POLYANILINE AND GRAPHENE BASED SYMMETRIC AND ASYMMETRIC
SOLIDE-STATE SUPERCAPACITOR

A Thesis

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ABSTRACT

The great demands of electronics is stimulated the development of portable energy storage devices. Supercapacitors show great potentials with its high power density and fast charge-discharge rate. Graphene material has advantages of high surface area, good electrical conductivity and is a promising material for fabrication of the electrical double layer capacitors. But the inevitable stacking between graphene sheets restricts the performance of the materials. Polyaniline (PANI) exhibits high intrinsic specific capacitance and good environmental stability, which is a promising candidate for pseudo capacitors. However, the shrinkage and swelling of PANI in charge-discharge process give the material mechanical degradation and less cycle stability.

Here, we fabricate polyaniline/graphene composite electrode and get the synergistic effect of the electrochemical performance from the two materials. The specific capacitance is significantly improved and the energy density of devices is also enhanced. The improvement comes from the combination of two materials. Meanwhile the morphology of the PANI also plays an important role in device performance. The nano-arrays we got in this study is uniform nano-dot and nano-fiber. We investigated different synthesis environments influencing the morphology of PANI and got morphology of nano-dot and nano-fiber. The uniform nano-array of PANI alleviates the aggregation of graphene sheet and thus gives an increase of surface area and pathways of ion diffusion.
Liquid electrolyte based supercapacitors has problem with high-cost package, electrolyte leakage, large-scale production and flexibility of device. However, with the solid-state supercapacitors fabrication we resolve this problem.

In our study, we fabricate both symmetric and asymmetric solid-state supercapacitors configuration. The symmetric supercapacitors can reach specific capacitance as 639 F/g high and the stability of device is 70% retention after 10,000 charge-discharge cycles. Both of these characteristic is higher than that of graphene based devices. To improve the work voltage of supercapacitors, we develop asymmetric supercapacitors configuration with PANI/graphene composite as positive electrode and graphene as negative electrode. The asymmetric device configuration can reach work voltage two times higher as that of symmetric device and the energy density is also enhanced 46%. The tandem devices we made can enlighten the blue LED over seventy seconds.
ACKNOWLEDGEMENTS

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CHAPTER I

ELECTROCHEMICAL SUPERCAPACITOR

1.1 Energy storage

With great development of portable electronics these days, it’s an attractive research attention for energy storage device. The applications of the energy storage device tends to be more flexible, portable and higher efficiency.\textsuperscript{1-3} Currently existing energy conversion storage device is various including fuel cell, battery, and capacitor et al. Shown with Figure 1.1, supercapacitors (SCs) bridge gaps between batteries and conventional capacitors in terms of the energy density and power density.\textsuperscript{4} Due to the different mechanism of the charge accumulation for SCs, the storage and delivery of charges happen quickly thus leading to the higher power density compared with batteries, which gives high potential for various application of SCs in back-up power systems, hybrid electric vehicles and industrial energy management systems.\textsuperscript{5,6} The global market size for the supercapacitor in 2014 was recorded at roughly US$ 3.8 billion and is expected with a compound average growth rate (CAGT) of 21.3% in
following years (2014-2019). The great demand of the application will absolutely drive the continuous development in the technology to improve the performance of the SCs performance. In our study, we want to improve the performance of supercapacitor base on graphene/PANI composite electrode and get synergistic effect of the two electrode material.

1.2 Two kinds of Supercapacitor

Based on the charge accumulations happening on the electrodes, there are two kinds of supercapacitor, electrical double layer capacitor (EDLC) and pseudo capacitor. For EDLC the storage of charges is achieved through electrostatic adsorption, which means great reversibility for device but gives low capacitance and energy density meanwhile. Carbon material is with the characteristics of good conductivity, a mitigation for the cycle degradation and cheap fabrication, which results it in an excellent candidate for electrodes in EDLC. Pseudo capacitors derive from fast and reversible redox reactions on electrodes, which exhibits an increased capacitance and fast charge-discharge rate for device. However, the stability of pseudo capacitors suffers from redox reactions on electrodes. Transition metal oxide and conducting polymers, like polyaniline (PANI), polypyrrole, and polythiophene, attracted great attention for the use of electrode in pseudo capacitors due to the characteristics of high power density and energy density.
1.3 Electrode materials for SCs

According to the different kinds of SCs, the material for electrodes is included with use of EDLC and that of pseudo capacitor. Mostly carbon material is used for the electrode of the EDLC. And metal oxide and conducting polymer are material used for the pseudo capacitor. Therefore, in the following part we will divide these three kinds of material.

![Figure 1.1 Ragone plot for different energy storage technologies.](image)

**Figure 1.1 Ragone plot for different energy storage technologies.**

1.3.1 Carbon electrode

Carbon material shows great advantages for the application as the electrode material over sufficient abundance, chemical stability, high specific area, good conductivity and wide operating temperature range. Usually the cyclic voltammetry (CV) curves for the carbon based supercapacitors have good shape of rectangular and the galvanostatic charge-discharge curves of that also shows symmetric triangle shape, which indicates a characteristic of electrochemical double layer capacitor and the material is well capacitive. As the charge accumulations happen on the interface of electrode and
electrolyte, the surface area of the carbon material accessible for electrolyte ions is a truly important factor to limit device performance. Therefore carbon nano tubes, activated carbon, carbon areogels and graphene are coming into our sight with their advantage over high surface area.\textsuperscript{15-18} Two-dimensional graphene nano-sheets show attractive potential with high electrical conductivity, high surface area, good mechanical property and easily chemical modified.\textsuperscript{19-22}

Figure 1.2 (a) CV curves of an activated mesocarbon microbeads (AMCMBs)/CNTs compound electrode at different scan rates (10, 40, 80, and 160 mV s\textsuperscript{-1}); (b) galvanostatic charge–discharge curves of the AMCMBs/CNTs compound electrode at a constant current of 0.5A g\textsuperscript{-1}.\textsuperscript{14}

1.3.2 Metal oxide

Metal oxide has large energy density for application as electrode due to the electrochemical reactions happening between the electrodes and ions in electrolyte. To satisfy the requirement for the application, the metal oxide usually should have characteristics: good conductive material, more than one oxidation state and easily intercalated with ions.\textsuperscript{23} According to this, there are several materials investigated like
Ruthenium oxide, manganese oxide, cobalt oxide, nickle oxide and vanadium oxide etc.

Ruthenium oxide (RuO$_2$) is extensively attractive for its wide potential window, good conductivity, high specific area, long cycle life and high rate capacity. The specific area of the material truly influences the device performance by providing more capable metal centers for redox reactions. Also, the amorphous structure facilitate the redox reaction both on the surface and the bulk of the powder, which gives it superior device performance than crystalline structure. Therefore, the synthesis parameter plays an important role, like temperature etc. As the redox reaction for the material happens through the hopping of alkaline ions and H$^+$ ions in H$_2$O and OH$^-$ sites, the combination of water with RuO$_2$ will significantly enhance the cation diffusion in the electrode layer. It is reported that the hydrous RuO$_2$ (RuO$_2.0.5$H$_2$O) can reach capacitance as 970F/g. And the water content can absolutely derive different device performance. Sugimoto et al. has reported the water content dependence of device performance, shown in Table 1. However, the drawbacks for the ruthenium oxide is mainly its high cost and harmfulness for environment, which restricts its widely commercial application.

