One-dimensional nanostructured materials for energy storage applications

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**ONE-DIMENSIONAL NANOSTRUCTURED
MATERIALS FOR ENERGY STORAGE APPLICATIONS**

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SCHOOL OF ELECTRICAL AND ELECTRONIC ENGINEERING

2017

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Summary

This thesis covers the applications of one dimensional nanostructured materials in energy storage devices such as lithium-ion batteries (LIBs) and micro-supercapacitors (MSCs). Besides energy storage devices fabrication, integration of energy storage devices with microelectronic devices is also included. The chapter 1 introduces the background, motivations, objectives and major contributions of this thesis.

Chapter 2 presents two important one-dimensional (1D) nanostructured materials, vertical-aligned carbon nanotubes (VACNTs) array and silicon nanowires (SiNWs) array, produced with our own techniques. The corresponding experimental details and morphology characterizations are given in this chapter as well.

In chapter 3, fabrication processes and electrochemical performances of two novel LIBs anodes basing on 1D nanostructured materials are introduced. The great contribution of 1D nanomaterial in improving the LIBs performance has been proved.

Chapter 4 describes two superior planar micro-supercapacitors manufactured through using 1D nanostructured materials. In which, the unique 1D nanostructures greatly strengthen the current delivery capability and stability of MSCs, even on the soft substrate.

Development of an integrated supercapacitor with a photodetector on the same 1D nanostructured materials based substrate is shown in chapter 5. It demonstrates that two components are able to function well in a microelectronic system for a high portability.

Finally, chapter 6 provides the conclusive remarks and recommendation for future work of 1D nanostructured materials applied for energy storage devices.

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List of Abbreviations

SiNWs	Silicon nanowires
LIB	Lithium-ion battery
EDLC	Electrical double layer capacitors
SWNTs	Single wall carbon nanotubes
MWNTs	Multi wall carbon nanotubes
MSC	Micro-supercapacitor
1D	One-dimensional
EIS	Electrochemical impedance spectra
CNT	Carbon nanotube
VACNT	Vertical-aligned carbon nanotubes array
SEM	Scanning electron microscope
TEM	Transmission electron microscope
AFM	Atomic force microscope
SEI	Solid electrolyte interphase
SC	Supercapacitor
CVD	Chemical vapor deposition
PECVD	Plasma enhanced chemical vapor deposition
MACE	Metal assisted chemical etching
AAMs	Anodic alumina membranes
CE	Coulombic efficiency
AAO	Anodic aluminum oxide
CV	Cyclic voltammetry
GV	Galvanostatic voltammetry
UV	Ultraviolet

1. Introduction

1.1 Introduction and background

1.1.1 Energy storage devices

Energy, as one of the hottest topics in 21st century, has attracted a lot of attention during recent decades. Due to the fast consumption of unsustainable energy sources like fossil-fuel, there is a significant demand for people to efficiently exploit sustainable and environmental friendly energy sources such as solar energy, wind energy and tidal power *etc.* However, these renewable and clean energy sources are obtained from nature and existed in the form of instability.

Energy storage, a necessary intermediate for expediently and smartly using the clean energy sources, has become a worldwide research focus and many efforts have been made to improve the storage performance and stability of the energy storage devices. As we know, the oldest energy storage approaches of human beings could be dated back to age of Teras. At that time, primitive people made fire by carrying the natural carbon based objects like woods and charcoals which are of very low capacity. Later, around one thousand years ago, coal was discovered and it was found that compared with woods and charcoals, the coal could store much more energy based on the same mass and volume. In the next hundreds years, there was a variety of fuels with high capacity found by human beings and all of these natural fuels, such as oil, natural gas and petroleum, have been collected and stored as energy carriers. As different types of fuels possess different properties and performances, the concept of energy storage formed and some relative studies began to be conducted on this field [1].

Because of continuous increase of power consumption nowadays, it is necessary to increasingly apply other kind of energy sources instead of fossil fuels because the amount of fossil fuels in the world is limited and environmental pollution problems have become much more serious. Thus, how to effectively and flexibly use unstable power sources as mentioned in first paragraph has become a greatest challenge for human beings continuous improvement. As a result, different types of energy storage devices have been studied and manufactured.

Energy storage devices have been studied extensively recently. Different kinds of approaches have been realized according to different mechanisms. For example, mechanical storage, energy could be stored in a form of gravitational potential energy of water, compressing air or spinning flywheels; thermal storage, energy is usually stored depended on the temperature changes as heat energy; electrochemical storage, energy could be stored in the electrochemical cells and easily transferred to electrical energy through chemical reactions. Among all these storage approaches, electrochemical storage plays the most important role in our daily life and various commercial products based on this mechanism are fabricated, such as rechargeable batteries, flow batteries, supercapacitors and so on. Every product has its own advantages and disadvantages. Within all these products, two major products of excellent energy storage capabilities, Lithium-ion batteries (LIB) and supercapacitor (SC), have dominated the present market and made great contributions in our daily life. Regarding to the huge worldwide requirements, LIBs and SCs are used not only in nearly all the portable electrical equipment and electronic devices, but also in large power facilities recently, like electric vehicles and large-scale grids [2-4]. So nowadays research and design attentions of energy storage devices are focused on these two products.

LIB, as a member of the rechargeable battery family, is widely used in consumable electronics. Usually one battery cell contains two electrodes, as shown in Figure 1-1. One is positive electrode and the other is negative electrode which can be also called as cathode and anode respectively. These electrodes are separated by a separator which only allows ions moving from anode to cathode during the discharge process to form a working current in the external circuit. Intercalations and de-intercalation of lithium ions at electrodes are the major storage mechanism of LIBs which represent the transformation between electrical energy and chemical energy. From the schematic diagram, one can see the chemical reactions occur within the whole electrode. As the lithium ion is the smallest metal ion in the world so that LIBs always exhibit an outstanding energy density by volume which is an important criterion to judge the performance of energy storage devices [5-7]. However, charges transporting speed at the electrodes

of LIBs would be constrained by the slow diffusion of lithium ions through the bulk active materials. Due to this formidable kinetic problem, the issue of how to increase the power density of LIBs is one of the most important challenges for current LIBs industry.

Figure 1-1 Schematic diagram of a common lithium-ion cell. During charging, lithium ions flow to the anode through the electrolyte and electrons flow from the external circuit. During discharge the directions are reversed, generating useful power to be consumed by the device. The figure is reproduced from Ref. [8].

Similar to LIBs, all the SCs have a layered structure as displayed in Figure 1-2, two electrodes and a separator are assembled in the sandwich structure, but SCs store charges with different mechanisms. According to the mechanisms, SCs could be divided into two categories: One is electrical double layer capacitors (EDLC) and the other is faradic pseudo-capacitors. The energy stored in EDLC relies on the absorption and desorption of ions at the surface of electrodes. In contrast, in pseudo-capacitors, reversible faradic reaction occurring at the surface of electrodes is the dominated energy storage mechanism [9-10]. Usually the pseudo-capacitors present a higher specific capacitance compared with double layer capacitors. As the charges transfer only occurs at the surface or near surface of the electrodes, the current response and peak power delivery capability of SCs are much better than those of LIBs. However, as the contributions of the bulk electrodes are very limited, the specific energy densities of SCs calculated based on volume and mass are not as high as LIBs. So enhancing the areal, stack and specific capacitance of SCs are the primary research interest for the scientists working in this field.

Figure 1-2 Schematic diagrams of (a) a two-cell supercapacitor device basing on EDLC and (b) the electric double layer structure based at a positively charged electrode surface. The figure is reproduced from Ref. [11].

1.1.2 One-dimensional nanostructured materials

With the rapid development of nanotechnology at the beginning of 21st century, one-dimensional nanostructured materials show a profound impact in various applications and have already been employed in nano-electronics, composite materials, and energy storage *etc.* [12]. Fabrication and synthesis of one-dimensional nanostructured materials with different morphologies (tubes, wires, rods, fibers, etc.) and their corresponding applications are under extensive research. Due to the unique structure of one-dimensional nanostructured materials, great unique electrical, chemical, physical and biological properties have been observed and discussed in a lot of papers and books [13-15]. One particular characteristic of one-dimensional nanostructured materials is the tremendous surface to volume ratio which largely increases the exposure areal of materials with the same volume. Therefore, one-dimensional nanostructured materials exhibit promising potential for high performance sensing and energy harvesting applications [16-17].

Generally speaking, almost every type of traditional materials has its own one-dimensional nanostructured counterpart and these one-dimensional nanostructured materials could be classified according to their composition i.e. elements, oxides, nitrides, polymers, carbon nanotube (CNT) and composites, etc. [12] Scientists working in different applications start to replace the traditional materials with these unique one-dimensional nanostructured materials. Interestingly, the performances of many applications have been apparently improved. Therefore, basing on the traditional energy storage materials, the electrochemical scientists also make lots of efforts on synthesis of various corresponding one-dimensional nanostructured materials for enhancing the storage capabilities. Encouragingly, due to the unique morphology and outstanding conductivity of one-dimensional nanostructured materials, researchers find have demonstrated a significant improvement in specific capacity and cycling performance after applying these nanostructured materials. Among all of these one-dimensional nanostructured materials, some of them have been demonstrated as the promising candidates for next-generation energy storage materials and prepared to be put into industrial production.

Carbon nanotubes, as an important 1D nanomaterials, can be described as a rolled up graphene sheet. They could be classified into single wall carbon nanotubes (SWNTs) and multi wall carbon nanotubes (MWNTs). In the case of SWNTs, electrical characteristics are determined according to the chirality of SWNTs [18]. Due to two thirds of SWNTs are semi-conductive ones and with an average diameter of 1~2 nm. SWNTs always present low capacities and are not an ideal material for energy storage devices. However, MWNT has an excellent conductivity and ultrafast ions transporting speed due to its multi layered sidewalls and straight one-dimensional morphology. Therefore, MWNTs with various properties and architectures have been synthesized in different methods and been vastly applied for fabricating energy storage devices as well. Referring to Figure 1-3, a free-standing CNT paper acting as a flexible anode of a Lithium-ion battery, scientists have designed and proved some new concepts of lithium-ion batteries electrodes using CNTs, like flexible, conductive, wearable and additive-free electrodes for lithium-ion batteries have been realized and these fancy concepts become a new research focus for next generation energy storage devices. Apart from Lithium-ion batteries, applications of CNTs in supercapacitors have been widely studied as well. Figure 1-4 shows a pure CNT based micro-supercapacitor (MSC), in which a vertical-aligned CNT array is used as an active material for storing the charges and an electrode matrix for offering direct ions transporting pathways. Owing to the facile growing methods of CNTs, engineered nanostructure of electrodes could be achieved through modifying process conditions. Significant improvement of the performance of energy storage devices has been realized after introducing of CNT. In summary, CNTs, an excellent one-dimensional nanostructured material, is playing a very important role in the current energy storage material studies.

Figure 1-3 Photograph of a free-standing CNT paper prepared. (b) SEM image of the CNT network. (c) Image of CNT paper bent around a metal cylinder. The figure is reproduced from Ref. [18].

Figure 1-4 Design of MSC and material characterizations of CNTs. (a) Schematic and (b) SEM image of the structure of CNT based MSCs.(c–e) TEM images of individual single-, double-, and multi-wall CNTs. The figure is reproduced from Ref. [19].

One-dimensional nanostructured materials, like silicon nanowires, germanium nanowires, copper nanowires, *etc.*, are considered as another ideal 1D nanomaterials for improving the stability and cycling performance of energy storage devices. Different from CNTs, the capacitive properties of the 1D nanostructured materials usually are not very apparent and, as we know, pure elements show little faradic capacitance. Thus, the element based 1D nanostructured materials have always been applied in lithium-ion batteries instead of supercapacitors. For anodes of lithium ion batteries, the favorable one-dimensional nanomaterials are of not only an ultrahigh capacity of forming the products of MLi_x (M stands for the element, like Si, Ge, Al *etc.*), but also efficiently solve the volume expansion existed in the thin film based electrodes [20-23]. Because, during the charge/discharge processes of lithium-ion batteries, lithium ions insert into the electrodes and form metal alloys and the volume of the electrode would suffer a tremendous expansion, which always affects the working lifetime and capacity retention ability of batteries. Nevertheless, with the introduction of one-dimensional nanostructures, the volume expansion problem could be efficiently addressed attributed to the huge interspacing between nanowires or nanotubes. As showed in Figure 1-5, there is a large room reserved between silicon nanowires. In this way, when the lithium ions are inserted inside the nanowires, the interspacing between nanowires are able to release the expansion strain and makes the whole electrodes maintain their original structures.

Figure 1-5 SEM images of pristine Si nanowires before (a) and after (b) electrochemical cycling. The figures are reproduced from Ref. [24].

Beside 1D nanomaterials of one element, metal oxide constructed nanowires and nanotubes are widely used in both lithium-ion batteries and supercapacitors as well. Compared with CNTs, metal oxide one-dimensional materials always exhibit much higher specific capacities [25-27], because the storage mechanism of 1D metal oxide nanomaterials is similar with 1D alloy formed nanomaterials as they both rely on the chemical reactions occurred within the electrodes. In addition, metal oxides also have their own advantages. For lithium-ion batteries, metal oxides show a more stable cycling performance as the expanding strain of metal oxides during the lithiation process is always smaller than pure elements. For supercapacitors, as the mainly storage mechanism of metal oxide based electrode is faradic reaction occurred at the interface between the electrodes and electrolyte, metal oxide constructed one-dimensional materials could trap more charges and store more energies compared with pure conductive elements. Therefore, extensive studies have been focused on the metal oxide based one-dimensional materials. Surprisingly, different properties of 1D metal oxide nanomaterials could be obtained by synthesizing the 1D metal composite oxide nanomaterials, in which the properties of 1D nanomaterial can be largely changed through modifying the ratio of metal compositions in the nanomaterials. Figure 1-6 displays the TEM images and corresponding characterization results of NiCo_2O_4 nanowires. NiCo_2O_4 nanowires exhibit better performance in both lithium-ion batteries and supercapacitors compared with pure nickel or cobalt oxide nanowires, suggesting that metal composite oxides based 1D nanomaterial is another promising choice for the next generation energy storage devices.

Figure 1-6 (a) (b) TEM images, HRTEM image (c) and SAED pattern (d) of NiCo_2O_4 nanowires. The figures are reproduced from Ref. [28].

1.2 Motivations

Since the rapid development of nanotechnology in the last decade, one-dimensional nanostructured materials have been used in different applications due to their unique morphology and enhanced electronic characteristics. Along with the fast improvements of characterization approaches, like SEM, TEM and AFM, designing and fabricating the ideal engineered nanostructured materials become feasible. Therefore, expected one-dimensional nanostructured materials have been synthesized to satisfy the requirements of different applications. For energy storage devices, especially like lithium-ion batteries and supercapacitors, one-dimensional nanostructured materials show their outstanding performance when compared with the traditional thin film materials. Vast experiments have demonstrated that applying nanostructure is an efficient approach to optimize the performance of energy storage devices.

For lithium-ion batteries, enhancement of performance by employing one-dimensional nanostructured materials could be attributed to following three reasons: 1. Short charge transporting pathways through the one-dimensional structure effectively increase the high current delivery capability so that rate performance of lithium-ion batteries presents an apparent optimization. 2. Voids reserved in between the nanowire array or network is able to release the expansion strain when lithium ions inserted inside the active materials during the cycling. 3. Fabricating core-shell one-dimensional nanostructured composite is a promising method to combine the advantages of different materials together to enhance the performance of LIBs in all aspects.

