaningful. Specifically for 1D electrodes of the fiber-based micro-SCs, length based electrochemical

performance should also be carefully evaluated. For all the performance metrics that characterized for the fiber-based micro-SCs, energy and power densities are the most important ones that mainly determined their applicability in practical applications for the microelectronics and micro-devices. Thus, the main target for current research on fiber-based micro-SCs is to match the energy and power requirements of the emerging microelectronics, micro-devices and other practical small energy consuming applications.

1.3 Conclusion

In this chapter, I have introduced the basis of supercapacitors as the promising media for energy storage including the types of SCs which can basically be generalized to electric double layer capacitors and pseudocapacitors, common evaluation metrics for SCs and materials for SCs, especially electrode materials which generally come from three categories: carbonaceous materials, pseudocapacitive metal oxides/hydroxides and conducting polymers. Furthermore, I have briefly reviewed several developing trends of current SC research in order to meet developing performance demands from more diverse practical applications. An asymmetric SC has a pseudocapacitive positive electrode that can provide high capacitance storage and an EDL negative electrode that can contribute to high power density. The asymmetric SCs are favored in aqueous electrolyte system for providing higher energy densities due

to extended cell voltage windows. With the emergence of flexible and portable electric devices, there are increasing demands for light weight and flexible capacitive energy storage systems. Various types of flexible SCs have been discovered; while among them, the paper based flexible SCs have attracted a lot of interest and been particularly discussed. Besides flexibility and lightness, small sizes are favored for fast-developing microelectronics and micro-devices. Thus, micro-SCs including planar-type micro-SCs and fiber-based micro-SCs have been focused. Compared with planar-type micro-SCs, fiber-based micro-SCs cannot only realize small sizes with various desired designs, also exhibit higher flexibility and more importantly, wearability for matching developments of smart wearable devices and smart textiles.

1.4 Motivation, Objectives and Scope of This Thesis

Currently, though the SCs have been extensively researched, there still remains great potential to promote their electrochemical performance. An effective approach is to develop composite materials hybridizing highly conductive EDL materials with pseudocapacitive materials for getting synergistic effects. Nickel hydroxide ($\text{Ni}(\text{OH})_2$) is a promising pseudocapacitive material to increase the energy storage capacity of SCs. It has three common crystalline structures: amorphous (amor), α - and β - $\text{Ni}(\text{OH})_2$. There is a lack of good understanding on their pros and cons as SC electrodes. In Chapter II, the electrochemical

performance of MWCNTs/Ni(OH)₂ composites depending on the crystallinity of Ni(OH)₂ have been investigated. Three nanocomposites with thin layers (10-15 nm) of amor-, α -, and β -Ni(OH)₂ deposited on MWCNTs are synthesized and evaluated on electrodes. The amorphous Ni(OH)₂ based composite achieves highest specific capacitance and rate capability, while suffers severe decaying cycling stability. The results highlighted that the electrochemical performances of MWCNT/Ni(OH)₂ nanocomposites depend on the crystallinity of Ni(OH)₂, and the performances of electrodes change upon the crystalline structure transformation of Ni(OH)₂ under repeated redox reactions.

Since the superiority of amorphous Ni(OH)₂ in application as SC electrode materials have been demonstrated, improving the structure stability and corresponding electrochemical performance of amor-Ni(OH)₂ became the focal point in the next study. A coaxial ternary hybrid material was prepared comprising of amorphous Ni(OH)₂ deposited on MWCNTs wrapped with conductive polymer (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)) and investigated for SC applications in Chapter III. The polymer layer prevents the degradation of the nanostructure and dissolution of Ni ion during repeated charge-discharge cycling for 30000 cycles, a phenomenon which often plagues Ni(OH)₂ nanomaterials. Furthermore, using the ternary Ni(OH)₂ hybrid and the reduced-graphene-oxide/carbon nanotube hybrid as the positive and negative electrodes, respectively, the assembled asymmetric supercapacitors exhibited

highest energy density of 58.5 Wh kg^{-1} at the power density of 780 W kg^{-1} as well as long cycle life (86% capacitance retention after 30000 cycles). The ternary hybrid architecture design for amorphous Ni(OH)_2 can be regarded as a general approach to obtain pseudocapacitive materials for SCs with both high energy density, excellent rate capability and long cycle life.

Modern portable electronic devices create a strong demand for flexible energy storage devices. Paper based nanocomposites are attractive as sustainable materials for such applications. In Chapter IV, I directly explored the hydroxyl chemistry of cellulose fibers of rice paper to synthesize hybrid ternary nanocomposites, comprised of rice paper, SWCNTs and manganese oxide nanoparticles. The functional groups on cellulose fibers could react with adsorbed permanganate ions, resulting in uniformly depositing manganese oxide nanoparticles. SWCNTs coated on top of manganese oxides formed a highly conductive network connecting individual manganese oxide particles. Using the hybrid ternary composites as electrodes, the assembled two-electrode SCs were demonstrated high performance in capacitance, energy, power, and cycle stability. In addition, the nanocomposites showed good mechanical strength and excellent mechanical flexibility that their capacitance has negligible changes after bending more than 100 times. These findings suggested that opportunities exist to further explore the rich chemistry of cellulose fibers for innovative energy applications.

Though the paper-based SCs exhibited excellent flexibility and have great potentials in developing flexible energy storage systems for portable devices, they fail to meet the fast growing demands of small-sized electronics and power consuming devices, and are also not qualified with new trends for wearable applications. In addressing these issues, fiber-based micro-SCs have been discovered and applied. However, as compared to conventional SCs, the history of fiber-based micro-SCs is quite short that they have not been extensively investigated. Especially, most previous studies on fiber SCs mainly focused on reporting methods for fiber preparations or merely increase the electrochemical values through novel structure design or incorporation of pseudocapacitive materials, but rare made efforts to better fit the wide range of power demands of practical applications. In Chapter V, a series of RGO/MWCNT hybrid carbon fibers for micro-SC applications have been reported. A unique method is developed for scaled synthesis and diameter control of nitrogen doped RGO/MWCNT porous fibers by one-step-one-pot confined hydrothermal self-assembly and simultaneous reduction. The diameters of the hybrid carbon fibers cross a wide range from 30 to 240 μm , while still keeping good electrical conductivity, high ion-accessible surface area and mechanical strength. Yarn micro-SCs were fabricated with these different-diameter and different-length carbon fibers, which could successfully cover a broad range of energy and power and satisfy a variety of requirements from volumetric to length performance,

without compromising excellent long term cyclic stability and flexibility.

Chapter II Nickel Hydroxide-carbon Nanotube Nanocomposites as Supercapacitor Electrodes: Crystallinity Dependent

Performances

(This chapter is reproduced with permission from Jiang, W; Zhai, S; Wei, L; Yuan, Y; Yu, D; Wang, L; Wei, J; Chen, Y*; Nickel hydroxide-carbon nanotube nanocomposites as supercapacitor electrodes: crystallinity dependent performances, *Nanotechnology*, 2015, *accepted*. Copyright 2015, IOPscience)

2.1 Background Introduction

As introduced above, supercapacitors are attractive energy storage devices because of their high power density, high rate capability and long cycle life.¹⁶ However, their energy density is much lower compared to batteries.⁹ Pseudocapacitive materials with fast reversible redox reactions can be used to increase the energy density of supercapacitor.¹³⁶ Among them, nickel hydroxide (Ni(OH)_2) is a promising candidate because of its high specific capacitance of 2082 F g^{-1} (in a potential window of 0.5 V), low cost, and environmental friendliness.²⁸ A critical obstacle for Ni(OH)_2 's practical applications is its low electrical conductivity at $\sim 10^{-15} \Omega^{-1} \text{ m}^{-1}$ ²⁴⁵, which restricts redox reactions to its surface. Thus, most of bulk Ni(OH)_2 used in supercapacitor electrodes would remain as inefficient dead volume.^{117,119} Researchers have created different nanostructures to increase the electrolyte accessible surface area of Ni(OH)_2 ,

including nanoparticles,¹⁹⁴ one-dimensional (1D) nanowires,¹¹⁶ nanorods,¹¹⁴ nanotubes,¹¹² nanoribbons,¹¹⁷ 2D nanoplates,¹¹⁹ mesoporous films,¹¹¹ 3D flowers,²⁴⁶ hollow structures,¹²² thin layer coatings²⁴⁷ and other structures.^{8,125,248} Further, these nanostructured Ni(OH)₂ have been combined with conductive nanomaterials or polymers to generate conductive network imbedded nanocomposites.^{8,190,248} In particular, multi-walled carbon nanotubes (MWCNTs) have proved to be an ideal choice as conductive networks because of their high electrical conductivity, large specific surface area, and relatively low cost.^{35,249-251} Various MWCNT/Ni(OH)₂ nanocomposites have been fabricated as supercapacitor electrodes.^{128-130,132,194,249,252,253}

Ni(OH)₂ has two main crystalline polymorphs: α - and β -Ni(OH)₂. α -Ni(OH)₂ has layered structures with some interlayer space to host intercalated anions or water molecules. In contrast, β -Ni(OH)₂ has a hexagonal closest-packed structure of Ni²⁺ and OH⁻ ions without other intercalated ions.^{254,255} Both crystalline polymorphs have shown good capacitive performances.^{28,256} Ni(OH)₂ also has amorphous (amor) structures. Some studies showed that amor-metal oxides or hydroxides have better capacitive performances than their crystalline counterparts.^{133,257-261} Recently, a few studies have used amor-Ni(OH)₂ as supercapacitor electrodes.^{190,259-261} Liu *et al.* used a rapid freezing micro-emulsion method to prepare amor-Ni(OH)₂ as electrochemical electrodes.²⁶¹ Li *et al.* synthesized amor-Ni(OH)₂ by high voltage electrolysis and demonstrated

the high capacitance of 2,188 F/g.²⁵⁹ However, there is still a lack of good understanding of the pros and cons of different forms of Ni(OH)₂. In particular, to our knowledge, no study has symmetrically evaluated the performance of MWCNT/Ni(OH)₂ nanocomposites as supercapacitor electrodes with different crystalline structures.

In this chapter, I synthesized MWCNT/Ni(OH)₂ nanocomposites with different Ni(OH)₂ crystallinity, including amor-Ni(OH)₂, α -Ni(OH)₂, and β -Ni(OH)₂. Their morphology and physiochemical properties were examined by scanning electron microscope (SEM), transmission electron microscopy (TEM), N₂ physisorption, X-ray diffraction (XRD) and thermogravimetric analysis (TGA). More importantly, I compared their performances as supercapacitor electrodes in terms of their specific gravimetric capacitance, rate capability, equivalent series resistance (ESR), and stability upon repeated charges/discharges. MWCNT/amor-Ni(OH)₂ with distorted structures has the highest specific capacitance, the best rate capability, but the worst stability among the three nanocomposites. My results highlight that the performances of MWCNT/Ni(OH)₂ nanocomposite based supercapacitor electrodes depend on the crystallinity of Ni(OH)₂, and the performances change upon Ni(OH)₂'s crystalline structure transformation after repeated redox reactions.

2.2 Experimental Section

2.2.1 Prepare of the MWCNT/Ni(OH)₂ nanocomposites

Figure 2.1 Schematic illustration of the synthesis of the three MWCNT/Ni(OH)₂ nanocomposites.

MWCNTs with the average diameter of ~10 nm (CNano Technology, FloTube 9000) were first washed in 37% HCl for 2 h to remove metal catalyst residues, and then functionalized in 65% HNO₃ for 4 h to introduce oxygen-containing functional groups on their surface. The treated MWCNTs can be well dispersed in the aqueous solution. The synthesis of MWCNT/amor-Ni(OH)₂ includes two steps,²⁶² shown as path A in Figure 2.1: formation of MWCNT/Cu₂O and etching/precipitation. First, CuCl₂ (0.8 M, 1 mL) was added slowly to MWCNT dispersion (0.075 mg/mL, 400 mL) containing trisodium citrate (Na₃C₆H₅O₇) (0.001 M) under continuous stirring. Next, NaOH (0.1 M, 32 mL) was hereby added dropwise. Afterwards, ascorbic acid (0.1 M, 15 mL) was hereby added

dropwise and then aged for 5 h with the color of the mixture changing from black to dark green. MWCNT/Cu₂O was collected by filtration, and then washed with water and ethanol. Second, MWCNT/Cu₂O and NiCl₂·6H₂O (100 mg) were dispersed in ethanol/water (volume ratio of 1:1, 100 mL) by sonication for 30 min. Afterwards, Na₂S₂O₃ (0.05 M, 30 mL) was hereby added dropwise under continuous stirring. MWCNT/amor-Ni(OH)₂ was collected by filtration. MWCNT/ α -Ni(OH)₂ was synthesized by oxidizing Ni²⁺ using K₂S₂O₈ in the presence of MWCNTs as shown by path B in Figure 2.1. Briefly, NiCl₂·6H₂O (100 mg) was added to MWCNT dispersion (0.3 mg/mL, 100 mL) containing Na₃C₆H₅O₇ (0.001 M) under continuous stirring. Next, K₂S₂O₈ (0.08 M) and ammonia (0.17 M) solution (5 mL) was added dropwise. After continuous stirring for 30 min, MWCNT/ α -Ni(OH)₂ was collected by filtration. MWCNT/ β -Ni(OH)₂ was synthesized using a slightly different approach (Path C in Figure 2.1). Ammonia solution (0.1 M, 20 mL) was added dropwise into MWCNT dispersion (0.3 mg/mL, 100 mL) containing Na₃C₆H₅O₇ (0.001 M) and NiCl₂·6H₂O (100 mg) at 80 °C under constant stirring. After stirring for 3 h, MWCNT/ β -Ni(OH)₂ was precipitated in 12 h.

2.2.2 Characterization of the MWCNT/Ni(OH)₂ nanocomposites

Morphology of synthesized nanocomposites was examined by a field emission SEM (FE-SEM) (JEOL, JSM6701) at 5 kV and TEM (JEOL, JEM-2010) at 120

kV. Crystallographic structures of the nanocomposites were studied using a powder XRD system (Bruker AXS D8) with Cu-K α radiation and selected area electron diffraction (SAED) performed by the TEM. The specific surface area and pore size distribution was measured using a surface area analyzer (QuantaChrome, Autosorb-6B) and analyzed by Brunauer–Emmett–Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. TGA (Perkin Elmer, Diamond FTA32 TG/DTA) was applied to determine the mass loading of Ni(OH) $_2$ in the nanocomposites.

2.2.3 Fabrication of the supercapacitor

Supercapacitor electrodes were fabricated by mixing MWCNT/Ni(OH) $_2$ nanocomposites with carbon black (Super P) and polyvinylidene fluoride (PVDF) at the mass ratio of 8:1:1, and then dispersed in N-methyl pyrrolidone (NMP) by sonication. Stainless steel sheets (1 $\times$ 3 cm) were used as current collectors. Each electrode contains ~6 mg of MWCNT/Ni(OH) $_2$ (pasted in an area of 1 $\times$ 1 cm) as active materials with a thickness of ~250 μ m, , similar to the electrodes used in commercial supercapacitors.²⁶³ The electrochemical tests were carried out using a three-electrode cell configure with a platinum wire as the counter electrode and saturated calomel electrode (SCE) as the reference electrode in 1 M KOH aqueous electrolyte. Cyclic voltammetry (CV), galvanostatic charge/discharge and capacitance retention tests were done using one potentiostat (CHI 660D).

The electrochemical impedance spectroscopy (EIS) was carried out using another potentiostat (VersaSTAT 4).

2.3 Results and Discussion

MWCNT/Ni(OH)₂ nanocomposites were synthesized at mild solution conditions as described in the experimental session. Na₃C₆H₅O₇ as a surfactant serves to anchor Ni²⁺ ions preferentially near the outer surface of MWCNTs. When alkaline solutions were added, Ni(OH)₂ is expected to nucleate predominantly on the outer surface MWCNTs. Commonly used Ni(OH)₂ synthesis methods all yield crystalline Ni(OH)₂.²⁵⁹ In this work, a two-step method²⁶² was used to deposit amor-Ni(OH)₂ on MWCNTs. Cu₂O was first deposited on MWCNTs as a sacrificing template. Next, it was etched by Na₂S₂O₃ solution to form [Cu₂(S₂O₃)_x]^{2-2x} complexes. This synchronously generates OH⁻ ions, which precipitate Ni²⁺ to form amor-Ni(OH)₂.²⁶² The chemical reactions are shown as:

Figure 2.2 SEM and TEM (insets) images of (a) MWCNT/amor-Ni(OH)₂, (b) MWCNT/α-Ni(OH)₂, (c) MWCNT/β-Ni(OH)₂ nanocomposites and (d) acid treated MWCNTs.

Morphology of MWCNT/Ni(OH)₂ nanocomposites and acid-treated MWCNTs was examined by SEM and TEM as shown in Figure 2.2. Acid treated MWCNTs have intact tube structures with a diameter of ~10 nm. TEM images in Figure 2.2 show that the outer surface of MWCNTs is coated with a thin layer of Ni(OH)₂. The diameter of MWCNT/Ni(OH)₂ nanocomposites increases to 15-20 nm. No aggregation of large Ni(OH)₂ particles were observed, suggesting uniform deposition of Ni(OH)₂ on MWCNT surfaces.

Figure 2.3 (a) XRD patterns of crystalline and amor-Ni(OH)₂ deposited on MWCNTs. (b) N₂ adsorption/desorption isotherms and the pore distribution (inset) of MWCNT/Ni(OH)₂ nanocomposites.

The crystalline structure of MWCNT/Ni(OH)₂ nanocomposites was surveyed by XRD as shown in Figure 2.3a. The reflections along (003), (006), (101) and (110) planes from Ni(OH)₂ on MWCNT/ α -Ni(OH)₂ match with that of rhombohedral α -Ni(OH)₂ (JCPDS 38-715). The XRD patterns of MWCNT/ β -Ni(OH)₂ have reflections from (001), (100), (011), (012), (110) and (111) planes, which is consistent with that of hexagonal brucite structured β -Ni(OH)₂ (JCPDS 14-0147). The XRD patterns of these two nanocomposites both display a weak peak, which can be attributed to the (002) diffraction peak (marked by a dash line) of MWCNTs (Figure 2.4a). MWCNT/amor-Ni(OH)₂ only exhibits this weak peak from MWCNTs, suggesting the amorphous structure of Ni(OH)₂. This was further confirmed by SAED using TEM (the insert of Figure 2.2a). The SAED pattern (Figure 2.4b) only exhibits diffraction rings of graphitic layers with (002)

and (100) planes from MWCNTs. The broad and misty halo shown in the SAED pattern confirms the amorphous structure of Ni(OH)_2 in MWCNT/amor- Ni(OH)_2 .

Figure 2.4 (a) XRD patterns of acid treated MWCNTs, (b) SAED pattern of MWCNT/amor- Ni(OH)_2 , (c) N_2 adsorption/desorption isotherms of MWCNT/ Ni(OH)_2 (d) TGA profiles of MWCNT/ Ni(OH)_2 nanocomposites and acid treated MWCNTs.

N_2 physisorption was carried out to determine the specific surface area and pore size distribution of the nanocomposites. Figure 2.3b shows their N_2 adsorption/desorption isotherms. The specific area of MWCNTs (Figure 2.4c) is $202 \text{ m}^2 \text{ g}^{-1}$ before Ni(OH)_2 deposition. It decreases to 155, 118 and $101 \text{ m}^2 \text{ g}^{-1}$ for MWCNT/amor- Ni(OH)_2 , MWCNT/ α - Ni(OH)_2 and MWCNT/ β - Ni(OH)_2 ,

respectively. The pore size distribution was determined from their N₂ adsorption isotherms. The three nanocomposites have similar narrow pore size distribution centered around 4-5 nm. MWCNT/amor-Ni(OH)₂ has the smallest average pore size centered at 4.1 nm and the largest pore volume of 0.836 cm³ g⁻¹. MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂ have the average pore size at 5.0 and 5.4 nm, respectively. MWCNT/ β -Ni(OH)₂ has the lowest pore volume of 0.486 cm³ g⁻¹.

The mass loading of Ni(OH)₂ in nanocomposites was determined by TGA (Figure 2.4d). TGA thermograms show two major weight lost steps, attributing to the decomposition of Ni(OH)₂ and oxidization of MWCNTs, respectively. The mass loading of Ni(OH)₂ is similar at 50.1, 52.2 and 49.1 wt% for MWCNT/amor-Ni(OH)₂, MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂, respectively.

The electrochemical performance of materials as supercapacitor electrodes can be evaluated from the following aspects: (1) the specific capacitance of the materials, which limits the energy density of supercapacitors; (2) the rate capability, the change of capacitive performances at different CV scan rates or charging current densities, which controls the power density as well as how fast assembled supercapacitors can be safely charged; (3) ESR, which affects the power density of assembled supercapacitors; and (4) stability, how many charge/discharge cycles electrodes can withstand without losing significant

portion of their original energy storage capacity.

Figure 2.5 (a) CV curves of MWCNT/Ni(OH)₂ electrodes measured at 5 mV/s; (b) cathodic peak potential shifts at different CV scan rates; (c) specific capacitance as a function of scan rate calculated from CV curves; (d) specific capacitance normalized based on the mass of Ni(OH)₂ as a function of CV scan rates.

I first examined the three MWCNT/Ni(OH)₂ nanocomposites using CV at the potential window of 0 to 0.5 V (vs. SCE) in the three-electrode cell configuration in 1 M KOH aqueous electrolyte. CV curves were collected at different scan rates from 5 to 100 mV s⁻¹ (Figure 2.5a and Figure 2.6a-c). Figure 2.5a shows that CV curves at 5 mV s⁻¹, which have two strong redox peaks from the reversible

Faradaic reaction between Ni(II) and Ni(III):

Figure 2.6 CV curves of (a) MWCNT/amor-Ni(OH)₂, (b) MWCNT/α-Ni(OH)₂ and (c) MWCNT/β-Ni(OH)₂ collected at different scan rates. Galvanostatic charge/discharge profiles of (d) MWCNT/amor-Ni(OH)₂, (e) MWCNT/α-Ni(OH)₂ and (f) MWCNT/β-Ni(OH)₂ collected at different current densities.

The shape of CV curves is different among the three nanocomposites. MWCNT/amor-Ni(OH)₂ has much sharper anodic (oxidation) and cathodic (reduction) peaks as well as the highest peak current density as listed in Table 2.1, which indicates that MWCNT/amor-Ni(OH)₂ has higher electrochemical reactivity.²⁶⁴ The potential difference between the anodic and cathodic peaks ($E_a - E_c$) can be considered as a measure of pseudocapacitive reaction reversibility, with smaller values indicating better redox reaction reversibility.^{112,252} This value

is 0.124 V for MWCNT/amor-Ni(OH)₂, which is smaller than that of MWCNT/ α -Ni(OH)₂ (0.131 V) and MWCNT/ β -Ni(OH)₂ (0.167 V) (Table 2.1). Furthermore, I also tracked the changes in cathodic peak potentials at different scan rates (Figure 2.5b). MWCNT/amor-Ni(OH)₂ not only shows the highest cathodic peak potential, but also has the least decline with the increase of CV scan rate. In contrast, MWCNT/ β -Ni(OH)₂ shows the lowest cathodic peak potential, and has the largest peak potential drop with the increase of CV scan rate.

Table 2.1 The anodic (i_a) and cathodic (i_c) peak currents and the potentials (E) of the MWCNT/Ni(OH)₂ nanocomposites at the CV scan rate of 5 mV/s

MWCNT/Ni(OH) ₂ nanocomposites	i_a (A/g)	i_c (A/g)	E_a (mV)	E_c (mV)	$E_a - E_c$ (mV)
MWCNT/amor-Ni(OH) ₂	39.5	32.4	0.388	0.264	0.124
MWCNT/ α -Ni(OH) ₂	26.5	19.8	0.353	0.222	0.131
MWCNT/ β -Ni(OH) ₂	20.1	15.8	0.368	0.202	0.167

The specific capacitance C_s (F/g) of electrode materials, which can be calculated from their CV curves based on the following equation:

$$C_s = Q / 2m\Delta V = (\int idV) / 2km\Delta V \quad (2.4)$$

where m (g) is the mass of electroactive materials in electrodes, ΔV (V) is the scanned voltage window, and Q is the voltammetric charge integrated from anodic and cathodic sweeps. i (A) is the current density and k (V/s) is the scan rate. Figure 2.5c illustrates C_s of the three MWCNT/Ni(OH)₂ electrodes at

different CV scan rates. MWCNT/amor-Ni(OH)₂ has the specific capacitance of 1495 F g⁻¹, exceeding both crystalline counterparts, MWCNT/ α -Ni(OH)₂ at 1308 F/g and MWCNT/ β -Ni(OH)₂ at 1114 F/g, by 14 and 34%, respectively. The CV curves of acid treated MWCNTs without Ni(OH)₂ were also measured (Figure 2.7). Their rectangular shaped CV curves of MWCNTs come from the electric double layered (EDL) capacitance of MWCNTs. C_s of MWCNTs is 53 F g⁻¹ at 5 mV s⁻¹, which is much smaller compared with that of MWCNT/Ni(OH)₂ nanocomposites. I assume that the EDL capacitance contributed by MWCNTs in MWCNT/Ni(OH)₂ nanocomposites is similar to that of the acid treated MWCNTs. Since the loading contents of Ni(OH)₂ are very close in all the three MWCNT/Ni(OH)₂ composites (50.1 %, 52.2 %, and 49.1 % for MWCNT/amor-Ni(OH)₂, MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂, respectively), the observed variation in capacitance among the composites has negligible effect from the amount of Ni(OH)₂. Based on the mass loading of Ni(OH)₂ in the three nanocomposites, the specific capacitance normalized to the mass of Ni(OH)₂ is determined to be 2984, 2506 and 2269 F g⁻¹ for MWCNT/amor-Ni(OH)₂, MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂, respectively (Figure 2.5c). The Ni(OH)₂ based specific capacitances are much higher than those reported for pure amor-, α - or β -Ni(OH)₂^{82,84,259,260,265,266}. They are also higher than that of previously reported crystalline Ni(OH)₂ based MWCNT/Ni(OH)₂ or graphene/Ni(OH)₂ composites.^{26,119,129,267} The higher C_s can be attributed to

MWCNTs as imbedded conductive networks in MWCNT/Ni(OH)₂ nanocomposites, which help to achieve efficient and fast electron transfer. Moreover, as shown in SEM and TEM images in Figure 2.2, both amorphous and crystalline Ni(OH)₂ forms a thin layer about 5-10 nm on conductive MWCNTs. The thin layer structure reduces the ion diffusion distance and enlarges the electrolyte accessible surface area. With the increase of CV scan rates from 5 to 100 mV s⁻¹, C_s decreases (Figure 2.5b and 2.5c) because of the polarization of electrodes and the declining redox reversibility⁸⁵. MWCNT/amor-Ni(OH)₂ shows the best capacitance retention at 47%. In comparison, MWCNT/ α -Ni(OH)₂ retains 42%, and MWCNT/ β -Ni(OH)₂ retains only 36%.

Figure 2.7 (a) CV curves of acid treated MWCNTs; (b) the specific capacitance of MWCNT/Ni(OH)₂ nanocomposites as a function of discharge current density.

C_s of the MWCNT/Ni(OH)₂ nanocomposites was further evaluated by galvanostatic charge/discharge tests (Figure 2.6d-f) following the equation:

$$C_s = i / [-m(dV / dt)] \approx i / [-m(\Delta V / \Delta t)] \quad (2.5)$$

where i (A) is the discharging current, ΔV (V) is the discharge voltage range and Δt (s) is the discharge time. MWCNT/amor-Ni(OH)₂ has a specific capacitance of 1503 F g⁻¹ at the discharge current of 3 A g⁻¹, which is similar to the CV result at 5 mV s⁻¹. The specific capacitance is 1326 and 1139 F g⁻¹ for MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂, respectively, at 3 A g⁻¹. From the galvanostatic charge/discharge curves, I can estimate the coulombic efficiency from the ratio between the discharged time and charged time.²⁶⁸ MWCNT/amor-Ni(OH)₂ has a high coulombic efficiency of 90%, while MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂ show poorer coulombic efficiency at 86 % and 83 %, respectively. Figure 2.7b shows the specific capacitances as a function of discharge current density based on the total mass of MWCNT/Ni(OH)₂ nanocomposites and Ni(OH)₂. They are similar to those observed from CV curves (Figure 2.5c and 2.5d). All these results consistently show that MWCNT/amor-Ni(OH)₂ has the best specific capacitance and rate capability, while MWCNT/ β -Ni(OH)₂ has the worst capacitance performances among the three nanocomposites.

Next, I used EIS to characterize the charge transport characteristics of the three MWCNT/Ni(OH)₂ nanocomposites. Figure 2.8a shows their Nyquist plots. The interception on the Z_{re} axis in the high frequency region indicates the equivalent

series resistance of the electrodes. The semicircles occurring between the high frequency region and the medium frequency region represent the Faradic redox reaction whose charge transfer resistance can be estimated by the diameter of the semicircle. The straight lines at the medium frequency region show the diffusion behaviors of electrolyte ions in the electrode materials and at the electrode/electrolyte interface. Among the three nanocomposites, MWCNT/amor-Ni(OH)₂ has the smallest semicircle and the quickest increase at the medium frequency region. This indicates that amor-Ni(OH)₂ has the smallest diffusion resistance, which allows electrolyte ions to reach its surface and complete Faradic redox reactions efficiently. This is in line with the highest cathodic peak potential and the lowest peak potential drop observed in the CV results (Figure 2.5b).

Figure 2.8 (a) Nyquist plots of MWCNT/Ni(OH)₂ nanocomposites; (b) cyclic stability test measured at the charge/discharge current of 10 A g⁻¹, the inserts show discharge curve profiles before and after 3000 charge/discharge cycles; (c) nyquist plots of MWCNT/amor-Ni(OH)₂ and MWCNT/ α -Ni(OH)₂ before and after 3000 charge/discharge cycles; (d) XRD patterns of MWCNT/amor-Ni(OH)₂ and MWCNT/ α -Ni(OH)₂ before and after 3000 charge/discharge cycles.

The stability of the three MWCNT/Ni(OH)₂ nanocomposites as supercapacitor electrodes was studied using cyclic charge/discharge tests at 10 A/g. The change of their C_s is shown in Figure 2.8b. MWCNT/amor-Ni(OH)₂ only retains 64% of its initial capacitance after 3000 charge/discharge cycles. It drops from 1092 to 980 F/g within 200 cycles, and gradually declines to 698 F/g thereafter till 3000

cycles. In comparison, MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂ retains 75 and 83% their initial capacitance, respectively. The insets of Figure 2.8b show the discharge curves of the three nanocomposites measured before (left) and after (right) 3000 charge/discharge cycles. Before repeated cycles, the discharge time (indicating specific capacitance) of MWCNT/amor-Ni(OH)₂ is clearly longer than that of the MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂. After repeated cycles, their discharge time becomes similar. The performance deteriorations of MWCNT/amor-Ni(OH)₂ and MWCNT/ α -Ni(OH)₂ can also be observed by comparing their Nyquist plots before and after 3000 charge/discharge cycles as shown in Figure 2.8c. The increased radius of semicircles and declined slope of straight lines in the medium frequency region indicates that their diffusion resistant increases after repeated Faradic reaction and ion intercalation/deintercalation.