Compared with RuO$_2$, manganese oxide is lower cost, less toxicity, high capacitance (ranging from 1100F/g to 1300F/g). The capacitance of manganese oxide mainly attributes from the oxidation state transition between Mn(III)/Mn(II), Mn(IV)/Mn(III), and Mn(VI)/Mn(IV). In spite of this, the CV curves of manganese oxide also show similar rectangular shape (Figure 1.3), which indicates similar to non-faradic mechanism for energy storage.
Similar to the RuO$_2$, the crystallinity also has influence on the capacitance performance. The trade-off of conductivity and ions transport exists for crystallinity issue. Moreover, the specific area and low conductivity is a concern for good performance of this material. To solve this problem, different dopants can be used to address. Metals like cobalt$^{28,35,41}$, nickle$^{38-40}$, molybdenum$^{42}$ are helpful to improve the performance. Additionally, carbon materials such as activated carbon, carbon nano tube and graphite and conducting polymer can also be utilized to promote the conductivity.

Table 1.1 Specific capacitance calculated by cyclic voltammetry at different scan rates for RuO$_2$.xH$_2$O$^{27}$

1.3.3 Conducting polymer

Conducting polymer is investigated for their low cost, good conductivity, high specific capacitance and environmental friendly. As there is no structural alternations for polymer during charge-discharge process, the reversibility of conducting polymer is high$^{23}$ and the capacitance comes not only from the surface of the material but also from the entire bulk.$^{43}$ Widely investigated polymers are polyaniline (PANI), polypyrrol (PPy) and polythiophene (PTh)$^{44-47}$.

PPy

Polypyrrol is considered to be a promising material for the application of the electrode in supercapacitors due to the characteristic of high conductivity, high capacitance, good stability and low cost.$^{48-50}$ The application of PPy is mostly on the composite material with carbon or metal oxide. In this way, the synergistic effects of materials show better device performance and avoid the degradation of the PPy during charge-discharge
process. Jiayou Tao et al. reported an electrochemical deposition method to integrate PPy/MnO$_2$/carbon fiber and thus fabricated flexible supercapacitor device with specific capacitance of 69.3 F cm$^{-3}$. Cheng Zhou et al.

Table 1.1 Specific capacitance calculated by cyclic voltammetry at different scan rates for RuO$_2$.xH$_2$O$^{27}$

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<tr>
<th>Scan rate/mV s$^{-1}$</th>
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<td>200</td>
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Figure 1.3 CV curves of MnO$_2$-based electrodes in 1 M Na$_2$SO$_4$ electrolyte with scan rate of 5 mV/s. (a) MnO$_2$ obtained by using CNT and (b) MnO$_2$ obtained by using mesoporous carbon.$^{37}$
synthesized PPy on the CoO nanowire with the nickel template and got the specific capacitance as high as $2223 \text{ F g}^{-1}$.\textsuperscript{49} The significant improvement in device performance comes from the decrease of the equivalent series resistance, which is attributed to the enhancement of the composite conductivity and the electronic contact between CoO and current collector. The combination of PPy and carbon material like carbon nanotube, graphene etc. is also widely reported. Li Li Zhang et al. has reported the sandwich structure of graphene oxide sheets and PPy and the device performance with capacitance 500 F/g and high rate performance.\textsuperscript{50}

**PANI**

Among these conducting polymers, PANI is expected to be a good candidate for electrodes because of its high capacitance, cheap fabrication cost, and environmental stability.\textsuperscript{51,52} However, due to the shortcoming of mechanical stability in charge-discharge process, it is difficult to get high cycle stability of device with only utilization of PANI. It is necessary for application of composite material to enhance electrochemical performance. The composite electrode material with graphene and PANI gives synergistic effect of both graphene and PANI. Jingjing Xu et al. fabricated hierarchical nano-composite with PANI and graphene oxide sheet and got the enhanced capacitance $555 \text{ F g}^{-1}$.\textsuperscript{53} Qiong Wu et al. reported the PANI nano-fiber and graphene composite with filtration method and enhance the performance of devices exhibiting high cycle stability and specific capacitance of $210 \text{ F g}^{-1}$.\textsuperscript{54}
1.4 Solid-state device

Solid-state supercapacitor devices show attractive advantages over portable energy storage, flexibility and wearable characteristics. Compared with the liquid-based supercapacitor, the solid state device doesn’t have problem to avoid like high-cost package, electrolyte leakage, thus it leads to difficulty to fabricate small scale and flexible supercapacitors with liquid electrolyte.\(^\text{55}\) When comes to solid state device, it is a challenge for the ion diffusion between the electrode and electrolyte.

1.4.1 Flexible electrodes

The large surface area and good ion contact is extremely important for electrode. The material used for flexible solid state electrode are mostly carbon material such as carbon particles\(^\text{56-58}\), two-dimensional graphene\(^\text{59-60}\), carbon nanotubes\(^\text{61-64}\) and carbon nanofibers\(^\text{65}\), which ascribes to their good mechanical property, high electrical conductivity and large surface area.

For better characteristics of flexibility, light-weight and porous structure, it is an attractive method for growth of carbon material on a substrate.\(^\text{66-69}\) Hu et al. reported their work about CNT growth on paper.\(^\text{66}\) With adsorbed CNT inks, the paper is coated with conformal layer of CNT and then is used for flexible electrode. The sheet resistance is 10Ω/sq. And the specific capacitance is as high as 200F/g (current density 1A/g). Also, Zheng et al. gave the idea of graphene-paper, which shows graphene paint cellulose paper,\(^\text{67}\) and the areal specific capacitance can reach as high as 2.3mF/cm\(^2\). Later on, cotton textiles and synthetic sponge are also chosen as the substrate.
Compared with the approach mentioned above, the approach fabricating freestanding film is also promising. Graphene is considered a good candidate for the fabrication of freestanding film because of its high surface area and inter-sheet force. Yang et al. reported the novel simple method to get freestanding film through filtration method. They fabricated wet chemical converted graphene (CCG) sheets in a similar parallel structure and well separated. And they got the specific capacitance as high as 215F/g (mass loading 0.45mg/cm²) and the device shows good rate capability. (Figure 4) With this approach, the outstanding conductivity and high specific area characteristic for graphene are got and thus it improves the ion diffusion and then the electrochemical characteristic of the material.

Faradaic materials like metal oxide and conducting polymers is proved to have high specific capacitance. However, the detrimental drawback of these material is either poor conductivity (e.g. MnO₂) or poor cycle stability, which restricts the widely application of these materials in supercapacitor. To enhance the energy density of carbon materials and mitigate the shortcoming of the faradaic materials, it is commonly a strategy to incorporate faradaic material with carbon material. Minkyu Kim et al. has fabricated the PANI/graphene composite electrode with high electrical conductivity and crystallinity. They use solution process method with camphorsulfonic acid (CSA) and changed the compact coil conformation of PANI to expanded coil conformation thus improving the electrical conductivity and inter-molecular conformation. Hu et al. reported electrodeposition method for integrate MnO₂ with CNT and freestanding graphene. They deposit MnO₂ on CNT-enabled textile and get device performance
with areal capacitance of 2.8F/cm². And the composite electrode MnO₂/graphene they fabricated also achieve areal capacitance of 1.42F/cm² at mass ratio 9.8mg/cm².⁶⁶

1.4.2 Gel polymer electrolyte

Solid-state electrolyte is the most important component for flexible solid-state devices. The requirement for good solid state electrolyte should be high ion conductivity, excellent mechanical properties, good stability.

