Controlled synthesis of manganese-based heterostructures for supercapacitor application

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**CONTROLLED SYNTHESIS OF MANGANESE-
BASED HETEROSTRUCTURES FOR
SUPERCAPACITOR APPLICATION**

TAN HUI TENG

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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List of Abbreviations

AC	Activated carbon
BET	Brunauer–Emmett–Teller
Cu-MnO@carbon	Carbon coated Cu-containing MnO
CNT	Carbon nanotubes
CV	Cyclic voltammetry
Cu-MnO@carbon	Carbon coated Cu-containing MnO
EC	Electrochemical capacitor
EDLC	Electrical double layer capacitance
EDX	Energy dispersive X-ray spectroscopy
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
FESEM	Field-emission Scanning Electron Microscope
GCD	Galvanic charge/discharge
GF	Graphite Felt
HRTEM	High resolution Transmission Electron Microscope
ICP	Inductively Coupled Plasm
MWCNT	Multi-walled carbon nanotube
NMP	1-Methyl-2-pyrrolidone
NR	Nanorod
NS	Nanosheet
NT	Nanotube

ODE	1-Octadecene
PANI	Polyaniline,
PEDOT	Poly(3,4-Ethylenedioxythiophene)
PPy	Polypyrrole
PTh	Polythiophene
PVDF	Polyvinylidene fluoride
SC	Supercapacitor
SCE	Saturated calomel electrode
STEM-DF	Scanning transmission electron microscopy dark field
TEM	Transmission Electron Microscope
TMO	Transition metal oxides
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
1-D	One dimensional
2-D	Two dimensional
3-D	Three dimensional

Abstract

The invention of SC fills the performance gap between the conventional capacitors and batteries in terms of energy and power densities. Since the scientific breakthrough in electrode material is an answer to the technological bottleneck of SCs, extensive research is recently focusing on the development of advanced functional materials in nanoscale. Although nanoengineering has been regarded as a powerful tool to tailor the intrinsic properties of the electrode materials, incompetence of single-phase electrode nanomaterials handicaps the SCs from realizing their full potential. Hence, the concept of “heterogeneous nanostructures” was implemented to compensate the intrinsic disadvantages of the single-phase nanomaterials *via* the synergistic effect in hope of making a great leap in electrochemical performances. Herein, this thesis explored the possibility of improving the energy densities of SCs without sacrificing their power density using nanosized manganese-based heterostructures (*e.g.* MnO, MnOOH, MnO₂).

The low electronic conductivity and dissolution problems of the MnO have hindered it from further electrochemical enhancement. In response to the aforementioned issues, monodispersed Cu-MnO@carbon nanostructures were synthesized *via* a facile solution-based method. The electronic conductivity is significantly improved in the presence of metallic Cu. Besides, the unique architecture of Cu-MnO@carbon heterostructures preserves excellent electrical integrity of the electrode *via* the conductive Cu “nanobridges” that provide efficient electron transfer pathway between the active materials and the current collector. On the other hand, the amorphous carbonaceous shell acts as a protective layer to attain structural integrity and prevent the dissolution of MnO.

The incorporation of the carbon-based materials is proved to induce excellent cycling stability of the SCs. In this regard, successful attempt has been made on controlled synthesis of MnOOH NTs on highly conductive GF as flexible SC electrode using a hydrothermal method. As the freestanding electrode excludes the addition of binder, the ESR of the electrode is greatly reduced, giving rise to higher power density. With the NTs structure, the active surface area of the MnOOH can be completely accessible to electrolyte ions besides having shorter charge transport length and greater ability to withstand the structural deformation. Hence, the hollow-structured MnOOH shows great promise in electrochemical system which can be reflected by its high specific capacitance. On the other hand, less capacitance fading is experienced by the MnOOH NTs electrode due to the presence of GF scaffold that contributes to the electronic conductivity and mechanical support.

To have further enhancement in energy density, the incorporation of pseudocapacitive materials with rationally designed architecture is of paramount important. In an attempt to explore the possibility of boosting the SC performance using the ternary composites with well-defined morphology, $V_2O_5@MnO_2/Fe_2O_3$ core-shell NTs with tunable interior dimensions were synthesized *via* a facile aqueous-based method. In addition, functionalization of the $V_2O_5@MnO_2$ NTs with other TMOs results in ternary composites with diverse composition, $V_2O_5@MnO_2/M$ NTs ($M = Fe_2O_3, Co_2O_3/Co(OH)_2, Ni(OH)_2$). The versatility of this synthetic protocol provides a platform to fabricate complex ternary composites in a more benign way. It is found that the rationally designed tubular morphology endows them with good permeability of electrolyte ions for

maximum utilization of the electroactive sites. Hence, high specific capacitance is achieved accompanied by excellent cycling stability.

Besides discussion on the fundamental reason that may make the engineered nano-sized manganese-based heterostructures viable candidates for SC application, evaluation of their practicability in device level will be covered as well. In this regard, the manganese-based heterostructures (positive electrodes) were assembled into pouch-type asymmetric SC (using CNTs as the negative electrodes). Preliminary result shows that their power and energy densities are comparable to those commercial products, indicating that they hold great promise as the energy storage device.

1. Introduction

1.1 Background

In the past few decades, continuous burning of fossil fuels (*e.g.*, petroleum, coal and natural gas) has intensified the global warming issue. In an effort to combat the soaring greenhouse gases emission that caused by the combustion of these finite resources, the society is racing towards the use of renewable resources that offer sustainable energy without sacrificing environmental quality. This trend has spurred up the development of energy storage system that converts chemical energy into electrical energy and tremendous effort has been devoted into three major categories of energy storage devices, which are fuel cells, batteries and SCs. Basically, they follow different charge storage mechanisms to deliver their electrochemical energy, leading to large discrepancy in energy and power densities. In Ragone plot¹ shown as Figure 1.1, fuel cell represents a class of energy storage devices that can store the largest amount of energy per unit weight/volume at the expense of its low efficiency and cost effectiveness. Batteries solved the problems of fuel cell by having relatively stable cycling performance but the slow energy delivery rate of batteries is still not able to meet the expectations. Conventional capacitor is well-known for their high power density. Nevertheless, achieving higher energy density for conventional capacitor remains a great challenge even though it can release the stored chemical energy within several milliseconds. Hence, SCs that combined the battery-type faradiac reaction emerged as a promising energy storage device to fill the

gap of power density between fuel cells, batteries but is still able to exhibit relatively high energy density and long calendar life characteristics owned by the ECs.

Figure 1.1. Ragone plot illustrating the relationship of power and energy density for various energy storage systems. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials (¹), copyright (2008).

Insatiable market demand for power and energy requirements of many applications that convey substantial energy in pulse especially the mobile communication products, roll-up displays and electric vehicles has promoted rapid development of SCs for the past decades. Research in materials chemistry lies at the heart of the technological breakthrough in SCs.² However, the implementation of conventional bulk single-phase materials as the SC electrode has brought about limited improvement in power and energy densities whose performances are hindered by their intrinsic properties. In pursuit of improved electrochemical performances, continuous effort has to been devoted to

tailoring the properties of the electrode materials for future SC applications that can meet the rising demand for affordable and green energy.

1.2 Motivation

Traditional SCs are constructed by carbonaceous materials with high surface area and electronic conductivity that convey the energy in the form of EDLC. Even though exceptionally high power density can be achieved, these materials show unsatisfied energy density. By moving beyond the conventional EDLC charge storage mechanism, pseudocapacitive TMOs, especially the manganese-based materials could be the alternatives to bring about incremental enhancement. Manganese-based materials have been regarded as the potential candidates, not only attributing to their high theoretical capacitance (~ 1370 F/g),³ but also their natural abundance, low cost and less toxicity. Although their multiple valance states and various allotropic forms endow them with high degree of tunability in property and functionality, some of their intrinsic properties have impeded them from realizing their full potential. To overcome these bottlenecks, effective strategy in materials design and synthetic protocol has to be developed.

In recent decades, nanoengineering becomes a trend in providing new perspectives on material research. Some of the hindrances faced by the conventional bulk material can be mitigated by applying the nanoscaling concept which constrains the spatial arrangement of functional materials down to nanometer level. It can be used to tailor the intrinsic properties of bulk materials in micron-size such as low electronic conductivity, mechanical stability, and kinetics issue that are associated with the charge diffusion rate

and the charge transfer pathway. Compared to the bulk counterpart, the unusual chemical and electronic properties of the nano-sized materials can be explained as follows:^{4,5}

1. The high surface-to-volume ratio of the nanostructures endows them with sufficiently high interfacial contact area between the active materials and the electrolyte ions. On the other hand, the rate of electrolyte replenishment and kinetics for charge/discharge processes can be significantly improved.
2. Nanostructures inherently possess high surface energy which can significantly enhance their surface reactivity towards electrochemical reactions, enabling them to exhibit both the microscopic bulk and nanoscopic surface properties.
3. Reducing the dimension of material to nanoscale can shorten the diffusion length for electron/ions transport, accelerating the diffusion rate.
4. Tensile strain and structural distortion generated can be better accommodated by the nanostructures.

As the trade-off of using nanoelectrodes, some concerns still remained:

1. The high surface energy and surface area of nanomaterials may induce an increase in undesirable side reactions, leading to self-discharge and poor cycle life.
2. Agglomeration of the nanostructures may sacrifice a number of accessible surface area for electrochemical reaction.

Nanomaterials are difficult to control owing to their low thermodynamic stability and high surface side reactions as compared to most of the microstructured materials. With these in mind, recent research in material chemistry has made tremendous effort in surface modification engineering for nanomaterials to ensure the progressive development will not be hindered by the detrimental effect incurred by nanoscaling.

Incompetence of conventional single-phase nanomaterials remains the bottleneck for making further technological breakthrough to meet the expectation of future energy storage system. To propel rapid progress in the development of high-efficiency SCs, utilization of heterogeneous nanostructures as electrodes opens up a new avenue for realizing the goal of achieving enhanced capacitive performance that derived from compensating the intrinsic shortages or synergistically combining the advantages of individual component.⁶ On the other hand, rationally designed architecture of a heterostructure is able to raise novel distinguishable properties not exhibited by either of the constituent materials alone. One sparkling success of current hybridization approach is reflected in the improving capability of the individual component. However, the fabrication of multi-component structures are challenging due to the increased complexity of the material system. Base on this point, tremendous attention has to be paid on developing efficient synthetic strategies to construct advanced functional materials with well-defined compositions and architectures. Besides, in-depth study has to be done on investigating the contribution of each component in the charge storage mechanism of SCs, so that further insight into better electrode design and fabrication can be provided.

1.3 Objectives and Research Scopes

The ultimate goal of this thesis is to improve the energy density of SCs without sacrificing their power density. Working towards implementing structural and compositional complexity to nanomaterials could potentially position the SC devices with further improvement in electrochemical performance. From this perspective, the objective of this thesis is to investigate the manganese-based nanomaterials that can deliver higher specific

capacitance than that of carbonaceous materials as the alternative SC electrodes. The sub-objectives are summarized as follows:

1. Developing effective methodology to synthesize manganese-based multi-component nanostructures with well-defined morphology and composition for capacitive enhancement

Electro-active surface area is regarded as a crucial parameter in SCs since the energy is converted from the surface mediated electrochemical reaction occurs at the electrodes. Several promising strategies can be used to increase the surface area, for instances, reducing the size and tailoring the morphology of the active materials. This causes the research field is overwhelmed with the concept of synthesizing nanostructures with tailored morphology which is believed to be able to construct more reaction interfaces and reduce the charge transport pathway. As mention above, heterostructures emerged as a new class of potential candidates in SCs due to their enhanced properties as compared to their single-phase counterparts. Nevertheless, the heterostructures have to be constructed in a logical way so that both of the constituents can realize their full potential. With this in mind, rational design in architecture of a composite is of paramount important. Although synergistic effect may induce enhancement in electrochemical performance by increasing the complexity of the functional materials, great challenges remain in developing effective strategy in material synthesis. Hence, novel synthetic routes are employed in this thesis to prepare manganese-based multi-component nanostructures and to demonstrate precise control on the morphology and composition of the heterostructures.

2. Investigate the contributions of the incorporated species in the manganese-based multi-component nanostructures towards the charge storage of SCs

As future prospect, further breakthrough in energy storage system may lie in the fundamental understanding on the relationship between the electrode materials and their electrochemical characteristics (*e.g.*, the kinetics of electron/ion transport at the electrode/electrolyte interface) which is critical for future optimization of synthesis parameters and material properties. Hence, noteworthy investigation has to be made on understanding the role of different components of a heterogeneous system in the charge storage of SCs and their contribution in enhancing the properties of manganese-based nanomaterials. In this thesis, one of the focuses is to present a systematic study on the correlations of electrochemical performance and charge storage mechanism with morphology, surface area, and electronic conductivity of the as-prepared nanomaterials.

1.4 Thesis Organization

The thesis organization can be divided into several sections.

Chapter 1 introduces the important role of SCs in recent energy storage and conversion system and points out the challenges for achieving the high-performance SCs. Based on this research justification, the thesis objective and scope were established, aiming to develop effective strategy to synthesize multi-component nanostructures for capacitive enhancement. In parallel, the contributions of each component of the heterostructures to their electrochemical performances will also be investigated in detailed.

Chapter 2 gives an overview of the developmental history and fundamentals of SCs. Then, several important parameters of SCs will be discussed, including different type of

charge storage mechanisms, electrode materials, and electrolytes. Examples reported in literature are provided in each section.

Chapter 3 includes application of solution-based method synthesized monodispersed Cu-MnO@carbon heterostructures as SC electrode. The intimate contact between the Cu and MnO preserves the electrical integrity of the electrode, in which the conductive Cu “nanobridge” provides efficient electron transfer pathway between the MnO and the current collector. On the other hand, the amorphous carbonaceous shell evidently gives a protective layer to attain structural integrity. Hence, enhancement in electrochemical performance is obtained which can be reflected by the enhanced cycling stability and rate capability of the heterostructures.

Chapter 4 demonstrates the hybridization concept by coupling the pseudocapacitive MnOOH with highly conductive GF as flexible SC electrode. Successful attempt has been made on controlled synthesis of MnOOH nanostructures with tunable morphology. Moreover, the time-dependent experiments interpret their mechanistic transformation. With the tubular structure, the active surface area of the MnOOH can be completely accessible to electrolyte ions besides having shorter charge transport length and greater ability to withstand the structural deformation. Hence, the hollow-structured MnOOH shows great promise in electrochemical system by showing high specific capacitance and excellent cycling stability.

Chapter 5 introduces a facile method to synthesize multi-component NTs ($\text{V}_2\text{O}_5@\text{MnO}_2$ and $\text{V}_2\text{O}_5@\text{MnO}_2/\text{Fe}_2\text{O}_3$) *via* an aqueous-based method. The rationally designed tubular morphology endows them with good permeability of electrolyte ions for maximum utilization of the electro-active sites while the epitaxial grown MnO_2 imposes

mechanical support to V_2O_5 against structural collapse upon long-term cycling. The incorporation of Fe_2O_3 suppresses the hydrogen evolution that causes the electrode polarization and enlarges the working potential of aqueous electrolyte to greater extent. Hence, high specific capacitance is achieved accompanied by excellent cycling stability. In addition, functionalization of the $\text{V}_2\text{O}_5@\text{MnO}_2$ NTs with other TMOs results in ternary composites, $\text{V}_2\text{O}_5@\text{MnO}_2/\text{M}$ NTs ($\text{M} = \text{Co}_2\text{O}_3/\text{Co}(\text{OH})_2, \text{Ni}(\text{OH})_2$) illustrates the versatility of this synthetic protocol in fabricating complex ternary nanocomposites in a more benign way.

Chapter 6 demonstrates the practical application of manganese-based heterostructures. The construction of asymmetric SCs that use carbon-based materials as the negative electrode and the high-capacitance faradaic manganese-based heterostructures as positive electrode overcomes the energy limitation of a three-electrode system. The energy density of the manganese-based asymmetric SCs is greatly enhanced as compared with the commercial SCs without sacrificing their long cycle life and high power density.

Chapter 7, a summary of my thesis work and some recommendation for future works are presented.

2. Literature Review

2.1 History of Supercapacitors

The development of ECs can be categorized into several stages: starting from electrostatic capacitor to electrolytic capacitor and finally comes to a mature stage, electrostatic double-layer capacitor, also known as SCs.⁷ Indeed, the concept of generating electrical energy from the electrical double layer formed at the interfacial region between the electrolyte and electrode materials was advocated in late 1800s. Until 1957, a patent filed by Becker, officially disclosed the invention of a “real” SC device using porous carbon electrodes.⁸ Subsequently, it was commercialized in 1971, symbolizing this energy storage device took step towards practical implementation in the market.⁹ On the following years, the unique attributes of SCs have raised tremendous demands in various applications, spurring research development to obtain improvement in their electrochemical performances in terms of power and energy densities. Besides increasing the capacitive values of SCs, industry and research field also make effort in doing device miniaturization to tailor the dimension and weigh of SCs. Over the past few decades, rapid development in nanoscience paved a new way for technological breakthrough in SCs, boosting the device performance to several-fold capacitive enhancement. In the near future, SCs is projected to have increasingly widespread applications in global, for instances, communication devices, back-up power devices, hybrid electric vehicles, automotive, and public transport.

2.2 Principles of Supercapacitors

A SC with double-electrodes configuration is constructed of a pair of closely spaced electrodes containing the electro-active materials (anode and cathode) attached to the current collector, electrolyte and a permeable separator sandwiched between the parallel electrodes. The device architecture is shown in Figure 2.1.

Figure 2.1. Schematic representation of a two-electrode SC with symmetric configuration. Above shows its corresponding equivalent circuit and below shows its potential differences. Reprinted from Ref.¹⁰ Copyright (2012), with permission from John Wiley & Sons.

Generally, there are two types of testing configurations, which are double-electrode and three-electrode systems (Figure 2.2). Although the three-electrode configuration is always employed to investigate the electrochemical performance of the active materials in laboratory, the symmetric/asymmetric double-electrode cell bears a closer resemblance to actual commercial SCs.¹¹ In a three-electrode setup, the applied voltage across the

working electrode is measured with respect to a particular reference electrode. In contrast, the applied voltage is distributed between two electrodes in the double-electrodes system, which is lower than that of the three-electrode system at a fixed scanning potential. Hence, electrode polarization is rarely occurred in the double-electrodes system (hydrogen evolution at the negative side and oxygen evolution at the positive side) although the applied potential range exceeds the thermodynamically stable potential of water (1.23 V).

Figure 2.2. Schematic representation of a (a) double-electrodes system and (b) three-electrodes system.

From this point of view, the potential across the three-electrode setup is twice of the double-electrodes system, giving rise to higher specific capacitance.¹² In a double-electrode configuration, the cell can be pictured as two capacitors arranged in series (Figure 2.1) and hence, the specific capacitance of a cell, C_t can be expressed as:¹⁰

$$\frac{1}{C_t} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1)$$

where C_1 and C_2 represent the specific capacitance of the positive and negative electrodes, respectively. Based on equation (1), the specific capacitance of an individual electrode will be twice of the total specific capacitance of the cell. It is worth noting that the gravimetric capacitance can be expressed per unit gram or area with the relationship of:¹⁰

$$C_{SA} (\mu F \text{ cm}^{-2}) = \frac{C_g (F \text{ g}^{-1})}{SA (m^2 \text{ g}^{-1})} \times 10^2 \quad (2)$$

where C_{SA} , and C_g are the capacitance per unit area, and capacitance per unit gram, respectively. SA is the specific surface area of the electrode materials.

There are many ways of defining the overall electrochemical performances of SCs. In term of capacitance calculation, CV and GCD measurement are employed. In the former case, the specific capacitance is dependent on the integrated area under the CV loop according to the following equation:¹⁰

$$C_t = \frac{Q}{m V} = \frac{1}{m V v} \int_{V^-}^{V^+} I(V) dV \quad (3)$$

where Q represents the total charge calculated by integration of the enclosed CV loop, m is the total mass of the active materials on two electrodes, v is the scan rate used during the positive and negative sweeps, and V is the operating potential window of the cell.

Otherwise, GCD technique measures the linear relationship of capacitance with the charge/discharge time under constant current condition, which can be derived from the following equation:¹⁰

$$C_t = \frac{I}{m dV/dt} \quad (4)$$

where I is the discharge current, V is the discharge potential after IR drop. To summarize, the value of dV/dt represents slope obtained from the discharge curve. In the case of non-linear response for most of the pseudocapacitive materials, it is suggested to calculate the specific capacitance using the two datum points derived from the discharge curve, $dV/dt = (V_{max} - \frac{1}{2} V_{max})/(t_2 - t_1)$, where t_1 and t_2 represent the discharge time of V_{max} and $\frac{1}{2} V_{max}$, respectively.¹²

Generally, two important parameters, energy (E) and power (P) densities, are used to evaluate the performance of energy storage devices. Energy density represents the total

amount of charges stored in SCs per unit mass or volume, whereas the power density is synonymous to the rate of charges being delivered upon discharging. The equations used to express these two parameters are as follows:¹³

$$E = \frac{1}{2} CV^2 \quad (5)$$

$$P = \frac{V^2}{4MR_s} \quad (6)$$

C is the specific capacitance of the electrode material, V is the operating voltage of the cell, M is the mass of both electrodes, and R_s is the ESR in ohms. Here, the ESR is deduced from the following equation:¹³

$$ESR = \frac{\Delta V}{|I_{charge}| + |I_{discharge}|} \quad (7)$$

ΔV represents the voltage different between the highest and second highest point. I_{charge} and $I_{discharge}$ represent magnitude of the charge and discharge currents, respectively.

These equations hint that effort can be made on optimizing three variables mentioned above (specific capacitance, voltage window and ESR) to achieve electrochemical improvement. It is worth noting that the three-electrode configuration may incur large error in calculating the energy and power densities due to overestimation of its specific capacitance. In the double-electrode system, the voltage passes through both of the oppositely positioned electrodes has to be optimized for higher specific capacitance. In this regard, larger energy density can be achieved by having optimum mass ratio between the positive and negative electrodes, and the corresponding equation can be expressed as follows:¹⁴

$$R = \frac{m_+}{m_-} = \frac{C_- \times \Delta E_-}{C_+ \times \Delta E_+} \quad (8)$$

where R is the mass ratio, m_+ and m_- , are the mass of the positive and negative electrodes, respectively, C_+ and C_- are the specific capacitance of the positive and negative electrodes, respectively, ΔE_+ and ΔE_- are potential window of the positive and negative electrodes, respectively.

On the other hand, the EIS is always conducted to probe the dynamic behavior at the electrode/electrolyte interface. The expression of impedance (Z) can be simplified as:¹³

$$Z = Z' + jZ'' \quad (9)$$

in which Z' and Z'' could be defined as the real and imaginary part of impedance, respectively.

Besides aforementioned methodologies, the specific capacitance can also be evaluated using the imaginary part of impedance and can be expressed as a function of angular frequency (ω , equal to $2\pi f$).¹³

$$C = \frac{-1}{2\pi f Z'' m} \quad (10)$$

where f is the frequency.