I propose that the observed electrochemical performance differences among the three nanocomposites and the performance changes during the repeated charge/discharge cycles are all related to their crystalline structures. α -Ni(OH)₂ has a more disordered structure than β -Ni(OH)₂ because various anions (*e.g.* NO₃⁻, CO₃²⁻, Cl⁻, SO₄²⁻, etc.) can reside among the interlayer space of α -Ni(OH)₂^{82,248,269}. Amor-Ni(OH)₂ has a more disordered structure than α -Ni(OH)₂. According to the Ni(OH)₂/NiOOH redox reaction (equation 2.3), generated protons have to diffuse between the solid electrode phase where they are created

and the liquid electrolyte/solid electrode interface to react with OH⁻. Defects within Ni(OH)₂ make it easier for protons to penetrate, which increase the interfacial boundary area, leading to shorter diffusion path and faster charge transfer rate²⁷⁰. In contrast, the more ordered or defect-free crystalline structures increase the diffusion resistance for redox reaction. In my results, the pore volume of amor-Ni(OH)₂ is indeed much larger than that of β -Ni(OH)₂. Further, I can also compare the cathodic peak current change at different scan rates. It is well established that the cathodic peak current i_p (A) follows the Randles-Sevcik equation for diffusion-controlled redox reactions:^{176,271}

$$i_p \sim n^{3/2} A C D^{1/2} \nu^{1/2} \quad (2.6)$$

where n is the number of electrons transferred during the redox reaction, A (cm²) is the effective surface area of electrode, C (mol cm⁻³) is the concentration of the diffusion species in the bulk of electrolyte, D (cm² s⁻¹) is the diffusion coefficient and ν (V s⁻¹) is the CV scan rate. Corrections between i_p and $\nu^{1/2}$ and its linear fittings of the three nanocomposites are shown in Figure 2.9. The fitting results suggest that the effective surface area and diffusion coefficient ($AD^{1/2}$) of MWCNT/amor-Ni(OH)₂ is 1.7 and 1.9 times of that of MWCNT/ α -Ni(OH)₂ and MWCNT/ β -Ni(OH)₂, respectively. Based on these results, I can conclude that the higher specific capacitance, better rate capability, and lower equivalent series resistance of MWCNT/amor-Ni(OH)₂ all can be attributed to the more disordered

structure of amor-Ni(OH)₂, as compared to the more ordered α -Ni(OH)₂ and β -Ni(OH)₂.

To understand the performance changes over repeated charge/discharge cycles, XRD was used to monitor the crystalline structure transition of Ni(OH)₂. Figure 2.8d shows that amor- and α -Ni(OH)₂ transforms to β -Ni(OH)₂ with the characteristic XRD peaks at 19.31° (diffraction of Ni(001)) and 38.34° (diffraction of Ni(011)). The weak Ni(003) diffraction peak of α -Ni(OH)₂ can still be seen. Some previous studies suggest that α -Ni(OH)₂ is not stable in alkaline solution, and would convert to β -Ni(OH)₂^{83,272}. I immersed as-prepared MWCNT/amor-Ni(OH)₂ and MWCNT/ α -Ni(OH)₂ in KOH solution (1 M) for 5 days, and no phase change was detected. Thus, I conclude that the crystalline transformation of Ni(OH)₂ observed in this study comes from the repeated redox reaction other than any solution effect. The repeated ion intercalation/deintercalation of the Ni(OH)₂/NiOOH redox reaction drives atoms in the disordered Ni(OH)₂ to form thermodynamically more stable β -Ni(OH)₂²⁷³. Further, the thin layer structure of Ni(OH)₂ deposited on MWCNTs also facilitates this transformation. The performances of MWCNT/amor-Ni(OH)₂ and MWCNT/ α -Ni(OH)₂ become similar to that of MWCNT/ β -Ni(OH)₂ after this structural change. I propose that a potential approach to obtain high performance MWCNT/Ni(OH)₂ nanocomposites as supercapacitor electrodes with better stability would be to protect the distorted structure of amor-Ni(OH)₂ so it would

withstand the repeated redox reaction without structural transformation

Figure 2.9 Correction between cathodic peak currents and square root scan rates, and their linear fittings by the Randles-Sevcik equation. (a) MWCNT/amor-Ni(OH)₂, (b) MWCNT/ α -Ni(OH)₂ and (c) MWCNT/ β -Ni(OH)₂.

2.4 Conclusion

Three MWCNT/Ni(OH)₂ nanocomposites were synthesized with thin layers (10–15 nm) of amor-, α -, and β -Ni(OH)₂ deposited on conductive MWCNTs. The mass loading of Ni(OH)₂ is analogous ranging from 49.1 to 52.2 wt% with comparable narrow pore size distribution centered around 4–5 nm. The nanocomposites were fabricated into supercapacitor electrodes with mass loading of 6 mg/cm² and thickness of ~250 μ m, similar to the electrodes used in commercial supercapacitor electrodes. Electrochemical tests carried out in 1 M KOH aqueous electrolyte show that MWCNT/amor-Ni(OH)₂ has the highest specific capacitance of 1495 F g⁻¹ or 2984 F g⁻¹ based on the mass of total active materials or Ni(OH)₂ at the scan rate of 5 mV s⁻¹, which exceeds that of MWCNT/ α -Ni(OH)₂ by 14% and that of MWCNT/ β -Ni(OH)₂ by 34%.

MWCNT/amor-Ni(OH)₂ also shows better rate capability when the CV scan rate is increased from 5 to 100 mV s⁻¹ or the discharge current is increased from 3 to 50 A g⁻¹. Better performances can be attributed to their disordered structure, which increase the effective surface area and reduce diffusion resistance for redox reactions. However, the superior performances of MWCNT/amor-Ni(OH)₂ gradually deteriorate to the same level as that of MWCNT/ β -Ni(OH)₂ over 3000 charge/discharge cycles because the disordered Ni(OH)₂ transforms to more ordered β -Ni(OH)₂. These findings point to the research direction of using MWCNT/amor-Ni(OH)₂ nanocomposites as high perform supercapacitor electrodes by improving the structural stability of amor-Ni(OH)₂.

Chapter III Ternary Hybrids of Amorphous Nickel Hydroxide-carbon Nanotube-conducting Polymer for Supercapacitors with High Energy Density, Excellent Rate Capability and Long Cycle Life

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3.1 Background Introduction

Engineering pseudocapacitive materials at the nanoscale level to allow a large fraction of redox reactions to take place on the surface or near-surface region of pseudocapacitive materials is paramount to the development of supercapacitors with both high energy density, high rate capability and long cycle life.

Ni(OH)₂ in amorphous phase has been demonstrated to achieve higher capacitance and energy density due to more grain boundaries and ion diffusion channels in the disordered structure compared to the crystalline phase. However, the key issues of applying the amorphous Ni(OH)₂ in practical supercapacitors lie in its short cycle life and unstable crystalline structure.

The electrical conductivity of Ni(OH)_2 is very low at around $10^{-15} \Omega^{-1} \text{m}^{-1}$.²⁷⁴ Thus, the redox reactions can only take place on its surface, and most of Ni(OH)_2 is inaccessible to electrolyte ions and remains as dead volume in supercapacitors.^{275,276} Several approaches have been explored to address the issues caused by the low electrical conductivity of Ni(OH)_2 including aforementioned forming hybrid structures with highly conductive carbon nanotubes,^{26,277-280} Even though these nanoscale engineering approaches can improve the electrical conductivity of Ni(OH)_2 , the constructed nanoscale structures often degrade and Ni ions dissolve into electrolytes after repeated charge/discharge cycles, which can result in short cycle life of supercapacitors.^{16,26,281-284}

In this chapter, with the aim of constructing supercapacitors with both high energy density, good rate capability and long cycle life, I have designed and synthesized a novel ternary hybrid electrode material comprising of multiwalled carbon nanotubes (MWCNTs), amorphous(amor)- Ni(OH)_2 and poly (3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) as high performance pseudocapacitive materials. Other than the commonly used crystalline Ni(OH)_2 , a thin layer of disordered amor- Ni(OH)_2 was deposited on conductive acid-treated MWCNTs by using a “coordinating etching and precipitating” method, which enabled efficient redox reactions to take place mostly on the surface of Ni(OH)_2 . To prevent the dissolution of Ni ions into

electrolytes and preserve the nanoscale structures amor-Ni(OH)₂ upon long charge/discharge cycles, a conductive polymer layer was further wrapped around the MWCNT/amor-Ni(OH)₂. Such a unique hybrid architecture design results in Ni(OH)₂ pseudocapacitive materials with ultrahigh specific capacitance and long cycle life. Asymmetric supercapacitors fabricated with the MWCNT/amor-Ni(OH)₂/PEDOT:PSS as positive electrodes and reduced graphene oxide (rGO)/CNT hybrids as negative electrodes have demonstrated one of the highest energy densities among Ni(OH)₂ based supercapacitors with excellent rate capability and long cycle life.

3.2 Experimental Section

3.2.1 Synthesis of MWCNT/amor-Ni(OH)₂

MWCNTs (diameter of 10 nm, FloTube 9000, CNano Technology) were first refluxed in 37 % HCl to remove metal catalyst residues, and then in 65 % HNO₃ for 4 h to introduce oxygen-containing functional groups. The MWCNT/amor-Ni(OH)₂ was synthesized in two steps. In the first step, the co-precipitation process was used to obtain MWCNT/Cu₂O. CuCl₂ (1 mL, 0.8 M) solution was slowly dropped into MWCNT (30 mg in 400 mL) aqueous dispersion containing 1 mM trisodium citrate in 10 min. Next, NaOH (32 mL, 0.1 M) solution was added dropwise. After stirring for another 10 min, ascorbic acid (15 mL, 0.1 M) was added dropwise, and kept stirring for 30 min before the mixture was aged

for 5 h statically. The black mixture gradually turned into dark green color. The resulting MWCNT/Cu₂O was collected by filtration, and then washed by deionized water and ethanol. In the second step, the *in situ* etching-precipitation process was used to convert Cu₂O into amor-Ni(OH)₂. The collected MWCNT/Cu₂O and Ni(NO₃)₂·6H₂O (120 mg) were dispersed in ethanol/H₂O (volume ratio= 1:1, 100 mL) by sonication for 30 min. Afterwards, Na₂S₂O₃ (30 mL, 0.05 M) aqueous solution was slowly added into the dispersion dropwise under continuous stirring, followed by ageing for another 2 h under stirring. Last, the MWCNT/amor-Ni(OH)₂ powders were obtained by filtration, washing with deionized water, and dried at 60 °C for 12 h. For electrochemical characterization of MWCNT/amor-Ni(OH)₂ in the three-electrode cell, MWCNT/amor-Ni(OH)₂ (about 3.5 mg) and PVDF (as binders) were first mixed at a mass ratio of 9:1 in *N*-methyl pyrrolidone (NMP) by sonication. Then, the mixed electrode material slurry was coated on a 1 × 1 cm area at one end of a carbon cloth (total 1 × 3 cm in rectangle shape), followed by drying at 100 °C in a vacuum oven. The carbon cloth coated with MWCNT/amor-Ni(OH)₂ was used as the working electrode.

3.2.2 Synthesis of MWCNT/amor-Ni(OH)₂/PEDOT:PSS

PEDOT:PSS solution (2 mg in 154 mg of water dispersion of 1.3 wt%) was added dropwise into the MWCNT/amor-Ni(OH)₂ aqueous dispersion (18 mg, 30 mL) under stirring. The mixture was further stirred for 5 h. Afterwards, the resulting

solids were collected by filtration. It was noted that the filtrate became colorless, different from the initial blue PEDOT: PSS solution, indicating that PEDOT: PSS was anchored on the hybrid. MWCNT/amor-Ni(OH)₂/PEDOT:PSS electrodes were prepared using the similar method as described earlier without adding PVDF binders.

3.2.3 Synthesis rGO/CNT hybrid

The hybrid was synthesized using a modified method from our previous publication.³⁰ Briefly, graphene oxide (GO) was prepared by the modified Hummers' method using natural graphite. CNTs (1.4 nm in diameter, Carbon Solution) were also treated in HCl and HNO₃ similar to the MWCNTs as described above. A homogeneous GO/CNT (at the mass ratio of 3:1) mixture was obtained by sonicating predetermined amount of acid treated CNTs in GO (10 mL, 2 mg/mL) aqueous solution. The mixture was then transferred to a Teflon lined stainless steel autoclave for 18 h hydrothermal treatment at 180 °C. Afterwards, the rGO/CNT hybrid was freeze-dried and crushed into powders. The rGO/CNT electrodes were fabricated using PVDF as binder.

3.2.4 Assembly of asymmetric supercapacitor

MWCNT/amor-Ni(OH)₂/PEDOT:PSS and rGO/CNT were used as positive and negative electrodes, respectively, at the mass ratio of 1:3.5. The two film electrodes and a piece of separator membrane (Nippon Kodoshi Co.) were

sandwiched together to form the complete device.

3.2.5 Material characterization

The morphology of the materials was examined by SEM (JEOL, JSM6701, 5 kV) and TEM (JEM-2010, JEOL, 120.0 kV). The crystallographic structures of the materials were characterized by a powder XRD system (Bruker, AXS D8) and the selected area electron diffraction (SAED) performed by JEM-2010 TEM. The chemical composition of the material surfaces was analyzed by XPS (PHI, Quantera). The specific surface areas of the materials were measured using a surface area analyzer (QuantaChrome, Autosorb-6B) and calculated by the Brunauer–Emmett–Teller method. Samples were degassed at 120 °C for 10 h under vacuum (<0.01 mbar) before the surface area test. The mass loading of Ni(OH)₂ was determined in thermogravimetric analysis (Perkin Elmer, Diamond FTA32 TG/DTA).

3.2.6 Electrochemical characterization

The electrochemical tests of various materials were performed using a three-electrode cell in 1 M aqueous KOH electrolyte with a platinum wire as the counter electrode, a saturated calomel electrode as the reference electrode, and the working electrode prepared as described early. The performance of the asymmetric supercapacitors was evaluated by measuring the assembled two-electrode cells. Cyclic voltammetry (CV), galvanostatic charge/discharge and

capacitance retention tests were carried out by the potentiostat (CHI 660D). EIS spectra were taken by the potentiostat (VersaSTAT 4).

3.3 Results and Discussion

3.3.1 Synthesis of hybrid materials

Figure 3.1 Schematic illustration of the MWCNT/amor-Ni(OH)₂/PEDOT:PSS ternary hybrid synthesis procedure.

It has been a significant challenge to directly synthesize amor-Ni(OH)₂, because all commonly used methods result in crystalline Ni(OH)₂.²⁸³ I have utilized a two-step procedure to achieve this as illustrated in Figure 3.1. First, Cu₂O nanocrystals were anchored onto the nitric acid-treated MWCNTs²⁸⁵ through *in situ* reduction of Cu(OH)₂ to Cu₂O by ascorbic acid (Vitamin C, C₆H₈O₆) at room temperature. Next, the “coordinating etching and precipitating” method was used to replace Cu₂O nanocrystals with amor-Ni(OH)₂.²⁸⁶ Alkaline S₂O₃²⁻ ions etched Cu₂O to generate Cu⁺ and OH⁻ ions. The OH⁻ ions synchronously combined with Ni²⁺ to form amor-Ni(OH)₂. The chemical reactions are as shown:

Amor-Ni(OH)₂ was deposited on the MWCNTs, resulting in a coaxial hybrid denoted as MWCNT/amor-Ni(OH)₂. The coaxial hybrid was further wrapped with the water soluble conducting polymer at a mass ratio of 9:1 between MWCNT/amor-Ni(OH)₂ and PEDOT:PSS to form the final MWCNT/amor-Ni(OH)₂/PEDOT:PSS ternary hybrid. In this ternary architecture design, I took advantage of the following synergistic effects. Firstly, MWCNT with excellent conductivity, large specific surface area, and relatively low cost serves as an ideal conductive template for the amor-Ni(OH)₂ deposition. Secondly, instead of crystalline Ni(OH)₂, either α -crystalline or β -crystalline Ni(OH)₂, which is commonly used as pseudocapacitive material,^{29,279,280,287,288} amor-Ni(OH)₂ is chosen in this work since disorders in crystalline Ni(OH)₂ can greatly improve their electrochemical efficiency.^{276,289} However, few studies have employed amor-Ni(OH)₂ in supercapacitors because of its synthesis difficulty. Recently, only few methods including freezing micro-emulsion²⁹⁰ and high voltage electrolysis²⁸³ were reported to produce bulk amor-Ni(OH)₂. In this study, I have applied a simple but effective “coordinating etching and precipitating” method to deposit a thin layer of amor-Ni(OH)₂ on the MWCNTs. Thirdly, wrapping of the MWCNT/amor-Ni(OH)₂ with a conducting polymer can significantly reduce the contact resistance among the metal oxide/hydroxide deposited MWCNTs as observed in previous studies,^{157,275,291,292} while achieving a long cycle life by preventing the irreversible dissolution of Ni ions from the amor-Ni(OH)₂ into

electrolytes. Such conducting polymers even have the potentials to replace insulating polymer binders, such as polytetrafluoroethylene and polyvinylidene fluoride (PVDF), commonly used in supercapacitor electrode fabrication.²⁷⁵

3.3.2 Structural characterization of the hybrids

Figure 3.2 SEM images of (a) nitric acid treated MWCNTs and (b) Cu₂O deposited MWCNTs.

The morphologies of the synthesized hybrid materials were first examined by scanning electron microscope (SEM). The nitric acid treated MWCNTs have a diameter of 10–15 nm with their structure intact after introducing carboxyl groups on their side walls (Figure 3.2). After depositing Cu₂O, their diameters increase to around 20 nm (Figure 3.2b). Figure 3.3a shows SEM images of the coaxial MWCNT/amor-Ni(OH)₂ hybrid. MWCNTs are uniformly covered with Ni(OH)₂, and the surface becomes much rougher compared to that of the acid treated MWCNTs. Their diameters increase to about 15–20 nm, suggesting that a thin layer of Ni(OH)₂ was deposited. Figure 3.3b shows SEM images of the

ternary hybrid. Although the diameter of the hybrid is observed to have no significant change before and after PEDOT:PSS wrapping, which suggests the formation of a thin layer of polymer coating, the individual hybrid ropes are found to stick more compactly together with the polymer coating. The transmission electron microscope (TEM) images in Figure 3.3c and d confirm that the thickness of $\text{Ni}(\text{OH})_2$ on the MWCNTs is below 5 nm. The selected-area electron diffraction (SAED) patterns shown on Figure 3.3c and d only exhibit the diffraction rings from graphitic layers in the MWCNTs at their (002) and (100) planes. The broad and misty halo shown in the SAED patterns confirms that the deposited $\text{Ni}(\text{OH})_2$ is amorphous.

Figure 3.3 SEM images of (a) MWCNT/amor- $\text{Ni}(\text{OH})_2$ and (b) MWCNT/amor- $\text{Ni}(\text{OH})_2$ /PEDOT:PSS. TEM images and the corresponding SAED patterns of (c)

MWCNT/amor-Ni(OH)₂, (d) MWCNT/amor-Ni(OH)₂/PEDOT:PSS, (e) MWCNT/amor-Ni(OH)₂ after 3000 charge and discharge cycles, and (f) MWCNT/amor-Ni(OH)₂/ PEDOT:PSS after 3000 cycles.

Next, X-ray diffraction (XRD) patterns of the MWCNT, MWCNT/Cu₂O, MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS are shown in Figure 3.4a. MWCNTs display an intensive (002) peak at 25.40° and a minor (100) peak at 42.58°, originating from their graphite-like nature.²⁹³ After depositing Cu₂O, these two peaks become much weaker, while the characteristic peaks of the Cu₂O crystal at the (110), (111), (200) and (311) planes appear at 29.34°, 36.19°, 42.05° and 61.11°, respectively.²⁹⁴ Similarly, the MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS exhibit the weak (002) peaks from the MWCNTs, indicating that the surface of the MWCNTs are mostly covered by Ni(OH)₂. The absence of any crystalline Ni(OH)₂ characteristic peaks confirms the amorphous structure of the deposited Ni(OH)₂, which is in good agreement with the SAED results in Figure 3.3.

Figure 3.4 (a) XRD patterns of MWCNT, MWCNT/Cu₂O, MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/ PEDOT:PSS, (b) Comparison between XRD patterns of MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/ PEDOT:PSS before and after 3000 charge and discharge cycles. XPS spectra of (c) MWCNT/amor-Ni(OH)₂ and the insert shows the Ni 2p spectrum, (d) MWCNT/amor-Ni(OH)₂/ PEDOT:PSS and the insert shows the S 2p spectrum.

Figure 3.5 XPS spectra of (a) C 1s and (b) O 1s in MWCNT/amor-Ni(OH)₂.

Further, X-ray photoelectron spectroscopy (XPS) was used to characterize the chemical characteristics of the MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS. Figure 3.4c shows that the surface of MWCNT/amor-Ni(OH)₂ mainly contains Ni, O, C, and a small amount of Cu from the residues of the unetched Cu₂O. The C 1s spectrum (Figure 3.5a) has peaks at 284.6 and 285.3 eV from the sp² and sp³ hybridized C atoms. The C atoms in C-O, C=O and COO- structures also give peaks at 286.2, 287.4 and 289.1 eV, respectively.²⁹⁵ The O 1s spectrum (Figure 3.5b) has one main peak at 531.2 eV from O atoms in Ni-O structures and three other peaks at 531.8, 532.5 and 533.7 eV from O atoms in carbonyl, phenol and carboxyl groups, respectively.²⁴⁵ The C and O XPS spectra indicate that nitric acid treatment introduces oxygen-containing functional groups on the MWCNTs, which not only improve their surface wettability but also generates anchoring sites for Ni(OH)₂ deposition.³⁵ The insert of Figure 3.4c displays the enlarged Ni 2p XPS spectrum with two major peaks of Ni 2p_{3/2} (856.2 eV) and Ni 2p_{1/2} (873.6 eV) and their corresponding satellite peaks. The spin-energy separation between the two Ni 2p peaks is at 17.4 eV, agreeing with previous findings on amor-Ni(OH)₂.²⁸³ XPS spectrum of the MWCNT/amor-Ni(OH)₂/PEDOT:PSS is shown in Figure 3.4d. The XPS peaks resulting from Ni, O and C are similar to those observed on the XPS spectrum of the MWCNT/amor-Ni(OH)₂. In addition, S 2s (163.1 eV) and S 2p (168.6 eV) peaks from S atoms in the PEDOT: PSS are observed.^{291,296}

Figure 3.6 (a) Nitrogen adsorption/desorption isotherms of acid treated MWCNTs, MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/ PEDOT:PSS. (b) Thermogravimetric analysis profiles of acid treated MWCNTs, amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂.

Furthermore, the specific surface areas of the hybrids are determined from their N₂ adsorption/desorption isotherms (Figure 3.6a). The MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS have a specific surface area of 161 and 127 m²g⁻¹, respectively, which are smaller than that of the pristine MWCNTs (200 m²g⁻¹). The mass loadings of amor-Ni(OH)₂ on MWCNTs were also determined by thermogravimetric analysis (TGA) (Figure 3.6b). There are two major weight lost steps on the TGA profile of the MWCNT/amor-Ni(OH)₂, which correspond to amor-Ni(OH)₂ and MWCNTs, respectively. The mass loading of amor-Ni(OH)₂ on MWCNTs was determined to be 49.5 wt% from TGA. Since the MWCNT/amor-Ni(OH)₂/PEDOT:PSS contains 10 wt% PEDOT:PSS, the mass loading of amor-Ni(OH)₂ in the ternary composite is about 44.6 %. I have explored the option of further increasing the mass loading of amor-Ni(OH)₂ by

depositing more Cu_2O . However, I have found that either the Cu_2O forms large particles, which cannot be completely etched, or crystalline $\text{Ni}(\text{OH})_2$ appears on the MWCNTs after replacement. Thus, the mass loading of amor- $\text{Ni}(\text{OH})_2$ at around 50 wt% is the optimal loading found in this study.

3.3.3 Specific capacitance and rate capacity of the hybrids

Figure 3.7 CV curves of (a) MWCNT/amor- $\text{Ni}(\text{OH})_2$ and (b) MWCNT/amor- $\text{Ni}(\text{OH})_2$ / PEDOT:PSS at different scan rates in aqueous 1.0 M KOH electrolyte. (c) CV cuvers of MWCNT and MWCNT/PEDOT:PSS at the scan rate of 10 mV/s in in aqueous 1.0 M KOH electrolyte. (d) The specific capacitance as function of scan rate of MWCNT/amor- $\text{Ni}(\text{OH})_2$ and MWCNT/amor- $\text{Ni}(\text{OH})_2$ / PEDOT:PSS.

I first evaluated the electrochemical performance of the hybrids by cyclic

voltammetry (CV) and galvanostatic charge/discharge measurements using a three-electrode cell in 1 M aqueous KOH electrolyte. The MWCNT/amor-Ni(OH)₂ was fabricated into electrodes using PVDF as a binder (with the mass ratio of 9:1), while the MWCNT/amor-Ni(OH)₂/PEDOT:PSS was directly used as working electrodes because the PEDOT:PSS coating can hold the materials together without the need of additional polymer binders. In addition, MWCNTs mixed with PVDF binder (with the mass ratio of 9:1) and MWCNTs wrapped with PEDOT: PSS (with the mass ratio of 9:1) without Ni(OH)₂ (denoted as MWCNT/PEDOT:PSS) were also measured as reference samples. Figure 3.7a and b show the respective CV curves of MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS with the potential window from 0 to 0.5 V (vs. saturated calomel electrode) at different scan rates. There are two intense redox peaks attributed to the reversible Faradaic reaction between Ni(II) and Ni(III):

The specific gravimetric capacitance (C_s , F g⁻¹) of electrode materials can be calculated using the voltammetric charge integrated from their CV curves according to the equation:

$$C_s = \frac{1}{2V_{\text{vm}}} \int_{V_-}^{V_+} i(V) dV \quad (3.4)$$

where the positive and negative sweeps of current i (V) are integrated to obtain the total voltammetric charge. v is the scan rate, and V ($V = V^+ - V^-$) represents the scanned potential window. V used in this study is 0.5 V. m is the mass of the electrode materials. Figure 3.7d shows that C_s of the MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS is 1540 and 1454 Fg⁻¹ at the scan rate of 5 mVs⁻¹, respectively. These are based on the total mass of all active materials in the measured electrodes including MWCNTs, amor-Ni(OH)₂, and PEDOT:PSS. CV curves of the two reference samples, MWCNTs and MWCNT/PEDOT: PSS, under a scan rate of 5 mVs⁻¹, are shown in Figure 3.7c. The MWCNTs display a rectangular shape, which is typical for EDLC. MWCNT/PEDOT:PSS also shows a rectangular-like shape but with a bulge around 0.22 V which is related to the redox reaction of PEDOT.²⁹⁷ C_s of the two reference samples determined from their CV curves are 58 and 80 Fg⁻¹, respectively, which is similar to previously reported results.^{160,297} Comparing the C_s of the two references samples to those of the two amor-Ni(OH)₂ hybrids, I can conclude that the contribution from EDLC by MWCNTs and PEDOT:PSS to the total capacitance of the hybrids is much smaller (less than 3.8 and 5.2 %) than the pseudocapacitance from the amor-Ni(OH)₂. In order to better compare the performance of amor-Ni(OH)₂ found in this study with the existing literature data reported for Ni(OH)₂ based materials, I have further calculated the specific gravimetric capacitance (C'_s) of the hybrids based on the mass of amor-Ni(OH)₂

only. It should be noted that amor-Ni(OH)₂ counts for 49.5 wt% of the MWCNT/amor-Ni(OH)₂ and 44.6 wt% of the MWCNT/amor-Ni(OH)₂/PEDOT:PSS. C'_s is 3111 and 3262 Fg⁻¹ for MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS, respectively, as shown in Figure 3.7d. To our knowledge, this is one of the highest gravimetric specific capacitances among all reported Ni(OH)₂ materials measured using a three-electrode cell^{26,111,171,278,279,281,283,284,287,298,299} (see Table 3.1), suggesting that efficient surface redox reactions can take place on the thin layer of disordered amor-Ni(OH)₂ deposited on the MWCNTs. It is worth mentioning that my result is more than two times higher than that of the previously reported pure amor-Ni(OH)₂ (1677 Fg⁻¹) at the same scan rate of 5 mVs⁻¹.²⁸³ The large specific gravimetric capacitance in this study can be attributed to the synergistic effects in the ternary hybrid architecture as discussed above.

Figure 3.7d further displays the rate capability of the two hybrids. C'_s of the MWCNT/amor-Ni(OH)₂ decreases from 3111 to 1648 Fg⁻¹ with 53% capacitance retention, when the CV voltage scan rate increases from 5 to 100 mV s⁻¹. In comparison, the MWCNT/amor-Ni(OH)₂/PEDOT:PSS exhibits significant improvement, 71.9% of its capacitance being retained. Its rate capability outperforms many previously reported Ni(OH)₂ materials^{26,29,171,194,245,279,281-283,287,298,299} (see Table 3.1 for detailed comparison). The rate capability of pseudocapacitive materials is usually limited by their charge transfer rate and ion

diffusion resistance. In the uniquely-designed hybrids, the abundance defects within the amor-Ni(OH)₂ can improve ion diffusion, which facilitates the efficient transformation between Ni(OH)₂ and NiOOH.³⁰⁰ The MWCNTs serve as conductive highways for electrons. The thin Ni(OH)₂ layer prompts the fast and efficient electron transportation between Ni(OH)₂ and MWCNTs. Moreover, the conductive PEDOT: PSS can further reduce the electron transfer resistance among MWCNT/amor-Ni(OH)₂ ropes, as reflected by the higher capacitance retention observed in the MWCNT/amor-Ni(OH)₂/PEDOT:PSS.

The specific gravimetric capacitance of electrode materials can also be calculated from their galvanostatic charge/discharge curves at different current densities using:

$$C_s = \frac{i}{dV/dt} \quad (3.5)$$

where i is the discharging current and dV/dt is the slope of the discharge curves. The galvanostatic charge/discharge curves of MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/PEDOT:PSS at the current density from 3 to 20 A/g are shown in Figure 3.8. The calculated C_s and the observed rate capability from the charge/discharge curves are similar to those obtained from their CV curves as shown in Figure 3.7d. The detailed comparison with the previously reported data obtained using charge/discharge curves is listed in Table 3.1, Figure 3.9 also shows that the MWCNT/amor-Ni(OH)₂/PEDOT:PSS has high Coulombic

efficiencies (near 100 %) at the charge/discharge current density up to 20 A/g, indicating that a large fraction of the redox reactions take place on the surface or near-surface region of amor-Ni(OH)₂ in the two hybrids.

Figure 3.8 Galvanostatic Charge/discharge curves of (a) MWCNT/amor-Ni(OH)₂ and (b) MWCNT/amor-Ni(OH)₂/ PEDOT:PSS in a three-electrode cell with 1 M aqueous KOH electrolyte at different current densities.

Figure 3.9 Columbic efficiency of MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/ PEDOT:PSS in a three-electrode cell with 1 M aqueous KOH electrolyte at different current densities.