For supercapacitors, the considerations of using one-dimensional nanostructured materials are as follows: 1. Similar with LIBs, the direct electrons transporting channels significantly enhance the current delivery capability of supercapacitors which are able to further increase the power density of supercapacitors. 2. As the energy storage mechanism of supercapacitor is mainly determined by the interface area between electrode and electrolyte, one-dimensional nanostructured materials show a superior specific capacitance due to their ultrahigh surface to volume ratios. 3. Apart from acting as active materials, one-dimensional nanostructured array and

network are also promising matrix and template for loading other active materials with high theoretical capacitance which is considered a facile method to further increase the capacitance.

Beside electrode fabrication, how to smartly apply these nanomaterials to energy storage devices is also a challenge. Along with continuous miniaturization trend of new-generation microelectronic devices, integrating suitable power suppliers on the same substrate to drive these small-scale microelectronic devices is a very promising concept. It is noted that integration of the energy storage devices on microelectronic devices could realize self-power and portability of the micro electronic devices. Therefore, the high integration of nowadays microelectronic devices with light weight, small volume and high energy storage capacity energy storage devices are under high demand. Many efforts have been made on fabricating the high performance energy storage devices. 1D nanostructured materials based energy storage devices with ultrahigh specific capacities and excellent power delivery capability could meet the above requirements. Moreover, 1D nanomaterial has been already used in a lot of microelectronic applications like sensors, solar cell, transistors, *etc.* Therefore, integrating 1D nanostructured materials constructed power sources with microelectronic devices is of great interests and potentials.

1.3 Objectives

We aim to develop high electrochemical performance electrodes for LIBs based on 1D nanostructured materials. Through introducing 1D nanomaterials, we expect to enhance both the specific capacities and cycling performance of the electrodes.

Beside LIBs, we also try to improve the capacitive performance of SCs by employing the 1D nanostructured materials. More attention is focused on the fabrication of micro-supercapacitors (MSCs), a new type energy storage unit

After proving the electrochemical performance improvements of LIBs and SCs by applying 1D nanomaterials, we aim to integrate these novel energy storage devices with traditional microelectronic devices on same substrate to form a completed electronic system. In this way, features of portability and self-powered could be realized.

1.4 Major contributions

- Successfully synthesized low density vertical-aligned CNT array on different substrates such as stainless steel, silicon wafer, quartz substrate and carbon cloth.
- Developed a large-scale low-cost method to fabricate vertical-aligned silicon nanowires and demonstrated the morphology controllable capability.
- Designed and fabricated a superior anode for LIBs with tin coated vertical-aligned CNT array. Good cycle stability has been achieved by employing the vertical-aligned CNT array.
- Developed a copper-silicon core-shell nanotube array based LIB anodes which exhibit an outstanding electrochemical performance.
- Grew nanostructured MnO_2 coated vertical-aligned CNT array on patterned electrodes to optimize the performance of high rate MSCs.
- Developed a metal-free SWNT/carbon/ MnO_2 hybrid electrodes for good performance coplanar MSCs on flexible substrate.
- Integrated a UV detector with a supercapacitor on the same vertical-aligned silicon nanowires substrate for realizing a self-powered system.

2. Fabrication of one-dimensional nanostructured materials

2.1 Synthesis of low density vertical-aligned carbon nanotube arrays

2.1.1 Introduction

Since first observations of CNTs, a lot of methods have been reported to fabricate large-scale and well-shaped CNT array. Due to the rapid development of CNT array based electronic devices, like polymer fillers [29], gas sensors [30], transistors [31], and electrochemical cells [32], critical morphology of CNT array are required referring to the specific applications. Therefore, many efforts have been made to grow the high quality and well-arranged vertical-aligned carbon nanotubes array (VACNT). Including laser ablation [33], chemical vapor deposition [34] and arc discharge [35] *etc.* Among all these methods, plasma-enhanced chemical vapor deposition is found to be the most promising and stable approach to grow highly vertically aligned CNT array with the highest grow rate and best repeatability. After successful growth of VACNT on silicon oxide substrate [36], a lot of other substrates have been employed for growing VACNT array as well. For the energy storage applications, VACNT array has been grown on nickel foil substrate, in which nickel foil with VACNT is able to act as an excellent current collector of ultrahigh surface to volume ratio. [37]

Apart from good current collectors, outstanding electrochemical performance of VACNT array based negative electrode has been demonstrated. [38] The as-prepared VACNT array exhibited reversible specific capacity as high as 782 mAh g⁻¹ which is nearly twice of the theoretical value of commercial graphite anode. Moreover, due to VACNT array is highly conductive and there is still great interspacing volume reserved, scientists have further deposited active materials with higher theoretical specific capacities on VACNT array. Fan *et al.* demonstrated a high performance lithium ion battery anode basing on well-designed CNT-silicon core-shell nanotube array. The good conductive vertically aligned CNT core and large inter-wire spacing could effectively optimize the conductivity of silicon and well accommodate strain generated during long-term cycling processes respectively. [39] Beside LIBs, Liu *et al.* successfully deposited

manganese oxide on a VACNT array to fabricate an outstanding electrode for high-performance supercapacitor. Through cathodic deposition of manganese oxide, the specific capacitance of the supercapacitor was significantly enlarged almost 10 times. [40]

To satisfy the requirements of energy storage applications, good quality VACNT arrays grown on conductive substrates are in high demand. Employing suitable conductive substrates acting as the current collectors could effectively improve the electrochemical performance of the energy storage devices and realize flexible and bending electrodes. Recently, Shen's group has synthesized various nanostructured materials on carbon clothes, a 3-dimensional and flexible current collector, for the anodes of lithium ion batteries. Outstanding performances, *i.e.*, ultrahigh capacity, long life cycles and good rate capability have been achieved. [41] For integration with new generation microelectronic devices, embedding energy storage units on the chips has attracted lots of attention recently. Maboudian's group has demonstrated porous silicon nanowires synthesized via a lithography compatible wet etch technique and encapsulated in an ultrathin carbon sheath, as high performance electrochemical micro-supercapacitor electrodes. [42] As-prepared carbon coated silicon nanowires were fabricated on silicon wafer and extremely high energy storage density of these wafer technology compatible supercapacitors has been achieved.

Growing VACNT array on a flexible substrate and patterned electrodes is a promising approach to apply the VACNT array in these new type energy storage devices. Owing to the unique morphology of VACNT array, the performance of the energy storage devices is supposed to be significantly improved.

2.1.2 Experimental details

VACNT array directly grown on stainless steel and carbon cloth were obtained in two steps: an ultrathin Ni/Al₂O₃ bi-layer catalyst was deposited using an electron beam evaporation system. The density and diameters of VACNT array could be well controlled by changing the thickness of nickel metal film. After deposition of the catalyst, the VACNTs grew in a mixture of ammonia/acetylene (240/60 sccm) gas atmosphere under 120 W plasma at 800 °C for 15 mins.

The structure and morphology of electrodes were characterized by field-emission scanning electron microscopy (SEM, LEO 1550 Gemini) and Transmission electron microscopy (TEM, JEM 2100F JEOL).

2.1.3 Results and discussion

Figure 2-1 Low magnification (a) and high magnification (b) top view SEM images of the VACNT array on stainless steel substrate. Low magnification (c) and high magnification (d) tilted view SEM images of the VACNT array on a stainless steel substrate.

To cooperate with the energy storage devices, we grew the VACNT array directly on the stainless steel (with a diameter of 15.5 mm) which was matched with the commercialized coin cell mode of CR2032. Because the stainless steel substrate contains different metal compositions which would form alloys with nickel catalyst during the high temperature growing process, an ultrathin alumina film was deposited on the substrate first to separate the nickel catalyst and stainless steel current collector. However the thickness of this spacer film was found to be very important as vertically growing mechanism of VACNT is mainly depended on the strong electrical field applied between two electrodes of the PECVD chamber. As we know, alumina is not a conductive material and thick spacer film would greatly affect the electrical field formed along the CNT growing direction. According to our experimental results, we find the thickness of 10 nm alumina is a suitable parameter for VACNT growth on stainless steel electrode.

Top view and tilted view SEM images of the VACNT array grown on the stainless steel substrate are presented in Figure 2-1. As the catalyst film is ultrathin, we have to choose the stainless steel substrate with low roughness. In this way, one can see from the low magnification SEM image that the VACNTs grown on stainless steel electrode are uniformly spread on the substrate and diameters of VACNTs are very similar. In high magnification SEM images, we could observe that most VACNTs are of similar morphology, 3 μm in height and 200 nm in diameter. Moreover the interspacing between VACNTs offers enough volume for further deposition of other active materials which makes this VACNT on stainless steel electrode an ideal candidate for high performance current collectors.

Figure 2-2 SEM images of 80 times (a), 5000 times (b), 10000 times (c) and 20000 times (d) magnification for the VACNT array grown on carbon cloth.

Due to the continuously increasing requirement of energy storage units with high energy densities and power capabilities, scientists have studied various active materials and measured their electrochemical performance. Apart from enhancing the specific capacities of active materials, people find that optimizing the morphology of the current collectors is also an effective approach to improve the performance of energy storage devices. As enlarging the interface area between current collectors and active material could decrease the charge transporting distance from active materials to current collectors, power density of the cells would be greatly increased. Therefore, many new types of current collectors other than traditional flat metal electrodes have been studied. By using these nanostructured based current collectors, improvements of the electrochemical performance have been demonstrated.

We have tried to grow the high quality VACNT array on a carbon cloth substrate and the results are shown in Figure 2-2. As presented in Figure 2-2a and 2-2b, we could see that the whole surface of carbon cloth was fully covered with the VACNT array and uniformity of this CNT array was very good. Different from the VACNT array grown on the metal substrate or stainless steel substrate, the catalyst of VACNT growth on the carbon cloth did not require spacer film as the carbon cloth does not react with catalyst in high temperature. Only one layer of nickel was deposited on the substrate as the catalyst. Interestingly, we could observe that although we used the same thickness of nickel metal as catalyst, the average diameter of VACNT grown on carbon cloth was slightly smaller than that of VACNT grown on the flat substrates. We suggest that it was caused by the special morphology of carbon cloth substrate as one can see that the carbon cloth was constructed by many carbon micro fibers which formed the three dimensional structures with an ultrahigh surface to volume ratio. The practical thickness of nickel catalyst on this 3D substrate was actually less than the expected value. In summary, the VACNT array grown on the carbon cloth substrate to form the unique 3D nanostructured electrode has been successfully achieved.

Figure 2-3 SEM images of 100 times (a), 500 times (b), 2000 times (c) and 5000 times (d) magnification for the VACNT array grown on the patterned silicon interdigital electrodes.

Along with continuous downsize of the microelectronic devices, power consumption of wafer based devices has been greatly decreased and traditional power sources with huge size are no longer necessary for driving these new microelectronics devices. In addition, the concepts of flexibility and portability for microelectronics devices have been demonstrated already. Embedding power supply components on the chips to realize the full portability for the wafer based applications are just around the corner. For these purposes, we have fabricated 3D silicon interdigital electrodes on silicon wafer which are promising planar geometrical designed electrodes for on chip MSC.

After demonstrating that the VACNT array is able to be grown on the flat metal current collectors and 3D carbon based current collectors, we have tried to grow the VACNT array on patterned electrodes as well. Figure 2-3 presents different magnification SEM images of the VACNT array grown on the 3D silicon interdigital electrodes on silicon oxide/silicon substrate. As shown in Figure 2-3a, 3D interdigital silicon electrodes on substrates through wafer process technology has been well manufactured. From Figure 2-3b, we can observe that the width and height of the silicon electrode are well-defined to 100 μm and 20 μm , respectively. Figure 2-3c is the tilted SEM image of the edge of silicon electrode. One could find that even at the surface of the edge, VACNT array could grow uniformly. This VACNT array grown all over the silicon based electrodes suggests the integration potential between silicon wafer and 1D nanostructured VACNT array.

2.1.4 Conclusion

In this part, we have successfully grown high quality VACNT array with similar diameters and uniform distribution on several different substrates. It has been demonstrated that VACNT array could grow on the commercial current collectors for battery and supercapacitor. Apart from the flat metal current collectors, 3D carbon cloth substrate has been also employed for growing VACNT array. It proved that growing VACNT on carbon cloth substrate could largely increase the surface to volume ratio of the electrode and through using this new type of electrodes. Flexible energy storage devices could be realized. Moreover, it has been demonstrated that VACNT could successfully grow on the 3D micro silicon walls

to form the composite planar interdigital electrodes as well which exhibits a great compatibility between VACNT and wafer technology.

2.2 Fabrication of diameters controllable vertical-aligned silicon nanowires array

2.2.1 Introduction

Besides CNTs, as we mentioned in the first chapter, SiNWs array have attracted intensive research interest recently due to their great promising properties in various applications [43-48]. For energy storage applications, the issue of significant volume expansion of Si during lithiation/de-lithiation processes than would be efficiently accommodated via replacing the traditional bulk or micron sized Si particles with SiNW arrays directly grown on stainless steel current collectors. It was confirmed that the electrochemical performance of Si anodes could be obviously improved [45, 46].

Basically, the fabrication methods of SiNW arrays can be divided into two approaches, bottom up and top down. Vapor-liquid-solid (VLS) is the most popular bottom up method [49] which is always to be used for growing randomly arranged SiNWs. For producing vertically aligned SiNWs array, either employing a template [50] or using SiCl_4 as the precursor [51] is required. However, there is a big problem with the VLS method *i.e.* the catalyst contamination caused by high temperature diffusion of gold catalyst into SiNWs [52]. As the metal affect the life-time and diffusion lengths of minority carriers in the SiNWs, metal defects are highly undesirable in electronic applications. Apart from metal contamination, large scale applications of SiNWs array produced through the VLS process are very difficult to be realized due to its critical growing conditions of high temperature and specific gas atmosphere.

Unlike the bottom up methods of fabricating SiNWs array, SiNWs are usually prepared by etching Si wafer with top down methods. Diameters, spacing and locations of SiNWs array are well controlled according to the reactive ion etching (RIE) in combination with a high-resolution-lithography technique [53]. The drawback of this method is the limited aspect ratio, especially referring to the

SiNW array with small interspacing. Moreover, the cost of this method is very high. Metal assisted chemical etching (MACE), as a newly developed top down method [54, 55] has attracted much research interests in recent years. In a typical MACE process, a Si wafer deposited with catalyst metals is immersed in an aqueous solution which contains HF and an oxidizing agent (H_2O_2) to perform catalyzed chemical etching process. Although the etching mechanisms are still under argument, the general understanding of the etching process has been widely accepted: (1) when a Si wafer coated with catalysts is immersed into the mixed etching solution, the oxidant in the solution would be preferentially reduce at the surface of the metal catalyst because of the catalytic effect of the metal. (2) The holes generated during the reduction reaction are penetrated into the Si bulk which is in contact with the catalysts and causes oxidation of Si from top to the bottom. (3) The oxidized Si is etched away by the HF solution and then the fresh Si is exposed for oxidation. As the concentration of holes at the metal/Si interface is much higher, the etching rate of the Si beneath the catalysts is much faster when compared with the bare bulk Si. As a result, the Si beneath the catalysts would be continuously dissolved and bare Si almost reserves its original state so that SiNWs are formed [55]. Although this is a simple, scalable and cost-effective approach, the diameter and interspacing of SiNW array are not easily controllable in the MACE method, which is mainly caused by the random distribution of the metal particles shaped catalyst. It should be pointed out that the parameters, like SiNW diameter and interspacing, actually play an important role in lots of applications.

