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CARBON-BASED NANOCOMPOSITES FOR ENERGY STORAGE

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

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Abstract

As portable consumer electronics become the necessities in one's daily life, energy storage systems which act as the primary power sources are attracting rising attention in their development. One of the great challenges is to develop ecologically friendly, low cost and sustainable energy storage system. The performance of these storage systems, for example, supercapacitors and lithium ion batteries, is strongly reliant on their materials of choice for electrode. Hence, much interest has been garnered in looking for innovative and advanced material that can overcome current technology hurdles.

In this dissertation, various carbon based nanocomposites have been explored to enhance the performance of the energy storage device by synergistic integration of the conductive carbon nanomaterials and reactive nanomaterials. Novel carbon-based nanostructured-composites that can be utilized as the electrode material for constructing lithium ion batteries and supercapacitor has been synthesized. If suitable, carbon based nanocomposites has been demonstrated to fabricate flexible energy storage systems. With wearable electronics leading the trend of next generation consumer electronics, designing and fabrication of flexible, inexpensive, lightweight, and high-performance energy storage devices would be the future for energy storage systems.

This dissertation starts with a short introduction of energy storage systems, followed by literature reviews on lithium ion batteries and supercapacitors. Then, from chapter 4 to 6, the carbon-based nanocomposite synthesized would be

discussed. In Chapter 4, the synthesis of interwoven network of MnO₂ nanowires and multi-walled carbon nanotubes (MWCNTs) is described. Working as the lithium ion battery anode material, this nanocomposite reveals superior performance by synergistically integrating the two composite materials. Also, with the MWCNT network bendability and strength, a bendable full battery is constructed and examined. Chapter 5 discusses the synthesis of core-shell-structured metal-nitride nanowires with a 3D carbon substrate and its performance for supercapacitor. The electrode exhibits excellent volumetric capacitance and good cycling life stability, attributed to the synergistic integration of vanadium nitride and titanium nitride, as well as the microporous 3D carbon substrate. Chapter 6 describes the doping of conducting polymer (polypyrrole) with graphene quantum dots via electro polymerization. The feasibility of enhancing the capacitive performance of electropolymerized PPy by doping with GQDs is examined. Last but not least, in chapter 7, a general conclusion for all chapters and recommendation for future research work is provided.

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Abbreviation

2D	Two-dimensional
3D	Three-dimensional
Ag	Silver
AgCl	Silver chloride
CO ₂ ,	Carbon dioxide
Co ₃ O ₄	Cobalt oxide
CuO	Copper oxide
CuO	Copper
DER	Distributed energy resource systems
EDLC	Electrical double layer capacitance
EESS	Electrical energy storage systems
FE-SEM	Field-emission scanning electron microscope
GO	Graphene oxide
GQDs	Graphene Quantum Dots
H ₂ SO ₄	Sulphuric acid
HEVs	Hybrid electric vehicles
HRTEM	High resolution transmission electron microscopy
KCL	Potassium chloride
KCl	Potassium chloride
KMnO ₄	Potassium permanganate
KOH	Potassium hydrochloride
Li	Lithium
LIB	Lithium ion batteries
LiFePO ₄	Lithium iron phosphate
LiMn ₂ O ₄	Lithium manganese oxide
LiPF ₆	Lithium hexafluorophosphate
MnO ₂	Manganese oxide
MWCNTs	Multi-wall carbon nanotubes
N	Nitrogen
NH ₄ Cl	Ammonium chloride
NiCd	Nickel Cadmium
NiO	Nickel oxide

NO _x	Nitrogen oxide
O	Oxygen
PANI	Polyaniline
pHEVS)	Plug in hybrids electric vehicles
Ppy	Polypyrrole
PVDF	Polyvinylidene fluoride
Py	Pyrrole
RuO ₂	Ruthenium(IV) oxide
S	Sulphur
Si	Silicon
SnO ₂	Tin oxide
SO ₂	Sulfur dioxide
TEM	Transmission electron microscope
TiN	Titanium nitride
TiO ₂	Titanium oxide
V ₂ O ₅	Vanadium oxide
VN	Vanadium nitride
VO	vanadium oxide
WO ₃	Tungsten oxide
XRD	X-ray powder diffraction
ZnO	Zinc oxide

Chapter 1

Introduction

1.1 Background of electric energy storage systems

In an era where portable consumer electronic devices such as cell phones, PDAs, tablets, laptops are becoming the necessities in one's daily life, energy storage systems which act as the primary power sources are attracting rising attention in their development. Be it to power up consumer electronics, medical devices, hybrid electric vehicles or to provide energy storage for power plant, the need for environmental friendly and efficient energy storage systems is enormous.

Due to their intermittent and cyclic nature, electric energy storage systems also has an important role in bridging the electricity generation and demands, particularly for the electrical energy generated from renewable and sustainable sources such as solar, wind and geothermal. By storing electrical energy in batteries or chemical fuels and using such energy later, it can radically improvise the energy efficiency, reliability and energy security for the conventional power plants. At the same time, emission of greenhouse gases and air pollutants such as CO₂, SO₂ and NO_x can be reduced. ^[1]

Figure 3.1 (a) Schematic representation of a battery, with requirements on electron and ion conduction. (b) Schematic representation of supercapacitor. (c) Schematic representation of fuel cell. Reproduced with permission from. [2] Copyright 2004, American Chemical Society.

Energy storage systems can be classified into batteries, fuel cells, and supercapacitors. Although there exist differences between storage and conversion mechanisms, there are certain similarities in the electrochemical properties of these systems. [2] For the three systems, common traits are that the energy-providing processes take place at the phase boundary of the electrode-electrolyte interface and that electron and ion transport are separated. Besides that, all three system are made up of two electrodes in contact with an electrolyte solution. Figure 1.1 show the basic operation mechanisms of the three systems, note that the requirements on ion and electron conduction in Figure 1.1a are the same for batteries, fuel cells and supercapacitors. [2] In this dissertation, we will focus on batteries (i.e. Lithium ion battery) and supercapacitors.

So far, batteries are much widely utilized in market. They are the primary power sources for portable consumer electronics such as mobile phones, wearable electronics or laptops. Supercapacitors, which are similar to batteries but with

higher power and longer cycle life, can also be used in consumer electronics as well as in automotive applications.

1.1.1 Li-ion batteries

Batteries can store chemical energy and when needed convert this chemical energy into electrical energy to power up various application. Batteries are divided into 3 main classes that is the primary batteries (discharged once and discarded), secondary batteries (rechargeable batteries that can be discharged and re-charged to restore their original condition) and specialty batteries (for specific purpose, mainly non-widely used military and medical batteries).^[2]

Since lithium has the highest gravimetric and volumetric theoretical energy density for all solid electrode, Li-ion battery is the most attractive energy storage systems among all types of batteries.^[1] However, as rechargeable battery based on metallic lithium anode will form lithium dendrite during charging and hence short the two electrodes, acceptable cycling life is not achievable.^[3] The current widely used Li-ion batteries are based on the use of lithium intercalation/alloying compounds for both anode and cathode. These materials have enhanced not just cycling life but also safety and rate capability.^[1]

As a member of the family of rechargeable batteries, Li-ion battery are widely used in portable consumer electronics. Lithium batteries were first proposed by M.S Whittingham in the 1970s.^[4] In the following decades, scientists strived to examine the mechanism and to develop the positive and negative electrode materials as well as the electrolytes for Li-ion batteries.^[5-8] It was until 1991 when Sony and Asahi Kasei released the first commercial Li-ion battery.

Figure 1.2 Schematic representation of a lithium - ion battery. Negative electrode (graphite), positive electrode (LiCoO₂), separated by a non - aqueous liquid electrolyte. Reproduced with permission from. [9] Copyright 2008, John Wiley and Sons.

Li-ion battery is made up of three basic components, the anode, cathode and electrolyte, schematically shown in Figure 1.2. During discharge, lithium ions move through the electrolyte from the anode (negative electrode) to the cathode (positive electrode) as the electrons flow through the external circuit. During recharge, both lithium ions and electrons are driven back in the reverse direction by an external voltage to store the electrical energy as chemical energy.

1.1.2 Supercapacitor

Supercapacitors, are sometimes known as electrochemical capacitors, ultracapacitors or hybrid capacitors. The capacitance value of a supercapacitor is contributed by the double-layer capacitance and pseudocapacitance. ^[10-11]

The double-layer capacitance involves storing the electrical energy attained by separation of charge in a Helmholtz double layer at the interface between the surface of a conductive electrode and an electrolyte. On the other hand,

pseudocapacitance involves the storage of the electrical energy with electron transfer, which is achieved by redox reactions with specifically adsorbed ions from the electrolyte, intercalation of atoms in the layer lattice or electrosorption, underpotential deposition of hydrogen or metal adatoms in surface lattice sites which result in a reversible faradaic charge-transfer.^[10-11]

Supercapacitors are classified into 3 families, that is the double-layer capacitors (with carbon or derivatives electrodes), pseudocapacitor (with metal oxides or conducting polymer electrode) and hybrid capacitor (with asymmetric electrodes that exhibit both double-layer capacitance and pseudocapacitance).

