

CRANFIELD UNIVERSITY

Shujun He

Carbon Nano Materials based Composites for Energy Storage

School of Aerospace, Transport and Manufacturing
(ATM)

MSc by Research

Academic Year: 2021 - 2022

Supervisor: Dr David Ayre

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This thesis is submitted in partial fulfilment of the requirements for
the degree of MSc by Research in Manufacturing

ABSTRACT

The development of human industrial technology has increased the requirement for electric energy. At present, the rapid development of various smart devices has led to an increasing demand for high-performance batteries. The emergence of various wearable devices has led to a need for flexible electrodes. Aerogels and paper, as two good flexible porous materials, have attracted many scholarly studies in recent years. Combining carbon materials, which have excellent electrochemical properties, with aerogel and paper can result in flexible electrodes with good performance. This research presents a series of aerogel and carbon paper samples prepared using three different production processes. For the aerogel samples, the effects of graphene addition and manufacturing route were investigated. The study resulted in a recommended material and process to produce a porous aerogel sample with high electrochemical cycle stability. For carbon paper samples, the relationship between variables such as surfactant, paper, conductive material and the sample properties was examined. Initial work indicates that carbon paper manufacturing routes are simpler than others reported elsewhere and provide materials that have electrochemical properties with potential for use as electrodes in supercapacitors and other energy storage devices. Of course, cost and environmental protection have also been considered in this project.

Key words: Graphene; PVDF; Aerogel; CNT; Carbon paper; Electrochemical; Energy storage; Dipping process

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Notations

CVD	Chemical Vapour Deposition
CNT	Carbon Nanotube
GO	Graphene Oxide
rGO	Reduced Graphene Oxides
CPs	Conductive Polymers
MOF	Metal-organic framework
Ag NPs	Silver Nanoparticles
Sc	Supercapacitor
LIBs	Lithium-ion batteries
BFCs	Biofuel cells
GPNs	Graphene nanoplates
SEM	Scanning electron microscope
FT-IR	Fourier Transform Infrared
CV	Cyclic voltammetry
GCD	Galvanostatic charge-discharge
HF	Hydrogen fluoride
Vc	Vitamin C
ITO	Indium tin oxides
LBL	Layer-by-layer self-assembly

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1. Introduction

1.1 Background of the study

In recent years, with rapid advances in electronics technology, more and more electronic devices are being developed in the direction of thinness, flexibility and wearability (see Figure 1-1). For example, companies such as Samsung and LG have launched curved screen phones and are planning to develop a new generation of products that can be folded and bent ^[10].



Figure 1-1 Trends in electronic equipment
(Samsung Electronics, 2019)

One of the biggest challenges in the development of flexible electronics is the thin and flexible electrochemical energy storage devices that are compatible with it. Traditional products such as lithium-ion batteries and supercapacitors are rigid, and when bent or folded, they can easily cause separation of electrode materials and collectors, affecting electrochemical performance and even leading to short circuits and serious safety problems ^[4]. Therefore, in order to adapt to the development of next-generation flexible electronic devices, flexible energy storage devices have become a research hotspot in recent years.

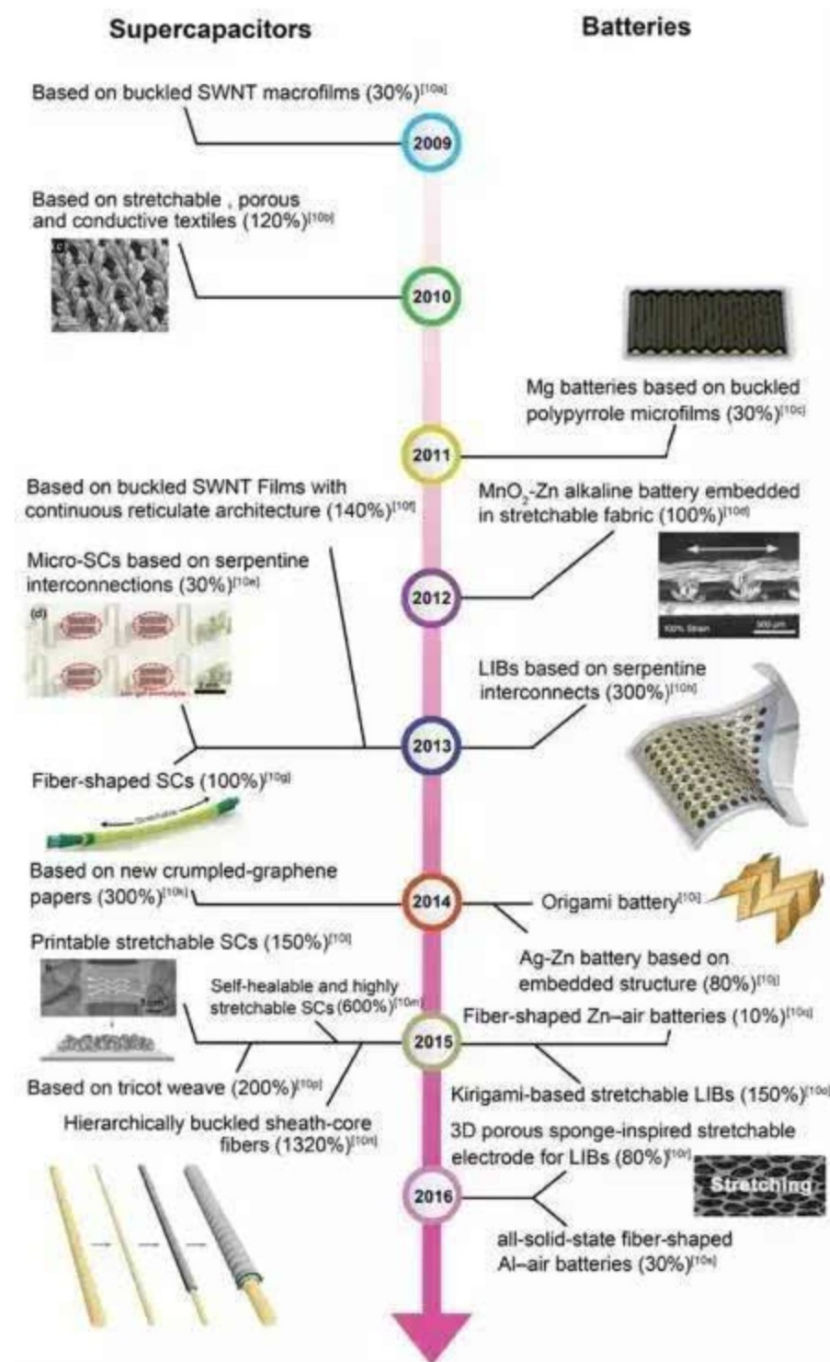


Figure 1-2 History of flexible energy storage devices ^[7]

In 2016, Cui Yi's group at Stanford University published a review in Adv. Mater. summarising the development of flexible and scalable energy storage devices in recent years (Figure 1-2).

Lithium-ion batteries have high energy density, good cycling performance and good

stability, and are the most ideal candidates for the development of flexible energy storage devices. The supercapacitor, on the other hand, has high power density, can achieve high current fast charging and discharging, long service life and other excellent performance, which can make up for the shortage of lithium batteries [12]. Currently, flexible Li-ion batteries and supercapacitors face three problems: 1) the design and preparation of flexible electrodes; 2) the stability of the electrochemical properties of the device during the bending and folding process; and 3) high energy density and high-power density.

In lithium-ion batteries and supercapacitors, the main types of flexible electrodes are as follows:

(1) 2D paper electrode

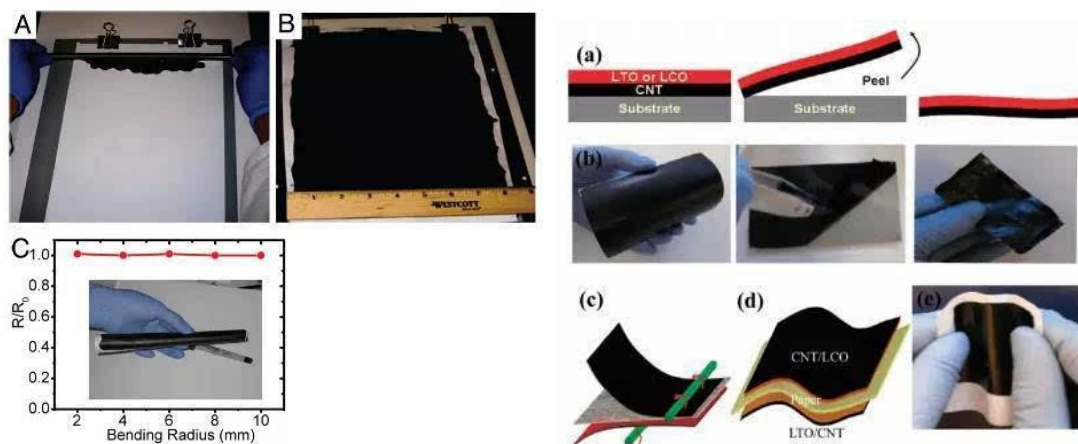


Figure 1-3 Carbon/ paper (IRN, 2016) Figure 1-4 CNT/ paper (QianxunWeb, 2017)

As shown in figure 1-4, carbon paper is flexible and there has been a lot of research on carbon nanotube (CNT) paper, graphene paper and carbon paper containing active materials, prepared in a variety of ways, from very simple methods like coating method (Figure 1-3) to some complex methods like vacuum filtration (Figure 1-5), CVD, in situ hydrothermal deposition and more [13].