To realize SiNW arrays with controlled diameters and interspacing, a straightforward and common used approach is to pattern the catalyst film on the silicon wafer. This has been successfully proved by using nano-spheres (polystyrene spheres or silica spheres) [56-58] or anodic alumina membranes (AAMs) [59-61] as the sacrificial templates. Both methods are capable of producing periodic SiNW arrays, but not easy for large scale fabrication processes. For nano-spheres based methods, assembling a well-aligned monolayer nano-sphere array on wafer through spin coating or drop casting techniques is very difficult to be realized in large area, although wafer scale closely decorated silica

sphere monolayer has been demonstrated via a Langmuir-Blodgett method, requirements of fabrication processes are very high [62]. In addition to AAM fabrication, a critical pattern transfer is required to transfer the AAM pattern onto the catalyst mesh. Recently, some groups have made some great developments on producing SiNW arrays with controllable diameters. Ruiyuan et al [63] de-wetted a thin silver film to create pin holes and used this random arranged silver nanoparticles thin film as the catalyst to etch silicon wafer. As de-wetting process easily turns a silver film into nanoparticle array, the diameters and number density of the nanoparticles, or resulting SiNWs, could not be controlled. In contrast, Azeredo et al [64] deposited a thin layer of gold onto de-wetted silver nanoparticles and they chemically etched away the silver nanoparticles to leave a gold film with many nano-holes. In this way, the Au mesh pattern was employed to fabricate SiNWs. However, Ag particles could not be fully removed, non-uniformly distributed of SiNWs array produced are not suitable for large scale SiNW arrays applications.

In this part, we demonstrate a reliable, scalable and cost-effective method to fabricate one-dimensional vertical-aligned SiNW arrays with controllable diameters and interspacing. In this technique, a simple de-wetting process combined with a reverse step is utilized to synthesize a randomly well-spaced metal particle monolayer which was used to etch SiNW arrays.

2.2.2 Experimental details

Figure 2-4 Schematic of the fabrication process to produce SiNW arrays with a sacrificial template.

Figure 2-4 presents a schematic of our fabrication processes. In our experiments, both p-type or n-type Si wafer could be used as the substrates. After a cleaning process, a thin layer of Ag was deposited on the wafer via electron beam evaporation. Subsequently the wafer was annealed in a quartz tube at 800 °C under Argon atmosphere for two minutes to transfer the Ag film into a monolayer Ag nano-particles mask. Then a Ti/Au bi-layer catalyst is sequentially deposited on the Si wafer and an ultrasonic treatment was applied to remove the sacrificial Ag particles obtain a catalyst mesh. Finally, the wafer was immersed into an etching solution containing deionized water, HF and H₂O₂ to obtain a vertically aligned SiNW array. The antireflection performances of the SiNW arrays were measured by a PerkinElmer Lambda 950 UV-Vis-NIR spectrometer.

2.2.3 Results and discussion

Figure 2-5a shows a scanning electron microscopy (SEM) image of de-wetted Ag nanoparticles on the surface of Si. The metal particles are naturally well spaced. After removing the sacrificial Ag particles, obtained Ti/Au catalyst mesh is presented in Figure 2-5b. From this SEM image, one can see that nearly all the Ag particles were removed which ensures no residual Ag particles remained to affect the distribution of SiNWs array. The beneath Ti layer was very important here and mainly has two functions. First, it significantly strengthens the adhesion between Au catalyst film and Si substrates so that the catalyst film is able to survive after strong ultrasonic treatment. Second, it plays a great role in forming a uniform Au film as it is well-known that the several catalyst metals (e.g. Au, Ag) possess poor adhesion to extremely flat Si wafer. [56, 60] Moreover, we found that, only with an extra Ti inter-layer between Au and Si, the Au metal could form a thin continuous uniform film with a thickness down to 10 nm otherwise some discrete areas would form. Upon immersion in etching solution, Ti layer was immediately etched away by HF solution which makes Au film is directly in contact with bulk silicon wafer, acting as an effective catalyst for continuous promoting the silicon etching. Figure 2-5c displays a top-view SEM image of a SiNW array fabricated using this approach, indicating that SiNWs was well matched with the same pattern of the sacrificial de-wetted metal particles. A tilted angle SEM image of the as-

prepared SiNW array is shown in Figure 2-5d. One can find the vertically aligned SiNWs were well spaced on the silicon wafer and the diameter and spacing of the SiNWs are determined by morphology of sacrificial metal nanoparticles. In addition, it is noted that the lengths of the SiNWs are very uniform which is consistent with other MACE based SiNWs fabrication methods.

Figure 2-5 SEM images of (a) the de-wetted Ag particles, (b) the obtained Ti/Au metal mesh, (c) top view of the SiNWs array and, (d) tilted angle view of the SiNWs array.

With this method, the diameters of SiNWs were determined by the dimensions of de-wetted metal particles, so through modulating the thickness of Ag thin film, the diameters of SiNWs are able to be controlled. Figure 2-6 shows capability of this method for producing the different diameters SiNWs array by changing thickness of Ag films. The diameters of SiNWs were in a range from 40 nm to 100 nm with 10 nm Ag film. Due to the diameters are much smaller than the lengths of SiNWs, the SiNWs were found to lean each other forming a SiNW bundle as presented in Figure 2-6b. Figure 2-6c and Figure 2-6d present the SiNWs manufactured via 30 and 50 nm thick pre-deposited Ag film respectively. Obviously, the SiNWs array fabricated with 30 nm thick Ag film had a much larger diameter than that of SiNWs array etched with 10 nm thick Ag film. Along with the thickness of Ag film increasing from 10 nm to 50 nm, the average diameters of resulting SiNW arrays correspondingly increased from 90 nm to 420 nm as well.

Figure 2-6 SEM images of (a) de-wetted Ag particles synthesized with 10nm Ag film, (b) SiNWs fabricated with 10nm Ag film, (c) the de-wetted Ag particles synthesized with 30nm Ag film, (d) the SiNWs fabricated with 30nm Ag film, (e) the de-wetted Ag particles synthesized with 50nm Ag film and (f) The SiNWs fabricated with 50nm Ag film.

The SEM in Figure 2-6 show that with the diameters of SiNWs increase, the interspacing of SiNW arrays consistently increase while the density of SiNWs decrease. Nevertheless, in spite of changing the de-wetting metal thickness, the nanoparticles coverage area remains at a similar value in Figure 2-7. We could conclude that the etching rates of this method are maintained at a stable level for etching different thickness samples. In this way, the length of different diameters SiNWs could be well controlled. As the silicon nanowires array are usually applied in optical applications, we have compared the optical reflectivity of the SiNW arrays with different diameters and same lengths (around 3 μm). From Figure 2-8, one can see the reflectivity of the SiNW array decreases along with the deposited Ag films thickness increasing from 10 nm to 50 nm. Encouragingly, the SiNW arrays showed a promising candidate material for light trapping devices as the reflectivity at a specific wavelength could be obtained through adjusting the diameters of SiNWs.

Figure 2-7 Average diameters and area coverages of Ag nanoparticles with different Ag deposition thicknesses.

Compared to previous nano-spheres and AAM methods which are used to produce the highly periodic SiNWs, the SiNWs array fabricated in our method are of an aperiodic interspacing. However, a good periodicity is not necessarily required in many applications, especially referring to SiNWs array based energy storage devices. In addition, simulation reported recently indicates that aperiodic SiNW arrays with random interspacing could achieve 2.35 times higher the power conversion efficiency than the ordered counterparts [65]. In terms of the repeatability and process simplicity, our method is more advantageous than the complicated template assisted methods especially when the applications do not require strict periodicity and highly diameter uniformity.

Figure 2-8 Reflectivity of SiNWs arrays fabricated with different thickness Ag films.

2.2.4 Conclusion

We have demonstrated a novel method to fabricate large scale SiNW arrays with controllable diameters and interspacing. The method relies on a simple de-wetting process to fabricate a monolayer of well-spaced metal nanoparticles on Si substrate. The metal nanoparticles are then used as a sacrificial template to pattern a gold mesh catalyst, which is used to catalyze solution for etching Si underneath it, forming SiNW array. This technique can be easily up-scaled for mass production of SiNW arrays.

3. One-dimensional nanostructured materials for LIB anodes

3.1 Sn coated carbon nanotube array for high performance LIB anodes

3.1.1 Introduction

According to the high demand of high energy density and long-life time lithium-ion batteries anodes, several active materials such as silicon (Si), germanium (Ge), lithium (Li) and tin (Sn) have been developed to increase the performance of the present commercial carbon based anodes (theoretical capacity of 372 mAh g^{-1}) [66-70]. Among all these materials with a higher theoretical capacity, a lot of attention has been focused on metal Sn due to its high theoretical specific capacity of 992 mAh g^{-1} for forming the alloy “ $\text{Li}_{22}\text{Sn}_5$ ” [71] and the abundant existence of Sn on earth. Nevertheless, one important issue of Sn-based anode is the significant volume expansion during lithium ion inserted inside the electrode, causing the material pulverization and poor cycling performance. [72]

For addressing this challenging problem, several approaches based on nanotechnology have been applied. For example, Sn nanoparticle based anodes are fabricated with an ultrahigh surface to volume ratio which has obviously enhanced electrochemical performance of Sn based lithium-ion batteries. [73] Unfortunately, although interspacing between Sn nanoparticles could release expansion force during the lithium ions insertion process and extend the life time of the battery cell, aggregation of Sn nanoparticles would still occur after dozens of charge/discharge cycles and damage the electrode structure, leading to a rapid capacity fading. [74, 75] To solve this problem, carbon materials have been employed with Sn for carbon/Sn composite anode. The reported approaches can be classified into two strategies: one is to use carbon materials as spacing buffer layers to avoid Sn nanoparticle aggregation [76, 77]. The other is to employ carbon based nanostructure (carbon nanoparticle [78], carbon nanotube (CNT) [77, 79], graphene nano-sheet [80, 81] and CNT network [82]) to support the active material and optimize the conductivity of the whole electrode.

Among these carbon templates, 1D nanostructures based matrix (CNT and carbon fibers) have attracted lots of attention based on their unique morphology which is able to offer a direct pathway for electrons transporting. In addition, the interspacing between nanostructures makes lithium ions much easier to penetrate inside the electrode. [83, 84] Owing to introducing of 1D carbon nanostructures, both the cycling stability and the energy density of Sn based anodes present a great improvement. For example, Sn/carbon core-shell nanowire constructed anodes exhibited a reversible capacity as high as 525 mAh g⁻¹ after one hundred cycles. [85] Besides, a Sn coated nitrogen doped carbon nanofibers based anode also showed an outstanding specific capacity of 682 mAh g⁻¹ after charge/discharge 200 cycles. [86] These excellent performance anodes with Sn/carbon nanostructure should be attributed to special characteristic offered by 1D nanostructure, in which voids and interspacing existed between the nanowires, effectively accommodating volume expansion during the formation/decomposition of Li_xSn alloys. [82, 85-87]

However, although a lot of 1D nanostructured Sn/C composite anodes have been fabricated and different degrees of improvement in the electrochemical performance have been achieved, deep studies of strain accommodation, conductivity improvement and cycling stability enhancement, are very necessary. Because most of these CNT and carbon nanofibers applied in the electrodes were arranged randomly, the strain released and aggregation of Sn at nanowires in the high density regions would occur due to this highly non-uniform interspacing distribution. [88] In addition, high-rate charge/discharge for Sn based electrodes is still a challenge and it is noted that when the current density is above 0.5 C, the initial high specific capacity would greatly decrease after 200 cycles. [89-91]

To solve the mentioned problems, we applied our VACNT array to fabricate a high performance VACNT/Sn based anode. In this anode, the well-aligned inter-wire spacing offers a sufficient expansion volume for Sn coated VACNT array after lithium insertion. [92] Moreover, as our VACNT array was directly grown on the stainless steel current collectors, binders and additives were not required to further decrease the resistance, shorten lithium-ions diffusion distance and improve the electrochemical impedance of the electrode. [93]

3.1.2 Experimental details

Fabrication processes of Sn coated VACNT array anodes were in two steps: (1) well-spaced vertical aligned CNT arrays were synthesized on stainless steel current collectors with the method we described previously. Briefly speaking, an ultrathin Ni/Al₂O₃ bi-layer catalyst was deposited in an E-beam system [84]. The sample then was loaded in a PECVD chamber to grow VACNT array in a mixture of ammonia/acetylene (240/60 sccm) gas atmosphere under 120 W plasma at 800 °C. (2) Sn was coated with Denton magnetron sputtering system in which a Sn target (99.999%) was sputtered at 100 W under pure Argon atmosphere.

The mass loadings of Sn were measured by comparing the mass difference of the substrate each time before and after CNT growth and Sn deposition with an analytical balance (Mettler Toledo XP 26, 0.002 mg), respectively.

Electrochemical characterizations were carried out using a standard CR-2032 coin cell, which were assembled in a glove box (Innovative Technology) with a pure lithium foil as the counter electrode. The electrolyte used in this work was composed of 1 M lithium hexafluorophosphate (LiPF₆) dissolved in ethylene carbonate and dimethyl carbonate (EC/DMC, 1:1 by volume). The galvanostatic charge/discharge and cyclic voltammetry measurements were tested through a multichannel battery tester (Neware, BTS-610) and an electrochemical workstation (AUTOLAB, M 101), respectively.

3.1.3 Results and discussion

Figures 3-1a and 3-1b present the tilted SEM images of the VACNT array before and after Sn deposition, respectively. It is noted that uniform interspacing between CNT was reserved and a significant diameters increasing from 20nm to 100nm indicated that Sn was successful coated on VACNT array. Even after depositing a thick Sn film, the residual inter-wire spacing was sufficient to release the strain and prevent metallic Sn from aggregation. For further demonstration that VACNT nanostructure has much more interface area compared with flat electrode, control samples without VACNT array were prepared when conducting the Sn deposition

process. We found that Sn mass loading on the VACNT sample ($0.3\text{-}0.6\text{ mg cm}^{-2}$) was a factor of 1.3~1.4 larger than that of the flat Sn film sample.

Figure 3-1 Tilted view SEM images of bare VACNT array (a) and Sn coated VACNT array (b).

From the TEM image of a single Sn coated CNT (Figure 3-2a), one can see that CNT core was very straight and presented a smooth surface morphology which could demonstrate that a direct and efficient pathway for electrons transporting has been achieved in this vertical aligned CNT nanostructure. However, due to the intrinsic characteristic of Sn [94], referring to Figure 3-2a, Sn nanoparticles were likely to be formed aggregation instead of a uniform thin layer. Consistently with the previous reported results [94-96], rough surface would be beneficial for the battery performance because it not only increases the surface to volume ratio, but also promotes electrolyte to penetrate inside the nanowires array and directly react with active materials. Figure 3-2b presents the high resolution TEM image of crystalline Sn nanoparticles [87] rooted on the VACNT, which further demonstrates Sn nanoparticles are successfully coated on VACNT.

Figure 3-2 (a) TEM images of a single Sn coated VACNT (a) and zoom-in high resolution TEM image at the area of metal Sn.

To measure the electrochemical performance of the as-prepared Sn coated VACNT array based anode, a coin-cell of CR2032 was assembled with a lithium foil as the counter electrode. All the cells were measured in a potential window of 5 mV to 2.5 V for fully utilizing the capacity of Sn. The cyclic voltammetry curves for the first several cycles are displayed in Figure 3-3a. Three apparent reaction peaks at 0.29, 0.51 and 0.62 V were obtained in the 1st discharge curve and they could be attributed to the alloying formation processes of Li_xSn and solid electrolyte interphase (SEI) layer formation, respectively. [97] Afterwards, the following three anodic curves and two cathodic curves are almost overlapped, suggesting an excellent electrochemical reversibility of this electrode. Two apparent cathodic peaks at (0.36 and 0.64 V) and a series of anodic peaks at (0.51, 0.64, 0.73, 0.79 V) in the repeatable CV curves correspond to the potential stages in the first three lithiation/de-lithiation plots of Figure 3-3b, in consistence with other reported results [89, 95-97]. Moreover, it should be pointed out that VACNT arrays have an ignorable contribution to the storage capability as there is no current peak regarding to the lithium intercalation into carbon has been observed in charge/discharge profiles of Figure 3-3.