Figure 1.4 Photograph of flexible SSG films (a), (b), Schematic of cross-section of SSG films (c), specific capacitance of SSG films (e).⁷⁰

and wide potential window.⁷² In general, there are three parts consisting of gel polymer electrolyte: the host component with polymer framework, the plasticizer using organic/aqueous solvent, and a supporting electrolytic salt.⁵⁵ The used host polymer are commonly poly(ethylene oxide) (PEO),⁷³ poly(vinyl alcohol) (PVA),⁷⁴,⁷⁵ poly(methyl methacrylate) (PMMA),⁷⁶ poly(vinylidene fluoride) (PVDF) etc. The commonly used
plasticizers are usually ethylene carbonate (EC), ethyl methyl carbonate (EMC), propylene carbonate (PC) etc.\textsuperscript{73,76,77,78,79} Actually, in real application more than one type of solvent is used to improve the ionic conductivity, potential window. When it comes to electrolytic salt, the commonly used three types of electrolytic salt are lithium ion salt, proton ion salt and other ion salt.

There are several types of lithium gel polymer electrolyte. The commonly used host polymers are including PMMA, PVA, PVDF. Huang et al. reported their polymer electrolyte with poly(ethylene glycol) mixing poly (acrylonitrile) as host, dimethyl formamide (DMF) as a plasticizer and LiClO$_4$ as electrolytic salt showing good ionic conductivity (6.9×10$^{-3}$ S/cm) and wide potential widow (2.1V).\textsuperscript{78} However, compared with the aqueous gel polymer electrolyte, the detrimental drawbacks for the organic polymer solvents are toxic, high cost and flammable. The application of the aqueous gel polymer electrolyte is more cheap and stable. Wang et al. developed aqueous gel electrolyte, PVA as the host, distilled water as solvent and LiCl as the electrolytic salt, which exhibits good characteristics with both mechanical stability and suppressing the chemical dissolution.\textsuperscript{80} For example, with the utilization of the LiCl/PVA electrolyte, VO$_x$ electrode has high cycle stabilities (retention 85\% after 5000 cycles).\textsuperscript{80,81}

Proton gel polymer electrolyte consists of proton donor, polar solvent and polymer host. Commonly proton conducting gel polymer electrolyte uses sulfuric acid (H$_2$SO$_4$), phosphoric acid (H$_3$PO$_4$) as proton donor and PVA is also widely used polymer matrix. The ionic conductivity for this kind of electrolyte is usually ranging from 10$^{-4}$ to 10$^{-2}$ S cm$^{-1}$ at room temperature. Recently Wu et al. developed a redox-mediated gel polymer
electrolyte by blending p-benzenediol (PB) with PVA-H$_2$SO$_4$ gel polymer electrolyte and the ionic conductivity can reach 34.8 mS cm$^{-1}$ with PB concentration optimization.$^{75}$

With the metal oxide electrode extensively investigated, alkaline gel polymer electrolyte is widely used in solid-state supercapacitor. There are various alkaline gel polymer electrolyte, such as PEO/KOH/H$_2$O,$^{82,83}$ potassium poly (acrylate) (PAAK)/KOH/H$_2$O,$^{84,85}$ and PVA/KOH/H$_2$O.$^{80,86}$ Yang et al. developed PVA polymer electrolyte doped with KOH.$^{86,87}$ The PVA/KOH/H$_2$O polymer electrolyte has high conductivity on the order of 10$^{-2}$ S cm$^{-1}$.

1.5 Devices

In general, two electrode devices can be regarded as two capacitors in series. The overall capacitance can be expressed as following equation.$^{88}$

$$\frac{1}{C_T} = \frac{1}{C_P} + \frac{1}{C_N}$$

Where the $C_T$ represents the overall capacitance of the device, $C_P$ means the capacitance of positive electrode and $C_N$ is the capacitance of negative electrode. When the material for two electrodes is the same, namely, $C_P = C_N$ the devices are symmetric supercapacitor. And for the case that two different materials are used for electrode respectively, the devices are asymmetric supercapacitor. In the following part, we will discuss that two types of supercapacitors.
1.5.1 Symmetric devices

Carbon material is extensively investigated due to excellent characteristic of conductivity and flexibility. Kaempgen et al. fabricated single-walled carbon nanotubes based thin films and combine with gel electrolyte PVA/H$_3$PO$_4$ and got the device performance of 36 F/g (current density 30mA/mg). And the solid-state device also reaches high energy density of 6Wh/kg and power density of 23kW/kg. As mentioned above, substrate can be used for flexible electrode growth. Paper are good candidate for that approach. Kang et al. developed flexible electrode fabrication with deposition CNT directly on office paper by drop-dry method, which exhibits good electrochemical performance with energy density of 3.5Wh/kg. In spite of CNTs, graphene-based materials are also attractive interest recently. Graphene-based materials have various advantages over good mechanical properties, large surface area and low cost. However, the re-stacking of graphene sheets caused by Van Der Waals force induces the capacitance far away from the intrinsic capacitance of material and thus restricts their application. El-Kady et al. fabricated un-stacking graphene via standard Light Scribe DVD optical drive and reduced graphite oxide to graphene. The produced films shows excellent mechanical properties, high electrical conductivity and specific area. The fabricated devices show high flexibility under bending condition and remarkable cycle stability.

Faradic materials exhibit much higher capacitance compared with carbon-based materials. There are also extensively studies to fabricate faradic material solid-state devices. Yuan et al. has studied a facile electrochemical deposition method for
PANI/Au/paper electrode. And the electrodes exhibit high cycle stability without any decay after 10,000 cycles and high energy density of 10 mWh cm\(^{-3}\) at power density of 3 W cm\(^{-3}\). Metal oxides are also extensively studied for application of flexible electrodes. RuO\(_2\) is a promising candidate for the supercapacitor electrode. Chen et al. reported hybrid thin film with RuO\(_2\) nanowire/SWCNT. And the device exhibit a specific capacitance of 138 F/g, energy density as high as 18.8 Wh/kg and power density of 96 kW/kg. MnO\(_2\) is regarded as promising alternative for RuO\(_2\) with its low-cost and high specific capacitance (1400 F/g). To enhance the conductivity of the MnO\(_2\), it is an effective approach to combine it with high conductivity material. Zhou et al. reported flexible electrodes fabrication via flame synthesis method and electrochemical deposition and got CNPs/MnO\(_2\) hybrid material. The devices exhibit highly flexible and good capacitive performance.