Table 3.1 Comparison of electrochemical performances of Ni(OH)₂ based materials

Ref.	Materials	Voltage range, V	Electrolyte (aqueous)	C _s , ^[1] F g ⁻¹	C _s , ^[2] F g ⁻¹	Rate capability	Cycle life ^[3]
279	β-Ni(OH) ₂ / graphene	0~0.55	1 M KOH	887 @5mV/s	1267 @ 5mV/s	20% decrease from 5 to 40 mV/s	No obvious change, 2000, @ 28 A/g
26	β-Ni(OH) ₂ /graphene foam	0~0.5	6 M KOH	166 @0.5 A/g	1560 @0.5 A/g	30% decrease from 0.5 to 10 A/g	65%, 1000, @10 A/g
287	α-Ni(OH) ₂ /graphene	0~0.7	1 M KOH	1250 @5 mV/s	3138 @5 V/s	50% decrease from 5 to 40 A/g	95%, 1000
171	β-Ni(OH) ₂ /CNT	-0.1~0.5	6 M KOH	1392 @5 mV/s	1536 @5 mV/s	21% decrease from 0.1 to 0.4 A/g	
194	β-Ni(OH) ₂ /MWCNT	0~0.7	2 M KOH	1487 @5 mV/s		32% decrease from 5 to 100 mV/s	96%, 1000, @100 mV/s
29	α-Ni(OH) ₂ /graphene	-0.1~0.45	6 M KOH	1480 @5 mV/s		65% decrease from 5 to 50 mV/s	
301	β-Ni(OH) ₂ /MWCNT	0~0.5	KOH	1735 @5 mV/s		18% decrease from 5 to 100 mV/s	94%, 6000, @20 mV/s
282	α-Ni(OH) ₂ /CNT	0~0.5	6 M KOH	1302.5 @5 mV/s		38% decrease from 5 to 20 A/g	51.8%, 1000, @5 A/g
288	β-Ni(OH) ₂ /RGO	0~0.55	6 M KOH	1551.8 @2.67 A/g		24% decrease from 2.67 to 21.33 A/g	102%, 2000, @5.33 A/g
245	β-Ni(OH) ₂ /graphene	0~0.6	6 M KOH	1503 @2 mV/s		73% decrease from 2 to 100 mV/s	96.5%, 6000, @50 mV/s

302	α -Ni(OH) ₂ /RGO	0~0.6	6 M KOH	1760.7 @5 mV/s			
278	α -Ni(OH) ₂ /CNT/Ni foam	0~0.4	6 M KOH		3300 @5 mV/s	33% decrease from 0.5 to 10 A/g	
281	Conformal Ni(OH) ₂ (A mix of α and β -Ni(OH) ₂ and 4Ni(OH) ₂ ·NiOOH)	-0.15~0.75	1 M KOH		1370 @5 mV/s	73% decrease from 5 to 50 mV/s	78%, 2000, @20 A/g
111	Nanoporous β -Ni(OH) ₂	0~0.5	6 M KOH		1765 @2 mV/s	47% decrease from 2 to 100 mV/s	
283	Amorphous Ni(OH) ₂	0~0.5	1 M KOH		1677 @5 mV/s	43% decrease from 1 to 20 mV/s	76%, 10000, @100 mV/s
298	Amorphous Ni(OH) ₂	0~0.5	2 M KOH		1689 @5 mV/s	48% decrease from 1 to 20 mV/s	95%, 1200, @5 A/g
299	Al-Co doped α -Ni(OH) ₂ /graphene	-0.1~0.4	6 M KOH		2257 @2 mV/s	30% decrease from 2 to 50 mV/s	77%, 1000, @50 mV/s
284	Ni-Co layered hydroxides	-0.1~0.55	2 M NaOH		1289 @1 A/g	30% decrease from 1 to 20 A/g	82%, 2000, @5 A/g
This work	MWCNT/Amor-Ni(OH) ₂ /PEDOTPSS	0~0.5	1 M KOH	1454 @5 mV/s	3262 @5 mV/s	28% decrease from 5 to 100 mV/s	92%, 3000, @10 A/g

[1] C_s : Specific capacitance calculated based on the total mass of active materials on the electrode;

[2] C_s' : Specific capacitance normalized on the mass of the nickel (or nickel-cobalt) hydroxide on the electrode;

[3] Cycle life: capacitance retention, cycles, @ current.

3.3.4 Improved cycle life of the ternary hybrid

Figure 3.10 (a) Cycle life of MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/ PEDOT:PSS measured at 10 A g⁻¹ in a three-electrode cell with 1 M aqueous KOH electrolyte. (b) EIS Nyquist plots of MWCNT/amor-Ni(OH)₂ and MWCNT/amor-Ni(OH)₂/ PEDOT:PSS before (solid spots) and after (open spots) the 3000 charge and discharge cycles as shown in (a). The insert shows the enlarged portion at the high frequency region.

As discussed above, nanoscale structure degradation and Ni ion dissolution are the two key issues compromising the cycle life of many previously reported Ni(OH)₂ nanomaterials. The cycle lives of the two hybrids were evaluated by galvanostatic charge/discharge tests at 10 A g⁻¹ in a range of 0-0.5 V in 1 M KOH aqueous electrolyte. Figure 3.10a shows that C_s of the MWCNT/amor-Ni(OH)₂ drops rapidly from 1103 to 987 F g⁻¹ after 200 cycles, and then gradually to 756 F g⁻¹ thereafter at 3000 cycles. The instability of the MWCNT/amor-Ni(OH)₂ is also substantiated by the change in its electrochemical impedance spectroscopic

(EIS) measurements. Figure 3.10b shows that the composite has much larger equivalent series resistance (from the x-intercept of the Nyquist plot) and higher charge transfer and ion diffusion resistance (from radius of the semicircles and the Warburg region on the Nyquist plot). These electrochemical performance changes are correlated to the structural changes of Ni(OH)₂. XRD patterns in Figure 3.4b indicate that the amor-Ni(OH)₂ is gradually transformed to β -crystalline Ni(OH)₂ with the appearance of its characteristic peaks at 19.31° (*i.e.* diffraction of Ni(001)) and 38.34° (*i.e.* diffraction of Ni(011)). I have also observed the formation of Ni(OH)₂ crystals on the TEM image shown in Figure 3.3e. The SAED pattern exhibits the diffraction rings from Ni(001) and Ni(011). These structural changes are not surprising as previous studies have reported that α -Ni(OH)₂ is not stable in alkaline solution and can be transformed to β -crystalline Ni(OH)₂.^{83,300,303} Upon multiple charge/discharge cycles, the ion diffusion inside the amor-Ni(OH)₂ supported on MWCNTs may facilitate the formation of the thermodynamically more stable β -Ni(OH)₂.

An important design consideration in the ternary hybrid is the wrapping of MWCNT/amor-Ni(OH)₂ with PEDOT:PSS so that the cycle life of the MWCNT/amor-Ni(OH)₂ can be extended while keeping their excellent specific capacitance and rate capability. Figure 3.10a shows that the ternary hybrid retains 92% of its original capacitance after 3000 cycles. This performance is not only much better than that of the MWCNT/amor-Ni(OH)₂, but also superior to many

previously reported Ni(OH)₂ materials (see Table 3.1 for details).^{26,170,278,281,283,299}

The improved cycle life of the ternary hybrid can be corroborated with the minimum changes in its equivalent series resistance and ion diffusion resistance (see Figure 3.10b). XRD (Figure 3.4b) and TEM (Figure 3.3f) results also confirm that amor-Ni(OH)₂ in the ternary hybrid has minor structural changes after 3000 charge/discharge cycles.

I further extended the cycling test of the MWCNT/amor-Ni(OH)₂/PEDOR:PSS to 30000 cycles at the current density of 20 A g⁻¹ in the three-electrode cell in order to demonstrate its long-term stability under high current density (Figure 3.11). The electrode retains about 85% of its original capacitance after 20000 cycles, and still has 77% of its original capacitance after 30000 cycles. As shown in the inserts of Figure 3.11, the charge-discharge profiles at different cycling stages (three cycles from each stage) show minor changes in their shapes except for the slightly decreased charge-discharge time. This further confirms the excellent stability of the ternary hybrid.

Figure 3.11 Cyclic test of MWCNT/amor-Ni(OH)₂/ PEDOT:PSS electrode extended to 30000 cycles measured at 20 A g⁻¹ in a three-electrode cell with 1 M aqueous KOH electrolyte. The insert shows the charge-discharge profiles at the different cycling stages during the test.

3.4.5 Performances of asymmetric supercapacitors

To evaluate the practical supercapacitor applications of the ternary hybrid, I have fabricated asymmetric supercapacitors using the MWCNT/amor-Ni(OH)₂/PEDOT:PSS as positive electrodes and the rGO/CNT hybrid as negative electrodes. The active electrode materials were coated on two pieces of carbon cloth (1 × 1 cm), and then sandwiched with a membrane separator in 1 M aqueous KOH electrolyte. The cell voltage was set as the sum of the potential windows of the positive (0–0.5 V) and negative (-1.0–0 V) electrodes at 1.5 V.²⁹

Figure 3.12 (a) SEM image of the freeze-dried rGO/CNT hybrid, (b) Nitrogen adsorption/desorption isotherm of the freeze-dried rGO/CNT hybrid, (c) CV curves and (d) galvanostatic charge/discharge curves of the rGO/CNT hybrid electrodes measured with a voltage window of 0 to -1 V in a three-electrode cell with 1 M aqueous KOH electrolyte.

The rGO/CNT hybrid was used in this study because of it has better electrochemical performances compared to commonly used activated carbon electrodes.^{30,169,278} The carbon hybrid with a mass ratio of 3:1 between rGO and CNTs was obtained following the previously reported hydrothermal synthesis method.^{30,33,228} The rGO/CNT hybrid is porous (see the SEM image on Figure 3.12a) with a specific surface area of 364 m²/g measured by N₂ physisorption (Figure 3.12b). The rGO/CNT hybrid was pressed into film electrodes to

assemble asymmetric supercapacitors. The CV curves of the rGO/CNT electrode measured using a three-electrode cell 1 M aqueous KOH electrolyte with the scanning voltage from -1 to 0 V are shown in Figure 3.12c. The rectangle-like CV curves indicate its EDLC behavior. No obvious IR drops are observed on its galvanostatic charge/discharge curves (Figure 3.12d), indicating that it has low internal resistances. The rGO/CNT hybrid has a specific capacitance of 203 F g⁻¹ at the current density 1 A g⁻¹, and retains 75% of this specific capacitance when the discharge current was increased to 20 A g⁻¹.

The charge stored by each electrode in an asymmetric supercapacitor depends on the specific capacitance (C_s) of electrode material, the potential window (ΔV) and the mass of electrode materials (m). To balance the charge stored in the two electrodes, the mass ratio of electrode materials is adjusted according to:

$$\frac{m^+}{m^-} = \frac{C_s^- \times \Delta V^-}{C_s^+ \times \Delta V^+} \quad (3.6)$$

In an assembled supercapacitor, the mass loading of the MWCNT/amor-Ni(OH)₂/PEDOT:PSS hybrid is about 3.5 mg cm⁻² and that of the rGO/CNT hybrid is about 12 mg cm⁻². The total active materials in each assembled supercapacitor of 1×1 cm² in size are about 15.5 mg.

Figure 3.13 (a) CV curves of the assembled MWCNT/amor-Ni(OH)₂/PEDOT:PSS//rGO/CNT asymmetric supercapacitor at different scan rates in 1 M aqueous KOH electrolyte with a 1.5 V voltage window. (b) Galvanostatic charge/discharge curves of the assembled asymmetric supercapacitor at different current densities. (c) The specific capacitance of the supercapacitor measured from CV curves at different scan rates. (d) The specific capacitance of the supercapacitor measured from charge/discharge curves at different current densities.

Figure 3.13a shows the CV curves of the assembled two-electrode asymmetric supercapacitor with a voltage scan rate from 5 to 150 mV s⁻¹. The CV curves show two redox peaks, which are much broader than those in Figure 3.7b. Its galvanostatic charge/discharge curves at the current density from 1 to 20 A g⁻¹

are shown in Figure 3.13b. The specific capacitance of the supercapacitor can be determined using:

$$C_{\text{cell},m} = \frac{C_{\text{cell}}}{m^+ + m^-} \quad (3.7)$$

where C_{cell} are obtained using either the CV curves or galvanostatic discharge curves based on equations similar to the equation (3.4) and (3.5), but measured on the two-electrode supercapacitor instead. As shown in Figure 3.13c and 3.13d, the asymmetric supercapacitor demonstrates excellent rate capability and the C_{cell} decreases from 179.8 to 109.6 F g⁻¹ when the galvanostatic discharge current increases from 1 to 20 A g⁻¹, or from 159.4 to 102.3 F g⁻¹ when the voltage scan rate increases from 5 to 150 mV s⁻¹.

The gravimetric specific energy ($E_{\text{cell},m}$) and power ($P_{\text{cell},m}$) density of the supercapacitor are obtained from the equations:

$$E_{\text{cell},m} = C_{\text{cell},m} \Delta V^2 / (2 \times 3600) \quad (3.8)$$

$$P_{\text{cell},m} = E_{\text{cell},m} \times 3600 / t_{\text{discharge}} \quad (3.9)$$

where $t_{\text{discharge}}$ is the discharge time.^[25, 48]

As shown in the Ragone plot on Figure 3.14a, the specific energy density of the supercapacitor reaches 58.5 Wh kg⁻¹ at the power density of 780 W kg⁻¹, and retains at 30.8 Wh kg⁻¹ with the high power density of 11.5 kW kg⁻¹. To our

knowledge, the asymmetric supercapacitor based on the MWCNT/amor-Ni(OH)₂/PEDOT:PSS has one of the highest specific energy and power densities among all reported Ni(OH)₂ based supercapacitors using similar calculation methods.^{82,278,283,304,305} The detailed comparison between my results with the previously reported data is listed in Table 3.2.^{26,85,171,278,283,306-308}

Figure 3.14 (a) Ragone plot of the assembled MWCNT/amor-Ni(OH)₂/PEDOT:PSS//rGO/CNT asymmetric supercapacitor in comparison with Ni(OH)₂ based symmetric supercapacitors reported in the literature. Photographs showing two asymmetric supercapacitors in series to (b) light up two LED

indicators in red and green simultaneously, and (c) drive a motor (video is shown in SI) after charging for 8 s at 20 A g^{-1} .

To demonstrate that the supercapacitors can be used as efficient power sources for practical applications, two $1 \times 1 \text{ cm}^2$ supercapacitors were connected in series to light up two light-emitting diode (LED) indicators (green: 3.0–3.2 V, 20 mA and red: 2.0–2.2 V, 20 mA) for about 9 min after being charged to 3 V in 8 s at the current density of 20 A g^{-1} (see Figure 3.14b). Moreover, the two supercapacitors in series were also used to drive a motor (Mabuchi RF-500TB, 330 mW) (see Figure 3.14c and watch the movie in SI).

Figure 3.15 Cycle life of the assembled asymmetric supercapacitor upon 30000 charge and discharge cycles in 1 M aqueous KOH electrolyte at 10 A/g galvanostatic charge-discharge current with a potential range of 0 to 1.5 V. The inserts show the first and last 10 cycles of charge/discharge profiles of during the test.

More importantly, the key advantage of the asymmetric supercapacitor is its long cycle life resulting from the uniquely designed ternary hybrid structure in the MWCNT/amor-Ni(OH)₂/PEDOT:PSS. Figure 3.15 shows that the supercapacitor can retain 90% of its original capacitance after 5000 charge/discharge cycles at 10 Ag⁻¹ and still maintain at 86% after 30000 cycles. The initial ten cycles and last ten cycles of the voltage profiles in the insert of Figure 3.15 show minor changes. The stability performance of the assembled asymmetric supercapacitor is similar to that of its positive electrode, MWCNT/amor-Ni(OH)₂/PEDOT:PSS, measured in the three-electrode cell test, which suggests that the cycling performance of the asymmetric supercapacitor is mainly controlled by its positive electrode. The performance of the asymmetric supercapacitor at the first few thousand cycles is evolving. The initial slight increase may be attributed to the improvement of electrode surface wettability and electrolyte ion accessibility.²⁴⁵ And the following decline may be caused by irreversible surface dissolution of unstable active materials and solid electrolyte interface (SEI) reactions, which have been observed in some previous studies.^{29,85,245,307-309} In the ternary hybrid, the conducting polymer coating help to stabilize the electrodes by reducing the dissolution of active materials and SEI reactions. Thus, the observed declining trend was extended to about 3000 cycles, in contrast to the fast decay within 1000-2000 cycles observed in many previous reports.^{29,85,245,307-309} After the unstable Ni(OH)₂ on the surface is dissolved and

the formation of stable SEI, the performance of the asymmetric supercapacitor became more stable. This cycle life outperforms most of the previously reported $\text{Ni}(\text{OH})_2$ based supercapacitors (see Table 3.2).^{26,29,85,171,278,283,306-308} The asymmetric supercapacitor tested in two electrode cell has better cycling performance compared to the electrode tested in three-electrode cell. This may be due to two reasons. First, the three-electrode cell test uses a much larger volume of aqueous electrolyte solution compared to that used in the two-electrode asymmetric supercapacitor. When the electrode materials are immersed in a large volume of electrolyte in the three-electrode cell, the irreversible dissolution of the active materials into electrolyte is more likely to happen because of the fast mass transfer. Second, the three-electrode cell test is an open system where the electrode materials are exposed to the oxygen dissolved in electrolyte from air. In contrast, the partially sealed two-electrode asymmetric supercapacitor significantly limits the oxygen exposure of electrodes.

Table 3.2 Comparison of electrochemical performances of Ni(OH)₂ based asymmetric supercapacitors

Ref.	Asymmetric supercapacitors	Rate capability		Energy density/ Power density (Wh/kg)/(W/kg)	Cyclic stability
		Measured by CV	Measured by charge-discharge		
26	β -Ni(OH) ₂ /UGF VS a-MEGO		119 F/g @1 A/g	13.4 Wh/kg @85000 W/kg	63.2 % retention after 10000 cycles at 5 A/g
29	α -Ni(OH) ₂ /graphene VS porous graphene	218.4 F/g @1 mV/s		77.8 Wh/kg @174.7 W/kg	75.1 % retention after first 150 cycles and 94 % after 3000 cycles at 100 mV/s
		~63 F/g @ 50 mV/s		13.5 Wh/kg @15200 W/kg	
278	α -Ni(OH) ₂ /CNT/Nickel foam VS Activated carbon (AC)		112.5 F/g @2.5 mA/cm ²	50.6 Wh/kg @95 W/kg	83 % retention after 3000 cycles at 50 mA/cm ²
			72.2 F/g @50 mA/cm ²	32.5 Wh/kg @1800 W/kg	
307	β -Ni(OH) ₂ nanosheets/nickel foam VS AC		105.8 F/g @2 mA/cm ²	36.2 Wh/kg @100.6 W/kg	92 % retention after 1000 cycles at 5 mA/cm ²
			44.9 F/g @20 mA/cm ²	10.5 Wh/kg @687.3 W/kg	
171	Ni(OH) ₂ /CNT VS AC		96 F/g @0.1 A/g	40 Wh/kg @100 W/kg	92 % retention after 2000 cycles at 0.5 A/g
			76.8 F/g @1.5 A/g	32 Wh/kg @1500 W/kg	
306	Ni-Co hydroxide/graphene/CNT VS AC/FWCNT		150 F/g @0.3 A/g	41 Wh/kg @210 W/kg	
			106 F/g @6 A/g	29 Wh/kg @4200 W/kg	
85	NiCo layered double hydroxide/graphene VS AC	~87 F/g @5 mV/s		35.5 Wh/kg@875 W/kg	90 % retention after 2000 cycles at 4 A/g
		~57 F/g @80 mV/s		20.7 Wh/kg @8750 W/kg	

111	Nanoporous Ni(OH) ₂ VS AC	192 F/g@0.9 A/g	68 Wh/kg @ ~1300 W/kg ~6.4 Wh/kg @44000 W/kg	90 % retention after 10000 cycles at 18 A/g
283	Amorphous Ni(OH) ₂ VS AC	153 F/g @5 mV/s 54 F/g @50 mV/s	35.7 Wh/kg @490 W/kg 12.6 Wh/kg @1670 W/kg	97 % retention after first 5000 cycles and 81 % after 10000 cycles at 50 mV/s
This work	MWCNT@amor-Ni(OH) ₂ @PEDOT:PSS VS RGO/SWCNT hybrid	159 F/g @5 mV/s	179.8 F/g @1 A/g 58.5 Wh/kg@780 W/kg	90 % retention after first 5000 cycles and 86 % after 30000 cycles at 10 A/g

3.4 Conclusion

I have successfully synthesized the coaxial ternary hybrid material with a thin layer (< 5 nm) of amorphous $\text{Ni}(\text{OH})_2$ deposited on nitric acid treated MWCNTs as the core and a thin conductive polymer (PEDOT:PSS) layer wrapping the core. The amorphous $\text{Ni}(\text{OH})_2$ was deposited by a novel “coordinating etching and precipitating” method, which enables large fraction of redox reactions to take place on the surface or near-surface region, resulting in high pseudocapacitance and excellent rate capability. The ternary hybrid has a gravimetric specific capacitance of 3262 F g^{-1} at 5 mV s^{-1} in 1 M aqueous KOH electrolyte and retains 71.9% of its capacitance at 100 mV s^{-1} . More importantly, the PEDOT: PSS layer prevents the degradation of the nanoscale structure of amorphous $\text{Ni}(\text{OH})_2$ and Ni ion dissolution upon repeated charges/discharges, resulting in a long cycle life (92% capacitance retention over 3000 cycles and 77% retention over 30000 cycles under the high current of 20 A g^{-1}). This makes the ternary hybrid superior to most of the previously reported $\text{Ni}(\text{OH})_2$ materials. The assembled asymmetric supercapacitor using the ternary hybrid as the positive electrode and the rGO/CNT hybrid as the negative electrode exhibits a gravimetric specific energy density of 58.5 Wh kg^{-1} at a power density of 780 W kg^{-1} , and retains at 30.8 Wh kg^{-1} with a high power density of 11.5 kW kg^{-1} . The supercapacitor holds 86% of its original capacitance after 30000 cycles and outperforms most of the

previously reported $\text{Ni}(\text{OH})_2$ based supercapacitors. Further, two supercapacitors, connected in series, are capable of lighting up two LED indicators simultaneously and driving a motor, demonstrating the excellent practical application potentials. The synthesis method of amorphous $\text{Ni}(\text{OH})_2$ and the unique ternary hybrid design that I have demonstrated can be regarded as a general approach to obtain high performance pseudocapacitive materials for supercapacitors with high energy density, rate capability and long cycle life.

Chapter IV Hybrid Ternary Rice Paper-manganese Oxide-carbon Nanotube Nanocomposites for Flexible Supercapacitors

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4.1 Background Introduction

Modern portable electronic devices create a strong demand for flexible energy storage devices.^{47,177-180} Supercapacitors are attractive because of their capability to deliver high power with long cycle life.^{9,12,17,310,311} Hybrid composite electrodes are often used to increase the capacitance, cycling life and rate performance of supercapacitors by combining high surface area nanostructured carbons with pseudocapacitive metal oxides.^{62,106,136,275,312-318}

As mention above, cellulose paper is a cheap, recyclable and sustainable material and has recently expanded its applications into supercapacitors.^{179,319-323} In 2007, Pushparaj *et al.* infiltrated plant cellulose dissolved in an ionic liquid at room temperature into multi-walled carbon nanotube (CNT) forests to form a paper-like composite.³¹⁹ Hu *et al.* reported the first study using conventional cellulose paper in 2009.³²⁰ They applied CNT ink onto Xerox paper using a Meyer rod coating method to form conductive paper, which was then used as

active electrodes and current collectors in supercapacitors.³²⁰ It was also reported that ink-jet printing can be used to prepare the CNT-paper composite.³²¹ Kang *et al.* reported the first synthesis of hybrid electrodes containing electrochemically deposited MnO₂ onto CNT-paper, which improved the energy density of supercapacitors.³²¹ Recently, the active materials used in paper based supercapacitors was expanded to multi-layer graphene hand-drew on Xerox paper,³²² while bacterial nanocellulose paper and filter paper were explored as supercapacitor electrode substrates for graphene based materials.^{197,323}

Figure 4.1 Primary and secondary hydroxyl groups on cellulose fibers.

A common approach in these studies is that cellulosic paper is used as a substrate to support active electrode materials, *i.e.* carbon nanomaterials, metal oxides, or their hybrids. The physical properties of paper, such as excellent flexibility and large porosity, are capitalized in these materials. Paper is held together through hydrogen bonding between the hydroxyl groups of interconnected cellulose fibers. Cellulose is a semi crystalline microfibrillar linear polysaccharide of β -1, 4-linked D-glucopyranose, which contains plenty of primary and secondary hydroxyl groups (Figure 4.1). Those hydroxyl groups make the cellulose fibers quite hydrophilic which can be easily wetted by

aqueous electrolyte and can also be capable of holding the aqueous electrolyte within fibers for long time. On the other hand, owing to their potential reductive activity, the hydroxyl groups offer reactive sites for chemical functionalization on cellulose fiber surfaces.³²⁴⁻³²⁷ I expect that the chemical properties of paper are as important as its physical properties, in particular, when material hybrids, such as metal oxides are to be deposited. Few studies have explored this area.

In this chapter, hybrid ternary nanocomposites, comprised of rice paper, MnO₂ and single-walled carbon nanotube (SWCNT) were synthesized. I intentionally compared two different synthesis approaches. One is to use paper as physical substrates for supporting active materials, while the other employs the hydroxyl chemistry of paper for direct deposition of MnO₂ nanoparticles. The morphologies and physicochemical properties of these two types of nanocomposites were studied by scanning electron microscope (SEM), physisorption, thermogravimetric analysis (TGA), and X-ray diffraction (XRD) and transmission electron microscopy (TEM). The nanocomposites were further fabricated into two-electrode supercapacitors. Their electrochemical characteristics show that the nanocomposites synthesized by direct depositing MnO₂ on paper have better electrochemical performance. The mechanisms for the two synthesis approaches were discussed. The deposition temperature of MnO₂ was optimized. In addition, the mechanical strength and flexibility of the composites and assembled supercapacitors were demonstrated.

4.2 Experimental Section

4.2.1 Preparation of functionalized SWCNT ink

The SWCNTs (AP-SWCNT, Carbon Solution Inc., batch: AP-407) were first purified by oxidation at 450 °C in air for 1 h and refluxing in 37% hydrochloric acid for another 1 h to remove amorphous carbon and metal impurities. The purified SWCNTs were further refluxed in concentrated nitric acid (Sigma, 65.0 %) for 4 h to graft carboxylic groups on their surface. The HNO₃ functionalized SWCNTs contain small carbonaceous fragments and functionalized large tube bundles, which can be easily dispersed in deionized (DI) water without obvious sediments through mild magnetic stirring. The dispersion was further centrifuged at 2000 *g* (4100 RPM on Hitachi Preparative Ultracentrifuge CP 80WX) for 1 h, and the supernatant containing small carbonaceous fragments was decanted. The deposited carbon was redispersed in DI water by bath sonication, and then was centrifuged at 50000 *g* (20800 RPM) for 1 h to remove large bundles. The resulting supernatant containing well dispersed SWCNTs was used as functionalized SWCNT ink. The concentration of SWCNT ink was adjusted by a standard concentration calibration curve using its absorption at 958 nm measured on an ultraviolet–visible–near-infrared (UV–Vis–NIR) spectrometer (Varian 5000).³²⁸

4.2.2 Synthesis of paper-based hybrid ternary composites

Two approaches were used to synthesize paper-based hybrid ternary composites. As illustrated in Figure 4.2, the composite synthesized from Path A is denoted as “SWCNT–MnO₂–paper”. The pristine rice paper (Shanghai deligao stationery Co., Ltd.) was first dipped into 0.1 M KMnO₄ aqueous solution (pH = 7) at 80 °C for 10 min to deposit MnO₂, resulting in the “MnO₂–paper” composite. After washing away the KMnO₄ residues, the dried MnO₂–paper was placed on a nylon filter membrane (0.22 μm pore). Then, SWCNTs (0.5 mg SWCNT/ per cm²) were coated on MnO₂ by filtration. The composite from Path B is denoted as “MnO₂–SWCNT–paper”. Paper was cut into round disks with the diameter of 4.7 cm, and placed on top of the nylon filter membrane. SWCNTs were first deposited on the paper by vacuum filtering SWCNT ink at a pressure of 600 mbar through paper and membrane, resulting in the “SWCNT–paper” composite. The amount of deposited SWCNTs was fixed at around 0.5 mg SWCNT/cm² by using specific amount of SWCNT ink. The SWCNT–paper was dried, and then dipped into 0.1 M KMnO₄ aqueous solution (pH = 7) at 80 °C for 10 min to deposit MnO₂.

Figure 4.2 Schematic illustration of the two synthesis approaches for the paper-based hybrid ternary nanocomposites.

4.2.3 Physiochemical and mechanical properties of nanocomposites

The morphology of pristine paper, MnO_2 -paper, MnO_2 -SWCNT-paper, SWCNT-paper, and MnO_2 -SWCNT-paper was first examined by a field-emission SEM (FESEM) (JEOL, JSM6701) at 5 kV. Their specific surface areas were measured by a surface area analyzer (Autosorb-6B, QuantaChrome) and calculated by the Brunauer–Emmett–Teller (BET) method. Prior to each measurement, the samples were degassed at 120 °C for 10 h under vacuum (<0.01 mbar). Thermogravimetric analysis (TGA, Perkin Elmer Diamond FTA32 TG/DTA) was applied to determine the mass loading of MnO_2 . The elemental composition of composites was obtained by their energy dispersive spectra (EDS) using FESEM at 20 kV. The phase and composition of MnO_2 in the composites was studied by XRD (Bruker AXS D8) with Cu-K radiation and a high-resolution

transmission electron microscopy (HRTEM) (JEOL-JEM3010) at 200 kV. The mechanical tensile stress of nanocomposites was measured by a tensile/compression tester (Instron 5543 Single Column Testing System).

4.2.4 Assembly of supercapacitors and electrochemical measurements

The paper based ternary nanocomposites were cut into 1×1 cm square electrodes. Each supercapacitor consists of two electrodes of the same type of materials, two platinum foils (Sigma, 99.99%) as current collectors, a piece of membrane (Nippon Kodoshi Co.) as separator, and 0.5 M Na_2SO_4 aqueous solution as electrolyte. All components were sandwiched together and sealed between two pieces of polypropylene (PP) films. The electrochemical performance of capacitors was measured using an electrochemical station (CHI 660D) by cyclic voltammetry (CV), galvanostatic charge and discharge, electrochemical impedance spectroscopy (EIS), and capacitance retention test. CV measurements were conducted in the applied potential difference window of 0–1 V at scan rates of 10, 20, 50, 100, 200 mV/s. Galvanostatic charge/discharge tests were operated under a constant charge/discharge current density of 0.5, 1, 2, 5 A/g within the applied potential difference ranging from 0 to 1 V. In EIS tests, the frequency range was within 0.01 and 100,000 Hz with 5 mV amplitude, and open circuit potential was applied as dc bias potential. The capacitance retention test was carried out at a constant current density of 2 A/g from 0 to 1 V for 3000

charge/discharge cycles. The bending test of assembled supercapacitors was conducted using 0.5×1.5 cm rectangle-size electrodes. Conductive silver gel (Aldrich) was placed on the 0.5×0.5 cm areas at both end of electrodes as current collectors without using Pt foils.

4.3 Results and Discussion

4.3.1 Morphology of nanocomposites

Figure 4.3 Surface water wettability comparison between (a) regular printing paper (Paperone premium copier, APRIL group, 80 g/m^2) and (b) rice paper (Shanghai deligao stationery Co., Ltd.). Rice paper shows much better water wettability.

Figure 4.4 SEM images of rice paper and paper-based nanocomposites. (a) Rice paper is composed of porous cellulous fibers, (b) the enlarged view of the porous surface of cellulous fibers, (c) MnO₂ particles directly deposited on paper, (d) SWCNT-MnO₂-paper nanocomposite, (e) SWCNTs filtered on paper, (f) MnO₂-SWCNT-paper nanocomposite. The inserts are the enlarged views of SEM images.