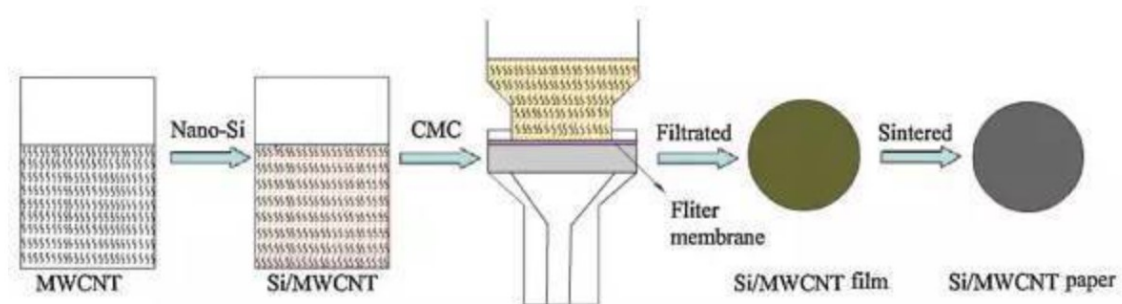


Figure 1-5 Vacuum filtration method (Large Electronics, 2018)

(2) Porous electrodes

The active material is filled in the pores of the porous electrode, i.e. it is not easily detached and the expansion of the active material during the charging and discharging process is solved ^[15].

(3) Fabric electrodes

Carbon fiber fabrics are also good fluid collectors and the deposition of active substances on the surface not only enables flexibility but also reduces the use of adhesives ^[3].

Although these electrode materials can solve the problem of flexible electrodes, how to further improve the active specific surface area and conductivity of the materials and thus improve the specific capacity of the battery has become the main challenge in the design of flexible electrode materials and structures.

1.2 Aims and Objectives

The aims and objectives of the present study can be stated as following:

Investigate the fabrication methods of novel electrodes for energy storage and the factors that affect electrode performance.	1. To perform a review of current porous electrode materials and production methods. 2. To perform a review of current conductive paper and their applications. 3. Understanding the production of graphene composite aerogels and the preparation of carbon composite paper under laboratory conditions. 4. To characterize the prepared samples in various ways and test their electrochemical properties. 5. To explore the influence of different factors on sample performance and study the mechanism.
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Table 1 Aims and Objectives

2. Literature Review

2.1 Electrode material

2.1.1 Carbon materials

Carbon materials have become advantageous electrode materials for electric double layer capacitors due to their high specific surface area and excellent electrical conductivity. In addition, carbon materials also have abundant allotropes, microstructures of various shapes, and materials with various dimensions (one-dimensional carbon nanotubes ^[1], to two-dimensional graphene ^[2], and three-dimensional aerogels ^[3]) (see Figure 2-1).

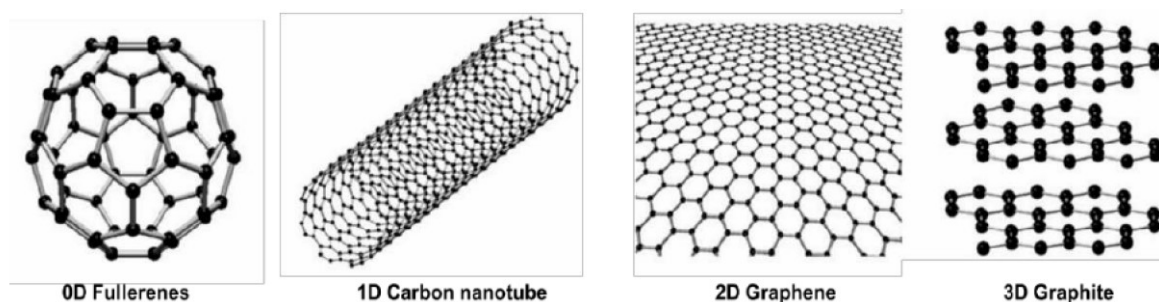


Figure 2-1 Carbon nanomaterials exhibiting different dimensionalities ^[3]

The structural properties of these materials lay the foundation for a wide range of applications. On the other hand, carbon materials are abundant in nature, easy to obtain, simple to handle in industrial production, low cost, less pollution in the production process, and carbon materials have good adaptability to acid and alkali and can be used in a wide temperature range. The structure is stable within the range, so carbon materials have become the preferred electrode materials for commercial production of supercapacitors ^[9]. At present, the carbon materials commonly used in the energy industry are as follows:

(1) Carbon nanotubes (CNT)

Carbon Nanotubes are seamless cylindrical structures wound from single or multiple layers of graphene, with open or closed ends ^[4]. Perfect carbon nanotubes are composed of carbon atoms arranged in a hexagonal lattice structure except for the ends. Carbon nanotubes rolled from a single layer of graphene are called single-walled carbon nanotubes (SWNTs), while carbon nanotubes composed of multiple layers of graphene are called multi-walled carbon nanotubes (MWNTs). Because of its unique physical, chemical, mechanical and electrical properties, carbon nanotubes have always been a hot material in various applied research projects.

(2) Graphene

Graphene is a sheet material with a hexagonal honeycomb lattice structure composed of carbon atoms with SP^2 hybrid orbitals, and its thickness is only the size of a single atom, which is a two-dimensional structure of carbon nanomaterials ^[5]. Due to its unique molecular structure, graphene has a series of outstanding physical and chemical properties, and it is the main material for the research and development of advanced functional materials. Graphene has a high theoretical specific surface area ($2600 \text{ m}^2\text{g}^{-1}$), and its thermal conductivity (up to $5300 \text{ Wm}^{-1}\text{K}^{-1}$) and mechanical strength are superior to those of graphite. In the single-layer graphene sheet, each carbon atom can contribute an unbonded electron, so the single-layer graphene has excellent electronic conductivity, and its electrical conductivity is as high as 10^8 Sm^{-1} . The optical transmittance of single-layer graphene is extremely high, but its absorption of visible light and near-infrared wavelengths is significantly enhanced when the graphene sheets are clustered together ^[6]. Graphene has excellent thermal, electrical, optical, and mechanical properties, providing it with broad application prospects in the fields of composite materials, energy storage, electronic devices,

and biomedicine [7]. The main preparation methods of graphene include mechanical exfoliation, chemical vapor deposition, silicon carbide epitaxial growth, redox, and electrochemical intercalation. Among them, the redox method can prepare reduced graphene oxide in large quantities, which is one of the most important methods for preparing graphene. Graphene Oxide, a graphene derivative prepared by oxidation, has a large number of oxygen-containing functional groups modified on its surface (Figure 2-2), which can form non-covalent forces with other functional materials, including van der Waals forces, π - π stacking, electrostatic interactions, hydrogen bonding, hydrophobic interactions, and ionic cross-linking, etc. [8]. As the precursor of graphene, graphene oxide is more processable and expandable, and can be processed into fibers, films and porous materials, and can also further expand the functions and application scope of graphene through modification and compounding [9].

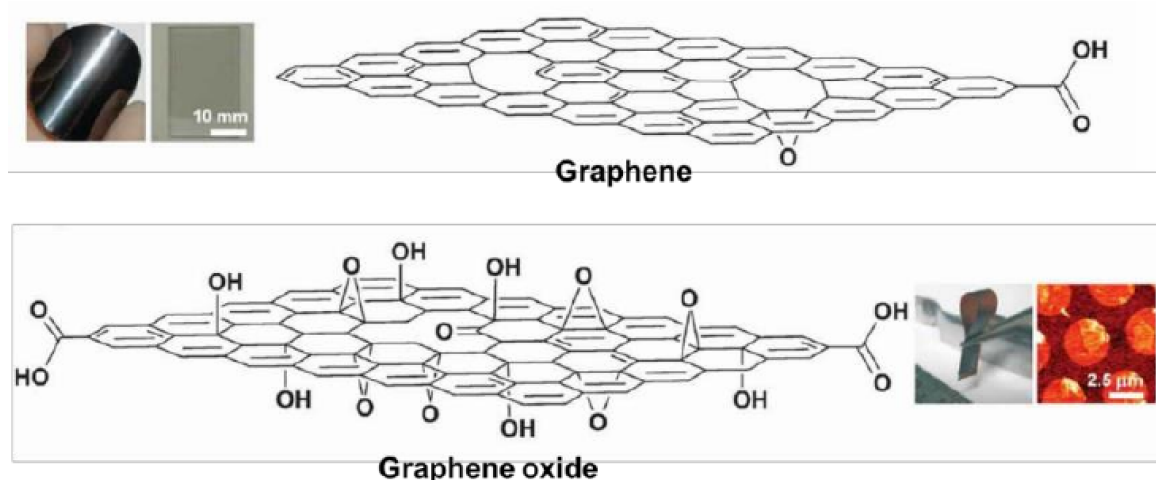


Figure 2-2 Schematic model of the graphene and graphene oxide [8]

(3) Carbon black

Carbon black is a kind of black powdery substance produced by incomplete combustion of hydrocarbons in the air. Its main body is carbon, and it also contains a small amount of oxygen, hydrogen, sulfur and nitrogen. Carbon black particles are an existing form of amorphous carbon, which are disordered or

short-range ordered three-dimensional materials, which have both SP^2 and SP^3 hybrid carbon atoms ^[10]. Carbon black particles are extremely fine, with an average diameter of only 5~30nm, and agglomerate into chain or grape-like aggregates with a size of 0.2~1.4 μ m. Carbon black has the advantages of excellent light absorption ability, coloring property, weather resistance, electrical conductivity and chemical stability, etc., and has a wide range of sources and low prices.