When this frequency-dependent behavior is expressed as a function of ω , the equation in describing the capacitive behavior can be simplified as:¹³

$$Z(\omega) = Z'(\omega) + jZ''(\omega) = \frac{1}{j\omega C(\omega)} \quad (11)$$

$$C(\omega) = \frac{1}{j\omega[Z'(\omega) + jZ''(\omega)]} \quad (12)$$

$$C(\omega) = \frac{-[jZ'(\omega) + Z''(\omega)]}{\omega|Z(\omega)|^2} \quad (13)$$

Capacitance (C) can also be expressed at a function of ω .¹³

$$C(\omega) = C'(\omega) + jC''(\omega) \quad (14)$$

$$C(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} - \frac{-Z'(\omega)}{\omega|Z(\omega)|^2} \quad (15)$$

$$C'(\omega) = \frac{-Z''(\omega)}{\omega|Z(\omega)|^2} \quad (16)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \quad (17)$$

where the $C'(\omega)$ and $C''(\omega)$ represent the real and imaginary parts of capacitance.

The graphic expressions of $C'(\omega)$ and $C''(\omega)$ as function of frequency are illustrated in Figure 2.3a and 2.3b, respectively. Figure 2.3a reveals that the $C'(\omega)$ is frequency dependent at lower frequency range and becomes more frequency independent upon discharging at constant current condition. In Figure 2.3b, $C''(\omega)$ reaches a maximum value at frequency, f_0 , or can be described as the inverse of the relaxation time in the system, $1/\tau_0$. This value illustrates the number of time required to be fully discharge with more than 50% efficiency, indirectly translating the rate capability of a SC.¹⁵ Figure 2.3c presents a typical Nyquist plot (Z' against Z'') obtained in symmetric configuration which comprises of a semicircle showing the blocking behavior (induced by charge transfer resistance or intrinsic electronic properties of the electrode) at high frequency region and a straight line showing capacitive behavior (more inclined to 90° is much closer to an ideal SC device) at low frequency region. At the middle frequency region, deviation from vertical line can be observed. The crossing of these two lines leads to a so-called “knee frequency”, in which the SCs are completely converted from a resistor to a capacitor beyond this frequency.¹³ In the electrical equivalent circuit, C_l , Z_p , and C_e are limiting capacitance, Warburg impedance and double-layer capacitance (also known as constant phase elements, CFEs), respectively. R_b can be the expression for a series of resistance, which consists of ionic resistance of the electrolyte, intrinsic resistance of the active

materials as well as the contact resistance between the electrode and the current collector. R_e is the charge transfer resistance induced by the double-layer capacitance at electrode surface.¹⁶

Figure 2.3. Evolution of the (a) real; (b) imaginary capacitance versus frequency; (c) Nyquist plot of EIS recorded by using a two-electrode mode, together with the equivalent circuit for impedance analysis.¹³

On the basis of discussion on the fundamentals of SC, several issues governing the electrochemical performance are worth to be pinpointed. Apparently, the factors influencing the specific capacitance of SCs lie on the properties of electrode materials, operating potential window and also ERS according to equations (5) (energy density) and (6) (power density). Since the specific capacitance is determined by the electro-active materials, interplay among the morphology, architecture and composition of the active materials is the key to realize a high-performance SC. On the other hand, the energy density is proportional to the square of operating voltage which is highly dependent on the electrolytes being used in the cell. Commonly used electrolytes can be classified into two categories which are liquid (aqueous, organic and ionic liquid) and solid electrolytes. It is

highly desirable to have electrolyte with higher ionic conductivity and wider thermodynamically stable potential range. Pro and cons are found for the recent electrolyte system, thus, we have to strike a balance between the issues raised from different type of electrolytes. Lastly, the ESR of the cell is governed by the intrinsic properties of the electrode materials as well as the electrode fabrication process. Recent progress made towards electrode material engineering has successfully tailored the some of the unfavorable effect of their intrinsic properties. In the latter case, the presence of electro-inert binders can potentially induce greater internal resistance. By understanding the rationale behind this perspective, binder-free approach emerged to be a solution to reduce unnecessary impedance in achieving high power density.

2.3 Charge Storage Mechanism of Supercapacitors

Further insight into the development and optimization of SC devices can be arisen through fundamental studies on charge/discharge behavior of SCs. On the following sections, the characteristics different charge storage mechanisms of SC will be discussed in details: (1) EDLC; (2) pseudocapacitance.

2.3.1 EDLC

Apart from the conventional electrostatic capacitors and electrolytic capacitors, the EDL capacitors do not contain the dielectric layer in between. It stores energy originated from the electrostatic charge separation at the electrolyte/electrode interfaces without involving the charge transfer reactions. The ion absorption and desorption interactions during the charge/discharge processes are schematically depicted as follows (Figure 2.4):

Figure 2.4. Charge and discharge mechanism of electric double layer capacitor.

Upon charging (voltage is applied to the system), the ions within the electrolyte solution are drawn towards two oppositely charged electrodes and accumulate at the electrolyte/electrode interfacial region. In this absorption process, electrode polarization is generated to form double-layer charge, which can be expressed as follows:¹⁰

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (18)$$

where ϵ_r , ϵ_0 , A and d are representations of the electrolyte dielectric constant, vacuum permittivity (8.854×10^{-12} F m⁻¹), surface area of the electrode immersed in the electrolyte, the thickness of electrical double layer, respectively. As compared to the other two conventional capacitors, the d value generated from the charge separation in EDL capacitors can be significantly reduced, giving rise to higher specific capacitance, as illustrated in Figure 2.5. Upon discharging, ion desorption process occurs and the electrolyte ions are released back to the bulk solution and recombine with their oppositely charged counterparts.

Figure 2.5. Construction of three main types of capacitors: electrostatic, electrolytic and electrochemical.¹⁷

Classic theories used to describe the EDLC consist of Helmholtz model, Gouy–Chapman model, and Stern model, as depicted in Figure 2.6.¹⁸ Helmholtz model was the first version assuming that the EDLC is originated from a compact layer of oppositely charged ions. This theory was further modified by Louis Georges Gouy and David Leonard Chapman after taking the ion diffusion within the solution into consideration. However, overestimation on the specific capacitance was found and the Stern model was established to combine both theories in describing the EDLC charge storage mechanism.

Figure 2.6. (a) The Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model. Inner and outer Helmholtz plane are denoted as IHP and OHP, respectively. The

IHP is defined as the distance of specifically adsorbed ions while the OHP is defined as non-specifically adsorbed ions. d is defined as the double layer distance in the Helmholtz model. ϕ_0 and ϕ represent the potentials at the electrode surface and the electrode/electrolyte interface, respectively. Reproduced from Ref. ¹⁸ with permission from The Royal Society of Chemistry.

When nanoporous materials are used, the classical theories fail to describe the linear relationship between the capacitance and surface area. Therefore, the surface curvature effect is taken into account in recent theories. An approach advocated by Vincent Meunier and co-workers demonstrated that the EDLC of the active materials, especially the carbon family can be tuned by the pore size, which provided further insight into the dynamic behavior of electrolyte in response to different pore dimensions.^{19,20} In this regard, DFT calculation and experimental data reveal the equations in calculating different type of capacitances when the pore curvature is taken into account. When the pore size is larger than the mesopore regime (> 50 nm), the capacitance calculation sticks to the conventional EDLC model. For mesoporous feature (2-50 nm), the capacitance can be derived from equation 19, where the solvated counterions are aligned in cylinder shape surrounded the pore wall.²⁰ By reducing the pore size to < 2 nm, the confined space of micropores only allow the solvated/desolvated counterions to line up in the pore due to the spatial restriction, which can be described in equation 20.²⁰

$$C/A = \frac{2\pi\epsilon_r\epsilon_o}{\ln b/a} \quad (19)$$

where a and b represent the outer and inner radii of the cylinder, respectively.

$$C/A = \frac{\epsilon_r \epsilon_0}{b \ln b/a_0} \quad (20)$$

where a_0 and b represent the radius of the solvated counterions and radius of the micropores, respectively.

The biggest advantage of the EDL capacitors is their long calendar life with almost no capacitive fading as compared to other energy storage and conversion systems. The underlying cause may be attributed to the highly reversible non-faradaic reactions occur at the electrode/electrolyte interface. Without the charge transfer reaction, there is no material degradation issue on the electrode (pulverization effect), making the EDL capacitors stable up to millions of cycles. Nevertheless, the EDLC derived from the charge separation is still not able to meet the commercial market expectation in terms of specific energy density.

2.3.2 Pseudocapacitance

Unlike the EDLC that physically accumulates charges, the pseudocapacitance is originated from the charge transfer process of an individual reactant molecule in the bulk phase, endowing them with higher capacitance as compared to the EDLC charge storage mechanism. Since electron transition process follows the Nerstian behavior resembling to batteries, the electrode materials should possess redox capability to maintain the charge balance by chemisorptions of electrolyte ions upon the continuous charge/discharge processes. The pseudocapacitance, or so-called a thermodynamically favored redox

reaction is proportional to the charge accumulated due to the electron transfer process (dq) as a function of potential (dV), according to the following equation:²¹

$$C = \frac{dq}{dV} \quad (21)$$

The correlation between the potential and the charge generated during the adsorption/desorption reactions can be expressed as:²¹

$$E = E^0 - \frac{RT}{nF} \ln \left(\frac{X}{1-X} \right) \quad (22)$$

$$C = \left(\frac{RT}{m} \right) \frac{X}{E} \quad (23)$$

in which E , R , T , n , F , X , m are the potential (V), ideal gas constant (8.314 J mol⁻¹ K⁻¹), temperature (K), number of electrons, faraday constant (96500 C mol⁻¹), fraction of surface coverage, molecular weight, respectively. Charge transfer process of pseudocapacitors that exploits the faradaic reaction to tunnel the electrons across the current collector/electrode interfaces can be done through different mechanisms:²¹ (1) underpotential deposition (UPD); (2) redox pseudocapacitance; (3) intercalation pseudocapacitance,

UPD is also called 2-D adsorption pseudocapacitance, involving the faradaic absorption/desorption of metal ions or protons on the surface of metallic active materials (e.g. Au, Pt, Rh, and Ru) with applied potential to form a stable intermediate in the aqueous medium (Figure 2.7a). This reversible process is highly dependent on the availability of the 2-D monolayer coverage of absorbed atoms (Ag, Pb, and H) and this dramatically hinders its further development.^{22,23}

Redox pseudocapacitor is analogous to a surface or near surface electrochemisorption process that accompanied by the charge transfer process (Figure

2.7b). Transient change in valence states of active materials occurs with concomitant faradaic charge transfer during charging/discharging. Materials such as reducible TMOs (RuO_2 , MnO_2 , Fe_2O_3) and redox polymers (PANI, PPy) have been widely investigated as the potential candidates to exhibit redox pseudocapacitance.²⁴

Intercalation pseudocapacitance is arisen from the phenomenon of cations intercalate into the 2-D crystalline lattice of layered host materials (Figure 2.7c). Such a behavior is associated with the rigid layered lattice framework that can provide 2-D pathway for ion transportation with minimum structural distortion. Materials that meet these requirements are Nb_2O_5 , V_2O_5 , MoS_2 , and MoO_3 .^{25,26}

Figure 2.7. Schematic diagram of different type of pseudocapacitive charge storage mechanisms.

2.3.3 Comparison between EDL Capacitors and Pseudocapacitors

As depicted in Figure 2.8, an ideal capacitors exhibit a rectangular shape (indicated as 1, green line). However, polarization sometime occurs when the system is exposed of different kinds of resistivity (indicated as 2, orange line). The highly reversible electrostatic electrolyte/electrode interfacial reaction of EDLC enables the CV curve to exhibit an almost symmetrical loop but showing a voltage delay (ΔV) when the potential is sweeping reversely (indicated as 3). This phenomenon is more obvious for pseudocapacitive materials, in which the distorted rectangular CV curve is due to the slow kinetics during the electron transfer process. On the other hand, the distinguishable redox couple (indicated as 4) always presents for materials with pseudofaradaic properties.²⁷ Indeed, redox pseudocapacitance is limited by electronic conductivity and the charge diffusion across the electrolyte/electrode interfaces, giving rise to voltage delay.

Figure 2.8. Typical charge/discharge voltammetry characteristics of an EC. Reprinted from Ref.²⁷ Copyright (2012), with permission from Elsevier.

Despite of having much higher specific capacitance than the EDLC, short cycle life is a problematic issue for the redox species due to the dissolution and structural deformation after repeating phase transformation in the charge/discharge process. It is worth noting that the charge storage of intercalation pseudocapacitance is impeded by the cation diffusion rate in the lattice structure of the host materials, restricting the SC charging rate. To have a clear picture on these two important charge storage mechanisms, Table 2.1 summarizes the characteristic of EDL capacitors and pseudocapacitors in different aspects.²⁸ In summary, the power density of EDL capacitors is superior but their energy density is still limited by the charge storage mechanism that relies on electrostatic in origin. On the other hand, the energy density of pseudocapacitors is comparable to batteries, their energy density is limited by the kinetics problem that are associated with the charge transfer process of the active materials.

Table 2.1 Comparison of EDL capacitors and pseudocapacitors.

EDL capacitors	Pseudocapacitors
Non-faradaic	Faradaic
Electrostatic energy storage	Electrochemical energy storage
Highly reversible	Slow reaction kinetics
Lower energy density	High energy density

2.4 Electrode Materials

As the energy density is proportional to the specific capacitance, the key for achieving high-performance SCs lies at the electrode materials. There are some common traits for electrode materials to reach this goal despite of adapting to different charge storage mechanisms, which are (1) high surface area active materials to increase the surface-to-

volume ratio, providing maximum contact surface between the active materials and electrolyte ion; (2) porous structure to guarantee easy accessibility for ion penetration, avoiding sacrifices of surface area due to stacking or blockage of active sites. In this part, potential electrode materials that be will be briefly introduced.

2.4.1 Carbon-based Materials

In this family, carbon nanostructures ranging from zero to 3 are being reported. They hold advantages of being low-cost, versatile, chemically stable in different environments, highly conductive and can operate at wide temperature range.

AC represents the first generation of carbon materials used in SCs owing to their high specific surface area for accumulation of charges. They can be derived from various precursors, such as natural biomass,²⁹ coal,³⁰ and petroleum coke,³¹ making them versatile in structure and surface texture based on different activation processes. In literature, their electrochemical performances varied significantly even though they all possess exceptionally high surface area, attributing to their pore structure. In this regard, optimum pore size is required to facilitate the ion penetration but not limiting the accessibility and mobility of the ions within the electrode. In short, better-performing ACs basically belongs to those who have high specific surface area and optimum pore size.

Besides, 2-D graphenes with micron lateral size and nano dimension thickness are well-known SC electrode materials. Without any stabilization treatment, the unprocessed graphenes exhibit relatively low electrochemical response, but exceptionally high specific capacitance can be achieved after the activation process that increases the surface area and prevents their re-stacking in solvents. Engineering of graphenes properties can be done

through surface modification and techniques such as thermal treatment³², colloidal chemical method³³, incorporation of spacers (small organic molecules and nanoparitics),³⁴ and crumpling of graphene sheets³⁵ *et. al.* have been reported in literature.

CNTs inherit some of the intrinsic properties of graphenes but their micron-size axes allow them to exhibit higher electronic conductivity and mechanical strength besides solving the re-stacking problem of graphenes.^{36,37} Additionally, ion diffusion can be facilitated by having the open-ended tunnel for electrolyte percolation. The entanglement of network provides CNTs with resilient and robust framework. Hence, freestanding SC electrode can be readily formed by incorporating the CNTs with foreign species (metals, transition metal) using drying or vacuum filtration method.³⁸ Bundled CNTs that caused from the strong van der waals interaction between their basal planes are not desirable because the agglomeration problem may reduce their surface area and accessibility of ions

Recent development of SCs also focuses on heteroatoms (O, N, P) incorporated carbons.³⁹⁻⁴¹ Depending on the type of precursors used in the synthetic step, diverse combination of carbon composition can be prepared. The doped-species can potentially change the electronic properties of the carbon by altering the electron density on the graphitic surface and affecting the electron affinity of the carbon materials. Recent reports also illustrated that the substitution of carbon with foreign atoms in the graphitic six-membered ring induces pseudo-capacitive properties due to the presence of reducible functional groups, giving rise to additional enhancement in specific capacitance.

Recently, 3-D carbon framework is a hot topic to be explored.⁴² The robust and interconnected 3D network is able to minimize the diffusion pathway by providing higher permeability of electrolyte ions to penetrate beyond the surface region. Besides, the

excellent mechanical strength of 3D carbon network constructs a rigid architecture for electrochemical reactions.^{43,44} Continuous effort was also done on developing freestanding 3D carbon electrode that avoids the addition of binders during the fabrication process.⁴⁵⁻⁴⁷ The binder-free concept of 3D carbon electrode aims at reducing the ion transport resistance of the electrodes that leads to large IR drop and eliminating the “dead” mass induced by the electro-inert binders.

2.4.2 Pseudocapacitive Materials

Recent progress in pseudocapactors has been done on investigating the electrochemical properties of metal oxides/hydroxides, metal sulfides, pre-doped materials and also redox polymers. Their electrochemical properties have strong correlation with their crystal structures, hydration properties and surface area. Despite of having high energy storage, semiconductor materials are inferior in resisting degradation upon cycling due to their low electronic conductivity and low charge transfer kinetics.⁴⁸ Apart from those semiconductors, the conducting polymers (PEDOT, PANI, PPy) emerged as important electrode materials that can compensate their disadvantages. However, the challenge for polymers is to retain their structural rigidity in response to continuous swelling and shrinking processes without compromising their cycle life.

2.4.2.1 Metal Oxides

Among the TMOs, ruthenium dioxide (RuO_2) represents the state-of-the-art in SCs as their have relatively high theoretical specific capacitance in wide operational potential (1.4 V) based on their high electronic conductivity and multiple valance states for electron

transition ($\text{Ru}^{2+} \leftrightarrow \text{Ru}^{3+}$, $\text{Ru}^{3+} \leftrightarrow \text{Ru}^{4+}$, $\text{Ru}^{4+} \leftrightarrow \text{Ru}^{6+}$). In addition, their highly reversible faradaic response allows them to present good cycling stability. Two different phases of RuO_2 are found to be electro-active, which are rutile phase RuO_2 and hydrated $\text{RuO}_2 \cdot x\text{H}_2\text{O}$. Fundamental studies have been done on investigating the electrochemical protonation charge storage mechanism of RuO_2 , which can be simplified as follows:^{49,50}

Hydrous $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ has been investigated before to understand the effect of structural water on their electronic conductivity and ion diffusion rate.⁵¹ It was also found that the amorphous $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ shows higher specific capacitance than the crystalline RuO_2 due to the flexibility of amorphous state to perform lattice rearrangement upon ion intercalation/deintercalation, allowing more active sites for redox reaction. Although RuO_2 -based materials are promising candidates, their expensive cost and limited abundance in nature make them impractical for widespread application.

Alternatively, manganese oxides, especially MnO_2 holds great promise in the future. From the ecological standpoint, MnO_2 shows more cost-effective compared to expensive RuO_2 . Indeed, MnO_2 possesses several advantages as promising pseudocapacitive materials: (1) abundant in nature; (2) low toxicity; (3) valence states varying from +2 to +7 that allow facile electron transition among their oxidation states (MnO , Mn_3O_4 , Mn_2O_3 , MnOOH , MnO_2); (4) rich in structural chemistry by having diverse crystal structures (Figure 2.9); (5) capable in forming different kinds of allotropes, in which different spatial arrangement of MnO_6 octahedra (vertices or edges sharing of subunits) can result in manganese polymorphs with different tunnel size (Table 2.2).⁵² On the other hand, diverse

tunnel structure of MnO_2 enables it to be used to accommodate the electrolyte ions with different radii in the framework organized by the interconnected MnO_6 octahedra.^{53,54} In addition to the aforementioned factors, the surface area, morphology, defect chemistry and pore structures may also affect their electrochemical performances.⁵⁵

Figure 2.9. Different crystal structures of manganese oxides. Reprinted with permission from ⁵². Copyright (2008) American Chemical Society.

Table 2.2. Tunnel structures of MnO_2 allotropes.⁵²

Allotropes	Tunnel	Sizes (Å)
$\alpha\text{-MnO}_2$	(1×1) , (2×2)	1.89, 4.6
$\beta\text{-MnO}_2$	(1×1)	1.89
$\gamma\text{-MnO}_2$	(1×1) , (1×2)	1.89, 2.3
$\delta\text{-MnO}_2$	Interlayer distance	7.0

Notably, MnO_2 has unique electrochemical properties, in which pseudocapacitance that are associated with surface and bulk charge storage reactions, respectively participate in the charge/discharge processes. The former one is a fast faradaic response involved the electrolyte ions adsorption/desorption on the electrode surface, following equation 26. This interfacial reaction causes a change in the oxidation states of Mn, varying between

+4 and +3 while the electrolyte cations play role in maintaining charge balance of the Mn species.⁵⁶ Additionally, intercalation/deintercalation of electrolyte ions into the crystalline lattice layer of MnO₂ is an alternative pathway to yield pseudocapacitance, following equation 27. Different from the previous case, changes in valence state is related to the incorporation of the electrolyte cations into the crystalline lattice of layered MnO₂ and eventually, the lattice dilation process induces the reduction of Mn⁴⁺ to Mn³⁺.⁵⁷

where C⁺ represents the electrolyte cations (H⁺, Li⁺, Na⁺, K⁺).

Nevertheless, similar to other TMOs, the intrinsically low electronic conductivity ($10^{-5} \sim 10^{-6} \text{ S cm}^{-1}$)⁵⁸ and proton diffusion rate ($6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$)⁵⁹ of manganese oxides remains a great challenge to be overcome. On the other hand, the irreversible transformation of Mn(II) and Mn(IV) species have limited their operating potential due to the dissolution phenomenon at these unstable states. Hence, redox reaction of manganese species is always restricted between the Mn(IV) and Mn(III).⁶⁰

Other than manganese oxides, V₂O₅ also has various oxidation states (V⁵⁺, V⁴⁺, V³⁺, V²⁺) to achieve facile electron transition. Similar to Nb₂O₅, MoO₃, and TiS₂, the layered crystalline structure of V₂O₅ provides them with van der Waals gap for cation intercalation according to following equations:^{61,62}

Besides having redox pseudocapacitance based on the surface reactions, the structural characteristics of V₂O₅ endow them with an additional faradaic intercalation

pseudocapacitance. The rigid crystalline lattice network allows reversible cations transportation along the interlayer gap followed by the reduction of vanadium ion to retain the charge neutrality.²⁶ Hence, these two important contributions are expected to give them higher level of charge storage capability. Since the kinetics of intercalation mechanism is not impeded by the solid-state diffusion, the intercalation pseudocapacitance accompanied by the redox pseudocapacitance would be a benefit for V_2O_5 to realize a high-performance SC.²⁵

Among various TMOs, iron oxides (Fe_2O_3 , Fe_3O_4 , $FeOOH$) are promising candidates that are able to show redox pseudocapacitance at low potential range (below 0 V vs. SCE).⁶³ This intrinsic characteristic of iron oxides allows them to kinetically push the hydrogen evolution to more negative limit in aqueous medium.⁶⁴ Hence, iron oxides could be used to replace the conventional carbon-based anodes in asymmetric SC at the expense of cycling stability due to their lower electronic conductivity of iron oxides as compared to the carbonaceous materials.⁶⁵ The charge storage mechanism of iron oxides involves the reversible transition of the Fe^{3+}/Fe^{2+} redox couple, but the effect of counter ion in maintaining the charge balance is yet to be determined.⁶⁶

2.4.2.2 Metal Hydroxides

Layered metal hydroxides such as $Ni(OH)_2$ and $Co(OH)_2$ have been long investigated as the SC electrode materials by exploiting their reversible redox properties. $Ni(OH)_2$ can achieve 2675 F g^{-1} in basic solution⁶⁷ while $Co(OH)_2$ can deliver specific capacitance as high as 3108 F g^{-1} .⁶⁸ However, both of these electrode materials have narrow working potential, resulting in lower energy densities.