Rice paper is a flexible, porous and low density ($\sim 30 \text{ g/m}^2$) material with excellent water wettability as compared with standard printing paper (see Figure 4.3 for comparison of their contact angle). As such, rice paper was used in study

to help adsorb SWCNT ink and KMnO_4 aqueous solution. SEM images in Figure 4.4a and b show that rice paper is composed of porous cellulosic fibers with diameters around 15–20 μm . The cellulosic fibers have relatively smooth surfaces. A closer look (Figure 4.4b) of their surfaces shows abundant nanoscale pores. Figure 4.4c–f show the SEM images of the two types of paper-based ternary composites which were fabricated. MnO_2 particles that were directly deposited on rice paper (Figure 4.4c) as described by Path A in Figure 4.2 are well dispersed on the cellulosic fiber surfaces with diameters around 20–70 nm. Afterwards, SWCNTs were filtered on top of MnO_2 particles to form the SWCNT– MnO_2 –paper composite. Figure 4.4(d) shows that the SWCNTs filtered on top of MnO_2 particles have aggregated into small bundles of 10–20 nm in diameter. The nanotube bundles cover individual MnO_2 particles, and interconnect them in a large nanotube network. Figure 4.4e shows that a dense layer of SWCNT network covers cellulose fibers after the SWCNTs were filtered on the paper as described by Path B in Figure 4.2. Figure 4.4f shows that individual MnO_2 particles, deposited on the nanotube network, are aggregated into large particles of a few hundred nanometers in diameter, and they are significantly larger than the MnO_2 particles directly deposited on rice paper shown in Figure 4.4c.

SEM images show that the morphologies of the two hybrid ternary composites are different. Their specific surface area was measured through N_2 physisorption. Figure 4.5a shows their N_2 adsorption/desorption isotherms. According to the

BET classification, the isotherms of pristine paper and SWCNT–paper belong to the type II adsorption. The isotherms of the two composites are more like that of the type IV with a drop in their desorption branches at $\sim 0.5 P_0$, which suggests the existence of mesopores. The calculated BET surface area of pristine paper, SWCNT–paper, MnO₂–SWCNT–paper and MnO₂–SWCNT–paper are 6.2, 14.3, 26.7 and 41.6 m²/g, respectively. Comparing the two hybrid ternary composites at similar MnO₂ loading (see the discussion of TGA results), the MnO₂–SWCNT–paper composite has much larger surface area, suggesting the existence of smaller MnO₂ nanoparticles, which is consistent with the SEM results. However, it should be noted that the measured specific surface area are relatively small. It could be related to the conglomeration of nanotubes.³²⁹ In a previous study, it was found that the oxygenated functional groups on SWCNTs may prevent N₂ accessing most their surfaces and the small measured BET surface areas reflect only the outer surface of SWCNT aggregates.³³⁰ The existence of functionalized SWCNT bundles in the hybrid ternary composites may have blocked the access of N₂ into their internal surfaces.

Figure 4.5 (a) Physisorption isotherms of composites. (b) TGA profiles of composites. (c) EDS spectra of MnO₂–SWCNT–paper and MnO₂–SWCNT–paper composites. The inserts show the SEM images where EDS spectra were obtained. (d) XRD patterns of composites. (e) HRTEM images of MnO₂ particles on the MnO₂–SWCNT–paper composite.

4.3.2 Physicochemical properties of nanocomposites

The mass loading of MnO₂ in the composites was measured by TGA. Figure 4.5b shows TGA profiles of pristine paper, SWCNT–paper, MnO₂–SWCNT–paper and MnO₂–SWCNT–paper composites. When the programmed oxidation temperature reaches 600 °C in air, both paper and SWCNT-paper were totally oxidized. In contrast, for the two hybrid ternary composites, most of SWCNTs and paper are consumed when the programmed oxidation temperature reaches 450

°C, and their TGA profiles become flat plateaus. On the other hand, there are two weight-loss stages in TGA curves of pristine and SWCNT-paper samples, while only one stage is observed in SWCNT-MnO₂-paper and MnO₂-SWCNT-paper samples. In the first stage (270 -350 °C) of pristine paper and SWCNT-paper, the weight loss can be attributed to the combustion of hemicellulose and cellulose. While in the second stage (350-500 °C), the lignin starts burning in air. KMnO₄ is a strong oxidizer. After treatment in potassium permanganate solution, lignin would be partially oxidized. This leads to lower oxidation temperature of treated paper. Moreover, SWCNTs can also be partially oxidized. Thus, the MnO₂-SWCNT-paper composite could be burn at even loewer temperature than SWCNT-MnO₂-paper sample. The remaining residues are from deposited MnO₂. The content of MnO₂ is 21.4 and 26.9 wt% for the SWCNT-MnO₂-paper and MnO₂-SWCNT-paper composites, respectively. Under the same KMnO₄ aqueous solution concentration, deposition temperature and time, more MnO₂ can be deposited on SWCNTs than on paper. The weights of SWCNTs and MnO₂ deposited on paper in different composites were summarized in Table 4.1.

The chemical properties of the nanocomposites were further characterized by EDS and XRD. The spectra in Figure 4.5c indicate the presence of manganese (Mn), carbon(C), oxygen (O), potassium (K) and platinum (Pt). Pt is likely from the sputter coating during SEM sample preparation. The MnO₂-SWCNT-paper nanocomposite has higher K content than SWCNT-MnO₂-paper. It was

proposed that hydrated K ions can be stuffed into the tunnel cavity of MnO₂ crystal structures.^{331,332} The formation of larger MnO₂ particles on the MnO₂–SWCNT–paper nanocomposite may have incorporated more K ions. Further, the carbon(C) peaks are much weaker on the MnO₂–SWCNT–paper, due to the fact that MnO₂ particles are deposited on top of SWCNT layers. XRD diffraction patterns of the two nanocomposites are shown in Figure 4.5d. The MnO₂–SWCNT–paper shows diffraction peaks at 12.5, 16.8, 22.3, 28.6, 37.4, 46.7, 49.6, 56.1, 59.9, 65.1, 69.0 and 78.4°, which are indexed to the (110), (200), (220), (310), (211), (301), (411), (600), (521), (002), (541) and (402) surfaces, respectively. Its structure matches with a tunnel structure of α -MnO₂ (JCPDS 44-0141) with tetragonal phase [space group: *I4/m* (87)].^{333,334} In comparison, the XRD pattern of the SWCNT–MnO₂–paper nanocomposite, though contains three characteristic peaks at around 37° and 66.3° marked by arrows in Figure 4.5d which indicating the existence of MnO₂, shows much weaker and broader, suggesting that the amorphous nature of the MnO₂.²⁷⁵ The crystal structure of MnO₂ particles on the MnO₂–SWCNT–paper nanocomposite was confirmed by HR-TEM. Figure 4.5e shows the microstructure of MnO₂ particles. Their polycrystalline subunits have two interplanar spacings between crystalline planes at 0.318 and 0.507 nm, which corresponds to the spacing of (310) and (200) planes of α -MnO₂, respectively.

4.3.3 Performances of assembled supercapacitors

Figure 4.6 Electrochemical characteristics of two-electrode supercapacitors fabricated using MnO₂-SWCNT-paper and SWCNT-MnO₂-paper nanocomposites. (a) CV curves at the scan rate of 20 mV/s. (b) Galvanostatic charge/discharge curves at the current density of 1 A/g. (c) Nyquist plots of supercapacitors from 0.01 to 100 000 Hz, and the insert shows the schematic illustration of the EC. (d) Capacitance retention as a function of cycle number. Supercapacitors were charged/discharged at a constant current density of 2 A/g from 0 to 1 V for 3000 cycles.

Figure 4.7 Cyclic voltammetry curves of two-electrode supercapacitors fabricated using SWCNT-paper, MnO₂-SWCNT-paper and SWCNT-MnO₂-paper composites at the scan rate of 10, 50 and 100 mV/s.

The nanocomposite electrodes were assembled as two-electrode symmetric supercapacitors, as illustrated on the insert of Figure 4.6c. Figure 4.6a shows their CV curves at the scan rate of 20 mV/s. The CV curve of the SWCNT-paper supercapacitor without MnO₂ is close to rectangle, indicating its double-layer capacitor behavior. On the other hand, the CV curves of two MnO₂ composite supercapacitors deviate from the rectangular shape. Because the enclosed areas of CV curves are proportional to the capacitance of supercapacitors, Figure 4.6a

shows that the pseudo-capacitance contribution resulting from MnO₂ is significant. The observed CV curves are similar to previous studies.^{292,335-337} In addition, the SWCNT–MnO₂–paper supercapacitor has much higher capacitance than the MnO₂–SWCNT–paper supercapacitor. Under different scan rates at 10, 50 and 100 mV/s (see Figure 4.7); the same trend between SWCNT–MnO₂–paper and MnO₂–SWCNT–paper supercapacitors is observed. The supercapacitors were further studied in galvanostatic charge/discharge tests at the current density of 1A/g (over active materials, *i.e.* SWCNTs and MnO₂ in assembled supercapacitors) in the applied potential difference window of 0–1.0 V. Their gravimetric specific capacitance was calculated according to the following equation:

$$C_s = \frac{2I}{-m(\frac{dV}{dt})} \approx \frac{2I}{-m(\frac{\Delta V}{\Delta t})} \quad (4.1)$$

where C_s (F/g) is the specific capacitance of active electrode materials, m (g) is the weight of active materials in one electrode, I (A) is the discharging current, $\Delta V/\Delta t$ (V/s) is the average slope of a discharge curve in the applied potential (1.0 V). The specific capacitance of SWCNT–MnO₂–paper is 260.2 F/g, which is 42 % higher than that of MnO₂–SWCNT–paper at 183.3 F/g. Both of them are much higher than the SWCNT–paper at 60.4 F/g. I further compared charge/discharge curves of the SWCNT–MnO₂–paper supercapacitor under different current densities from 0.5 to 5 A/g. As shown in Figure 4.8, the time duration increases

with the decreasing current. The capacitance drops when the charge/discharge current increases from 0.5 to 1 A/g, and shows less changes when the charge/discharge current further increases from 1 to 5 A/g. This indicates that the SWCNT–MnO₂–paper supercapacitor could perform steadily in a wide range of currents. Figure 4.6c shows the Nyquist plots of supercapacitors in the frequency region from 100000 to 0.1 Hz. The equivalent series resistance (R_s) of supercapacitors can be determined at the first intersection of the Z_{re} axis at the high-frequency region on the Nyquist plots. The R_s is attributed to the resistance of electrolyte, the internal resistance of electrode, and the interfacial resistance between electrode and current collector.^{338,339} R_s of the SWCNT–MnO₂–paper EC is 3.27 Ω , which is lower than that of the MnO₂–SWCNT–paper supercapacitor at 4.02 Ω . The slope of 45° portion in the plot is called the Warburg impedance, representing the frequency dependence ion diffusion behavior between electrode interface and electrolyte. And both MnO₂ incorporated composites have larger Warburg resistance than that of SWCNT–paper which is close to an EDLC. Increased obstruction and higher length variations in ion diffusion among large MnO₂ aggregates and SWCNTs could explain the longer Warburg region on MnO₂–SWCNT–paper electrode.³³⁹ I further compared energy density (E) and power density (P) of the assembled supercapacitors:

$$E = \frac{1}{2 \times 3.6} C_{cell} V^2 = \frac{1}{8 \times 3.6} C_s V^2 \quad (4.2)$$

$$P = \frac{V_{cut-off}^2}{4R_s m} \quad (4.3)$$

E is specific energy density in Wh/kg, C_{cell} is the capacitance of assemble supercapacitors in F/g, C_s is the specific capacitance of electrode active materials in F/g, V is the operating voltage window in volts. P is the specific power density in kW/kg, $V_{cut-off}$ is the operating voltage window (measured in volts and obtained from the discharge curve excluding the IR drop), R_s is the internal resistance of the device estimated from their EIS results while m is the weight of active materials in one electrode in unit of g. As shown in Table 4.1, the SWCNT–MnO₂–paper supercapacitor has higher power and energy density than that of the MnO₂– SWCNT–paper supercapacitor. To evaluate the stability of composite electrodes, the capacitance retention tests were carried out, and results are shown in Figure 4.6d. The SWCNT–paper supercapacitor retains more than 95 % of its original capacitance after 3000 charge/discharge cycles, which are consistent with previous studies.³³⁰ The two MnO₂ composite electrodes suffer a fast drop in the first few hundred cycles but are subsequently stabilized. The MnO₂–SWCNT–paper EC retains 85% of its original capacitance while the SWCNT–MnO₂–paper supercapacitor retains 88%. Overall, based on various electrochemical tests, I found that the hybrid ternary nanocomposites comprised of paper, MnO₂, and SWCNTs can significantly increase the capacitance and energy density of the assembled supercapacitors (3-4 times), as compared to SWCNT paper supercapacitors. The two different synthesis approaches produce

nanocomposites with different performances, and the SWCNT–MnO₂–paper nanocomposite has better electrochemical characteristics than the MnO₂–SWCNT–paper nanocomposite.

Figure 4.8 (a) Galvanostatic charge-discharge curves of the two-electrode supercapacitors fabricated using SWCNT–MnO₂–paper composites at the current density of 0.5, 1, 2 and 5 A/g. (b) The gravimetric specific capacitance of the two-electrode EC at different current density.

Table 4.1 Summary of electrochemical characteristics of supercapacitors fabricated using paper based nanocomposites.

Nanocomposites	SWCNT weight (mg/cm ² paper)	MnO ₂ weight (mg/cm ² paper)	Specific capacitance (C _s , F/g)	Energy density (E, Wh/kg)	Power density (P, kW/kg)
SWCNT–paper	0.52±0.08	-	60.4	2.12	163.0
MnO ₂ –SWCNT–paper	0.50±0.08	1.12±0.06	183.3	6.3	38.4
SWCNT–MnO ₂ –paper	0.51±0.06	0.77±0.09	260.2	9.0	59.7

4.3.4 Growth mechanisms of nanocomposites

Figure 4.9 Schematic illustration of the reaction mechanism of paper-based hybrid ternary nanocomposites: (a–c) SWCNT– MnO_2 –paper, and (d–f) MnO_2 –SWCNT–paper. (a) The proposed reactions between KMnO_4 and surface functional groups on paper. (b) The MnO_2 particles deposited on paper. (c) Filtered SWCNTs covering MnO_2 particles. (d) SWCNTs covering paper. (e) The proposed reaction mechanism of MnO_2 formation on SWCNT surfaces. (f) The MnO_2 particles deposited on SWCNTs.

I propose that the different electrochemical behaviors of two paper-based hybrid ternary nanocomposites can be attributed to their structural differences resulting from their synthesis methods. As illustrated in Figure 4.9, MnO_2 was directly deposited on the rice paper in the SWCNT– MnO_2 –paper nanocomposite. Due to the good water wettability of the rice paper, KMnO_4 aqueous solution can easily reach the reaction sites on the paper. The chemical functional groups (primary

and secondary hydroxyl groups) on cellulose fibers react directly with adsorbed permanganate ions. Because cellulose fibers are not electrically conductive, electrons generated are taken up by permanganate ions locally, resulting in the deposition of MnO_2 nanoparticles, as illustrated in Figure 4.9a. MnO_2 nanoparticles deposited on cellulose fibers block the access of MnO_4^- ions to the MnO_2 covered fiber surface. The reaction between permanganate ions and cellulose fiber would stop at that specific reaction site, which prevents the formation of large MnO_2 particles. As illustrated in Figure 4.9b, MnO_2 particles can be deposited on most surfaces of cellulosic fibers, and their size is relatively uniform. This is confirmed by the SEM image shown in Figure 4.4c. Figure 4.9c illustrates that SWCNTs filtered on MnO_2 -paper form a network connecting individual MnO_2 particles, which is verified by the SEM image shown in Figure 4.4d. The poor electrical conductivity and low stability are major problems hindering the application of MnO_2 as pseudocapacitive electrode materials.³³³ In the SWCNT- MnO_2 -paper, SWCNTs act as an efficient conductive network connecting individual MnO_2 nanoparticles, which improve the overall conductivity of the nanocomposite. Moreover, the gaps among MnO_2 nanoparticles and SWCNTs allow easy access of electrolyte ions to MnO_2 . Overall, the structure of SWCNT- MnO_2 -paper is favorable for its application as capacitor electrodes. In contrast, when SWCNTs were first filtered on paper in the MnO_2 -SWCNT-paper, a dense layer of SWCNTs covered reactive sites of

cellulous fibers (Figure 4.9d), supported by the SEM in Figure 4.4e. When the SWCNT–paper is exposed to KMnO_4 aqueous solution, MnO_4^- ions can react directly with cellulose molecules as well as the carboxylic groups on SWCNTs,^{330,340} resulting in MnO_2 deposition.^{295,333,340} As illustrated in Figure 4.9e, electrons generated from the oxidation of SWCNTs can easily travel along the conductive surface of SWCNTs, as proposed in previous study,³⁴⁰ which can be picked up by MnO_4^- ions at other locations.³⁴⁰ Thus, the deposition of MnO_2 particles is not restricted to the localized reaction sites as compared to that on cellulous fibers, leading to the formation of more aggregated and crystalline MnO_2 particles on SWCNTs (see Figure 4.9f).³⁴⁰ This is supported by their SEM image (Figure 4.4f), XRD (Figure 4.5d), and TEM image (Figure 4.5e). Studies have shown that only a thin surface layer of manganese oxide is involved in the pseudocapacitive redox process^{341,342} and high surface area plays a significant role in high specific capacitance of the MnO_2 based capacitors.³⁴² The larger and more crystalline MnO_2 particles have much smaller surface area, poorer electrical and ionic conductivities, resulting in lower specific capacitance and energy density shown in Figure 4.6.

4.3.5 Further optimization of compositions synthesis temperature

Figure 4.10 Thermogravimetric analysis profiles of the SWCNT-MnO₂-paper composites synthesized at different MnO₂ deposition temperature from 25 to 100 °C. The insert shows the increase of MnO₂ loading with the increase of deposition temperature.

Figure 4.11 SEM images of MnO₂ particles directly deposited on rice paper by reacting with 0.1 M KMnO₄ solution for 10 min at different temperature: (a) 25, (b) 60, (c) 80, and (d) 100 °C.

Since the nanocomposites produced from the Path A have better electrochemical performances, their synthesis conditions were further optimized. The deposition of MnO₂ on paper depends on its deposition temperature. SWCNT–MnO₂–paper nanocomposites synthesized at 25, 60, 80 and 100 °C were compared. As shown in Figure 4.10, the loading of MnO₂ was determined by TGA. With the increase reaction temperature from 25 to 100 °C, MnO₂ nanoparticles deposited on paper increases from 12 to 35 wt%. When reaction temperature was further increased, the entire paper would be oxidized. Thus, the composite would lose its flexibility. Moreover, the size and morphology of deposited MnO₂ particles also show significant changes. As shown in Figure 4.11, with the increase in the deposition temperature, more cellulosic fiber surface was covered by MnO₂, and MnO₂ particles also grow from around 20 nm at 25 °C into large aggregates of more than 200 nm at 100 °C. The morphology and phase purity of MnO₂ particles were further characterized by TEM. As shown in Figure 4.12. Porous amorphous MnO₂ particles were deposited on rice paper at the four reaction temperatures. Similar to SEM results, with the increase of reaction temperature, MnO₂ particles grow into aggregates. Those porous amorphous MnO₂ particles are favorable for electrochemical capacitor applications.¹³⁶

Figure 4.12 TEM images of MnO₂ directly deposited on surface of rice paper fiber at different temperature: 25, 60, 80, and 100 °C.

Figure 4.13 Electrochemical characteristics of two-electrode supercapacitors fabricated using SWCNT–MnO₂–paper nanocomposites synthesized at different temperatures. (a) CV curves at the scan rate of 20 mV/s. (b) Galvanostatic charge/discharge curves at the current density of 1 A/g over active materials in electrodes.

By coating the same amount of SWCNTs on top of deposited MnO₂, the SWCNT–MnO₂–paper nanocomposites were fabricated into symmetric two-electrode supercapacitors. As shown in Figure 4.13a, the enclosed areas of CV curves increase with the increase of deposition temperature from 25 to 80 °C, indicating more pseudo-capacitance contributions resulting from MnO₂ with the increase of their loading in the nanocomposites. However, when the deposition temperature further increases to 100 °C, the enclosed area becomes smaller. A similar trend can also be observed on their galvanostatic charge/discharge tests shown in Figure 4.13b. The electrochemical characteristics of supercapacitors were summarized in Table 4.2. At a low deposition temperature, MnO₂ deposited on cellulose fiber surfaces are well dispersed nanoparticles, which are interconnected by SWCNTs. The performance of the SWCNT–MnO₂–paper supercapacitors is comparable with other studies using MnO₂ incorporated SWCNT electrode supercapacitors.^{43,295,321} With the increase of deposition temperature, more MnO₂ particles are deposited, leading to higher capacitance and energy density. It was also reported by previous studies showing that relatively higher ratio of MnO₂ in MnO₂–SWCNT composite electrodes could achieve higher specific capacitance thanks to the much higher capacitance contributed from pseudocapacitance of MnO₂ than pure SWCNTs for electrodes.^{295,338} However, there is an upper limit for ratio of MnO₂ in SWCNT-based composites. When reaction temperature reached 100 °C, the fabricated

composite showed declining specific capacitance show in Table 4.2. In aqueous system, the MnO₂ based electrodes undergo intercalation and deintercalation of protons and or alkali ions such as Na⁺ and K⁺ into MnO₂ surface as well as redox reactions of Mn⁴⁺/Mn³⁺ couple.³⁴³ The growth of large aggregates of MnO₂ nanoparticles at high deposition temperature leads to lower utilization efficiency, since diffusion controlled ion intercalation and deintercalation and redox reactions tend to take place on surface under high speed CV or high current charge/discharge, and the inner mass of MnO₂ could not be fully utilized, which was also discussed in section 4.3.4. On the other hand, larger charge-transfer resistances within and among large MnO₂ particles, would result in lower power density, which may explain the fading specific power density as temperature grew. The advantage of higher specific capacitance of MnO₂ over SWCNTs and the disadvantage of lower utilization efficiency and poorer electronic conductivity on thicker and larger MnO₂ particles would reach a balance. Based on results shown in Table 4.2, the deposition temperature around 80 °C is the optimum condition for synthesizing the SWCNT–MnO₂–paper nanocomposite for supercapacitor applications. Seen from SEM images in Figure 4.11, the MnO₂ nanoparticles deposited at 80 °C were uniform and higher density compared with prepared from 25 and 60 °C, but did not aggregate as severely as those on 100 °C prepared composite. The morphology advantage of 80 °C deposited MnO₂ may contribute to reach the balance near this temperature.

Table 4.2 Electrochemical characteristics of supercapacitors fabricated using SWCNT–MnO₂–paper nanocomposites synthesized at different temperatures.

Preparation temperature (°C)	SWCNT weight (mg/cm ² paper)	MnO ₂ weight (mg/cm ² paper)	Specific capacitance (C _s , F/g)	Energy density (E, Wh/kg)	Power density (P, kW/kg)
25	0.52 ± 0.05	0.38 ± 0.08	211.4	7.3	118.1
60	0.55 ± 0.07	0.56 ± 0.06	229.4	7.9	82.9
80	0.51 ± 0.06	0.77 ± 0.09	260.2	9.0	59.7
100	0.48 ± 0.11	1.42 ± 0.25	240.7	8.4	30.5

4.3.6 Mechanical properties of flexible devices

Figure 4.14 (a) The mechanical tensile stress of nanocomposites bending and (b) folding tests of two-electrode supercapacitors fabricated using SWCNT–MnO₂–paper nanocomposites: CV curves at the scan rate of 20 mV/s measured at different bending and folding conditions.

Paper based nanocomposites are suitable for flexible energy storage devices. The mechanical tensile stress of MnO₂–paper, MnO₂–SWCNT–paper, and SWCNT–MnO₂–paper nanocomposites was measured. As shown in Figure 4.14a, the two hybrid ternary nanocomposites have much higher mechanical tensile stress than

the MnO₂-paper at (7.29 MPa). This can be contributed to the existence of SWCNTs. Moreover, the SWCNT-MnO₂-paper nanocomposite (17.32 MPa) has higher tensile stress than MnO₂-SWCNT-paper (12.64 MPa), which may be due to the fact that SWCNTs in the SWCNT-MnO₂-paper nanocomposite are not exposed to oxidation by KMnO₄. To show the high physical stability of the deposited MnO₂ on paper by the direct reaction deposition method in composite SWCNT-MnO₂-paper, a dried 80 °C fabricated SWCNT-MnO₂-paper was examined by bending/folding and being blown by a rubber suction bulb. No MnO₂ partocles fell off from the paper upon several times of bending and folding. Not only did the MnO₂ on paper keep stable in dry, it was also stable in water and even under violent shake. To demonstrate the flexibility of the SWCNT-MnO₂-paper nanocomposite, bending/folding tests were carried out on supercapacitors fabricated with the SWCNT-MnO₂-paper nanocomposite synthesized at 80 °C. As illustrated in Figure 4.15, bending at 90° and folding of 180° were exerted on the assembled rectangle shape Supercapacitors. Figure 4.14b shows their CV curves under different conditions. There are minor changes in their CV curves. The capacitance calculated decreases less than 5% when the supercapacitor is bent at 90°, and has about 10% drop when the supercapacitor is folded at 180°. More importantly, Figure 4.14b shows that the supercapacitor has negligible changes in its performance after bending 100 times. These results suggest that the SWCNT-MnO₂-paper nanocomposite has excellent mechanical flexibility.

Figure 4.15 Photographs of the assembled rectangular shape supercapacitors fabricated using SWCNT–MnO₂–paper composites under different bending test conditions. (a) flat, (b) bending at 90°, and folding of 180°.

4.4 Conclusion

The hydroxyl chemistry of cellulose fibers was explored to synthesize hybrid ternary nanocomposites comprised of rice paper, MnO₂, and SWCNTs. I compared two approaches: one mainly uses paper as a supporting substrate; the other utilizes paper as an active material. MnO₄⁻ ions can react with SWCNTs to form large MnO₂ aggregates in the first case. In contrast, MnO₄⁻ ions directly react with functional groups on cellulose fibers, resulting in uniform deposition of MnO₂ nanoparticles on cellulose fibers, which enhance the specific capacitance of the nanocomposite. Moreover, SWCNTs coated on top of MnO₂ form a highly conductive network connecting individual MnO₂ particles, leading to fast charge transfer rate. Increasing MnO₂ deposition temperature increases MnO₂ loading; however, it also leads to the formation of large MnO₂ particles with high charge and diffusion resistances. The optimum deposition temperature was found at around 80 °C. Using the hybrid ternary nanocomposite as electrodes,

the two-electrode supercapacitors achieved the specific capacitance of 260.2 F/g at the 1 A/g charge-discharge current density in 0.5 M aqueous Na₂SO₄ solution. They also demonstrated high performance in maximum specific energy (9.0 Wh/kg), specific power (59.7 kW/kg), and cycle stability (12% drop after 3000 cycles). Moreover, the SWCNT–MnO₂–paper nanocomposite has a tensile stress of 17.32 MPa. The assembled supercapacitors show excellent mechanical flexibility and its capacitance has negligible changes after bending more than 100 times. The synthesis approach is easily scalable for large-scale industrial production which increases the potential of applying this sustainable new hybrid ternary nanocomposite in flexible energy storage devices. Moreover, those findings suggest that the rich chemistry of cellulose fibers can be further explored for innovative energy applications.

Chapter V Space-confined Assembly of Hybrid Carbon Fibers for Capacitive Energy Storage: Realizing Built-to-order Concept in Micro-supercapacitors

5.1 Background Introduction

The rapid development of portable and wearable electronics, implantable biosensors, remote and mobile environmental sensors, microelectromechanical systems (MEMS) and nano-robotics creates great demands for micro-scale energy storage devices.²²⁴ Micro-batteries are the current device of choice, however, they are suffering from low power densities, sluggish charge/discharge processes and limited cycle life.^{45,190,224} Micro-supercapacitors (micro-SCs) are promising alternatives as they can provide higher power densities, faster charge/discharge rates, and much longer lifetimes.²²⁶⁻²²⁸ In particular, fiber-based micro-SCs using 1-dimensional (1D) fibers as electrodes have emerged as a strong candidate because of their several unique advantages.¹⁹⁰ First, using 1D fibers with diameters ranging from micrometers to millimeters, micro-SCs can be created small in size and light in weight. Second, their wire-shaped structures are highly flexible with excellent wearability. Third, fiber-based micro-SCs can be further woven or knitted into various desired shapes and locations, offering great design versatility. Forth, they can be easily integrated with other fiber-based energy harvesting devices or sensors to form integrated multifunctional

systems.^{30,232,344-347}

Various fibers have been fabricated to serve as electrodes, current collectors or both for fiber based micro-SCs, which include carbon fibers,^{189,235,236} graphene fibers,^{30,111,240-242,348} carbon nanotube (CNT) fibers,^{172,239,349,350} hybrid/composite fibers containing different types of carbon materials and pseudocapacitive materials, such as metal oxides and conductive polymers.^{172,188,189,235,349} Among them, the carbon-based fiber electrodes have been most extensively researched in recent two years because of their superiority in low densities, excellent conductivity and good mechanical properties. Those carbon fibers have been mainly synthesized through several common approaches, including wet spinning from neat condensed CNT or graphene oxide (GO) dispersions,^{237,351-355} dry spinning from CNT arrays or aerogels,³⁵⁶⁻³⁵⁹ direct scrolling of CNT or GO films,³⁶⁰⁻³⁶² tube-confined hydrothermal synthesis,^{30,243,266,363} and conventional carbon fibers as cores for electroactive material deposition.^{189,235,236,364} However, the rigorous conditions such as chlorosulfonic acid²³⁷ and fuming sulfuric acid³⁶⁵ used for wet-spinning and high cost from producing CNT arrays as precursors for dry-spinning severely limit the CNT based carbon fibers from scalability and widely practical applications.³⁶⁶ Meanwhile, the conventional carbon fiber suffers from low surface area and poor gravimetric performance. In contrast, graphene based carbon fibers are favored in achieving higher surface area and easy preparation of graphene fiber fabrication precursors. The most studied

method for graphene fiber fabrication is wet-spinning from GO liquid crystal phase.³⁶⁶ An extra step is needed to reduce the spun GO fibers either by chemical methods using toxic or caustic agents, or by high-temperature thermal methods. In addition, the wet-spun GO fibers often exhibit relatively low tensile strength resulted from low alignment of GO sheets along the fiber axial direction.³⁶⁷ More importantly, it is difficult to control the diameters of the spun fibers in the coagulation media. Recent developed one-step tube-confined hydrothermal technique has successfully incorporated CNTs into the graphene fibers, which were achieved much improved electrochemical performance due to synergistic effects of the hybrid structures.³⁰ Nevertheless, very little effort has been dedicated to tune the physical dimensions of fibers (diameter and length) in previous research.

The physical dimension of fibers (diameter and length) dramatically affects the energy storage performances of used in micro-SCs.^{224,226} However, no systematic studies have been carried out on this aspect. More importantly, the power requirements of micro-scale devices are very diverse,^{45,225} for example, pacemakers only need a power of 1 microwatt,³⁶⁸ radio frequency identification tags require a power of 1 to 100 microwatts,³⁶⁹ implantable neural stimulator chips need a power of hundreds of microwatts,^{370,371} sensors for blood glucose monitoring³⁷² and cortical implant systems³⁷³ require a power of several miniwatts. Thus, it is critical to be able to tailor the structure of fiber electrodes

to create micro-SCs with diverse energy storage capacities.