(4) Activated carbon

Activated carbon is composed of irregularly arranged microcrystalline carbon with cross-connected micropores. It is a kind of powdery or granular porous carbon material with high pore structure, high specific surface area and rich surface chemical groups. The sources of activated carbon are abundant, and it is produced from carbon-rich organic materials such as wood, bamboo and fruit shells, and mineral resources such as coal ^[11]. Activated carbon has the advantages of stable chemical and physical properties, insoluble in water and organic solvents, recyclable, low price and simple preparation process.

2.1.2 Conductive polymers

Conductive polymers (CPs) are also important electrode materials for supercapacitors. Conductive polymers, such as polyaniline ^[12] (PANI), polypyrrole ^[13] (PPy), and polythiophene ^[14] (PTh), which are commonly used in current research, have good pseudocapacitive effects. The pseudocapacitive effect is mainly due to the adsorption and de-intercalation of ions in the electrolyte by the conductive polymer. Conductive polymers have a remarkable feature. Whether its pseudocapacitive effect can be exhibited is related to the voltage between the conductive polymer and the electrolyte.

Due to the pseudocapacitance effect, the specific capacity of conductive

polymers is much higher than that of electric double layer materials. According to the literature, the specific capacity of supercapacitors using pure PANI to fabricate electrodes is as high as 815 F/g, which is much higher than ~150 F/g of carbon materials. However, conductive polymers also have many problems. One of the most serious problems is that the volume of conductive polymers will change during the ion adsorption and deintercalation process of pseudocapacitive effect ^[15]. This change will cause the structure of the conductive polymer to be gradually destroyed with the increase of the number of cycles during the cycle. Therefore, simply using conductive polymers as electrode materials for supercapacitors has no practical application value. In the current research, a series of methods have been adopted to solve the volume change of conductive polymers. At present, according to the reported literature, the more effective means are:

- (1) To control the structure and morphology of conductive polymers, select supporting structures such as spherical and tubular ^[16].
- (2) Adopt different structures.
- (3) The strategy of using composite materials ^[17].

2.1.3 Metal oxide

Metal oxides and hydroxides are also popular electrode materials for supercapacitors currently studied. Among them, researchers most focus on metal ruthenium oxides ^[18], manganese oxides ^[19], cobalt oxides ^[20], nickel oxides ^[21] and vanadium oxides ^[22]. Due to the properties of these metal oxides and hydroxides, they generally have several times higher specific capacitance than common carbon materials and better cycling stability than conducting polymers.

According to the published literature, the following factors affect the performance of metal oxides and hydroxides in supercapacitors: specific surface area, bound

water content, crystallinity, and particle size. Unlike conducting polymers, the pseudocapacitive reactions of metal oxides are concentrated on their surfaces. Therefore, the high specific surface area can increase more active sites for the reaction and enhance the pseudocapacitive performance of the material. In addition, according to the literature, the presence of bound water can enhance the diffusion of ions in the electrode material, therefore, higher bound water content can improve the performance of the material. In addition, the degree of crystallinity of the material can also affect the properties of the material. The higher the crystallinity of the material, the more stable its structure is, which makes it difficult for ions in the electrolyte to diffuse in the electrode, so that the redox reaction is limited to the surface and reduces the performance of the material. In addition, the smaller the particle size, the shorter the diffusion path of ions in the electrode material, and the better the performance.

2.1.4 Metal-organic framework

In addition to the above traditional electric double layer capacitor materials, some researchers have also studied the application of metal-organic framework (MOF) structure in supercapacitors [23]. The remarkable features of MOF structure are large specific surface area, high porosity and relatively stable structure. However, MOF structures are generally not very conductive due to their high porosity. They adopted a MOF structure with higher conductivity among MOFs that have been found so far, $\text{Ni}_3(\text{HITP})_2$, as the electrode without any additives for supercapacitors. The MOF structure of $\text{Ni}_3(\text{HITP})_2$ has a specific surface area of $630 \text{ m}^2/\text{g}$ and an electrical conductivity of 5000 S/m . The supercapacitor made with it has a specific capacitance of 112 F/g at a current density of 0.05 A/g , and a specific surface area normalized specific capacitance of $18 \mu\text{F/m}^2$. It also has good cycling performance, with a retention rate of 90% after 10,000 cycles at a current density of 2 A/g . However, it is worth noting that after increasing the current

density, the performance of the supercapacitor assembled with this material attenuates greatly, which can be attributed to the structure of this material. Therefore, this material cannot be used in applications requiring high current. But it also inspired researchers to open up the application of MOF structures in the field of supercapacitors.

2.2 Graphene Aerogel

2.2.1 Introduction to graphene aerogels

Aerogels are wet gels prepared by the sol-gel method. After removing most of the solvent, air is used as a medium to fill the space network of the gel with rich pore structure, very low apparent density and low thermal conductivity. In 1931, S.S. Kistler et al. ^[24] of Stanford University first used the sol-gel method to prepare SiO₂ hydrogel with Na₂SiO₃ as raw material, and obtained SiO₂ aerogel after supercritical drying (Figure 2-3a). As a result, aerogel, an ultra-light material with a special structure, has entered people's history. With the exploration and development of aerogel materials, metal oxides (Al₂O₃^[25], TiO₂^[26], MgO^[27], etc.), organic silicon sources (methyl orthosilicate ^[28], ethyl orthosilicate aerogel materials such as esters ^[29], etc.), sulfides ^[30], carbon (graphene ^[31], carbon nanotubes ^[32], etc.) were synthesized. While organosilicon sources were used as raw materials, organic solvents were used. Instead of inorganic solvents, the preparation process is simplified, the preparation method and desolvation process are also continuously improved. The aerogel samples obtained by a single sol-gel method and supercritical drying technology are gradually broadened to a series of materials with a gel network structure and the dispersion medium is gas.

As an important part of aerogel materials, a series of carbon aerogels prepared from carbon materials have broad application prospects due to their excellent electrical conductivity. The excellent electrical conductivity and the large specific

surface area and porous structure of aerogels mean aerogels have great application prospects in energy storage, environmental protection, catalyst supports, sensors, etc.

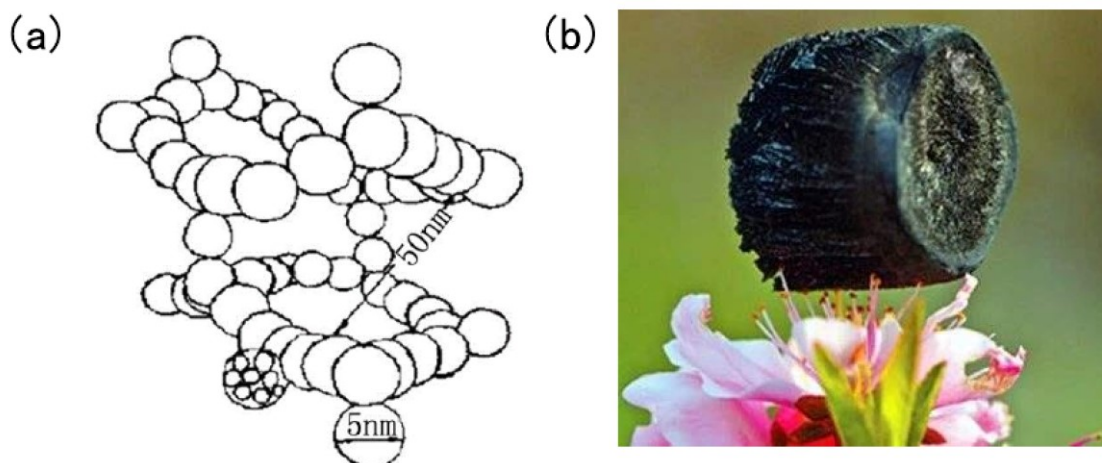


Figure 2-3 (a) Structure diagram of SiO₂ aerogel [24]; (b) Graphene aerogel [24]

2.2.2 Preparation method of graphene aerogel

2.2.2.1 Hydrothermal reduction method

The hydrothermal reduction method is the most commonly used method for preparing graphene hydrogels. Using graphene as a precursor, the graphene will self-assemble during hydrothermal process. After drying, a graphene aerogel with a macroscopic three-dimensional assembly structure is obtained.

In 2010, Shi Gaoquan et al. [33] used graphene oxide dispersion as the precursor solution for the first time, reacted in a hydrothermal kettle at 180 °C for 12 h, and successfully prepared three-dimensional graphene hydrogels. As shown in figure 2-4, the hydrogel has excellent mechanical, electrical, thermal properties and rich pore structure. Gao Chao et al. [34] of Zhejiang University successfully prepared a composite aerogel containing carbon nanotubes and graphene by freeze-drying, with ultra-low density (0.16 mg/cm³) and good elasticity, becoming the lightest material in the world at that time. Hossein et al. [35] fabricated composite aerogels with 3D porous structure using graphene and PVDF.

The researchers achieved the successful preparation of graphene aerogels by hydrothermal method. At the same time, by adding metal oxides, the nanoparticles were supported on the graphene sheets to achieve functionalized graphene aerogels. Wu et al. [36] supported ferric oxide (Fe_3O_4) nanoparticles in aerogels by a hydrothermal method. Due to the porosity and large comparative area of the aerogel materials, when the catalyst particles were uniformly supported on the aerogels, increasing the contact area between the catalyst and the reactant, thus improving the catalytic performance of the composite. Xu et al. [37] embedded ferromagnetic Fe_3O_4 nanoparticles in aerogels, making the aerogels ferromagnetic. By adding a magnetic field, the self-compression and extrusion of aerogels can be realized, with intelligent controllability and magnetic drive.