The charge storage mechanism of $\text{Ni}(\text{OH})_2$ depends on the electrochemical reaction of the $\text{Ni}^{3+}/\text{Ni}^{2+}$ redox couple in response to anionic electrolytes, which can be generally expressed as follows:⁶⁹

However, the charge storage mechanism of $\text{Co}(\text{OH})_2$ is distinct from $\text{Ni}(\text{OH})_2$. Besides having simultaneous oxidation of $\text{Co}(\text{OH})_2$ to CoOOH , further transformation of CoOOH to CoO_2 is a plausible route, giving rise to two pairs of redox peaks during CV measurements.⁶⁸ Hence, the general expressions for the quasi-reversible redox reaction of $\text{Co}(\text{OH})_2$ can be written as:⁶⁸

2.4.2.3 Conducting Polymers

Conductive polymers such as PANI, PPy, PTh, and PEDOT are new class of electro-active materials that make use of the unique doping/de-doping chemistry associated with their π -conjugated electrons along the carbon backbone.⁷⁰⁻⁷² Both the electrical double layer and pseudocapacitive charge storage mechanisms are exhibited by the conducting polymers. The former one is derived from the surface electrostatic reaction while the latter one is arisen from the facile electron transition along the polymeric π -conjugated chains. Most of the conducting polymers are electrochemically or chemically synthesized through the polymerization of their corresponding monomers, which can be divided into *p*- or *n*-doping polymers. Based on this, they adopt to different charge storage mechanisms, in

which conductive polymers are *p*-doped with anions in oxidation reaction (equation 33), and inversely, *n*-doped with cations in reduction reaction (equation 34).⁷³

Restriction to the polymers lies at their structural fragility when they are subjected to repeating swelling and shrinking during charge and discharge, giving rise to large amount of irreversible capacitances.⁷⁴ In addition, the limitation of this class of materials is their narrow window potential, generally less than 1 V in aqueous electrolytes. Over-oxidation by extending the operating potential may catalyze the breakdown of polymers.⁷⁵ Hence, much effort has to be devoted to looking for better cell configuration to increase the operating voltage for greater energy density.

2.4.3 Hybrid Structures

The heterostructured electrode materials that are being designed in nano-regime provide an alternative platform in adding functionalities and synergistic properties to the single-phase nanostructures. Therefore, research trend reflect enthusiasm towards synthesis of hybrid structures that constructed by more than one component in a unique architecture to compensate their intrinsic disadvantages such as low electronic conductivity, slow reaction kinetics and low mechanism strength. Generally, hybrid structures can be categorized into (1) core-shell hybrid structures; (2) segmented heterostructures; (3) branched heterostructures; and (4) nanoparticles-decorated hybrid structures. On the other hand, vast combination of electrode materials is available in meeting the growing energy demands, including metal/metal oxides, polymers/metal oxides, and also carbon/metal

oxides. Positive synergistic results generated from each component of the hybrid structures further convinced the research society that their multi-functional properties make great contribution in providing electrochemical enhancement.

2.4.3.1 Mixed Metal Oxides Heterostructures

The combination of multiple metal oxides in core-shell architectures are desirably achieved for capacitive enhancement. In this regard, the core region is usually consisted of species with higher electronic conductivity to act as a conductive scaffold for electron transfer between the current collector and the shell species. In addition, they are usually engineered for higher surface area to obtain larger contact area with the electrolyte ions. From the surface electrochemical point of view, the construction of core-shell structures could possibly reduce the surface energy of the electrode materials and subsequently become more resistive to side reactions that may cause undesirable consequences.⁴⁸ For instances, 1-D core-shell structures consist of conformal coating of MnO₂ on SnO₂ was synthesized by Yan *et. al.* (Figure 2.10).⁷⁶ It was found that the low electronic conductivity problem of MnO₂ (5 – 74 S cm⁻¹) was mitigated by having SnO₂ core (5 – 74 S cm⁻¹) to conduct enhanced electron transfer between the current collector and the MnO₂ shell layer compared to the single-phase MnO₂. Owing to this unique architecture, the hybrid structures could provide specific capacitance of 637 F g⁻¹ (based on MnO₂) at 2 mV s⁻¹ in neutral aqueous solution and demonstrated excellent cycling stability by exhibiting less than 1.2% capacitive fading after 2000 cycles.

Figure 2.10. (a-b) FESEM images of the SnO₂/MnO₂ composites; (c) TEM image of the SnO₂/MnO₂ composites. Its corresponding SAED pattern was shown in the inset of (c). (d) HRTEM image of a single SnO₂/MnO₂ composites recorded from the marked area in (c). (e-f) STEM image and the line-scanning elemental mapping across the SnO₂/MnO₂ nanowires (as indicated in (e)). Reprinted with permission from ⁷⁶. Copyright (2008) American Chemical Society.

In another report, ZnO₂ was functioned as the transportation pathway to maximize the utilization of the nanoporous MnO₂ shell layer by having enhanced electron transfer between the active materials and the current collector (Figure 2.11). On the other hand, the ZnO₂ experienced little structural deformation upon cycling due to its electrochemical stable nature, serving as the rigid scaffold to provide mechanical support. As a result, the specific capacitance of the ZnO₂ NR MnO₂ shell composites could reach 675 F g⁻¹ at 10 mV s⁻¹ (based on MnO₂), significantly surpassing the single-phase MnO₂ NTs counterparts.⁷⁷

Figure 2.11. SEM images of (a-b) ZnO NRs and (c-d) ZnO/MnO₂ composites; (e-f) TEM images of ZnO/MnO₂ composites. Reproduced from Ref. ⁷⁷ with permission from The Royal Society of Chemistry.

Although the hybrid nanostructures mentioned above have further boosted their electrochemical performance, the main concern is the existence of “dead-mass” or “dead-volume” in the hybrid system, where the core compartment contributes little to the overall specific capacitance. Therefore, TMOs that are electro-active were purposely used as the substituents in order to reach full utilization of all the components of the heterostructures. In this regard, Xia *et. al.* synthesized Co₃O₄@NiO core-shell heterostructures with the aid of hydrothermal and chemical bath deposition methods (Figure 2.12).⁷⁸ Improved electrochemical properties of these hybrid structures in term of cycling performance could be attributed to the nanoporous structures that made the electrolyte penetration became easier across the interfaces and endowed them with higher exposure of electro-active surface area (Co₃O₄ core) beyond the surface region (NiO shell). Furthermore, the core-shell configuration constructed a firm architecture to prevent drastic structural

deformation of the heterostructures. Owing to the unique core-shell architecture, these heterostructures could deliver specific capacitance as high as 853 F g^{-1} at 2 A g^{-1} .

Figure 2.12. TEM images of (a-b) Co₃O₄ nanowire; (c-f) Co₃O₄@NiO core@shell nanowire; (e) NiO nanoflake shell region; (f) porous characteristic of the Co₃O₄ core region. (g) STEM-EDX elemental mappings of Co and Ni. Reprinted with permission from ⁷⁸. Copyright (2008) American Chemical Society.

2.4.3.2 Carbon/Metal Oxides Heterostructures

In literature, significant progress has been made on using carbon-based hybrids in reducing agglomeration of the supported nanostructures and more importantly, acting as the conductive scaffold and mechanical support for another species. In this regard, carbonaceous materials such as CNTs, graphenes, carbon fibers, and carbon textiles are those successful examples for deposition of nanostructures with significant capacitive improvement in terms of cycling stability, energy and power densities.

The incorporation of ultrathin graphene NSs, a 2-D sp^2 hexagonal carbon network, with pseudocapacitive materials could provide improved cycling stability and rate

capability in the presence of electrochemically stable graphitic EDL capacitors. In this regard, the combination of MnO_2 and graphene has been widely investigated in the past. For example, graphene oxides- MnO_2 nanocomposites synthesized by a simple heating-up method in a mixture of H_2O and isopropyl alcohol was reported by Chen *et. al.* (Figure 2.13).⁷⁹ Enhanced capacitive performances highly dependent on the highly conductive graphene scaffold to provide effective electron/charge transfer pathway.

Figure 2.13. (a-b) Low magnification TEM images of GO and MnO_2 nanostructures; (c-d) TEM bright-field and dark-field images of CMG3; (e-f) HRTEM images of MnO_2 nanostructures. Reprinted with permission from ⁸⁰. Copyright (2008) American Chemical Society.

It was found that the 2-D graphene structures can be transformed into 3-D network using a sacrificial template route. The morphological characterizations of the 3-D graphenes/ MnO_2 network after removal of the nickel foam template was illustrated in Figure 2.14. The advantages of graphenes were inherited, additionally, the porous

structure generated was beneficial for ease penetration of electrolyte ions and guaranteed fully utilization of the active surface area.⁸¹

Figure 2.14. (a) SEM image of the 3-D graphene networks after removing the nickel foam template; (b) TEM image of a single layer graphene. Inset is its corresponding SAED pattern; (c) SEM images of the samples with 0.85 mg cm^{-2} mass loading. (d) TEM image of the MnO_2 with 120 min deposition time. Reprinted with permission from ⁸². Copyright (2008) American Chemical Society.

Based on previous successful attempts on building 3-D network, Mazloumi *et. al.* demonstrated a general approach to fabricate mesoporous vertically aligned CNT/metal oxides (C, Zn, Mn) hybrid structures using microwave-chemical process.⁸³ *In-situ* growth of metal oxides on CVD-grown 1-D CNTs forest provided intimate contact between the current collector with the active materials, significantly reducing the contact resistance induced by the incorporation of electro-inert binder. Besides, the low electronic conductivity problem of the TMOs can be mitigated and resulted in capacitive enhancement.

2.4.3.3 Polymers-based Heterostructures

Problems such as volumetric shrinkage and reduction in conductance in the de-doping process may cause undesirable ohmic polarization to happen. Therefore, the conducting polymers coupling with TMO heterostructures are demonstrated to solve these problems. On the other hand, by exploiting their flexible organic framework to protect the attached particles against dissolution in electrolytes (too acidic or basic) and excellent electronic conductivity of polymers, the electrochemical properties of attached TMO species can be enhanced. Wide variety of polymers make the synthetic process more versatile, in which hydrophobic, hydrophilic and amphiphilic polymeric building blocks can be used as the template to support the deposition of inorganic materials. Conducting polymers such as PEDOT, PANI and PPy were used previously.

For example, MnO₂ nanoparticle enriched PEDOT nanowires and MnO₂/PEDOT coaxial nanowires could achieve 250 and 210 F g⁻¹ at 5 mA cm⁻² current density.^{84,85} On the other hand, coaxial PANI-MnO₂ heterostructures were successfully synthesized *via* a two-step approach (hydrothermal method to prepared MnO₂ nanowires and surfactants-assisted polymerization to prepare conformal coating of PANI) to give uniform coating of PANI conducting polymer on 1-D MnO₂ (Figure 2.15).⁸⁶ Even at relatively high current density (2 A g⁻¹), the specific capacitance of PANI-MnO₂ can still deliver 498 F g⁻¹, which was apparently greater than the values of single-phase MnO₂ (377 F g⁻¹) and PANI (324 F g⁻¹). Enhanced cycling stability was found for the PANI-MnO₂ nanocomposites as they exhibited only 5% of capacitive fading over 5000 cycles (single-phase MnO₂ and PANI were 18% and 30%, respectively). The authors attributed these observations to the enhanced electronic conductivity of the composites in the presence of conducting

polymers to reduce the active materials/electrolyte interfacial charge transfer resistance and the PANI protecting layer endowed them with higher resistivity against dissolution of MnO_2 upon long-term cycling.

Figure 2.15. SEM image of (a) MnO_2 nanowires, (b) MnO_2 /PANI coaxial nanowires, and (c) PANI. TEM image of (d) MnO_2 nanowires and (e) MnO_2 /PANI coaxial nanowires. (f) TEM-EDX analysis of MnO_2 /PANI coaxial nanowires Reproduced from Ref. ⁸⁶ with permission from The Royal Society of Chemistry.

Resembling to the synthetic method mentioned above, Qu *et. al.* used oxidative polymerization of PPy on the surface of V_2O_5 with the aid of anionic surfactant, dodecylbenzenesulfonate (DBS^-) to prepare V_2O_5 @PPy core-shell structures (Figure 2.16).⁸⁷ Well-defined V_2O_5 @PPy nanostructures exhibited superior energy density and cycling stability due to the synergistic effect between the conducting polymers and the V_2O_5 . Here, the incorporation of redox polymer increased the specific capacitance of the composites (162 and 308 F g^{-1} for V_2O_5 and V_2O_5 @PPy, respectively at 100 mA g^{-1}) and improved the charge transfer kinetics of the the heterostructures. Such promising results

again drew the research attention in combining the polymeric species with pseudocapacitive material in pursuit of further technological breakthrough.

Figure 2.16. (a-b) SEM images of the bare V₂O₅ nanoribbons and the PPy@V₂O₅ nanocomposites; (c) TEM image of PPy@V₂O₅ core-shell-structure. Reprinted from Ref. ⁸⁷ Copyright (2012), with permission from John Wiley & Sons.

2.4.3.4 Ternary Structures

New trend was established on synthesizing advanced electrode materials with multi-functionality and diversity in compositions. The construction of ternary structure is one of the alternatives in satisfying current demands for being high-performance in terms of energy and power densities.

In this regard, ternary structure consisted of MnO₂/CNT/PEDOT:PSS was successfully synthesized by Hou *et. al.*⁸⁸ By addressing the electronic conductivity problem of MnO₂ by depositing MnO₂ on the mechanical stable CNT backbone, enhanced electrochemical performances could be obtained. More surprisingly, the addition of conducting polymer as the outermost layer improved the charge transfer kinetics by making stronger adhesion between the MnO₂/CNT nanocomposites and the current collectors. Besides, the intertwined network formed a mesoporous structure for easy penetration of electrolytes, giving rise to excellent electrochemical performances, in

which specific capacitance of $\text{MnO}_2/\text{CNT}/\text{PEDOT:PSS}$ (200 F g^{-1}) was higher than the single-phase MnO_2 (129 F g^{-1}) and $\text{MnO}_2/\text{PEDOT:PSS}$ (132 F g^{-1}) at 5 mA cm^{-2} .

Successful attempt in preparing $\text{WO}_{3-x}@\text{Au}@\text{MnO}_2$ core-shell nanowires on carbon fabric was achieved in literature.⁸⁹ The combination of WO_{3-x} , Au, and MnO_2 in a unique architectures resulted in several electrochemical improvements: (1) direct growth of active materials on current collector improved the electron transfer rate; (2) reduced internal resistance was obtained by having conductive Au metal as linkers. Thus, the ternary nanocomposites could deliver 588 F g^{-1} of specific capacitance at scan rate of 10 mV s^{-1} and exhibited good cycling stability over 5000 cycles.

Figure 2.17. (a) Schematic representation of the fabrication process of $\text{WO}_{3-x}@\text{Au}@\text{MnO}_2$ NWs. SEM images of (b-c) WO_{3-x} NWs; (d) $\text{WO}_{3-x}@\text{Au}$ NWs; (e) $\text{WO}_{3-x}@\text{Au}@\text{MnO}_2$ NWs on carbon fabrics. Reprinted from Ref. ⁸⁹ Copyright (2012), with permission from John Wiley & Sons.

Similar to the 3-D $\text{WO}_{3-x}@\text{Au}@\text{MnO}_2$ core-shell nanowires, $\text{Co}_3\text{O}_4@\text{Pt}@\text{MnO}_2$ nanowire arrays was synthesized to boost the electronic conductivity of MnO_2 species.⁹⁰

In addition, the author claimed that the attached Pt nanoparticles can endow size confinement effect on MnO_2 to promote homogeneous nucleation of MnO_2 and hence, greatly enhanced the loading efficiency of MnO_2 species on Co_3O_4 support. This led to a specific capacitance of 539 F g^{-1} at 1 A g^{-1} while obtaining almost no capacitance fading over 5000 cycles.

Figure 2.18. SEM images of (a-b) Co_3O_4 NAs; (c-d) $\text{Co}_3\text{O}_4@\text{Pt}$ NAs; (e-f) $\text{Co}_3\text{O}_4@\text{Pt}@\text{MnO}_2$ NAs. Reprinted by permission from Nature Publishing Group: Nature Materials (⁹⁰), copyright (2008).

2.5 Electrolyte

As discussed above, the influences of electrolyte in energy and power densities from the aspects of operational potential window and internal resistance (ESR) have spurred the research development in this area to realize the full potential of SCs. There are two main categories of electrolytes, which are liquid (aqueous and non-aqueous) and solid (gel).

2.5.1 Aqueous

Aqueous electrolytes that consist of acids (H_2SO_4 , HCl), alkalis (LiOH , NaOH , KOH), and neutral salts (LiCl , NaCl , KCl) are widely used in despite of their narrower thermodynamically stable window potential (1.23 V) as compared to organic and solid electrolytes. From the ecological point of view, use of aqueous electrolytes is more environmental benign, cost-effectiveness, and safe. On the other hand, the ionic conductivity of water is several orders of magnitude higher than the organic electrolyte because the sizes of cations in aqueous electrolytes are much smaller than that of solvated ions in organic electrolytes, making the electrolyte ions easier to approach the electrode surface and penetrate beyond the surface region of the electrode. The hydrated ion radii of different cations can be arranged as follows:⁹¹

Table 2.3. Ionic and hydrated ion radii of different alkaline cations.

Alkaline Cations	Ionic Radius (Å)	Hydrated Ion Radius (Å)
Li^+	0.90	3.82
Na^+	1.17	3.58
K^+	1.49	3.31
Me_3N^+	2.85	3.47
Et_3N^+	3.48	4.00
Pr_3N^+	3.98	4.52
Bu_3N^+	4.37	4.94

Recently, focus has been directed to optimize the cell configuration in aqueous electrolyte. By having a symmetric/asymmetric SC arrangement, window potential can be adjusted to 2.7 V without showing significant electrode degradation. Such appealing

results have sparked great interest in research again to obtain further improvement of aqueous system.

2.5.2 Organic Electrolytes

Commercial used electrolytes are organic-based liquids, for examples, quaternary alkyl ammonium salts in propylene carbonate or acetonitrile. Although wider electrochemical window of organic electrolytes (beyond 2.5 V) is beneficial for greater energy density, some issues still remain to be overcome. Most reports reveal the safety issues of organic electrolytes due to their highly flammable properties. On the other hand, the lower ionic conductivity seems to be an adverse impact in their rate capability performance. Higher electrical resistivity of organic electrolyte could be attributed to the bulkier organic side chains owned by the cations, giving them slower molecular movement in the electrolyte. The ionic conductivity of commonly used electrolytes can be arranged as follows:⁹²

Table 2.4. Ionic conductivity of different electrolytes at 1 mol dm⁻³, 25 °C.

Electrolytes	Solutions	Ionic Conductivity (mS cm ⁻¹)
NaCl	H ₂ O	89.9
KCl	H ₂ O	111.9
HCl	H ₂ O	332.8
Et ₄ NBF ₄	PC	13
	AN	56
LiPF ₆	PC	5.8
	AN	50
LiClO ₄	PC	5.6
	AN	32

2.5.3 Solid Electrolytes

The practical implementation of solid-type polymer electrolyte in SCs was envisaged by the motivation to miniaturize this energy storage device. This concept makes use of the freestanding polymeric gel matrix to encapsulate the ionic additives within the framework as the solid electrolyte. The rigid organic framework of gel polymeric electrolyte is maintained while the ionic species are extracted from the polymeric host. In the later development, the solid polymeric electrolytes are branching into two categories, which are aqueous and non-aqueous. The aqueous polymer gel electrolytes can be elucidated as dissolving the acidic (H_2SO_4) or alkaline (KOH) molecules into a mixture of polymers and solvents. On the other hand, non-aqueous type solid electrolyte substitutes the aqueous components with either organic solvents or electrolytic salts in different polymer systems. Recent year, all-solid-state SCs have been invented by using the solid gel as the electrolyte but it is still in its infancy. The device performance is inferior as compared to those liquid electrolytes, owing their low ionic conductivity and also the limited concentration of salt additives within the electrolyte. Hence, on-going studies are hoped to bring out workable solutions to these issues.

2.6 Summary and Current Status

To meet the ever-increasing energy demands, SC electrode materials that are capable of exhibiting high energy density, good rate and cycling stability are highly desirable. With regard to the aforementioned criteria, bulk materials can no longer fulfill the promise for the next-generation of energy storage devices. Fortunately, current nanoscale science and technology has been hailed as a sparkling success in improving the electrochemical

performances by restricting the electrode materials to nanometer level. By implementing the nanomaterials as SC electrode, both the bulk and surface properties of the nanostructured materials are uncovered. Nanostructuring is an efficient way to increase the surface-to-volume ratio per unit mass and create more electro-active interfaces. By reducing the particle to nano-dimension, the ion diffusion length can be shortened, the inner stress can be alleviated, and reaction kinetics can be improved significantly, giving rise to higher reactivity towards electrochemical reactions.

Single-phase nanostructures are lack of competency due to the limitation in their intrinsic properties. Integrating different components into a single system allow an increase in the degree of structural and compositional complexity on the nanoscale, paving a new way towards enhanced functional improvement. By manipulating different distinct properties of individual component in a multi-component system, tailorable functionality can be achieved for use in novel applications. Research community are directing to a new trend of synthesizing multi-component nanostructures with well-defined morphology, architecture and composition, symbolizing a new milestones in nano-world. Along with this line, the properties of electrode materials play crucial role in determining the overall electrochemical performance of SCs. Hence, rational design on electrode materials is essentially important.