1.5.2 Asymmetric Devices

Even though the supercapacitors have advantage over high power density compared with batteries, the energy density of that is not high enough for potential application. And the increase of energy density will sacrifice the power density and cycle life, which is not desirable for device performance. A promising approach to increase the energy density is to fabricate the asymmetric supercapacitors with large potential window. The asymmetric devices are including two parts, the faradic electrode and capacitor-type electrode. Carbon-based materials are commonly used for negative electrode. Lee reported asymmetric solid-state devices using ionic liquid functionalized chemically
modified graphene (IL-CMG) as negative electrode and hydrous RuO$_2$-IL-CMG composite as positive electrode.\textsuperscript{95} The asymmetric device can reach voltage as high as 1.8V and achieve high energy density of 19.7Wh/kg at power density of 0.5 kW/kg. In addition to this, there are many attempts for low-cost fabrication of asymmetric device. Gao et al. fabricated asymmetric device with free-standing CNTs/graphene for negative electrode and Mn$_3$O$_4$ as the positive electrode. The asymmetric device can reach operating voltage 1.8V high and energy density 32.7Wh/kg (current density 0.5A/g).\textsuperscript{96} For flexible electrode material fabrication, carbon fiber is chosen as a promising substrate for the metal oxide growth. Lu et al. fabricated asymmetric supercapacitors using carbon cloth as substrate and deposited hydrogen-treated TiO$_2$-MnO$_2$ core-shell nanowires.\textsuperscript{97} The H-TiO$_2$/MnO$_2$ electrodes exhibits the specific capacitance of 449.6 F/g (at scan rate of 10 mV/s). The asymmetric device yielded energy densities of 59 Wh/kg (0.30 mWh/cm$^3$) and it also reaches high voltage as high as 1.8V. Even though the carbon-based material is a good choice for the utilization as anode because of its good conductivity and high surface area, the further improvement of device performance can be achieved by replacing it with metal oxide such as molybdenum oxide and iron oxide.\textsuperscript{98-100} Jian Chang et al. recently developed the asymmetric device configuration as graphene/MnO$_2$/graphene/MoO$_3$.\textsuperscript{102} The graphene composite material improves the electrical conductivity for the metal oxide and the large difference in work function for these two material gave rise of the potential window for device. The as-prepared asymmetric device yielded a specific capacitance of 307 F/g at current density of 200 mA/g and high energy density of 42.6 Wh/kg at voltage of 2.0V. The core-shell
structure with two metal oxide is also applied to improve the electrical conductivity. Zhou et al. reported their work using tungsten oxide nanowires as scaffold to support MoO$_{3-x}$. The cathode for asymmetric configuration is PANI nanowires and they reached energy density of 1.9 mWh/cm$^3$ at power density of 0.73 W/cm$^3$ (at work voltage 1.9V high). With the specific structure the device shows excellent cycle stability with 75% capacitance retention after 10,000 cycle test (at current density 5 mA/cm$^2$).

1.6 Evaluation of supercapacitors

As supercapacitors are energy storage device, it is important parameter to measure the capacity of charges the devices store and the rate of charge-discharge. The measurement of supercapacitor devices includes electrochemical cyclic voltammetry (CV), galvonal-static charge-discharge and electrochemical impedance spectroscopy (EIS).

1.6.1 Cyclic voltammetry

The measurement is carried out for the electrode with the chosen electrolyte and record cyclic voltammograms of the electrode. As the accumulation of the charges occurs on the surface of electrode, the electrical field is established and the specific capacitance can be expressed as following equation:

$$C_s = \frac{|Q|}{m \Delta V} = \frac{1}{sm \Delta V} \int_{v_{low}}^{v_{high}} i dv \quad (1)$$

where $C_s$ means specific capacitance, $Q$ is the amount of charges, $m$ is weight of the
electrode, $\Delta V$ is working potential, $s$ is scan rate, $i$ is current. Based on the equation above, it is easy to judge the capacitance of electrode with the area of the CV curves.

1.6.2 Galvonal-static Charge-discharge

The measurement for the charge-discharge test is applied constant current on the supercapacitor device and discharge time is used to evaluate the device capacitance. The calculation equation is shown as following:

$$ C_s = \frac{it}{m\Delta V} $$

(2)

where $C_s$ is specific capacitance, $\Delta V$ is working voltage for the device. As shown with the equation (2), discharge time is an important parameter to evaluate the amount of specific capacitance.

1.6.3 Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy is also important characterization for the capacitance of devices. The signal is collected with wide range of frequency (1mHz-1MHz) when the device is applied small amplitude of alternative voltage at the open-circuit potential.\(^\text{13}\) The capacitance can be expressed with Bode plot. The capacitance of device is related to the imaginary part of impedance $|Z|$ and frequency $f$ and calculated with equation: $C = 1/(2\pi f |Z|)$. The Bode plot is $\log|Z|$ vs. $\log f$ curve and the capacitance is the linear portion of the curve. Also the Nyquist plot can express the EIS and is imaginary part of impedance ($Z''$) vs. real part of the impedance ($Z'$). The interception of curve and x-axis at high frequency shows the equivalent series resistance of the device which is attributed to the contact between electrode and electrolyte, the
contact between electrode and substrate and the intrinsic resistance of electrode. The radius of the semi-circle curves indicates the charge transfer resistance of device. At low frequency, the device shows capacitive characteristic performance thus for ideal capacitance performance the curves should be parallel to the imaginary impedance axis. For the real situation, the line is inclined 45°-90° angle against the imaginary axis impedance.

1.6.4 Energy density and power density

The energy density (E) of device is an important parameter to characterize the energy capacity of device and the power density (P) indicates the discharge rate. The two parameters can be calculated as following equations:

$$E = \frac{1}{2} CV^2$$  \hspace{1cm} (3)

$$P = \frac{1}{4R_s} V^2 = \frac{E}{t}$$  \hspace{1cm} (4)

where C means the capacitance of electrode, V means the working voltage, $R_s$ means inner resistance of the device and t means the discharge time. According to the equation (3) and (4), it is reasonable approaches to enhance E and P by increase the capacitance of electrode and working voltage of device. To increase the working voltage, there are two ways to achieve. One method is utilizing non-aqueous electrolyte with wide potential window (2-3V). The other is for the asymmetric device configuration
2.1 Introduction

The portable and wearable energy storage devices show great convenience in the real application and get great research interest these days due to great demand for energy storage devices. Based on this motivation, the energy storage devices are extensively developed towards light-weight, flexible and high power density devices.\textsuperscript{1–3} The restriction for the application of existing batteries is low power density, short cycle life and long charging time\textsuperscript{103} and the performance of the conventional capacitor exhibits lower energy density. Supercapacitors, known as electrochemical supercapacitors, have got attention with its characteristic of high power density, great capacitance, long cycle time and low cost.\textsuperscript{104–106} However, the liquid-based supercapacitor has shortcomings with high cost of packaging and less flexibilities for real application. The solid-state supercapacitors show great potential for the application of portable energy storage. Nevertheless, the ion diffusion is limited because of the solid-state electrolyte, thus the fabrication in electrode is necessary to offset this limitation.
The agglomeration of graphene sheets due to van der Waals force restricts the performance of the material compared with its ideal performance. Conducting polymers PANI is expected a good candidate for electrodes use with its high capacitance, lower fabrication cost, easy synthesis and environmental stability. Nevertheless the mechanical degradation during charge-discharge process is a detrimental shortcoming for its long cycle stability. The composite electrode material has synergistic performance of graphene and PANI and performs both advantages of the two materials. Jingjing Xu et al. reported hierarchical nano-composite of PANI/graphene oxide sheet and got the enhancement of specific capacitance 555 F g\(^{-1}\). Qiong Wu et al. developed the PANI nano-fiber and graphene composite and enhanced performance of devices of high cycle stability and specific capacitance of 210 F g\(^{-1}\).

In this work, we coat PANI nano-arrays on the surface of free-standing graphene film via in situ polymerization. The composite electrodes exhibit great electrochemical performance with high capacitance of 573 F g\(^{-1}\) at current density of 0.5 A g\(^{-1}\), energy density 12.21 W h kg\(^{-1}\) at power density of 9.01 kw kg\(^{-1}\) and great rate capacity with high retention of specific capacitance when the current intensity increases. The device is flexible showing barely change of performance with the bending angle and after bended for several times. The cycle stability of the device retains 70.1% of the initial specific capacitance after 10000 charge-discharge cycles with current density of 10 A g\(^{-1}\).
2.2 Experiment

In this study, we used graphite material and filtration method to get free-standing graphene film for electrode application.

2.2.1 Materials

Aniline, sulfuric acid (H_2SO_4), hydrazine, ammonia water, ammonium persulfate (APS) and poly (vinyl alcohol) (PVA) (molecular weight: 89,000-98,000 g/mol) were purchased from Sigma-Aldrich and used without further purification. Graphite powder is used to synthesize GO.