The difference between double-layer capacitors and pseudocapacitor is shown schematically in Figure 1.3.^[12] In general, double-layer capacitors have high power capabilities, due to the fast sorption and desorption of ions, but a low specific energy.^[13] Pseudocapacitor undergo a redox reaction to store charge in the bulk of the material and thereby increase the energy stored and reduce self-discharge. Significant drawback of pseudocapacitor is the relatively low power due to the slow diffusion of ions within the bulk of the electrode.^[13]

Figure 1.3 Comparison of charging of (a) double-layer capacitor (carbon) and (b) pseudo-capacitor (conducting polymer). Reproduced with permission from. [12] Copyright 2011, Elsevier.

1.2 Motivations and Objective

With ever-rising energy demand, emerging environmental concern and limited energy resources, one of the great challenges in this era is undeniably developing ecologically friendly, low cost and sustainable energy storage system. The performance of these energy storage systems, such as supercapacitors and lithium ion batteries, is strongly dependent on their electrode materials. Hence, much interest has been garnered in looking for innovative and advanced material that can overcome current technology hurdles.

For its relatively lower cost and better mechanical stability, carbon materials such as graphite, carbon nanotubes have been explored as electrode materials for both lithium ion batteries and supercapacitors. ^[9,14-17] In lithium ions batteries, carbon materials have been used as anode material whereas in supercapacitors, carbon electrodes are used for harnessing double-layer capacitance. In both cases, the performance is limited by its active surface area and pore size.^[14-18]

In this dissertation, various carbon based nanocomposites have been explored to enhance the performance of the energy storage device by synergistic integration of the conductive carbon nanomaterials and reactive nanomaterials. Novel carbon-based nanostructured-composites that can be used as the electrode material for lithium ion batteries and supercapacitor has been synthesized.

The specific objectives are as follows: (1) To synthesize carbon-based nanocomposites as electrode material for energy storage systems. (2) To enhance the performance of the energy storage device by synergistic integration of the conductive carbon nanomaterials and reactive nanomaterials. (3) If suitable, to

utilize the as synthesized nanocomposites to fabricate flexible energy storage systems. With wearable electronics leading the trend of next generation consumer electronics, designing and fabrication of flexible, inexpensive, lightweight, and high-performance energy storage devices would be the future for energy storage systems.

1.3 Organization of Dissertation

In this dissertation, various carbon-based nanocomposites that can be used to enhance the performance of the energy storage device has been designed and examined. Chapter 1 introduces the background of electric energy storage systems and gives a short summary of lithium ion batteries and supercapacitors. It also provides an overview of the motivation and objectives of this dissertation. Chapter 2 reviews on development of electric energy storage systems, with focus on lithium ion batteries and supercapacitors. Chapter 3 lists the chemicals that was utilized and their sources. Equipment that was used for characterizing the nanocomposites synthesized were also included. Details methodology can be found in subsequent chapters. In Chapter 4, a facile one-pot synthesis of interwoven network of MnO₂ nanowires and multi-walled carbon nanotubes (MWCNTs) is described. The performance of the carbon based nanocomposites is also examined and illustrated. Chapter 5 discusses the synthesis of hybridized core-shell-structured metal-nitride nanowires with a 3D carbon substrate and its performance for supercapacitor. Last but not least, Chapter 6 describe the doping on conducting polymer (polypyrrole) with graphene quantum dots via electropolymerization.

1.4 References

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Chapter 2

Literature Review

2.1 Electrical energy storage systems (EESS)

Electrical energy storage systems operate by converting generated electrical energy into a storable form. The deposited energy can then be re-converted back into electricity when necessary — regardless of energy demand, generation cost or generation means. ^[1-6] Electrical energy storage systems can be applied in various sectors. Other than handheld devices and green vehicles, with their intermittent and recurring nature, electrical energy storage systems can connect electricity and demands, especially for energy harnessed from sustainable and green sources such as wind, geothermal and solar power. By using electrical energy storage systems in conventional power plants, power efficiency, reliability and security can be improved while simultaneously reducing greenhouse gas and air pollutants emission. ^[1-7] Economically-wise, cheap and consistent energy is crucial. This could be achieved with electrical energy storage systems which offer full-fledged means to enhance steadiness and reliability of grid. ^[8]

2.1.1 Background

Utility companies realized that supply electrical energy storage systems would be beneficial for power network since power stations often need to shut down during nighttime in early 20th century, and turn to lead-acid accumulators for direct current network supply. ^[2-4] With this, pumped hydroelectric storage, which

is now widely applied — up to 99% of global storage capacity, was introduced in 1929. ^[2,8,9] In recent years, interest in investing pumped hydroelectric storage has dropped as global regulatory environment has changed, tougher environmental regulations has been implemented. The drop can also be attributed to the growing usage of renewable energy sources as the major electricity source. ^[3-6] With the mentioned difficulties and current advancement in developing new electrical storage systems, practical usage of emerging storage systems now show great potential. ^[6]

2.1.2 Significance of EESS

In electricity generating industries, storage facilities are rare as the rural power plants transport electricity directly to consumers via the transmission and distribution network. As electricity generated by the plant must be used exactly so, wastage occur as demands for electricity changes with usage time and season. Hence, plants are usually oversized to meet maximum demands, render them to be inefficient and costly. However, if there exist access to large scale EESS, plants can be designed to fulfil only average electrical demand, making the plant more environmental friendly and efficient in energy generation [6, 10]. On the other hand, EESS also plays an vital part in the application of sustainable and eco-friendly distributed energy resource systems (DER). As DER has smaller capacity and higher occurrence of line fault, sudden voltage drops and drastic load changes could occur and this can be compensated by EESS which can deliver continuous power supply when sudden voltage drop occurs [6]. Furthermore, EESS is crucial for its role in harnessing electricity from renewable energy sources. Electricity generating

systems that built on these sources are fundamentally intermittent and uncontrollable. By storing excess electricity generated when demand is low and allowing it to be used when demand is higher, EESS can help renewable energy supply systems to overcome its intermittency and allow it to be used extensively [6].

2.1.3 Classification of EESS

EESS can be categorized based on their function and the form used to store electrical energy [6].

In sorting according to functions, EESS are basically divided into 1) those that intended for power quality and reliability and 2) those intended for energy management. Capacitor, supercapacitor, flywheel and batteries are among EESS designed for high power rankings but comparatively smaller energy content while pumped hydroelectric storage, fuel cell, solar cell etc. are for managing energy [6].

Based on the form that is used to store electricity, EESS can be classified into four major categories, namely electrical, mechanical, chemical and thermal. Electrical energy storage is represented by two types of energy storage, electrostatic storage (eg. supercapacitors) and magnetic storage (eg. superconducting magnetic energy storage). On the other hand, mechanical energy storage included potential energy storage like pumped hydroelectric storage system and kinetic energy storage system such as flywheels. There are three kinds of chemical energy storage, namely electrochemical storage (eg. batteries including lithium ion and nickel metal hydride), chemical storage (eg. fuel cells) and thermochemical energy storage (eg. solar metal). Lastly, thermal energy storage could be further categorized into low temperature storage (E.g. cryogenic energy storage system) and high temperature

storage, represented by heat systems. A schematic representative of organization of electrical energy storage systems is shown in Figure 2.1.

Figure 2.1 *Classification of electrical energy storage systems*

In this disseratation, we will focus on two types of electrochemical energy storage systems, specifically lithium ion batteries (LIB) and supercapacitors.

2.2 Lithium Ion Batteries (LIB)

2.2.1 Introduction to batteries

Batteries are devices that are used to directly power various applications owing to its capability to convert chemical energy to electricity. From studies of electricity to development of telegraph, telephone and electric cars today, batteries play a vital role in electrical advances today for their part as the major source of electricity before the electric generator and electric grid.