Figure 3-3 (a) The cyclic voltammetry and (b) charge/discharge curves of Sn coated VACNT array anode at 1st, 2nd and 3rd cycle.

To more systematically evaluate the cycling stability of this novel 1D nanostructured composite anode, galvanostatic measurements with different current densities of 0.2 C and 0.5 C (1 C equals to 990 mA g⁻¹) were conducted. The corresponding plots of charge/discharge capacity and coulombic efficiency versus cycle numbers are exhibited in Figure 3-4a and Figure 3-4b, respectively. The reversible capacity of the Sn coated VACNT array anode was able to reached 878.6 mAh g⁻¹ of its first cycle at the rate of 0.2 C and even when cycled after 400 cycles, the electrode still remained a superior reversible specific capacity as high as 930.8 mAh g⁻¹. When the battery was cycled at a higher current density of 0.5 C, a high initial charge specific capacity of 424.6 mAh g⁻¹ has been realized. As presented in Figure 3-4b, we could observe an excellent capacity retention performance over cycling more than thousand cycles was achieved in which an average Coulombic efficiency of 99.37% and a specific capacity of 380.9 mAh g⁻¹ at the 1000 cycle demonstrate great improvement after we applied 1D nanostructured on this novel anode. Interestingly, there is a similar trend within all the galvanostatic measurements under different cycling current densities, the capacities decreased in the first tens of cycles and subsequently slightly recovered to their initial value. As we know, this significant drop of the specific capacity has been observed for the first tens cycles in a lot of anode cases. A common acceptable explanation for this phenomenon is that the irreversible SEI layer formation plays a great contribution in the initial charge/discharge processes and then capacity would recovery after a few initial cycles probably due to a polymeric gel-like film formation of kinetically activated electrolyte degradation [98-100]. Especially for the nanostructured based Sn electrodes, the same capacity increasing effect has also been found as well. [85-87, 101] Apart from the traditional cycling measurements, a rate performance test was performed at various current densities from 0.1 C to 1.0 C. As illustrated in Figure 3-4c, excellent rate stability has been demonstrated and this electrode was able to stably work under different current rates even after 200 cycles. In addition, when we reset the current rate back to 0.1 C, the specific capacity could recover to the initial value of 953.5 mAh g⁻¹.

Figure 3-4 The plots of reversible capacity retention and Coulombic efficiency versus cycle numbers at 0.2 C (a) and 0.5 C (b). (c) Lithiation/de-lithiation capacity and CE cycled at different current rates from 0.2 C to 1.0 C. (d) The reversible capacities for pure VACNT array sample, flat Sn film sample and Sn coated VACNT the array sample.

For more straightforward evolution on the electrochemical performance improvement by applying this novel structure and quantitative explanation of the VACNT structure contribution to the total capacity, control experiments were carefully carried out through fabricating and comparing three different types of samples, *i.e.*, a pure VACNT sample, flat Sn film sample and Sn coated VACNT array sample. All the described samples were prepared under the same experimental conditions for VACNT growing process and the mass density of the VACNT arrays was approximate 0.2 mg. The flat Sn film sample and Sn coated VACNT array sample were also deposited in the same batch. Figure 4-4d compares the reversible specific capacities of these three samples in 100 cycles. We could tell the contribution of the VACNT is as low as 30 mAh g⁻¹, less than 10% of the initial specific capacity of the Sn based samples. From the contrast of the planar Sn film and Sn coated VACNT array, it is clearly noted that a remarkable enhancement in the cycling performance for introducing the VACNT array in the electrodes. Although both of them would degrade at first tens of cycles, the Sn coated VACNT array sample slowly stabilized at an outstanding specific capacity of 606.1 mAh g⁻¹ at the 100 cycle which was nearly five times higher than that of the flat Sn film sample.

3.1.4 Conclusion

In this experiment, we have demonstrated that by applying 1D nanostructure VACNT array to fabricate a Sn/VACNT composite anode, a great electrochemical performance improvement has been achieved probably due to the large interspacing and excellent electron transport pathway formed by the well-aligned VACNT array. From the measurement results, this novel Sn decorated VACNT array anode presented a superior capacity retention capability in different electrochemical tests and an excellent reversible capacity of 930.8 mAh g⁻¹ after 400 cycles at a current rate of 0.2 C and a reversible capacity of 380.9 mAh g⁻¹ after 1000 cycles at current rate of 0.5 C. In addition, even after 200 cycles, the electrode still showed very high rate performance and good stability.

3.2 SiNWs assisted fabrication of copper/silicon nanotube array for LIB anodes

3.2.1 Introduction

To satisfy the increasing requirement of high energy density LIBs, silicon as a very promising active anode material with the highest specific capacity of 4200 mAh g⁻¹ [102] attracts a lot of attention recently. Besides lithium ion storage capability, environment friendly and abundance of silicon make it an ideal choice for mass production. However, pristine silicon anode has a tremendous volume expansion problem during lithiation process which would cause the structural pulverization and capacity fading after tens of cycles [67, 103-104]. Encouragingly, it has been found that applying nanostructure on silicon based anode is an effective approach to accommodate volume expansion issue and maintain the performance for long cycles. As a result, various silicon nanostructured based electrodes, like hollow nano-spheres [105], nanowires [24], nanotubes [106] and 3D nanostructure [107], etc. were studied to improve Si anodes performance recently. Although better cycling performances of mentioned nanostructured Si anodes have been achieved, these electrodes still could not satisfy the requirements of long life cycling LIBs.

Nowadays, instead of only employing pure nanostructure, composite materials based core-shell nanostructures rooted on the current collectors are seen as a new development direction. In which, the robust nanostructure materials function as the supporter not only offers a strong mechanical template for the shell material, but also largely increases the electrodes transporting speed on the base of forming a 1D direct pathway. Compared with traditional electrodes, binder and additives are not essential in these electrodes which could largely decrease the internal resistance of battery cell to perform a high rate capability. In 2008, a novel anode constructed of crystalline-amorphous core-shell silicon nanowires was fabricated by Cui group [108] which firstly demonstrated that the unique core-shell nanostructure was able to realize the ultrahigh specific capacity of silicon anodes. After that, several groups have tried other materials with higher conductivity to further optimize the performance of silicon based anodes. Wang et al. [77] and Fan et al. [79] have

reported novel VACNT-silicon core-shell nanowire arrays for high performance LIBs where CNT arrays made a great contribution to the stability and conductivity. Apart from carbon nanotubes, copper nanowire array was also employed as a core material to fabricate copper-silicon nano-cable arrays for superior anodes [109]. Compared with CNT arrays, copper nanowires anchored at copper foil offered much better adhesion between current collectors and active silicon. Beside traditional nanowires and nanofibers, to increase the accessible surface area between silicon and electrolyte, silicon nanotubes array [110] and sealed silicon nanotubes array [111] were investigated as well for developing the surface to volume ratio of electrodes and remaining more volume for accommodating expansion strain during the charge-discharge processes. In addition, to further enhance the electrochemical performance of silicon nanotube array, a new type of double-wall silicon nanotube array [112] was reported where the silicon nanotubes were extra coated with a thin silicon oxide layer. Due to the growth of solid-electrolyte interface (SEI) at silicon oxide layer, the structure of silicon nanotube array was much more stable and achieving long life cycle [113, 114] of the battery.

However even though a significant development has been realized through applying core-shell nanowire or nanotube structures, some problems still exist. Usually, the core nanowires are fabricated with high temperature conditions [24, 111, 115] on the substrates such as stainless steel which may cause unexpected changes to batteries performance when the temperature is too high [116]. Another important reason for the capacity degradation of these anodes is the detachment of 1D nanostructured active materials from the current collectors caused by the stress produced through Li ions insertion [46]. Therefore the adhesion between the nanowires and the current collectors plays a significant role in the stability performance of 1D nanostructure based anodes.

In this experiment, we present a novel core-shell Cu/Si composite anode with unique 1D cone-shaped nanostructure and the copper nanotubes array act as both current collector and structure supporter to hold the amorphous silicon shells. In this design (Figure 3-5a), inner core and substrate are of the same material, naturally having much stronger adhesion than other similar electrodes [117].

Besides, this special cone-shaped side layer morphology partly increases the contact interface area between silicon and copper, as well as the contact area between the array and substrate. Therefore, detachment of active materials from the collector tends to be avoided during the cycling process [95]. Figure 3-5b illustrates the cross section of this core-shell nanotubes, in which the single uncapped Cu nanotube offers more volume for silicon expansion towards inside [112] and there is a significant increase of the surface to volume ratio which could greatly decrease electrons transporting resistance within the electrode [118].

3.2.2 Experimental details

Figure 3-5 (a) Schematic illustration contrast between a traditional 1D nanostructure and as-designed nanostructure. (b) Cross section illustration of the fabricated nanotube. (c) Fabrication process of the copper-silicon core-shell arrays.

Figure 3-5c displays the fabrication process for as-prepared copper-silicon core-shell nanotubes array. The core copper nanotube array was produced through sputtering metal copper on a silicon nanowire template which was synthesized through the MACE technique [119]. After copper deposition, the sample then was immersed into a KOH etchant solution to etch away the silicon template forming copper nanotubes array which was a free-standing substrate shown in Figure 3-6. Because of the shadow effect of sputtering deposition, a slope sidewall of copper nanotube was formed [120]. From the tilted SEM image (Figure 3-6b), one can see the thickness of this copper nanotube array substrate is approximate several micrometers (sputtering times is around 2 hours). The amorphous silicon shell was deposited with plasma enhanced CVD (PECVD). Raman scattering of the nanotube arrays before silicon coating and after silicon coating was conducted to confirm amorphous silicon deposition.

3.2.3 Results and discussion

Figure 3-6 Top view (a) and cross-section view (b) SEM images of copper nanotube array; tilted view (c) and top view (d) SEM images of copper-silicon core-shell nanotube array. (e) Top part TEM image of a single copper-silicon core-shell nanotube. (f) Low magnification TEM image of a single copper-silicon core-shell nanotube.

The tilted and top view SEM images of the copper-silicon array are exhibited in Figure 3-6c and Figure 3-6d respectively. This interconnected nanotube arrays were a promising substrate for high performance electrodes highly interconnected nanowires was able to prevent individual unit detached from the substrate during lithiation process. [46, 84, 105] In addition, applying silicon nanowire array as template could avoid introducing contaminations as some metal oxide particles have been observed by using Anodic Aluminum Oxide (AAO) template [121] and zinc oxide template [122] to fabricate silicon based anodes. Figure 3-6e exhibits a TEM image of a single core-shell nanotube. We can clearly find that the practical nanotube morphology was well consistent with our design presented in Figure 3-5 and the thickness of copper layer was very thin when compared with the amorphous silicon coating shell. Such a structure offered a high silicon mass loading ratio (0.3 mg cm^{-2}) of the whole electrode (3 mg cm^{-2}) while achieving high conductivity between amorphous silicon and current collectors. The low-magnification TEM image of Figure 3-6f evidences the unique cone-shaped morphology of nanotube and a large area at the interface has been formed.

The electrochemical performances of the copper-silicon core-shell nanotube arrays were measured in the standard CR-2032 coin cells. All the samples were cycled in a potential window of 0.01-1.2 V (vs. Li⁺/Li) to fully utilize the capacity of amorphous Si [79]. Figure 3-7a shows the specific capacities and coulombic efficiency versus cycle number for initial 400 cycles at a current density of 0.2 C (1 C=4200 mAh g⁻¹). Regarding to the first cycle, an ultrahigh specific capacity of 2473 mAh g⁻¹ was achieved. After 400 cycles, it still maintain an average coulombic efficiency of 98.44%, reversible specific capacity as high as 1506 mAh g⁻¹, indicating that the average fading rate of this electrode was less than 0.1%. Moreover, after stabilization process of electrode, only a slight degradation in reversible capacity of the electrode was observed after approximate 400 cycles. Figure 3-7b presents the discharge/charge potential to specific capacity profiles of 2nd, 20th, 100th and 200th cycle at a constant current density of 0.2 C. Comparing the profiles between 20th and 200th cycle, no apparent difference can be found,

strongly suggesting that the as-designed electrode still remains its novel structure during the volume expansion upon such long cycles.

Figure 3-7 (a) Lithiation/de-lithiation specific capacities and coulombic efficiency in a function of cycle numbers at a current rate of 0.2 C. (b) The potential to specific capacity profiles of the Cu-Si core-shell structures at different cycles.

To further evaluate the current delivery capability of this copper-silicon core-shell nanotubes array based anode, a rate performance test was conducted under different current rates from 0.3 C to 12 C and 5 cycles were performed at each current rate. After experiencing the highest current rate of 12 C, the electrode could still remain stable of its initial electrochemical performance and nanostructure when the current rate was returned to 0.3 C. Excellent specific capacities were obtained of 2079, 1846, 1625, 1316, 1013, 633 and 411 mAh g⁻¹ at 0.3 C, 0.5 C, 1 C, 2 C, 4 C, 8 C and 12 C respectively as displayed in Figure 3-8. When the current was set back to 0.3 C, the specific capacity of electrode was recovered to 2025 mAh g⁻¹ which was approximately the same as the initial value.

Figure 3-8 Capacity retentions of the copper-silicon core-shell nanotubes array anode at different current rates from 0.3 C to 12 C.

From these experiments results, the impressive cycling performance and rate performance of this 1D nanostructure have been demonstrated. We attributed the improvements to the novel core-shell vertical nanostructure. (1) The free-standing copper nanotubes array substrate functions as both nanostructure matrix and current collector of electrode which could greatly enhance electrons transporting speed and increase the energy density of the whole electrode. (2) Owing to the vertical-aligned core-shell nanotubes array, volume expansion problem has been effectively overcome. As shown in Figure 3-9a, the top view SEM image of this electrode after 400 cycles proves that although amorphous silicon has suffered a tremendous expansion, it was still attached to the copper nanotubes. (3) Different from common 1D nanostructured array, this engineered copper nanotube array has a cone-shaped sidewall and was tightly attached to the bottom current collector. In Figure 3-9b, the side-view SEM image of the electrode after cycled 400 cycles demonstrates that the silicon stayed being coated on the copper nanotubes and maintained its original morphology. In addition, there is an extra bonding force between the contacts of this highly interconnected 1D nanostructure for improving the stability of whole electrode.

Figure 3-9 Top view (a) and side view (b) SEM images of the core-shell nanotube array based electrode after 400 cycles.

3.2.4 Conclusion

We have successfully fabricated a free-standing and binder-free copper-silicon core-shell nanotubes array based electrode which showed outstanding electrochemical performance. Owing to the vertical-aligned nanostructure and feasible template used in this method, the as-prepared anode was of a long cycle life for lasting up to 400 cycles with average capacity fading rate of less than 0.1% per cycle and realizing an impressive specific capacity of 2473 mAh g⁻¹. Moreover, the electrode is able to maintain an excellent structure with a specific capacity as high as 1506 mAh g⁻¹ after 400 cycles and even after undergoing 12 C high current rate test, the reversible capacity kept at 97.4% of initial value when the current rate was returned to 0.3 C. To our best knowledge, this is the first time to use customized silicon nanowire array as the template to fabricate 1D nanotubes array. Encouragingly, the developed architecture could be applied on other functional nanostructured materials as well.