3. Colloidal Synthesis of Carbon Coated Cu-MnO Heterostructures

3.1 Introduction

The important breakthrough in energy storage system can be traced back to the implementation of nano-sized electrode materials, endowing them with unexpected electrochemical kinetics by exhibiting both the bulk and surface properties.⁹³ Followed by this pioneer research discovery, successful attempts were also made on demonstrating the contribution of nanostructural features of TMOs in tailoring the energy storage and conversion system.⁹⁴ In effort to explore TMOs as the electrode materials, MnO has been rarely reported for SC application. In order to compensate its intrinsic disadvantages of being low electronic conductivity, hybridization approaches were always adopted to reduce the detrimental effects encountered. Apart from direct growth of TMOs on carbonaceous materials such as graphenes^{95,96}, CNTs^{97,98} to increase the electronic conductivity, the 3-D metallic scaffolds that anchoring with the current collector such as nickel foam⁹⁹, copper nanocables¹⁰⁰, stainless steel foil¹⁰¹ revolutionize current scientific research. The integrated conductive pathway provides efficient electron transport highways *via* the intimate contact between the active materials and the current collector, giving rise to better electron transfer and rate capability. However, the constraints imposed by nanostructure engineering remained a research concern owing to their higher surface energy. Upon restricting the dimension to nano-regime, the surface energy of nanoparticles becomes inevitably high, making them have strong tendency to agglomerate.

In addition, they are also highly reactive towards side reactions and subsequently induced some uncontrollable phenomena such as depletion of electrolytes, self-discharge and shorter usage life.⁹³ Hence, some research groups also exploited the conformal coating of mesoporous amorphous carbon on the nanoparticles surface as the protective matrix to address the severe agglomeration and dissolution issues.^{102,103}

In literatures, the high-temperature solution-based method was extensively applied in chemical synthesis to precisely control the dimension and geometry of the nanoparticles without sacrificing their size uniformity. The production of highly uniform nanoparticles is achieved by having steric constrain of the organic surfactants and solvents to give homogenous growth of nuclei. In colloidal chemical synthesis, a kinetic model was proposed in the past to describe the formation mechanism of nanocrystals using heating-up method.¹⁰⁴ In process I, the precursor (P) thermally decomposes to its monomeric unit (M) upon heating. Upon accumulation of the monomer, the reaction solution eventually becomes supersaturated.¹⁰⁵

In process II, the energy barrier of nucleation is overcome and the nucleation process occurs when the solution reaches a critical point in which crystal C_x is formed from the x monomers followed by abrupt decrease in the concentration of monomer.

In process III, any crystals smaller than the critical sized nuclei possess a thermodynamic tendency to dissolve and any crystals larger than the critical sized nuclei shall be thermodynamically driven to grow.

Different from the heating-up method, the hot injection method was widely studied as to induce spontaneous supersaturation upon injection of highly active reactants at high temperature into a surfactant-containing system.^{106,107} The introduction of highly reactive species into a hot solution may induce instantaneous decomposition of the precursors and the reaction solution becomes highly supersaturated. This will lead to rapid nucleation (so-called burst nucleation) to occur followed by the diffusion-controlled growth of the nanocrystals. Monomers in the solution are eventually exhausted in this stage and Ostwald ripening process takes place, in which the monomer dissolves from the smaller particles will precipitate on the larger particles.¹⁰⁸ Although monodispersed nanocrystals have been successfully synthesized by many research groups, it is still of great challenge to synthesize heterostructures in the hopes of enhancing their effectiveness. On the other hand, multiple fabrication steps approach has made the hybridization approach much more complicated.

Here, we reported a facile non-hydrolytic heating-up method to synthesized colloidal Cu-MnO heterostructures that afford high crystallinity and narrow size distribution. The versatility of this synthetic approach provides a platform for *in-situ* growth of metallic Cu that allows strong coupling between the conductive species with the electrochemical active materials. Therefore, promising electrochemical performances were achieved by breaking down the obstacles that are associated with the electronic conductivity and dissolution issues of MnO. In this regard, the metallic copper made contribution in enhancing the electron transfer process to guarantee electronic integrity of the electrode. On the other hand, the protective layer of amorphous carbon surrounded the MnO nanoparticles that formed after annealing was able to sustain the tensile stresses and

prevent dissolution of active materials upon the phase transformation. The synergistic effects that are reflected by the stability performance and rate test allowed Cu-MnO heterostructures to experience less capacitive fading upon cycling and preserve higher capacitance at high rate measurement. Since this solution-based method is versatile for synthesis of TMOs, it might pave a new way for lighter and longer calendar life SCs for commercial use.

3.2 Experimental Details

3.2.1 Synthesis of Metal-oleate

Metal-oleates complex were synthesized using a modified method according to a reported procedure.^{109,110} Using the Mn-oleate as an example, the preparation steps were described as follows: MnCl_2 (2 mmol) and Na-oleate (4 mmol) were dispersed in 10 and 20 mL methanol, respectively in separate bottle to obtain clear solutions. After that, the manganese precursor solution was added dropwise into the Na-oleate solution and highly viscous brownish precipitate can be observed instantly under sonication. The Mn-oleate complex was washed with methanol for several times to remove the residual sodium salts and stored in vacuum oven overnight to evaporate the solvent completely. The preparation step for Cu-oleate was resembled to Mn-oleate, except the MnCl_2 was substituted with $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

3.2.2 Synthesis of MnO Nanoparticles

The MnO nanoparticles were synthesized by thermal decomposition of manganese-oleate precursors under protection of argon. In the synthetic steps, the Mn-oleate complex was

redispersed in 20 mL of ODE in a three neck round bottom flask. Then, 10 mL of the solution (0.5 M) was transferred into a round bottom flask and degassed at 120 °C for 1 h to get rid of the moisture content. Subsequently, the temperature was raised to 300 °C within 15 min and refluxed for 10 min to allow the precursors being thermally decomposed. The heating mantle was then removed and the mixture was cooled to room temperature naturally. The MnO nanoparticles were precipitated and washed with hexane/acetone (volume ratio 3:1) for several times, followed by drying process in 50 °C vacuum oven overnight.

3.2.3 Synthesis of Cu-MnO Heterostructures

In the synthesis of Cu-MnO heterostructures, 10 mL of Mn-oleate (0.5 M) was added into a round bottom flask containing 20 mL ODE and degassed at 120 °C for 1 h under protection of argon. The mixture was hold at 300 °C for 10 min before the temperature was stabilized at 200 °C. Subsequently, different volume of Cu-oleate (0.1 M) was injected rapidly into the mixture and aged for 5 min. 0.1 and 0.5 mL of Cu-oleate solution added were denoted as 0.1Cu-MnO and 0.5Cu-MnO, respectively. The Cu-MnO heterostructures were precipitated and washed with hexane/acetone (volume ratio 3:1) for several times to remove the excess surfactants, followed by drying process in 50 °C vacuum oven overnight.

3.2.4 Synthesis of Carbon Coated Cu-MnO Heterostructures

In order to transform the organic surfactants into a thin layer of carbon shell surrounding the MnO and Cu-MnO nanoparticles, thermal annealing step was involved to perform the

carbonization process. The as-prepared samples were annealed under protection of argon at 400 °C for 1 h with 2 °C min⁻¹ ramping rate. Carbon coated MnO, 0.1Cu-MnO and 0.5Cu-MnO were denoted as MnO@C, 0.1Cu-MnO@C and 0.5Cu-MnO@C, respectively.

3.3 Synthesis and Characterizations of Carbon Coated Cu-MnO

The colloidal Cu-MnO@carbon heterostructures were synthesized *via* a thermal decomposition of oleate-chelated precursors in non-coordinating hydrocarbon solvent, as depicted in Figure 3.1.

Figure 3.1. Schematic representation of the proposed formation mechanism of Cu-MnO heterostructures.

In brief, pyrolysis of the carboxylate salts (Mn-oleates and Cu-oleates) in ODE solvent at elevated temperature produced highly crystalline Cu-MnO nanoparticles with narrow size distribution by taking the advantages of the homogeneous nucleation and growth of their corresponding oleate precursors in ODE solvent. Owing to the higher reactivity of Cu-oleate precursors, the Cu nanocrystals were epitaxially grown on MnO in

the latter stage by injecting the precursors into the solution at lower temperature. The one-pot synthesis method not only functionalized the MnO with metallic Cu, but also induced the anchoring of the capping agents (oleates) on the surface of MnO simultaneously. Hence, the bulky organic molecules could stabilize the nanoparticles against Brownian motion-driven aggregation. With the aim to carbonize the capping layer into amorphous carbon on the surface of MnO, annealing process was executed at 400 °C under argon protection.

The XRD patterns shown in Figure 3.2a evidenced the formation of rock-salt structure of highly crystalline MnO@C. Sharp diffraction peaks located at 34.9°, 40.6°, 58.8°, 70.3° and 73.9° can be indexed to the (111), (200), (220), (311) and (222) planes, respectively of cubic phase MnO (JPDS 78-0424).¹¹¹ No characteristic peaks were observed for crystalline impurities besides a broad hump appeared at 23° that ascribed to the amorphous glass holder. In the presence of Cu foreign species, the peaks intensity of the MnO was attenuated gradually while the diffraction peaks of elemental Cu emerged for 0.1Cu-MnO@C and 0.5Cu-MnO@C, illustrating in Figure 3.2b-c, respectively. These peak positions were consistent with the metallic copper (JCPDS 04-0836) with face-centered cubic (*fcc*) arrangement.¹¹² On the other hand, the crystallographic information also showed gradual enhanced diffraction peaks for Cu with increasing the concentration of Cu-oleate precursor.

Figure 3.2. XRD pattern of the as-prepared samples: (a) bare MnO; (b) 0.1Cu-MnO; (c) 0.5Cu-MnO.

Furthermore, the TEM and BF-STEM were employed for morphological and compositional analyses, respectively. Figure 3.3 provided the TEM and HRTEM images of the as-prepared samples with different of Cu- to Mn-oleates concentration ratio as well as the EDX elemental mapping for the as-prepared samples. The narrow particle size distribution of the MnO@C and Cu-MnO@C heterostructures shown in Figure 3.3a, 3.3d and 3.3g suggested that the surfactant-assisted thermal decomposition approach is promising in producing monodispersed nanoparticles. More precisely, the bare MnO@C nanoparticles were found to be achievable in the size range of 5–8 nm.

Figure 3.3. Structural characterizations of the as-prepared samples: (a-c) TEM images, HRTEM images and the EDX mapping of MnO, respectively; (d-f) TEM images, HRTEM images and the EDX mapping of 0.1Cu-MnO, respectively; (g-i) TEM images, HRTEM images and the EDX mapping of 0.5Cu-MnO, respectively. The regions marked in (d) and (g) were magnified in (e) and (h), respectively. The scale bars in (c), (f), (i) are 10 nm.

The lattice d-spacing of MnO@C shown in Figure 3.3b was estimated to be 0.222 nm, which was consistent with the diffraction peak corresponding to the MnO (200) plane.¹¹³ In the subsequent step, the epitaxial growth of Cu species on MnO can be

evidenced from the observation of Cu (111) with 0.208 nm lattice d -spacing and Mn (200) planes with 0.222 nm lattice d -spacing co-existing in Figure 3.3e and 3.3h, which was indicative of epitaxial growth of Cu on MnO nanoparticles.¹¹⁴ Additionally, the compositional information of Cu species extracted from the TEM-EDX shown in Figure 3.4 was also in consistent with such observation. Coupling with the compositional EDX mapping in BF-STEM, the elemental distribution of Mn and Cu could be evidently perceived in Figure 3.3f and 3.3i. In this case, no preferential growth of Cu on MnO nanoparticles was observed, giving rise to random elemental distribution of Cu on the surface of MnO.

Figure 3.4. TEM EDX elemental analysis of (a) 0.1Cu-MnO and (b) 0.5Cu-MnO.

Upon increasing the concentration of Cu to 0.6 M, severe particle agglomeration was found, as illustrated in Figure 3.5. When the concentration of Cu monomers become extremely high in the reaction solvent, the Cu nanoparticles tend to form individual cluster instead of following the epitaxial growth mechanism on the surface of MnO. In addition, the ICP results shown in Table 3 further confirmed the co-existence of the Mn and Cu species and also resolved the metal contents of Cu-MnO@carbon heterostructures, in which the molar ratio of Cu:Mn increased (0.06:1 and 0.2:1 for 0.1Cu-MnO and 0.5Cu-MnO, respectively) with increasing the concentration of Cu precursors.

Figure 3.5. TEM images of Cu-MnO with the addition of 0.6 M of Cu-oleate precursors.

Table 3.1. Elemental composition of the heterostructures.

Entry	Metal Content ^a		Molar ratio (Cu:Mn)
	(wt.%)		
	Cu	Mn	
0.1Cu-MnO	3.08	42.92	0.06:1
0.5Cu-MnO	11.29	49.71	0.20:1

^a Metal content was tested by ICP.

3.4 Formation Mechanism of Carbon Coated Cu-MnO

The concept of complete separation between the nucleation and growth steps is always applied in attempt to synthesize monodispersed nanoparticles that synonymous with high surface area and shorter ions/charges transport pathways for surface-mediated electrochemical reactions.¹¹⁵ Hence, metal-oleates were used as metal-surfactant precursors to induce homogeneous nucleation and growth in the synthetic step, which can eliminate the undesirable nucleation of intermediate phases during the growth process.¹⁰⁸

The schematic representation of the plausible formation mechanism of colloidal Cu-

MnO@carbon heterostructures was proposed as Figure 3.3. When the Mn-oleate complex was heated in non-coordinating solvent ODE, the thermal energy transformed the oleate precursors into MnO nanoparticles at 300 °C. In preparing the Cu-MnO heterostructures, hot injection above the decomposition temperature of Cu-oleate was executed to drive a high supersaturation level in the reaction solution instantaneously, inducing the Cu nanoparticles tend to grow on the surface of MnO to reduce the free energy of heterogeneous nucleation. In contrast to the sequential addition of precursors, great discrepancy in chemical reactivity between the Mn- and Cu-oleates caused the formation of discrete Cu and MnO nanoparticles instead of forming Cu-MnO heterostructures when both of them were heated to 300 °C simultaneously (as illustrated in Figure 3.6). As a result, the high reaction temperature caused Cu to grow larger at the decomposition temperature of MnO, significantly affected the uniformity in particle size and morphology.

Figure 3.6. TEM images of (a) 0.1Cu-MnO; (b) 0.5Cu-MnO where both the Mn and Cu precursors were mixed and heated simultaneously to 300 °C for 10 min.

Current successful synthesis of monodisperse nanocrystals lied on the steric stabilization of the anionic oleate molecules. The long chain oleates of the precursors can

contribute in different aspects: (1) function as the coordinating agents to stabilize the metal salts in hydrocarbon solvent; (2) prevent rapid coalescence of nuclei during the growth process *via* the steric repulsion of their bulky chains. To achieve full utilization of the surface-chelated organic molecules, the *in-situ* carbonization the organic surfactants can be done through the post-synthesis thermal annealing process under inert gas to provide a protective layer (~ 2 nm) with amorphous nature surrounded the nanoparticles (Figure 3.7).¹⁰³ The HRTEM images of the as-prepared samples shown here further confirmed the amorphous state of the carbon matrix by showing no distinct lattice fringes. Furthermore, the existence of the poorly crystalline conformal carbon coating of the as-prepared samples was further examined using Raman spectroscopy, where the D band and G band of graphitic materials were manifested at $\sim 1580\text{ cm}^{-1}$ and $\sim 1340\text{ cm}^{-1}$, respectively, as shown in Figure 3.8.

Figure 3.7. TEM images of (a) 0.1Cu-MnO; (b) 0.5Cu-MnO where both the Mn and Cu precursors were mixed and heated simultaneously to $300\text{ }^{\circ}\text{C}$ for 10 min.

Figure 3.8. Raman spectra of the as-prepared samples.

3.5 Electrochemical Measurements

In Figure 3.9a, typical rectangular CV curves were observed for all the as-prepared samples at scan rate of 2 mV s^{-1} . Here, the bare carbon substrate showed a relatively small CV loop as compared to the other as-prepared samples and hence, their capacitive contribution could be neglected in this case. On the other hand, no obvious redox peaks were observed for MnO containing samples, evidencing the unique electrochemical properties of MnO that resembled to MnO_2 in performing charge/discharge process in a pseudo-constant rate.¹¹⁶ Here, it is worth noting that the metallic copper is an electro-inert species besides of providing enhancement in electronic conductivity (no redox peaks were found for Cu). Based on these CV curves, the current response of the as-prepared samples

can be arranged in the following order: $\text{MnO@C} < 0.1\text{Cu-MnO@C} < 0.5\text{Cu-MnO@C}$ at 2 mV s^{-1} . Evidently, increasing the concentration of Cu led to significant capacitive enhancement. Different from the highly reversible redox reactions at low scan rate, the MnO@C showed distorted CV curve when the scan rate was increased to 200 mV s^{-1} , which could be due to the slow kinetics of MnO that resulted in voltage delay in response to fast scan rate, as shown in Figure 3.9b. On the contrary, the Cu-containing samples (0.1Cu-MnO@C and 0.5Cu-MnO@C) could still exhibit an almost intact rectangular CV curve at high scan rate, indicating the important role of Cu in improving the redox reaction kinetics of MnO by increasing the electronic conductivity of the hybrid structures. By integrating the enclosed CV loop of the as-prepared sample at 200 mV s^{-1} , 0.5Cu-MnO@C could achieve the highest specific capacitance, followed by 0.1Cu-MnO@C and MnO@C samples, exhibiting similar trend as the low scan rate results.

Figure 3.9. CV of the as-prepared samples at different scan rate: (a) 2 mV s^{-1} and (b) 200 mV s^{-1} .

From the GCD curves measured at low current densities (*e.g.* 0.5 and 1 A g^{-1}), the specific capacitance of the Cu-containing samples (0.1Cu-MnO@C and 0.5Cu-MnO@C) outperformed the MnO@C .

Figure 3.10. GCD curves of the as-prepared samples at different current densities: (a) 0.5 A g⁻¹; (b) 1 A g⁻¹; (c) 2 A g⁻¹; (d) 10 A g⁻¹.

It was believed that the 0.1Cu-MnO@C sample was able to strike a balance between the good electronic conductivity endowed by the Cu species and the sufficient amount of electro-active MnO to undergo redox reaction, giving rise to the highest specific capacitance at low scan rate. Such observation hinted that higher concentration of Cu reduced the specific capacitance, confirming that Cu species do not have capacitive contribution. Gradual increase in current density to 2 A g⁻¹ resulted in reverse observation, in which 0.5Cu-MnO@C surpassed the other two as-prepared samples in terms of specific capacitance. The 0.5Cu-MnO@C sample was beneficial from its excellent electronic conductivity that allowed it to experience less capacitance fading in response to higher

charge/discharge rate. At current density as high as 10 A g^{-1} , similar trend was observed and the Cu effect became more apparent, giving rise to large discrepancy in specific capacitance between the bare MnO@C and the Cu-MnO@C heterostructures.

As shown in Figure 3.11a, the rate capability of the Cu-containing samples was apparently greater than the bare MnO@C. At 0.5 A g^{-1} , the specific capacitance of the as-prepared samples evaluated for MnO@C, 0.1Cu-MnO@C and 0.5Cu-MnO@C were 203 F g^{-1} , 235 F g^{-1} and 218 F g^{-1} , respectively. As the current density increased to 2 A g^{-1} , the specific capacitance of 0.5Cu-MnO@C sample is the highest, 168 F g^{-1} , followed by 0.1Cu-MnO@C (155 F g^{-1}) and MnO@C (127 F g^{-1}). The retention percentage of the as-prepared samples could be arranged in the following order: 0.5Cu-MnO@C (43%) > 0.1Cu-MnO@C (35%) > MnO@C (8%). Even at scan rate as high as 10 A g^{-1} , the 0.5Cu-MnO@C was able to deliver 94 F g^{-1} , surpassing the other two samples. It indicated that faster electrochemical response could be obtained in the presence of higher Cu content to make successive redox reaction.

Figure 3.11. (a) Specific capacitance of the as-prepared samples at different current densities; (b) cycling performance of the as-prepared samples.

Besides, better cycling stability of 0.5Cu-MnO@C was obtained as compared the bare MnO@C and 0.1Cu-MnO@C, in which 0.5Cu-MnO@C retained 86%, 0.1Cu-MnO@C retained 80% and Cu-MnO@C retained 71% of their initial specific capacitance, respectively after 1000 cycles (Figure 3.11b). The initial discrepancy in specific capacitance between the 0.1Cu-MnO@C and 0.5Cu-MnO@C samples became smaller upon cycling, and finally the specific capacitance of 0.5Cu-MnO@C surpassed 0.1Cu-MnO@C after 350 cycles.

Furthermore, EIS was performed to confirm that the metallic Cu contributed to the overall electronic conductivity of the electrode. As shown in Nyquist plot (Figure 3.12a), all the as-prepared samples showed similar blocking behavior at high frequency region by exhibiting almost constant value in ESR, $4.9 (\pm 0.2) \Omega$ (Z' real axis intercept).¹¹⁷ Subsequently, different behavior in charge transfer resistance of the electrodes was perceived by comparing the diameter of the semicircle magnified as the inset of Figure 3.12a, where the ohmic resistance of the as-prepared samples can be arranged in order as follows: MnO@C (0.26Ω) > 0.1Cu-MnO@C (0.12Ω) > 0.5Cu-MnO@C (0.06Ω).¹¹⁸ This observation provided concrete evidence that the electronic conductivity increased with increasing the Cu content as the thickness of the amorphous carbon layer coated on the surface of MnO that may affect the charge and electron diffusion was almost the same.

It has been proposed that the behavior of SC changed from a resistor to a capacitor at the “knee frequency” (at -45° phase angle), and a pure capacitor could be reached after this transition point.¹³ Based on the Bode diagram shown in Figure 3.12b, the frequency at phase angle of -45° for the MnO@C, 0.1Cu-MnO@C, and 0.5Cu-MnO@C was estimated to be 3.46, 9.08, and 14.02 Hz, respectively and their corresponding the relaxation time (τ_0

$= 1/f)^{119}$ to reach a pure capacitor was 289, 110, and 71 ms, respectively. This interpreted that the incorporation of Cu species was useful in providing enhanced capacitive response of the SC. On the other hand, the Nyquist plot (Figure 3.12a) showed an almost -90° phase angle vertical line that resembled to the ideal capacitor for all the three samples at low frequency region, which can also be visualized in Bode diagram (Figure 3.12b) at 0.01 Hz (-76, -80, and -84 degree for MnO@C, 0.1Cu-MnO@C, and 0.5Cu-MnO@C, respectively).

Figure 3.12. (a) Nyquist impedance plots, and (b) Bode diagram of the as-prepared samples.

Based on our preliminary result, the Cu-containing heterostructures exhibited enhanced electrochemical performances as compared to the single-phase MnO. The enhanced electrochemical performance of the Cu-MnO@carbon heterostructures can be attributed to the following aspect: Incorporation of metallic Cu could be signified as a bridge to conduct integrated charge transfer between the MnO active materials and the current collector and it was beneficial for maintaining the electrical integrity of the electrode. By addressing the electronic conductivity issue of MnO, the charge transfer resistance could be reduced and capacitive response could be remarkably improved. The

positive effect could be implied from the excellent rate capability measurement. The schematic representation of the integrated charge transfer process between the active materials and the current collector was depicted as Figure 3.13.