In this study, I demonstrate a novel space-confined assembly approach to fabricate hybrid carbon fibers containing nitrogen doped reduced graphene oxide and multiple walled carbon nanotube method for scaled synthesis and diameter control of nitrogen doped rGO/MWCNT porous fibers by one-step-one-pot confined hydrothermal self-assembly and simultaneous reduction. The diameters of the hybrid carbon fibers cross a wide range from 30 to 240 μm , while still keeping good electrical conductivity, high ion-accessible surface area and mechanical strength. Yarn micro-SCs were fabricated with these different-diameter and different-length carbon fibers, which could successfully cover a broad range of energy and power and satisfy a variety of requirements from volumetric to length performance, without compromising excellent long term cyclic stability and flexibility.

5.2 Experimental Section

5.2.1 Synthesis of GO

GO was prepared from expandable graphite (DL50, Qingdao Henglid Graphite Co., Ltd.) following previously studies.^{240,374,375} Briefly, expandable graphite were thermally expanded under 1050 °C for 15 s. The expanded graphite was used as the precursor for GO synthesis. 1 g expanded graphite was added into 200 mL sulfuric acid (Merck, 98 %) in a three-neck flask under stirring. Then, 5

g KMnO_4 was slowly added into the solution and kept stirring at 30 °C for 24 h. Next, the flask with the mixture was put into an ice bath followed by slowly adding of 200 mL deionized water and 50 mL H_2O_2 into the mixture, changing the colour of the mixture to light brown after 30 min stirring. The brown dispersion was washed and centrifuged with HCl solution (water : 37 % HCl =9:1 in volume) for three times, and further washed and centrifuged with deionized water until the pH of the supernatant above 5. The concentration of the condensed GO were adjusted to about 10 mg mL^{-1} .

5.2.2 Scaled synthesis of carbon hybrid fibers in different diameters

MWCNTs (diameter of 10 nm, FloTube 9000, CNano Technology) were refluxed in 65 % HNO_3 for 4 h to increase surface hydrophilicity by introducing oxygen-containing functional groups on CNT walls, and further washed and adjusted to 2.5 mg mL^{-1} aqueous solution by sonication. A homogenous GO/CNT dispersion with GO/CNT mass ratio of 4 : 1 was prepared by mixing same volume of acid treated MWCNT solution and GO solution by stirring and then added with ethylenediamine ($\sim 2 \mu\text{g mL}^{-1}$ in the final solution). The dispersion was injected into my home-designed shape confined multiple fiber reactors (illustrated in Figure 1). The reactors were heated at 180 °C for 12 h. After cooling down, the wet fibers were poured out from the reactors into a water reservoir. Final hybrid fibers were obtained after drying the wet fibers in air for 12 h.

5.2.3 Characterization of the different diameter hybrid fibers

The structure and morphology of the carbon fibers were characterized by scanning electron microscope (FESEM, JEOL, JSM6701, 5kV). The conductivity of the fibers were measured by a Keithlink four-point probe station (probe spacing 1.6 mm, probe pin diameter 40.6 μm). The chemical composition of the fibers was analyzed by energy-dispersive X-ray spectroscopy (EDX) equipped with the FESEM (JEOL, JSM6701) and X-ray photoelectron spectroscopy (XPS) using a PHI Quantera scanning X-ray microprobe. Nitrogen adsorption-desorption isotherms were measured by QuantaChrome Autosorb-6B static volumetric instrument at 77 K and the Brunauer–Emmett–Teller method was used for the calculation of specific surface area. Tensile stress of the different diameter fibers was measured by Instron 5543 tensile testing system. The electrical conductivity of fibers was tested on a Kethley 4200 SCS multimeter.

5.2.4 Fabrication and characterization of all-solid-state two-ply micro-SCs

The PVA/H₃PO₄ polymer gel electrolyte was prepared by adding 6 g poly(vinyl alcohol) powder (PVA, molecular weight: 89,000 – 98,000, Sigma-Aldrich) and 6 g H₃PO₄ (Merck) into 60 mL deionized water under stirring. Then, the mixture was heated to 90 °C under stirring until solution became clear. Two hybrid fibers with the same diameter and length were immersed into the gel electrolyte with one reserved end (2 – 3 mm) of each fiber still above the solution for several

minutes. After drying for 1h, the fibers were stuck together parallelly with predetermined overlap length. The reserved end of each fiber was connected with a metal wire by silver paste. Multiple electrolyte coated fibers were also put in parallel on a PET film to make a micro-SC array either in serial or in parallel. Supercapacitor performance was investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge methods (CHI 660E).

5.2.5 Electrochemical performance calculation of the two-ply all-solid-state micro-SCs

The capacitance of the two-electrode symmetric micro-SC was calculated from both the charge/discharge curves at different current densities:

$$C_{T,CD} = It_{Disch} / \Delta V \quad (5.1)$$

where I (A) is the discharge current, t_{Disch} (s) is the discharge time and ΔV (V) stands for the potential window, and CV curves at different scan rates:

$$C_{T,CV} = Q / 2\Delta V = (\int idV) / 2k\Delta V \quad (5.2)$$

where Q (C) is the voltammetric charge integrated from anodic and cathodic sweeps, ΔV (V) is the scanned voltage window and i (A) is the current density and k (V/s) is the scan rate.

The volumetric and length capacitance, C_V (F cm⁻³) and C_L (F cm⁻¹), of micro-

SC were calculated by normalizing the total capacitance from either CV or charge/discharge, C_T , based on the volume and length of the device, respectively:

$$C_V = C_T / V_T, \text{ and } C_L = C_T / L \quad (5.3)$$

Where $V_T(\text{cm}^3)$ and $L(\text{cm})$ are the total volume and effective length of the micro-SC device.

The specific capacitance of the fiber electrode in the micro-SC either based on volume or on effective length of single electrode was obtained as following:

$$C_{s,V} = 2C_T / V_s, \text{ and } C_{s,L} = 2C_T / L \quad (5.4)$$

where $V_s(\text{cm}^3)$ is the volume of single electrode and $L(\text{cm})$ is the effective length of the electrode.

The volumetric and length energy density, $E_V(\text{Wh cm}^{-3})$ and $E_L(\text{Wh cm}^{-1})$ of the fiber micro-SCs were calculated from the capacitance results of galvanostatic charge/discharge:

$$E_V = \frac{1}{2} C_V \Delta E^2 / (3600 \text{ s/h}) \quad (5.5)$$

$$\text{and } E_L = \frac{1}{2} C_L \Delta E^2 / (3600 \text{ s/h}) \quad (5.6)$$

where the 3600 s/h is the time factor to change the unit of time from second to hour.

Corresponding, the volumetric and length power density, P_V (W cm^{-3}) and P_L (W cm^{-1}) of the fiber micro-SCs were also calculated from results of galvanostatic charge/discharge and directly using the results of energy density:

$$P_V = E_V \times (3600 \text{ s} / h) / t_{\text{Disch}} \quad (5.7)$$

$$\text{and } P_L = E_L \times (3600 \text{ s} / h) / t_{\text{Disch}} \quad (5.8)$$

5.3 Results and Discussion

A unique approach to control the structure of nanomaterials is the space-confined synthesis, where chemical synthesis is taken place inside the void spaces of host materials. There is a wide range of inorganic, organic or organometallic materials with 1-D tunnel, 2-D layer and 3-D framework structures.³⁷⁶ Their cavity dimensions vary widely in size, from barely being able to accommodate the smallest ionic or molecular guests all the way up to millimeters.³⁷⁶ This approach has been used to confine the structure of nanomaterials during chemical reaction or self-assembly, resulting in many novel composite materials.³⁷⁷⁻³⁸³ In recent years, hydrothermal reaction has also been used to create various carbon composite structures.^{64,384-392} Individual glass tubes and fused silica capillary columns were used as hydrothermal reactors to confine the formation of carbonaceous fibers.³⁹³⁻³⁹⁵ However, there are two key limitations by using individual glass tubes or capillary columns: first, only one fiber can be synthesized in one reactor, limiting the scalability of producing large amount of

carbonaceous fibers with similar properties; and second, the diameter of carbonaceous fibers cannot be easily changed once the reactor is fabricated, limiting the flexibility of producing fibers with different diameters. Here we designed a new type of hydrothermal reactors with space confinement fillers to address both limitations. As illustrated in Figure 5.1a, the fillers with multiple cylindrical tunnels were fabricated using machine processable material, *i.e.* Teflon. Thus, it is convenient to change their specifications to create tunnels of different diameters and areal density. The multiple cylindrical tunnels have either uniform diameter or different diameters (see Figure 5.1c). The space confinement fillers were placed inside the Teflon liner of common hydrothermal autoclaves. Aqueous dispersion of carbonaceous precursors was then added into the autoclave to carry out hydrothermal reactions.

Figure 5. 1 (a) Schematic illustrations of hydrothermal reactors with space

confinement fillers containing cylindrical tunnels of the same diameter and (c) different diameters. (b) Photographs of wet rGO/MWCNT hybrid fibers with uniform diameters and (c) multiple diameters obtained in one hydrothermal synthesis batch. (e) Photograph of dried rGO/MWCNT hybrid fibers of different diameters. (f) Schematic illustration of an all-solid-state two-fiber symmetric SC in PVA/H₃PO₄ gel electrolyte supported on PET film (upper) and a photograph of five fiber-based micro-SCs in different diameters (bottom).

GO sheets and surface functionalized MWCNTs were selected as carbonaceous precursors for assembling hybrid carbon fibers. Graphene sheets are widely regarded as a promising electrode material for capacitive energy storage because of their ultrahigh surface area, good conductivity, as well as high mechanical and chemical stability. However, strong interactions among graphene sheets cause them to stack together, which decreases electrolyte ion accessibility for capacitive energy storage. GO sheets can be prepared from expanded graphite as described in the Experimental session. They are well dispersed in aqueous solution because of their abundant surface functional groups. Through hydrothermal reactions, GO sheets can be partially reduced and aggregated into rGO composites with large ion accessible surface area. The average lateral size of GO sheets used in this work is around 40 μm determined by atomic force microscopy (AFM), shown in Figure 5.2. Due to their relatively large size, holey defects with diameters of 1 to 3 μm were observed in Figure 5.2, which are

beneficial for ion permeability.^{396,397} CNTs were added to decrease the stacking of graphene sheets.^{394,398,399} Here, surface functionalized MWCNTs with diameter of ~ 10 nm and length of ~ 10 μm were used because their relatively low cost. In our view, they are more promising as electrode materials compared to single walled carbon nanotubes (SWCNTs) for practical micro-SC applications. GO and MWCNT was mixed together at the mass ratio of 4:1 based on our previous optimization of GO and SWCNT mixtures.³⁹⁴ In addition, a small amount of ethylenediamine (EDA) was also added into aqueous carbon dispersions because EDA can serve as both a reductant and nitrogen dopant for GO during hydrothermal reactions.³⁹⁴ The aqueous solution containing GO, MWCNT and EDA was loaded into hydrothermal autoclaves with space confinement fillers. Depending on the filler used, many rGO/MWCNT hybrid fibers with uniform diameter or different diameters can be synthesized in one synthesis batch as shown in Figure 5.1b and 5.1d.

Figure 5. 2 AFM image of the large GO single layer sheet. Height profiles marked by different colors on the AFM image shown on the right. Scale bar: 10 μm .

In this work, we focused on five different rGO/MWCNT hybrid fibers in diverse diameters synthesized from fillers with the channel diameter of 0.3, 0.5, 1, 1.5 and 2 mm. They were denoted as fiber-1, fiber-2, fiber-3, fiber-4 and fiber-5, respectively (see Figure 5.1e and Table 5.1). An rGO fiber was also prepared using the channel with the diameter of 0.5 mm as a reference. Due to the self-assembly of carbonaceous precursors during hydrothermal synthesis, the diameter of as-synthesized wet fibers was smaller than the channel diameter of fillers. After drying in air, the diameter of fibers further shrank. The average diameter of the dry rGO fiber is $42 \pm 4 \mu\text{m}$, which is smaller than that of the fiber-2 ($48 \pm 5 \mu\text{m}$) synthesized using the same 0.5 mm channels. The morphology of dry fibers was characterized using scanning electron microscope (SEM). Both their side view and the cross-section of fracture ends are shown in Figure 5.3. The images of rGO fiber are shown in Figure 5.4, displaying that rGO sheets stack compactly together. In contrast, Figure 5.3f shows that MWCNTs stay among rGO sheets, reducing their stacking. This may contribute to the larger diameter of the fiber-2 in comparison to the rGO fiber. Comparing among rGO/MWCNT hybrid fibers, their diameter increases proportionally to the confinement channel used in their synthesis (Table 5.1). The diameter of the fiber-5 is almost 8 times that of the fiber-1, which is 60 times in volume per length. Table 5.1 indicates that the density of hybrid fibers decrease from 1.15 ± 0.05 to $0.92 \pm 0.04 \text{ g/cm}^3$ with the increase of their diameter from fiber-1 to fiber 5. We

propose that the change in density can be explained by the capillary effect in hydrothermal synthesis. The aqueous dispersion of GO sheets and MWCNTs was drawn into the capillary-like channels due to capillary effect. The capillary pressure could be estimated from the Young-Laplace equation: $p_c = (2\gamma \cos\theta)/r$, where p_c is capillary pressure, γ stands for interfacial tension, θ is the wetting angle and r is the effective radius which is the radius of the space confinement channels. Thus, the capillary pressure is inversely proportional to the channel diameter, leading to more compacted assembly of hybrid fibers in smaller-diameter channels.

Figure 5. 3 SEM images of rGO/MWCNT hybrid fibers at different diameters with their fracture end area shown in the inset images: (a) Fiber-1; (b) Fiber-2; (c) Fiber-3; (d) Fiber-4; (e) Fiber-5. (f) A enlarged view of fracture end area of a hybrid fiber.

Figure 5.4 (a) Photograph of rGO fibers prepared by the shape-confined multiple fiber reactor; (b) FESEM image of the rGO fiber with the fracture end area in the inset; (c) Enlarged view of fracture end area.

The mechanical properties of fibers were characterized using a tensile testing system. Their stress-strain profiles are shown in Figure 5.5. The calculated Young's modulus and tensile strength are listed in Table 5.1. The rGO fiber has a Young's modulus and tensile of 9.7 GPa and 180.5 MPa, respectively, which is comparable to previous reported wet-spinning rGO fibers^{241,353,400,401} and hydrothermal rGO fibers^{394,402}. The hybrid fibers show poorer mechanical properties compared to the rGO fiber. With the increase of hybrid fiber diameter, both Young's modulus and tensile strength decrease, which can be attributed to their less compacted structures after inserting MWCNTs. On the other hand, MWCNTs provide a conducting network among rGO layers, improving the inter-sheet charge transfer in rGO composites.⁴⁰³ Electrical conductivity of the fibers was measured by a four-point probe station. The rGO fiber has an electrical conductivity of 7.8 S/cm, which is comparable to previously reported rGO fibers.^{394,402} The electrical conductivity of the fiber-2 is more than three times higher at 31.6 S/cm. The electrical conductivity decreases slightly with the

increase of hybrid fiber diameter due to the less compacted structure of larger-diameter hybrid fibers.

Table 5.1 Physiochemical, mechanical and electrical conductivity rGO/MWCNT hybrid fibers and rGO fiber.

Fiber	Confined channel diameter (mm)	Fiber diameter (μm)	Density (g cm^{-3})	Modulus (GPa)	Tensile strength (MPa)	Conductivity (S cm^{-1})
rGO fiber	0.5	42 ± 4	0.68 ± 0.04	9.7 ± 0.4	180.5 ± 7.2	7.8 ± 0.8
Fiber-1	0.3	30 ± 2	1.06 ± 0.06	7.4 ± 0.3	183.2 ± 7.5	34.5 ± 2.0
Fiber-2	0.5	48 ± 5	0.98 ± 0.04	6.6 ± 0.2	153.7 ± 6.2	31.6 ± 1.6
Fiber-3	1	121 ± 8	0.95 ± 0.06	4.5 ± 0.3	115.9 ± 5.0	26.5 ± 1.2
Fiber-4	1.5	188 ± 11	0.87 ± 0.04	3.4 ± 0.2	88.1 ± 7.1	23.4 ± 1.5
Fiber-5	2	236 ± 10	0.83 ± 0.03	2.5 ± 0.3	65.9 ± 6.5	22.9 ± 1.4

Figure 5.5 Stress-strain curves of the five different diameter hybrid fibers as well as the rGO fiber.

Energy Dispersive X-ray spectroscopy (EDX) and X-ray Photoelectron Spectroscopy (XPS) were used to characterize the chemical composition of

hybrid fibers. EDX mapping (Figure 5.6) displays that C, O, and N are uniformly distributed in the hybrid fibers. XPS spectra in Figure 5.7 indicate that the hybrid fibers contain mostly C and O with the additional 4-5 at% of N. High resolution C1s and N1s spectra of the fiber-2 were further studied. The main peak at 284.5 eV in the C1s spectrum (Figure 5.7) comes from sp^2 C. The fitted peaks at 286.5, 287.5 and 289.0 eV correspond to C in C-OH, C=O and O-C=O states, respectively.⁴⁰⁴ The peak at 285.6 eV can be attributed to C bound to doped N atoms.⁴⁰⁵ Figure 5.7 show peaks at 398.6, 400.2 and 401.5 eV, corresponding to pyridinic, pyrrolic and graphitic N, respectively. The peak at 399.4 eV can be ascribed to amine moieties or other sp^3 -C and N bonds.⁴⁰⁶ These findings are consistent with our previous study that EDA can dope N into rGO sheets in hydrothermal conditions.³⁹⁴

Figure 5. 6 (a-e) FESEM images of the hybrid carbon fibers with different diameters with their EDX elemental (C, O and N) mapping images in the insets: (a) Fiber-1; (b) Fiber-2; (c) Fiber-3; (d) Fiber-4; (e) Fiber-5.

Figure 5. 7 (a) XPS spectra of wide survey of the different diameter fibers; (b) C 1s spectrum of Fiber-2; N 1s spectrum of Fiber-2.

We first compared the electrochemical performances of the rGO fiber and the fiber-2 in a three-electrode configuration in 1 M H₂SO₄. Cyclic voltammetry (CV) curves Figure 5.8 shows that scanned at 5 mV s⁻¹ showed the capacitance divergence of the two carbon fibers. The reversible cathodic and anodic peaks on the CV curves indicated the existence of pseudocapacitive process during the test, which may be dedicated to the contribution of the oxygen and/or nitrogen containing functional groups. The specific capacitance of the two fiber electrode in the aqueous electrolyte was evaluated by galvanostatic charge/discharge at diverse current densities (figure 5.8). The specific capacitive values normalized on the electrode volume calculated from the discharge curves were displayed as

a function of volumetric current density (figure 5.8). The hybrid fiber, fiber-2, obtained a specific volumetric capacitance of 210 F cm^{-3} at current of 110.5 A cm^{-3} , more than twice of the value of the rGO fiber which was taken from an even lower current of 72.2 A cm^{-3} . Moreover, the hybrid fiber achieved a much better capacitance retention of about 60 % even the charge/discharge current was increased to 1658 A cm^{-3} , while the rGO fiber had already suffered almost 68 % capacitance loss when current reached 1083 A cm^{-3} , indicating the superiority in capacitive performance of carbon nanotube incorporated rGO composite based micro-SCs than those formed of the pure rGO,^{237,241,394,407,408} which may attribute to the synergistic effect of the hybrid porous structures including rGO offering higher surface area and MWCNTs providing highly conductive scaffold and preventing severe stacking of rGO.

Figure 5. 8 Comparative electrochemical study of fiber-2 and rGO fiber in a three-electrode configuration in 1 M H₂SO₄. (a) Comparative CV curves of fiber-2 and rGO fiber measured at 5 mV s⁻¹; (b) Galvanostatic charge/discharge curves of the rGO fiber at different current densities; (c) Galvanostatic charge/discharge curves of fiber-2 at different current densities; (d) Specific volumetric capacitance of fiber-2 and rGO fiber as a function of current density.

Figure 5. 9 CV curves of the five different diameter fiber two-ply all-solid-state micro-SCs measured at different scan rates.

Since I have demonstrated the capacitive advantages of hybrid fiber over rGO fiber with similar diameter and prepared in the same diameter reactor channels, I further investigated the electrochemical capacitive performance of the five types of hybrid fibers with different diameters when applied them as micro-SC electrodes. Two of each diameter hybrid fibers were assembled parallelly into a

two-ply all-solid-state fiber micro-SC using PVA-H₂SO₄ solid electrolyte. Each micro-SC had an overlapping electrode length of around 1 cm, while the effective volumes dependent on the diameters of the electrode fibers as well as the surrounding solid electrolyte, which were estimated to be $\sim 1.9 \times 10^{-5}$, $\sim 4.1 \times 10^{-5}$, $\sim 2.7 \times 10^{-4}$, $\sim 6.3 \times 10^{-4}$ and $\sim 9.2 \times 10^{-4}$ cm³. Since the volumetric and length capacitance or energy/power density are more meaningful in evaluation of electrochemical performance for such fiber type micro supercapacitive devices than the gravimetric values based on active electrode materials,^{30,45,409} I mainly studied the volumetric and length based performance in this work. Firstly, CV techniques were utilized to measure the specific capacitance of each diameter hybrid fiber electrode. CV curves of the five two-ply all-solid-state micro-SCs were measured at scan rates from 2 to 50 mV s⁻¹ (Figure 5.9). CV curves all exhibit rectangular shapes when scanned at low rates and still remained replete when the scan rates increased for fiber-1 and fiber-2, indicating their lower charge transfer resistance and good electrical conductivity as electrodes in the assembled micro-SCs. However, for those thicker fibers, the CV curves became more lean and spindle-like at higher scan rates, which may result from the lower conductivity (Table 5.1) and the longer ion diffusion distance with the expanding of the fiber diameters. Figure 5.10a gave the CV@5 mV s⁻¹ results of the five hybrid fiber formed micro-SCs normalized on the volumes of each electrode, intuitively showing the CV area size variations which accounted for the specific

volumetric capacitance growth with diminishment of the fiber diameters. A comparison of all the specific volumetric capacitance of the five hybrid fiber micro-SCs calculated from CV results at different scan rates was displayed in Figure 5.10b. Fiber-1 achieved best specific volumetric capacitance of about 281 F cm⁻³, which is higher than the values of most previously reported fiber based all-solid-state micro-SCs^{111,189,236,239,242,361,410} and also many other type of micro-SCs.²²⁶⁻²²⁸ In contrast, when the CV@5 mV s⁻¹ results were processed based on the length of the device electrodes, the results reversed from above volumetric performance (Figure 5.10c): the fiber-5 exhibited largest specific length capacitance of 53 mF cm⁻¹, followed by fiber-4 then fiber-3; fiber-1 and fiber-2 only obtained 3.8 % and 8.6 % of the specific capacitance per length of fiber-5 measured at same scan rate, mainly attributed to their gaps in diameters. The length performance achieved by fiber-5 is among the highest reported value for fiber electrodes including graphene fibers,^{241,242,244,259,348} carbon nanotube assembled fibers,^{238,349,411} conventional carbon fiber substrate composite fibers¹⁸⁹ and metal wire substrate composite fibers.^{188,345,412} As shown in Figure 5.10b and 5.10d, fiber-1 had the best rate performance when the scan rates increased than those thicker fibers, which remained nearly 70 % of the specific capacitance when scan rates increasing from 2 to 50 mV s⁻¹.

Figure 5. 10 Electrochemical cyclic voltammetry (CV) performance of the two-ply micro-SCs with different diameters. (a) CV curves based on volumetric performance measured at 5 mV s^{-1} ; (b) Specific volumetric capacitance as a function of scan rate; (c) CV curves based on length performance measured at 5 mV s^{-1} ; (d) Specific length capacitance as a function of scan rate.

Figure 5. 11 Galvanostatic charge/discharge curves of the five different diameter fiber two-ply all-solid-state micro-SCs measured at different current densities.

I had evaluated the specific capacitance of the hybrid fiber electrodes in the solid state symmetric micro-SCs. More importantly, the overall capacitive performance of those fiber micro-SCs was studied using galvanostatic charge/discharge. The charge/discharge results of the five diameter fiber devices measured at multiple current densities from 42 mA cm^{-3} up to around 850 mA cm^{-3} were all shown in Figure 5.11. Figure 5.12a showed the triangular shape charge/discharge curves of all the five devices with measuring currents around 42 mA cm^{-3} as a clear representative of the total capacitance. The volumetric and length performance normalized to the whole devices were calculated from the discharge times and illustrated in Figure 5.12b and 5.12c. Similarly as above, the thinner fiber formed devices were better at volumetric capacitance, while the thicker ones did much more outstanding when measured by length. Volumetric capacitance of 41.7 F cm^{-3} and 22.9 F cm^{-3} were calculated both from nearly 42 mA cm^{-3} on fiber-1 and fiber-5 micro-SC, respectively, between which values covered the performance of fiber-2, fiber-3 and fiber-4 devices successively. Similar situations could also be found in results from other discharge currents. Larger capacitance gaps were observed on diameter depended length performance (Figure 5.12c). The fiber-5 micro-SC could reach the best device capacitance per length up to 21 mF cm^{-1} and experienced a wide range of performance from 7.7 to 21 mF cm^{-1} . And for fiber-1 device, a length capacitance ranged from 0.8 to 0.47 mF cm^{-1} at different discharge currents.

Figure 5. 12 Electrochemical galvanostatic charge/discharge performance of the two-ply micro-SCs with different diameters. (a) CV curves based on volumetric performance all measured at around $42\ mA\ cm^{-3}$; (b) Specific volumetric capacitance as a function of current density; (c) Specific length capacitance as a function of current density; (d) Length depended device capacitance of the fiber-1 and fiber-5 assembled two-ply all-solid-state micro-SCs: volumetric capacitance measured at volumetric current density of $85\ mA\ cm^{-3}$ and length capacitance measured at constant currents of $1.6\ \mu A$ for fiber-1 micro-SCs and $80\ \mu A$ for fiber-5 micro-SCs.

Figure 5. 13 Galvanostatic charge/discharge curves of 0.5, 1, 2.5, 5 cm two-ply all-solid-state micro-SCs: (a) and (b) measured at the same volumetric current density of about 85 mA cm^{-3} from fiber-1 assembled micro-SCs (a) and fiber-5 assembled micro-SCs (b); (c) fiber-1 assembled micro-SCs measured at constant current of $1.6 \text{ } \mu\text{A}$ (equivalent to about 85 mA cm^{-3} current density for the 1 cm fiber-1 micro-SC); (d) fiber-5 assembled micro-SCs measured at constant current of $80 \text{ } \mu\text{A}$ (equivalent to about 85 mA cm^{-3} current density for the 1 cm fiber-5 micro-SC).

The measurement was extended to different length of the solid state micro-SCs. Two series of different length devices were fabricated using the thinnest fiber, fiber-1, and the thickest fiber, fiber-5, each of which included effective length of 0.5, 1, 2.5 and 5 cm. Considering the resistance dependent on the total fiber

volumes and the capacitive performance clearly influenced by the charge/discharge currents, I had applied two types of currents in the measurement. Firstly, those devices were measured at the same volumetric current density of about 85 mA cm^{-3} based on their effective device volumes (Figure 5.13a and 5.13b). Then, two constant currents, 1.6 and $80 \text{ } \mu\text{A}$, were loaded on the fiber-1 series devices (equivalent to about 85 mA cm^{-3} current density for the 1 cm fiber-1 micro-SC) and the fiber-5 series (equivalent to about 85 mA cm^{-3} current density for the 1 cm fiber-5 micro-SC), respectively (Figure 5.13c and 5.13d). With the same volumetric discharge current density, the shorter devices attained longer discharge time. And when keeping the current constant for each diameter devices, the longer devices had the longer discharge time. While both measurement gave the smaller IR drop at the beginning of the discharge curves from the shorter devices which was caused by the internal resistance of the fiber electrodes. The increasing of the electrode length brought the larger internal resistance. Figure 5.12d showed the calculated results of the length depended performance of above devices. Both series of different length micro-SCs suffered a volumetric capacitance and length capacitance decline as the length extending. 41.3 F cm^{-3} was got by the 0.5 cm fiber-1 micro-SC at 85 mA cm^{-3} , reduced to 35.9 F cm^{-3} as length doubled to 1 cm, and was further pulled back to 31.2 and 26.7 F cm^{-3} for length of 2.5 and 5 cm, respectively. For fiber-5 different length micro-SCs, a linear decreasing curve of the length capacitance was observed with

increase of device length measured at constant current of $80 \mu\text{A}$, from 18 mF cm^{-1} of the 0.5 cm device to 12 mF cm^{-1} of the 5 cm device. Though the fiber micro-SCs experienced a drawback in capacitance when increasing the device length, the fiber-1 micro-SCs still remained 65 % volumetric capacitance and the fiber-5 micro-SCs kept 67 % of the length capacitance when the device length extended to ten times. On the other hand, the 5 cm length is more than enough for a micro-SCs whose footprint areas are usually in the millimeter to centimeter scale.⁴⁵ In contract, the performance variations along different length as well as different diameters gives more choices to meet specific energy and power requirements of the micro-SC applications.

Figure 5. 14 (a) Galvanostatic charge/discharge curves of one, two and three

fiber-5 two-ply micro-SC connected in series; (b) Galvanostatic charge/discharge curves of one, two and three fiber-5 devices connected in parallel; (c) Cyclic life of fiber-1 and fiber-5 two-ply micro-SCs. Inset: Schematic of a fiber-1 integrated device and a fiber-5 integrated device, photographs of the two alignment devices powering a LED, respectively. (d) Capacitance retention of the fiber-1 and fiber-5 micro-SCs during 1000 cycles of up to 120° bending as illustrated in the schematic and photograph in the inset.

To further satisfy diverse energy storage needs for potential applications, the 1 cm fiber-5 micro-SCs were studied both in series (Figure 5.14a) and in parallel (Figure 5.14b) as a demonstration. The voltage windows of the serial devices could be multiplied by the device numbers to 2 or 3 V, while no change for the parallel ones. Seen from Figure 5.14a, when two or three devices were connected in series, the charge/discharge time did not apparently change when operated at the same current. The charge/discharge time doubled or tripled in two or three parallel aligned devices at the same operation current as shown in Figure 5.14d. As a demo of concept, a fiber-1 integrated device with five fiber-1 two-ply micro-SC connected in parallel then three of the five-parallel alignments connected in series and a fiber-5 integrated device with five fiber-5 two-ply micro-SC connected in parallel, then two of the five-parallel alignments connected in series were fabricated and able to power a LED light individually (illustrated in the inset of Figure 5.14c). The results indicated that the fiber micro-SCs were feasible to

extend or scale up to multiple serial or parallel alignments for practical complex applications.

The long term cyclic stability of the two-ply solid state fiber micro-SCs were evaluated on the fiber-1 and fiber-5 devices under repeated charge/discharge at around 850 mA cm^{-3} current. Figure 5.14c showed that about 86 % and 92 % of initial capacitance were retained for the fiber-1 micro-SC and fiber-5 micro-SC, respectively, after 10000 test cycles, demonstrating their excellent stable electrochemical performance under high current long life test. Moreover, the mechanical flexibility of the fiber micro-SCs were verified by repeated bending at 120° (illustrated in the inset of Figure 5.14d) of the fiber-1 and fiber-5 devices for 1000 times. As shown in Figure 5.14d, the initial capacitance tested without bending was marked as number 0 of bending times. Only as negligible as about 1 % capacitance decline on bending was detected as compared with the initial capacitance. The thinnest fiber-1 micro-SC retained nearly 96 % capacitance after 1000 bending times, indicating its outstanding mechanical flexibility and electrochemical stability which is essential for flexible and wearable electronics. The thickest fiber-5 device was also able to preserve 89 % capacitance after bending 1000 times. The bending result gap between fiber-1 and fiber-5 devices may be caused by the reason that the thicker fiber may be easier to suffer structure damages than the thinner fibers during bending.