4. One-dimensional nanostructured materials for micro-supercapacitors

4.1 Optimization of coplanar high rate supercapacitors by applying VACNT array

4.1.1 Introduction

Along with the rapid development of microelectronic industry, micro-systems integrated with embedded power sources are in highly demand. [123] However, to introduce common LIBs and sandwiched supercapacitors, *etc.* directly on integrated circuits (IC) is still very challenging, because downsizing and planar geometric design are difficult for these devices. [124]

Planar micro-supercapacitors (MSCs), as a newly-developed micro energy storage device, have attracted significant attention [125]. Compared with commercial power supplier products, planar MSCs theoretically could deliver higher power densities [126]. Moreover wafer process technology could be employed to manufacture the planar MSCs, making MSCs environmental friendly and seamlessly integrated with other functional microelectronic devices. [127]

Commonly two approaches have been used for enhancing the MSCs: (1) utilization of novel nanomaterials, including onion-like carbon [128], reduced graphene oxide [129], graphene quantum dots [130] and graphene oxide/CNT composite [131], *etc.* and (2) introducing of novel thin film fabrication technique, like inject printing [132], in-situ photoresist-derived [133] and layer-by-layer assembling [134], *etc.* Although these approaches make great contributions in MSCs performance improvements, to satisfy the practical requirements of some micro-systems, the power delivery capability are not sufficient regarding to some applications requiring ultrafast rate performance [135] and sufficient peak power [136]. To this end, some groups have attempted to fabricate MSCs with high power densities. A graphene-based MSC [137] has demonstrated with an ultrafast rate up to 3.6 ms, nevertheless, although graphene presented an outstanding conductivity and a good capacitance property, the ultrathin thickness of graphene limited the areal capacitance of the MSC. A 3D nanostructured planar MSC based on the high

dense vertical-aligned CNT array [138] did increase the areal energy density of capacitor, reaching a maximum power density of 0.115 W cm^{-2} , but an obvious drawback of pure CNT based MSCs was the low theoretical capacitance [139] of 120 F g^{-1} compared with other functional materials [140].

To optimize the high rate MSCs, we have designed three types of nanostructured MSCs through introducing a low density VACNT array and MnO_2 nanosheets: (1) symmetric bare VACNT arrays based MSC (D1); (2) symmetric MnO_2 nanosheets deposited onto VACNT arrays based MSC (D2); (3) asymmetric hybrid MSC (D3) where a $\text{MnO}_2/\text{VACNT}$ array and a bare VACNT array functioned as the positive and negative electrodes, respectively. The *in-situ* grown VACNT array efficiently reduced the interfacial resistance and the straight morphology of VACNT array [23] not only tremendously increased the surface to volume ratio, but also accelerated liquid electrolyte penetration into the electrode. According to the volumetric energy density E (mWh cm^{-3}) relationship ($E = C_s (\Delta V)^2 / 7200$), where C_s refers to stack capacitance (mF cm^{-3}) and ΔV (V) refers to operating potential window, it is expected to have a large specific capacitance C_s [141] for MSC (D2) and broadened working potential range ΔV for the asymmetric structure of MSC (D3).

Here, we have successfully fabricated the three types of MSCs and interestingly, enhancement in energy density of MSC (D2) has been proved and asymmetric designed MSC (D3) was found to exhibit an outstanding electrochemical behavior with a high potential window.

4.1.2 Experimental details

A conventional photolithography technique was used to pattern the interdigital electrodes. Subsequently, a four-layer-metal of $\text{Ti}/\text{Au}/\text{Al}_2\text{O}_3/\text{Ni}$ thin film was deposited on the quartz substrate. After a lift-off step, VACNT arrays grew in a mixture of ammonia/acetylene (240/60 sccm) gas atmosphere under 120 W (PECVD) at 800°C [23] to form MSC D1. MnO_2 nano-sheet was electrodeposited on the VACNT array according to Ref. 147. Briefly speaking, the electrodes with VACNT on the substrate were immersed in an aqueous mixed solution of 20 mM $\text{Mn}(\text{NO}_3)_2$ and 100 mM NaNO_3 and a constant current density of $66.7 \mu\text{A cm}^{-2}$ was continuously applied for 10 minutes in a two-electrode setup. For MSC D2, both

electrodes were deposited with MnO₂ nano-sheet. Only one electrode was electrodeposited for MSC D3. The deposited specific mass loading of MnO₂ nano-sheet was approximately 1.1 mg cm⁻².

The morphology characterizations of as-fabricated MSCs were conducted with an optical microscope, a field-emission scanning electron microscopy (SEM, LEO 1550 Gemini) and a Raman system, respectively. Electrochemical characterizations of all the MSCs were carried out through an electrochemical workstation (AUTOLAB, M 101) in a 0.5 M Na₂SO₄ aqueous electrolyte. All electrochemical impedance spectroscopy (EIS) plots were tested in the frequency ranging from 100 kHz to 1 Hz.

4.1.3 Results and discussion

Figure 4-1 Schematics of all MSCs structures and fabrication flows: (1) symmetric VACNT arrays MSC (D1); (2) symmetric MnO₂ nano-sheets coated VACNT arrays MSC (D2); (3) asymmetric MSC (D3).

Figure 4-2 (a) Optical image of patterned multi-layer metal electrodes. Figure (b) and (c) are optical images in terms of position b and position c, respectively. Microscopical images of (d), (e) and (f) indicates the interdigital electrodes of MSC D1, D2 and D3, respectively.

The fabrication flow charts of the three planar MSCs are shown in Figure 4-1 and the dimensions of the interdigitated electrodes are indicated in images of Figure 4-2b. One can see the width of interdigitated electrodes and the interspacing in this work were precisely controlled to be 100 μm . Figures 4-2d, 4-2e and 4-2f are the optical images of the MSC D1, D2 and D3 respectively. The light color areas refer to the quartz substrate, the red areas correspond to well-separated VACNT arrays and the dark areas are MnO_2 nanosheets decorated VACNT arrays. From the results, the uniform interdigitated electrodes have been achieved for all MSCs and the red alternating with black fingers was successfully realized in MSC D3.

Figure 4-3 Low (a) and high (b) magnification tilted view SEM images of VACNTs array with well interspacing; low (c) and high (d) magnification SEM images of MnO₂ nano-sheets deposited VACNTs array.

Figure 4-3 presents the morphology characterizations of VACNT arrays and MnO₂ nanosheets decorated VACNT arrays. From the low magnification SEM images of VACNT before and after MnO₂ nanosheets deposition, we could observe both VACNT and MnO₂ nanosheets were uniformly grown and ultra-straight multi-wall VACNT was individually rooted on the current collectors. The as-grown CNT was approximately 60 to 80 nm in diameter and several micrometers in length. To our understanding, this low density and uniform interspacing between CNTs is favorable for electrolyte penetrating into the bottom of the VACNT array and could tremendously enlarge the contact interface area between active materials and ionic electrolyte. In addition, the highly straight 1D nanostructure could effectively offer short electrons transporting channels from the electroactive electrodes to the bottom conductive metals. As shown in Figure 4-3d, MnO₂ nanosheets were successfully deposited on VACNT array and the as-synthesized MnO₂ nanosheets were likely to stick together to form the flower-like hierarchical architecture was consistent with some similar reports. [142]

Figure 4-4 The Raman spectras of the VACNT array with and without MnO₂ nanosheets deposition at different wave numbers.

The Raman spectra of the VACNT arrays with and without MnO₂ nanosheets deposition are shown in Figure 4-4. The disordered band (D band of 1360 cm⁻¹) and the graphite band (G band of 1580 cm⁻¹) of VACNT are very obvious before MnO₂ nanosheets deposition. However no Raman features above 1000 cm⁻¹ are observed after coating MnO₂ nanosheets, further suggesting that the VACNT array has been covered with MnO₂ nanosheets. Figure 4-4a shows the Raman peaks after MnO₂ nanosheets deposition and one can see a strong Raman signal centered at 630 cm⁻¹ was detected which can be assigned to Mn(IV)-O bond vibration in MnO₂. [143] Besides, some small Raman peaks around 300 cm⁻¹ appeared as well which was supposed to be caused by other types of Mn-O bond vibrations like Mn(III)-O bond in Mn₂O₃. The Raman results suggest that most of manganite oxides grown on the VACNT array were MnO₂ [144] and a small amount of Mn₂O₃ was existed in the oxide composite, in which the Faradaic redox reactions (Mn(IV)/Mn(III) redox couples) would occur within the composite electrodes during charge/discharge cycles and we believed it would benefit to the pseudo-capacitor performance of the MSCs.

Figure 4-5 CV curves of pure VACNT constructed MSC D1 at low scan rates from 1000 mV s^{-1} to 5000 mV s^{-1} (a) and high scan rates from 10000 mV s^{-1} to 50000 mV s^{-1} (b).

To evaluate the electrochemical performance of VACNT array, CV measurements of MSCs at different scan rates were performed in the same 0.5 M Na_2SO_4 aqueous electrolyte. The results were exhibited in Figure 4-5a and Figure 4-5b for slow scan rates (1 V s^{-1} to 5 V s^{-1}) and fast scan rates (10 V s^{-1} to 50 V s^{-1}), respectively. The curves presented were nearly symmetric and rectangles in shape, suggesting that efficient electric double layers at the interface of VACNT array and ideal capacitive nature of MSC D1 were successfully confirmed. Encouragingly, even at the tenfold scan rates, the CV curves still kept their original shapes, clearly demonstrating the high power capability of this VACNT composed MSC D1. Besides, the rapid current response at each potential scanning reversal indicated the ideal electrolytic ions accessibility of penetrating inside the electrodes owing to the special architecture of VACNT array with sufficient interspacing. Even at the highest scan rate of 50000 mV s^{-1} the superior electrochemical properties of MSC were exhibited which was comparable with some high-power MSCs of carbon materials developed by other groups [124, 134]. However, from the charge/discharge currents densities and the small shape shifts at the edge of the potential window, we believed that this bare VANCT array could function as a good matrix for a high rate MSC and it was able to operate very well at ultrafast scan rates, the specific capacitance of MSC D1 was still far away from our requirements because of the poor storage capacitance of high-temperature synthesized CNTs and small active materials mass loading.

Figure 4-6 CV curves of MnO₂ nanosheets/VACNT constructed MSC D2 at low scan rates (a) from 1000 mV s⁻¹ to 5000 mV s⁻¹ and high scan rates from 10000 mV s⁻¹ to 50000 mV s⁻¹ (b). (c) Comparisons of the current densities in a function of scan rates between MSC D1 and MSC D2. (d) Galvanostatic measurements of MSC D2.

Introducing of novel electroactive material MnO_2 nanosheets onto the VACNT array could be an efficient approach to increase the specific capacitance of the electrode meanwhile to remain the superior power density. Figure 4-6 displayed the CV measurements of MSC D2 at different scan rates and the corresponding CV curve of D1 was included for comparison as well. Impressively, almost symmetric and rectangle curves have been observed at low scan rates (Figure 4-6a) and there was also a significant improvement in electrochemical performance of MSC D2. Moreover, even at a scan rate as high as 50000 mV s^{-1} (Figure 4-6b), only slight delay of current response could be noticed, indicating the good conductivity between active materials and current collectors further promoting the high current delivery capability of MSC D2 even after non-conductive MnO_2 nanosheets coating. The green curves in Figures 4-6a and 4-6b referred to the CV results of MSC D1 at 5 V s^{-1} and 50 V s^{-1} , respectively. A straightforward rise of current density in MSC D2 demonstrated that capacitance enlargement was successfully achieved via coating MnO_2 nanosheets. Furthermore, the currents as a function of scan rates of MSCs from 60 mV s^{-1} to 50000 mV s^{-1} in Figure 4-6c gave a clear evidence for the contribution of MnO_2 nanosheets deposition in reaching the great energy density. Note that a linear dependence of current versus the scan rate was found below the scan rate of 10 V s^{-1} and the corresponding current density slightly decreased along with the scan rate increase which was probably attributed to the limitation of ions diffusing speed at ultrahigh scan rates. [145] Encouragingly, MSC with MnO_2 nanosheets achieved an ultrahigh current delivery capacity of 7, 13 and 24 mA cm^{-2} at 10, 20 and 50 V s^{-1} , respectively, approximately 40 times larger than pure VACNT MSC. According to the galvanostatic charging and discharging plots exhibited in Figure 4-6d, there were almost ideal triangle shape have been observed and no significant voltage drop was found at the beginning of each discharge process demonstrating the good capacitive behavior and the low internal resistance of VACNT/ MnO_2 constructed MSC D2.

Figure 4-7 CV measurements of MSC D3 at low (a) and high (b) scan rates with a fixed potential window. (c) CV measurements of MSC D3 at a series of working voltages with a constant scan rate of 10 V s^{-1} . (d) Corresponding galvanostatic tests of MSC D3.

As discussed in the introduction, enlarging the working potential of MSC is a promising method not only to improve the energy density, but also to satisfy high operation voltages applications. To this end, an asymmetric MSC D3 was fabricated and its CV curves at different scan rates were shown in Figure 4-7. For better understanding the electrochemical properties of MSC D3, corresponding CV curves of MSC D1 were included for comparison. Interestingly, all the curves recorded at different scan rates exhibited nearly symmetric profiles within this expanding working potential and this asymmetric electrodes design successfully broadened the potential of MSC meanwhile maintained the excellent capacitive performance. In contrast to pure VACNT based MSC D1, one can see that current densities of MSC D3 have an apparent rise, indicating the contribution of MnO₂ nanosheets to the electrode specific capacitance. Owing to the asymmetric design, a MnO₂/VACNT array and a bare VACNT array functioned as the positive and negative electrodes, the working voltage of MSC D3 would be broadened and to further evaluate the electrochemical performance of MSC D3, we measured the CV curves of MSC at larger cell working potentials from 1.2 to 2.0 V in the same 0.5 M Na₂SO₄ aqueous electrolyte. As shown in Figure 4-7c, a smooth stretch of the rectangular CV curve was attained along with the potential increase at a fixed scan rate of 10000 mV s⁻¹ and no notable change of CV profile was observed even at the highest operating voltage of 2.0 V. These results suggested that there was no violent polarization reaction occurred at the electrodes and from the galvanostatic testing results presented in Figure 4-7d, the linear symmetric charging and discharging plots predicted a good capacitive behavior of the fabricated asymmetric MSC.

Figure 4-8 EIS plots (a) from 1 to 100000 Hz (inset refers to zoom in image of high frequency part) and (b) impedance phase angle vs frequency plots.

Electrochemical impedance spectra (EIS) of all MSCs are presented in Figure 4-8a (inset is a zoom in figure of high frequency region). The measurements proved the fast ion transporting characteristics of as-prepared MSCs, even after MnO₂ nanosheets deposition. From the magnification Nyquist plots of the high-frequencies, MSC D1 had the smallest equivalent series resistance which was attributed to that the non-conductive MnO₂ nanosheets coating would decrease the conductivity of electrodes in MSC D2 and D3. However this resistance increase was not significant suggesting the electrochemical performance of MSCs were not greatly affected. A small semicircle has been found at the high frequency region of MSC D3 which was attributed to the weak pseudo-capacitive contribution during the cycling process caused by Faradaic redox reaction of Mn(IV)/Mn(III) redox couples. For better understanding of EIS measurements results, we also plotted the profiles of phase angle as a function of frequency (Figure 4-8b). Note that all phase angles of the MSCs were close to 90 degrees below 10 Hz and within this low frequency range, the MSCs were able to behave comparable with a traditional electrical capacitor (whose equivalent circuit is a resistance and a capacitor in series) as the phase angle of 90 degrees was an index of an ideal capacitor [146]. To investigate high power capability of different MSCs, we compared the frequencies at the phase angle of 45 degrees (f_0) for the all MSCs (note that $f_0=1/\tau_0$, where τ_0 is the corresponding time constant and refers to the minimum time required for a supercapacitor to discharge its stored energy with an efficiency of 50 percent). Apparently, pure VACNT based MSC D1 could release its energy much faster than MSC D2 and MSC D3, but ultrafast discharging capabilities of tens milliseconds were achievable for all three MSCs.