2.2.2 Preparation of graphene film

GO is prepared with modified Hummers method from graphite. The RGO is synthesized with following method: mixing 25μL hydrazine, 175μL ammonia water and 12.5mL graphene oxide solution with a concentration of 1 mol/L together, and then putting the mixture in 90℃ oil bath for 60 min. After cooled to room temperature, reduced GO solution is filtered with cellulose membrane with pore size of 0.05μm and then immerse the film in the water overnight to remove the remaining ammonia and hydrazine. Then peel the film off from membrane and cut it to the square size of 1cm×1cm, thus we get graphene film.

2.2.3 Preparation for graphene/PANI composite

Aniline was dissolved in 1M H_2SO_4 solution. Graphene films were immersed into aniline/H_2SO_4 solutions with aniline concentration of 0.015M, 0.03M, 0.04M and
0.05M respectively for 30 min to diffuse the aniline monomer on the surface of film. The initiator ammonium persulfate (APS) was added with a mole ratio of 1:4 to aniline monomer and the reaction interval is 24 h. Then the film was washed with deionized (DI) water for three times.

2.2.4 Assembly of device

The electrolyte is prepared as the following method: mixing the PVA 5 g, H₂SO₄ 5 g and DI water 50 ml together and stirring them strongly at 85 °C until the mixture is transparent. For the better diffusion of the ion in the electrolyte, the composite film is immersed in the 1 M H₂SO₄ solution overnight. The graphene/PANI composite film was pasted on the substrate of polyimide (PI) film coated with 100 nm gold. The electrolyte is then cast on the two composite films respectively. After the evaporation of solvent in electrolyte, the two halves of device were assembled together with a separator of hydrophilic polypropylene (PP) film (CELGARD 3501) inserted.

2.2.5 Electrochemical measurement

The sandwiched supercapacitor with two electrodes as shown is carried out with cyclic voltammetry (CV) test at a potential range from 0-0.8 V, electrochemical impedance spectroscopy (EIS) measurement in frequency range of 10⁵-10⁻² Hz and galvano-static charge-discharge test under different current densities using GARMY reference 3000 electrochemical workstation.
2.2.6 Characterization

Scanning electron microscopy (SEM S-2150 microscope (Hitachi, Japan)) was employed to characterize the morphology of the graphene film and graphene/PANI composite film. Fourier transform infrared (FT-IR) spectra was obtained on FT-IR Bruker Inc over the range of 4000 to 400 cm$^{-1}$ with KBr method. Raman spectra were collected from 1800 to 1100 cm$^{-1}$ on a Thermo Scientific DXR Raman Microscope with a 532 nm laser source. The conventional four-point technique was used to measure the electrical conductivities of the samples.

2.3 Results and Discussion

To demonstrate the composite, we used characterization method with SEM images, Raman spectra and FT-IR spectra. Also, the electrochemical performance is also shown.

2.3.1 Characterization

Figure 2.1 shows SEM images of pristine graphene film and graphen/PANI nano composite film with different magnification. In Figure 2.1a and 2.1b, graphene morphology is silk-like and wrinkled, which is in correspondence to the intrinsic characteristics of graphene. From the Figure 2.1c and 2.1d illustration, we see the uniform nano arrays coating on the surface of the graphene. It is clear to prove the composite of graphene and PANI. The uniform PANI nano array facilitates the conductivity of electrode by creating more ballistic pathway of ions, which is ascertained with change of conductivity in the following part. Schematic illustration in
Scheme 2.1 visually shows preparation procedure of graphene/PANI composite film. After reduced GO solution, graphene film is got with filtration method and then is coated with PANI. The uniformed nano arrays of PANI shorten the ion diffusion pathway and improve the electrochemical performance.

We performed Raman spectroscopy as characterization for the change of film composite (Figure 2.2a). For GO and RGO spectra, there appear two prominent peaks displaying at 1340 cm\(^{-1}\) referred to D mode corresponding to the structural defects and at 1580 cm\(^{-1}\) assigned to G mode related to the first order scattering of the \(E_{2g}\) mode observed to sp\(^{2}\)-carbon domains.\(^{108,109}\) As Figure 2.2a shown, the intensity ratio of D band to G band (I\(_D\)/I\(_G\)) increases for RGO compared with that for GO, which indicates the reduction process has increased the defect content or edged area of the RGO sheets.\(^{108,110}\) Furthermore, the decreased size of RGO sheets may also lead to the structural defect and cause an increase of the ratio (I\(_D\)/I\(_G\)). After polymerization of PANI, there are four distinguishable peaks observed in Figure 2.2a. The 1170 cm\(^{-1}\) band is ascribed to C—H bending of the quinoid rings. The vibrations at 1339 cm\(^{-1}\) and at 1480 cm\(^{-1}\) in the spectrum are assigned to C—N\(^{+}\) stretching in bipolar form and C=N stretching of the quinoid ring respectively. The band at 1580 cm\(^{-1}\) is ascribed to C=C stretching of the quinoid ring.\(^{111}\) These peaks is attributed to the inter-molecular \(\pi-\pi\) stacking resulting in mixing of p\(_z\) orbitals for the basal plane of RGO with valence orbitals for quinoid rings of PANI backbones, which improves the charge transfer and as a result increases charge density.\(^{108}\)
The composite of the film is also furthered demonstrated with FT-IR spectroscopy measurement. (Figure 2.2b) In the spectrum of GO, the adsorption band at 3387 cm\(^{-1}\) is assigned to the -OH stretching mode in -COOH.\(^{112}\) The bands at 1729 cm\(^{-1}\) and 1605 cm\(^{-1}\) are attributed to the C=O in -COOH and the C-O bond in C-OH respectively.\(^{53,112}\)

For the spectrum of graphene/PANI, new peak observed at 1258 cm\(^{-1}\) is assigned to the C=N stretching modes, which again proves the successful coating of PANI on graphene.\(^{53}\)

### 2.3.2 Electrochemical performance

The electrochemical performance for devices is evaluated with the cyclic voltammetry (CV) curves and galvanostatic charge-discharge tests with the use of electrochemical workstation. As shown in Figure 2.3 a, the CV curves of graphene/PANI electrode devices have larger area than that of pristine graphene.
electrode devices, which shows great improvement in device capacitance. The two remarkable peaks for CV curves of graphene/PANI devices are attributed to the redox of PANI, corresponding to its redox transition between the pernigraniline form and emeraldine form. The quasi-rectangular shape with a pair of peaks for graphene/PANI CV curves indicates the combination of EDLC and pseudo capacitor. The similar rectangular shape for graphene electrode devices shows an ideal performance of EDLC. And the smaller area of the graphene CV curve is due to the absence of PANI in electrodes and the compact structure of graphene sheets. Figure 2.3b gives the galvanostatic charge-discharge curves of devices with current density of 1 A g\(^{-1}\). The test is performed to calculate the specific capacitance of device according to the following equation:

\[
C_s = \frac{It}{m\Delta V}
\]