The high volumetric energy and power densities were constituted in the Ragone plots and compared with the corresponding performance of previous reported fiber-shaped micro-SCs as well as two commercial energy-storage devices as shown in Figure 5.15a. All the five different diameter hybrid fiber assembled micro-SCs got relatively superiority in volumetric energy and power densities, especially the fiber-1 one which achieved a highest volumetric energy density of 5.8 mWh cm^{-3} , which is among the highest volumetric energy densities achieved by the fiber-based micro-SCs and is better than many recent published studies working on fiber-shaped SCs including 3.4 mWh cm^{-3} of the wet-spin rGO/DWCNT fiber-shaped SCs,²⁴¹ 3.5 mWh cm^{-3} of the wet-spin rGO/CNT@CMC yarn SCs,²⁴² about 4.1 mWh cm^{-3} of the rGO-MoS₂ fiber micro-SCs, 0.22 mWh cm^{-3} of the carbon/MnO₂ fiber micro-SCs,²³⁵ 2 mWh cm^{-3} of the carbon fiber/PANI VS functionalized carbon fiber asymmetric fiber-shaped SCs,²³⁶ 1.1 mWh cm^{-3} of the PPy@MnO₂@rGO@metal wire yarn SCs¹⁸⁸ and 2.2 mWh cm^{-3} of the Ni fiber@Ni(OH)₂ and ordered mesoporous carbon fiber SCs.⁴¹³ This volumetric energy density also surpassed the value about 0.6 mWh cm^{-3} of the commercial 5.5 V/100 mF SC and is even comparable to the 4 V/500 μAh thin film lithium battery.⁴¹⁴ Figure 5.15b showed length energy and power density distribution of the five hybrid fiber micro-SCs and their comparisons with the length performance of other fiber-shaped CSs. A highest length energy of $2.8 \text{ } \mu\text{Wh cm}^{-1}$ and a highest length power of $379 \text{ } \mu\text{W cm}^{-1}$ were

gained by the fiber-5 micro-SC with a length energy range from 2.8 to 1 $\mu\text{Wh cm}^{-1}$ and a length power range covering from 19 to 379 $\mu\text{W cm}^{-1}$. Both the length energy and power density of the fiber-5 micro-SCs exceeded those of many reported fiber-shaped SC studies, including the rGO/DWCNT fiber-shaped SCs (maximum energy about 29 nWh cm^{-1} and maximum power about 6.5 $\mu\text{W cm}^{-1}$),²⁴¹ carbon fiber/MWCNT coaxial fiber SCs (maximum energy about 0.74 $\mu\text{Wh cm}^{-1}$ and maximum power about 687 $\mu\text{W cm}^{-1}$),¹⁸⁹ MnO_2/CNT fiber and CNT fiber asymmetric SCs (maximum energy 46.6 nWh cm^{-1} and maximum power 61.6 $\mu\text{W cm}^{-1}$),²³⁸ rGO/CNT@CMC yarn SCs (maximum energy about 47.1 nWh cm^{-1} and maximum power 2.6 $\mu\text{W cm}^{-1}$),²⁴² CNT/ MnO_2 /polymer fiber SCs (maximum energy 0.75 $\mu\text{Wh cm}^{-1}$ at the power of 19.3 $\mu\text{W cm}^{-1}$)⁴¹¹ and carbon fiber/PANI and functionalized carbon fiber asymmetric fiber-shaped SCs (maximum energy 1.4 $\mu\text{Wh cm}^{-1}$ at the power of 119 $\mu\text{W cm}^{-1}$).²³⁶ Seen from Figure 5.15a and 5.15b, the energy and power densities of fiber-2, fiber-3 and fiber-4 devices either based on device volumes or normalized by the device effective length were all distributed between the thinnest fiber-1 and thickest fiber-5 devices and aligned following the order of the hybrid fiber diameters, indicating the capability of tailoring the energy or power of the micro-SCs within the range by controlling the device electrode diameters. With my methods, I succeeded to prepare rGO/CNT fibers with different diameters and length and applied them as electrodes for the micro-SCs. As illustrated in Figure 5.15c, a

wide distribution of energy and power was displayed on the plot with the energy ranging from $<0.1 \mu\text{Wh}$ to nearly $10 \mu\text{Wh}$ and the power even ranging across four order of magnitude area from $0.2 \mu\text{W}$ to about $1950 \mu\text{W}$ and formed an area marked by light blue within which all the energy and power could be covered by the hybrid fiber micro-SCs. The marked energy and power areas I had achieved from the porous hybrid carbon fiber micro-SCs is much broader than those of many other planer-shaped or fiber-shaped micro-SCs could reach. If integrated with specific microelectronics, my fiber micro-SCs are capable of satisfying a large part of the power requirements for general micro-devices including pacemakers,³⁶⁸ RFIDs,³⁶⁹ implantable biosensor or micro medical devices,³⁷⁰ and micro-energy harvesting devices such as micro fuel cells and micro solar cells,⁴¹⁵ as shown in figure 5.15c.

Figure 5. 15 Energy and power of the hybrid fiber micro-SCs: Volumetric (a) and length (b) energy and power densities of the five different diameter fiber micro-SCs were compared with previously reported fiber-shaped micro-SCs; Device energy and power distributions of the fiber micro-SCs as well as several recently reported micro-SCs. The power consumption of several types of microelectronics and micro-power sources were also marked.

5.4 Conclusion

I have successfully developed a scaled synthesis method for diameter control of nitrogen doped rGO/MWCNT porous fibers by one-step-one-pot multi-fiber confined hydrothermal self-assembly and simultaneous reduction. The prepared hybrid fibers showed both good electrical and mechanical properties. A series of fiber micro-SCs were fabricated using the hybrid fibers with diameters ranging from 30 to 240 μm and assembled parallelly into two-ply all-solid-state fiber micro-SCs using PVA-H₂SO₄ solid electrolyte. The hybrid fiber micro-SCs was observed to exhibit diameter dependent electrochemical performance. The volumetric performance including capacitance, energy and power densities increased with the decrease of the diameters of the fiber electrodes, while the length performance went inversely to the volumetric performance changing trend. A highest device volumetric capacitance of 41.7 F cm⁻³ was obtained from the thinnest fiber-1 electrode with the corresponding best specific volumetric capacitance of 281 F cm⁻³ and a largest device length capacitance of 21 mF cm⁻¹ was measured on the thickest fiber-5 electrode with the related best specific length capacitance of 53 mF cm⁻¹. The performance of the other fibers with diameters in the middle was all distributed between the above two devices and ranked along the order of the hybrid fiber diameters. The performance range was further expanded by extending the device length from 0.5 to 5 cm which gave a series of length-dependent performance. All diameter devices showed good rate

capability. Both the thinnest fiber-1 and thickest fiber-5 devices exhibited long cyclic lifetime, excellent flexibility and mechanical stability, and good ability in extended serial and parallel integration. The device volumetric energy and power densities could be up to 5.8 mWh cm⁻³ and 423 mW cm⁻³ on fiber-1 micro-SC and the device length energy and power densities could reach highest 2.8 μWh cm⁻¹ and 379 μW cm⁻¹ from fiber-5 device. More importantly, a broad range of energy and power distribution was achieved that could cover a wide variety of energy and power demands from micro-SCs for different applications. This work would open up the possibility of realizing built-to-order concept in microsupercapacitors.

Chapter VI Conclusions and Outlook

6.1 Conclusions

Supercapacitor has become one of the most promising energy storage devices to meet the expanding demands of the world energy consuming styles. Recent advances in materials has revealed that the development of novel electrodes for SCs from hybrid materials, especially nano-carbon based composite materials, has been extensively researched and demonstrated to effectively improve the electrochemical performance of the SCs. On the other hand, with the development of SCs and diversified demands in powering applications, more novel properties are required of SCs. Flexibility, wearability and miniaturization are among the currently favored characteristics from SCs for trending applications including portable and flexible devices, smart wearable devices and smart textiles, and microelectronics and micro-devices. In this thesis, some successful improvements have been demonstrated that may help to address those issues.

Firstly, the electrochemical performance of the highly interested pseudocapacitive material, Ni(OH)_2 has been enhanced by hybridizing it with highly conductive MWCNTs. Three different species of crystallinity of Ni(OH)_2 (α , β and amorphous) were deposited on MWCNTs, respectively, with analogous mass ratios. Electrochemical performance divergence was detected on electrodes

fabricated from those three different-crystalline Ni(OH)_2 based composites in a three-electrode testing system in 1 M KOH aqueous electrolyte, showing that MWCNT/amor- Ni(OH)_2 has the highest specific capacitance based either on the mass of total active materials or merely on Ni(OH)_2 . MWCNT/amor- Ni(OH)_2 also has most superior rate capability with increasing CV scan rates or discharge currents. Results indicated that the disordered structures helped to promote the effective surface area and reduce diffusion resistance for redox reactions that consequently increase the electrochemical performance but have resulted in deteriorating cycling stability.

Above study has inspired us to further investigate into the MWCNT/amor- Ni(OH)_2 nanocomposites as high perform SC electrodes by improving the structural stability of amor- Ni(OH)_2 . Then, a thin conductive polymer (PEDOT:PSS) was utilized to wrap on the MWCNT/amor- Ni(OH)_2 nanocomposites to form a coaxial ternary hybrid material. An extremely high gravimetric specific capacitance of 3262 F g^{-1} was achieved from the ternary hybrid composite fabricated electrode in 1 M aqueous KOH electrolyte. And the long term cycling life (92% capacitance retention over 3000 cycles and 77% retention over 30000 cycles under the high current of 20 A g^{-1}) was apparently improved after the protection of PEDOT: PSS layer. An asymmetric SC was assembled using the ternary hybrid as the positive electrode and the rGO/CNT hybrid as the negative electrode for achieving high energy density. The specific

energy density of the asymmetric SC reached 58.5 Wh kg^{-1} at a power density of 780 W kg^{-1} , and retained at 30.8 Wh kg^{-1} with a high power density of 11.5 kW kg^{-1} . Especially, an outstanding cycling stability was obtained for 30000 cycles. The utilization of amorphous Ni(OH)_2 in the CNT based composites and the unique ternary hybrid design have been demonstrated to be a general approach to get high performance pseudocapacitive materials for SCs with high energy density, rate capability and long cycle life.

Besides electrode materials for high capacitance, energy and power densities, the modern trends of portable electronics have created a strong demand for flexible energy storage devices. Novel rice paper based flexible electrodes were successfully designed and prepared. The hydroxyl chemistry of cellulose fibers was taken advantages in synthesizing hybrid ternary nanocomposites comprised of rice paper, MnO_2 , and SWCNTs. A uniform layer of MnO_2 nanoparticles was deposited on cellulose fibers through directly reactions of MnO_4^- ions with functional groups on paper cellulose fibers. SWCNTs provided a highly conductive network in connecting individual MnO_2 particles, helping to prompt fast charge transfer. Furthermore, an optimum deposition temperature for MnO_2 deposition has been discovered, which can lead to a high capacitance and retain good mechanical strength. The flexible ternary hybrid composites were evaluated in the two-electrode SCs, getting a excellent specific capacitance among flexible electrodes of 260.2 F/g in neutral aqueous solution as well as good cycling

stability and tensile strength. The flexible SC also showed excellent electrochemical stability in mechanical bending for more than 100 times. The approach guided a significance in large-scale production flexible energy storage devices using the sustainable materials.

The fast growing demands of small-sized flexible electronics and power consuming devices cannot be simply satisfied with the regular flexible SCs, but instead, the micro-SCs. Moreover, the new trends for wearable applications even require the fiber-based micro-SCs. Therefore, we successfully developed scaled synthesis of diameter control of nitrogen doped rGO/MWCNT porous fibers by one-step-one-pot multi-fiber confined hydrothermal self-assembly and simultaneous reduction. A series of fiber electrodes with different diameters were fabricated and assembled into two-ply all-solid-state fiber micro-SCs. The electrochemical performance of the hybrid fiber micro-SCs could be tuned through the electrode diameters. A highest device volumetric capacitance was seized from the thinnest fiber micro-SC and a largest device length capacitance was measured on the thickest one. The performance was further tailored depended on the device length. The hybrid fiber micro-SCs also exhibited long cyclic lifetime, excellent flexibility and mechanical stability, and good ability in extended serial and parallel integration. With the tailorability of the micro-SC electrode diameters, the energy and power of the fiber micro-SCs could be tuned to satisfy a wide range of demands for practical micro-device applications. This

may open up a pathway to realize built-to-order concept in micro-SCs.

6.2 Outlook

Though tremendous efforts have been made on discovering new electrode materials and novel designs of device configurations for SCs, the electrochemical performance, especially energy and power densities, which are the core parameters in evaluating SCs, are still behind the feasible expectations for wide-spread energy storage applications. Stemming from the results and discussions made in this thesis, several research perspectives are suggested and elaborated as follow.

6.2.1 Amorphous metal oxides/hydroxides for high performance electrode materials.

Studies have demonstrated that the amorphous crystallinities have advantages in achieving high pseudocapacitance on several metal oxides/hydroxides including RuO_2 , MnO_2 and $\text{Ni}(\text{OH})_2$.^{28,133,136} Thus, there is a need to extend the candidate pool by preparing more pseudocapacitive metal oxides/hydroxides with amorphous structures and evaluating them as electrode materials. However, the synthesis of amorphous metal oxides/hydroxides is not a simple job. Therefore, to discover general synthesis methods will effectively shorten the distance to success. Furthermore, amorphous mixed metal oxides/hydroxides may be more favored in out-performing the single metal materials due to the easy phase

tenability and electrochemically synergistic effects such as complementary redox currents and improved electrical conductivity. In addition, constructing hybrid materials of the poor-electrical-conductivity amorphous metal oxides/hydroxides with highly conductive components would always be an efficient way to achieve higher energy and power densities simultaneously.

6.2.2 Improving performance of asymmetric supercapacitors by balancing both high performance electrodes.

The asymmetric SCs are favored in addressing the energy issue by extending the voltage windows of the SCs. One critical research target in SC developments is to discover novel couples of high performance positive and negative electrodes for the asymmetric SCs. However, previous research were mostly focused on developing better positive electrode materials for the asymmetric SCs. Judging from equation 1.4 in Chapter I, no matter how high the capacitance of the one electrode can reach, the total capacitance of an asymmetric SC is mainly limited by the other electrode with lower capacitance. Thus, more efforts should be made to develop higher performance negative electrode materials for the aqueous asymmetric SCs and to optimize the total device performance by balancing the performance of these two electrodes.

6.2.3 Paper based flexible supercapacitors with high performance using cheap and scalable manufacturing methods

The most outstanding advantage of the paper based flexible SCs is their biodegradability and environmental friendliness, which makes them ideal candidates for single-use-and-throw-away applications when integrated with e.g. environmental sensors, body monitors for sports, blood or saliva testers in a single piece of paper. In order to correspond to this trend, cheaper and more easily scalable methods have to be developed for manufacturing such disposable paper based SCs. Printing technologies have been extensively applied in printed electronics industry. They have also been studied to fabricate paper based SCs and are promising to realize scalable manufacture with low cost.⁴¹⁶ However, in previous studies, the printed SCs on paper are mainly based on carbon materials and a few using conducting polymers.^{417,418} Thus, the energy densities of the printed SCs were limited. There is a need to modify the printing processes in fabricating paper based SCs, especially the electrode materials for printing. Incorporation of high performance metal oxides/hydroxides into the printing precursor with the carbon materials can be an effective approach in improving the energy of the electrodes. However, the existence of the metal oxides may decrease the quality of the printing precursors like poor dispersion, changed viscosity or decreased stability that affect the printing efficiency. Therefore, a lot of efforts may have to be made to investigate the printable electrode materials for

high performance paper based flexible SCs.

6.2.4 Novel designs of fibers for higher performance of fiber micro-SCs

Though plenty of fiber electrodes have been fabricated for SC applications, currently-developed fiber micro-SCs are still far away from commercial micro-batteries in terms of energy densities for practical applications. Thus, a major research target is to improve capacitance of fiber micro-SCs without sacrificing the power densities, excellent long cycling life and mechanical flexibility. Potential approaches can be extracted for novel designs of fiber structures and nanoscale sizes with large ion accessible surface area, fiber compositions and chemistry with higher electrical conductivity and larger pseudocapacitive performance from heteroatoms doping. Hybrid electrode materials accommodated with EDL-type nanocarbons and pseudocapacitive materials have been demonstrated to be one of most promising candidates for high performance regular-sized SCs, while studies of such hybrid materials for fiber micro-SCs are few. Thus, more efforts should be made to investigate into the elaborately designed EDL-pseudocapacitive hybrid materials for micro-SC fiber electrodes.

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Publications and Conference

Journal Papers

- (1) **Jiang, W.**; Zhai, S.; Wei, L.; Goh, K.; Karahan, H. E.; Yuan, Y.; Yu, D.; Wei, J.; Chen, Y.*; Space-confined assembly of hybrid carbon fibers for capacitive energy storage: realizing built-to-order concept in micro-supercapacitors, 2015, *Energy & Environmental Science* (revised).
- (2) **Jiang, W.**; Wei, L.; Zhai, S.; Yuan, Y.; Yu, D.; Zhang, Q.; Wei, J.; Chen, Y.*; Nickel hydroxide-carbon nanotube nanocomposites as supercapacitor electrodes: crystallinity dependent performances, *Nanotechnology*, 2015, 26, 314003 (10pp).
- (3) **Jiang, W.**; Yu, D.; Zhang, Q.; Goh, K.; Wei, L.; Yong, Y.; Jiang, R.; Wei, J.; Chen, Y.*; Ternary hybrids of amorphous nickel hydroxide-carbon nanotube-conducting polymer for supercapacitors with high energy density, excellent rate capability and long cycle life, *Advanced Functional Materials*, 2015, 25, 1063–1073
- (4) **Jiang, W.**; Zhang, K.; Wei, L.; Yu, D.; Wei, J.; Chen, Y. *, Hybrid ternary rice paper–manganese oxide–carbon nanotube nanocomposites for flexible supercapacitors, *Nanoscale*, 2013, 5, 11108-11117.
- (5) Zhai, S.; **Jiang, W.**; Wei, L.; Karahan, H. E.; Yuan, Y.; Ng, A.K.; Chen, Y*, All-carbon solid-state yarn supercapacitors from activated carbon and carbon fibers for smart textiles, *Materials Horizons*, 2015, DOI: 10.1039/C5MH00108K.
- (6) Wei, L.; **Jiang, W.**; Yuan, Y.; Goh, K.; Yu, D.; Wang, L.; Chen, Y.*; Synthesis of free-standing carbon nanohybrid by directly growing carbon nanotubes on air-sprayed graphene oxide paper and its application in supercapacitor, *Journal of Solid State Chemistry*, 2015, 224, 45–51.

- (7) Wei, L.; **Jiang, W.**; Goh, K.; Chen, Y.*, Mechanical reinforcement of polyethylene using n-alkyl group functionalized multi-walled carbon nanotubes: effect of alkyl group carbon chain length and density, *Polymer Engineering and Science*, 2014, 54, 336–344.
- (8) Yu, D.; Zhai, S.; **Jiang, W.**; Wei, L.; Goh, K.; Chen, X.; Jiang, R.; Chen, Y.*, Transforming pristine carbon fiber tows into high performance solid-state fiber supercapacitors, *Advanced Materials*, 2015, DOI: 10.1002/adma.201501948.
- (9) Yuan, Y.; Wei, L.; **Jiang, W.**; Goh, K.; Jiang R.; Lau, R.; Chen, Y.*, Sulfur induced chirality changes in single-walled carbon nanotube synthesis by ethanol chemical vapor deposition on Co/SiO₂ catalyst, *Journal of Materials Chemistry A*, 2015, 3, 3310–3319.
- (10) Yu, D.; Wei, L.; **Jiang, W.**; Wang, H.; Sun, B.; Zhang, Q.; Goh, K.; Si, R.; Chen, Y*, Nitrogen Doped Holey Graphene as Efficient Metal-Free Multifunctional electrochemical catalysts for hydrazine oxidation and oxygen reduction, *Nanoscale*, 2013, 5, 3457-3464.
- (11) Wei, L.; Karahan, H. E.; Goh, K.; **Jiang, W.**; Yu, D.; Birer, O.; Chen, Y.*, High performance metal-free electrocatalyst for hydrogen evolution reaction from bacteria derived carbon, *Journal of Materials Chemistry A*, 2015, 3, 7210-7214.
- (12) Yu, D.; Qian, Q.; Wei, L.; **Jiang, W.**; Goh, K.; Wei, J.; Zhang, J.; Chen, Y*, Emergence of fiber supercapacitors, *Chemical Society Reviews*, 2015, 44, 647–662.
- (13) Goh, K.; Setiawan, L.; Wei, L.; **Jiang, W.**; Wang, R.; Chen, Y.*, Fabrication of novel functionalized multi-walled carbon nanotube immobilized hollow fiber membranes for enhanced performance in forward osmosis process, *Journal of Membrane Science*, 2013, 446, 244–254.
- (14) Yu, D.; Goh, K.; Wang, H.; Wei, L.; **Jiang, W.**; Zhang, Q.; Dai, L.; Chen,

Y.*, scalable synthesis of hierarchically-structured carbon nanotube/graphene fibers for capacitive energy storage, *Nature Nanotechnology*, 2014, 9, 555-562.

Conferences

- (1) **Jiang W.**; Wei J.; Chen Y., Hybrid Ternary Paper–Manganese Oxide–Carbon Nanotube Nanocomposites for Flexible Supercapacitors, 7th International Conference on Materials for Advanced Technologies, July. 2013, Singapore.

References

- (1) Dunn, B.; Kamath, H.; Tarascon, J.-M. *Science* **2011**, 334, 928.
- (2) Hadjipaschalis, I.; Poullikkas, A.; Efthimiou, V. *Renew. Sust. Energ. Rev.* **2009**, 13, 1513.
- (3) Haihua, Z.; Bhattacharya, T.; Duong, T.; Siew, T. S. T.; Khambadkone, A. M. *IEEE Trans. Power Electron.* **2011**, 26, 923.
- (4) Hill, C. A.; Such, M. C.; Dongmei, C.; Gonzalez, J.; Grady, W. M. *IEEE Trans. Smart Grid* **2012**, 3, 850.
- (5) Ibrahim, H.; Ilinca, A.; Perron, J. *Renew. Sust. Energ. Rev.* **2008**, 12, 1221.
- (6) *Electricity Energy Storage Technology Options: A White Paper Primer on Applications, Costs, and Benefits*, Electric Power Research Institute (EPRI), 2010.
- (7) Liu, C.; Li, F.; Ma, L.-P.; Cheng, H.-M. *Adv. Mater.* **2010**, 22, E28.
- (8) Choi, N.-S.; Chen, Z.; Freunberger, S. A.; Ji, X.; Sun, Y.-K.; Amine, K.; Yushin, G.; Nazar, L. F.; Cho, J.; Bruce, P. G. *Angew. Chem. Int. Ed. Engl.* **2012**, 51, 9994.
- (9) Simon, P.; Gogotsi, Y. *Nat. Mater.* **2008**, 7, 845.
- (10) Yan, J.; Wang, Q.; Wei, T.; Fan, Z. *Adv. Energy Mater.* **2014**, 4, 1300816.
- (11) Rolison, D. R.; Nazar, L. F. *MRS Bull.* **2011**, 36, 486.
- (12) Ghosh, A.; Lee, Y. H. *ChemSusChem* **2012**, 5, 480.
- (13) Zhang, L. L.; Zhao, X. S. *Chem. Soc. Rev.* **2009**, 38, 2520.
- (14) Becker, H. I.; Office, t. U. S. P. a. T., Ed.; General Electric Company: 1957.
- (15) Kötz, R.; Carlen, M. *Electrochim. Acta* **2000**, 45, 2483.
- (16) Wang, G.; Zhang, L.; Zhang, J. *Chem. Soc. Rev.* **2012**, 41, 797.
- (17) Conway, B. E. *Electrochemical Supercapacitors: Scientific*

Fundamentals and Technological Applications; Kluwer Academic/Plenum: New York, 1999.

(18) Long, J. W.; Bédanger, D.; Brousse, T.; Sugimoto, W.; Sassin, M. B.; Crosnier, O. *MRS Bull.* **2011**, *36*, 513.

(19) Conway, B. E.; Birss, V.; Wojtowicz, J. *J. Power Sources* **1997**, *66*, 1.

(20) Schultze, J. W.; Koppitz, F. D. *Electrochim. Acta* **1976**, *21*, 327.

(21) Koppitz, F. D.; Schultze, J. W. *Electrochim. Acta* **1976**, *21*, 337.

(22) Seredych, M.; Hulicova-Jurcakova, D.; Lu, G. Q.; Bandosz, T. J. *Carbon* **2008**, *46*, 1475.

(23) Wang, X.; Sun, G.; Routh, P.; Kim, D.-H.; Huang, W.; Chen, P. *Chem. Soc. Rev.* **2014**, *43*, 7067.

(24) Conway, B. E. *J. Electrochem. Soc.* **1991**, *138*, 1539.

(25) Zhang, S.; Pan, N. *Adv. Energy Mater.* **2015**, *5*, n/a.

(26) Ji, J.; Zhang, L. L.; Ji, H.; Li, Y.; Zhao, X.; Bai, X.; Fan, X.; Zhang, F.; Ruoff, R. S. *ACS Nano* **2013**, *7*, 6237.

(27) Lu, Q.; Lattanzi, M. W.; Chen, Y.; Kou, X.; Li, W.; Fan, X.; Unruh, K. M.; Chen, J. G.; Xiao, J. Q. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 6847.

(28) Feng, L.; Zhu, Y.; Ding, H.; Ni, C. *J. Power Sources* **2014**, *267*, 430.

(29) Yan, J.; Fan, Z.; Sun, W.; Ning, G.; Wei, T.; Zhang, Q.; Zhang, R.; Zhi, L.; Wei, F. *Adv. Funct. Mater.* **2012**, *22*, 2632.

(30) Yu, D.; Goh, K.; Wang, H.; Wei, L.; Jiang, W.; Zhang, Q.; Dai, L.; Chen, Y. *Nat. Nanotechnol.* **2014**, *9*, 555.

(31) March, N. H.; Rubio, A. *J. Nanometer.* **2011**.

(32) Shen, J. M.; Liu, A. D.; Tu, Y.; Foo, G. S.; Yeo, C. B.; Chan-Park, M. B.; Jiang, R. R.; Chen, Y. *Energ. Environ. Sci.* **2011**, *4*, 4220.

(33) Cheng, Q.; Tang, J.; Ma, J.; Zhang, H.; Shinya, N.; Qin, L.-C. *Phys. Chem. Chem. Phys.* **2011**, *13*, 17615.

(34) Zhao, X.; Johnston, C.; Grant, P. S. *J. Mater. Chem.* **2009**, *19*, 8755.

- (35) Sathiya, M.; Prakash, A. S.; Ramesha, K.; Tarascon, J. M.; Shukla, A. K. *J. Am. Chem. Soc.* **2011**, *133*, 16291.
- (36) Hahm, M. G.; Leela Mohana Reddy, A.; Cole, D. P.; Rivera, M.; Vento, J. A.; Nam, J.; Jung, H. Y.; Kim, Y. L.; Narayanan, N. T.; Hashim, D. P.; Galande, C.; Jung, Y. J.; Bundy, M.; Karna, S.; Ajayan, P. M.; Vajtai, R. *Nano Lett.* **2012**, *12*, 5616.
- (37) Tamailarasan, P.; Ramaprabhu, S. *J. Phys. Chem. C* **2012**, *116*, 14179.
- (38) Jha, N.; Ramesh, P.; Bekyarova, E.; Itkis, M. E.; Haddon, R. C. *Adv. Energy Mater.* **2012**, *2*, 438.
- (39) Huang, C.-W.; Wu, C.-A.; Hou, S.-S.; Kuo, P.-L.; Hsieh, C.-T.; Teng, H. *Adv. Funct. Mater.* **2012**, *22*, 4677.
- (40) Hu, S.; Rajamani, R.; Yu, X. *Appl. Phys. Lett.* **2012**, *100*.
- (41) Gao, H.; Xiao, F.; Ching, C. B.; Duan, H. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2801.
- (42) Gao, H.; Xiao, F.; Ching, C. B.; Duan, H. *ACS Appl. Mater. Interfaces* **2012**, *4*, 7020.
- (43) Chen, P. C.; Shen, G. Z.; Shi, Y.; Chen, H. T.; Zhou, C. W. *Acs Nano* **2010**, *4*, 4403.
- (44) Randles, J. E. B. *Discuss. Faraday Soc.* **1947**, *1*, 11.
- (45) Beidaghi, M.; Gogotsi, Y. *Energ. Environ. Sci.* **2014**, *7*, 867.
- (46) Yu, G.; Xie, X.; Pan, L.; Bao, Z.; Cui, Y. *Nano Energy* **2013**, *2*, 213.
- (47) Nyholm, L.; Nystrom, G.; Mihranyan, A.; Stromme, M. *Adv. Mater.* **2011**, *23*, 3751.
- (48) Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. *Science* **2006**, *313*, 1760.
- (49) Pandolfo, A. G.; Hollenkamp, A. F. *J. Power Sources* **2006**, *157*, 11.
- (50) Bose, S.; Kuila, T.; Mishra, A. K.; Rajasekar, R.; Kim, N. H.; Lee, J. H. *J. Mater. Chem.* **2012**, *22*, 767.
- (51) Frackowiak, E.; Béguin, F. *Carbon* **2001**, *39*, 937.

- (52) Barbieri, O.; Hahn, M.; Herzog, A.; Kätz, R. *Carbon* **2005**, *43*, 1303.
- (53) Kierzek, K.; Frackowiak, E.; Lota, G.; Gryglewicz, G.; Machnikowski, J. *Electrochim. Acta* **2004**, *49*, 515.
- (54) Iijima, S. *Nature* **1991**, *354*, 56.
- (55) Zhou, K. G.; Mao, N. N.; Wang, H. X.; Peng, Y.; Zhang, H. L. *Angew. Chem. Int. Ed. Engl.* **2011**, *50*, 10839.
- (56) Hu, L.; Wu, H.; Cui, Y. *Appl. Phys. Lett.* **2010**, *96*, 183502.
- (57) Compton, O. C.; Nguyen, S. T. *Small* **2010**, *6*, 711.
- (58) Futaba, D. N.; Hata, K.; Yamada, T.; Hiraoka, T.; Hayamizu, Y.; Kakudate, Y.; Tanaike, O.; Hatori, H.; Yumura, M.; Iijima, S. *Nat. Mater.* **2006**, *5*, 987.
- (59) Lu, Z.; Chang, Z.; Liu, J.; Sun, X. *Nano Res.* **2011**, *4*, 658.
- (60) Taberna, P.-L.; Chevallier, G.; Simon, P.; Plé, D.; Aubert, T. *Mater. Res. Bull.* **2006**, *41*, 478.
- (61) Bordjiba, T.; Mohamedi, M.; Dao, L. H. *Adv. Mater.* **2008**, *20*, 815.
- (62) Lee, S. W.; Kim, J.; Chen, S.; Hammond, P. T.; Shao-Horn, Y. *ACS Nano* **2010**, *4*, 3889.
- (63) Ma, S. B.; Ahn, K. Y.; Lee, E. S.; Oh, K. H.; Kim, K. B. *Carbon* **2007**, *45*, 375.
- (64) Meng, C.; Liu, C.; Chen, L.; Hu, C.; Fan, S. *Nano Lett.* **2010**, *10*, 4025.
- (65) Zhou, C.; Kumar, S.; Doyle, C. D.; Tour, J. M. *Chem. Mater.* **2005**, *17*, 1997.
- (66) Zhou, Y.; Qin, Z.-Y.; Li, L.; Zhang, Y.; Wei, Y.-L.; Wang, L.-F.; Zhu, M.-F. *Electrochim. Acta* **2010**, *55*, 3904.
- (67) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. *Science* **2004**, *306*, 666.
- (68) Wang, Y.; Wu, Y.; Huang, Y.; Zhang, F.; Yang, X.; Ma, Y.; Chen, Y. *J. Phys. Chem. C* **2011**, *115*, 23192.