Figure 3.13. Schematic representation of the charge transfer process between the active materials and the current collector.

To further investigate the implication of carbon coating on the nanoparticles, post-mortem morphological analyses of the MnO@C and Cu-MnO@C heterostructures were conducted, as shown in Figure 3.14. It was found that the pulverization process was suppressed, retaining the particles size as those before cycling even though denser packing density of the nanoparticles after cycling was observed. Therefore, we believed that the spatial restriction of the graphitic layer has cushioned the structural deformation during the faradaic redox reactions besides preventing the agglomeration upon cycling by restricting the random migration of the nanoparticles.

On the other hand, the dissolution of Mn^{+2} was suppressed after the carbon coating, which could be evidenced from the ICP results shown in Table 3.2. It was found that the concentration of Mn of the as-prepared samples in the electrolyte after 1000 cycles was relatively small as compared to the MnO commercial powder, showing the important role

of the amorphous carbon layer in preventing the dissolution of Mn^{2+} caused by the irreversible redox reaction of MnO.

Figure 3.14. TEM images of the electrodes after cycling for 1000 cycles: (a) MnO@C; (b) 0.1Cu-MnO@C; (c) 0.5Cu-MnO@C.

Table 3.2. ICP results of the as-prepared samples in the electrolyte after 1000 cycles.

Entry	Mn Metal Content ^a (wt.%)
MnO Powder	5.3
MnO@C	2.4
0.1Cu-MnO@C	2.3
0.5Cu-MnO@C	2.4

^a Metal content was tested by ICP.

3.6 Summary

In present study, the colloidal chemical approach provided an effective protocol to synthesize uniform Cu-containing MnO@C heterostructures, which can be summarized as the thermal decomposition and hot injection strategies. The monodispersed Cu-containing MnO@C heterostructures in nano-dimension were readily transformed into a core-shell hybrid after executing the thermal carbonization step under argon protection. It was found

that the embedded metallic Cu preserved excellent electrical integrity between the electrochemical active species and the current collector. In addition, rationally designed on the architecture of the Cu-containing MnO@C heterostructures endowed them with integrated charge transfer capability and enhanced capacitive response, giving rise to significant improvement in electrochemical performances. It was also revealed that the conformal carbon coating prevented the structural deformation and Mn^{2+} dissolution upon cycling. Since the synthesis of heterostructures with different compositions falls within the realm of possibility, versatile hybrid system can also be developed to empower the SC with capacitive enhancement responses.

Although the incorporation of metallic copper is able to increase the electronic conductivity of the active material (MnO) and improve the kinetics of the SC electrode, the electro-inert nature of these species may lead to lower energy density of SC. Thus, the substitution of metallic copper with other conductive materials that have capacitive contribution could pave a new direction to provide further improvement to the SCs.

4. Controlled Synthesis of MnOOH Nanotubes/Graphite Felt

4.1 Introduction

Electrochemical reaction that exploits the fast faradaic responses between $\text{Mn}^{\text{IV}}\text{O}_2$ and $\text{Mn}^{\text{III}}\text{OOH}$ has been widely investigated.¹²⁰⁻¹²³ In contrast to MnO_2 , MnOOH is less being reported in the past although it inherent the redox capability for facile electron transfer process.^{124,125} According to the structure-activity dependent relationship, the morphology of the active materials plays vital role in determining their electrochemical performances.¹²⁶ In this regard, the unique structural properties of NTs are advantageous for surface-mediated reaction, making them receive considerable attention for pseudocapacitor application.^{127,128} As compared to the solid core counterparts, the NTs are endowed higher surface area by exposing their inner walls for electrochemical reactions. Furthermore, the hollow interiors with good permeability enable the active surface area to be fully accessible to electrolyte ions. However, the synthesis of MnOOH with controlled geometry and dimension remains a great challenge in research field.

Although high energy density can be benefited from the pseudocapacitive characteristic of MnOOH, its semiconductive properties of being less capable of withstanding tensile strain and poor electronic conductivity nature cause them suffering from poor rate capability and shorter cycle life.⁸² Since the carbonaceous materials such as CNTs¹²⁹⁻¹³¹, graphenes¹³²⁻¹³⁴, AC textiles¹³⁵ and carbon fibers^{136,137} fulfil the requirements to provide mechanical support besides having high electronic conductivity,

they represent the environmental benign supports to mitigate the constraints that hindered MnOOH from realizing their full potential. Hence, hybridization approach to couple MnOOH and carbonaceous materials into a hybrid system has been recognized as a bridge to fill the gap between these two materials and compensate their intrinsic disadvantages.

Hydrothermal synthesis of nanomaterials can be described as the action of water under elevated temperature and pressure in a confined space, bringing about chemical reactions that are not able to perform under ambient aqueous-based condition. The water solvent behaves differently beyond its critical point, where the supercritical fluid emerged (also known as liquid-vapor co-existence phase), as shown in Figure 4.1.

Figure 4.1. Phase diagram of water, adopted from reference ¹³⁸. Reprinted with permission from AAAS.

From the ecological standpoint, hydrothermal reaction holds several advantages over conventional methods. Unlike many methods that require substantial energy and cost for operation, hydrothermal treatment makes use of environmental friendly and cheap solvent for low temperature processing. In term of safety conscience, water shows great potential to be recycled after being used and is convenient to be disposed if recycling is not possible. More importantly, highly crystalline nanomaterials can be achieved by the

unique pressure-temperature interaction of water beyond the critical point under low-temperature hydrothermal reaction.

Traditionally, the electrode fabrication step involves the addition of binders such as PVdF or nafion to enhance the adhesion of active materials to the current collector. However, degradation of the electrochemical performance is always observed as the result of inducing internal resistance of the non-conductive agents, besides blocking the reaction surface area of the electrode.¹³⁹⁻¹⁴¹ With this in mind, one of the critical aspects falls to developing binder-free approaches that can produce freestanding electrode to reduce the reliability to the conventional fabrication steps. Towards the vision for flexible SC, low cost and mass density GF that can provide conductive scaffold and unique 3-D mesh-like structures for ease of electrolyte ions penetration represents the environmental benign electrical double layer materials that capable of achieving long cycle life with good capacitive retention.

Herein, we presented a facile hydrothermal synthesis of freestanding nanostructured MnOOH/GF composites as efficient ECs. With the architecture of *in-situ* growth MnOOH on filamentary microstructure GF flexible substrate, non-conductive binders can be excluded. Nonetheless, the successful synthesis of MnOOH NTs has been demonstrated and significant capacitive enhancement was observed attributing to their unique tubular structure. More remarkably, shape-controlled synthesis of MnOOH was accomplished and the formation mechanism can be described as a rolling process of NSs into NTs intermediate stage followed by the infilling process of nanoparticles to transform the NTs to NRs as a function of reaction time. By coupling the binder-free approach in fabricating

the freestanding and flexible electrode, superior electrochemical performances were observed, implying the feasibility of these composites in SC application.

4.2 Experimental Details

4.2.1 Synthesis of MnOOH NTs/GF

The commercial available GF was firstly cut into 1 cm x 5 cm and refluxed in 3 M nitric acid to remove the impurities and to induce hydrophilic functional groups on the GF surface. After that, the GF was rinsed with deionized water for several times and dried in vacuum oven overnight for further usage. In the subsequent step, the GF was act as the support for MnOOH deposition. MnOOH NTs can be prepared by immersing the GF in deionized water (35 mL), followed by dropwise addition of KMnO_4 solution (2 mL, 0.1 M) under sonication condition (30 min) in a 50 mL Teflon lined pressure vessel. The Teflon lined autoclave was then hydrothermally treated in an electric oven preheated to 190 °C for 3 h. For the synthesis of NSs and NRs, the hydrothermal duration was set at 45 min and 6 h, respectively. After the allowed reaction duration, the autoclave was cooled to room temperature naturally and the as-prepared samples were rinsed with considerable amounts of deionized water to get rid of the remaining reactant and undesirable side products. The samples were then dry in vacuum oven overnight to remove the residual water. The as-prepared samples were denoted as MnO_2 NSs/GF, MnOOH NTs/GF, and MnOOH NRs/GF for 45 min, 3 h, and 6 h reaction time, respectively. The as-prepared samples can be directly used as the binder-free SC electrodes for electrochemical measurement.

4.2.2 Synthesis and Characterizations of MnOOH NTs/Graphite Felt

In-situ growth of MnOOH on GF can be achieved *via* a facile hydrothermal method, which was illustrated in Figure 4.2.

Figure 4.2. Schematic representation of the preparation steps for the composites.

Initially, GF was heated in concentrated nitric acid at 100 °C for 6 h to induce some hydrophilic functional groups on its surface that serve as the anchor point for metal cations deposition.^{142,143} Subsequently, the acid-treated GF was soaked in a precursor solution of KMnO₄ with vigorous sonication to introduce homogeneous dispersion of the MnO₄⁻ anion onto the GF surface. The core-shell structure was formed by reduction of MnO₄⁻ anions on GF under hydrothermal condition, finally leading to the formation of MnOOH nanostructures on the surface of GF. The appearances of the as-prepared samples were displayed in Figure 4.3. In Figure 4.3a, the colour of the electrodes changed from black to brown, indicating the successful deposition of manganese species on the surface of GF. The freestanding GF-based electrodes could be directly used for testing without prior fabrication. On the other hand, the foldable capability of the composite shown in Figure 4.3b indicated that it is strong and enough to withstand structural deformation under applied stress.

Figure 4.3. (a) Appearance of the as-prepared composites at different reaction times; (b) foldable ability of the freestanding electrode.

XRD diffraction patterns shown in Figure 4.4 provided the crystallographic information of the bare GF and the sample after 3 h hydrothermal treatment. The broad diffraction peaks at 25° and 44° shown in Figure 4.4a can be ascribed to the (002) and (100) planes of GF, respectively (JCPDS 41-1487).¹⁴⁴ In addition, the 3 h hydrothermally treated sample can be referred to manganite γ -MnOOH with monoclinic phase (JCPDS 41-1379).¹⁴⁵ The main diffraction peaks located at 26.4° , 34.2° , 35.9° , 37.5° , 40.0° , 41.4° , 51.7° , 54.2° , 55.4° , 56.6° , 62.4° , 65.5° , 65.7° can be indexed to the $(\bar{1}11)$, (020), (111), (200), $(\bar{1}21)$, $(\bar{2}02)$, (210), (022), $(\bar{2}22)$, $(\bar{3}11)$, $(\bar{1}31)$, (131), (202) planes of γ -MnOOH, respectively. On the other hand, no crystalline impurity phases were detected other than the alumina holder peak observed at 38° (JCPDS 04-787).¹⁴⁶ Due to the small grain size of the nanostructures, the diffraction peaks were relatively weak even though they were synthesized under harsh hydrothermal conditions.

Figure 4.4. XRD pattern of the (a) GF and (b) MnOOH/GF composites. Reprinted from Ref. ¹⁴⁷ Copyright (2012), with permission from John Wiley & Sons.

The morphology of the sample was investigated by SEM and TEM, which was summarized in Figure 4.5. Before undergoing the hydrothermal treatment, the carbon scaffold with 10 μm diameter with smooth surface, shown in Figure 4.5a, functioned as a support for nucleation of the manganese species. The SEM images in Figure 4.5b illustrated the surface of GF after the deposition of MnOOH. Rougher texture can be observed and the thickness of the GF was apparently greater than the uncoated precursor, indicating the conformal coating of nanostructured MnOOH on the carbonaceous skeleton. When the rough surface was magnified, a mat of interwoven 1-D nanostructures with the length of several micrometers was observed on the GF surface, as shown in Figure 4.5c. Investigating by TEM, these 1-D nanostructures were NTs with diameter in the range of 20–50 nm and their hollow interiors were clearly seen in Figure 4.5d.

Figure 4.5. (a-c) SEM images, (d-f) TEM images, and (g) HRTEM images of MnOOH NTs/GF. The region 1 and 2 marked in panel d were magnified in e and f, respectively. Reprinted from Ref. ¹⁴⁷ Copyright (2012), with permission from John Wiley & Sons.

The high magnification TEM images (Figure 4.5e-f) indicated that the NTs were mostly open-ended with the wall thickness of ~15 nm and inner diameter of ~20 nm. The HRTEM image (Figure 4.5g) of one NT revealed its polycrystalline nature and the lattice information further confirmed the formation of MnOOH, where the 0.24 nm and 0.34 nm lattice *d*-spacings matched the (002) and ($\bar{1}11$) planes of its crystallographic structure, respectively.

4.3 Formation Mechanism of MnOOH NTs/GF

The time-dependent experiment was investigated to understand the formation mechanism of the MnOOH NTs. The results indicated that the morphology and structures of MnOOH could be tuned by varying the reaction duration. When the reaction time was set to be 45 min, lamellar structure evolved and densely covered the GF surface (Figure 4.6a-c). It was noted that the NSs (Figure 4.6b) illustrated by TEM tend to stack together and formed aggregates, which was consistent with the SEM observation. Further magnifying the view of the edge region of the aggregates as shown in Figure 4.6c, ultrathin NSs with submicrometers in lateral size could be clearly seen. The HRTEM (Figure 4.6d) revealed that the NSs were constructed by self-assembled polycrystallines with grain size of ~5 nm and the lattice *d*-spacing of 0.31 nm could be index to the (002) plane of MnO₂. Furthermore, XRD peaks of the NSs sample (Figure 4.6e) could be ascribed to the formation of δ -MnO₂ (JCPDS 80-1089) that has a layered structure.¹⁴⁸ The 2-D NSs were believed originating from the aggregation of MnO₆ octahedra in the solution and the condensation of these monomers has driven them packing into NS morphology, following an oriented attachment mechanism.

Figure 4.6. (a) SEM images; (b-c) TEM images; (d) HRTEM images; (e) XRD pattern of the MnO₂ NSs/GF.

With increasing reaction time to 3 h, the MnO₂ was reduced to MnOOH.^{149,150} The TEM observations (Figure 4.7a-b) depicted the intermediate stage that the hierarchical NSs eventually scrolled into a roll. The rolling of the NSs was related to the tendency for

the reduction in surface energy and obtaining saturation level of the free bonds from the NSs boundary under elevated temperature and pressure during the hydrothermal treatment. Previously, the rolling mechanism was also suggested in explaining the transformation mechanism of 2-D NSs into 1-D structures.^{151,152}

Figure 4.7. (a-b) TEM images taken at 1 h showing the rolling process. Reprinted from Ref. ¹⁴⁷ Copyright (2012), with permission from John Wiley & Sons.

Further extending the reaction time to 6 h, the morphology of the sample was changed to rod shape with length of $\sim 1\ \mu\text{m}$ and diameter of $\sim 100\ \text{nm}$, as shown in Figure 4.8a-c. The HRTEM image of one NR, shown in Figure 4.7d, displayed that it was polycrystalline with the grain size of 5-10 nm and the lattice d -spacing of 0.24 and 0.34 nm could be index to the (002) and ($\bar{1}11$) planes of MnOOH, respectively. Resembled to the crystal structure obtained at 3h, the NRs formed at 6 h could be ascribed to the γ -MnOOH.

Figure 4.8. (a) SEM images; (b-c) TEM images; (d) HRTEM images; (e) XRD pattern of the MnOOH NRs/GF.

This observation indicated the infilling process of NTs with nanoparticles, which was evidenced by the observation of the sample (Figure 4.9a-b) taken in intermediate state (4 hours reaction time). This phenomenon was related to the heterogeneous nucleation of

nanocrystallites on the surface of the NTs and ultimately the tubular interior was filled with the newly formed nanoparticles.

Figure 4.9. (a-b) TEM images taken at 4 h showing the infilling process. Reprinted from Ref. ¹⁴⁷ Copyright (2012), with permission from John Wiley & Sons.

Having a strong correlation between the surface area and the capacitance, BET measurement was conducted to provide detailed information on the surface texture of the GF and the composites (Table 4.1).

Table 4.1. Physical properties of the as-prepared samples.

Entry	Mass loading (mg cm ⁻³)	BET surface area ^[a] (m ² g ⁻¹)
GF	-	10.2
MnO ₂ NSs/GF	1.25	105.3
MnOOH NTs/GF	2.85	153.7
MnOOH NRs/GF	3.83	109.5

^[a] The values calculated were based on the total mass of the composites.

Bare GF that constructed in micron size can only provide BET specific surface area of 10.2 m² g⁻¹. After incorporation of the manganese species, the BET specific surface

area increased significantly, showing that the tailored morphology can give rise to higher surface-to-volume ratio. From the BET analysis, the specific surface area of the as-prepared samples can be arranged as the following order: MnOOH NTs/GF > MnOOH NRs/GF > MnO₂ NSs/GF > GF.

As shown in Figure 4.10, the N₂ adsorption/desorption isotherm of bare GF was indicative of its non-porous structure.¹⁵³

Figure 4.10. Nitrogen adsorption and desorption isotherms of the as-prepared samples. Reprinted from Ref. ¹⁴⁷ Copyright (2012), with permission from John Wiley & Sons.

The MnO₂ NSs/GF showed a typical type IV isotherm with a pronounced hysteresis loop. This suggested the mesoporous characteristics of the NSs, which constructed the interspaces between the small crystallites.¹⁵⁴ The BET specific surface area of the NSs (105.5 m²g⁻¹, Table 4.1) was lower than that of the NTs, indicating the intimate stacking of NSs has blocked some of the active-site accessibilities. The isotherms of MnOOH NTs/GF resembled to the MnO₂ NSs by having hysteresis loop in the relative pressure range of 0.4 to 1, illustrating that this sample also showed mesoporous characteristics.

Meanwhile, the MnOOH species have strong tendency to arrange into monoclinic packing driven by the external heat energy and the crystallinity of the as-prepared samples was improved significantly with increasing reaction time suggested by the enhanced XRD peak intensity (Figure 4.8e). From the BET analysis of the NRs, the capillary condensation effect of N₂ became less apparent and adopted to a type II isotherm, hinting gradual loss of the mesoporous structure as time proceeded. The obtained BET specific surface area of the NRs reduced to 109.3 m² g⁻¹ (Table 4.1) because the densification process sacrificed a number of active sites from the interiors. Based on these characterization results, the morphological evolution of MnOOH on the surface of GF can be schematically represented as Figure 4.11.

Figure 4.11. Schematic representation of the formation mechanism. Reprinted from Ref.

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4.4 Electrochemical Measurements

The redox reaction between various valence states of manganese ions upon chemisorption or physisorption can be used to represent the charge storage reaction at the electrode,^{125,155} as follows:

where C^+ and A^- represent the cation and anion, respectively in the electrolyte.

Figure 4.12a-b showed the CV curves of the as-prepared samples at 2 and 100 mV s^{-1} , respectively. At scan rates of 2 mV s^{-1} , all the as-prepared samples maintained an almost rectangular CV loop. It hint the good kinetic reversibility and low contact resistance of the active materials, in which the electrolyte ions could penetrate beyond the surface region and the diffusion rate was able to keep pace with the chemical reaction occurred on the electrode surface.¹⁵⁶ At high scan rate (100 mV s^{-1}), the diffusion rate of electrolyte ion was slower with respect to the scan rate to access all the available active sites of the electro-active species to undergo redox reactions, causing the rectangular-shape CV curve to be slightly distorted.¹²⁶ Although the intrinsic features of GF have prompted them to be kinetically reversibility and excellent cycling stability, its specific capacitance derived from the electrostatic interaction between the oppositely charged species is limited. The area of the CV loop of the pure GF that represent the total number of electron being transferred during the electrochemical reaction was significantly smaller than those with manganese species attached. On the other hand, no obvious redox peaks were observed from the voltammograms for the manganese-based GF composites synthesized at different reaction time, evidencing the unique electrochemical properties of the manganese species in performing charge/discharge process in a pseudo-constant rate.¹¹⁶

Figure 4.12. CV of the as-prepared samples at scan rate of (a) $2 mV s^{-1}$; (b) $100 mV s^{-1}$.

The galvanostatic charge/discharge curves were measured at $1 A g^{-1}$ to evaluate their specific capacitance (Figure 4.13) and the results were summarized in Table 4.2.

Figure 4.13. GCD curves of the as-prepared samples at current density of $1 A g^{-1}$.

Apart from the conventional fabrication method, the GF was used as the active materials as well as the current collector. Therefore, the electrical double layer charge storage reaction of GF that governed by the electrostatic charge separation has to be taken into consideration.¹⁵⁷ In this case, the bare GF can only deliver a specific capacitance of $60 F g^{-1}$ at $1 A g^{-1}$ without addition of pseudocapacitive materials. In contrast, the specific capacitance was significantly enhanced for the manganese-based GF composites. In brief,

the as-prepared samples can be arranged in the order of increasing capacitance as follows:

GF < MnO₂ NSs/GF < MnOOH NRs/GF < MnOOH NTs/GF.

Table 4.2. Specific capacitance of the as-prepared samples at 1 A g⁻¹.

Entry	Specific Capacitance ^a (F g ⁻¹)
GF	60
MnO ₂ NSs/GF	137
MnOOH NTs/GF	498
MnOOH NRs/GF	268

^a Specific capacitance calculated from GCD curves.

This manifested the structural effect on the electrochemical performances, in which the NTs that possess the highest BET surface area can achieve the highest specific capacitance. Owing to the unique architecture, the tubular structure of MnOOH is beneficial for maximizing the utilization of the active materials by activating the inner walls as the active sites for electrochemical reactions. Furthermore, the hollow interiors can shorten the diffusion length for charge transport by allowing the electrolyte ions to pass through their interior tunnels and replenishing the electrolyte depleted region effectively.¹⁵⁸ Thus, the overall capacitance of the MnOOH NTs/GF was boosted to the highest value, surpassing the MnOOH NRs/GF and MnO₂ NSs/GF.

To have better illustration on the specific capacitances of the as-prepared MnOOH/GF composites as a function of current densities, the electrochemical results were illustrated in Figure 4.14. It was found that the MnOOH NTs/GF exhibited good rate capability by retaining specific capacitance of 145 F g⁻¹ at a high current density of 10 Ag⁻¹. Comparatively, GF, MnO₂ NSs/GF, MnOOH NRs/GF can only achieve specific

capacitances of 36 F g^{-1} , 61 F g^{-1} , 51 F g^{-1} , respectively, at 10 A g^{-1} . Again, these results have proved the positive impacts obtained from the tubular morphology.

Figure 4.14. Specific capacitance of the as-prepared samples as a function of current densities.