where I, t, m and \(\Delta V\) represent given current (A), discharge duration (s), mass of electrode material (g) and potential deviation (V) respectively. The nearly triangle shape of galvanostatic charge-discharge curve for devices indicates the capacitance of devices is mainly originated from electric double layer capacitance and with good reversibility. The longer discharge duration of device based on graphene/PANI
electrode is ascribed to the synergistic effect of the two materials. And it can be seen that the device based on the electrode with 0.03M PANI concentration shows the best capacitance performance of 573 F g\(^{-1}\) at current density of 0.5 A g\(^{-1}\) according to the figure. For the discharge curve, there are two stages distinguished from the slope change of discharge curve. The first stage ranging from 0.8V to 0.4V shows short discharge duration attributed to the EDLC characteristics. And the latter stage in range of 0.4 to 0V performs longer discharge duration indicating the combination of EDLC and faradic capacitor. For all conditions, the specific capacitance decreases with the increase of current density. As applied with the larger current density, both the inner material of electrodes and the surface of that are used for the charge storage. The retention of specific capacitance is as high as 79.7% when the current density is increasing from 0.5 A g\(^{-1}\) to 10 A g\(^{-1}\), which shows good rate capacity of device.
capacitance for the device with composite electrodes is greatly improved compared with pristine graphene electrode device. The Nyquist plot (Figure 2.3d) is employed to show different ion diffusion and impedance characteristic of device. The intersection of the impedance curve and x-axis at high frequency gives the equivalent series resistance (ESR). The radius of semicircle response for high frequency displays the charge transfer resistance for device. The linearity of the curve at low frequency range is used to exhibit the Warburg resistance. The ESR for graphene/PANI 0.03M and graphene is 3.06 Ω and 3.56 Ω respectively according to the Fig. 6d. It comes from the improvement of electrode conductivity from 0.28 S cm\(^{-1}\) for graphene to 0.90 S cm\(^{-1}\) for graphene/PANI. The radii of the semicircle response in the curve demonstrate the less charge transfer resistance of graphene/PANI 0.03M than graphene. At low frequency range the linearity of curve indicates ideal performance of device with composite electrode material due to the improvement of ion diffusion and transportation in electrolyte. Thus we ascertain the advantage that graphene/PANI electrode has over electrochemical characteristic.

To test the flexibility and feasible application of device, we bend the device at different angles and with several times at 180°. The CV curves (Figure 2.4a) show no significant change after bending at angles. After bending for 250 times there is nearly the same performance of device shown with Figure 2.4b, and 2.4c. Therefore the flexibility of electrode is demonstrate. The energy densities and power densities are also important parameters for the depiction of the device performance, which can be illustrated with Rogone plot as Figure 2.5a shows. It shows significant improvement in
the energy density for graphene/PANI based devices. The maximum energy density for 0.03M device is 12.21 W h kg\(^{-1}\) obtained at power density of 9.01 kw kg\(^{-1}\) and it remains 6.75 W h kg\(^{-1}\) with an increase of power density to 14.35 kW kg\(^{-1}\), which shows good rate capacity of device in accordance to the result got from Figure 2.3c, indicating the operation of the device is suitable with high power density and energy density at high charge-discharge current density. For the graphene-based device, the highest energy density is 4.09 W h kg\(^{-1}\) at power density of 12.94kw kg\(^{-1}\). The improved energy storage performance comes from the optimization of structure for the electrode material, which facilitates the ion diffusion in the device and avoid the agglomeration of graphene sheets.

The cycle stability is a crucial parameter to show the stability of the device during charging/discharging cycle. The lethal limitation for the use of PANI is the degradation coming from the shrinkage and swelling of the material. As shown with Figure 2.5b, the retention of the initial capacitance is as high as 70.1% after 10000 cycles with current density of 10 A g\(^{-1}\), which is comparable higher than the reported results.\(^{108, 109}\) The increase of the specific capacitance compared with the initial capacitance is due to the activation of the electrode with more ion diffused into the electrode.

The excellent electrochemical performance of the supercapacitor exhibits the synergistic effect of graphene/PANI and inhibits the deficiency of PANI. For the real application of the supercapacitor, we use three devices assembly in series to lighten the red LED after charged to potential 2.4V in 2.05s. (Figure 2.6)
2.4 Conclusion

In summary, using the free-standing graphene film made by vacuum filtration method, graphene/PANI composite electrode is successfully fabricated with in-situ polymerization. Solid-state electrolyte with sulfuric acid and PVA is used to fabricate the supercapacitor device. At suitable concentration of PANI (0.03M), the performance of...
The great rate capacity is ascertained with 79.7% retention of specific capacitance as the current density increases from 0.5 A g\(^{-1}\) to 10 A g\(^{-1}\). The cycle stability of device is 70.1% retention after 10000 charge-discharge cycles and proves great possibilities for the real application of the device. The high flexibilities are also demonstrated with bending test in this study, which shows no significant change of the electrochemical properties.

![Figure 2.4](image)

**Figure 2.4** CV curves for different bending angle (a), CV curves at 20mV/s after bending times (b), Galvanostatic charge discharge curves at current density of 1A/g after bended treatment.
The outstanding device performance results from the synergistic effect of graphene and PANI in ion diffusion and unique structure of the composite. The solid-state

Figure 2.5 Ragone plots (Power density vs energy density) of the graphene, 0.015M graphene/polyaniline(GP), 0.03M GP, 0.04M GP and 0.05M GP based supercapacitors (a), cycle stability of the 0.03M based supercapacitor after charge-discharge for 10000 cycles (b).

Figure 2.6 CV curves at 100mV/s of single device and three devices in series (a), photographs for the light red LED with charged tandem divices(b). supercapacitor fabricated in this study shows great potential in real application with its characteristic of light-weight, high energy density and power density, long cycle stability. Above all, the flexible devices we produced have much more advantages for the real application.
CHAPTER III

ASYMMETRIC SUPERCAPACITOR BASED ON GRAPHENE POLYANILINE
NANOFIBER COMPOSITE ELECTRODE

3.1 Introduction

The composite material with graphene and PANI shows great advantage on the device performance with the synergistic effect of two materials. The film morphology will truly influence the surface area of electrode and thus the ion diffusion in the device. Several works have reported different morphology of PANI. Qiong Wu et al. reported the composite electrode with graphene and PANI nanofiber.\textsuperscript{54} The PANI nanofiber results in efficient pathway for ion diffusion and avoids the aggregation of graphene sheets. The free-standing graphene films have various advantages over flexibility and conductivity compared with graphene mixture of binder. The chemical converted graphene is proved with high electrical conductivity and surface area.

Energy density is related to the capacitance and working voltage of supercapacitor. The asymmetric configuration of supercapacitors can achieve high working voltage of the device and show high energy density. The asymmetric supercapacitors based on
PANI are reported with the integral of carbon material such as graphene and carbon nanotube and can reach working voltage as high as 1.6V. The significant improvement of energy density is two times that of symmetric configuration device. The other utilization of the PANI in asymmetric supercapacitor is combined with metal oxide and carbon material. Jintao Zhang et al. has fabricated asymmetric supercapacitor using RGO-RuO$_2$ composite as positive electrode and RGO-PANI as negative electrode and the energy density with the asymmetric configuration is as high as 26.3 Wh/kg.$^{113}$

In this work, we fabricate free-standing graphene film by filtration method and synthesize PANI nanofiber by in-situ polymerization on the graphene film. We characterize the symmetric two-electrode supercapacitor device performance and test the cycle stability of device. The specific capacitance is as high as 639.74 F/g and energy density is approximately 13.59 Wh/kg, which is a comparable high performance according to the reported results. And the asymmetric configuration devices can reach energy density 19.97 Wh/kg and work voltage as high as 1.6V, which exhibits significant improvement compared with symmetric device configuration. Our symmetric configuration also shows good cycle stability with retention 49.47% of initial capacitance after 10,000 cycles.