(69)Cheng, Y.; Lu, S.; Zhang, H.; Varanasi, C. V.; Liu, J. *Nano Lett.* **2012**, *12*, 4206.

(70)Yan, Z.; Ma, L.; Zhu, Y.; Lahiri, I.; Hahm, M. G.; Liu, Z.; Yang, S.; Xiang, C.; Lu, W.; Peng, Z.; Sun, Z.; Kittrell, C.; Lou, J.; Choi, W.; Ajayan, P. M.; Tour, J. M. *ACS Nano* **2012**, *7*, 58.

(71)Fan, Z.; Yan, J.; Zhi, L.; Zhang, Q.; Wei, T.; Feng, J.; Zhang, M.; Qian, W.; Wei, F. *Adv. Mater.* **2010**, *22*, 3723.

(72)Zhu, Y.; Li, L.; Zhang, C.; Casillas, G.; Sun, Z.; Yan, Z.; Ruan, G.; Peng, Z.; Raji, A.-R. O.; Kittrell, C.; Hauge, R. H.; Tour, J. M. *Nat Commun* **2012**, *3*, 1225.

(73)Ania, C. O.; Khomenko, V.; Raymundo-Piñero, E.; Parra, J. B.; Béguin, F. *Adv. Funct. Mater.* **2007**, *17*, 1828.

(74)Wang, D.-W.; Li, F.; Liu, M.; Lu, G. Q.; Cheng, H.-M. *Angew. Chem. Int. Ed. Engl.* **2008**, *47*, 373.

(75)Xu, B.; Wu, F.; Chen, R.; Cao, G.; Chen, S.; Zhou, Z.; Yang, Y. *Electrochem. Commun.* **2008**, *10*, 795.

(76)Hu, S.; Zhang, S.; Pan, N.; Hsieh, Y.-L. *J. Power Sources* **2014**, *270*, 106.

(77)Wang, G.; Wang, H.; Lu, X.; Ling, Y.; Yu, M.; Zhai, T.; Tong, Y.; Li, Y. *Adv. Mater.* **2014**, *26*, 2676.

(78)Li, J.; Wang, X.; Huang, Q.; Gamboa, S.; Sebastian, P. J. *J. Power Sources* **2006**, *158*, 784.

(79)Hao, P.; Zhao, Z.; Tian, J.; Li, H.; Sang, Y.; Yu, G.; Cai, H.; Liu, H.; Wong, C. P.; Umar, A. *Nanoscale* **2014**, *6*, 12120.

(80)Trasatti, S.; Buzzanca, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1971**, *29*, A1.

(81)Li, J.; Zhao, W.; Huang, F.; Manivannan, A.; Wu, N. *Nanoscale* **2011**, *3*, 5103.

(82)Lu, P.; Liu, F.; Xue, D.; Yang, H.; Liu, Y. *Electrochim. Acta* **2012**, *78*, 1.

(83)Freitas, M. B. J. G. *J. Power Sources* **2001**, *93*, 163.

- (84) Patil, U. M.; Gurav, K. V.; Fulari, V. J.; Lokhande, C. D.; Joo, O. S. *J. Power Sources* **2009**, *188*, 338.
- (85) Han, D.; Xu, P.; Jing, X.; Wang, J.; Yang, P.; Shen, Q.; Liu, J.; Song, D.; Gao, Z.; Zhang, M. *J. Power Sources* **2013**, *235*, 45.
- (86) Toupin, M.; Brousse, T.; Bédanger, D. *Chem. Mater.* **2004**, *16*, 3184.
- (87) Peng, L.; Peng, X.; Liu, B.; Wu, C.; Xie, Y.; Yu, G. *Nano Lett.* **2013**, *13*, 2151.
- (88) Huang, H. J.; Wang, X. *Nanoscale* **2011**, *3*, 3185.
- (89) Hou, Y.; Cheng, Y. W.; Hobson, T.; Liu, J. *Nano Lett.* **2010**, *10*, 2727.
- (90) Hu, L.; Chen, W.; Xie, X.; Liu, N.; Yang, Y.; Wu, H.; Yao, Y.; Pasta, M.; Alshareef, H. N.; Cui, Y. *ACS Nano* **2011**, *5*, 8904.
- (91) Qorbani, M.; Naseri, N.; Moshfegh, A. Z. *ACS Appl. Mater. Interfaces* **2015**, *7*, 11172.
- (92) Yang, Q.; Lu, Z.; Sun, X.; Liu, J. *Sci. Rep.* **2013**, *3*.
- (93) Jing, M.; Yang, Y.; Zhu, Y.; Hou, H.; Wu, Z.; Ji, X. *Electrochim. Acta* **2014**, *141*, 234.
- (94) Xia, X.-h.; Tu, J.-p.; Mai, Y.-j.; Wang, X.-l.; Gu, C.-d.; Zhao, X.-b. *J. Mater. Chem.* **2011**, *21*, 9319.
- (95) Ma, Z.; Huang, X.; Dou, S.; Wu, J.; Wang, S. *J. Phys. Chem. C* **2014**, *118*, 17231.
- (96) Yang, W.; Gao, Z.; Wang, J.; Wang, B.; Liu, L. *Solid State Sci.* **2013**, *20*, 46.
- (97) Wang, Z.; Ma, C.; Wang, H.; Liu, Z.; Hao, Z. *J. Alloys Compd.* **2013**, *552*, 486.
- (98) Wang, H.; Xu, Z.; Yi, H.; Wei, H.; Guo, Z.; Wang, X. *Nano Energy* **2014**, *7*, 86.
- (99) Qu, Q.; Yang, S.; Feng, X. *Adv. Mater.* **2011**, *23*, 5574.
- (100) Perera, S. D.; Patel, B.; Nijem, N.; Roodenko, K.; Seitz, O.; Ferraris, J. P.; Chabal, Y. J.; Balkus, K. J. *Adv. Energy Mater.* **2011**, *1*, 936.

- (101) Wee, G.; Soh, H. Z.; Cheah, Y. L.; Mhaisalkar, S. G.; Srinivasan, M. *J. Mater. Chem.* **2010**, *20*, 6720.
- (102) Kim, I.-H.; Kim, J.-H.; Cho, B.-W.; Lee, Y.-H.; Kim, K.-B. *J. Electrochem. Soc.* **2006**, *153*, A989.
- (103) Yang, Y.; Kim, D.; Yang, M.; Schmuki, P. *Chem. Commun.* **2011**, *47*, 7746.
- (104) Deng, W.; Ji, X.; Chen, Q.; Banks, C. E. *RSC Adv.* **2011**, *1*, 1171.
- (105) Wu, Z.-S.; Wang, D.-W.; Ren, W.; Zhao, J.; Zhou, G.; Li, F.; Cheng, H.-M. *Adv. Funct. Mater.* **2010**, *20*, 3595.
- (106) Hu, C.-C.; Chang, K.-H.; Lin, M.-C.; Wu, Y.-T. *Nano Lett.* **2006**, *6*, 2690.
- (107) Kim, Y.-T.; Tadai, K.; Mitani, T. *J. Mater. Chem.* **2005**, *15*, 4914.
- (108) Sugimoto, W.; Makino, S.; Mukai, R.; Tatsumi, Y.; Fukuda, K.; Takasu, Y.; Yamauchi, Y. *J. Power Sources* **2012**, *204*, 244.
- (109) Lang, J.-W.; Kong, L.-B.; Wu, W.-J.; Luo, Y.-C.; Kang, L. *Chem. Commun.* **2008**, 4213.
- (110) Xia, X.-h.; Tu, J.-p.; Wang, X.-l.; Gu, C.-d.; Zhao, X.-b. *J. Mater. Chem.* **2011**, *21*, 671.
- (111) Sun, G.; Liu, J.; Zhang, X.; Wang, X.; Li, H.; Yu, Y.; Huang, W.; Zhang, H.; Chen, P. *Angew. Chem. Int. Ed. Engl.* **2014**, *53*, 12576.
- (112) Cai, F.-S.; Zhang, G.-Y.; Chen, J.; Gou, X.-L.; Liu, H.-K.; Dou, S.-X. *Angew. Chem. Int. Ed. Engl.* **2004**, *43*, 4212.
- (113) Cao, F.; Pan, G. X.; Xia, X. H.; Tang, P. S.; Chen, H. F. *J. Power Sources* **2014**, *264*, 161.
- (114) Lakshmi, V.; Ranjusha, R.; Vineeth, S.; Nair, S. V.; Balakrishnan, A. *Colloids Surf. A Physicochem. Eng. Asp.* **2014**, *457*, 462.
- (115) Vidhyadharan, B.; Zain, N. K. M.; Misnon, I. I.; Aziz, R. A.; Ismail, J.; Yusoff, M. M.; Jose, R. *J. Alloys Compd.* **2014**, *610*, 143.
- (116) Jiang, H.; Li, C.; Sun, T.; Ma, J. *Chem. Commun.* **2012**, *48*, 2606.

- (117) Yang, D.; Wang, R.; Zhang, J.; Liu, Z. *J. Phys. Chem. B* **2004**, *108*, 7531.
- (118) Behm, N.; Brokaw, D.; Overson, C.; Peloquin, D.; Poler, J. *J. Mater. Sci.* **2013**, *48*, 1711.
- (119) Wang, H.; Casalongue, H. S.; Liang, Y.; Dai, H. *J. Am. Chem. Soc.* **2010**, *132*, 7472.
- (120) Ren, Y.; Gao, L. *J. Am. Chem. Soc.* **2010**, *93*, 3560.
- (121) Mondal, C.; Ganguly, M.; Manna, P. K.; Yusuf, S. M.; Pal, T. *Langmuir* **2013**, *29*, 9179.
- (122) Wang, Y.; Gai, S.; Li, C.; He, F.; Zhang, M.; Yan, Y.; Yang, P. *Electrochim. Acta* **2013**, *90*, 673.
- (123) Yan, X.; Tong, X.; Wang, J.; Gong, C.; Zhang, M.; Liang, L. *Mater. Lett.* **2013**, *95*, 1.
- (124) Zhao, D.-D.; Bao, S.-J.; Zhou, W.-J.; Li, H.-L. *Electrochem. Commun.* **2007**, *9*, 869.
- (125) Duan, G.; Cai, W.; Luo, Y.; Sun, F. *Adv. Funct. Mater.* **2007**, *17*, 644.
- (126) Jianwei, L.; Jeremy, E.; Jun, L. *Chem. Mater.* **2010**, *22*.
- (127) Wei, W. F. W. W. F.; Cui, X. W.; Chen, W. X.; Ivey, D. G. *Chemical Society Reviews* **2011**, *40*, 1697.
- (128) Shahid, M.; Liu, J.; Shakir, I.; Warsi, M. F.; Nadeem, M.; Kwon, Y.-U. *Electrochim. Acta* **2012**, *85*, 243.
- (129) Wang, Y.-g.; Yu, L.; Xia, Y.-y. *J. Electrochem. Soc.* **2006**, *153*, A743.
- (130) Salunkhe, R. R.; Lin, J.; Malgras, V.; Dou, S. X.; Kim, J. H.; Yamauchi, Y. *Nano Energy* **2015**, *11*, 211.
- (131) Gund, G. S.; Dubal, D. P.; Shinde, S. S.; Lokhande, C. D. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3176.
- (132) Tang, Z.; Tang, C.-h.; Gong, H. *Adv. Funct. Mater.* **2012**, *22*, 1272.
- (133) Zheng, J. P.; Jow, T. R. *J. Electrochem. Soc.* **1995**, *142*, L6.

- (134) Lee, H. Y.; Goodenough, J. B. *J Solid State Chem.* **1999**, *144*, 220.
- (135) Lee, H. Y.; Manivannan, V.; Goodenough, J. B. *Cr. Acad. Sci. II C.* **1999**, *2*, 565.
- (136) Wei, W.; Cui, X.; Chen, W.; Ivey, D. G. *Chem. Soc. Rev.* **2011**, *40*, 1697.
- (137) Ni, J.; Lu, W.; Zhang, L.; Yue, B.; Shang, X.; Lv, Y. *J. Phys. Chem. C* **2009**, *113*, 54.
- (138) Liu, R.; Lee, S. B. *J. Am. Chem. Soc.* **2008**, *130*, 2942.
- (139) Subramanian, V.; Zhu, H.; Vajtai, R.; Ajayan, P. M.; Wei, B. *J. Phys. Chem. B* **2005**, *109*, 20207.
- (140) Jiang, H.; Sun, T.; Li, C.; Ma, J. *J. Mater. Chem.* **2012**, *22*, 2751.
- (141) Yan, W.; Ayvazian, T.; Kim, J.; Liu, Y.; Donavan, K. C.; Xing, W.; Yang, Y.; Hemminger, J. C.; Penner, R. M. *ACS Nano* **2011**, *5*, 8275.
- (142) Yan, W.; Kim, J. Y.; Xing, W.; Donavan, K. C.; Ayvazian, T.; Penner, R. M. *Chem. Mater.* **2012**, *24*, 2382.
- (143) Zhao, X.; Zhang, L.; Murali, S.; Stoller, M. D.; Zhang, Q.; Zhu, Y.; Ruoff, R. S. *ACS Nano* **2012**, *6*, 5404.
- (144) Fischer, A. E.; Pettigrew, K. A.; Rolison, D. R.; Stroud, R. M.; Long, J. W. *Nano Lett.* **2007**, *7*, 281.
- (145) Yan, J.; Fan, Z.; Wei, T.; Qian, W.; Zhang, M.; Wei, F. *Carbon* **2009**, *47*, 3371.
- (146) Lang, X.; Hirata, A.; Fujita, T.; Chen, M. *Nat. Nanotechnol.* **2011**, *6*, 232.
- (147) Li, Q.; Wang, Z.-L.; Li, G.-R.; Guo, R.; Ding, L.-X.; Tong, Y.-X. *Nano Lett.* **2012**, *12*, 3803.
- (148) Yang, D. *J. Power Sources* **2012**, *198*, 416.
- (149) Yoo, H. N.; Park, D. H.; Hwang, S.-J. *J. Power Sources* **2008**, *185*, 1374.
- (150) Zhang, Z.-a.; Lai, Y.-q.; Li, J.; Liu, Y.-x. *J. Cent. South Univ. T.* **2007**,

14, 638.

(151) Kang, J.; Hirata, A.; Kang, L.; Zhang, X.; Hou, Y.; Chen, L.; Li, C.; Fujita, T.; Akagi, K.; Chen, M. *Angew. Chem. Int. Ed. Engl.* **2013**, *125*, 1708.

(152) Li, Y.; Xie, H. *Ionics* **2010**, *16*, 21.

(153) Ragupathy, P.; Park, D. H.; Campet, G.; Vasan, H. N.; Hwang, S.-J.; Choy, J.-H.; Munichandraiah, N. *J. Phys. Chem. C* **2009**, *113*, 6303.

(154) Devaraj, S.; Munichandraiah, N. *J. Electrochem. Soc.* **2007**, *154*, A80.

(155) Shi, Y.; Peng, L.; Ding, Y.; Zhao, Y.; Yu, G. *Chem. Soc. Rev.* **2015**.

(156) Dubal, D. P.; Lee, S. H.; Kim, J. G.; Kim, W. B.; Lokhande, C. D. *J. Mater. Chem.* **2012**, *22*, 3044.

(157) Snook, G. A.; Kao, P.; Best, A. S. *J. Power Sources* **2011**, *196*, 1.

(158) Sivaraman, P.; Kushwaha, R. K.; Shashidhara, K.; Hande, V. R.; Thakur, A. P.; Samui, A. B.; Khandpekar, M. M. *Electrochim. Acta* **2010**, *55*, 2451.

(159) Xue, M.; Li, F.; Zhu, J.; Song, H.; Zhang, M.; Cao, T. *Adv. Funct. Mater.* **2012**, *22*, 1284.

(160) Antiohos, D.; Folkes, G.; Sherrell, P.; Ashraf, S.; Wallace, G. G.; Aitchison, P.; Harris, A. T.; Chen, J.; Minett, A. I. *J. Mater. Chem.* **2011**, *21*, 15987.

(161) Zang, J.; Li, X. *J. Mater. Chem.* **2011**, *21*, 10965.

(162) Malinauskas, A. *Polymer* **2001**, *42*, 3957.

(163) Long, J. W.; Bédanger, D.; Brousse, T.; Sugimoto, W.; Sassini, M. B.; Crosnier, O. *MRS Bulletin* **2011**, *36*, 513.

(164) Peng, C.; Zhang, S.; Zhou, X.; Chen, G. Z. *Energ. Environ. Sci.* **2010**, *3*, 1499.

(165) Qu, Q.; Zhang, P.; Wang, B.; Chen, Y.; Tian, S.; Wu, Y.; Holze, R. *J. Phys. Chem. C* **2009**, *113*, 14020.

(166) Fan, Z.; Yan, J.; Wei, T.; Zhi, L.; Ning, G.; Li, T.; Wei, F. *Adv. Funct.*

Mater. **2011**, *21*, 2366.

(167) Liu, J.; Zhang, L.; Wu, H. B.; Lin, J.; Shen, Z.; Lou, X. W. *Energ. Environ. Sci.* **2014**, *7*, 3709.

(168) Chen, L.-F.; Huang, Z.-H.; Liang, H.-W.; Guan, Q.-F.; Yu, S.-H. *Adv. Mater.* **2013**, *25*, 4746.

(169) Tang, C.-h.; Yin, X.; Gong, H. *ACS Appl. Mater. Interfaces* **2013**, *5*, 10574.

(170) Park, H. W.; Ju, Y. T.; Park, S.-M.; Roh, K. C. *RSC Adv.* **2014**, *4*, 567.

(171) Wang, Y.-g.; Yu, L.; Xia, Y.-y. *Journal of The Electrochemical Society* **2006**, *153*, A743.

(172) Chen, X.; Qiu, L.; Ren, J.; Guan, G.; Lin, H.; Zhang, Z.; Chen, P.; Wang, Y.; Peng, H. *Adv. Mater.* **2013**, *25*, 6436.

(173) Zhang, J.; Jiang, J.; Li, H.; Zhao, X. S. *Energ. Environ. Sci.* **2011**, *4*, 4009.

(174) Wang, Y.-G.; Wang, Z.-D.; Xia, Y.-Y. *Electrochim. Acta* **2005**, *50*, 5641.

(175) Nagaraju, D. H.; Wang, Q.; Beaujuge, P.; Alshareef, H. N. *J. Mater. Chem. A* **2014**, *2*, 17146.

(176) Wang, X.; Sumboja, A.; Lin, M.; Yan, J.; Lee, P. S. *Nanoscale* **2012**, *4*, 7266.

(177) Nishide, H.; Oyaizu, K. *Science* **2008**, *319*, 737.

(178) Rogers, J. A.; Someya, T.; Huang, Y. G. *Science* **2010**, *327*, 1603.

(179) Scrosati, B. *Nat. Nanotechnol.* **2007**, *2*, 598.

(180) Tarascon, J. M.; Armand, M. *Nature* **2001**, *414*, 359.

(181) Yu, C.; Masarapu, C.; Rong, J.; Wei, B.; Jiang, H. *Adv. Mater.* **2009**, *21*, 4793.

(182) Chou, S.-L.; Wang, J.-Z.; Chew, S.-Y.; Liu, H.-K.; Dou, S.-X. *Electrochem. Commun.* **2008**, *10*, 1724.

- (183) Wang, D.-W.; Li, F.; Zhao, J.; Ren, W.; Chen, Z.-G.; Tan, J.; Wu, Z.-S.; Gentle, I.; Lu, G. Q.; Cheng, H.-M. *ACS Nano* **2009**, *3*, 1745.
- (184) Li, Z.; Mi, Y.; Liu, X.; Liu, S.; Yang, S.; Wang, J. *J. Mater. Chem.* **2011**, *21*, 14706.
- (185) Liu, F.; Song, S.; Xue, D.; Zhang, H. *Adv. Mater.* **2012**, *24*, 1089.
- (186) Wang, L.; Li, C.; Wang, D.; Dong, Z.; Zhang, F. X.; Jin, J. *J. Nanosci. Nanotechnol.* **2013**, *13*, 5461.
- (187) Jin, Y.; Chen, H.; Chen, M.; Liu, N.; Li, Q. *ACS Appl. Mater. Interfaces* **2013**, *5*, 3408.
- (188) Huang, Y.; Hu, H.; Huang, Y.; Zhu, M.; Meng, W.; Liu, C.; Pei, Z.; Hao, C.; Wang, Z.; Zhi, C. *ACS Nano* **2015**, *9*, 4766.
- (189) Le, V. T.; Kim, H.; Ghosh, A.; Kim, J.; Chang, J.; Vu, Q. A.; Pham, D. T.; Lee, J.-H.; Kim, S.-W.; Lee, Y. H. *ACS Nano* **2013**, *7*, 5940.
- (190) Yu, D.; Qian, Q.; Wei, L.; Jiang, W.; Goh, K.; Wei, J.; Zhang, J.; Chen, Y. *Chem. Soc. Rev.* **2015**, *44*, 647.
- (191) Sawangphruk, M.; Srimuk, P.; Chiochan, P.; Krittayavathananon, A.; Luanwuthi, S.; Limtrakul, J. *Carbon* **2013**, *60*, 109.
- (192) Jost, K.; Stenger, D.; Perez, C. R.; McDonough, J. K.; Lian, K.; Gogotsi, Y.; Dion, G. *Energ. Environ. Sci.* **2013**, *6*, 2698.
- (193) Du, J.; Zhou, G.; Zhang, H.; Cheng, C.; Ma, J.; Wei, W.; Chen, L.; Wang, T. *ACS Appl. Mater. Interfaces* **2013**, *5*, 7405.
- (194) Dubal, D. P.; Gund, G. S.; Lokhande, C. D.; Holze, R. *ACS Appl. Mater. Interfaces* **2013**, *5*, 2446.
- (195) Dubal, D. P.; Holze, R. *J. Power Sources* **2013**, *238*, 274.
- (196) Gui, Z.; Zhu, H.; Gillette, E.; Han, X.; Rubloff, G. W.; Hu, L.; Lee, S. B. *ACS Nano* **2013**, *7*, 6037.
- (197) Weng, Z.; Su, Y.; Wang, D.-W.; Li, F.; Du, J.; Cheng, H.-M. *Adv. Energy Mater.* **2011**, *1*, 917.
- (198) Yun, T. G.; Oh, M.; Hu, L.; Hyun, S.; Han, S. M. *J. Power Sources* **2013**, *244*, 783.

- (199) Pasta, M.; La Mantia, F.; Hu, L.; Deshazer, H.; Cui, Y. *Nano Res.* **2010**, 3, 452.
- (200) Shi, S.; Xu, C.; Yang, C.; Chen, Y.; Liu, J.; Kang, F. *Sci. Rep.* **2013**, 3.
- (201) Kaempgen, M.; Chan, C. K.; Ma, J.; Cui, Y.; Gruner, G. *Nano Lett.* **2009**, 9, 1872.
- (202) Yu Jin, K.; Haegeun, C.; Chi-Hwan, H.; Woong, K. *Nanotechnology* **2012**, 23, 065401.
- (203) Roberts, J. C. *The Chemistry of Paper*; The Royal Society of Chemistry: Cambridge, UK, 1996.
- (204) Tobj örk, D.; Österbacka, R. *Adv. Mater.* **2011**, 23, 1935.
- (205) Hu, L.; Cui, Y. *Energ. Environ. Sci.* **2012**, 5, 6423.
- (206) Jin, W.; Linlin, L.; Chui Ling, W.; Srinivasan, M. *Nanotechnology* **2012**, 23, 495401.
- (207) Kang, Y. J.; Chun, S.-j.; Lee, S.-s.; Kim, B.-y.; Kim, J. H.; Chung, H. *ACS Nano* **2012**, 6, 6400.
- (208) Pushparaj, V. L.; Shaijumon, M. M.; Kumar, A.; Murugesan, S.; Ci, L.; Vajtai, R.; Linhardt, R. J.; Nalamasu, O.; Ajayan, P. M. *P. Natl. Acad. Sci. USA* **2007**, 104, 13574.
- (209) Hu, L.; Choi, J. W.; Yang, Y.; Jeong, S.; La Mantia, F.; Cui, L.-F.; Cui, Y. *P. Natl. Acad. Sci. USA* **2009**.
- (210) Weng, Z.; Su, Y.; Wang, D.-W.; Li, F.; Du, J.; Cheng, H.-M. *Advanced Energy Materials* **2011**, 1, 917.
- (211) Zheng, G.; Hu, L.; Wu, H.; Xie, X.; Cui, Y. *Energy Environ. Sci.* **2011**, 3368.
- (212) Hu, L.; Zheng, G.; Yao, J.; Liu, N.; Weil, B.; Eskilsson, M.; Karabulut, E.; Ruan, Z.; Fan, S.; Bloking, J. T.; McGehee, M. D.; Wagberg, L.; Cui, Y. *Energ. Environ. Sci.* **2013**, 6, 513.
- (213) Nyström, G.; Mihranyan, A.; Razaq, A.; Lindström, T.; Nyholm, L.; Strømme, M. *J. Phys. Chem. B* **2010**, 114, 4178.

- (214) Mihranyan, A.; Nyholm, L.; Bennett, A. E. G.; Strømme, M. *J. Phys. Chem. B* **2008**, *112*, 12249.
- (215) Johnston, J. H.; Moraes, J.; Borrmann, T. *Synthetic Met.* **2005**, *153*, 65.
- (216) Nyström, G.; Razaq, A.; Strømme, M.; Nyholm, L.; Mihranyan, A. *Nano Lett.* **2009**, *9*, 3635.
- (217) Hu, L.; Choi, J. W.; Yang, Y.; Jeong, S.; La Mantia, F.; Cui, L.-F.; Cui, Y. *Proceedings of the National Academy of Sciences of the United States of America* **2009**, *106*, 21490.
- (218) Kang, Y. J.; Kim, B.; Chung, H.; Kim, W. *Synthetic Met.* **2010**, *160*, 2510.
- (219) Kang, Y. J.; Chun, S.-J.; Lee, S.-S.; Kim, B.-Y.; Kim, J. H.; Chung, H.; Lee, S.-Y.; Kim, W. *Acs Nano* **2012**, *6*, 6400.
- (220) Weng, Z.; Su, Y.; Wang, D.-W.; Li, F.; Du, J.; Cheng, H.-M. *Adv. Energy Mater.* **2011**, *1*, 917.
- (221) Hu, S.; Rajamani, R.; Yu, X. *Applied Physics Letters* **2012**, *100*, 104103.
- (222) Zheng, G.; Hu, L.; Wu, H.; Xie, X.; Cui, Y. *Energy & Environmental Science* **2011**, *4*, 3368.
- (223) Kang, Y. J.; Kim, B.; Chung, H.; Kim, W. *Synthetic Metals* **2010**, *160*, 2510.
- (224) El-Kady, M. F.; Kaner, R. B. *Nat Commun* **2013**, *4*, 1475.
- (225) Wang, Z. L. *Nano Today* **2010**, *5*, 512.
- (226) Chmiola, J.; Largeot, C.; Taberna, P.-L.; Simon, P.; Gogotsi, Y. *Science* **2010**, *328*, 480.
- (227) Gao, W.; Singh, N.; Song, L.; Liu, Z.; Reddy, A. L. M.; Ci, L.; Vajtai, R.; Zhang, Q.; Wei, B.; Ajayan, P. M. *Nat. Nanotechnol.* **2011**, *6*, 496.
- (228) Beidaghi, M.; Wang, C. *Adv. Funct. Mater.* **2012**, *22*, 4501.
- (229) Wu, Z.-S.; Feng, X.; Cheng, H.-M. *Nat. Sci. Rev.* **2013**.

- (230) Pech, D.; Brunet, M.; Dinh, T. M.; Armstrong, K.; Gaudet, J.; Guay, D. *J. Power Sources* **2013**, 230, 230.
- (231) Yoo, J. J.; Balakrishnan, K.; Huang, J.; Meunier, V.; Sumpter, B. G.; Srivastava, A.; Conway, M.; Mohana Reddy, A. L.; Yu, J.; Vajtai, R.; Ajayan, P. M. *Nano Lett.* **2011**, 11, 1423.
- (232) Cai, X.; Peng, M.; Yu, X.; Fu, Y.; Zou, D. *J. Mater. Chem. C* **2014**, 2, 1184.
- (233) Jost, K.; Dion, G.; Gogotsi, Y. *J. Mater. Chem. A* **2014**, 2, 10776.
- (234) Bae, J.; Song, M. K.; Park, Y. J.; Kim, J. M.; Liu, M.; Wang, Z. L. *Angew. Chem. Int. Ed. Engl.* **2011**, 50, 1683.
- (235) Xiao, X.; Li, T.; Yang, P.; Gao, Y.; Jin, H.; Ni, W.; Zhan, W.; Zhang, X.; Cao, Y.; Zhong, J.; Gong, L.; Yen, W.-C.; Mai, W.; Chen, J.; Huo, K.; Chueh, Y.-L.; Wang, Z. L.; Zhou, J. *ACS Nano* **2012**, 6, 9200.
- (236) Jin, H.; Zhou, L.; Mak, C. L.; Huang, H.; Tang, W. M.; Chan, H. L. W. *Nano Energy* **2015**, 11, 662.
- (237) Behabtu, N.; Young, C. C.; Tsentalovich, D. E.; Kleinerman, O.; Wang, X.; Ma, A. W. K.; Bengio, E. A.; ter Waarbeek, R. F.; de Jong, J. J.; Hoogerwerf, R. E.; Fairchild, S. B.; Ferguson, J. B.; Maruyama, B.; Kono, J.; Talmon, Y.; Cohen, Y.; Otto, M. J.; Pasquali, M. *Science* **2013**, 339, 182.
- (238) Xu, P.; Wei, B.; Cao, Z.; Zheng, J.; Gong, K.; Li, F.; Yu, J.; Li, Q.; Lu, W.; Byun, J.-H.; Kim, B.-S.; Yan, Y.; Chou, T.-W. *ACS Nano* **2015**, 9, 6088.
- (239) Meng, Q.; Wu, H.; Meng, Y.; Xie, K.; Wei, Z.; Guo, Z. *Adv. Mater.* **2014**, 26, 4100.
- (240) Aboutalebi, S. H.; Jalili, R.; Esrafilzadeh, D.; Salari, M.; Gholamvand, Z.; Aminorroaya Yamini, S.; Konstantinov, K.; Shepherd, R. L.; Chen, J.; Moulton, S. E.; Innis, P. C.; Minett, A. I.; Razal, J. M.; Wallace, G. G. *ACS Nano* **2014**, 8, 2456.
- (241) Ma, Y.; Li, P.; Sedloff, J. W.; Zhang, X.; Zhang, H.; Liu, J. *ACS Nano* **2015**, 9, 1352.
- (242) Kou, L.; Huang, T.; Zheng, B.; Han, Y.; Zhao, X.; Gopalsamy, K.; Sun, H.; Gao, C. *Nat Commun* **2014**, 5, 3754.