The term “battery” can trace its source from the military and was originally used to describe a group of weaponries that operates together. It was first used by Benjamin Franklin in 1748 to describe a connected set of Leyden Jars. [11] In 1836, when the first industry standard battery, the Daniell cell, was invented by John Frederic Daniell, which was later used to power the electrical telegraph

Today, there are basically two classes of batteries, which are namely primary batteries and secondary batteries. Primary batteries are capable of powering devices as soon as produced. Yet, their active components could be used up during discharge and hence making them non-rechargeable. Occasionally, in certain applications such as the telegraphic network, the timeworn electrodes in primary batteries can be changed to restore the battery power.[12,13] Secondary batteries also known as rechargeable batteries, on the other hand, can power devices by discharging and then be recharged to approximately initial state with an external power source.[12] Even though the recharge-ability is not infinite as a result of

active materials loss, electrolyte loss and internal deterioration, secondary batteries remain as a good system for electricity storage.[6, 12]

Rechargeable batteries which is the oldest form of electricity storage must first be charged before use, usually have lower storage capability when compared to its primary counterparts. The extra storage necessities for rechargeability and long process restrict the choice of the chemical systems. [12-15] Examples of rechargeable batteries include lead acid batteries, NiCd batteries, NaS batteries, NANI batteries and Li ion batteries (LIB) [16]

A typical make up of rechargeable batteries consist of the following 4 parts. As illustrated in figure 2.1: (1)The anode, which is also termed as negative electrode provides the electrons; then thru the electrochemical reaction, the anode undergo oxidation. (2) The cathode, which is also termed as positive, is the opposite of anode. It accepts electrons and undergo reduction when the reaction occur. (3) The electrolyte function as the medium for electron movement between the positive and the negative electrodes. (4) Lastly, the separators is placed in between the two for electrical insulation purpose.

Figure 2.2 Chargeable cell/battery diagram. Reproduced with permission from [16], Copyright 2009, Elsevier

2.2.2 Background of Lithium Ion batteries (LIB)

Accountable to more than half transportable devices market, LIB , were first anticipated in the 1970s by M.S Whittingham. [17] It became real when Bell Labs established a functional graphite anode to replace lithium metal. In the next decades, scientists strived to examine the mechanism and to develop the positive and negative electrode materials as well as the electrolytes for Li-ion batteries. [18-21] It was until 1991 when Sony and Asahi Kasei introduced the first commercial LIB. Since then, material developments and enhancement have brought forward developments in terms of energy density (75 to 200Wh.kg) and cycle life (10000 cycles). [6]

LIB is founded on using Li ion-intercalation compound. The ions travel via the electrolyte situated in between the positive and negative electrode, as shown in previous chapter, Figure 1.2. LIBs surpass other available batteries such as NiCd, and Lead acid by providing high specific power. The success of LIB can be credited to Li low molecular weight as well as its ionic size which is small enough to benefit the diffusion. High-output voltages and energy density is enabled by its relatively low redox potentia. Its excellent rate capability and extended cycle life has also contributed to its success whether in portable electronics market , power tools equipment or the next generation of HEVs or plug in hybrids (pHEVS), as long as the enhancement can be achieved without disregarding long term stability, price and safety. [22]

2.2.3 Challenges for LIB

At present, main challenges in the progression of LIB technology includes, (1) Inadequate and lower than theoretical capacity; (2) Diminishing capacity with cycling rate; (3) Insufficient power density for proposed usage. (4) Low energy efficiency due to huge losses during charge/discharge, especially when the cycling rates is high. (5) it has limited cycling lifetime (capacity fading)

As many electrode materials such as LiFePO_4 [23] have insufficient electronic conductivity, highly conductive particles like carbon black are often used to enhance conductivity. Binder like Polyvinylidene fluoride (PVDF) are mixed with the active materials and conductive particles and pressed onto current collector foil or foam. For effective usage of active electrode materials, for exmaple, carbon and active materials must be in close contact, and simultaneously maintain connection to the metal substrate for efficient electron collection during cycling.

Unfavorable changes in electrode microstructure during cycling would worsen the performance as it would be harder to connect between electrode materials and this in turn would cause diminishing capacity that is due to active electrode materials electrical isolation.

Generally, existing LIB performance is restricted by the weakening in microstructure caused by the expanding or contracting of volume, transforming of material phase, changes in the morphology of the electrode active materials throughout cycling.

Considerable changes in the sizes, distribution, forms, and connectivity during cycling can cause unwanted rearrangement or separation of phases. This would result in the active materials encountering electrical isolation and subsequently causes capacity diminishing. It can also cause diminishing connectivity between active material and hence lead to higher current assembly and charge transfer resistance. Other than that, it leads to falling electro-active reactants transportation to the active sites. This in turn creates higher resistance during mass transfer and turn causing the charge/discharge rate to reduce.. As an example, lithium dendrite which forms during charging (morphology change) can lead to fractional short of the anode and cathode. This will eventually result in disastrous battery operation failure.

Volume changes caused by lithium intercalation may result in strain and stress build up in the electrodes. This stress and strain will eventually cause the active electrode material to pulverize or the electrode to disintegrate mechanically. This would subsequently make the attainable capacity and operating rates during

cycling gradual diminish. This is because more active materials is electrically isolated from current collectors, carbon particles are less connected, and the transferring electro-active species to/from active sites is hindered due to increased resistance. This change in volume is unavoidable during charge/discharge cycling. This is especially so for alloying compound with Li. As an illustration, $\text{Li}_{4.4}\text{Si}$ is approximately four times larger in molar volume when compare to Si. During the Li ion interaction in and from Si, large recurring volume change occur which inevitably damages the electrodes, and hence caused poor performance and capacity that is lower than theoretical value.[24]

Besides changes in morphology, size, and microstructure during cycling, the phase transformation (changes in crystal structure) may also occur. New phases with poor electronic or ionic conductivity forms. This then causes the feasibility for Li^+ intercalation degrade and make it harder to retain capacity. As an instance, LiMn_2O_4 at high cycling rate would have its phase deviates from the better performed cubic structure to the diminished capacity tetragonal structure. This structural phase change may be inherent to a certain structure under particular circumstances. Nanostructures effectively improve the phase transformation kinetics and hence help in lessening unwanted performance. For example, more shallow transformation in structure was observed when LiMn_2O_4 nanowires (ultrathin/ dia. $<10\text{ nm}$) were used as positive electrode. This phenomena is observed with good capacity retention and high reversibility [25].

Other than the above, in battery system like Li/S, there may be insulating reaction byproducts covering the surface of active electrode. This would then block

electro-active species transportation to the active sites which in turn decrease the total activity on the coated surface [26]

2.2.4 Nanostructures advantages in LIB enhancement

From bulk materials to nano-sized particles, it enabled the electrode responses that is impossible for micrometer-sized particles.[27] The reduced size greatly enhances (1) the Li intercalation rate as now shorter distance is involved and (2)the electron transport within the particles. [28] With higher surface area, there is a higher contact area for electrode and the electrolyte. This in turn allow higher Li-ion flux across the interface of electrode/electrolyte. By modifying the chemical potentials for Li ions and electrons of extremely small particles, it can result in an alteration of electrode potential hence thus affect the reaction thermodynamics.. [29] For nanoparticles, the composition range for solid solutions existence is more widespread, [30] and hence allowing better tolerance to the strain associated with intercalation. However, nanostructures also has its cons [31] as it is harder to synthesize and control the size of nanoparticles. It higher surface area with the electrolyte can contribute to additional unwanted by-reactions. Also it would be harder to maintain the contact between particles. Comparing to its micrometer-sized counterparts synthesized from same materials, nanosized materials in general has a lower density. Hence to use the same mass of material, the volume would have to be increased, this in turn results in volumetric energy density reduction. [31]

2.2.5 Methods to improve anode performance

In order to minimize recurring capacity fading and irreversible first cycle capacity of anodes based on alloy, various methods are developed to deal with the harmful effects of the and to ease the by-reaction.

One of it is to dispersing active materials within a composite matrix in order to be used for cushioning the huge changes in active particles volume. With this, we can maintain the electrode structures and the electronic connectivity between the conductive phase and active materials [32, 33]. To uphold the stability of the microstructures in the negative electrode, the matrix which function as a host must be capable of rapid electron and Li ions transfer. [34] the matrix which function as a host also acts as a buffer zone during cycling in order to prevent the active particles from aggregating. [34,35] Depends on the host phase type, the composite negative electrode include (a) inactive type which is made up of electrochemically inert and active particles [36-39], (b) active type with lithiation reactive matrix[40-42], (c) Carbon composite matrix with improved conductivity carbon-matrix composite [43-46] and (d) 3D porous structures for higher tolerance of expanding volume [47-49].

2.3 Supercapacitors

2.3.1 Background of supercapacitors

Earliest patented supercapacitors can trace back to 1957. However, it was until the 1990s that supercapacitor start to garner attention for its ability to enhance the power source in hybrid vehicles [71] With acknowledgement that that supercapacitor can complement batteries in strong energy by acting as the substitute power supplies and hence prevent power interruptions., many others follow suit in supercapacitor development. [72]

Equipped with benefits like high power density, high efficiency, long shelf life, ecological friendly and wide range of operating temperatures, supercapacitor are much preferred for applications in electric or hybrid vehicles, portable consumer electronics, power supplies, and solar cell energy storage system. [71, 74-79]

Supercapacitors are basically classified into 3 families: (1) the double-layer capacitors which is made up with carbon or derivatives electrodes; (2) pseudocapacitor which is with metal oxides or conducting polymer electrode; and (3) hybrid capacitor which consists asymmetric electrodes that exhibit both double-layer capacitance and pseudocapacitance. [12]

Generic differences between double-layer capacitors and pseudocapacitor has been previously mentioned in Chapter 1.