Figure 4-9 Comparisons of three MSCs in specific area capacitance (a), specific stack capacitance (b) and specific energy density (c). (d) Cycling performances of three MSCs, in which MSC D1 and D2 were cycled in 0-0.8 V and MSC D3 was cycled in 0-1.2 V.

To systematically evaluate these two approaches, we compared the electrochemical performances of three MSCs in different aspects. For practical considerations, all the capacitances and energy densities of MSC D1 and MSC D2 were calculated in a working potential range of 0-0.8 V, while asymmetric MSC D3 was conducted in a higher potential window of 1.2 V. Figure 4-9a and Figure 4-9b present the areal capacitance C_a and stack capacitance C_s of the MSCs, respectively, which were calculated with the following equations:

$$C_{\text{MSC}} = \frac{1}{v \cdot (V_{\text{max}} - V_{\text{min}})} \int_{V_{\text{min}}}^{V_{\text{max}}} I(V) dV \quad 4 - 1$$

$$C_a = \frac{C_{\text{MSC}}}{A_{\text{MSC}}} \quad 4 - 2$$

$$C_s = \frac{C_{\text{MSC}}}{V_{\text{MSC}}} \quad 4 - 3$$

where v is the scan rate (mV s^{-1}), V_{max} and V_{min} stand for the maximum and minimum potential of the working cell, respectively. $I(V)$ refers to the discharge current (A) in the CV measurements, A_{MSC} and V_{MSC} are the areal and volume (thicknesses of electrodes are evaluated through SEM images) of the MSC. Encouragingly, an impressive areal capacitance of 0.91 mF cm^{-2} at 1000 mV s^{-1} for MSC D2 was obtained. At a high scan rate of 50000 mV s^{-1} , the areal capacitance of MSC D2 still remained 0.48 mF cm^{-2} , around 47 times higher than that of MSC D1. The areal capacitance is very promising compared with previous reported values at the similar scan rates, *i.e.* reduced graphene oxide MSC ($462 \text{ } \mu\text{F cm}^{-2}$) [15], graphene/CNT carpet MSC (2.16 mF cm^{-2}) [24], Graphene/ MnO_2 /silver nanowires ternary film based MSC ($16 \text{ } \mu\text{F cm}^{-2}$) [7] and graphene MSC ($80.9 \text{ } \mu\text{F cm}^{-2}$) [23]. Although both areal and stack capacitance would decrease with scan rate increase, a volumetric capacitance of 9.09 F cm^{-3} at 1000 mV s^{-1} was achieved at a ultrahigh rate up to 50000 mV s^{-1} and a stack capacitance of 4.79 F cm^{-3} was attained for MSC D2, nearly 25 times larger than that of MSC D1. For MSC D3, the decay phenomenon was not obvious and only a slight drop of stack capacitance from 1.39 F cm^{-3} at 1000 mV s^{-1} downward to 0.83 F cm^{-3} at 50000 mV s^{-1} was observed. Figure 4-9c exhibits the calculated volumetric energy density E (mWh cm^{-3}) of three MSCs according to the relationship of $E = C_s (\Delta V)^2 / 7200$. Different from the specific capacitance, the energy density of MSC D3 was more comparable

with MSC D2 because the enlargement of the cell potential window ΔV apparently enhanced the energy storage capacity of MSC D3. Remarkably, MSC D2 and MSC D3 delivered a volumetric energy density of 0.81 mWh cm^{-3} and 0.27 mWh cm^{-3} , respectively, in the liquid ionic electrolyte. These values are comparable or even better than some other nanomaterials constructed MSCs, like graphene quantum dots [130], graphene oxide/ MnO_2 [141], MWCNT/ V_2O_5 nanowires [127] and monolithic carbide-derived carbon films [124]. Figure 4-9d presents the cycling tests of three MSCs and overall the excellent stabilities of all MSCs have been achieved. According to the systematic comparisons, these two approaches of optimizing the high rate electrochemical performance MSC were proved with different advantages. Excellent enhancement in areal and stack capacitance were demonstrated for MSC D2 and a successful high potential window broadening has been achieved attributed to the asymmetric design of MSC D3. More importantly, because the fabrication processes of the as-fabricated MSCs are compatible with conventional wafer process technologies for microelectronic devices, the integration of the MSCs with other electronic devices on the same chip becomes feasible.

4.1.4 Conclusion

Employing VACNT array, we have developed three types of coplanar micro-supercapacitors (MSCs) to optimize the area and volumetric capacitance, energy density, rate performance, operation potential window and cycling performance of the MSCs. In comparison with pure VACNT based MSC, the MnO_2 coated VACNT based MSC presented tremendous improvements in both areal and volumetric capacitances. Meanwhile, the MSC with VACNT and MnO_2 coated VACNT electrodes successfully demonstrated a broadened operation potential window. In addition, the advanced MSCs maintain outstanding high power delivery capability, high rate performance and superior cycling stability. The developed MSCs are able to be integrated with other microelectronic devices on the same substrate.

4.2 Metal-free hybrid electrode for high performance coplanar micro-supercapacitor

4.2.1 Introduction

Flexible electronics has been attracted a lot of attentions. Several types of soft electronic devices have been demonstrated recently [148]. To further realize these impressive concepts of portable and flexible microelectronic systems, flexible energy storage devices with light weight, small volume and high energy storage capacity are highly demanded. [149-150] In addition, some pioneer studies of miniaturized sensors and energy harvesters integrated with micro power sources have been reported recently. For example, a power pack based on an organometallic perovskite solar cell and a supercapacitor has been fabricated. This type of power source could offer continuous electric power output through a supercapacitor to store the energy harvested by the solar cell. [127] Moreover some sensors and energy storage devices have been successfully integrated on the same substrate as well, in which the embedded supercapacitors were able to drive the sensors and functional devices for long period [151-153].

As a novel type of energy storage devices, micro-supercapacitors (MSCs) are of superior power density, long cycling lifetime and ultrahigh rate capability compared with micro batteries and traditional sandwich structured supercapacitors [130, 134, 154]. Several revolutionary features of MSCs, like planar geometric design, easily transferred to soft substrate and environmental protection, make MSCs considered as the most ideal power sources for miniaturized microelectronic devices. [155-156] As a result, a great deal of attention has been focused on planar MSCs, for which many nanomaterials such as metallic VS_2 [157], MnO_2 /graphene [140], reduced graphene oxide [126] and multiwall CNTs [158] have been employed as their electrodes. Among them, composites of transition metal oxides and carbon materials [123, 147, 159] are considered as one of the most promising active materials for future MSCs. Note that incorporation of transition metal oxides is an effective approach to improve the specific capacitance of pure carbon based electrodes which usually have impressive electrical conductivity and excellent capacitive property, but possess a low specific capacitance. [158, 160-162]

Apart from incorporation of different active materials into MSCs, various fabrication techniques have also been reported to fabricate rational electrodes of planar MSCs, like ink jet printing [132], layer-by-layer assembling [134] and laser direct writing [135]. It is well known that the electrochemical performance of MSCs depends on both the width of current collectors and interspaces between the current collectors. A rational processing technique with high resolution is critical to enhance capacitance performance of MSCs. [163] Photolithography, a traditional wafer processing technique, is widely used to fabricate high performance planar MSCs. It could provide a facile control of interdigital electrode dimensions and compatible with the fabrication mainstream of integrated circuits [164]. Additionally, several groups [133, 153] have demonstrated photoresist-derived porous carbon to be of very promising electrochemical capacitive behavior recently.

In this section, we report on a novel design and fabrication process of a superior hybrid electrode for high-performance coplanar MSCs on a soft substrate. In the MSCs, traditional metal current collectors with little electrochemical capacitance were replaced by a composite of single-wall carbon nanotube (SWNT) network and photoresist-derived porous carbon. By using carbon electrodes instead of metal electrodes (like Ti/Au), a tremendous improvement in the specific capacitance for the entire electrode has been achieved. Due to a high-temperature carbonized porous carbon and high density SWNT network serving as the frame of the current collector, this collector exhibits an outstanding electrical conductivity and robust structure stability. Besides, we find that a further significant enhancement in the specific capacitance and energy density can be achievable through adding manganese oxide (MnO_2) nano-flowers onto the carbon composite current collectors.

4.2.2 Experimental details

Figure 4-10 Fabrication flow charts and photograph of designed MSC on a soft substrate.

The fabrication processes are presented in Figure 4-10. A uniform catalyst (ferritin) was firstly spin coated on a flat quartz substrate and then high density SWNT network grown in a chemical vapor deposition (CVD) system [29]. Subsequently, photoresist AZ5214 based electrodes were photolithographically patterned on the substrate with a Mask Aligner and then the sample was placed into a thermal CVD furnace. After purifying the system with Argon gas, the sample was heated up to 300 °C and held for half an hour in mixture of argon/hydrogen (200/50 sccm) gas atmosphere. Carbonization of the patterned photoresist was carried out at a high temperature of 1050 °C in the same gas atmosphere for 2 hours. After carbonization, the sample was treated by oxygen plasma with a power of 10 W for 30 seconds to remove the SWNT network that is not covered by the carbonized porous carbon patterns and form interdigital electrodes of the MSC. Different densities of MnO₂ Nano-sheets are then electrodeposited onto this all carbon materials based electrodes in the following processes: the sample is immersed in an aqueous solution of 20 mM Mn(NO₃)₂ and 100 mM NaNO₃ and a fixed current density of 60 $\mu\text{A cm}^{-2}$ was applied for the time from 100 s to 600 s, respectively. A conventional transfer process [29] was conducted and the optical image of the MSC on a soft polymer substrate was exhibited in Figure 4-10.

The morphology and material characterizations of the as prepared hybrid electrodes were studied using a field-emission scanning electron microscopy (SEM, LEO 1550 Gemini) and a Raman system (WITec) under a 532 nm wavelength excitation, respectively. A two-electrode measurement setup was applied to measure electrochemical performance of MSCs in a 0.5 M Na₂SO₄ aqueous electrolyte in an electrochemical workstation (AUTOLAB, M 101). For solid-state MSC manufacture, the as-prepared MSC was covered with a typical solid electrolyte which is prepared through mixing 6 g H₃PO₄, 6 g PVA and 60 ml DI water and then heating up to 90 °C under vigorous stirring. All the cyclic voltammetry tests were operated in a potential window of 0-0.8 V and all electrochemical impedance spectroscopy (EIS) plots were tested in a frequency ranging from 0.01 Hz to 100 kHz.

4.2.3 Results and discussion

Figure 4-11 Low magnification (a) and high magnification (b) SEM images of the carbon electrodes on SWNT network after carbonized process. (c) SEM image of substrate surface between electrodes before after oxygen plasma treatment. (d) Raman spectrum of as-grown SWNT network (red) and SWNT/carbon film (blue).

The SEM image of the SWNT/carbon electrode without O₂ plasma treatment is shown in Figure 4-11a. From the corresponding Raman spectrum in Figure 4-11d (in red), we can find a large G band ($\sim 1580\text{ cm}^{-1}$) from the as grown SWNT film. The high ratio of G band to D band ($\sim 1360\text{ cm}^{-1}$) indicates that this SWNT network was of high quality. The high density SWNT network was used as a frame of a carbon electrode to reinforce the adhesion and mechanical stability of the amorphous carbon film. It was found that the electrodes without SWNT network would fracture when they were peeled off from the quartz substrate, while the electrodes with high density SWNT beneath retained their structural integrity. To demonstrate the stability of the SWNT network under high temperature annealing treatments, a high magnification SEM image at the edge of patterned photoresist-derived carbon on SWNT electrode after carbonized process is presented in Figure 4-11b. We can observe that SWNT network still remained its structural integrity. With photolithography method, the width of the electrodes and the gap in between are well defined to 100 μm . After oxygen plasma treatment, nearly all the uncovered SWNTs were successfully removed, referred to Figure 4-11c. Figure 4-11d shows the Raman spectra of SWNT/carbon composite (in blue) and bare SWNT network (in red) which demonstrates the SWNT network was conformably covered by the photoresist-converted carbon and these metal-free current collectors were mainly constructed by amorphous carbon.

Figure 4-12 (a) CV curves of SWNT/carbon composite electrode at three scan rates of 100, 200 and 500 mV s^{-1} . Comparisons of CV curves between SWNT/carbon electrode (in red) and pure carbon electrodes (in blue) at 1000 mV s^{-1} (b), 2000 mV s^{-1} (c) and 5000 mV s^{-1} (d). (e) Galvanostatic charge/discharge curves of SWNT/carbon electrode at the current density of 0.5, 1.0 and 2.0 $\mu\text{A}/\text{cm}^2$. (f) Complex plane plots of the impedance spectrums for pure carbon and SWNT/carbon electrodes and inserted is the zoom in image at high frequency region.

To evaluate the electrochemical performance of these all carbon based current collectors, we have conducted cyclic voltammetry (CV), galvanostatic charge/discharge measurements. Figure 4-12a is the CV curves of SWNT/carbon composite electrode recorded at different scan rates from 100 to 500 mV s^{-1} . The CV curves of nearly rectangular shape indicate that excellent electrical double layer capacitances were formed within these all carbon materials based electrodes. Rapid current response at the voltage reversals demonstrated that even without traditional metal current collectors, fast charge propagation at electrodes could still be realized, probably due to outstanding conductivity of hybrid carbon film consisting of high density SWNT network and carbon coating. The CV curves between pure carbon electrode and SWNT/carbon composite electrode at higher scan rates from 1000 mV s^{-1} to 5000 mV s^{-1} were compared. According to the CV curves of 1000 mV s^{-1} in Figure 4-12b, the current response of the pure carbon film based electrodes was slightly slower than that of the SWNT/carbon hybrid electrode at the voltage reversal periods. Moreover, when further increasing the scan rates to 2000 mV s^{-1} (Figure 4-12c), distortion of CV curve became more apparent. Up to a scan rate of 5000 mV s^{-1} (Figure 4-12d), the electrode without SWNT was not even able to reach the maximum current density probably because the charge transporting speed within the electrodes could not catch the ultrafast voltage scanning rate. This suggests that by employing high-density SWNT network as the frame of the carbon film, a distinct improvement of the performance of the current collector can be achievable. Galvanostatic charge/discharge measurements are presented in Figure 4-12e. Triangular shape of all curves and no obvious voltage drop at the beginning of every discharge indicate good capacitive behavior of these hybrid carbon electrodes. Besides, from electrochemical impedance spectra (EIS) curves and corresponding zoom in image at the high frequency region in Figure 4-12f, the approximate equivalent series resistance of the electrode has decreased from 1823 ohms for pure carbon electrodes to 323 ohms for SWNT/carbon electrodes, further demonstrating that SWNT network could increase the conductivity of the carbon hybrid current collectors.

To integrally study the electrochemical performance of this carbon hybrid current collector, we calculated areal capacitance (C_A) and stack capacitance (C_S) basing on following equations:

$$C_A = \frac{I}{A \cdot \frac{dV}{dt}} \quad 4 - 4$$

$$C_S = \frac{I}{S \cdot \frac{dV}{dt}} \quad 4 - 5$$

where I is the average current and dV/dt refers to the potential scan rate. A and S stand for the areal and volume of the electrode, respectively. It was found that the areal capacitance of this hybrid carbon electrode was $11.9 \mu\text{F cm}^{-2}$ at a scan rate of 200 mV s^{-1} which was much higher than that of all metal current collectors. As the thickness of this carbon electrode was approximately 270 nm , the calculated volume capacitance based on the all electrode at 50 mV s^{-1} was about 0.43 F cm^{-3} , which is already comparable with the capacitances of some reported advanced MSCs like graphene/CNTs carpet (1.08 F cm^{-3}) [19] and onion-like carbon (1.10 F cm^{-3}) [125] laser reduced graphene (3.10 F cm^{-3}) [154]. To further improve the capacitance of our MSCs, we have deposited MnO_2 nano-flowers on the all carbon based current collectors using electrochemical deposition technique.