Further investigation was also done on the cycling stability of the as-prepared composites. As shown in Figure 4.15a, the MnO_2 NSs/GF, MnOOH NTs/GF, MnOOH NRs/GF composites exhibited capacitance retention of 90%, 92% and 70%, respectively, upon charge and discharge after 1000 cycles. Minimum capacitance decay of the NTs composites could be attributed to their capability to withstand the structural deformation during the electrochemical reaction through their well-defined tubular structure. The concentric expansion and contraction force exerted on the tubular structure resulted in more symmetric deformation, making it under the threshold stress for structural collapse upon long-term cycling.^{159,160} As compared to the stress-induced effect on other manganese species containing samples, they tend to undergo deformation process due to lack of hollow structure to accommodate their volume change during redox transformation and hence, they suffered from rapid capacitance fading. Despite showing

relatively low specific capacitance, the highly reversible charge storage mechanism of GF rendered it exceptionally stable cycling performance (95% of retention after 1000 cycles). On the other hand, the contributions of GF as the scaffold for mechanical support and conductive “highway” to preserve electrical integrity of the manganese species should not be omitted also.

Figure 4.15. Cycling performance of the as-prepared samples prepared by binder-free method; (b) comparative study on the cycling performance of the binder-free MnOOH NTs/GF electrode and the conventional method fabricated MnOOH NTs and MnOOH NTs/GF electrodes.

Additionally, a control experiment was done on investigating the cycling stability of the binder-free MnOOH NTs/GF electrode and the conventional method fabricated MnOOH NTs and MnOOH NTs/GF electrodes, as shown in Figure 4.15b. Apparently, the implementation of binder-free approach during the fabrication step induced 92% of capacitance retention, which was greater than the conventional method fabricated MnOOH NTs and MnOOH NTs/GF electrodes that can only maintain 71% and 81% of their original specific capacitance, respectively. The underlying reason could be attributed to the introduction of electro-inert binders within the electrode that reduces the electronic

conductivity and lead to the severe degradation in cycling stability. In principle, the bare MnOOH NTs sample was expected to be capable of delivering higher specific capacitance as compared to the manganese-based GF composites because the total contribution of the bare MnOOH NTs was pseudocapacitance while the capacitance of manganese-based GF composites was partially derived from the EDLC.¹⁶¹ However, the bare MnOOH NTs were inferior as compared to the MnOOH NTs/GF composite. In this case, synergistic effect was manifested here in which improvement in electronic conductivity of the electrode after the incorporation of GF enabled the MnOOH NTs to realize their full potential. Without the conductive matrix, some of the MnOOH NTs became inactive towards redox reaction due to their low reaction kinetics.

In parallel, EIS measurement was conducted to investigate the adverse effect induced by the binder. It is known that the value of ESR is dependent on the resistance of the electrolyte combined with the electrical resistance at the electrode/current collector interface.^{162,163} Since same aqueous electrolyte was used, the ESR estimated from the EIS could be useful to examine the internal resistance at the electrode/current collector interface. Here, the Nquist plot shown as Figure 4.16 illustrated that the ESR value of the binder-free method fabricated electrode ($3.9\ \Omega$) was lower than the conventional method fabricated electrode ($5.1\ \Omega$) by comparing their intercept values at the Z' real part axis. On the other hand, it was further confirmed by estimated the ESR from the IR drop of their GCD curves. Based on above calculation, the ESR of the binder-free method and the conventional method fabricated electrode were estimated to be $4.2\ \Omega$ and $5.4\ \Omega$, respectively, which was in accordance with those ESR values calculated from the EIS. From the preliminary results, the binder-free approach that coupled the carbonaceous GF

with the manganese-based pseudocapacitive nanostructures was able to enhance the specific capacitance and to improve the cycling stability of the SC by improving the electronic conductivity of the manganese-based nanostructures. On the other hand, the exclusion of polymeric binder during the fabrication step is beneficial in reducing the internal resistance of the electrode, giving rise to better cycling stability.

Figure 4.16. Nyquist impedance plot of the as-prepared samples.

4.5 Summary

In summary, the tubular MnOOH nanostructures were synthesized *via* a facile hydrothermal method. The underlying mechanism can be depicted as the rolling mechanism that transformed the 2-D NSs to 1-D NTs. On the other hand, we found that the subtle interplay between the morphology and dimension is responsible for the remarkable properties of MnOOH as SC electrodes. In this regard, the tubular structure of MnOOH has contributed to different aspects: (1) both the exterior and interior surface of the active materials are subjected to chemical reactions; (2) reduces the mass and charge transport; (3) allows more freedom of expansion to accommodate their volume change

during redox transformation. As the results, the electrochemical performances of the MnOOH NTs surpassed the NSs and NRs. The significance of the present work also falls on the fundamental understanding on the mechanistic transformation process of MnOOH, which provides new platform for rational materials design. Hybridization between the carbonaceous and pseudocapacitive materials could synergistically overcome their intrinsic disadvantages, allowing them to realize their full potentials. Lastly, applying the binder-free concept in this scalable approach reduces the internal resistance of the electrode, making the fabrication of flexible SC electrode feasible for industrial use.

Recently, the SC electrodes that consist of more than one pseudocapacitive material have been the subject in numerous reviews. These composites show great prospect in commercial market as their energy densities are higher than those carbonaceous-pseudocapacitive combinations. On the other hand, enhancement in electrochemical performance shown by the binary structures has been a resounding success in material research. In contrast, the field of ternary composite with well-defined morphology and composition has less been explored although they hold great promise to fill the performance gap of current use SC devices.

5. Controlled Synthesis of $V_2O_5@MnO_2/Fe_2O_3$ Nanostructures

5.1 Introduction

Core-shell heterostructures have been demonstrated to exhibit improved physical and chemical properties for electronic, optics, catalysis and energy storage applications.^{88,164-167} Many synthetic strategies for the synthesis of core-shell nanostructures have been established in literature, for instances, chemical vapor deposition¹⁶⁸⁻¹⁷⁰, hydrothermal/solvothermal treatment¹⁷¹⁻¹⁷³, electrodeposition¹⁷⁴⁻¹⁷⁶ and solution-phase route.¹⁷⁷⁻¹⁷⁹ All of these approaches are promising to revolutionize the research field with the trend of preparing multi-components nanostructures, but some concerns remain: they are not easily scalable, use hazardous reactants and operate in a less energy-efficient way. Hence, developing new chemical route towards multi-component nanostructures with well-defined morphology and functionality that conducted at ambient condition using aqueous medium can pave a more cost-efficient and environmentally benign way for high-throughput synthesis.

Multi-component nanostructures are potential candidates for SC application owing to their enhanced capacitive performance that stemmed from compensating the intrinsic shortages or synergistically combining the advantages of individual component. In this study, the outstanding electrochemical performances of V_2O_5 have inspired us to couple it with MnO_2 into a single system. V_2O_5 is well-known for its rich redox chemistry and hence it can provide high pseudocapacitance that is associated with the reversible

electrochemical reactions. Compared with MnO_2 , V_2O_5 shows a different pseudocapacitive mechanism, termed intercalation pseudocapacitance as obtaining a structural characteristic that offers transport pathway for electrolyte cations through its crystalline interlayer spacing. By exploiting this highly reversible and stable ion insertion/extraction process *via* its open-framework structure, the V_2O_5 electrodes always show great promise in providing high energy density and rate capability performances.^{87,180} However, the structural instability of V_2O_5 has triggered detrimental effect upon cycling. As compared to MnO_2 and V_2O_5 , the electronic conductivity of Fe_2O_3 is much higher.¹⁸¹ More importantly, they show redox capability at low potential region and this intrinsic characteristic of Fe_2O_3 allows them to kinetically push the hydrogen evolution to more negative limit in aqueous medium.⁶⁴

MnO_2 shows high cycling stability but its energy density is not comparable to V_2O_5 .^{182,183} Thus, the combination of these two materials with rational designed architecture might lead to unprecedented electrochemical performances, in which the conformal coating of MnO_2 on V_2O_5 imposes constraint against its structural collapse and the V_2O_5 constituent contributes to its specific capacitance and rate capability.^{184,185} On the other hand, the coverage of Fe_2O_3 at the outermost layer may provide better electrical contact for electron transfer besides its capacitive contribution.

With this in mind, a $V_2O_5@MnO_2$ core-shell structure with hollow interior was synthesized to demonstrate the tailorability of multiple component nanostructures for properties tuning: (1) conformal deposition of more stable MnO_2 on the surface of tubular V_2O_5 could prevent its dissolution upon long-term cycling while the V_2O_5 exhibits higher specific capacitance and excellent electrochemical performance at high rate measurement;

(1) the deposition of Fe_2O_3 provide better electrical contact between the current collector and the composite; (3) with the unique hollow core-shell structure, the MnO_2 nanoflakes provided an open-framework for easy penetration of electrolyte to MnO_2 and V_2O_5 surfaces and the hollow tunnels of V_2O_5 enabled excellent accessibility of electrolyte to the inner wall regions, maximizing the electroactive surface area.

Herein, we demonstrated a facile chemical route for the construction of $V_2O_5@MnO_2$ core-shell NTs with tunable diameters of V_2O_5 nanowires (ranging from 40 nm to 350 nm) and MnO_2 thickness in aqueous medium under ambient condition (*e.g.* at room temperature and 1 atm). As the formation mechanism of $V_2O_5@MnO_2$ NTs relies on the aqueous chemistry of V_2O_5 under acidic environment, the free nitrate ions released from the redox deposition of MnO_2 chelate to the V_2O_5 core to form soluble oxonitrate complex, leading to the transformation of solid core into tubular structure. In addition, such a green strategy could also be extended to fabricate multilayer ternary composite NTs ($V_2O_5@MnO_2/M$, $M = Fe_2O_3, Co_2O_3/Co(OH)_2, Ni(OH)_2$). Further functionalized the $V_2O_5@MnO_2$ NTs with other reducible TMOs could be achieved by exploiting the difference in electrochemical potentials between the outermost MnO_2 layer with other foreign metal cation species in solution.¹⁸⁶ This preparation method opens up a platform for scalable synthesis of multi-component NTs with high tailorability in composition that is expected to hold great promise for energy storage system. In this work, demonstration of the $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs as the SC electrode also evidenced the practicality of multi-component nanostructures as they outperformed their single-phase counterparts.

5.2 Experimental Details

5.2.1 Room Temperature Synthesis of MnO_2 Nanoflakes

In a typical synthesis, $Mn(NO_3)_2 \cdot 4H_2O$ (0.1 mmol, 1.2 mL) and $KMnO_4$ (0.1 mmol, 1.8 mL) solutions were added sequentially into a beaker filled with deionized water (30 mL). The mixture was then stirred at room temperature for 3 h and the brownish precipitate was washed with deionized water before drying in oven overnight.

5.2.2 Synthesis of V_2O_5 Nanowires

The room-temperature synthesis of V_2O_5 nanowires was prepared according to a modified protocol based on our previous work.¹⁸⁷ In a typical synthesis, the commercial available V_2O_5 powder was dispersed in NaCl (1 mol, 200 mL) solution and the mixture was mechanically stirred at room-temperature for 3 days. Then, the mixture was centrifuged and washed with excess deionized water before drying in oven overnight. The V_2O_5 nanowires with 350 nm diameter were prepared hydrothermally according to our previous work.⁶² Briefly, commercial available V_2O_5 powder (1 mmol) was dissolved in deionized water (30 mL) accompanied by vigorous stirring. After then yellow powder was homogeneously dispersed, H_2O_2 (30 wt. % of H_2O_2 in H_2O , 5 mL) was added dropwise into the suspension to form a yellow solution followed by addition of $NH_4H_2PO_4$. After stirring for 15 min, the mixture was transferred into a 50 mL Teflon-lined pressure vessel for hydrothermal treatment at 180 °C for 48 h. Then, the mixture was centrifuged and washed with excess deionized water before drying in oven overnight.

5.2.3 Synthesis of $V_2O_5@MnO_2$ Heterostructures

The reaction parameters for the synthesis of $V_2O_5@MnO_2$ heterostructures were summarized in Table 5.1. Typically, V_2O_5 (5 mg mL^{-1} , 2 mL) solution was extracted and mixed with deionized water (30 mL). Then, $Mn(NO_3)_2 \cdot 4H_2O$ and $KMnO_4$ solutions were then added sequentially. A series of reactions was done by varying the concentration of Mn(II) and Mn(VII), in which the molar ratio between Mn(II):Mn(VII) was fixed at 3:2.

Table 5.1. Reaction parameter for the preparation of $V_2O_5@MnO_2$ ^a.

Entry	V_2O_5 (mg)	0.1 M $Mn(NO_3)_2 \cdot 4H_2O$ (mL)	0.1 M $KMnO_4$ (mL)
Mn-V-01	10	0.6	0.4
Mn-V-02	10	1.2	0.8
Mn-V-03	10	1.8	1.2
Mn-V-04	10	2.1	1.4
Mn-V-05	10	2.4	1.6

^a Reaction condition: 1 h, room temperature.

Due to the homogeneity of the Mn-V-03 sample, this sample was used for the time-dependent experiments. Typically, V_2O_5 (5 mg mL^{-1} , 2 mL) solution was extracted and mixed with deionized water (30 mL). $Mn(NO_3)_2 \cdot 4H_2O$ (0.1 mmol, 1.2 mL) and $KMnO_4$ (0.1 mmol, 1.8 mL) solutions were then added sequentially. The mixture was stirred at room temperature for 0.5 h and 3 h to obtain solid and hollow core-shell structures, which were denoted as $V_2O_5@MnO_2$ and $V_2O_5@MnO_2$ NTs, respectively.

5.2.4 Synthesis of $V_2O_5@MnO_2/Fe_2O_3$ Heterostructures

Since the synthesis of tubular $V_2O_5@MnO_2/M$ ($M = Fe_2O_3, Co_2O_3/Co(OH)_2, Ni(OH)_2$) heterostructures was similar, $V_2O_5@MnO_2/Fe_2O_3$ NTs were used to a demonstration. Solution of $V_2O_5@MnO_2$ NTs (1 mmol, 1 mL) was extracted and mixed with deionized water (5 mL). Anhydrous $FeCl_2$ (0.1 mmol, 100 μ L) were added dropwise into the $V_2O_5@MnO_2$ NTs solution and stirred at 80 °C for 1 h. Subsequently, the mixture was washed three times of deionized water and dried in vacuum oven overnight. For the synthesis of $V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$ and $V_2O_5@MnO_2/Ni(OH)_2$, anhydrous $CoCl_2$ (0.1 mmol, 200 μ L) and $NiCl_2$ (0.1 mmol, 200 μ L) were used, respectively, while the reaction conditions were otherwise identical to the synthesis of $V_2O_5@MnO_2/Fe_2O_3$.

5.3 Synthesis and Characterizations of $V_2O_5@MnO_2$ Heterostructures

Single-phase MnO_2 and V_2O_5 were synthesized using a scalable and room-temperature method and the $V_2O_5@MnO_2$ heterostructures could also be achieved *via* this methodology. In this regard, the crystal structures of the single-phase MnO_2 and V_2O_5 were determined by XRD (Figure 5.1), in which V_2O_5 (Figure 5.1a) is orthorhombic phase (JCPDS 41-1426, lattice constants: $a = 1.151$ nm, $b = 0.3565$ nm, $c = 0.4372$ nm, space group $Pmmn$)¹⁸⁸ and MnO_2 (Figure 5.1b) is tetragonal phase (JCPDS 44-0141, lattice constants: $a = b = 0.978$ nm, $c = 0.286$ nm, space group $I4/m$)¹⁸⁹.

Bare V_2O_5 were grown into wire-like morphology, shown in Figure 5.2a-b. The low magnification images showed the densely entangled nanowires with micron-sized longitudinal axis and < 100 nm diameter (Figure 5.2a). Higher magnification image

(Figure 5.2b) showed the smooth surface of V_2O_5 nanowires. Besides, the SEM images of MnO_2 showed irregular spheres stacking together (Figure 5.2c). Magnified SEM images revealed that a discrete sphere with wrinkle-like surface was hierarchically assembled by ultrathin nanoflakes of MnO_2 (Figure 5.2d).

Figure 5.1. XRD pattern of the single-phase (a) V_2O_5 and (b) MnO_2 , respectively. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

Figure 5.2. (a-b) SEM images of the V_2O_5 nanowires; (c-d). SEM images of MnO_2 nanostructures after 3 h reaction time. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

To synthesize the $V_2O_5@MnO_2$ nanostructures, V_2O_5 nanowires were reacted with different concentration of manganese precursors ($Mn(NO_3)_2 \cdot 4H_2O$ and $KMnO_4$) that fixed at 3:2 ratio in aqueous solution. The redox deposition of MnO_2 on the surface of V_2O_5 resulted in core-shell hybrid structures. In this regard, the concentration of Mn precursors played crucial role in maintaining the homogeneity in morphology. As shown in Figure 5.3a-b, the emergence of V_2O_5 nanowires with rough surface was indicative of the successful deposition of MnO_2 shell but most of the V_2O_5 nanowires were still preserved in their original morphology at very low concentration of Mn precursors (MV-01). 2-fold increase in the concentration of Mn precursors (MV-02) increased the number of $V_2O_5@MnO_2$ heterostructures but trace amount of uncoated V_2O_5 nanowires could still be observed from the SEM images (Figure 5.3c-d). When the reaction was conducted at higher concentration of Mn precursors (Mn-V-03), optimum amount of Mn precursors was achieved to produce large amount of uniformly coated V_2O_5 heterostructures. The diameter of the nanowires was greater than the bare V_2O_5 nanowires and hierarchically coated MnO_2 could be readily observed from the SEM images (Figure 5.3e-f). When the amount of Mn precursors was increased to higher concentration (Mn-V-04), $V_2O_5@MnO_2$ heterostructures with larger diameter (Figure 5.3g-h) were resulted. It was also found that the hierarchically porous MnO_2 shell became more obvious under SEM investigation. However, discrete nanoflakes that formed apart from the entangled nanowires were observed at extremely high concentration of Mn precursors (Mn-V-05), destroying the homogeneity in morphology (Figure 5.3i-j). Therefore, M-V-03 was employed as the precursor in the following synthesis (synthesis of $V_2O_5@MnO_2$ core-shell NTs and $V_2O_5@MnO_2/M$ core-shell NTs) due to its excellent homogeneity.

Figure 5.3. SEM images of the $V_2O_5@MnO_2$ core-shell heterostructures with different manganese precursors concentration: (a-b) Mn-V-01; (c-d) Mn-V-02; (e-f) Mn-V-03; (g-h) Mn-V-04; (i-j) Mn-V-05.

5.4 Synthesis and Characterizations of $V_2O_5@MnO_2/Fe_2O_3$ Nanotubes

The schematic representation for the synthesis of $V_2O_5@MnO_2/Fe_2O_3$ multi-component NTs was depicted as Figure 5.4, employing an aqueous-based chemical route.

Figure 5.4. Schematic representation of the proposed formation mechanism of $V_2O_5@MnO_2/Fe_2O_3$ core-shell NTs. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

The micron-scale length V_2O_5 was transformed from the commercial V_2O_5 powder by stirring the reaction mixture at room-temperature, in which the growth process of V_2O_5 nanowires could be described as the dissolution of bulk V_2O_5 followed by the homogeneous oriented-growth to form 1-D nanowires. As mentioned in the previous

section, the V_2O_5 with adjustable diameters were firstly synthesized as the scaffold for redox deposition of MnO_2 (reduction of Mn^{7+} accompanied by oxidation of Mn^{2+}) to form the $V_2O_5@MnO_2$ core-shell structure. Simultaneously, the selective chelate-promoted dissolution of the V_2O_5 induced regional depletion of the core region, forming the $V_2O_5@MnO_2$ NTs under the acidic condition. Subsequently, the realization of $V_2O_5@MnO_2/Fe_2O_3$ NTs was accomplished by the galvanic displacement reaction between the outermost layer of MnO_2 (0.91 V, MnO_2/Mn^{3+}) and the lower-oxidation-state Fe^{2+} (0.77 V, Fe^{3+}/Fe^{2+}) species,¹⁹¹ adopting the mechanism of reductive dissolution of Mn^{3+} and the oxidative deposition of the Fe_2O_3 .¹⁹² By manipulating this chemical reaction pathway, ternary nanocomposite with disparate combination of multi-layer NTs could be readily synthesized. In this regard, the epitaxial growth of oxides or hydroxides species on $V_2O_5@MnO_2$ NTs is highly dependent on their discrepancy in standard reduction potential with respect to MnO_2 . From our preliminary results, this concept could be generalized to the synthesis of $V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$ and $V_2O_5@MnO_2/Ni(OH)_2$ multi-component NTs.

Figure 5.5a indicated the amorphous nature of $V_2O_5@MnO_2$ NTs by showing no significant diffraction peaks in XRD analysis. Different from the crystalline phase of single component V_2O_5 nanowires and MnO_2 nanoflakes (Figure 5.1a-b), this explicit characteristic of the binary structure could be due to two primary factors: (1) the amorphization of V_2O_5 under strong oxidative environment that created by the addition of $KMnO_4$; and (2) the mild reaction conditions (*i.e.* 25 °C, 1 atm) attendant to the redox deposition of MnO_2 . In the absence of XRD diffraction peak could also be attributed to their extremely small grain size of the nanoparticles that beyond the detection limit of

XRD technique. To rule out this possibility, HRTEM was conducted to further confirm the nature of the $V_2O_5@MnO_2$ NTs. In Figure 5.5b, it was found that no lattice fringes could be observed in the HRTEM images for all the $V_2O_5@MnO_2$ NTs and the ring-like FFT patterns (inset of Figure 5.5b) were indicative of their non-crystalline characteristic. Based on these observations, we confirmed that the $V_2O_5@MnO_2$ NTs are in amorphous state.

Figure 5.5. (a) XRD pattern; (b) HRTEM images of the $V_2O_5@MnO_2$ core-shell NTs. Inset in (b) is its corresponding FFT pattern.

Therefore, XPS measurement that corrected using the C 1s core level taken at 284.6 eV as the binding energy reference was conducted to further investigate the valence states of the constituents. The core binding energies of 517.4 and 524.6 eV that originated from V $2p_{3/2}$ and V $2p_{1/2}$ (Figure 5.6a) were in accordance with those predominant peaks of V^{5+} in V_2O_5 .¹⁹³ In response to the binding energy of Mn $2p$ spin-orbit splitting shown in Figure 5.6b, Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks located at 642.5 eV and 654.3 eV with spin-energy separation of 11.8 eV were corresponded to Mn^{4+} .¹²⁶ The deconvolution of O 1s peak resulted in two peaks positioned at 531.7 and 530.4 eV (Figure 5.6a), attributing to

the existence of oxygen contents associated with the surface absorbed hydroxyl groups and metal-oxygen bonds (Mn-O/V-O), respectively. Based on the binding energies assigned to V, Mn and O, the compositions of the nanocomposite were proposed as V_2O_5 and MnO_2 , respectively.

Figure 5.6. (a) XPS O 1s and V 2p core-level spectra; (b) XPS Mn 2p core-level spectrum of the $V_2O_5@MnO_2$ core-shell NTs.