For electrochemically inactive double-layer capacitors, which involve carbon electrode materials, no electrochemical reaction occurs during

charge/discharge. The high-power capabilities involve pure physical charge accumulation due to the fast adsorption and desorption of ion at the electrode/electrolyte interface. When charging, electrons move from negative electrode to positive electrode via external circuit. Inside the electrolyte, positive ions move towards the negative electrode and vice versa. During discharge, the process is reversed. Between the electrode and the electrolyte, there is zero charge transfers and ion transfer. [72,78]

For electrochemically active pseudocapacitor electrode materials, such as metal oxide and metal nitride, faradaic reactions occur to store charge in the bulk of the material charge/discharge. [78–81] Faradaic reactions which is fast and reversible happen on the electrode materials surface when a potential is applied. The channel of charge through the double layer subsequently result in faradaic current transfer in the supercapacitor. Conducting polymers and metal oxides, like RuO_2 , MnO_2 , and Co_3O_4 are examples of materials that can undergo this type of redox reactions [79,82-84] In conductive polymer based electrodes, faradaic processes is contributed by the reversible adsorption, metal oxides redox reactions and revocable electrochemical dope/dedope.. [79] Faradaic processes can widen the working and rise the specific capacitance of the supercapacitors and hence shows larger capacitance values and energy density than a double-layer capacitors. [85-86] However, a pseudocapacitor typically suffers from comparatively lower power density and poor cycling stability. [87]

2.3.2 Components of supercapacitors

A typical supercapacitor has a construction that is corresponding to batteries, which consist of two electrodes, a separator in between the electrode and electrolytes.

Electrode material is the most significant component of a supercapacitor. Generally, the electrodes are made-up from highly porous and high surface area nanosize materials, in order to enhance the capacitance of supercapacitor.

There are 3 types of electrolyte for supercapacitor, namely (1) aqueous electrolyte, (2) ionic liquids, and (3) organic electrolyte. Aqueous electrolytes (such as KOH, H₂SO₄) that can be easily prepared, has a lower resistance and higher concentration of ions compare to organic electrolyte. With this electrolyte, supercapacitor may exhibit higher capacitance and higher power. However, aqueous one has a relatively small voltage window (1.2 V), hence restrict energy and power densities. Organic electrolytes are often recommended for its high voltage window (~3.5 V). However, it has a weak point of stringent preparation condition, where water content must be kept below 3–5 ppm. [71] Solvent free Ionic liquids is basically molten salt. It has low vapor pressure, high thermal and chemical stability, widespread electrochemical stability window (2 to 6 V) and high conductivity. The challenge of this type of electrolyte is to have a wider potential range combined with high conductivity in a extensive temperature range. [88-90]

2.3.3 Challenges for supercapacitors application

One of the challenges faced by supercapacitor is its low energy density (about 5 W h kg⁻¹) when compared with batteries (>50 W h kg⁻¹). When large

energy capacity is required, a larger supercapacitor should be constructed which in turn rising production cost. Other than that, supercapacitors have a low duration and a high self-discharging rate of 10–40% per day. In some applications, this has been considered a major obstacle to their practical use. [91] Industrial standards for commercialization also exists as a hurdle for supercapacitor applications. Currently, carbon/carbon supercapacitor with capacitance of 50–5000 F have become commercially available, the electrolyte used in such kind of supercapacitor is acetonitrile, which can give a cell voltage of 2.7 V with a typical specific energy of 4 W h kg⁻¹. This performance was achieved when charging the device at 400 W kg⁻¹ from 100% to 50% of the rated voltage. Although this kind of supercapacitor is commercially available, it is necessary to establish some general industrial standards such as performance, electrode structure, electrode layer thickness and porosity and so on. However, due to the variety of applications as well as limited commercial products, industrial standards are still unavailable.

2.3.4 Supercapacitor electrode materials enhancement

Ideally, supercapacitor electrode materials need to have the following criteria (1) high specific surface area (contribute to the specific capacitance), (2) controlled porosity (influences specific capacitance, rate capability), (3) high electronic conductivity, (affect rate capability, power density), (4) electroactive sites (enable pseudo-capacitance), (5) high thermal stability, (6) high chemical stability, (7) low costs of raw materials and manufacturing.

Today, most commercial available supercapacitors are made of inexpensive and corrosion resistant carbon electrodes. These supercapacitors have excellent

cyclic stability and long service lifetime since there is no electrochemical change. However, their maximum capacitance is restricted by the active electrode surface area and the pore size distribution (typically $0.15\text{--}0.4\text{ F m}^{-2}$, or $\sim 150\text{ F g}^{-1}$ for carbon). [93-94] Energy density on the other hand, is typically $3\text{--}5\text{ W h kg}^{-1}$, which is much lower than that of an for a lithium-ion battery ($10\text{--}250\text{ W h kg}^{-1}$).

In order to enhance specific capacitance and energy density, transition metal oxides that show excellent pseudo-capacitance, including RuO_2 , MnO_2 , ZnO , NiO , SnO_2 , Co_3O_4 , TiO_2 , CuO , V_2O_5 , Fe_2O_3 , WO_3 , etc are examined for the use as supercapacitor materials. The defects, functional groups, and grain boundaries serve as the excellent redox centres for the faradaic reactions. Metal oxide alone electrodes can deliver large specific capacitance and high energy density at a slow scan rate or low current density. [95-105] Practically, metal oxides are unsuitable to be use as standalone supercapacitor electrodes due to the following disadvantages. (1) High resistivity of metal oxides increases sheet resistance as well as charge transfer resistance of the electrode. This result in poor power density and rate capability; (2) Strain created during the charge/discharge processes causes the cracking of the electrode hence poor stability; (3) Hard to control pore distribution and porosity.

It is hence rational to develop a composite electrode containing both carbon and transition metal oxide as the supercapacitor electrode. This composite electrode is expected to concurrently possess high power density, high energy density, good rate capability and cyclic stability. The carbon nanostructures can function as the physical support as well as provide the channels for charge transport. The high

electronic conductivity of carbon nanostructures benefits to the rate capability and power density at a large charge/discharge current. The metal oxides are the main sources that store the charge and the energy. The electro-activities of metal oxides contribute to high specific capacitance and high energy density of the carbon nanostructure–metal oxide composite electrodes. A synergistic effect could be expected and the materials cost can be reduced. The compositional constituent, microstructure and physical properties of metal oxide–carbon composites govern the performance of the supercapacitor electrodes. The electrode porosity, electronic conductivity, pore size distribution, specific surface area affect the cell performance. Table 2.1 gives a comparison of carbon, metal oxide and metal oxide–carbon composite electrodes.

Table 2.1 Comparison of carbon, metal oxide and metal oxide–carbon composite as supercapacitor electrode. Reproduced with permission from [92], Copyright 2012, Royal Society of Chemistry

Electrode materials	Surface area	Pore size distribution	Specific capacitance	Conductivity	Rate capability	Stability	Cost
Carbon	High	Various ways to tailor	Low	High	High	Good	Low
Metal oxide	Normally low	Difficult to tailor	High	Low	Low	Poor	High
Metal oxide–carbon composite	Normally controlled by a carbon support	Various ways to tailor depending on the carbon support	High	Tunable, depending on the carbon support	Good	Good	Moderate

2.4 References

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Chapter 3

Experimental Approaches

3.1 Chemicals

All chemicals used in this dissertation were purchased from Sigma-Aldrich except for the following: potassium chloride (KCl) from Merck used. Multi-wall carbon nanotubes (MWCNTs) were obtained from NANOAMOR. The purity of the MWCNTs is >95%, with an outside diameter of 10-30 nm, while the inside diameter is 5-10 nm, with length of 5-15 μm . Vulcan CX-72 carbon black were purchased from Cabot Corporation.

All solutions were prepared using Milli-Q deionized water with a resistance of 18M Ω .cm. All chemicals were used as received.

3.2 Equipment

Field-emission scanning electron microscope (FE-SEM, JSM-6700F) was used to examine the morphology of carbon based nanocomposites synthesized. Transmission electron microscope (TEM, Tecnai G² 20) was used for high resolution transmission electron microscopy (HRTEM) to further examine the morphology and structures of nanocomposites produced.

Rigaku D/max 2400 X-ray diffractometer equipped with graphite monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$; scan rate = $0.02^\circ \cdot \text{s}^{-1}$) and Bruker D8 Avance diffractometer using Cu K α radiation were used to obtain XRD patterns to investigate the crystallographic information of the synthesized nanocomposites.

UV-visible spectrophotometer (Varian Cary 5000, USA) was used to measure the absorption spectra.

CHI-660D electrochemical workstation (Chenhua) was used for electrochemical measurement involving 3 electrode systems.

NEWARE battery tester were used for examining the electrochemical performance of lithium ion battery related material.