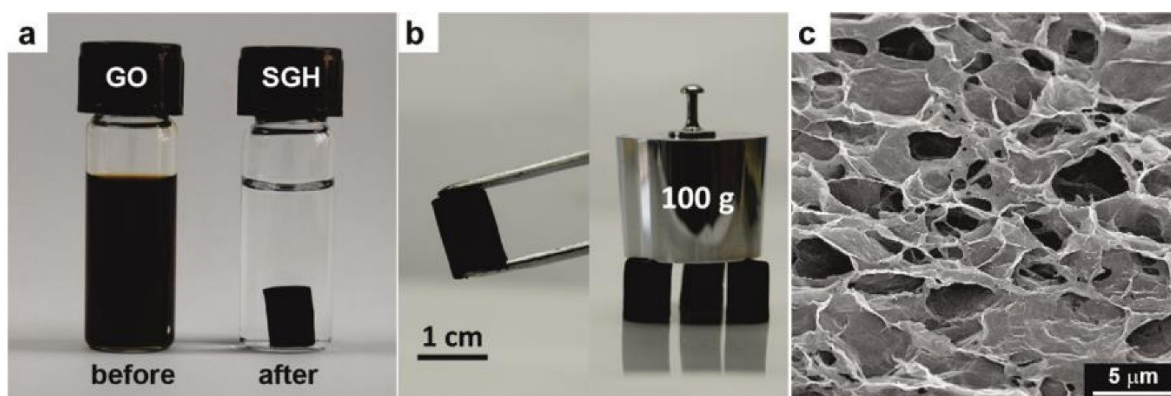


Figure 2-4 (a) Photographs of a 2 mg/mL homogeneous GO aqueous dispersion before and after hydrothermal reduction at 180°C for 12 h; (b) Photographs of a strong SGH (Self-assembled Graphene Hydrogels) allowing supporting weight; (c) SEM images of SGH [33]

2.2.2.2 Chemical reduction

The preparation of graphene aerogels by hydrothermal method requires high temperature and high pressure, and requires specialist equipment, so it cannot be prepared on a large scale, while the chemical reduction method is favored by researchers because of its milder reaction process and reaction conditions. At the

same time, it can be prepared on a large scale. The chemical reduction method usually uses mild reducing agents such as hydrazine [38], Vitamin C (Vc) [39], and sodium ascorbate [40] to reduce graphene oxide. In the reduction process, simple water bath heating is usually required to obtain excellent reduction effects to produce graphene hydrogels with uniform pore structure. Zhang et al. [41] successfully used oxalic acid and sodium iodide as the reaction system to reduce graphene oxide solution to prepare 3D graphene with low density and high porosity. Bai et al. [42] successfully prepared graphene aerogels with a three-dimensional structure by using the electrochemical reduction method and a three-electrode system. Chen et al. [43] prepared graphene/CeO₂ aerogels by a one-step in-situ electrochemical method.

2.2.2.3 Template method

During the reduction of graphene oxide, π - π stacking between graphene sheets is prone to occur. In order to controllably adjust the pore size and microstructure of graphene, the template method is a very effective preparation method. Chen et al. [44] prepared three-dimensional graphene foam by CVD method for the first time by using nickel foam as a template. In addition, PMMA, PS, SiO₂, polyurethane sponge, etc. are also commonly used as hard templates for the assembly of graphene 3D structures. Liu et al. [45] used melamine as a template to attach graphene oxide to the surface of the foam and then chemically reduced the melamine to prepare superelastic graphene aerogels of any shape after hydrogen fluoride (HF) etching, as shown in Figure 2-5 (a). In addition, there are soft templates assembled by organic solvents and graphene aqueous solutions through emulsion polymerization, Shi Gao et al. [46]. By mixing n-hexane droplets with graphene oxide aqueous solution to form an emulsion, graphene aerogels with good compressibility and elasticity were obtained after hydrothermal and freeze-drying.

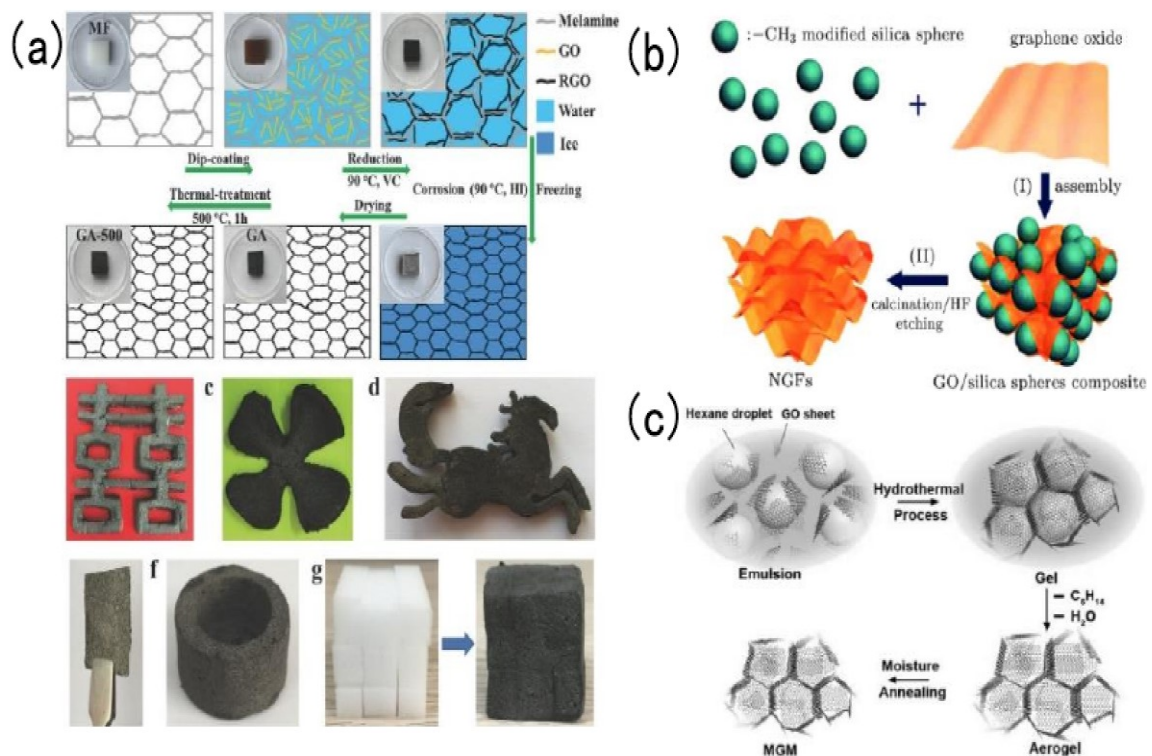


Figure 2-5 (a)Schematic showing the formation of graphene sponge and photographs of graphene sponge for different shapes; (b)Preparation of graphene aerogel depends on the template of PS; (c)Schematic illustration of the preparation of graphene aerogel depends on the template of n-hexane [45]

2.2.2.4 Cross-linking method

As a hydrophilic compound, graphene oxide is a stable solution state in water. By protonation of carboxyl groups in a strongly acidic environment, the effect of hydrogen bonds is strengthened, or through the interaction between crosslinking agents and graphene oxide, can cause agglomeration between graphene oxides to form a stable gelled structure. Generally, the gelation of graphene oxide sheets is promoted by enhancing the bonding force between graphene oxide sheets through hydrogen bonding. Shi Gao et al. [47] mixed GO with PVA and adjusted the pH to increase hydrogen bonds in an acidic environment to achieve gelation. In addition, when graphene hydrogels are prepared by cross-linking method, commonly used cross-linking agents include metal ions (Ca^{2+} , Mg^{2+} , Pb^{2+} , Cr^{3+} , etc.) [48], small polymer molecules, high molecular mass polymers [49], biological

macromolecules ^[50], etc.

2.2.2.5 Other methods

In addition, 3D printing methods ^[51] and other methods have been applied to prepare graphene aerogels. Liu et al. first freeze-dried high concentration of graphene oxide and then reduced the treated graphene oxide by using HI under hydrothermal conditions. Finally the obtained graphene aerogel was washed and further freeze-dried. The three-dimensional graphene thus prepared has very high mechanical strength and compressibility, and can be prepared in large quantities. Zhu et al. ^[52] reported a 3D printing technique called direct ink writing, and the graphene aerogels prepared by 3D printing were lightweight, conductive, and had excellent compressive properties.

2.2.3 Applications of graphene aerogels

2.2.3.1 energy storage material

Graphene aerogels, as porous materials with excellent electrical properties and large specific surface area, have a wide range of applications in lithium-ion batteries, supercapacitors and solar energy, etc. Bai Hua et al ^[53] from Xiamen University performed in situ assembly of polyaniline as well as graphene oxide at the molecular level and reduced graphene oxide to obtain an aerogel with a specific capacitance of 808 F/g. Sun et al ^[54] reacted pyrrole monomer with graphene oxide and prepared a graphene aerogel with a specific capacitance of 304 F/g. Qin et al ^[55] prepared graphene/MnO₂ three-dimensional composites with a specific capacitance of 560 F/g using a one-step hydrothermal method, and the specific capacitance decreased by 21% after 1000 cycles, showing excellent cycling stability. As shown in Figure 2-6, Li et al ^[56] prepared fibrous hydrogel electrodes by the macromolecular self-assembly of GO and polyaniline hydrogels.