- (243) Chen, Q.; Meng, Y.; Hu, C.; Zhao, Y.; Shao, H.; Chen, N.; Qu, L. *J. Power Sources* **2014**, *247*, 32.
- (244) Yu, D.; Goh, K.; Zhang, Q.; Wei, L.; Wang, H.; Jiang, W.; Chen, Y. *Adv. Mater.* **2014**, *26*, 6790.
- (245) Wu, Z.; Huang, X.-L.; Wang, Z.-L.; Xu, J.-J.; Wang, H.-G.; Zhang, X.-B. *Sci. Rep.* **2014**, *4*, 3669.
- (246) Kim, B. K.; Chabot, V.; Yu, A. *Electrochim. Acta* **2013**, *109*, 370.
- (247) Shakir, I.; Ali, Z.; Bae, J.; Park, J.; Kang, D. J. *RSC Adv.* **2014**, *4*, 6324.
- (248) Bitao, D.; Han, Z.; Jin, L.; Lusi, Z.; Guoxin, G.; Shujiang, D. *Nanotechnology* **2014**, *25*, 435403.
- (249) Nam, K.-W.; Kim, K.-H.; Lee, E.-S.; Yoon, W.-S.; Yang, X.-Q.; Kim, K.-B. *J. Power Sources* **2008**, *182*, 642.
- (250) Wang, Y.; Zhitomirsky, I. *Langmuir* **2009**, *25*, 9684.
- (251) Ruifeng, Z.; Chuizhou, M.; Feng, Z.; Qunqing, L.; Changhong, L.; Shoushan, F.; Kaili, J. *Nanotechnology* **2010**, *21*, 345701.
- (252) Zhang, L. L.; Xiong, Z.; Zhao, X. S. *J. Power Sources* **2013**, *222*, 326.
- (253) Chen, S.; Zhu, J.; Zhou, H.; Wang, X. *RSC Adv.* **2011**, *1*, 484.
- (254) Jeevanandam, P.; Koltypin, Y.; Gedanken, A. *Nano Lett.* **2001**, *1*, 263.
- (255) Oliva, P.; Leonardi, J.; Laurent, J. F.; Delmas, C.; Braconnier, J. J.; Figlarz, M.; Fievet, F.; Deguibert, A. *J. Power Sources* **1982**, *8*, 229.
- (256) Lu, Q.; Mellinger, Z. J.; Wang, W.; Li, W.; Chen, Y.; Chen, J. G.; Xiao, J. Q. *ChemSusChem* **2010**, *3*, 1367.
- (257) Jiang, W.; Zhang, K.; Wei, L.; Yu, D.; Wei, J.; Chen, Y. *Nanoscale* **2013**, *5*, 11108.
- (258) Li, H.; Gao, Y.; Wang, C.; Yang, G. *Adv. Energy Mater.* **2015**, *5*, 1401767.

- (259) Huang, T.; Zheng, B.; Kou, L.; Gopalsamy, K.; Xu, Z.; Gao, C.; Meng, Y.; Wei, Z. *RSC Adv.* **2013**, 3, 23957.
- (260) Fu, Y.; Song, J.; Zhu, Y.; Cao, C. *J. Power Sources* **2014**, 262, 344.
- (261) Liu, C.; Li, Y. *J. Alloys Compd.* **2009**, 478, 415.
- (262) Nai, J.; Tian, Y.; Guan, X.; Guo, L. *J. Am. Chem. Soc.* **2013**, 135, 16082.
- (263) Obreja, V. V. N.; Dinescu, A.; Obreja, A. C. *Int. Rev. Electr. Eng.-I* **2010**, 5.
- (264) Yuanyuan, L.; Guanghai, L.; Guotao, D.; Lide, Z. *Nanotechnology* **2006**, 17, 4278.
- (265) Park, H. W.; Ju, Y. T.; Park, S.-M.; Roh, K. C. *RSC Adv.* **2014**, 4, 567.
- (266) Cheng, H.; Dong, Z.; Hu, C.; Zhao, Y.; Hu, Y.; Qu, L.; Chen, N.; Dai, L. *Nanoscale* **2013**, 5, 3428.
- (267) Liu, C.-G.; Lee, Y.-S.; Kim, Y.-J.; Song, I.-C.; Kim, J.-H. *Synthetic Met.* **2009**, 159, 2009.
- (268) Yeager, M.; Du, W.; Si, R.; Su, D.; Marinković, N.; Teng, X. *J. Phys. Chem. C* **2012**, 116, 20173.
- (269) Liang, J.; Dong, B.; Ding, S.; Li, C.; Li, B. Q.; Li, J.; Yang, G. *J. Mater. Chem. A* **2014**, 2, 11299.
- (270) Zhu, G.; Xi, C.; Shen, M.; Bao, C.; Zhu, J. *ACS Appl. Mater. Interfaces* **2014**, 6, 17208.
- (271) Yan, J.; Sun, W.; Wei, T.; Zhang, Q.; Fan, Z.; Wei, F. *J. Mater. Chem.* **2012**, 22, 11494.
- (272) Van der Ven, A.; Morgan, D.; Meng, Y. S.; Ceder, G. *J. Electrochem. Soc.* **2006**, 153, A210.
- (273) Hu, G.; Li, C.; Gong, H. *J. Power Sources* **2010**, 195, 6977.
- (274) Deabate, S.; Henn, F.; Devautour, S.; Giuntini, J. C. *J. Electrochem. Soc.* **2003**, 150, J23.

- (275) Hou, Y.; Cheng, Y.; Hobson, T.; Liu, J. *Nano Lett.* **2010**, *10*, 2727.
- (276) Lu, Q.; Chen, J. G.; Xiao, J. Q. *Angew. Chem. Int. Ed. Engl.* **2013**, *52*, 1882.
- (277) Ghosh, D.; Giri, S.; Mandal, M.; Das, C. K. *RSC Adv.* **2014**, *4*, 26094.
- (278) Tang, Z.; Tang, C.-h.; Gong, H. *Advanced Functional Materials* **2012**, *22*, 1272.
- (279) Wang, H.; Casalongue, H. S.; Liang, Y.; Dai, H. *J. Am. Chem. Soc.* **2010**, *132*, 7472.
- (280) Xie, J.; Sun, X.; Zhang, N.; Xu, K.; Zhou, M.; Xie, Y. *Nano Energy* **2013**, *2*, 65.
- (281) Alhebshi, N. A.; Rakhi, R. B.; Alshareef, H. N. *J. Mater. Chem. A* **2013**, *1*, 14897.
- (282) Chen, S.; Zhu, J.; Zhou, H.; Wang, X. *RSC Advances* **2011**, *1*, 484.
- (283) Li, H. B.; Yu, M. H.; Wang, F. X.; Liu, P.; Liang, Y.; Xiao, J.; Wang, C. X.; Tong, Y. X.; Yang, G. W. *Nat Commun* **2013**, *4*, 1894.
- (284) Wang, X.; Yan, C.; Sumboja, A.; Yan, J.; Lee, P. S. *Adv. Energy Mater.* **2014**, *4*, n/a.
- (285) Wei, L.; Jiang, W.; Goh, K.; Chen, Y. *poly., Eng. Sci.* **2014**, *54*, 336.
- (286) Nai, J.; Tian, Y.; Guan, X.; Guo, L. *J. Am. Chem. Soc.* **2013**, *135*, 16082.
- (287) Chen, S.; Duan, J.; Tang, Y.; Zhang Qiao, S. *Chem. Eur. J.* **2013**, *19*, 7118.
- (288) Wang, Y.; Gai, S.; Niu, N.; He, F.; Yang, P. *J. Mater. Chem. A* **2013**, *1*, 9083.
- (289) Bernard, M. C.; Cortes, R.; Keddam, M.; Takenouti, H.; Bernard, P.; Senyarch, S. *J. Power Sources* **1996**, *63*, 247.
- (290) Liu, C.; Li, Y. *Journal of Alloys and Compounds* **2009**, *478*, 415.
- (291) Su, Z.; Yang, C.; Xu, C.; Wu, H.; Zhang, Z.; Liu, T.; Zhang, C.;

Yang, Q.; Li, B.; Kang, F. *J. Mater. Chem. A* **2013**, *1*, 12432.

(292) Yu, G. H.; Hu, L. B.; Liu, N. A.; Wang, H. L.; Vosgueritchian, M.; Yang, Y.; Cui, Y.; Bao, Z. A. *Nano Lett.* **2011**, *11*, 4438.

(293) Kim, Y. K.; Park, H. *Energ. Environ. Sci.* **2011**, *4*, 685.

(294) Park, J. C.; Kim, J.; Kwon, H.; Song, H. *Adv. Mater.* **2009**, *21*, 803.

(295) Shen, J.; Liu, A.; Tu, Y.; Wang, H.; Jiang, R.; Ouyang, J.; Chen, Y. *Electrochim. Acta* **2012**, *78*, 122.

(296) Xia, Y.; Sun, K.; Ouyang, J. *Energ. Environ. Sci.* **2012**, *5*, 5325.

(297) Lota, K.; Khomenko, V.; Frackowiak, E. *J. Phys. Chem. Solids* **2004**, *65*, 295.

(298) Fu, Y.; Song, J.; Zhu, Y.; Cao, C. *Journal of Power Sources* **2014**, *262*, 344.

(299) Chen, X.; Long, C.; Lin, C.; Wei, T.; Yan, J.; Jiang, L.; Fan, Z. *Electrochim. Acta* **2014**, *137*, 352.

(300) Van der Ven, A.; Morgan, D.; Meng, Y. S.; Ceder, G. *Journal of The Electrochemical Society* **2006**, *153*, A210.

(301) Shahid, M.; Liu, J.; Shakir, I.; Warsi, M. F.; Nadeem, M.; Kwon, Y.-U. *Electrochimica Acta* **2012**, *85*, 243.

(302) Yang, S.; Wu, X.; Chen, C.; Dong, H.; Hu, W.; Wang, X. *Chem. Commun.* **2012**, *48*, 2773.

(303) Oliva, P.; Leonardi, J.; Laurent, J. F.; Delmas, C.; Braconnier, J. J.; Figlarz, M.; Fievet, F.; Guibert, A. d. *Journal of Power Sources* **1982**, *8*, 229.

(304) Hu, C.-C.; Chen, J.-C.; Chang, K.-H. *J. Power Sources* **2013**, *221*, 128.

(305) Wang, H.; Liang, Y.; Mirfakhrai, T.; Chen, Z.; Casalongue, H.; Dai, H. *Nano Res.* **2011**, *4*, 729.

(306) Cheng, Y.; Zhang, H.; Varanasi, C. V.; Liu, J. *Energ. Environ. Sci.* **2013**, *6*, 3314.

(307) Huang, J.; Xu, P.; Cao, D.; Zhou, X.; Yang, S.; Li, Y.; Wang, G. *J.*

Power Sources **2014**, *246*, 371.

(308) Long, C.; Wei, T.; Yan, J.; Jiang, L.; Fan, Z. *ACS Nano* **2013**, *7*, 11325.

(309) Borges, R. S.; Reddy, A. L. M.; Rodrigues, M.-T. F.; Gullapalli, H.; Balakrishnan, K.; Silva, G. G.; Ajayan, P. M. *Sci. Rep.* **2013**, *3*.

(310) Winter, M.; Brodd, R. J. *Chem. Rev.* **2004**, *104*, 4245.

(311) Miller, J. R.; Simon, P. *Science* **2008**, *321*, 651.

(312) Xiong, S.; Yuan, C.; Zhang, M.; Xi, B.; Qian, Y. *Chem. Eur. J.* **2009**, *15*, 5320.

(313) Nam, K. W.; Kim, K. B. *J. Electrochem. Soc.* **2002**, *149*, A346.

(314) Zhang, X.; Shi, W.; Zhu, J.; Zhao, W.; Ma, J.; Mhaisalkar, S.; Maria, T. L.; Yang, Y.; Zhang, H.; Hng, H. H.; Yan, Q. *Nano Res.* **2010**, *3*, 643.

(315) Jianwei, L.; Jeremy, E.; Jun, L. *Chem. Mater.* **2010**, *22*, 5022.

(316) You, B.; Li, N.; Zhu, H.; Zhu, X.; Yang, J. *ChemSusChem* **2013**, *6*, 474.

(317) McKeown, D. A.; Hagans, P. L.; Carette, L. P. L.; Russell, A. E.; Swider, K. E.; Rolison, D. R. *J. Phys. Chem. B* **1999**, *103*, 4825.

(318) Feng, D.; Dingshan, Y.; Liming, D.; Ganguli, S.; Varshney, V.; Roy, A. K. *Chem. Mater.* **2011**, *23*, 4810.

(319) Pushparaj, V. L.; Shaijumon, M. M.; Kumar, A.; Murugesan, S.; Ci, L.; Vajtai, R.; Linhardt, R. J.; Nalamasu, O.; Ajayan, P. M. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 13574.

(320) Hu, L.; Choi, J. W.; Yang, Y.; Jeong, S.; La Mantia, F.; Cui, L.-F.; Cui, Y. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 21490.

(321) Kang, Y. J.; Kim, B.; Chung, H.; Kim, W. *Synth. Met.* **2010**, *160*, 2510.

(322) Zheng, G. Y.; Hu, L. B.; Wu, H.; Xie, X.; Cui, Y. *Energ. Environ. Sci.* **2011**, *4*, 3368.

(323) Kang, Y. J.; Chun, S. J.; Lee, S. S.; Kim, B. Y.; Kim, J. H.; Chung,

H.; Lee, S. Y.; Kim, W. *ACS Nano* **2012**, 6, 6400.

(324) Li, X.; Tabil, L. G.; Panigrahi, S. *J. Polym. Environ.* **2007**, 15, 25.

(325) Baiardo, M.; Frisoni, G.; Scandola, M.; Licciardello, A. *J. Appl. Polym. Sci.* **2002**, 83, 38.

(326) Paul, A.; Joseph, K.; Thomas, S. *Compos. Sci. Technol.* **1997**, 57, 67.

(327) Saito, T.; Kimura, S.; Nishiyama, Y.; Isogai, A. *Biomacromolecules* **2007**, 8, 2485.

(328) Attal, S.; Thiruvengadathan, R.; Regev, O. *Anal. Chem.* **2006**, 78, 8098.

(329) Lafi, L.; Cossement, D.; Chahine, R. *Carbon* **2005**, 43, 1347.

(330) Shen, J. M.; Liu, A. D.; Tu, Y.; Foo, G. S.; Yeo, C. B.; Chan-Park, M. B.; Jiang, R. R.; Chen, Y. *Energy Environ. Sci.* **2011**, 4, 4220.

(331) Luo, J.; Zhu, H. T.; Zhang, F.; Liang, J. K.; Rao, G. H.; Li, J. B.; Du, Z. M. *J. Appl. Phys.* **2009**, 105.

(332) Kai, K.; Yoshida, Y.; Kageyama, H.; Saito, G.; Ishigaki, T.; Furukawa, Y.; Kawamata, J. *J. Am. Chem. Soc.* **2008**, 130, 15938.

(333) Wang, K.; Zhao, P.; Zhou, X. M.; Wu, H. P.; Wei, Z. X. *J. Mater. Chem.* **2011**, 21, 16373.

(334) Meher, S. K.; Rao, G. R. *J. Power Sources* **2012**, 215, 317.

(335) Hu, L. B.; Chen, W.; Xie, X.; Liu, N. A.; Yang, Y.; Wu, H.; Yao, Y.; Pasta, M.; Alshareef, H. N.; Cui, Y. *ACS Nano* **2011**, 5, 8904.

(336) Yuan, L. Y.; Lu, X. H.; Xiao, X.; Zhai, T.; Dai, J. J.; Zhang, F. C.; Hu, B.; Wang, X.; Gong, L.; Chen, J.; Hu, C. G.; Tong, Y. X.; Zhou, J.; Wang, Z. L. *ACS Nano* **2012**, 6, 656.

(337) Yu, G. H.; Hu, L. B.; Vosgueritchian, M.; Wang, H. L.; Xie, X.; McDonough, J. R.; Cui, X.; Cui, Y.; Bao, Z. N. *Nano Lett.* **2011**, 11, 2905.

(338) Subramanian, V.; Zhu, H.; Wei, B. *Electrochem. Commun.* **2006**, 8, 827.

- (339) Stoller, M. D.; Park, S. J.; Zhu, Y. W.; An, J. H.; Ruoff, R. S. *Nano Lett.* **2008**, 8, 3498.
- (340) Jin, X.; Zhou, W.; Zhang, S.; Chen, G. Z. *Small* **2007**, 3, 1513.
- (341) Mathieu, T.; Thierry, B.; Daniel, B. *Chem. Mater.* **2004**, 16, 3184.
- (342) Mathieu, T.; Thierry, B.; Daniel, B. *Chem. Mater.* **2002**, 14, 3946.
- (343) Lee, H. Y.; Goodenough, J. B. *J. Solid State Chem.* **1999**, 144, 220.
- (344) Yang, Z.; Deng, J.; Sun, H.; Ren, J.; Pan, S.; Peng, H. *Adv. Mater.* **2014**, 26, 7038.
- (345) Jost, K.; Durkin, D. P.; Haverhals, L. M.; Brown, E. K.; Langenstein, M.; De Long, H. C.; Trulove, P. C.; Gogotsi, Y.; Dion, G. *Adv. Energy Mater.* **2015**, 5, 1401286.
- (346) Fu, Y.; Wu, H.; Ye, S.; Cai, X.; Yu, X.; Hou, S.; Kafafy, H.; Zou, D. *Energ. Environ. Sci.* **2013**, 6, 805.
- (347) Bae, J.; Park, Y. J.; Lee, M.; Cha, S. N.; Choi, Y. J.; Lee, C. S.; Kim, J. M.; Wang, Z. L. *Adv. Mater.* **2011**, 23, 3446.
- (348) Meng, Y.; Zhao, Y.; Hu, C.; Cheng, H.; Hu, Y.; Zhang, Z.; Shi, G.; Qu, L. *Adv. Mater.* **2013**, 25, 2326.
- (349) Zhang, Y.; Bai, W.; Cheng, X.; Ren, J.; Weng, W.; Chen, P.; Fang, X.; Zhang, Z.; Peng, H. *Angew. Chem. Int. Ed. Engl.* **2014**, 53, 14564.
- (350) Meng, Q.; Wang, K.; Guo, W.; Fang, J.; Wei, Z.; She, X. *Small* **2014**, 10, 3187.
- (351) Vigolo, B.; Pénicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. *Science* **2000**, 290, 1331.
- (352) Zhang, S.; Koziol, K. K. K.; Kinloch, I. A.; Windle, A. H. *Small* **2008**, 4, 1217.
- (353) Xu, Z.; Gao, C. *Nat Commun* **2011**, 2, 571.
- (354) Xu, Z.; Zhang, Y.; Li, P.; Gao, C. *ACS Nano* **2012**, 6, 7103.
- (355) Shin, M. K.; Lee, B.; Kim, S. H.; Lee, J. A.; Spinks, G. M.; Gambhir, S.; Wallace, G. G.; Kozlov, M. E.; Baughman, R. H.; Kim, S. J. *Nat Commun*

2012, 3, 650.

- (356) Jiang, K.; Li, Q.; Fan, S. *Nature* **2002**, 419, 801.
- (357) Zhang, M.; Atkinson, K. R.; Baughman, R. H. *Science* **2004**, 306, 1358.
- (358) Li, Y.-L.; Kinloch, I. A.; Windle, A. H. *Science* **2004**, 304, 276.
- (359) Vilatela, J. J.; Windle, A. H. *Adv. Mater.* **2010**, 22, 4959.
- (360) Pan, S.; Deng, J.; Guan, G.; Zhang, Y.; Chen, P.; Ren, J.; Peng, H. *J. Mater. Chem. A* **2015**, 3, 6286.
- (361) Sun, G.; Zhang, X.; Lin, R.; Yang, J.; Zhang, H.; Chen, P. *Angew. Chem. Int. Ed. Engl.* **2015**, 54, 4651.
- (362) Cruz-Silva, R.; Morelos-Gomez, A.; Kim, H.-i.; Jang, H.-k.; Tristan, F.; Vega-Diaz, S.; Rajukumar, L. P.; El ás, A. L.; Perea-Lopez, N.; Suhr, J.; Endo, M.; Terrones, M. *ACS Nano* **2014**, 8, 5959.
- (363) Dong, Z.; Jiang, C.; Cheng, H.; Zhao, Y.; Shi, G.; Jiang, L.; Qu, L. *Adv. Mater.* **2012**, 24, 1856.
- (364) Zhang, Z.; Xiao, F.; Xiao, J.; Wang, S. *J. Mater. Chem. A* **2015**, 3, 11817.
- (365) Ericson, L. M.; Fan, H.; Peng, H.; Davis, V. A.; Zhou, W.; Sulpizio, J.; Wang, Y.; Booker, R.; Vavro, J.; Guthy, C.; Parra-Vasquez, A. N. G.; Kim, M. J.; Ramesh, S.; Saini, R. K.; Kittrell, C.; Lavin, G.; Schmidt, H.; Adams, W. W.; Billups, W. E.; Pasquali, M.; Hwang, W.-F.; Hauge, R. H.; Fischer, J. E.; Smalley, R. E. *Science* **2004**, 305, 1447.
- (366) Cheng, H.; Hu, C.; Zhao, Y.; Qu, L. *NPG Asia Mater.* **2014**, 6, e113.
- (367) Xiang, C.; Young, C. C.; Wang, X.; Yan, Z.; Hwang, C.-C.; Cerioti, G.; Lin, J.; Kono, J.; Pasquali, M.; Tour, J. M. *Adv. Mater.* **2013**, 25, 4592.
- (368) Amin Karami, M.; Inman, D. J. *Appl. Phys. Lett.* **2012**, 100, 042901.
- (369) Joseph, A. P. In *IEEE Pervasive Comput.*; Thad, S., Ed. 2005; Vol. 4, p 18.
- (370) Olivo, J.; Carrara, S.; De Micheli, G. *IEEE Sensors J.* **2011**, 11, 1573.

- (371) Gudnason, G.; Bruun, E.; Haugland, M. *Analog Integr. Circ. S.* **2000**, 22, 81.
- (372) Ahmadi, M. M.; Jullien, G. A. *IEEE Trans. Biomed. Circuits Syst.* **2009**, 3, 169.
- (373) Silay, K. M.; Dondi, D.; Larcher, L.; Declercq, M.; Benini, L.; Leblebici, Y.; Dehollain, C. In *Circuits and Systems, 2009. ISCAS 2009. IEEE International Symposium on 2009*, p 533.
- (374) Aboutaleb, S. H.; Chidembo, A. T.; Salari, M.; Konstantinov, K.; Wexler, D.; Liu, H. K.; Dou, S. X. *Energ. Environ. Sci.* **2011**, 4, 1855.
- (375) Aboutaleb, S. H.; Gudarzi, M. M.; Zheng, Q. B.; Kim, J.-K. *Adv. Funct. Mater.* **2011**, 21, 2978.
- (376) Ozin, G. A. *Advanced Materials* **1992**, 4, 612.
- (377) Bose, A.; He, P. G.; Liu, C.; Ellman, B. D.; Twieg, R. J.; Huang, S. P. D. *Journal of the American Chemical Society* **2002**, 124, 4.
- (378) Chen, H. Y.; Wydra, J.; Zhang, X. Y.; Lee, P. S.; Wang, Z. P.; Fan, W.; Tsapatsis, M. *Journal of the American Chemical Society* **2011**, 133, 12390.
- (379) Fuertes, A. B. *Microporous and Mesoporous Materials* **2004**, 67, 273.
- (380) Gies, H.; Grabowski, S.; Bandyopadhyay, M.; Grunert, W.; Tkachenko, O. P.; Klementiev, K. V.; Birkner, A. *Microporous and Mesoporous Materials* **2003**, 60, 31.
- (381) Wang, Z. P.; Dornath, P.; Chang, C. C.; Chen, H. Y.; Fan, W. *Microporous and Mesoporous Materials* **2013**, 181, 8.
- (382) Zhan, B. Z.; White, M. A.; Sham, T. K.; Pincock, J. A.; Doucet, R. J.; Rao, K. V. R.; Robertson, K. N.; Cameron, T. S. *Journal of the American Chemical Society* **2003**, 125, 2195.
- (383) Zhu, G. S.; Qiu, S. L.; Gao, F. F.; Li, D. S.; Li, Y. F.; Wang, R. W.; Gao, B.; Li, B. S.; Guo, Y. H.; Xu, R. R.; Liu, Z.; Terasaki, O. *Journal of Materials Chemistry* **2001**, 11, 1687.
- (384) Byrappa, K.; Adschiri, T. *Progress in Crystal Growth and Characterization of Materials* **2007**, 53, 117.

- (385) Chen, L. F.; Zhang, X. D.; Liang, H. W.; Kong, M. G.; Guan, Q. F.; Chen, P.; Wu, Z. Y.; Yu, S. H. *Acs Nano* **2012**, *6*, 7092.
- (386) Chen, S.; Zhu, J. W.; Wu, X. D.; Han, Q. F.; Wang, X. *Acs Nano* **2010**, *4*, 2822.
- (387) Shen, J. F.; Yan, B.; Shi, M.; Ma, H. W.; Li, N.; Ye, M. X. *Journal of Materials Chemistry* **2011**, *21*, 3415.
- (388) Xu, Y. X.; Sheng, K. X.; Li, C.; Shi, G. Q. *Acs Nano* **2010**, *4*, 4324.
- (389) Zhi, M. J.; Xiang, C. C.; Li, J. T.; Li, M.; Wu, N. Q. *Nanoscale* **2013**, *5*, 72.
- (390) Bi, H. C.; Yin, K. B.; Xie, X.; Zhou, Y. L.; Wan, N.; Xu, F.; Banhart, F.; Sun, L. T.; Ruoff, R. S. *Advanced Materials* **2012**, *24*, 5124.
- (391) Dong, Z. L.; Jiang, C. C.; Cheng, H. H.; Zhao, Y.; Shi, G. Q.; Jiang, L.; Qu, L. T. *Advanced Materials* **2012**, *24*, 1856.
- (392) Yang, Z. Y.; Jin, L. J.; Lu, G. Q.; Xiao, Q. Q.; Zhang, Y. X.; Jing, L.; Zhang, X. X.; Yan, Y. M.; Sun, K. N. *Advanced Functional Materials* **2014**, *24*, 3917.
- (393) Meng, Y.; Zhao, Y.; Hu, C.; Cheng, H.; Hu, Y.; Zhang, Z.; Shi, G.; Qu, L. *Advanced Materials* **2013**, *25*, 2326.
- (394) Yu, D.; Goh, K.; Wang, H.; Wei, L.; Jiang, W.; Zhang, Q.; Dai, L.; Chen, Y. *Nat Nano* **2014**, *9*, 555.
- (395) Yu, D.; Goh, K.; Zhang, Q.; Wei, L.; Wang, H.; Jiang, W.; Chen, Y. *Advanced Materials* **2014**, *26*, 6790.
- (396) Zhao, X.; Hayner, C. M.; Kung, M. C.; Kung, H. H. *ACS Nano* **2011**, *5*, 8739.
- (397) Xu, Y.; Lin, Z.; Zhong, X.; Huang, X.; Weiss, N. O.; Huang, Y.; Duan, X. *Nat Commun* **2014**, *5*, 4554.
- (398) Yu, D. S.; Dai, L. M. *Journal of Physical Chemistry Letters* **2010**, *1*, 467.
- (399) Jha, N.; Ramesh, P.; Bekyarova, E.; Itkis, M. E.; Haddon, R. C. *Advanced Energy Materials* **2012**, *2*, 438.

- (400) Cong, H. P.; Ren, X. C.; Wang, P.; Yu, S. H. *Sci. Rep.* **2012**, 2, 613.
- (401) Jalili, R.; Aboutalebi, S. H.; Esrafilzadeh, D.; Shepherd, R. L.; Chen, J.; Aminorroaya-Yamini, S.; Konstantinov, K.; Minett, A. I.; Razal, J. M.; Wallace, G. G. *Advanced Functional Materials* **2013**, 23, 5345.
- (402) Dong, Z.; Jiang, C.; Cheng, H.; Zhao, Y.; Shi, G.; Jiang, L.; Qu, L. *Advanced Materials* **2012**, 24, 1856.
- (403) Yang, S.-Y.; Chang, K.-H.; Tien, H.-W.; Lee, Y.-F.; Li, S.-M.; Wang, Y.-S.; Wang, J.-Y.; Ma, C.-C. M.; Hu, C.-C. *Journal of Materials Chemistry* **2011**, 21, 2374.
- (404) Jiang, W.; Yu, D.; Zhang, Q.; Goh, K.; Wei, L.; Yong, Y.; Jiang, R.; Wei, J.; Chen, Y. *Advanced Functional Materials* **2015**, 25, 1063.
- (405) Jun, G. H.; Jin, S. H.; Lee, B.; Kim, B. H.; Chae, W.-S.; Hong, S. H.; Jeon, S. *Energy & Environmental Science* **2013**, 6, 3000.
- (406) Chen, P.; Yang, J.-J.; Li, S.-S.; Wang, Z.; Xiao, T.-Y.; Qian, Y.-H.; Yu, S.-H. *Nano Energy* **2013**, 2, 249.
- (407) Beidaghi, M.; Wang, C. *Advanced Functional Materials* **2012**, 22, 4501.
- (408) Byon, H. R.; Lee, S. W.; Chen, S.; Hammond, P. T.; Shao-Horn, Y. *Carbon* **2011**, 49, 457.
- (409) Gogotsi, Y.; Simon, P. *Science* **2011**, 334, 917.
- (410) Zheng, B.; Huang, T.; Kou, L.; Zhao, X.; Gopalsamy, K.; Gao, C. *J. Mater. Chem. A* **2014**, 2, 9736.
- (411) Choi, C.; Kim, S. H.; Sim, H. J.; Lee, J. A.; Choi, A. Y.; Kim, Y. T.; Lepro, X.; Spinks, G. M.; Baughman, R. H.; Kim, S. J. *Sci. Rep.* **2015**, 5.
- (412) Li, Y.; Sheng, K.; Yuan, W.; Shi, G. *Chem. Commun.* **2013**, 49, 291.
- (413) Dong, X.; Guo, Z.; Song, Y.; Hou, M.; Wang, J.; Wang, Y.; Xia, Y. *Adv. Funct. Mater.* **2014**, 24, 3405.
- (414) El-Kady, M. F.; Strong, V.; Dubin, S.; Kaner, R. B. *Science* **2012**, 335, 1326.
- (415) Cook-Chennault, K. A.; Thambi, N.; Sastry, A. M. *Smart Mater.*

Struct. **2008**, *17*, 043001.

(416) Zhang, Y.-Z.; Wang, Y.; Cheng, T.; Lai, W.-Y.; Pang, H.; Huang, W. *Chem. Soc. Rev.* **2015**, *44*, 5181.

(417) Keskinen, J.; Sivonen, E.; Jussila, S.; Bergelin, M.; Johansson, M.; Vaari, A.; Smolander, M. *Electrochim. Acta* **2012**, *85*, 302.

(418) Pettersson, F.; Keskinen, J.; Remonen, T.; von Hertzen, L.; Jansson, E.; Tappura, K.; Zhang, Y.; Wilén, C. E.; Österbacka, R. *J. Power Sources* **2014**, *271*, 298.