Fisher Scientific FS30 Ultrasonic Cleaner was used at maximum power.

3.3 Methodology

Specific experimental approaches are elaborated in details in the subsequent chapters.

Chapter 4

Interwoven network of MnO₂ nanowires and carbon nanotubes as anodes for flexible Li-ion battery

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4.1 Introduction

Developing flexible, inexpensive, lightweight, and high-performance energy storage devices for the emerging flexible optoelectronics has recently sparked tremendous interests and efforts ^[1-3]. In particular, flexible lithium-ion batteries (LIB) have been fabricated using electroactive nanomaterials and bendable current collectors ^[1-3]. However, the practical use of these flexible LIBs is limited by the non-trivial fabrication process, high cost, low capacity, cycling stability, and poor mechanical stability.

Manganese dioxide (MnO₂) is a low-cost earth-abundant material which has been extensively researched as cathode material for LIBs ^[4-6]. Recently, it has attracted considerable attention as anode material because of its high reversible capacity ^[7-10]. But, like other transition metal oxides, MnO₂ suffers from fast capacity loss and poor rate performance due to its poor electrical conductivity and

the large structural changes induced by intercalation and de-intercalation of lithium ions. ^[11,12]

At present, graphite and coke are commonly used as the LIB-anode materials for their low cost and low operation voltages. ^[10] The capacity of these bulk carbonaceous materials, however, is limited. Therefore, nanostructured carbon materials (graphene or carbon nanotubes) and electroactive metal oxides (including MnO₂) have been synergistically hybridized in order to attain high capacity, high conductivity, and less vulnerability to structural collapse ^[13-17]. For example, LIB anodes based on MnO₂ nanoflakes have been demonstrated ^[18]. However, these electrodes exhibit poor capacity or cycling stability.

We herein report a facile one-pot synthesis of interwoven network of MnO₂ nanowires and multi-walled carbon nanotubes (MWCNTs). We further demonstrate a bendable LIB equipped with such thin-film hybrid anode with improved capacity (891 mAh g⁻¹ at 100 mA g⁻¹) and cycling stability (88% capacity retention after 60 cycles

4.2 Experimental section

4.2.1 Preparation of manganese oxide (MnO₂) ultralong nanowires

A 10 mL mixture of 0.2 mmol of KMnO₄ and 0.2 mmol of NH₄Cl was prepared and sonicated for 1 h. Then, the mixture was transferred to a 25 mL Teflon-lined stainless steel autoclave and maintained 150 °C for 24 h. The resulting dark brown solids were then centrifuged, collected and dried at 50°C in vacuum oven.

4.2.2 Preparation of MnO₂-MWCNT composite

MWCNTs were obtained from NANOAMOR. They were sonicated in distilled water for 1 h, collected by centrifugation and then dried at 50 °C overnight. The purity of the MWCNTs is >95%, with an outside diameter of 10-30 nm, while the inside diameter is 5-10 nm, with length of 5-15 μ m.

MnO₂-MWCNT nanocomposites were synthesized by first mixing 25 mg of MWCNTs with 0.2 mmol of KMnO₄ and 0.2 mmol of NH₄Cl. The 10 mL mixture was then subjected to 1 hour sonication at room temperature. Then, the mixture was transferred into a 25 mL Teflon-lined stainless steel autoclave and maintained 150 °C for 24 h. The resulting black solids are then centrifuged for collection and then dried at 50°C in vacuum oven.

4.2.3 Characterization

The morphologies of the products were investigated using field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). High resolution transmission electron microscopy (HRTEM) was performed using Tecnai G² 20 instrument. X-ray diffraction (XRD) was performed with Bruker D8 Avance diffractometer using Cu K α radiation to investigate the crystallographic information of the products.

4.2.4 Electrochemical measurement

To fabricate the working electrode, a mixture comprising 80 wt% active material, 15 wt% conducting carbon black (Vulcan XC-72), and 5 wt% an organic binder (poly(vinylidene difluoride)) was prepared to form a slurry. The slurry was then pasted onto Cu foil and dried in vacuum oven overnight. Next, the coin cells were assembled in argon-filled glovebox. Moisture and oxygen contents are kept below 1 ppm. 1 M LiPF₆ in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. The cyclic voltammetry (CV) and galvanostatic charge-discharge properties were tested using a NEWARE battery tester. The electrochemical tests were performed between 0.1-3.0 V.

For bendable full battery assembly, LiFePO₄ coated on aluminium foil was used as a cathode. 1 M LiPF₆ in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate was used as the electrolyte. The anode was prepared by making a slurry comprising 80 wt% active material, 10 wt% super-P carbon, and 10 wt% PVDF

and coating the slurry onto flexible copper foil current collector. The electrolyte was injected in an argon filled glove box after the negative electrode, polymer separator and positive electrode were stacked together to make the battery core. The electrochemical tests were performed between 0.1-2.5 V using a NEWARE battery tester.

4.3 Results and Discussion

4.3.1 Proposed synthesis route

Figure 4.1 Schematic illustration of the synthesis route

The synthetic route is schematically illustrated in Figure 4.1. Multi-walled carbon nanotubes (MWCNTs) were firstly dispersed in the mixed solution of potassium permanganate (KMnO_4 , 0.2 mM) and ammonium chloride (NH_4Cl , 0.2 mM), with assistance of sonication (1 h). As a strong oxidizing agent, KMnO_4 is able to induce oxygenated groups onto MWCNTs which facilitate MWCNT dispersion and can serve as the nucleation sites for growth of MnO_2 . As previously reported ^[19,20], sonication of KMnO_4 solution can lead to formation of manganese oxides nanocrystals. In the subsequent hydrothermal condition (150 °C for 24 h), the sonochemically formed MnO_2 nanocrystalline seeds on the defect sites of MWCNTs grow into ultralong MnO_2 nanowires interweaving with MWCNTs. The percentage of the MWCNT in the resulting nanocomposite is estimated to be 60 wt%.

4.3.2 Material characterization

Figure 4.2. (a) XRD pattern of MnO₂-MWCNT nanocomposite (b-d) SEM images of MnO₂ nanowires, MWCNTs, and MnO₂-MWCNT nanocomposite respectively. Scale bars = 1 μm. Insets are the zoom-in image at a higher magnification with scale bar = 300 nm.

The X-ray diffraction (XRD) pattern as shown in Figure 4.2a exhibits several distinct peaks corresponding to the (110), (200), (310) and (411) planes in the standard alpha MnO₂ spectrum (JCPDS44-0141), confirming the successful integration of MnO₂ and MWCNT. The additional peaks at 26° and 54° can be

attributed to the (002) and (004) reflections of graphitic carbon (JCPDS 75-1621) from the MWCNTs.

The same hydrothermal process without MWCNTs produces straight ultralong MnO_2 nanowires (~ 70 nm in diameter and >10 μm in length) which can be observed in Figure 4.2b. In contrast, MWCNTs are curled with diameter of ~ 20 nm and length of 5-15 μm (manufacturer's specifications, also see Figure 4.2c. Hydrothermal synthesis with MWCNTs serving as the growth seeds, in comparison, yields an interwoven network of MnO_2 and MWCNTs (Figure 4.2d).

Figure 4.3 (a) TEM image of MnO_2 -MWCNT nanocomposite with scale bar = 100 nm. (b-c) HRTEM image of MWCNTs and MnO_2 nanowires in the nanocomposite. Scale bar = 10 nm..

TEM image of the nanocomposites further confirms the interwoven structure of the MnO_2 nanowires and the hollow MWCNTs in Figure 4.3a. The

distance between neighbouring fringes of MWCNT (Figure 4.3b) is measured to be ~ 0.35 nm, which is slightly larger than that of graphite (0.335nm) as the high curvature and strain results in higher inter-planar spacing.^[21] The inter-planar spacing of MnO₂ nanowires in the nanocomposite is ~ 0.31 nm, which corresponds to the (310) lattice planes of α -MnO₂ crystal.

4.3.3 Electrochemical performance of coin cell assembly

Figure 4.4 Electrochemical performance in 1M LiPF₆ electrolyte in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate. (a,b) MnO₂ ultralong nanowires /CNTs nanocomposites (c,d) MnO₂ ultralong nanowires ; (e) Capacity vs. cycle number curves of MnO₂/CNT nanocomposite electrode and the MnO₂ composite electrode at various current density. (f) Nyquist plots of MnO₂/CNT nanocomposite electrode and the MnO₂ composite electrode.