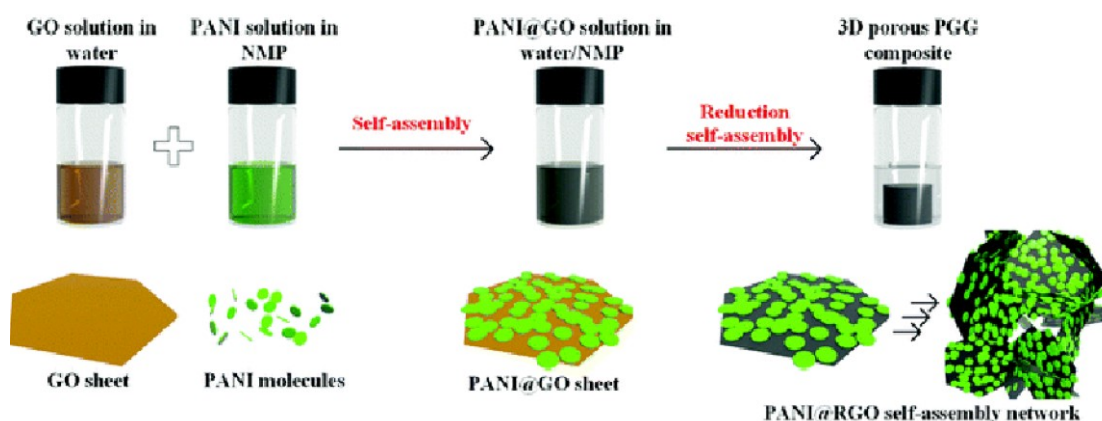


Figure 2-6 Schematic illustration of the solution-based self-assembly method for the preparation of PGGs ^[56]

2.2.3.2 Sensor

Graphene aerogels are widely used in sensors due to their very large specific surface area, which can maximize contact with analytes, and the rapid passage of charge carriers through the continuous graphene network structure, thereby improving analytical sensitivity. Zhang et al. ^[57] used La^{3+} ions and PEI to improve the strength of graphene oxide aerogels through cross-linking, which is oxidative compared to graphene and can be used as a monitor for some reducing gases. The overall conductive network of graphene aerogels shows attractive application prospects in sensors and other fields. Bao et al. ^[58] prepared three-dimensional graphene/ Co_3O_4 composites by thermal expansion method, which have high specific capacitance as supercapacitors, and can also achieve high sensitivity and high selectivity of glucose without enzyme detection. Injecting elastic polymers into the three-dimensional framework of graphene aerogels can construct elastic conductors with excellent performance.

2.2.3.3 Adsorbent

Because of the high hydrophobicity and large specific surface area of graphene aerogel, it has excellent adsorption capacity for hydrophobic organics and heavy metals, and has potential application value in environmental protection.

Song et al. ^[59] developed an ultralight nitrogen-doped graphene aerogel (NGA) using dopamine inspired by marine mussels. The synthesized NGA exhibits macroscopic assembly, mechanical stability, and flame retardancy, and has a high adsorption capacity for crude oil. Mi et al. ^[60] used graphene aerogel to treat Cu^{2+} in water, which showed strong pH sensitivity to the adsorption of copper ions, and could absorb and release copper ions by adjusting pH, and it could cycle use. As shown in Figure 2-7, Ge et al. ^[61] soaked the foam in graphene oxide by the template method, and obtained graphene foam after HI reduction. Using it as a Joule self-heating adsorbent can quickly clean up high-viscosity crude oil at sea, providing a new direction for efficient cleaning and recovery of high-viscosity crude oil spills.



Figure 2-7 (a) Illustration of the production process of the graphene sponge;
(b) Graphene foam adsorb high viscosity crude oil at sea ^[61]

2.2.3.4 Catalyst

To avoid agglomeration of nano-catalytic particles, and improve the catalytic efficiency of catalytic particle, use graphene aerogel as a catalyst carrier can

improve its dispersibility. At the same time, due to the porous structure and large specific surface area of the aerogel, the catalytic efficiency can be greatly improved. Su et al. ^[62] used GO and ammonium thiocyanate as precursors to prepare N and S co-doped 3D graphene-structured N/S-GFs by one-pot method, and the hybrid aerogel as a metal-free catalyst could accelerate oxygen, the sample shows good catalytic performance under alkaline conditions. Hou et al. ^[63] synthesized multi-layer MoS₂/nitrogen-doped graphene nanosheet aerogels (MoS₂/N-GAs) by hydrothermal method as a novel catalyst, which is effective in organic waste and microbial electrolysis cells (MECs) by electrochemical catalytic production of hydrogen.

2.3 Graphene/polymer composites

2.3.1 Introduction to graphene/polymer composites

Most of the physicochemical properties of graphene are altered during the assembly into three-dimensional network structures compared to two-dimensional graphene. This is caused by the quality of the dispersion, the interface and the binder properties. The good properties make graphene an excellent polymer filler. By regulating the structure of graphene aerogels, polymer composites are expected to achieve high electrical conductivity and excellent mechanical properties at low filler content, and at the same time, they can solve the problem of dispersion of two-dimensional graphene materials in polymers. And give composite materials some special functions. In addition, the functionalization of graphene aerogels can be achieved by introducing other polymer materials on the surface of aerogels.

2.3.2 Preparation and application of graphene/polymer composites

2.3.2.1 Co-assembly

Three-dimensional graphene/polymer composites prepared by co-assembly are

mainly composed of covalent bonds, hydrogen bonds and electrostatic adsorption between polymers or polymer monomers and graphene oxide or graphene. The three-dimensional graphene/polymer composites that can be prepared by co-assembly are mainly polymers that can interact with GO, such as polypyrrole^[64], polyaniline, polydopamine, polyacrylamide^[65], polyimide, PVA, polyethyleneimine, chitosan, sodium alginate^[66] and DNA and so on. Graphene/conductive polymer composites are mainly used in energy storage materials and sensors.

2.3.2.2 Template method

The template method is a method of preparing graphene/polymer composites through the self-assembly of graphene or graphene oxide and polymers by using polymer foams or microspheres as templates. The graphene/polymer composites prepared by the template method mainly include polystyrene (PS, natural rubber (NR), polyurethane (PU)^[67] (the preparation process is shown in Figure 2-8), polymethyl methacrylate (PMMA)^[68], ultra-high molecular weight polyethylene (UHMWPE)^[69], etc. Using a polymer with a complete three-dimensional network structure as a template to construct a graphene composite with a stable network structure can effectively improve the conductive properties of the polymer.

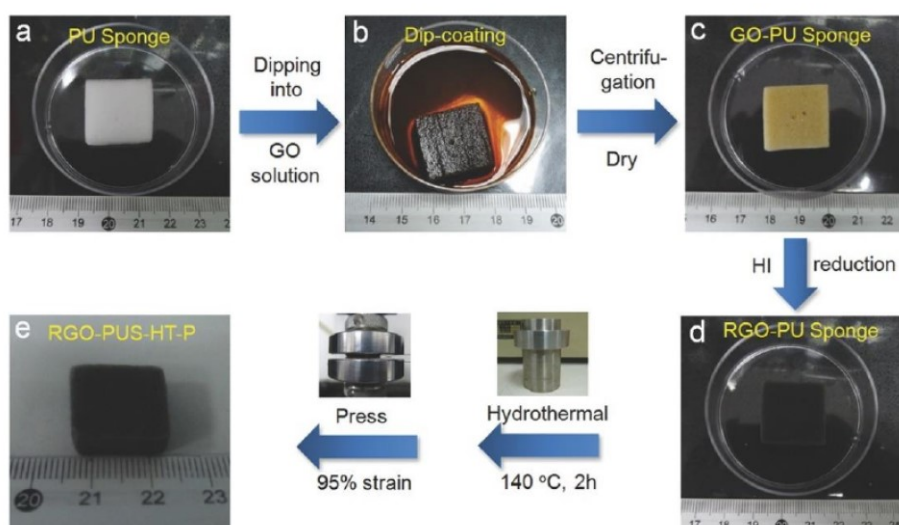


Figure 2-8 Fabrication process and pressure-sensing models of graphene-wrapped PU sponges ^[67]

2.3.2.3 Pre-construction

The pre-construction method is to obtain the three-dimensional graphene with complete structure through the template method, CVD method, directional freezing method and hydrothermal reduction self-assembly method. Then through the polymerization reaction or electrochemical deposition of the polymer, and vacuum-assisted method or impregnation method, polymers or polymer monomers and additives are introduced into the pre-constructed three-dimensional graphene, thereby obtaining a three-dimensional graphene/polymer composite material. The method is simple to operate and easy to produce on a large scale. Three-dimensional graphene/polymer composites prepared by pre-construction method, the polymers are mainly PDMS, EP, polyacrylamide ^[70], PVA ^[71] and polytetrafluoroethylene.