3.2 Experiment

Chemical converted free-standing graphene film is obtained with filtration method in this study. And the composite electrode is the combination of PANI and graphene.
3.2.1 Materials

Graphite powder (100 mesh, 99.9995% metal basis), phosphorous oxide and potassium persulfate were purchased from Alfa Aesar. Aniline, ammonium persulfate (APS), hydrazine, ammonia water, perchloric acid (HClO₄), sulfuric acid (H₂SO₄) and poly (vinyl alcohol) were bought from Sigma-Aldrich without further purification.

3.2.2 Preparation of chemical converted graphene film

Graphene oxide (GO) is synthesized as the literature reported by Hummers method. The chemical converted graphene (CCG) was prepared according to the method Dan Li et al. developed. Briefly, 25μL hydrazine, 175μL ammonia water were added into the 50ml graphene oxide aqueous solution (0.25mg/ml). Then the mixture was heated in oil bath for 60 minutes at 90°C and cooled down with room temperature. Successively, half of the mixture is filtered using cellulose membrane with pore size 0.05μm and the membrane is immersed in deionized (DI) water overnight to remove the residual hydrazine and ammonia water. Peel off the chemical converted graphene (CCG) film from the cellulose membrane and cut it into graphene film pieces with square of 1cm×1cm.

3.2.3 Preparation of PANI/CCG composite film

The graphene film is immersed in the aniline HClO₄ solution for three hours. The concentration of aniline monomer is 0.01M, 0.03M and 0.05M respectively. The APS solution is added into the above solution with mole ratio of 1:4 to aniline monomer.
And the mixture reacted for 24 hours and the composite film is washed with DI water for three times and immersed in 1M H₂SO₄ solution overnight before use.

### 3.2.4 Assembly of device

The supercapacitor device structure is two-electrode device that consists of current collector, electrodes, electrolyte and separator. The current collector is polyimide (PI) film coated with 100nm gold by thermal evaporation. The electrode is made from the CCG film and composite PANI/CCG film. The electrolyte used is gel polymer electrolyte. The host polymer is PVA, the solution is water and the electrolytic salt is sulfuric acid. The electrolyte is made of 1 gram PVA, 1 gram H₂SO₄ and 10ml DI water mixing and stirring at 85°C until the mixture is transparent. The separator we use is hydrophilic polypropylene (PP) (CELGARD 3501). The assembly process is pasting the electrode on the current collector, casting electrolyte on the electrode, inserting separator between two electrodes and assembling two halves.

### 3.2.5 Electrochemical measurement

The two-electrode supercapacitors are carried out with cyclic voltammetry test at range of potential based on device configuration, galvno-static charge-discharge test using different current and electrochemical impedance spectroscopy (EIS) test in range of frequency 10⁵-10⁻² Hz. All these measurement is done with GARMY reference 3000 electrochemical work station.
3.2.6 Characterization

Scanning electron microscopy (SEM S-2150 microscope (Hitachi, Japan)) is carried out for characterize the morphology of films. Fourier transform infrared (FT-IR) spectra was got on FT-IR Bruker Inc at the range of 4000 to 400 cm$^{-1}$. Raman spectra were obtained from the range of 1800 to 1100 cm$^{-1}$ on a Thermo Scientific DXR Raman Microscope using a 532 nm laser source.

3.3 Results and Discussion

The composite film is utilized for electrodes in this study. The characterization is important for the composite film we got. And electrochemical performance of composite electrode is also demonstrated.

3.3.1 Characterization

SEM images of the graphene film and composite film are shown as Figure 3.1 with different magnification. SEM images of GO shows uniform two-dimension nanosheets and smooth morphology, which is due to the intrinsic characteristic of graphene. To avoid the aggregation of graphene sheets in drying process, we prepared the samples with freeze-drying method. (Figure 3.1a, 3.1b) Normal drying processed graphene sample exhibits silk like and wrinkle morphology (Figure 3.1c). PANI nano-fiber morphology is demonstrated as Figure 3.1d, 3.1e show and the radius of nanofiber is approximately 90nm, which gives efficient pathway for ion transportation and avoids the mechanical degradation during charge-discharge process. Also, the nano fiber structure as show can also prevent the aggregation of graphene sheets. Thus it is proved
the composite electrode of these two materials. The GO is reduced by hydrazine and ammonia water and the film is obtained with the filtration method. The synthesis of PANI is based on in-situ polymerization and the CCG film is the substrate for PANI nano-fiber growth. The composite film is with good flexibility and able to be folded (Figure 3.1f).

Raman spectroscopy gives powerful proofs for the structure change of carbon materials. Therefore we performed Raman measurement for the different films we prepared. Figure 3.2a is the Raman spectra of the GO film, CCG film and PANI/graphene composite film. There are two prominent peaks for the spectra of three samples at 1330cm and 1590cm, which is attributed to D band and G band respectively. D band is the disorder band and correspond to the structure defect.\textsuperscript{108, 109}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{Figure 3.1 SEM images of dry-freezing graphene (a and b), normal process graphene (c) and graphene/PANI composite (d and e), photographs of flexible composite film (f)}
\end{figure}

It is known that the G band is ascribed to the first-order scattering of the E\textsubscript{2g} mode
observed for sp² carbon domains. The high disorder of graphite results in broader G band and higher intensity of D band compared with G band, thus the ratio of intensity between D band and G band can be used for a measurement of disorder. The Raman spectra of CCG shows an increase of ratio $I_D/I_G$, which indicates the increase of defect content or edage area in structure. Also, the decrease of size for graphene sheets may be the reason for the defect increase and thus lead to the increase of $I_D/I_G$. The spectra of PANI/graphene film shows two more peaks compared with that of CCG film, which is assigned to 1160 cm⁻¹ and 1485 cm⁻¹ and related to C-H bending of quinoid ring and C=N stretching of the quinoid ring. The appearance of these peaks may be caused by the prominent inter-molecular π-π stacking. Thus, it is demonstrated that the success polymerization of PANI on the CCG film.

We also performed FT-IR spectroscopy to corroborate the composite of PANI/graphene by comparing the spectroscopy of CCG, pristine PANI and PANI/graphene (Figure 3.2b). For the spectra of CCG film, the adsorption band at approximately 3840 cm⁻¹ is attributed to the -OH stretching mode on the functional groups of carboxyl groups, which is in correspondence with the reported data. The adsorption bands at 2925 cm⁻¹ and 2853 cm⁻¹ displayed on the spectroscopy is ascribed to symmetric variation and asymmetric stretching of -CH₂. These oxidant functional groups give more active sites for the PANI nucleation. For the composite electrode spectra, the new adsorption band at 1254 cm⁻¹ is attributed to the C=N stretching mode. Thus, it is proved the PANI coating on the graphene sheets.
3.3.2 Electrochemical performance

The electrochemical measurement is carried out using electrochemical workstation and the device performance is shown with cyclic voltammetry (CV) curves, galvanostatic charge-discharge curve and electrochemical impedance spectroscopy (EIS) curve. Shown with Figure 3.3a, the CV curves of 0.03M PANI/graphene device are quasi rectangular shape at different scan rates indicating ideal EDLC charateristics. And the two peaks are ascribed to the redox reaction happening on the electrode, which is due to the doping of hydrogen ions and de-doping of hydrogen ions from the PANI molecule. Figure 3.3b shows CV curves of different PANI concentration composite. It is clear that the area of CV curve for PANI/graphene composite electrode is larger than that of graphene electrode device, which indicates the great enhancement of capacitance for device. The CV curves of composite electrode device show the similar rectangular shape and two prominent peaks at charge and discharge process respectively. The CV curves exhibit synergistic effect of the two materials and show 0.03M PANI/graphene is the