Both MnO₂-MWCNT nanocomposite and pure MnO₂ nanowires are used as the anode material for lithium ion battery, and tested firstly in a coin-cell assembly. Comparing to the MnO₂ electrode (Figure 4.4a), the two oxidation peaks (at 1.2 and 2.4 V) in the cyclic voltammogram of MnO₂-MWCNT electrode (Figure 4.4c) are more prominent, indicating improved electrochemical kinetics. The four reduction peaks (at 0.1, 0.55, 1.2 and 1.7 V) corresponding to four consecutive Li⁺ intercalations disappear after the first cycle. This is attributable to the formation of solid electrolyte interface (SEI) and formation of metal from metal oxide during the electrolyte decomposition ($\text{MnO}_2 + 4\text{Li}^+ + 4\text{e}^- \rightleftharpoons 2\text{Li}_2\text{O} + \text{Mn}$) [22,23]. Similar to the previous report [18], both MnO₂ and MnO₂-MWCNT electrodes show a voltage plateau (between 0.4 – 0.5 V) during discharge process and two voltage plateaus (at ~1.2 and 2.4 V) during the charge process (Figure 4.4c and d). These plateaus are resulted from the redox reactions during Li⁺ insertion and extraction. It is noteworthy that the second (stabilized) discharge capacity of the MnO₂-MWCNT nanocomposite (891 mAh g⁻¹) is much higher than that of pure MnO₂ (530 mAh g⁻¹). This value is not too far from the theoretical limit (1230 mAh g⁻¹) [22] Figure 4.4e further demonstrates that the MnO₂-MWCNT electrode exhibits not only significantly higher capacity but also much improved cycling stability as compared to the MnO₂ electrode (88% capacity retention after 60 cycles vs. 38% retention after 50 cycles). The synergistic integration between MnO₂ nanowires and MWCNTs can be attributed, at least in part, to the fact that the MWCNT network interwoven with MnO₂ nanowires facilitates rapid charge transfer. Indeed, as shown by electrochemical impedance spectroscopy (EIS) measurements (Figure 4.4f), the

charge transfer resistance of the composite electrode is much smaller than that of the MnO₂ electrode (~ 35 vs. $\sim 58 \Omega$).

4.3.4 Electrochemical performance two-electrode full battery

Figure 4.5 (a) Assembly of bendable full battery. (b-d) Electrochemical performance of the full battery in 1M LiPF₆ electrolyte in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate. (b) Charge-discharge capacity at 100 mA g⁻¹; (c) Cyclic performance at different current densities. (d) Coloumbic efficiency at different current densities

A two-electrode full battery using a MnO₂-MWCNT or MWCNT anode was assembled as shown in Figure 4.5a. The cathode is a LiFePO₄ coated aluminium electrode which has a theoretical capacity of 170 mAh g⁻¹ (lower than that of MnO₂-MWCNT). Since such battery is cathode-limited, the current density of the battery is calculated based on the mass of LiFePO₄.

Figure 4.5b shows the charge-discharge cycles at a current density of 100 mA g⁻¹ and between 0.01 to 2.5 V. The initial (1st cycle) irreversible discharge capacity of the MnO₂-MWCNT anode is 875 mAh g⁻¹ and the subsequent reversible discharge capacity is stable. 40% of this discharge capacity can be attributed to the 60 wt% MWCNTs in the porous interwoven network (Figure 4.6). Figure 4.5c shows the cycling performance of the battery (0.01 to 2.5 V) at different current densities. As shown, the battery can retain a capacity as high as 928 mAh g⁻¹ (at 50 mA/g) after 50 charge-discharge cycles, approximately 80 % of the initial capacity. Coulombic efficiency during the cycling sustains at 95-97% (Figure 4.5d).

Figure 4.6 Charge discharge capacity in 1M LiPF₆ electrolyte in a 50:50 w/w mixture of ethylene carbonate and diethyl carbonate. (a) MnO₂-MWCNT anode
(b) MWCNT anode

Figure 4.7 (a) Discharge capacity at 50mA/g with different bending angle. Insets show bending at different bending angles. (b) Stability after bending at 90 degrees. Insets show 1 bending cycle and a lit red LED

We further demonstrate the bending of the battery to a large angle only causes a small loss in capacity (Figure 4.7a) and the bended battery exhibits stable cycling capacity (Figure 4.8). The battery after 100 cycles of bending still essentially retains its capacity (80.3%) and is able to lighten up a red LED (Fig. 4.7b).

Figure 4.8 Cyclic performance at different bending angle.

4.4 Conclusion

In summary, we successfully synthesize a porous interwoven network of MnO₂ ultralong nanowires and MWCNTs. In comparison to the poorly conductive MnO₂, the nanocomposite demonstrates superior capacity and cycling stability. The synergistic integration of the two materials can attributed to the highly conductive network provided by MWCNTs; 2) the interconnected porous structure that allows free Li⁺ ion transport and tolerance to the volume change caused by Li⁺ intercalation. In addition, the excellent flexibility and strength of MWCNT network renders the bendability of the nanocomposite electrode. The full battery equipped with such electrode offers high capacity, stability, bendability and low-cost.

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Chapter 5

TiN@VN nanowire arrays on 3D carbon for high-performance supercapacitors

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5.1 Introduction

Supercapacitors are energy storage devices offering high power density and low cost.^[1-5] Their performance critically relies on the choices of 1) active materials that ideally should exhibit high and stable electrochemical activities (thus pseudo-capacitance) and high conductivity to ensure low charge transfer impedance, and 2) electrode structures that ideally should be highly conductive for efficient charge transport and large surface area to achieve high power density.

As compared to the commonly used metal oxides, metal nitrides are the emerging active materials for high-performance supercapacitors because of their both high pseudo-capacitance and superior electrical conductivity.^[6-17] Among them, titanium nitride (TiN) and vanadium nitride (VN) has attracted considerable attention.^[18-21] However, the capacitance of these metal nitrides declines quickly in alkaline electrolyte solution due to their ineluctable transformation to oxides (TiO₂

or vanadium oxide (VO)) which is much less conductive and capacitive. To improve the poor cycling stability of TiN, solid-state electrolyte was used to prevent the oxidation of TiN, however, with sacrifice in performance as compared with liquid electrolyte.^[22]

Recently, graphene foam has been used as three-dimensional (3D) electrodes for supercapacitors.^[23,24] Such 3D carbon scaffold provides large surface area for abundant loading of active materials whereby enhancing the specific capacitance. Comparing to the conventional 2D electrodes, 3D architecture is obviously able to offer much larger areal or volume power density.^[25-39] But graphene foam is fragile and grown by costly chemical vapor deposition (CVD). In addition, its macroporous (>100 μm) structure is occupied by much void spaces which is undesirable for achieving high power density.

Herein, we hybridized core-shell-structured metal-nitride (TiN@VN) nanowires with a 3D carbon substrate. This hybrid electrode demonstrates high volumetric capacitance and good cycling stability. The high capacitance is attributed to the exceptional electrochemical properties of TiN and VN, as well as the vast surface area and conductive network provided by the microporous 3D carbon structure. The improved stability is resulted from preventing transformation of TiN into poorly conductive TiO_2 by the thin shell of vanadium nitride (VN).

5.2 Experimental sections

5.2.1 Preparation of conductive 3D carbon

The cotton was sunk in 5 mg/ml graphene oxide (GO) solution for 3 hours. The cotton fibers coated by GO were dried in vacuum oven at 80 °C for 12 hours and repeated 5 times. Then the pretreated cotton was heated in tube oven in the argon at 1000 °C for 1 hour.

5.2.2 Preparation of nanowires array of TiO₂ growth on the 3D carbon (3D carbon @TiO₂)

Nanowires array of TiO₂ was grown on the 3D carbon substrate as literature previously reported.^[1] For example, the 3D carbon substrate was immersed into the 0.2 M titanium isopropoxide of HCl solution and sealed in the autoclave and heated at 150 °C for 20 h. The product was washed completely with DI water and dried in vacuum oven at 80 °C for 12 hours.

5.2.3 Coating an ultrathin layer of vanadium oxide (VO)

3D carbon@TiO₂ was placed in the 12 mM vanadium isopropoxide/isopropanol alcohol solution and sealed in the autoclave and heated at 180 °C for 12 hours. The product was dried in the 80 °C for 12 hours.

5.2.4 Converting TiO₂@VO to TiN@VN

3D carbon@TiO₂@VO was finally converted to 3D carbon@TiN@VN by annealing in tube oven with NH₃ flow at 850 °C for 3 h.

5.2.5 Characterization

The morphology of the samples was examined by field-emission scanning electron microscope (FE-SEM, JSM-6700F) and transmission electron microscope (TEM, Tecnai G² 20). The XRD patterns were obtained using Rigaku D/max 2400 X-ray diffractometer equipped with graphite monochromatized Cu K α radiation (λ = 1.5406 Å; scan rate = 0.02 °·s⁻¹). Using a CHI-660D electrochemical workstation (Chenhua), the electrochemical measurements were carried out in a three-electrode system with 1.0 M KOH as the electrolyte solution.