2.3.2.4 Sol-gel method

Sol-gel method is a process in which a mixture of metal-organic compounds, metal-inorganic compounds or the above two as raw materials undergoes hydrolysis and polycondensation, and gradually gels and undergoes corresponding aging and drying treatments to obtain oxides or other compounds. In this process, the metal organic or inorganic compounds are generally used as raw materials, dissolved in a certain solvent to form a uniform solution, and then the ions in the solution are hydrolyzed and polycondensed under the action of catalysts and additives. By controlling various reaction parameters, a uniform solution is obtained. A dispersion system in which nanoparticles or clusters are uniformly dispersed in a liquid medium, that is, a sol, and the sol is then subjected to changes in temperature, stirring, and hydrolysis and polycondensation. Aggregation increases the viscosity of the dispersion system, and eventually

leads to a fluid liquid sol slowly changing into a certain elastic solid gel. Whether a sol can develop into a gel depends on whether the force between the colloidal particles can overcome the potential barrier during agglomeration. Therefore, by increasing the charge of the colloidal particles, the steric hindrance effect and the solvation effect, etc., the sol can be made more stable and the gelation is more difficult; otherwise, the sol will form a gel more easily. In general, the methods for preparing gels from sols include solvent evaporation, adding non-solvents, freezing, adding electrolytes, and using chemical reactions to generate insoluble substances.

Researchers have developed a variety of graphene/polymer aerogels. However, with the development of the times, the demand for flexible supercapacitors has been increasing, and materials suitable for flexible electrodes need to have good flexibility and capacitance retention in addition to good electrochemical performance. Therefore, the research on flexible electrode materials has always been one of the hot research fields of materials science.

2.4 Development of conductive paper

In recent years, with the development of electronic technology and the improvement of people's living standards, flexible conductive materials have received extensive attention. As shown in figure 2-9, Flexible conductive materials can be widely used in electronic products, smart clothing, energy storage devices, sensors and wearable devices ^[72]. According to the development trend of various electronic devices, flexible conductive materials should not only have high transparency, high conductivity and good flexibility, but also should meet the requirements of light weight, low manufacturing cost and mass production. Currently, there are various problems such as shortage of non-renewable resources and serious environmental pollution. Therefore, using renewable materials as raw materials to prepare high-performance electronic

devices with low processing costs has a good development prospect.

As the most abundant renewable resource on earth, cellulose is one of the most important chemical raw materials in the 21st century. Compared with glass and plastic, the traditional substrates for electronic devices, cellulose-based materials are tough, bendable, non-fragile and thermally stable which can be used as flexible substrates ^[73]. Combining cellulose with conductive materials can not only endow the cellulose-based materials with certain conductive properties, but also improve the biocompatibility and strength of the conductive materials. Usually, metal foil ^[74], plastic substrates ^[75] and glass ^[76] can be used as substrates in electronic devices. But these substrates have unavoidable disadvantages, such as heavy weight, weak bonding between functional materials and substrates, easy oxidation and poor durability ^[77]. In contrast, eco-sustainable, recyclable, lightweight and readily available flexible paper-based materials offer potential alternatives to conventional substrates ^[78]. Although pure cellulose paper materials are non-conductive, this limits the application of paper in electronics to some extent. However, cellulose fibers with various lengths and sizes have unique three-dimensional structures, and paper substrates can be composited with various conductive active materials, providing feasibility for the development and application of advanced electronic devices ^[79]. For example, conductive coatings are applied on the surface of cellulose paper ^[80], conductive fillers are added during the paper preparation process ^[81], or metals are grown in situ on the surface of cellulose fibers ^[82]. Paper, especially as a porous structural material, has obvious advantages in electrochemistry. Therefore, paper-based flexible electronic devices have the potential to become popular and even improve or solve the environmental pollution problems caused by electronic waste in the near future.

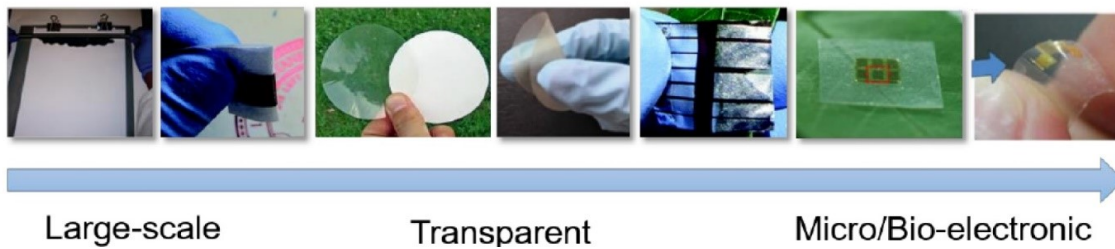


Figure 2-9 Development of the paper-based electronics: coating paper, transparent paper, paper-based solar cell and micro-electronics. ^[72]

2.4.1 Characteristics of paper as a conductive substrate

Flexible electronic products in various fields have greatly enriched and improved people's living standards, and also increased the demand for flexible substrates that can directly affect the performance of electronic products.

2.4.1.1 Advantages of paper-based electronic devices

- (1) Paper is a generally available renewable material with wide sources and low cost ^[83];
- (2) Paper is biodegradable and flammable, and can be safely disposed of through natural degradation or incineration, saving space for electronic waste disposal ^[84];
- (3) The cell lumen of cellulose can accommodate and deliver solutions. Liquid substances can flow through defined channels by capillary action of cellulose fibers, independent of external forces ^[85]. For batteries and capacitors, pores on the fiber walls and mesoporous channels inside the fibers can act as additional ion diffusion paths for the charge/discharge process;
- (4) Special properties of paper substrates (eg, hydrophobicity, transparency, and breathability) can be tailored to meet individual needs;
- (5) Paper with 3D porous structure, high surface area and certain thickness is easier to absorb and adsorb active substances, and can store more required

reagents. When paper is used as the electrode of a fuel cell, it can be used to store the electrolyte ^[86]. And most importantly, the two sides of the paper can also be selectively treated with different functions ^[87] to achieve the role of a separator;

(6) Cellulose is insoluble in common organic solvents, giving paper excellent chemical stability ^[88];

(7) Cellulose has high thermal stability, paper can exhibit higher dimensional stability under temperature changes, and has a lower thermal expansion coefficient than most plastics ^[89], which will expand the application of electronic devices scope and work environment.

(8) Cellulose paper has good biocompatibility, non-toxic and harmless, and can be directly used in biosensing, human body sensing and other fields.

2.4.1.2 Disadvantages of paper used in electronic devices

(1) Porous construction. On the one hand, the paper's porosity (and roughness) is advantageous for achieving good adherence of functional components to increase device performance ^[111]. On the other hand, the high surface roughness and porosity of functionalized paper typically results in lower conductivity than plastic substrates, and the inherent surface structure of paper will affect the resolution and structural accuracy of the produced electronic devices, which is not conducive to the precision Construction of electronic devices.

(2) Stability and durability. Paper is mechanically weaker than traditional substrates (metal, glass and plastic) and is therefore more prone to damage. Despite great progress in papermaking technology, most of the issues related to paper stability and durability have not yet been resolved, and paper-based materials will yellow, degrade, and be prone to fiber loss when exposed to natural air and sunlight ^[141]. Therefore, the outdoor environment, harsh natural environment, etc. have a great impact on paper-based electronic products.

(3) Humidity effects. Since paper is hygroscopic, even a small amount of moisture may generate a response current that affects the electrical properties of flexible devices on paper. In addition, humidity also affects the strength of the paper ^[97]. In order to achieve stable electrochemical performance, researchers laminate or coat plastic on the surface of paper to obtain a water-repellent surface, but this will be detrimental to paper recycling and environmental protection issues.

(4) Appropriate technology and new materials. There are reportedly many ways to fabricate electronic devices on paper. However, most are time-consuming or expensive. Because paper is more difficult to process and control than substrates such as plastic or glass, these factors have hindered the development of paper-based electronics ^[116]. Cost-effective, easy-to-operate fabrication and integration techniques are urgently needed to develop flexible paper-based electronic devices, and new materials more suitable for compounding with cellulose or cellulose paper should be explored.

(5) Miniaturized integratability. Most of the paper-based electronics are geared towards mass production and low-cost manufacturing techniques, while efforts should also be devoted to good design and construction for future-oriented applications such as miniaturized, fully integrated, portable and self-powered paper electronics ^[140]. In addition, natural and biocompatible paper-based materials can also be applied to precision electronic products such as human health system monitoring.

(6) Although great progress has been made in the development of paper-based electronic devices in recent years, and there are broad application studies in various fields, there is still a lack of relevant theoretical foundations, and there are many differences with the physical structure and chemical composition of paper substrates ^[120]. complex and directly related issues. Therefore, in the future, a deeper understanding of the geometry and chemical composition of cellulose

paper-based materials should be pursued rather than simply trying to use porous paper as a functional carrier for specific applications.

To summarise, while the use of paper to flexible electronics has piqued the interest of the scientific community, due to the large diversity of paper types, selecting the proper paper type is critical strategic relevance when fabricating electronic devices for a number of applications. Before building a specific flexible electrical gadget, the many qualities of paper must be thoroughly considered. Overall, the use of paper in electronic equipment has enormous promise, heralding a new era of green electronics.

2.4.2 Preparation method of conductive paper

2.4.2.1 Physical methods

The unique porosity of cellulose paper and the large number of hydroxyl groups on cellulose fibers make cellulose paper easy to combine with active conductive substances by physical methods^[90]. Therefore, a variety of different materials are used to composite with cellulose paper through different processes. Clearly, easy-to-operate and inexpensive physical methods are more competitive when designing and fabricating electronic components and devices, considering the requirements of emerging portable electronic devices^[91]. Inspired by paper-related functions in daily life (eg, handwriting, printing, and coating), conductive pathways can be constructed on paper substrates by means of common tools in life, such as pencils, inkjet printers, squeegees, and airbrushes, etc. As shown in Figure 2-10, the various physical methods used to improve the electrical conductivity of paper are listed.