Figure 4-13 SEM images of the surface for hybrid carbon electrode (a), the electrodes with MnO_2 depositions for 100 s (b), 200 s (c) and 400 s (d). (e) High magnification SEM image of fully covered electrode (d) Raman spectra before and after MnO_2 electrochemically deposition.

From SEM image of Figure 4-13a, we find after high temperature carbonized process, the surface of the carbon electrode was very uniform and stable. The diameters of MnO₂ nano-flowers and the coverage of MnO₂ can be well-controlled through deposition time. In our case, we employed different deposition times of 100 s, 200 s and 400 s under a constant current density to deposit MnO₂ onto the hybrid carbon electrodes. The corresponding SEM images after MnO₂ deposition are presented in Figure 4-13b, Figure 4-13c and Figure 4-13d respectively. Clearly, the hybrid carbon current collectors are covered with MnO₂ nano-sheets. The dimensions and coverage of MnO₂ nanostructures increased with the deposition time. It was also found that deposition time of approximately 400 s was sufficient to load MnO₂ nanostructures onto the entire surface of the hybrid carbon electrodes and further increasing the time did not increase MnO₂ loading. Figure 4-13e is an enlarged SEM image of fully covered composite electrode under 400 s and MnO₂ nano-sheets in our samples was similar with previous results [146]. In addition to morphology characterization, the Raman spectra before and after MnO₂ growth exhibited in Figure 4-13f. After deposition, the intensities of carbon peaks were apparently reduced. A strong new peak centered at 631 cm⁻¹ which can be assigned to Mn(IV)-O bond vibration in MnO₂ [143] is observed.

Figure 4-14 The CV curves (a) and GV curves (b) for SWNT/carbon electrode and SWNT/carbon electrodes with different MnO₂ Nano-sheets depositions. (c) The CV curves of the fully covered electrode tested at 20, 50 and 100 mV s⁻¹. (d) The GV curves of fully covered electrode tested at 5, 10 and 20 uA cm⁻². (e) Complex plane plots of the impedance spectra for SWNT/carbon electrodes and SWNT/carbon/MnO₂ (inserted is zoom in image at high frequency region). (f) Specific capacitance of SWNT/carbon/MnO₂ electrodes based solid MSC as a function of cycle number.

The electrochemical performance results of the different MSCs are revealed in Figure 4-14. Firstly, we compared the hybrid SWNT/carbon electrodes with the electrodes partially coated with MnO₂ nanostructures. Notably, from the CV curves (Figure 4-14a) and galvanostatic voltammetry (GV) curves (Figure 4-14b), an efficient and gradual enhancement of the capacitance was realized, where nearly ideal rectangular shapes of the CV curves and almost symmetric shapes of GV curves after MnO₂ loading, suggesting that the excellent capacitive behaviors of all MSCs were enhanced after MnO₂ nanostructure deposition. Along with increasing MnO₂ loading, both current densities of CV measurements and charging/discharging times of GV measurements significantly increased. With Equations 4-5 and 4-6, the calculated areal capacitance of sample with the 100 s MnO₂ deposition was increased from 11.9 $\mu\text{F cm}^{-2}$ to 54.2 $\mu\text{F cm}^{-2}$ at a scan rate of 50 mV s^{-1} and for the 200 s deposition device, the areal capacitance was effectively increased to 131.2 $\mu\text{F cm}^{-2}$. As presented in Figure 4-14c, the CV curves at different scan rates are studied. One can see the pseudo capacitive behavior of MSC became much more significant after more MnO₂ deposition is loaded. This can be attributed to enhancement of Faradaic redox reactions of Mn(IV)/Mn(III) redox couples [146] within the electrodes during the charge/discharge processes. Regarding to the GV curves in Figure 4-14d, several slight potential plateaus can be observed in both charge and discharge periods. Remarkably, the areal capacitance of the fully covered electrode reached 550 $\mu\text{F cm}^{-2}$ at a scan rate of 20 mV s^{-1} , almost 43.6 times larger than that of the electrode without MnO₂ nanostructure deposition. The stack capacitance was even increased to 20.4 F cm^{-3} . This value is much higher than those for planar carbon based MSC reported before. [19, 125, 130, 134, 154] From the high magnification Nyquist plots in Figure 4-14e, one could find an obvious semicircle appeared at the high frequency region after MnO₂ nanostructure loading, indicating that the enlarged capacitive property of MSC was realized and pseudo capacitance caused by Mn(IV)/Mn(III) redox couples does exist. However, there was a slight decrease in ESR for MnO₂ fully covered MSC. This could be attributed to two aspects. Firstly, MnO₂ is a material of high resistivity compared with graphited carbon and, secondly, electrons

transporting length could increase after MnO_2 coating. All these affect the conductivity of the entire electrode. Finally, to demonstrate applicability of our MSC, we have assembled this MSC in all solid-state with polymer based electrolyte on a soft substrate (Polyimide). Encouragingly, this metal-free SWNT/carbon/ MnO_2 hybrid electrodes based MSC remains 92.4% of the initial capacitance after 5000 cycles (Figure 4-14f), showing the long-life time and outstanding stability.

4.2.4 Conclusion

We have replaced the common metal current collectors with SWNT network and photoresist-derived carbon composite current collectors in planar MSCs. The good conductivity and superior electrochemical performance of the novel current collectors have been demonstrated. Moreover, we have successfully deposited MnO_2 nanostructures on the carbon hybrid collectors to further increase the energy storage capability of the MSCs. It is found that the MnO_2 nanostructure decorated carbon hybrid electrodes show higher areal capacitance and stack capacitance than those of carbon based collectors and metal collectors in MSC reported so far. The as-prepared MSCs present excellent electrochemical performance of high energy storage capability, long-life cycles and good rate performance on a soft substrate which could be a promising candidate for integration with new generation microelectronic devices in future.

5. Integration of energy storage devices with microelectronic devices

5.1 Integration of a UV detector and a supercapacitor on SiNWs array

5.1.1 Introduction

Low-cost and fast response ultraviolet (UV) photodetectors are in great demand for various applications, such as safety/security monitoring, environmental monitoring and space-to-space communication technologies, etc. [167-170] Many approaches, including p-n junctions [171], p-i-n photodiodes [172], Schottky barrier and metal-semiconductor-metal structures [173], have been utilized to improve the sensing performances and reduce the power consumption of UV detectors. Among these UV detectors, one-dimensional (1D) nanostructure based UV detectors have attracted a lot of attention. Ti_2O_3 nanowire [174], ZnO nanowire [175], and V_2O_5 nanowire [176] based detectors have shown excellent sensitivities to UV light due to the high surface to volume ratios of 1D nanostructures. [177]

In addition to the high sensitivity, research is also focused on reducing the power consumption of UV detectors. For example, photodetectors based on photo-electrochemical cells (PECs) [178] were of a “self-powered” function, or in other words, the detectors could function with the energy from the PECs without any external power source. [179] Note that resulting from miniaturization of the detectors, large driving power is no longer required so that “self-powered” detectors become feasible and promising. Indeed, integrated with tiny power sources, like a micro-batteries [180] or micro-supercapacitors (MSC) [154], the detector can have a very high integrability. Kim et al. [152] have successfully integrated a multi-walled carbon nanotube/ V_2O_5 nanowire based MSC with a SnO_2 nanowires UV sensor, in which the MSC was able to power the UV sensor. However, as the UV sensor and MSC were made of different nanomaterials, their devices were not seamlessly integrated and fabricated with complicated processes. It is noted that some semiconductor nanowires are both promising candidate materials for photo-response and energy storage devices. Hou et al. [181] developed a bi-functional nanosystem, in which flexible SnO_2 nanowires coated on

carbon cloth functioned as a fast response UV photodetector and the anode material of a binder-free lithium-ion batteries (LIB). However, despite the UV detector exhibited a high performance, the UV detector and battery were not integrated on the same substrate.

Taking the compatibility of silicon wafer technology into consideration, silicon nanowires (SiNWs) have been used for this “self-powered” UV photodetectors [182-183]. Moreover, energy storage devices like LIBs [22, 184-185] and MSCs [186] based on silicon nanowires have also shown high-power capacities and robust cycle lifetimes. Especially, the ultrathin carbon sheath on SiNWs in the MSC fabricated by Maboudian’s group [42] demonstrated the enabling of a high energy density MSC on a silicon substrate.

Figure 5-1 Fabrication process and structure of the UV detector.

In this section, we show our design and fabrication of a “self-powered” UV detector on a silicon substrate. The device structure and fabrication processes are shown in Figure 5-1. Vertically aligned SiNW array (Figure 5-1a) was prepared using a wet-etching method reported previously by our group [119], with which the SiNW array could be produced under a large scale at a low cost. Then, carbon walls were selectively grown on the predefined area of the SiNW array (Figure 5-1b) so that the carbon coated SiNWs array was used as the active material of the supercapacitor. A full MSC was assembled in a sandwich structure with a polymer solid electrolyte in between two carbon coated SiNW arrays as the electrodes (Figure 5-1c). After the MSC was assembled, it was fully charged in 80~100 seconds (Figure 5-1d) and then self-discharged through the UV detector which was constructed with SiNWs without carbon coating. Upon UV illumination (Figure 5-1e), the bare SiNW area exhibited a fast response and the photo-generated carriers would diffuse into the MSC due to concentration gradient of carriers over the whole electrode (Figure 5-1f) so that the current crossing the circuit was increased from the original self-discharge current. The external potential between the two electrodes of the MSC were increased in response to the intensity of UV light. By employing SiNWs as the photo response material and electrodes of the MSC, we could achieve three unique advantages: 1. because the UV sensor and MSC are based on the same SiNW array substrate, the fabrication processes were much simple. The high surface to volume ratio of SiNW array is favorable to fast UV detection and high energy storage capacity as well; 2. Due to the special design, the UV detector was of extremely low power consumption so that it functioned more than ten hours in one discharge process after the MSC was fully charged in less than 100 seconds; 3. The integrated device consisted of only solid materials and manufactured on the same silicon substrate. Thus, the device could be easily integrated with other devices on a silicon wafer.

5.1.2 Experimental details

SiNWs were synthesized using the technique discussed in our previous publication [119]. Briefly speaking, a thin layer of silver was deposited on a silicon wafer by electron beam evaporation and the wafer was then annealed in a high

temperature of 800 °C to form Ag particles. A Ti/Au bi-layer was sequentially deposited on the Si wafer and then the sacrificial Ag particles were removed by ultrasonic to obtain a Ti/Au bi-layer (catalyst) mesh. Finally, the wafer was immersed into an etching solution (89% deionized water, 10% HF and 1% H₂O₂) to obtain a vertically aligned SiNW array on the silicon substrate. The height of SiNWs was controlled by the etching time, temperature and the concentration of the etching solution. Interconnected carbon walls were incorporated through dropping cast sugar solution (2 mg sugar to 100 ml DI water) onto the SiNW array and annealing at 700 °C for 2 hours under Ar/H₂ protection atmosphere. A typical solid electrolyte was prepared through mixing 6 g H₃PO₄, 6 g PVA and 60 ml DI water and heating up to 90 °C under vigorous stirring. The complete MSC was assembled with two pieces of carbon wall interconnected SiNWs array facing each other, but separated by the mixture gel electrolyte. Drying naturally in air over 12 hours was necessary to have a high performance MSC.

The morphology and characterizations of bare SiNWs and carbon wall interconnected SiNWs were studied using the field-emission scanning electron microscopy (SEM, LEO 1550 Gemini) and the Raman system (WITec) under a 532 nm wavelength excitation, respectively. Electrochemical characterizations of the MSC and photo responsivity of self-powered detector were carried out through an electrochemical workstation (AUTOLAB, M 101). The UV photo response currents of the bare SiNWs array were performed at room temperature and recorded by Agilent B1500A. The UV light illumination was performed using Lamplic 365 nm UV LED flashlight.

5.1.3 Results and discussion

Figure 5-2 Tilt view SEM image (a) and cross-section view SEM image (b) of a bare SiNW array. Tilt view SEM image (c) and top view SEM image (d) of a carbon wall coated SiNWs array.

Figures 5-2a and Figure 5-2c present 15 degrees tilted SEM images of the bare SiNW array and carbon wall coated SiNW array, respectively. In comparison with Figure 5-2b, no apparent damage to the structure of SiNW array was found after carbon wall coating was introduced. Compared with the high magnification SEM images before (Figure 5-2b) and after (Figure 5-2c) carbon coating, one can see that the carbon walls were conformally connected to SiNWs. The ultrathin carbon walls could largely increase the surface interface area of the electrodes of the MSC. From the top-view SEM image of the carbon wall coated SiNW array (Figure 5-2d), each silicon nanowire was connected with more than one carbon wall on average although the positions of the carbon walls were random. Overall uniform distribution of the carbon walls and SiNWs was found and it is sufficient for supercapacitor application as a good periodicity is not necessary. As the SiNW array was produced by a diameter-controllable method of our group, the average diameter and length of the SiNWs array employed in this work were approximate 150 nm and 5 μm , respectively. The Raman scattering from the SiNWs array with and without carbon wall coating is shown in Figure 5-3. Two peaks at ~ 1360 and $\sim 1580\text{ cm}^{-1}$ corresponding to the disordered band (D band) and the graphitic band (G band) were clearly observed from the carbon walls. The high magnification SEM image in Figure 5-3 determined the thickness of the carbon walls was around 10 nm.

Figure 5-3 The Raman spectra of the SiNWs with/without carbon-wall coating. The inset: a high magnification top-view SEM image of a SiNW and a single carbon wall.

The symmetric electrochemical MSC consisted of two identical carbon coated SiNW arrays as the positive and negative electrodes and polyvinyl alcohol (PVA):H₃PO₄ was used as the solid electrolyte. The MSC characteristics were studied through cyclic voltammograms (CV) and galvanostatic charging/discharging testing in a symmetric two-electrode configuration. During the CV measurements, several scanning rates were applied from 1 mV s⁻¹ to 20 mV s⁻¹. The CV curves in Figure 5-4a exhibit symmetrical and nearly rectangular shapes at different scanning rates, indicating an excellent capacitive behavior because the carbon is a promising supercapacitor material for its outstanding stability and good conductivity. In addition, a control sample having two bare SiNW arrays as its electrodes without incorporation of any carbon walls presented a much lower current density (the black curve in Figure 5-4a) at corresponding scanning rate, strongly suggesting that the interconnected carbon walls in the electrodes of the MSC played a dominant role of enhancing its capacitance. In addition, the spacing between the two SiNW arrays and carbon walls were controlled to let the solid gel electrolyte penetrate into the electrodes to maintain a stable potential window within 0.8 V. The areal capacitance of the MSC was calculated from the galvanostatic charging/discharging results according to the relation of $C_{\text{areal}} = i / [(dt/dV) A]$ where i is the applied current, dV/dt is the slop of the discharge curve after IR (resistive component of the MSC) drop and A refers to the electrode areal of the MSC. From Figure 5-4b, an areal capacitance of approximate 6.8 mF cm⁻² was obtained from which we could calculate the volumetric capacitance of the MSC was 13.6 F cm⁻³. At different current rates, charge/discharge profiles revealed nearly symmetric triangle shapes, suggesting an excellent capacitive behavior of this MSC. In addition, the areal capacitance of the MSC was found to be more than 1000 times larger than that of the control sample where no any carbon walls were introduced, further confirming that the extremely thin interconnected carbon walls were responsible to the capacitive performance enhancement.