Figure 3.2 Raman spectra (a), FT-IR spectra (b) of graphene oxide (GO), chemical converted graphene (CCG) and graphene/polyaniline (PANI)
optimization of aniline concentration. When the concentration is less than this, there are sparse PANI grown on graphene sheets. And the growth of PANI is happened on the surface of graphene sheets via heterogeneous nucleation and the active sites of graphene sheets will reduce the energy barrier between graphene sheets surface and aniline solution inducing subsequently growth of PANI. Nevertheless, for large concentration of aniline monomer, it will stimulus homogeneous nucleation of PANI growth utilizing the aniline cell as soft-template and form the random morphology. The charge-discharge curves is also an important evaluation for electrochemical performance of supercapacitor. The specific capacitance can be calculated based on equation (2) thus the longer discharge time will lead to higher specific capacitance. The charge-discharge curves show that the discharge time increases for the composite electrode device. (Figure 3.3c) The 0.03M PANI/graphene electrode performs longest discharge time, which is in correspondence with the conclusion we get from CV curves. The change of charge-discharge curve slope shows the redox reaction happens during charge-discharge process and the similar triangle shape of the curves indicates the device with the characteristic of EDLC and high reversibility, which corroborates the synergistic effect of two materials for device performance. The specific capacitance will decrease with the current density increase because the smaller current density can activate both the inner and surface of material. (Figure 3.3d) The specific capacitance of composite electrode is larger than the graphene electrode for all conditions. The highest specific capacitance is 639.74 F/g at current density 0.5 A/g, which is a comparative high capacitance for graphene/PANI composite electrode. The retention of
specific capacitance is as high as 90.7\% and it shows excellent rate capacity of device.

The asymmetric configuration of device is composed of composite PANI/graphene as positive electrode and graphene as negative electrode. As Figure 3.4a shown, the CV curves of pristine graphene electrode exhibits nearly rectangle shape at work voltage 0-0.8V and indicates its ideal EDLC performance and high charge transport between electrode and electrolyte. Figure 3.4b shows the CV curves of the asymmetric device at different working voltage ranging from 0.8V to 1.6V. The CV curves at high work voltage show similar rectangular shape and a pair of peaks at approximately 0.4V indicating redox reaction and electrical double layer capacitance. The CV curves of device at high scan rate show quasi rectangular shape as it is applied high voltage 1.6V suggesting high capacitive performance. (Figure 3.4c) The charge-discharge curves (Figure 3.4d) at different work voltage exhibit symmetry similar triangle shape suggesting excellent capacitive performance. With different current density at 1.6V, the charge-discharge curves retain symmetric shape indicating high reversibility of device. (Figure 3.4e) And the voltage drop at low current density 0.5A/g is 0.04V, which reveals the high capacity of device. Figure 3.4f shows the specific capacitance and Coulombic efficiency v.s. work voltage of device. As the work voltage increases, the Coulombic efficiency decreases, which may be attributed to the decomposition of PANI at high voltage. Moreover, the Coulombic efficiency keeps 89.77\% and thus we choose 1.6V as work voltage for the asymmetric device.

Energy density and power density are very important two parameters for supercapacitor, which shows the energy storage characteristic of device. Ragone plot
(Figure 3.5a) shows energy density of different devices. The energy density for asymmetric devices shows 19.97 Wh/kg at power density of 7.61 kw/kg and retains 12.19 Wh/kg at power density of 17.27 kw/kg. It is clear that the asymmetric device exhibits higher energy density than symmetric configuration does. The 0.03M PANI/graphene composite electrode device has best performance compared with the

Figure 3.3 CV curves of the 0.03M graphene/polyaniline (GP) supercapacitor at different scan rates (a), CV curves at a scan rate of 20mV/s (b), Galvanostatic charge discharge curves (c), specific capacitance vs. current density (d) of graphene, 0.01M graphene/polyaniline (GP), 0.03M GP, and 0.05M GP based device.

of energy density compared with the CCG electrode device. The cycle stability of supercapacitor is a key parameter to evaluate the real application of device. The stability
test shown with Figure 3.5b is performed the cycle duration of device. The specific capacitance retains 49.47% of its initial capacitance.

Figure 3.4 CV curves of pristine graphene -0.8-0V at different scan rate (a), CV curves of asymmetric device with different work voltage at 100mV/s scan rate (b), CV curves of asymmetric device 0-1.6V at different scan rate (c), charge-discharge curves for different work voltage at current density 1A/g (d), specific capacitance, Coulombic efficiency vs. work voltage (e).
To testify the real potential application of the devices, we connected two asymmetric supercapacitors as tandem device. We used CV curves and charge-discharge to evaluate the tandem device performance. The work potential of the tandem device is extended to 3.2V. (Figure 3.6a) As for each supercapacitor the mass loading of electrode films is the same (1.1mg for each device), we applied the same current density as single device. The charge-discharge duration for tandem device is nearly the same as that for individual device suggesting the good capacitive performance of each supercapacitor. (Figure 3.6b) In addition, we charged the tandem device and light up a blue light-emitting diode (LED) which has lowest working potential about 3.0V. (Figure 3.7) And the LED can light over 70 seconds thus it proves the potential of real application for asymmetric supercapacitors.

Figure 3.5 Rogone plot for asymmetric device, graphene, 0.01M GP, 0.03M GP, 0.04M GP device (a), specific capacitance retention vs. cycle number (b)
3.4 Conclusion

We have fabricated PANI/grapheme composite electrode and proved its good utilization in symmetric and asymmetric configuration device. The composite film has advantage over light-weight and flexible. The solid-state device we fabricated resolve the high-cost package, safety issue and difficult transportation problems for liquid-electrolyte based supercapacitor. The electrochemical performance for PANI based

Figure 3.6 CV curves of single device and tandem device (a), galvnal-static charge-discharge curve for single device and tandem device (b).

Figure 3.7 Photograph of the blue LED powered up with two tandem devices for 70s.
symmetric supercapacitor can reach the specific capacitance of composite electrode as high as 639 F/g and exhibits excellent rate capacity (retention 90.7% at current density 10A/g). The asymmetric configuration device can perform work voltage 1.6V and energy density 19.97 Wh/kg at power density of 7.61kw/kg. The tandem asymmetric devices also show good performance and can light up blue LED for 70 seconds. In summary, with the flexible and light-weight characteristic, nano-fiber PANI/graphene composite film is proved of a promising material for supercapacitor electrode.
CHAPTER IV

CONCLUSIONS AND OUTLOOK

4.1 Conclusions

Graphene material has great potential for the application as the electrode for supercapacitor. The composite material based on graphene and PANI shows good electrochemical performance with both high capacitance and cycle stability as a result of the synergistic effect of the two material. The different synthesis environment will influence the morphology of PANI and give different device performance. In our study, we fabricated two types of composite electrode and got improvement electrochemical performance. The results show the concentration of aniline solution plays an important role for electrodes performance, which is due to the concentration leading to two kinds of nucleation, heteronucleation and homonucleation and trade-off for the amount grown on the surface and less conductivity. The asymmetric configuration in our study also shows energy densities enhancement over 40% and exhibits high potential window as 1.6V.
4.2 Outlook

Supercapacitors have widely potential application for the future energy storage field and the improvement for energy densities will still be an important problem to resolve. The application of the carbon material for electrode will absolutely reduce the expense of fabrication. However, low capacitance and energy densities restricts the advantage of the material. The composite material with Faradic material will enhance the device performance. The synthesis method for composite material will be towards less toxic and easier process method.
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APPENDIX

PUBLICATIONS