The low magnification SEM images shown in Figure 5.7a displayed densely entangled 1-D $V_2O_5@MnO_2$ nanostructures with uniform size, dominantly having micro-scale length ($\sim 10\ \mu m$). Successful conformal coating of the MnO_2 species could be evidenced by the rougher surface texture of the nanocomposites (inset of Figure 5.7a) that in contrast to the smooth surface of the bare V_2O_5 nanowires (Figure 5.2a-b) besides exhibiting the morphological characteristic of bare MnO_2 nanoflakes (Figure 5.2c-d). Moreover, the radial dimension (~ 60 - $70\ nm$) of the nanocomposites was apparently greater than the single-phase V_2O_5 nanowires ($\sim 40\ nm$). Magnifying the cross-sectional view of the broken interfaces as shown in Figure 5.7b, the hollow interiors of the NTs that encrusted with flaky sheath were readily visible. Furthermore, the TEM exposures disclosed a V_2O_5 hollow axial core that covered by the hierarchically assembled MnO_2

nanoflakes (Figure 5.7c). It was found that the tubular nanocomposite has ~ 7 nm of V_2O_5 inner wall thickness and ~ 10 nm of MnO_2 shell thickness, constructing the well-defined core-shell architecture.

Figure 5.7. (a-b) SEM images, (c) TEM image; and (d) Dark field STEM/EDX line scan profile; (e-g) elemental mappings of the $V_2O_5@MnO_2$ core-shell NTs. Inset of (d) illustrated the dark field STEM images of the $V_2O_5@MnO_2$ core-shell NTs. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

From the STEM/EDX line scan profile acquired across the core-shell nanowire (Figure 5.7d), both the V and Mn signals exhibited relatively high intensity at the edge region and reduced intensity at the core region, signifying the formation of tubular structure. Furthermore, Figure 5.7e-g illustrated the dark field TEM image and its corresponding elemental mappings, revealing the distribution of V and Mn in a single nanocomposite. This observation was in qualitative accordance with the results obtained from the radial line scan profile (Figure 5.7d) that gave evidence on the formation of $V_2O_5@MnO_2$ core-shell NTs.

This report also illustrated a benign chemical route for the preparation of compositionally diverse ternary tubular nanocomposites, $V_2O_5@MnO_2/Fe_2O_3$. The Fe-containing nanocomposite inherited the amorphous characteristic of the $V_2O_5@MnO_2$ NTs, as shown in the XRD and HRTEM analysis (Figure 5.8a-b).

Figure 5.8. (a) XRD pattern; (b) HRTEM images of the $V_2O_5@MnO_2/Fe_2O_3$ core-shell NTs. Inset in (b) is its corresponding FFT pattern.

In the XPS spectra, there was no obvious shift in binding energy illustrated in core-level spectra of V (Figure 5.9a) and Mn (Figure 5.9b) as compared to the $V_2O_5@MnO_2$ NTs. The Fe $2p_{3/2}$ and $2p_{1/2}$ peaks located at 711.5 and 724.6 eV (Figure 5.9c), respectively, with an associated satellite shoulders at 8 eV higher than the main peaks indicated that it was trivalent Fe_2O_3 .^{194,195}

Figure 5.9. (a) XPS O 1s and V 2p core-level spectra; (b) XPS Mn 2p core-level spectrum; (c) XPS Fe 2p core-level spectrum of the $V_2O_5@MnO_2/Fe_2O_3$ core-shell NTs with the addition of $FeCl_2$ (0.1 mmol, 100 μ L) precursor. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

SEM and TEM images shown in Figure 5.10a-c displayed that the surface texture, dimension, and more importantly, the NTs morphology of the initial $V_2O_5@MnO_2$ were preserved, evidencing the structural rigidity of the core-shell framework for cations substitution.

Figure 5.10. (a-b) SEM images, (c) TEM image; and (d) Dark field STEM/EDX line scan profile; (e-h) elemental mapping of the $V_2O_5@MnO_2/Fe_2O_3$ core-shell NTs. Inset of (d) illustrated the dark field STEM images of the $V_2O_5@MnO_2/Fe_2O_3$ core-shell NTs. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

As compared to the $V_2O_5@MnO_2$ NTs precursors, no drastic change in morphology of $V_2O_5@MnO_2/Fe_2O_3$ NTs was observed. The line scan profile (Figure 5.10d) of

$V_2O_5@MnO_2/Fe_2O_3$ NTs illustrated that the emergence of Fe signal was accompanied by significant depletion of Mn concentration after the displacement of Fe^{2+} species, which was in agreement with the element concentration derived from the integration of the XPS peaks and ICP quantitative analyses summarized in Table 5.2 and Table 5.3, respectively. Both results showed incremental loss of Mn content after the addition of Fe species. Furthermore, the compositional mappings (Figure 5.10e-f) clearly depicted uniform distribution of Fe^{2+} species over the entire NTs and signal for Mn was relatively weak. It is worth noting that the higher standard reduction potential V_2O_5 (0.95 V, V_2O_5/VO^{2+})¹⁹¹ as compared to the intimately contacted MnO_2 could enhance the chemical resistivity of V_2O_5 to be replaced, making the inner core layer less vulnerable to the galvanic process, which was in accordance with the line scan signal of V that exhibited similar intensity with the signal of Fe (Figure 5.10d).

Table 5.2. Surface composition derived from XPS analysis of the as-synthesized samples.

Entry	Surface Composition [At%]					
	Mn	V	Mn:V Ratio	Fe	Co	Ni
$V_2O_5@MnO_2$ NTs	14.6	6.7	2.2	-	-	-
$V_2O_5@MnO_2/Fe_2O_3$ 0.1 mmol	3.3	6.5	0.5	8.3		
$V_2O_5@MnO_2/Fe_2O_3$ 0.5 mmol	0.3	6.5	0.1	15	-	-
$V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$	9.4	6.7	1.4	-	2.7	-
$V_2O_5@MnO_2/Ni(OH)_2$	13.8	6.3	2.2	-	-	3.8

Table 5.3. Element content of the as-synthesized samples derived from ICP analysis.

Entry	Element Content [wt%]					
	Mn	V	Mn:V Ratio	Fe	Co	Ni
$V_2O_5@MnO_2$ NTs	16.87	17.29	0.976	-	-	-
$V_2O_5@MnO_2/Fe_2O_3$ 0.1 mmol	1.20	16.28	0.074	24.85	-	-
$V_2O_5@MnO_2/Fe_2O_3$ 0.5 mmol	0.38	16.09	0.024	37.02	-	-
$V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$	14.87	16.90	0.880	-	7.46	-
$V_2O_5@MnO_2/Ni(OH)_2$	16.25	16.36	0.993	-	-	9.27

The N_2 adsorption/desorption isotherms of the as-prepared sample were summarized in Figure 5.11. From the BET analysis of pure MnO_2 (Figure 5.11a), the hysteresis loop shown in the N_2 adsorption/desorption isotherm was indicative of its mesoporosity. In contrast, the absence of capillary condensation in pure V_2O_5 isotherm (Figure 5.11b) revealed its non-porous structure. Comparatively, $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs possessed isotherm (Figure 5.11c) resembled to pure MnO_2 , which could be interpreted as having mesoporous characteristics originated from the interstices between the interconnected MnO_2 nanoparticles. Therefore, similar surface texture and porosity were expected for $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs. As summarized in Table 5.4, the BET surface area estimated for $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs could reach 191.7 and 210.7 $m^2 g^{-1}$, respectively, which was apparently higher than their single-phase components, MnO_2 (71.1 $m^2 g^{-1}$) and V_2O_5 (33.7 $m^2 g^{-1}$). It was found that the sum of BET surface area of the single-phase MnO_2 and V_2O_5 is much smaller than the $V_2O_5@MnO_2$ hybrids, illustrating that rational design in architecture has reconstructed the surface which leads to higher surface-to-volume ratio.

Figure 5.11. N_2 absorption/desorption isotherms of (a) MnO_2 ; (b) V_2O_5 ; (c) $\text{V}_2\text{O}_5@\text{MnO}_2$ core-shell NTs; (d) $\text{V}_2\text{O}_5@\text{MnO}_2/\text{Fe}_2\text{O}_3$ core-shell NTs. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

Table 5.4. Specific BET surface area of the as-prepared samples.

Entry	BET surface area ^[a] ($\text{m}^2 \text{ g}^{-1}$)
V_2O_5	33.7
MnO_2	71.1
$\text{V}_2\text{O}_5@\text{MnO}_2$	191.7
$\text{V}_2\text{O}_5@\text{MnO}_2/\text{Fe}_2\text{O}_3$	210.7

5.5 Formation Mechanism of $V_2O_5@MnO_2/M$ Heterostructures

To have better illustration on the morphology evolution of the $V_2O_5@MnO_2$ NTs, V_2O_5 with larger lateral dimension, ~ 350 nm, was synthesized for redox deposition of MnO_2 . The time-dependent experiment shown in Figure 5.12 depicted the mechanistic transformation process for the NTs.

Figure 5.12. Time-dependent variation of the $V_2O_5@MnO_2$ core-shell NTs and their corresponding radial STEM/EDX line scan profiles: (a,d) 30 min reaction time; (b,e) 3 h reaction time; (c,f) 9 h reaction time. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

Firstly, solid core-shell $V_2O_5@MnO_2$ nanowires were formed at 1 h reaction duration under ambient condition (Figure 5.12a). The room-temperature heterogeneous nucleation occurred instantly on the V_2O_5 surface *via* the redox reaction between Mn^{2+} and Mn^{7+} , following the equation shown below:¹⁵¹

As an intermediate product that formed at 3 h reaction time, partially acidic etched core region could be clearly observed (Figure 5.12b). The tubular formation could be attributed to the chelation of nitrate ions that released from the redox deposition of MnO_2 to V_2O_5 under acidic environment, yielding soluble vanadium-based oxonitrate complex, $VO_2(NO)_3$:

Extending the incubation time of the nanocomposites in solution to 9 h consequently enlarged the tunnel dimension of V_2O_5 core (Figure 5.12c). On the other hand, the radial line scan profiles of their corresponded nanocomposites shown in Figure 5.12e-f further supported the concept that the evolution of tubular structure were initiated from the $V_2O_5@MnO_2$ solid core-shell structure to $V_2O_5@MnO_2$ core-shell NTs.

In the following step, galvanic replacement process took place to substitute the exposed MnO_2 layer with lower-oxidation-state Fe^{2+} to form $V_2O_5@MnO_2/Fe_2O_3$ ternary nanocomposite. The evolution of $V_2O_5@MnO_2/Fe_2O_3$ NTs was stimulated by the spontaneous oxidation-reduction reaction that driven by the standard reduction potential difference between these two reducible species. The proposed reaction mechanism in explaining the phenomenon of oxidative precipitation of Fe species promoted the dissolution of Mn species could be further proved by a control experiment that use high concentration of Fe^{2+} , in which almost complete depletion of Mn species was observed and its existence could be vaguely detected by XPS measurement (Figure 5.13b). The quantitative analysis in term of weight percentage of each component was summarized in Table 5.2. As compared to the binary $V_2O_5@MnO_2$ NTs, the concentration of Mn species in $V_2O_5@MnO_2/Fe_2O_3$ 0.1 mmol decreased significantly and the Mn depletion becomes

more apparent at high concentration of Fe^{2+} species, $V_2O_5@MnO_2/Fe_2O_3$ 0.5 mmol, which was in accordance with the ICP results (Table 5.3).

Figure 5.13. XPS O 1s and V 2p core-level spectra; (b) XPS Mn 2p core-level spectrum; (c) XPS Fe 2p core-level spectrum of the $V_2O_5@MnO_2/Fe_2O_3$ core-shell NTs with the addition of $FeCl_2$ (0.5 mmol, 100 μ L) precursor. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

When this synthetic approach was extended to Co and Ni, different behaviors were observed but both ternary nanocomposites remained in their amorphous state by showing no distinct XRD peaks and ring-like FFT pattern in HRTEM analysis (Figure 5.14a-b, Figure 5.15a-b for Co and Ni, respectively).

Figure 5.14. (a) XRD pattern; (b) HRTEM images of the $V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$ core-shell NTs. Inset in (b) is its corresponding FFT pattern.

Figure 5.15. (a) XRD pattern; (b) HRTEM images of the $V_2O_5@MnO_2/Ni(OH)_2$ core-shell NTs. Inset in (b) is its corresponding FFT pattern.

There was no obvious shift in XPS binding energy illustrated in core-level spectra of V (Figure 5.16a and 5.17a) and Mn (Figure 5.16b and 5.17b) as compared to the $V_2O_5@MnO_2$ NTs. The XPS analysis of the Co-containing ternary nanocomposites revealed that the core level of Co $2p_{3/2}$ (Figure 5.16c) could be deconvoluted into +2 (781.2 eV) and +3 (780.1 eV) oxidation states that belongs to $Co(OH)_2$ and Co_2O_3 , respectively.¹⁹⁶

Figure 5.16. (a) XPS O 1s and V 2p core-level spectra; (b) XPS Mn 2p core-level spectrum; (c) XPS Co 2p core-level spectrum of the $V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$ core-shell NTs with the addition of $CoCl_2$ (0.1 mmol, 200 μ L) precursor. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

In this regard, the underlying cause might be attributed to the higher standard reduction potential of Co^{3+}/Co^{2+} pair (1.82 V)¹⁹¹, resulting in competition between the hydroxide precipitation process to form $Co(OH)_2$ and the galvanic displacement process to yield Co_2O_3 . This phenomenon was further proved by having reduced amount of Mn displaced by Co species as compared to the $V_2O_5@MnO_2/Fe_2O_3$ ternary nanocomposite (Table 5.2).

On the contrary, the core level of Ni $2p_{3/2}$ with binding energy 855.7 eV (Figure 5.17c) revealed that the deposition of Ni species solely adopted to the hydroxide precipitation process as $Ni(OH)_2$.¹⁹⁷ The absence of oxidative precipitation reaction could also be evidenced from the amount of Mn species remaining in the Ni-containing $V_2O_5@MnO_2$ nanocomposite shown in Table 5.2, preserving almost the same amount of Mn species as the $V_2O_5@MnO_2$ NTs.

Figure 5.17. (a) XPS O 1s and V 2p core-level spectra; (b) XPS Mn 2p core-level spectrum; (c) XPS Ni 2p core-level spectrum of the $V_2O_5@V_2O_5@MnO_2/Ni(OH)_2$ core-shell NTs with the addition of $NiCl_2$ (0.1 mmol, 200 μ L) precursor. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

Moreover, ICP was conducted to further quantify the concentration of each element in the nanocomposites. The ICP results summarized in Table 5.3 revealed that the concentration of Mn decreased after the addition of Fe and Co while remained almost the

same after the addition of Ni, showing similar trend as the XPS analysis. On the other hand, the ICP results also showed that the V species is relatively inert towards the galvanic replacement process. Hence, we proposed that successful galvanic displacement reaction can only be achieved by having suitable redox potential, or otherwise the hydroxide precipitation will become the predominant process.

It is worth noting that the tubular core-shell architecture pertained for the Co and Ni-containing ternary nanocomposites with only compositional changes at the outermost layer (Figure 5.18a-h, Figure 5.19a-h for Co and Ni, respectively). This chemical route illustrated the versatility of aqueous-based synthetic protocol for accessing well-defined morphology with tunable composition.

Figure 5.18. (a-b) SEM images, (c) TEM image; and (d) Dark field STEM/EDX line scan profile; (e-h) elemental mapping of the $V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$ core-shell NTs. Inset of (d) illustrated the dark field STEM image of the $V_2O_5@MnO_2/Co_2O_3/Co(OH)_2$

core-shell NTs. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

Figure 5.19. (a-b) SEM images, (c) TEM image; and (d) Dark field STEM/EDX line scan profile; (e-h) elemental mapping of the $V_2O_5@MnO_2/Ni(OH)_2$ core-shell NTs. Inset of (d) illustrated the dark field STEM image of the $V_2O_5@MnO_2/Ni(OH)_2$ core-shell NTs. Reprinted with permission from ¹⁹⁰. Copyright (2014) American Chemical Society.

5.6 Electrochemical Measurements

As a demonstration of potential applications, the $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs were tested as the SC electrode in KCl aqueous electrolyte. At slow scan rate of 2 mV s^{-1} (Figure 5.20a), the CV curve of MnO_2 exhibited a symmetrical rectangular shape while the CV curve of V_2O_5 showed three pairs of redox peak (0.39/0.55, 0.03/0.11, -

0.59/-0.26 V *vs.* Ag/AgCl) over the entire scanning range. On the other hand, the CV curve of the $V_2O_5@MnO_2$ NTs was a combination of the electrochemical properties of its individual component, exhibiting the pseudo-constant charge/discharge rate of MnO_2 and intercalation/deintercalation reaction mechanism of V_2O_5 that allows penetration of cation into its 2-D crystalline lattice network, according to the following equations:^{25,116}

Enlarged CV loop with distinct redox peaks that resembled to the CV curve of V_2O_5 could be observed for $V_2O_5@MnO_2$ NTs. For $V_2O_5@MnO_2/Fe_2O_3$ NTs, new redox peaks for Fe_2O_3 emerged at low potential region, showing as humps at -0.93 and -0.79 V (*vs.* Ag/AgCl). As far as the Fe_2O_3 was concerned, this redox pair could be explained as the reversible faradaic conversion between the Fe^{3+} and Fe^{2+} . It was found that the V_2O_5 redox peaks experienced some potential shift, which could be due to synergistic interaction imposed by the other two species and caused variation in the reaction kinetics of V_2O_5 . Similar trend was observed at 100 mV s⁻¹ except small shifting of the redox peaks (Figure 5.20b). Cyclic voltammetric investigation of $V_2O_5@MnO_2$ NTs at 100 mV s⁻¹ hinted its excellent kinetic reversibility by attaining almost identical CV loop without significant alteration as compared to the CV loop obtained at low scan rate (Figure 5.20a). In addition, the redox peaks were more significant as the current response become stronger at high scan rate. From the experimental results, it was found that the water decomposition was suppressed and hydrogen overpotential was extended to lower potential for V_2O_5 ,

$V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$. Interestingly, the working potential of $V_2O_5@MnO_2/Fe_2O_3$ NTs could be extended to 2.4 V at the expense of cycling stability (slightly drop in cycling retention percentage as compared to those measurement scan in less than 2 V potential range due to the dissolution of electro-active materials at low potential), which was far greater than the thermodynamic stable operating potential of water.

Figure 5.20. CV of the as-prepared samples at different scan rate: (a) 2 mV s^{-1} and (b) 100 mV s^{-1} .

The GCD curves of the as-prepared samples from 0.5 to 10 A g^{-1} were illustrated in Figure 5.21. At low current density, symmetric V-shape charge and discharge curves were observed from MnO_2 nanoflakes, V_2O_5 nanowires, $V_2O_5@MnO_2$ NTs. Although V_2O_5 nanowires and $V_2O_5@MnO_2$ NTs displayed redox peaks in their corresponding CV measurements, no obvious redox plateaus were observed in the GCD curves, which is the pseudocapacitance induced by the iron species. Therefore, the charge and discharge curves exhibited a reaction plateau that symbolized to the redox reactions of Fe species below -0.5 V (vs. Ag/AgCl).

Figure 5.21. GCD curves at different current densities (a) MnO₂; (b) V₂O₅; (c) V₂O₅@MnO₂ NTs; (d) V₂O₅@MnO₂/Fe₂O₃ NTs.

On the other hand, the GCD curves at different current densities of the as-prepared samples were illustrated in Figure 5.22. At 0.5 A g⁻¹, the pure MnO₂ nanoflakes, pure V₂O₅ nanowires, V₂O₅@MnO₂ NTs and V₂O₅@MnO₂/Fe₂O₃ NTs could achieve 269, 444, 571 and 622 F g⁻¹, respectively, in which the V₂O₅@MnO₂ and V₂O₅@MnO₂/Fe₂O₃ NTs exhibited superior capacitive capabilities than those of single-phase V₂O₅ and MnO₂ nanoflakes. Similar trend was observed at current densities of 10 A g⁻¹, in which V₂O₅@MnO₂/Fe₂O₃ NTs could still achieve 245 F g⁻¹ and it was apparently higher than the pure MnO₂ nanoflakes (104 F g⁻¹), pure V₂O₅ nanowires (111 F g⁻¹), V₂O₅@MnO₂ NTs (190 F g⁻¹).

Figure 5.22. Specific capacitance of the as-prepared samples at different current densities.

The preliminary results shown in Figure 5.23 revealed that MnO_2 is a durable species in cycling test, giving rise to the highest capacitance retention percentage (94%) and the $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs inherited the good cycling stability of MnO_2 that retained 90% and 93%, respectively, of its original specific capacitance after 1000 cycles, surpassing V_2O_5 that undergoing rapid capacitive fading upon cycling. Despite of having exceptionally high specific capacitance in the beginning, the dissolution or structural collapse issue of V_2O_5 could be the prime factor leading to rapid capacitive fading in the subsequent cycles. Furthermore, the displacement of Fe_2O_3 at the outermost layer might improve its electronic conductivity and protective layer for V_2O_5 , giving rise to better long-term cycling stability as compared to the $V_2O_5@MnO_2$ NTs.

Figure 5.23. Cycling performance of the as-prepared samples scanning at 1 A g^{-1} .

Here, the electrochemical performances examined for the $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs exhibited distinguishable properties over conventional single-phase counterparts from different aspects. The observed electrochemical enhancement in term of specific capacitance could be attributed to the successful tailoring of morphological and interfacial properties of the $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs, endowing them with higher specific BET surface area as compared to their single-phase V_2O_5 and MnO_2 . With the unique hollow architecture, easy penetration and excellent accessibility of electrolyte were guaranteed for both the MnO_2 and V_2O_5 , maximizing the electro-active surface area and leading to optimum electrochemical performances. On the other hand, the design rationale for tubular $V_2O_5@MnO_2$ core-shell nanostructure was able to impose constraint against structural collapse of V_2O_5 by having conformal coating of MnO_2 on its surface while the protected V_2O_5 can exhibit higher specific capacitance and excellent electrochemical performance at high rate measurement.

In addition, the coverage of Fe species on the outermost surface might construct a protection zone for V_2O_5 and improved the electronic conductivity of the nanocomposite (electrical conductivity of MnO_2 ($10^{-5} - 10^{-6} \text{ S cm}^{-1}$)⁵⁸ < V_2O_5 ($10^{-2} - 10^{-3} \text{ S cm}^{-1}$)¹⁹⁸ < Fe_2O_3 ($10^{-1} - 10^{-2} \text{ S cm}^{-1}$)¹⁸¹). Notably, the operating voltage of the nanocomposites could be extended to 2.4 V and delayed the decomposition of water, pushing the hydrogen overpotential to lower limit.