5.3 Results and Discussion

5.3.1 Fabrication process

Figure 5.1. Fabrication of 3D carbon@TiN@VN electrode. The scale bars = 0.5 cm

The fabrication process is illustrated in Figure 5.1. Firstly, the commercially available cotton pad was dip-coated with graphene oxide (GO) solution (5 mg mL^{-1}), followed by annealing at 1000°C in the argon atmosphere in order to reduce GO and carbonize the cotton. The resulting carbon structure exhibits a high conductivity ($\sim 47 \text{ ohms cm}^{-2}$) and highly resistant to acid or alkali conditions.

5.3.2 Material characterization

Figure 5.2 SEM images of 3D carbon substrate (a), TiO_2 nanowires on 3D carbon (b and c), TiN@VN nanowires on 3D carbon (d). XRD pattern of 3D carbon @ TiN@VN (e)

As revealed by scanning electron microscopy (SEM), the 3D carbon is interwoven of carbon nanofibers and microporous (Figure 5.2a). TiO_2 nanowires (~ 100 nm in diameter, ~ 2 μm in length) array (NA) were then densely grown on the carbon substrate (Figure 5.2b and c) through a hydrothermal method reported elsewhere.^[22] Subsequently, an ultrathin layer (a few nm) of vanadium oxide (VO) was coated conformally around individual TiO_2 nanowires using another hydrothermal procedure (Figure 5.2d and 5.3a).^[40] Finally, annealing in ammonia atmosphere at 850 $^{\circ}\text{C}$ for 3 h converted $\text{TiO}_2\text{@VO}$ to TiN@VN nanowire arrays. All the Bragg peaks in X-ray diffraction (XRD) pattern of the annealed sample can

be unambiguously indexed to TiN (JCPDS No.38-1420) and VN phase (JCPDS No.35-0768) (Figure 5.2e).

Figure 5.3 TEM images of TiN@VN nanowire (a and b). Elemental mapping of Ti (c) and V (d) elements on the TiN@VN nanowire.

The high-resolution transmission electron microscopy TEM (HRTEM) reveals the perfect crystalline structure of the outer VN shell with an interplanar distance of ~ 0.235 nm corresponding to the (111) plane of VN (Figure 5.3b). The boundary between core-shell and the different crystalline orientation of TiN are clearly visible. The hybridized core-shell structure (TiN nanowire homogenously coated with an ultrathin VN shell) was further confirmed by elemental mapping of Ti and V (Figure 5.3c and d).

5.3.3 Electrochemical performance

Figure 5.4 (a) CVs of 3D carbon@TiN@VN electrode at various scan rates. (b) Charge-discharge curves of 3D carbon@TiN@VN at different current densities. (c) Comparison of charge-discharge curves from TiO_2 , TiN or TiN@VN nanowires on 3D carbon at 1 mA cm^{-2} . (d) The cycling stability of the volumetric specific capacitance of 3D carbon@TiN@VN and 3D carbon@TiN at 5 mA cm^{-2} .

Cyclic voltammograms (CV) between 0.2 V and -0.6 V of the 3D carbon@TiN@VN electrode was measured in a three electrode system at various scan rates in 1 M KOH electrolyte (Figure 5.4a). One pair of redox peaks can be clearly resolved at -0.1 V and -0.22 V, respectively, which correspond to the transformation between the II, III and IV ionization states of vanadium.^[41,42] From the charge-discharge voltage profile (Figure 5.4b), the volumetric specific

capacitance (C_s) is calculated according to the equation $C_s = (I \times \Delta t) / (V \times \Delta V)$, where I is the constant discharge current, Δt is the discharge time, V is the volume of the electrode, ΔV is the voltage difference between the voltage after ohmic drop at the beginning of discharging and the voltage at the end of discharging.^[43]

The specific capacitance of 3D carbon@TiN@VN electrode is found to be as high as $\sim 0.64 \text{ F cm}^{-2}$ (corresponding to volumetric C_s of $\sim 6 \text{ F cm}^{-3}$) at the current density of 1 mA cm^{-2} . The mass capacitance is $\sim 198.3 \text{ F g}^{-1}$ at a current density of 5 A g^{-1} . Even at a high current density of 10 mA cm^{-2} , the C_s still reaches 0.52 F cm^{-2} , suggesting the feasibility for fast charging/discharging.

In comparison, the C_s values of 3D carbon@TiN and 3D carbon@TiO₂ electrodes are largely reduced (0.58 F cm^{-2} and 0.35 F cm^{-2} , respectively) (Figure 5.4c).

The cycling stability of 3D carbon@TiN@VN electrode was examined by chronopotentiometry at a current density of 5 mA cm^{-2} . As shown in Figure 5.4d, C_s largely retains even after 4000 cycles. The decay of C_s demonstrates two phases: $<5\%$ capacitance loss after the first ~ 2000 cycles; a steeper loss ($\sim 14\%$) in the second phase. In remarkable contrast, the C_s of 3D carbon@TiN electrode degenerates rapidly during cycling, similar to the previous observation.^[22]

Figure 5.5 *Ti 2p core-level XPS spectra of the 3D carbon@TiN before (a) and after (b) 2000 cycles. Black line, red line and blue line are the experimental data, fitted curve and baseline in both (a) and (b), respectively. Others are fitted Gaussian peaks corresponding to the valence states of titanium.*

As revealed by X-ray photoelectron spectroscopy (XPS) before and after 2000 cycles, such drastic decay is accompanied by the conversion of TiN to TiO₂ (Figure 5.5). XPS snapshots of 3D carbon@TiN@VN electrode at different cycle numbers show that the VN thin-layer evolves essentially to VO after 1000 cycles as evidenced by the right-shift of the V 2p³ peak (Figure 5.6).^[44,45]

On the other hand, Ti-N peak remains essentially unaltered in the first 2000 cycles while it completely converts to Ti-O peak after 4000 cycles (Figure 5.7). Consistently, after 4000 cycles, the N 1s peak in XPS spectrum disappears, indicating the complete conversion from nitrides to oxides (Figure 5.8).

Figure 5.6 V 2p core-level XPS spectra of 3D carbon@TiN@VN at different cycles. Black line, red line and blue line are the experimental data, fitted curve and baseline in both (a), (b) and (c), respectively. Other lines are fitted Gaussian peaks corresponding to the valence states of vanadium.

Figure 5.7 Ti 2p core-level XPS spectra of 3D carbon@TiN@VN at different cycles (before, 1000, 2000 and 4000 respectively) . Black line, red line and blue line are the experimental data, fitted curve and baseline in all figures, respectively. Other lines are fitted Gaussian peaks corresponding to the valence states of titanium.

Figure 5.8 N 1s core-level spectra of 3D carbon@TiN@VN sample before (a) and after (b) 4000 cycles.

Figure 5.9 Nyquist plots for 3D carbon@TiN@VN nanowire array electrode before and after 4000 cycles.

As expected, the electrode impedance greatly increases after 4000 cycles because of the poor conductivity of metal oxides (Figure 5.9). Taken together, the first phase of Cs decay of 3D carbon@TiN@VN is mainly due to transformation of VN shell to VO shell while the second phase is resulted from transformation of TiN core to TiO₂.

5.4 Conclusion

The good capacitive performance of our hybrid electrode is attributable to the synergistic integration of two types of metal nitrides. TiO_2 nanowires provide low capacitance while TiN nanowires without shell are poorly stable because of their transformation to less conductive TiO_2 . It has been previously shown that CNT@VN composites also demonstrate poor cycling stability.^[32]

Here, VN shell plays dual roles. Firstly, transition between different ionization states of the mixed-valence vanadium element offers large pseudo-capacitance; secondly, VN shell protects TiN from being oxidized. On the other hand, TiN nanowires firstly serve as the highly-conductive electron collectors, and secondly may contribute to the total capacitance given the thin thickness of VN shell. Furthermore, the microporous 3D carbon substrate provides large (active) surface area and multiplexed conduction networks.

5.5 References

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Chapter 6

Graphene Quantum Dots doped Polypyrrole Nanocomposite For Supercapacitor

6.1 Introduction

Increasing concern over fossil fuel depletion and ecological issues has made the search of renewable energy sources that are environmental friendly become essential. Supercapacitors, also known as electrochemical capacitors and ultracapacitors^[1,2], are one of these potential energy sources for their ability to offer power and energy density that are superior to batteries and conventional capacitors^[3-7].

Supercapacitors generally involved two mechanisms for energy storage, which are pseudo-capacitance and electrical double layer capacitance (EDLC)^[8-10]. (1) Pseudo-capacitance, also known as redox supercapacitance, involves fast redox reactions of the electrode surface material and the electrolyte, which allows it to have capacitance-like performance^[8,11-12]. Conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and thiophene-based conducting polymers are often used as pseudo-capacitive material^[8]. (2) On the other hand, EDLC are derived from the non-Faradaic charge accumulation in the electrical double-layer of the electrolyte/

electrode surface interface ^[8,9]. Nanostructured carbon materials such as graphene and carbon nanotubes (CNTs) are often used as EDLC materials ^[13-16].