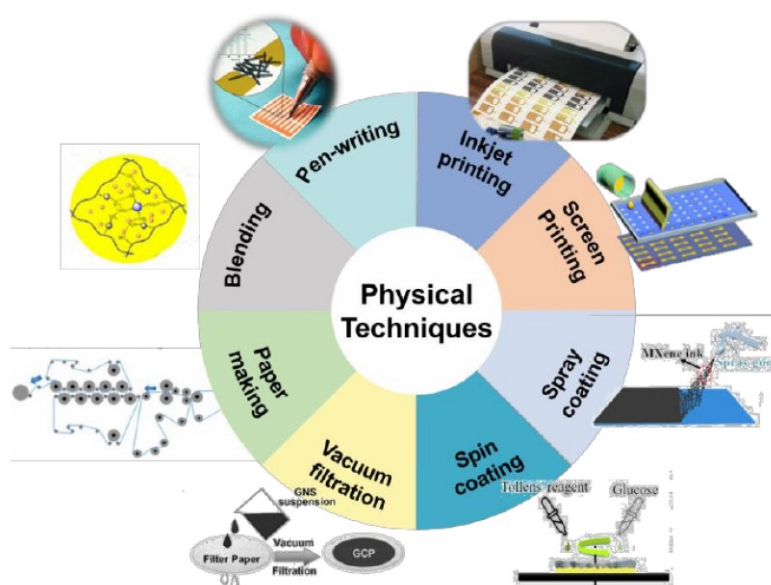


Figure 2-10 Physical techniques for obtaining conductive cellulose paper, including pen-writing, inkjet printing, screen printing, spray coating, spin coating, vacuum filtration, paper making and blending. [98, 105,108,110]

(1) Pen-writing

Using common office supplies, inexpensive and easy-to-use paper electronic components and even electronic devices can be designed and fabricated in minutes. The most common and easiest way is pen-write. According to the writing instrument, this method can be divided into two categories, pencil and ink pen [98, 99]. In order to obtain high-density and uniform graphite paper-based electrodes, the graphite tracks are generally obtained by means of cross-writing. For example, the writing direction is horizontal first, vertical in the second loop, and horizontal in the third loop [92]. With this writing style, the resulting paper-based electrodes have been applied in supercapacitors [93], humidity sensors, microfluidic devices [94] and anemometers [95] and other electronic devices.

In addition to solvent-free pencils, a variety of other writing instruments can also be used for writing purposes, including brushes, signature pens, fountain pens [96], and ballpoint pens, a range of ink-filled pens.

(2) Inkjet printing

To efficiently fabricate flexible paper electronics, inexpensive and efficient fabrication techniques are required. Inkjet printing is a common method for transferring electronic patterns onto flat substrates such as paper or plastic film. On this basis, Bollström and colleagues produced a hermetic barrier to prevent the penetration of the ink ^[97]. Using this barrier layer, a multilayer coating structure was successfully printed by the curtain coating technique. In addition, the researchers found that the smooth surface of the calendered paper significantly enhanced its printability, imparting strong conductivity and high resolution to the inkjet-printed silver ink. Because narrow, high-resolution printed wires require smoother substrate surfaces, high surface roughness has little effect on wider conductive paths. On the other hand, the special rough surface of paper is very beneficial for energy storage devices.

A common problem with inkjet printing is uneven drying of low-viscosity printing inks due to fast evaporation rates at the edges of printed structures, which can affect printing results, resulting in uneven patterns, known as the coffee ring effect ^[98]. To mitigate this adverse effect, inks should have high concentrations and low evaporation rates.

(3) Screen printing

Screen printing first originated in China and has a history of over 2,000 years. In this method, the screen printing plate pattern part of the mesh can pass through the ink, non-pattern part of the mesh cannot pass through the ink, printing in one end of the screen printing plate to add conductive ink, with a moving squeegee on the conductive ink pressure, the ink in the movement of the squeegee from the pattern part of the mesh extrusion to the paper or other desired substrate, the formation of conductive patterns ^[99]. Compared with pen-writing methods, screen

printing, like inkjet printing, has the advantages of fast, precise and repeatable deposition of a variety of functional materials on paper substrates.

(4) Spray/spin coating

Spray coating, which involves spraying coatings (paints, inks, varnishes, etc.) onto the surface of a device using air pressure or centrifugal force, is also used to build electrical component architectures on paper substrates. By spraying on paper, Edman et al. created flexible and lightweight functioning top-emitting devices ^[100]. Unlike conventional approaches, all functional components, including anodes, cathodes, and active materials, are obtained by spraying under typical conditions with a spray cannon. In addition, researchers developed paper-like flexible electronic devices Li_2S /reduced graphene oxide paper ^[101] and transparent paper electronic devices ^[102] using a simple rod coating technique. The rod coating technique is similar to blade surface coating in the papermaking process, and these results show that low-cost green electronics can be built in-line on inexpensive paper at a large scale through the paper machine coating process.

(5) Vacuum filtration

The paper substrate has a 3D porous structure, and pure cellulose paper, such as filter paper, has a large number of gaps between the fibers. The gaps allow other solvents, such as water, to pass through, while retaining insoluble materials. Therefore, paper can be used as a filter membrane, and conductive materials are filled on the surface or inside of cellulose fibers by vacuum filtration. Inkyum Kim obtained flexible and biodegradable light-weight transparent electrodes through continuous vacuum filtration of CNFs and silver nanowires, which can be applied to nanotriboelectric generators ^[103].

(6) Papermaking process

In the modern papermaking process, papermaking fillers are essential. The conductive active material can be directly added as a conductive filler, and the scale and industrialization of conductive functional paper can be realized without any changes to the papermaking process and papermaking machine. Gerhardt et al. successfully fabricated conductive fibers by assembling conductive ITO (indium tin oxides) nanoparticles onto wood fibers by LBL (layer-by-layer self-assembly), and made handsheets from these treated fibers by conventional papermaking methods. Positively charged ITO nanoparticles passed through negatively charged polyethylene amines and positively charged poly (sodium 4-styrene sulfonate) assembled to the surface of fibers ^[104].

(7) Dissolving and blending

After dissolving the cellulose and mixing it with the conductive functional material, the mixture of the conductive material and the cellulose is very uniform, and the combination is stable, resulting in the composite material exhibiting excellent mechanical and conductive stability even when stretched and bent. Although cellulose is insoluble in most organic solvents, it is soluble in some, including NaOH/aqueous urea, LiOH/urea, LiCl/N, N-dimethylacetamide, N-methylmorpholine-N oxide, and the ionic liquid 1-butyl-3-methylimidazolium acetate ^[105-107]. Huang Huadong et al. successfully prepared carbon nanotube/cellulose nanocomposite films using sodium hydroxide/urea aqueous solution as solvent ^[108]. The results show that after the cellulose is dissolved, the carbon nanotubes are uniformly dispersed in the cellulose matrix. Due to the formation of intermolecular hydrogen bonds between carbon nanotubes and cellulose chains, the prepared cellulose nanocomposite films not only have good electrical conductivity, but also have significantly improved mechanical properties.

2.4.2.2 Chemical methods

To increase the utility of paper substrates, two chemical procedures (in situ growth and polymerization) can be used in addition to the physical methods outlined above. The distinction between chemical and physical processes is that during chemical functionalization of paper, one group of chemicals is changed into another group of chemicals, involving the formation and breaking of chemical bonds between atoms. This section will highlight general chemical approaches for controlling the electrical characteristics of paper and their associated qualities. Figure 2-11 summarises materials typically employed in chemical modification of paper or paper-like electronics.

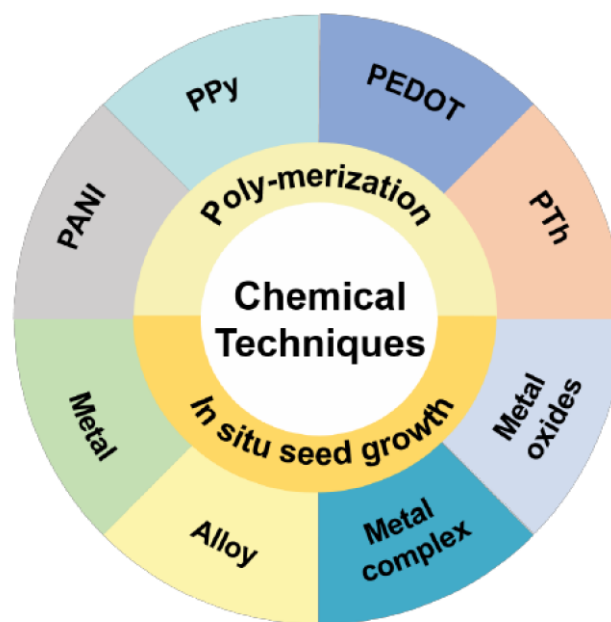


Figure 2-11 Chemical techniques for obtaining conductive cellulose paper. [109, 116, 120]

(1) In situ seed growth

Paper-based composites are obtained by traditional physical methods, in which the physical interaction between conductive materials and cellulose fibers is weak, and it is difficult for flexible electronic devices to maintain stable performance under severe conditions (bending, stretching, etc.). By in situ reduction and

growth of metal nanoparticles on the cellulose surface, stronger binding forces between particles and fibers can be achieved. Cellulose has a large specific surface area, a negative charge on the surface, and a large number of polar hydroxyl groups, which can bind a large number of transition metal ions. In situ growth of metal ions, which can enhance the interaction between active materials and cellulose fibers and control the structure of the resulting product by regulating the growth process ^[105]. So far, many electronic papers have been loaded with active nanomaterials by in situ growth methods, including Au ^[109], Ag ^[110, 111], Pt ^[112, 113], alloys ^[114, 115], and metals oxides ^[116, 117]. The metal nanomaterials loaded on the fiber surface not only improved the electrical conductivity of the fibers, but also had a certain promotion effect on the overall specific surface area of the composites ^[118]. Cellulose fibers serve as growth templates for these noble metals, which define the growth direction of metals, and fiber structures with good mechanical properties can also be used as scaffolds for flexible electronic devices ^[119].