5.7 Summary

In summary, $V_2O_5@MnO_2$ NTs were successfully synthesized using a scalable approach under ambient condition. In addition, the well-defined morphology but adaptive dimension of the $V_2O_5@MnO_2$ NTs could be tuned to meet the requirements of different applications. From the fundamental point of view, the mechanism for the transformation of solid to hollow core-shell structure could be attributed to the formation of soluble oxonitrate complex of vanadium upon redox deposition of MnO_2 . Notably, a facile aqueous-based synthetic protocol for accessing tubular ternary nanocomposites with tunable chemical compositions was also developed. The preliminary results manifested the versatility of this aqueous-based chemical route for expanding the binary $V_2O_5@MnO_2$ NTs to tubular $V_2O_5@MnO_2/M$ ($M = Fe_2O_3, Co_2O_3/Co(OH)_2, Ni(OH)_2$) ternary composite. In addition, the successful attempt in applying the multi-component $V_2O_5@MnO_2$ and $V_2O_5@MnO_2/Fe_2O_3$ NTs as SC electrode has prompted them to be implemented as the next generation energy storage devices with high power and energy density.

6. Asymmetric Supercapacitors

6.1 Introduction

It is known that the energy stored in a capacitor is a function of capacitance (C) and working potential (V), represented by the equation: $E = \frac{1}{2} CV^2$.^{199,200} As SC is progressing towards the ultimate goals of being high energy and power densities, development of hybrid SCs can usher in wider working potential for higher energy density without sacrificing the power density and cycling stability. Figure 6.1 depicted the schematic diagram of an asymmetric SC.⁵⁰

Figure 6.1. Schematic diagram of an asymmetric SC. Reproduced from Ref. ⁵⁰ with permission from The Royal Society of Chemistry.

It consists of negative and positive electrodes, electrolyte and a separator sandwiched between the parallel facing electrodes. Generally, non-faradaic reaction (electric double-layer adsorption/desorption) takes place at negative side and faradaic reaction (redox response) occurs at positive side.²⁰¹ The working principle involves the voltage-driven

migration of cations (Li^+ , Na^+ , K^+ , H^+ , *etc.*) or anions (OH^- , ClO_4^- , PF_6^- , BF_4^- , *etc.*) through the electrolyte towards the electrodes for reversible electrochemical reactions. Meanwhile, the electrons flow through the external circuit to maintain the charge balance.

Although most of the commercial organic electrolytes provide wider working potential, safety and high-cost issues remain.⁵⁰ Alternatively, aqueous electrolytes hold a number of advantages over the organic electrolytes: (1) high ionic conductivity of the aqueous electrolyte due to low viscosity and smaller hydrated ions;²⁰² (2) ecological friendly solvent that can be easily handled and recycled; (3) only produce environmental benign decomposition products that can be treated easily.²⁰³ However, one of the critical aspects for the aqueous-based SCs to achieve this goal is the limitation in operating potential range (1.23 V) arisen from the decomposition of water.^{204,205} In this regard, the use of asymmetric SCs is an answer to the limitation in energy density. Combining the advantages of using aqueous-based electrolytes, long cycle life asymmetric SCs with high energy and power density could be achieved. Several successful examples in literatures have been shown to be efficient, for instances, AC// PbO_2 ²⁰⁶⁻²⁰⁸, AC// MnO_2 ²⁰⁹⁻²¹¹ and AC// Ni(OH)_2 ^{212,213}. From the ecological standpoint, strongly acidic⁴¹ or basic²¹⁴ electrolytes may induce corrosion or dissolution problems at the electrode and therefore, the environmental friendly neutral aqueous-based electrolytes could be an ideal alternative for sustainable development of asymmetric SCs.

In this chapter, a comparative study was done to investigate the practicability of the as-prepared manganese-based nanomaterials by testing them in aqueous medium employing the asymmetric configuration. SC. In this double-electrode system, the

MWCNTs were used as the negative electrodes while the manganese-based nanocomposites were used as the positive electrodes.

6.2 Experimental Details

The asymmetric SC devices were fabricated at ambient condition using 1 M KCl aqueous electrolyte. Both the positive and negative electrodes were firstly coated on the carbon paper (except the binder-free MnOOH NTs/GF sample). Then, aluminum tab was attached to the current collector as both the negative and positive terminals for pouch cell while the filter paper was used as the separator to prevent electrical contact between the positive and negative electrodes. After that, the parallel facing electrodes were sealed in a polymer-coated aluminum foil using the heat press machine. The asymmetric SC can be schematically represented in Figure 6.2.

Figure 6.2. Schematic illustration of the asymmetric SC structure and the digital image of the polymer-coated aluminum foil pouch cell.

6.3 Electrochemical Measurements

The CV and GCD measurement of the MWCNTs negative electrode at different scan rates and current densities, respectively, were illustrated in the Figure 6.3.

Figure 6.3. (a) CV curves; (b) GCD curve of the MWCNTs electrode.

It is worth mentioning that the applied voltage is distributed equally on two electrodes with the same mass in a symmetric SC. In contrast, the voltage that splits between two electrodes is dependent on the capacitance of each electrode. Therefore, the charge balance in an asymmetric SC system can be described as follows:²¹⁵

$$q_+ = q_-$$

q_+ and q_- are the charges at positive and negative electrodes, respectively.

$$q = C \times \Delta V \times m$$

C , ΔV and m are the capacitance, working voltage and mass of the active materials, respectively.

To balance the charge stored within the positive and negative electrodes for maximum energy density, the mass ratio of the positive and negative electrodes was calculated using the following equation:²¹⁵

$$R = \frac{m_+}{m_-} = \frac{C_- \times \Delta V_-}{C_+ \times \Delta V_+}$$

The value of C_- and C_+ was estimated from the three-electrode system that used Ag/AgCl as the reference electrode and platinum mesh as the counter electrode. From the specific capacitance deduced from the three electrode system at 1 A g⁻¹, the mass ratio between the positive and negative electrode were summarized in Table 6.1. As the total cell voltage of the double-electrode system is the sum of the operating potential of the positive and negative electrodes, this asymmetric configuration could operate up to 2 V in aqueous medium (1 M KCl).

Table 6.1. Mass ratio of the as-prepared samples for asymmetric SC.

Entry	Specific Capacitance ^a	Voltage Range	Mass Ratio
	(F g ⁻¹)	(V)	($m_+:m_-$)
MWCNTs	82	1.0	-
0.5Cu-MnO@C	307	1.0	3.7:1.0
MnOOH NTs/GF	388	1.0	4.7:1.0
V ₂ O ₅ @MnO ₂ NTs	529	1.2	6.5:1
V ₂ O ₅ @MnO ₂ /Fe ₂ O ₃ NTs	588	1.0	7.2:1

^a The specific capacitance was calculated at 1 A g⁻¹.

Figure 6.4 showed the CV curves of the asymmetric SCs that constructed by MWCNT negative electrode and manganese-based heterostructures positive electrode at different potential window, ranging from 1 to 2 V (100 mV s⁻¹). Successive redox reactions of as-prepared manganese-based nanocomposites were observed by demonstrating no distorted rectangular shape up to 2 V of potential window. On the other hand, their corresponding CV curves also illustrated their good electrochemical

reversibility and stability from low to high scan rate (2 to 100 mV s^{-1}) within 2 V range without showing any polarization phenomenon caused by the H_2 and O_2 evolution. It could be due to the compensation effect that hindered the electrode polarization upon charge and discharge processes.¹⁰

Figure 6.4. CV curves of the asymmetric SCs scanned at 100 mV s^{-1} : (a) 0.5Cu-MnO@C ; (b) MnOOH NTs/GF ; (c) $\text{V}_2\text{O}_5\text{@MnO}_2 \text{ NTs}$; (d) $\text{V}_2\text{O}_5\text{@MnO}_2/\text{Fe}_2\text{O}_3 \text{ NTs}$.

Similar to the three-electrode configuration, the specific capacitance of the manganese-based nanocomposites was calculated from the GCD measurement at 1 A g^{-1} (Figure 6.5). The manganese-based asymmetric SCs showed an almost symmetric charge and discharge curves indicated their good reversibility and stability in response to redox reaction. It was found that the specific capacitance of the manganese-based

nanocomposites can be arranged in the following order: $\text{V}_2\text{O}_5@\text{MnO}_2/\text{Fe}_2\text{O}_3$ NTs (196 A g^{-1}) > $\text{V}_2\text{O}_5@\text{MnO}_2$ NTs (168 F g^{-1}) > MnOOH NTs/GF NTs (124 F g^{-1}) > $0.5\text{Cu}/\text{MnO}@C$ (64 F g^{-1}).

Figure 6.5. GCD curves of the asymmetric SCs: (a) $0.5\text{Cu-MnO}@C$; (b) MnOOH NTs/GF; (c) $\text{V}_2\text{O}_5@\text{MnO}_2$ NTs; (d) $\text{V}_2\text{O}_5@\text{MnO}_2/\text{Fe}_2\text{O}_3$ NTs.

On the other hand, the rate capability of the asymmetric SCs was evaluated by testing them at different current densities (Figure 6.6a). Remarkably, $\text{V}_2\text{O}_5@\text{MnO}_2/\text{Fe}_2\text{O}_3$ NTs was able to deliver 220, 196, 164, 140, and 104 F g^{-1} at 0.5, 1, 2, 3, and 5 A g^{-1} , respectively, surpassing the other three manganese-based asymmetric SCs. On the other hand, the cycling stability of the asymmetric SCs and the overall retention percentage of the as-prepared samples after 1000 cycles can be visualized in Figure 6.6b. As indicated

in Figure 6.5b, MnOOH NTs/GF experienced the least capacitance fading, followed by $V_2O_5@MnO_2/Fe_2O_3$ NTs, $V_2O_5@MnO_2$ NTs and $0.5Cu-MnO@C$.

Figure 6.6. (a) Specific capacitance at different current densities; (b) cycling stability test of the asymmetric SCs.

The energy and power densities of the manganese-based nanocomposites in asymmetrical two-electrode cell can be gleaned from the Ragone plot shown in Figure 6.7 and their overall electrochemical performances could be clearly visualized from Table 6.2.

Figure 6.7. Ragone plot of the asymmetric SCs.

Table 6.2. Overall electrochemical performances of the manganese-based asymmetric SCs.

Entry	Current Density (A g ⁻¹)	Specific Capacitance (F g ⁻¹)	Energy Density (W h kg ⁻¹)	Power Density (kW kg ⁻¹)
0.5Cu/MnO@C	0.5	22.2	12.2	14.3
	1	16.4	8.9	13.3
	2	12.2	6.7	10.9
	3	8.3	4.4	10.2
	5	5.1	2.8	8.7
MnOOH NTs/GF	0.5	35.2	19.4	25.0
	1	30.8	17.2	21.6
	2	25.2	13.9	19.6
	3	19.1	10.6	16.8
	5	13.1	7.2	12.6
V ₂ O ₅ @MnO ₂ NTs	0.5	48.2	26.7	11.5
	1	41.9	23.3	12.6
	2	37.2	20.6	11.4
	3	30.0	16.7	8.3
	5	17.8	10.0	7.3
V ₂ O ₅ @MnO ₂ /Fe ₂ O ₃ NTs	0.5	55.0	30.6	12.8
	1	49.1	27.2	11.8
	2	40.7	22.8	10.2
	3	35.0	19.4	9.6
	5	26.2	14.4	9.3

The energy and power densities of the as-synthesized manganese-based asymmetric SCs are comparable to the commercial lithium ion batteries and SCs, respectively, suggesting that they hold great promise toward practical implementation as SC electrode.

6.4 Summary

In this section, pouch-type assembly of the engineered manganese-based heterostructures in an asymmetric configuration will be demonstrated in hope of paving a new research direction to bring them one step further towards commercial implementation. The construction of asymmetric SCs that use carbon-based materials as the negative electrode and the high-capacitance faradaic positive electrode (manganese-based heterostructures) overcomes the energy limitation of a three-electrode system. Ultimately, the energy density of the manganese-based asymmetric SCs was greatly enhanced as compared with the commercial SCs without sacrificing their long cycle life and high power density.

7. Conclusions and Future Work

7.1 Conclusions

In this thesis, new strategies were developed to prepare nano-sized manganese-based heterostructures with well-defined morphology and fundamental understanding on their growth mechanisms was also developed. Precisely tuning the morphology and having rational design in architecture of manganese-based composites enable high surface area to be obtained, leading to higher specific capacitance. Furthermore, coupling the single-phase manganese species with foreign components gives rise to unprecedented electrochemical performances attributing to the synergistic effect. Here, the mutual interaction between the manganese species and the incorporated components can be interpreted from different aspects:

1. Improve the rate capability of the SC by coupling the single-phase MnO with metallic Cu to improve the electronic conductivity of the electrode. The conformal carbon coating prevents the MnO from dissolution upon long-term cycling.
2. Improve the cycling stability of the SC by *in-situ* deposition of MnOOH on conductive GF scaffold. The intimate contact at the epitaxial MnOOH/GF interfaces reduces the ESR and promotes the electron transfer between the active materials and the current collector.
3. Improve the specific capacitance of the SC by hybridizing MnO₂ with other pseudocapactive species to form multi-component nanostructures with well-defined composition and morphology.

Firstly, carbon coated Cu-MnO nanostructures were synthesized to compensate the low electronic characteristic of MnO besides constraining the structural deformation and dissolution of MnO upon long-term cycling in the presence of thin carbon layer. By decomposing the manganese and copper precursors in high boiling point organic solvents, the dimension and uniformity of the nanoparticles can be precisely controlled. Introduction of Cu nanoparticles promotes integrated charge transfer of the whole electrode by reducing the charge transfer resistance between the MnO active materials and the current collector. Improved rate capability was observed, hinting the feasibility of using intimate connected metallic species in tailoring the electronic conductivity of MnO. Therefore, the electrochemical performances of the hybrids surpassed the single-phase MnO. By executing the thermal annealing step, the physically chelated organic can be carbonized into amorphous protective layer to prevent the dissolution of MnO upon long-term cycling. Successful attempt on Cu-MnO@C hybrid provides a new platform for the preparation of other Cu-containing TMO heterostructures with narrow particle size distribution.

Secondly, freestanding electrodes that consisted MnOOH and GF were synthesized using a facile hydrothermal method. The surface area of the MnOOH species was tailored to increase the surface-to-volume ratio for greater capacitive enhancement. On the other hand, the binder-free concept was applied, aiming to avoid the conventional fabrication method that used electro-inert polymeric binders such as the PVDF and nafion. Therefore, the ESR of the electrode was reduced significantly by having more direct contact between the active materials and the carbon current collector and providing more efficient pathway

for electron transportation. As a result, the cycling stability of the binder-free composites was greatly improved as compared to the conventional method fabricated samples.

Lastly, the $\text{V}_2\text{O}_5@\text{MnO}_2$ core-shell NTs were successfully synthesized *via* a room-temperature aqueous-based method and further functionalization of the $\text{V}_2\text{O}_5@\text{MnO}_2$ NTs with other TMOs resulted in ternary composites, $\text{V}_2\text{O}_5@\text{MnO}_2/\text{Fe}_2\text{O}_3$ NTs. The *in-situ* growth of MnO_2 on V_2O_5 scaffold can enhance the capacitance of the nanocomposites by having contribution arises from the V_2O_5 with multiple valence states. On the other hand, the intrinsic disadvantages of V_2O_5 are also compensated by the good cycling performance of MnO_2 by forming core-shell architecture. Furthermore, the incorporation of Fe_2O_3 as the outermost layer may increase the electronic conductivity of the nanocomposites besides having capacitive contribution. Additionally, the hollow core-shell structures were presented to surpass its solid counterpart due to significant increase in accessible surface area and activation of the inner wall for electrochemical reactions.

The construction of asymmetric SCs that use carbon-based materials as the negative electrode and the high-capacitance faradaic positive electrode overcome the energy limitation of a three-electrode system. Owing to the significant increment in operating voltage, the overall energy density of the asymmetric configuration is greater than the three-electrode system as well as the symmetric double-electrode system besides inheriting long cycle life and high power characteristics of SCs.

In summary, enhancement in energy and power density was successfully achieved through nanoengineering and electrode material modification. In-depth study was done on investigating the contribution of the newly incorporated components in the charge storage

mechanism of SCs. Finally, the applicability of the nano-sized manganese-based heterostructures in pouch-type asymmetric SCs was also demonstrated.

7.2 Recommendation for Future Work

Present works have been successfully proven the feasibility of tailoring the physical as well as chemical properties of manganese species by adapting to different newly developed synthetic approach to accomplish the ultimate goal of realizing the full potential of the electrode materials. The following section recommends some possibility for future work to further develop a better electrode for commercial use.

7.2.1 Elemental Doping to Tune the Properties of Manganese Oxides

Although new and efficient synthetic strategies were developed to prepare novel hybrid nanostructures for greater electrochemical enhancement, this synthetic platform that derived from external reinforcements induces some problems. In the past, engineering on the intrinsic properties of manganese oxides by exploiting the doping effect has been less thoroughly investigated. In contrast to the surface absorbed deposition, successful doping is regarded as the substitution of foreign atoms to the host atoms, tuning the properties of the host species. In this regard, the incorporation of dopants within the lattice could lead to dramatic change in their electronic structure of the host species due to the electron affinity of the dopants. In general, the dopant concentration-dependent electronic conductivity is originated from the generation of carriers for conduction. Nevertheless, the concentration of dopant is limited since the host species tend to eliminate the dopants to maintain thermodynamic equilibrium and excess dopants will form segregated phase instead of the

non-stoichiometric form. Thus, this represents a promising approach to provide a platform for tailoring the intrinsic electronic properties and mass transfer efficiency of manganese species.^{216,217}

7.2.2 *In-situ* Characterizations

Systematic studies on the electrochemical characteristics of electrode materials have to be done to provide fundamental insight into reaction mechanism of SCs. In this regard, *in-situ* techniques are power tool in providing on-time analysis to probe the electrochemical reactions occurred within the electrode. On the other hand, *in-situ* observation the structural and compositional changes of the active materials is also beneficial for mechanistic study on particle behavior, and indirectly elucidate the origin of capacitance fading as well as charge-transfer resistance incurred. In contrast to *ex-situ* techniques, *in-situ* characterizations can minimize the analysis errors incurred by any compositional and structural changes after air exposure. Hence, efforts can to be devoted to investigating the reaction mechanism through: (1) *in-situ* XRD studies to probe the crystallographic structure of the reaction products; (2) *in-situ* TEM to provide insight into the structural transformation processes by observing the real-time information in transient states at atomic resolution; (3) *in-situ* ambient pressure XPS to identify how the electrons transport across the active materials/electrolyte interfaces by probing the valence state change of the active materials. By having further insight into the ion transport and phase transformation process upon reacting with the external environment, rational design of high-performance functional materials can be achieved in addressing some of the bottlenecks we faced nowadays.

7.2.3 All-Solid-State SCs for Electronic Device Applications

For the last few chapters, the hybridized electrode materials performed quite very well in three-electrode and double-electrode configurations. Nevertheless, a “real SCs” device has not been realized yet. Our recent setup possesses several drawbacks for practical application as compared to the all-solid-state SCs:²¹⁸ (1) a completely sealed package is required to prevent any leakage of liquid electrolyte; and (2) the setup is not flexible enough as liquid electrolyte occupy huge volume in a sealed system, hindering it from miniaturization. In contrast, an all-solid-state SC makes use of the gel-like polymer matrix as the electrolyte to separate the positive and negative electrodes, allowing them to have excellent flexibility and small in size.^{219,220} In this regard, preparation of solid or gel electrolytes that allow ion permeability but avoid any electric short circuit will be a great challenge.

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Appendices

Appendix 1 Electrode Preparations

The electrodes were prepared by dispersing the active materials, CNTs (conductive matrix) and 8 %wt. of PVDF (binder) in weight ratio of 7:2:1 in NMP. After homogeneous mixing, it was casted on carbon paper (current collector) with area of $1 \times 1 \text{ cm}^2$ and dried in vacuum oven at 50 °C for 12 h to remove the solvent.

Appendix 2 Characterizations

This chapter summarizes the material and electrochemical characterizations of the electrode materials. XRD, XPS, FESEM and TEM are employed for phase and morphology characterizations. Additionally, BET, ICP measurements are conducted to characterize their physical properties. Detailed descriptions of the electrochemical testing setup will be included as well. Besides, electrochemical characterizations such as GCD measurement, CV, cycling stability test and EIS are used to evaluate the electrochemical properties of the electrode materials.

Appendix 2.1 Materials Characterization Techniques

Appendix 2.1.1 X-ray Diffraction (XRD)

XRD measures the coherent scattering of x-ray of the materials and transforms it into the crystallographic information. Shimadzu XRD-6000 diffractometer and Bruker AXS D8

Advance diffractometer with Cu K α radiation ($\lambda = 0.15406$ nm) were used to investigate the crystal structure of the electrode materials.

Appendix 2.1.2 Field Emission Scanning Electron Microscopy (FESEM)

JEOL JSM-7600F field emission scanning electron spectroscopy was used for morphology investigation.

Appendix 2.1.3 Transmission Electron Microscopy (TEM)

JEOL JEM 2100F transmission electron microscope, operating at 200 kV was used for capturing HRTEM images and the STEM-DF was used to perform the EDX elemental mapping and line scan analyses.

Appendix 2.1.4 Brunauer-Emmett-Teller (BET)

Accelerated Surface Area and Porosimetry System (ASAP 2020) was used to measure the nitrogen adsorption/desorption isotherms at -196 °C. Before the measurement, all the as-prepared samples were degassed at 150 °C for 6 h under vacuum condition. The specific surface area was determined by BET method.

Appendix 2.1.5 X-ray Photoelectron Spectroscopy (XPS)

XPS measurements were performed on VG Escalab 250 spectrometer using Al K α 1846.6 eV anode. The binding energy was calibrated using C 1s peak at 284.6 eV as the reference.

Appendix 2.1.6 Inductively Coupled Plasma (ICP)

ICP (ICP Dual-view Optima 5300 DV ICP-OES system) was employed to measure the elemental contents. Concentrated hydrofluoric acid (40%) was used to digest the samples prior to the measurements.

Appendix 2.1.7 Raman Spectroscopy

The Raman spectroscopy was conducted using the WITec CRM200 confocal Raman microscopy system with a laser wavelength of 488 nm and a spot size of 0.5 mm. Calibration was done using the Si peak at 520 cm^{-1} as a reference.

Appendix 2.2 Electrochemical Characterizations

The electrochemical characterizations such as CV, GCD measurement, cycling test were carried out on Solartron analytical equipment (Model 1470E). The three-electrode system consists of Ag/AgCl reference electrode, Pt mesh counter electrode and working electrode that contained the active materials while the asymmetric double-electrode cell consist of two electrodes oppositely facing to each other. EIS measurements were conducted at open circuit potential on an impedance spectrum analyzer (Solartron, SI 1255B Impedance/gain-phase analyzer; computer software ZView) in the frequency range of 10 kHz to 0.01 Hz with an AC perturbation of 5 mV.

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Conference Presentation

1. Controlled Synthesis of Nanostructured Manganese Oxyhydroxide Nanotubes:
Implication for High-Power High-Energy Supercapacitor

H. T. Tan, X. Rui, W. Shi, C. Xu, H. Yu, H. E. Hoster, Q. Yan

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