PPy and its nanocomposites have been actively studied as a supercapacitor material for its low production cost, good conductivity, electrochemical properties despite its poor stability ^[17-25]. To garner the synergetic benefits of both pseudocapacitance and EDLC as well as for enhanced chemical stability, carbon materials such as graphite, graphene, single-walled nanotubes and multi-walled nanotubes have been used to synthesize carbon enhanced PPy nanocomposites ^[16-20].

Graphene quantum dots which are less than 100nm version of graphene sheet, are promising candidate for PPy enhancement. On the GQDs surface, there exists abundant hydroxyl (–OH), carbonyl (C=O), and carboxyl (–COO–) groups ^[26]. These functional groups cause GQDs to be highly negative charged, which can allow GQDs to interact well with positively charged PPy to form GQDs-doped PPy (PPy/GQDs). Besides that, due to its small size, GQDs is able to enhance the porosity of PPy and hence its capacitance. Herein, we proposed a novel material of PPy/GQDs that is used for supercapacitor.

6.2 Experimental

6.2.1 Materials

Pyrrole and Lithium perchlorate (LiClO_4) were purchased from Sigma-Aldrich. Potassium chloride (KCl) from Merck was used. All solutions were prepared using Milli-Q deionized water with a resistance of $18\text{M}\Omega\text{cm}$. All chemicals were used as received.

6.2.2 Material preparation

GQDs were prepared from Vulcan CX-72 carbon black (Cabot Corporation) by refluxed with concentrated nitric acid.^[26] The PPy was electrochemically deposited on the glassy carbon electrode using 0.85V in a solution of 0.1M Py and 0.07M LiClO_4 . PPy/GQDs or PPy/GO nanocomposite were deposited with the same conditions, but with 0.5mg/ml of GQDs or GO added to the deposition solution. After deposition, the electrochemical behaviours of PPy and PPy/GQDs film on glassy carbon electrodes were investigated in an electrolyte of 1M KCl. For SEM studies, PPy and PPy/GQDs films were deposited on glassy carbon and dried in vacuum at 80°C . Nanocomposites was weighed using ultra-microbalances.

6.2.3 Characterization

A three electrodes cell, with Ag/AgCl/saturated KCl electrode and platinum wire each as reference and counter electrodes, was used in all electrochemical experiments. Glassy carbon electrodes were used as working electrode. For each

use, glassy carbon electrodes was first polished to a mirror finish with 0.3 μ m alumina powder and then sonicated in deionized water to remove the residue powder. All electrochemical experiments were performed with a CHI-660B electrochemical station. The morphologies of the products were investigated using field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). All measurements were carried out at room temperature.

6.3 Results and discussion

6.3.1 Proposed mechanism

Figure 6.1 UV-vis absorption and PL emission spectra of GQDs in water solution. Inset: GQDs solution under UV light (left) and visible light (right)

Figure 6.2 Schematic representation of PPy/GQDs nanocomposite formation.

Circled in red: Proposed interactions between PPy and GQDs

GQDs with UV absorption peak at 228nm, as shown in Figure 6.1, were synthesized and used as dopant for PPy as mentioned in previous section. As suggested by Li and Qian ^[27], there are two different doping sites exist in pure PPy. The first site is at the positively charged conjugated chain whereas the second site is associated with the protonated pyrrole subunit on the PPy chain. In our design of experiment, GQDs are expected to interact with the positively charged conjugated PPy chain at first site, as shown in Figure 2. These interactions then allow GQDs to act as the nucleation sites for PPy chains to aggregate and form a highly porous film of PPy/GQDs.

6.3.2 Material characterization

SEM is performed to investigate the nature of PPy and PPy/GQDs nanocomposites (Figure 6.3). In Figure 6.3a, the pure PPy is shown to have the typical granular raspberry morphology^[28] while PPy/GQDs nanocomposite is shown to have highly microporous flower-like structures (Figure 6.3c). The particles of PPy/GQDs nanocomposite are smaller and much uniform than those of PPy (Figure 3b and d). As proposed, this surface morphology change of PPy/GQDs is due to the presence of GQDs which function as nucleation sites for the PPy chains. The presence of GQDs enhance the porosity of PPy/GQDs and hence the capacitance of the material which makes PPy/GQDs an excellent material for supercapacitor.

Figure 6.3 SEM images of PPy deposited on glassy carbon, (a) low magnification (b) high magnification; SEM imaged of PPy/GQDs (c) low magnification (d) high magnification

6.3.3 Electrochemical performance

Figure 6.4 Cyclic voltammograms behaviours of (a) PPy (b) PPy/GQDs and (c) PPy/GO

Figure 6.4 shows the cyclic voltammery results in order to characterize the capacitor performance of PPy/GQDs. The rectangular-like CV curves correspond to the ideal capacitive behavior of rapid current respond on potential reversal ^[29]. At a scan rate of 5 mV s⁻¹, PPy/GQDs nanocomposite exhibit higher capacitance that both PPy and PPy/GO. This can be explained by greater porosity of the PPy/GQDs surface morphology which offers larger surface area for charge transfers and hence rapid current respond.

Figure 6.5 Charge-discharge curve of (a) PPy and (b) PPy/GQDs

Constant current charge-discharge curves (Figure 6.5) obtained at a current density of 0.5 mA cm⁻² further prove that the capacitance of PPy/GQDs is much higher than that of pure PPy and are used to quantify the specific capacitance of the materials. Discharge capacitance is calculated by evaluating Figure 5, using eqn (1) ^[30],

$$C_m = I \times \frac{\Delta t}{\Delta V \times m} \quad (1)$$

where C_m is the specific capacitance, I is the charge/discharge current, Δt is the discharge time, ΔV is the potential change and m is the mass of material deposited on the electrode. The specific capacitance of PPy/GQDs is 138.0 F g⁻¹ which

exhibits a 45.6% Improvement when compared to PPy which has a calculated specific capacitance of 95.4 F g^{-1} . These calculated capacitance is consistent to the data obtained from CV curves.

Figure 6.6 Stability curve of PPy/GQDs nanocomposite after 1000 cycles

The stability of PPy/GQDs was examined by running charge-discharge at constant current. After being cycled for over 1100 cycles, the charge loss of PPy/GQDs is approximately 27% as shown in Figure 6.8.

Figure 6.7. Electrochemical impedance spectrometry graph of (a) PPy and (b) PPy/GQDs

EIS is generally used in examining the frequency respond of the supercapacitor materials as it provides information on electronic/ionic conductivity of materials as well as the equivalent series resistance ^[29]. EIS spectra usually consist of a semicircle part in the high frequency region and a linear part in the low frequency region. The size of the semicircle corresponds to the charge-transfer resistance of the material. Figure 6.7b observed PPy/GQDs has virtually no semicircle part, which indicates that PPy/GQDs has virtually no charge-transfer resistance as compared to pure PPy. This makes PPy/GQDs an excellent material for supercapacitors as it allows fast redox reactions. The linear part of PPy/GQDs also inclines more towards the imaginary axis, compared to pure PPy. This indicates that PPy/GQDs has better capacitive performance ^[27].

Figure 6.8 Plots of capacitance versus frequency for (a) PPy and (b) PPy/GQDs

Figure 6.8 shows the conversion capacitance obtained from the EIS spectra by using eqn (2)

$$C_m = -1/(2\pi mfZ'') \quad (2)^{[31]}$$

where C_m is the specific capacitance, f is the frequency, m is the mass of material deposited on the electrode and Z'' is the imaginary part of the EIS. As shown in

Figure 6.8, at low frequency, PPy/GQDs shows higher capacitance than pure PPy. For supercapacitors, majority of their capacitance is only available at low frequency^[32], thus, PPy/GQDs is again shown to have superior capacitive performance as compared to PPy.

6.4 Conclusion

In this report, we have examined the feasibility of enhancing the capacitive performance of electropolymerized PPy by doping with GQDs. Electropolymerized PPy/GQDs nanocomposites has a 45.6% improvement in specific capacitance when compared to PPy. The long cycle life and enhanced capacitive performance have demonstrated that PPy/GQDs can be an excellent choice as potential supercapacitor material.

6.5 Future work recommendation

Due to limitations of experiment, specific capacitance of electropolymerized PPy synthesized in this report, i.e. 95.4 F g^{-1} , is less than that reported by Chang et. al. i.e. 108 F g^{-1} [33]. Yet, the improvement percentage of PPy/GQDs from pure PPy is comparable to ~41% described by Wu et. al. [34] whom synthesized PPy/GQDs via in-situ polymerization.

For more in-depth exploration of the viability in using PPy/GQDs nanocomposites as supercapacitor electrode material, further optimization such as (1) adjusting the ratio of PPy to GQDs (2) varying the pH condition during electropolymerization (3) varying the electrolytes and characterization could be done. Construction of two-electrode system would also be beneficial in examine application of PPy/GQDs in supercapacitors.

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