Figure 5-4 (a) Cyclic voltammogram curves at different scan rates and (b) galvanostatic charging/discharging curves measured under different densities for the MSC and the control sample (in black).

To evaluate the UV detection sensitivity of the SiNW array, the time-resolved UV light response current was measured from a bare SiNW array under a bias voltage of 0.8 V, which corresponded to the maximum voltage of the MSC. During the measurements, the SiNW array with an area of 0.4 cm^2 was illuminated with 30 mW cm^{-2} UV light ($\lambda=365 \text{ nm}$), while the bulk silicon substrate acted as the back electrode (refers to Figure 5-5a). All the testing setups were covered with an alumina foil to avoid the environmental light affect. From the results shown in Figure 5-5b, a significant current increase upon the UV light illumination was observed. The detector preformed a stable response with a rise time (it stands for the time that current takes for rising to 63% of response current) of 1.0 s and a decay time (the time takes for decreasing by 63% of the response current) of 1.5 s. Figure 5-5c shows the repeatable response of the photocurrent under a periodic UV light rectangle pulses, strongly suggesting an outstanding stability of the detector. As the MSC and detector were integrated on the same silicon substrate, the high resistance of the substrate could have a negative impact on the sensitivity of the detector. Better performance of the integrated device could be achievable through optimizing the device structure and applied material.

Figure 5-5 (a) Schematic of bare SiNWs array UV light response. (b) Time-resolved current response to UV light of the UV detector at a bias voltage of 0.8 V. (c) The photoresponse upon a periodic UV light rectangle pulse excitation.

Figure 5-6 (a) The charge/self-discharge curves of the MSC integrated with UV detector from 0.3 to 0.8 V. (b) One complete charge/self-discharge curve from 0.2 to 0.8 V (The charging current was $20 \mu\text{A}/\text{cm}^2$ in the all measurements). The UV light potential response of this self-powered UV detector in fast decay regime (c) and slow decay regime (d). (e) Equivalent circuit of detector under UV illumination. (f) Photoresponse voltage of the device as a function of the incident UV ($\lambda=365 \text{ nm}$) intensity at the slow decay regime.

Integration of the UV detector with the MSC was implemented according to the schematic drawing in Figure 5-1, in which the ratio of the MSC area (carbon wall coated SiNWs array) to the sensing area (bare SiNWs) was around 0.67. Cycled charge/self-discharge measurements were performed in a potential range from 0.3 to 0.8 V, as shown in Figure 5-6a. In all the measurements, the MSC was charged to 0.8V with a constant current density of $20 \mu\text{A cm}^{-2}$ and followed with self-discharge through a voltmeter (Figure 5-1e). The repeatable voltage variations suggest that the embedded MSC is very stable. Figure 5-6b presents one complete charge/self-discharge curve in a potential window of 0.2-0.8V. It reveals that with a very short charging time (less than 100 s) and the MSC could self-discharge to 0.2 V in 10 hours. In other words, the MSC could power the UV detector for more than 10 hours after less than 100 s charging. From the discharge profile, it can be divided into two regimes: the potential range between 0.8 and 0.3 V refers to a fast decay process and the potential less than 0.3 V refers to a slow decay process. Upon UV light illumination, the external circuit potential increase (0.03-0.12 V) between the two electrodes of the MSC was clearly observed. Figures 5-6c and 5-6d show the UV light potential responses in the fast and slow decay process, respectively, with a maximum on/off potential ratio of 1.5. It has been suggested that the self-discharge process could be dominated with two mechanisms. In the fast decay regime, a diffusion process would affect the self-discharge as some ionic species in electrolyte form a high concentration near the surfaces of the electrodes [187]. During the slow decay regime, most diffusion capacitance of MSC would be consumed so that the MSC would behave like an ordinary capacitor. The device can be represented by an ideal capacitor C , a parallel resistor R_p and a series resistor R_s , see Figure 5-6e. R_p can be attributed to the current leakage through the double-layer capacitance which would exist all over the self-discharge process [188] and it is largely determined by the spacing between the two electrodes and the electrolyte used. It would be not affected by UV light illumination. In contrast, R_s is dominated by the resistance of the silicon substrate whose resistance would largely affected by UV light illumination. When the device was connected to a voltmeter, the internal resistance of the voltmeter, R_{in} , should be introduced to

complete the entire circuit. As R_{in} and R_p are of very large resistance, the voltage measured by the voltmeter can be approximately expressed as:

$$V_{out}(t) \cong \frac{R_{in}V_0}{R_s + R_{in}} \exp \left[-\frac{(R_{in} + R_p)t}{CR_{in}R_p} \right] \quad 5-1$$

where V_0 is the potential difference caused by the double-layer capacitance component of the MSC. Upon UV light illumination, photocarriers would be generated in the area of the UV sensing SiNWs and they could easily diffuse into the negative electrode of the MSC, causing a reduction in R_s , or an increase in the voltage V_{out} . Thus the increasing photoresponse voltage, V_{ph} is equal to δV_{out} : $V_{ph} = \delta V_{out}(t) \cong -V_{out}(t) \frac{\delta R_s}{R_s + R_{in}}$. During the slow decay process, the measured V_{ph} was found to be highly repeatable, ‘sitting’ on the slowly decayed discharge current. The photoresponse rising voltage V_{ph} is nearly linearly proportional to the series resistant variation δR_s . The incident UV light intensity dependence of the photoresponse voltage of this device at the slow decay regime is shown in Figure 5-6f. The induced photoresponse voltage, V_{ph} , follows a power-law relationship with the intensity, P : $V_{ph} \propto P^{0.245}$. The fitting result is consistent with other nanostructure based photo-detectors [174, 189] and the non-unity power law factor is thought to be caused by two reasons, i.e., (1) hole-trap saturation phenomenon could occur at high light intensities and (2) the complex electron-hole generation/recombination process for the semiconductor photodetector. [190]

5.1.4 Conclusion

A well-integrated device in which a micro-supercapacitor (MSC) and UV detector are fabricated on a common silicon substrate has been demonstrated. One-dimensional SiNW array on the silicon substrate functions as the UV sensing element, while SiNWs interconnected with ultra-thin carbon walls serve as the electrodes of the MSC. The excellent rate performance and high power density have been achieved for the MSC. The UV detector shows a maximum on/off potential ratio of 1.5. Upon charging in less than 100 s, the charged MSC is able to drive the detector for ~10 hours during its discharge process.

6. Conclusions and recommendation

6.1 Conclusions

This thesis focuses on the energy storage applications of 1D nanostructured materials, including CNTs and SiNWs *etc.* Due to large surface to volume ratio and unique properties, high quality CNTs and SiNWs are promising materials for fabricating new-generation high-performance energy storage devices. Instead of directly employing these two materials as the active electrodes, we have designed and fabricated some novel nanostructures based on these 1D nanomaterials.

We have successfully grown vertical-aligned CNT array on several different substrates which are good current collectors for electrochemical cells. A standard stainless steel for CR2032 mode coin cell has been applied as a substrate to support our VACNT array. In this way, we were able to directly measure the energy storage performances of VACNT array based anodes. Beside this traditional stainless steel current collector, we also used carbon cloth, a new-type microfibers constructed substrate, to fabricate flexible electrodes for LIBs. We also tried to grow VACNT array on patterned interdigital microelectrodes through wafer process technology. A pair of VACNT based planar electrodes for electrochemical cell has been achieved which demonstrated the integration potential between VACNT and micro energy storage devices.

Apart from CNTs, we also developed a reliable, scalable and cost-effective method to fabricate one-dimensional vertical-aligned SiNW arrays with controllable diameters and interspacing. In this technique, a simple de-wetting process of silver ultrathin film was deposited to synthesize a randomly well-spaced metal particle monolayer which functioned as the mask to etch SiNWs array. Through modulating the thickness of silver film, the dimensions and interspacing between nanoparticles could be well controlled. Therefore, the morphology of SiNWs array was simply defined by changing the thickness of de-wetting metals. From the experimental results of SiNWs arrays produced with different silver thickness, we found that the diameters of SiNWs array increased consistently with

the thickness of silver film increasing. This fabrication method is applicable for large-scale applications.

Subsequently, we have applied mentioned 1D nanomaterials to energy storage devices. Firstly, we have employed VACNT array to optimize the LIBs anode performance. After introducing 1D nanostructure VACNT array to the Sn/VACNT composite anode, a great electrochemical performance improvement could be achieved because of the large interspacing and excellent electron transport pathway formed by the well-aligned VACNT array. From the measurement results, this novel Sn decorated VACNT array anode presented a superior capacity retention capability in different electrochemical tests and an excellent reversible capacity of 930.8 mAh g⁻¹ after 400 cycles at a current rate of 0.2 C and a reversible capacity of 380.9 mAh g⁻¹ after 1000 cycles at current rate of 0.5 C. In addition, even after 200 cycles, the electrode still showed very high rate performance and good stability.

We also fabricated high performance LIBs anodes using SiNW arrays. Different from VACNT array, we did not use SiNWs array as the active materials or supporters. We employed SiNWs as the sacrificial template to fabricate a free-standing and binder-free copper-silicon core-shell nanotubes array based electrodes. Outstanding electrochemical performance of this superior anode has been demonstrated. Benefiting to the vertical-aligned nanostructure and feasible template used in syntheses, this anode was of a long cycle life for lasting 400 cycles with less than 0.1% capacity fading rate and was able to maintain an excellent structure stability with a specific capacity as high as 1506 mAh g⁻¹ after 400 cycles. Even after undergoing 12 C high current rate testing, the reversible capacity kept at 97.4% of initial value as long as the current rate was returned to 0.3 C. Encouragingly, this developed architecture could be applied on other functional nanostructured materials as well. We were the first to use customized silicon nanowire array as the template to fabricate 1D nanotube arrays.

We also paid our attention to a new type energy storage device i.e. micro-supercapacitors. At first, we used VACNT to enhance the specific capacitance, energy density, rate performance, operation potential window and cycling performance of the MSCs. The as-prepared symmetric MSCs presented

tremendous improvements in both areal and volumetric capacitance. Meanwhile, the asymmetric MSC successfully demonstrated a broadened operation potential window. In addition, the advanced MSCs maintain the outstanding high power delivery capability, high rate performance and superior cycling stability, suggesting that the developed MSCs can be integrated with other microelectronic devices on the same substrate.

As flexible and bendable energy storage devices will play a major role, we have replaced the common metal current collectors with SWNT network and photoresist-derived carbon composite current collectors in planar MSCs. The good conductivity and superior electrochemical performance of the novel current collectors have been demonstrated. Moreover, we have successfully deposited MnO_2 nanostructures on the carbon hybrid collectors to further increase the energy storage capability of the MSCs. It was found that the MnO_2 nanostructure decorated carbon hybrid electrodes showed higher areal capacitance and a good stability on flexible substrate. The as-prepared MSCs presented excellent electrochemical performance of high energy storage capability, long-life cycles and good rate performance on a soft substrate.

Last, we have realized the integration between energy storage devices and traditional microelectronic devices on the same substrate. Integrating the energy storage units with these low power consumption microelectronic devices is of great interests. Considering the outstanding electrochemical performance of 1D nanostructured materials, we have integrated a supercapacitor and UV detector on a silicon substrate, where one-dimensional SiNWs array functioned as a UV sensing element, while SiNWs interconnected with ultra-thin carbon walls served as the electrodes of the MSC. The excellent rate performance and high power density have been achieved for the MSC. The UV detector showed a maximum on/off potential ratio of 1.5. Upon charging in less than 100 s, the charged MSC was able to drive the detector for ~10 hours during its discharge process.

6.2 Recommendation

In this thesis, we have demonstrated the performance improvements of both LIBs and MSCs by applying 1D nanostructured materials, especially CNTs and SiNWs produced using our own approaches. Besides, we have also made a lot of efforts to integrate our 1D nanostructured materials constructed energy storage devices with the traditional microelectronics devices.

Although impressive improvements have been achieved, further efforts are required. Recently, some scientists have focused on sodium ion battery and lithium sulfide battery which are of higher energy densities. However, the cycling performance and stability of these two types of batteries could not meet the industry requirements. Therefore applying the 1D nanostructure to the electrodes of these batteries should be a promising approach to increase the life time and improve the capacity retentions capabilities.

For micro-supercapacitors fabricated in this thesis, the active materials are usually made of nanostructured metal oxide. 1D nanomaterials played a supporting role. Although, the 1D nanostructured materials could effectively enhance the cycling performance and electrons delivery capability, the energy densities and specific capacitance are constrained by the nature of active materials. Nevertheless, it has been found that metal sulfide and metal nitride could have much higher theoretical capacitance. Thus, replacing the metal oxide applied in this work with these new materials would be an interesting research topic.

Integration of energy storage devices with microelectronic devices would have significance in future electronics. New design is required to develop on-chip MSC together with the sensors/functional devices and this self-powered microelectronic system would be a new hot topic in the near future.

Publication

Journal paper

1. **Leimeng Sun**, Xinghui Wang, Kang Zhang, Jianping Zou, Zhiyu Yan, Xiaonan Hu and Qing Zhang* “Bi-functional electrode for UV detector and supercapacitor” *Nano Energy* 2015, 15, 445-452.
2. **Leimeng Sun**, Xinghui Wang, Kang Zhang, Jianping Zou, Qing Zhang* “Metal-free SWNT/carbon/MnO₂ hybrid electrode for high performance coplanar micro-supercapacitors” *Nano Energy* 2016, 22, 11-18.
3. **Leimeng Sun**, Xinghui Wang, Rahmat Agung Susantyoko, and Qing Zhang* “High performance binder-free Sn coated carbon nanotube array anode” *Carbon* 2015, 82, 282-287.
4. **Leimeng Sun**, Xinghui Wang, Rahmat Agung Susantyoko and Qing Zhang* “Copper-Silicon Core-Shell Nanotube Arrays for Free-Standing Lithium Ion Battery Anodes” *Journal of Materials Chemistry A* 2014, 2 (37), 15294-15297.
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6. Xinghui Wang†, **Leimeng Sun**†, Xiaonan Hu, Rahmat Agung Susantyoko, and Qing Zhang* “Ni-Si nanosheet network as high performance anode for Li ion batteries” *Journal of Power Sources* 2015, 280, 393-396. (†Contribute equally)
7. **Leimeng Sun**, Xinghui Wang, Wenwen Liu, Kang Zhang, Jianping Zou and Qing Zhang* “Optimization of coplanar high rate supercapacitors” *Journal of Power Sources* 2016, 315, 1-8.
8. Xinghui Wang†, **Leimeng Sun**†, Rahmat Agung Susantyoko, Qing Zhang* “A hierarchical 3D carbon nanostructure for high areal capacity and flexible lithium ion batteries” *Carbon* 2016, 98, 504-509. (†Contribute equally)
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Conference

1. **Leimeng Sun**, Xinghui Wang and Qing Zhang* "Asymmetric design for high voltage planar supercapacitor" Poster in *The International Conference on Materials for Advanced Technologies (ICMAT2015)* **2015.07**, Singapore.
2. Xinghui Wang, Cao Guan, **Leimeng Sun**, Rahmat Agung Susantyoko, Hongjin Fan, and Qing Zhang* "Hierarchical 3D nanocarbon based current collectors for flexible battery electrodes" Poster in *The International Conference on Materials for Advanced Technologies (ICMAT2015)* **2015.07**, Singapore.

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