(2) Poly-merization

Due to their inherent advantages of high energy density, electrical and optical stability, environmental friendliness, and high flexibility, various conducting polymers, including polyacetylene (PA), polyethylenedioxythiophene (PEDOT), polypyrrole (PPy), polythiophene (PTh), polyaniline (PANI) and their derivatives have been widely studied as electrocatalysts, photocatalysts and energy storage materials.

As one of the most popular conducting polymers, PPy possesses abundant microstructure and porosity, which is very suitable for flexible paper electronic devices, which has attracted great interest from researchers ^[120]. For example, Yuan Longyan et al. synthesized polypyrrole on the paper surface by soaking common printing paper in pyrrole monomer solution, then transferring the paper

to FeCl_3 solution (as oxidant) containing HCl (as dopant) ^[121]. After polymerization, a black conductive polypyrrole film doped with hydrogen ions was obtained with a conductivity of 15 Scm^{-1} . This conductive paper can be used as an electrode for solid-state supercapacitors with an area capacitance of 0.42 Fcm^{-2} . Cao Caiwan et al. used ferric iron as an oxidant to in situ polymerize PPy on the surface of cellulose paper, and then immersed the PPy/cellulose paper in the aqueous dispersion of GO to adsorb GO ^[120]. The three-dimensional porous structure of PPy has a good adsorption effect on GO, and the prepared hybrid paper has a very low sheet resistance ($1.7 \text{ }\Omega\text{cm}^{-1}$). In addition, the hybrid paper has good mechanical flexibility and excellent electrical conductivity, which can also be applied in all-solid-state flexible supercapacitors.

Similarly, due to its ease of synthesis, high electrical conductivity, large specific capacitance, and wide surface area, PANI produced by chemical or electrochemical polymerization has been extensively researched in energy storage devices. It has the potential to enhance the loading and stability of other active materials ^[122, 123]. PANI/gold/composite paper, for example, is frequently utilised as electrodes for all-solid-state SCs. Yuan Longyan et al. employed conventional printing paper made of cellulose fibres as the substrate ^[124] and a thin polymer film before evaporating an 80 nm-thick gold layer to overcome the weak adhesion between cellulose fibres and metal films. The vinyl alcohol layer alters the paper substrate before electroplating the PANI network on the Au/paper porous structure. Based on this, all-solid-state SCs were created. The all-solid-state SCs fabricated based on this technique exhibited high energy density (0.01 Whcm^{-3}) and power density (3 Wcm^{-3}), and were successfully applied to self-powered nanosystems.

In short, there are many ways to functionalize paper, both physical and chemical methods have their own advantages and disadvantages. Therefore, the

characteristics of the fibers, the internal structure of the paper, the properties of the active materials, and the characteristics of the target electronic device need to be fully considered before deciding which technique to adopt for functionalization.

2.5 Application of conductive paper in flexible electronics

The era of wearable electronic products is coming, and the big data industry and the Internet of things have inspired the unremitting pursuit of advanced electronic equipment in terms of performance, use, and aesthetics. The development of lightweight, environmentally friendly and flexible basic electronic devices is necessary to accelerate the arrival of the electronic age. Therefore, the preparation of emerging basic electronic units on paper will pave the way for the development of green electronics. E-paper has been significantly expanded into a wide variety of applications, including basic electronics, energy storage, power generation, batteries, sensing, and antennas, to name a few. In recent years, various materials and fabrication methods have been studied and demonstrated, paper-based electronics with equal or better performance and cost-effectiveness ratio. This section will introduce and discuss paper-based flexible electronics or applications over the past few years. Common paper-based electronic components and electronic devices are shown in the Figure 2-12.

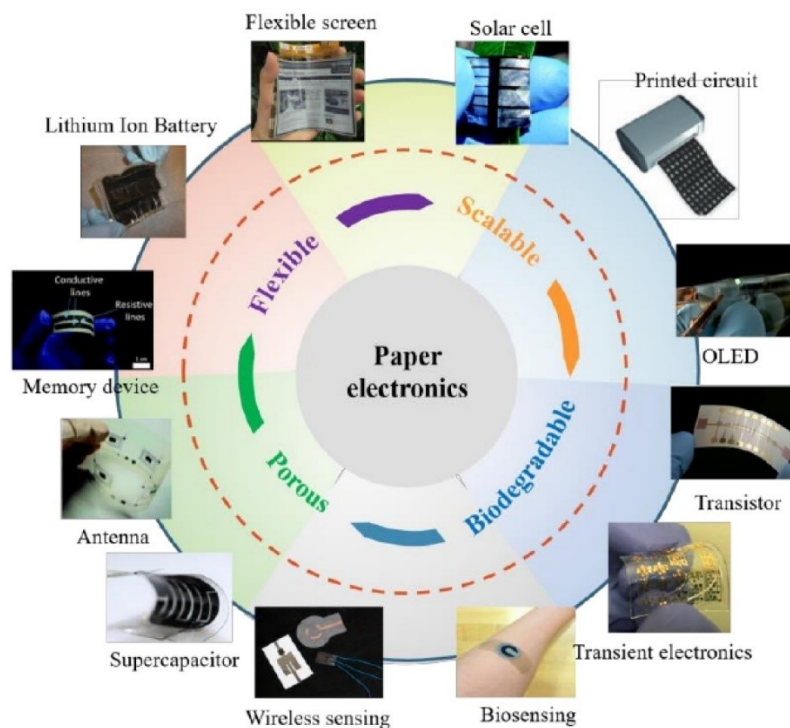


Figure 2-12 Diverse devices or applications of flexible electronics based on paper. [130, 136, 140, 142]

2.5.1 Supercapacitor

Supercapacitors, which have the advantages of fast charging and discharging rates and long cycle life, have higher energy density than traditional electrostatic capacitors and higher power density than batteries. [125-127]. Supercapacitors have great application prospects in electronic products, electric vehicles, and military products [128, 129]. Paper is composed of cellulose fibers with a diameter of about 20 μm , which contain many microfibrils composed of fibrils of tens of nanometers in diameter, giving the paper a rough and porous surface. This rough and porous surface is a natural advantage for supercapacitors, it facilitates the attachment of electrochemically active materials to the surface of cellulose, facilitates the adsorption of electrolytes, and also acts as a separator to prevent contact between the two electrodes [130, 131]. In addition, paper with certain mechanical

strength can also be used as a scaffold for supercapacitors to meet the needs of bendable and foldable flexible electronic devices.

Cellulose paper-based supercapacitors generally use carbon materials and conductive polymers as active materials. Wang Shiqun et al. ^[132] added graphene to cellulose fibers and synthesized polypyrrole in situ on the fibers. The resulting conductive paper has channels that allow electrons to move at high speed. A flexible wearable supercapacitor was fabricated with this paper, and its areal capacitance was as high as 363 mFcm^{-2} . Wu Xinyun et al. ^[133] polymerized pyrrole on the surface of a single CNC by in-situ chemical polymerization to obtain conductive cellulose nanocrystals. The supercapacitors made of the obtained materials have excellent electrochemical performance, and the scan rate is 0.01 Vs^{-1} has a capacitance of $248 \text{ F}\cdot\text{g}^{-1}$.

2.5.2 Biofuel cell

Biofuel cells (BFCs), a kind of devices that convert chemical energy contained in biodegradable organic matter into electrical energy, have recently received great attention.

BFCs built on paper will obtain the properties of paper-based flexible substrates, such as light weight, low cost, and environmental friendliness ^[134, 135]. In addition, BFC has the characteristics of moderate operating conditions (moderate ambient temperature and pH value), easy miniaturization, and high energy conversion efficiency, which broadens its application range, especially in the development of flexible energy devices. The first reported paper-based BFC dates back to 2010, in which gold sputtered carbon paper was used as the anode of the BFC, which was characterized by improved power generation ^[136]. Cyclic voltammetry analysis showed that *Shewanella* developed well on the gold sputtered carbon paper, indicating that the introduction of porous carbon paper is beneficial to the internal reproduction of microorganisms. In addition, the synthesized anode

material has rather high electrical conductivity and electrochemical performance as well as good biocompatibility, which contributes to the fast start-up of the reactor and enhanced current output. Zhang Lingling et al. used filter paper instead of carbon paper as the starting material for medium-free and small size (1.5 cm × 1.5 cm) BFC ^[137]. The ionic liquid-functionalized carbon nanotube composite material is used as a carrier to stably load glucose dehydrogenase (anode biocatalyst), which is beneficial to the direct electroreduction of O₂ by bilirubin oxidase (cathode biocatalyst).

2.5.3 Lithium-Ion battery

Because of its high energy density, lack of memory effect, extended cycle life, and environmental friendliness, lithium-ion batteries (LIBs) are a very promising power source for portable electronic devices. They are being employed in mobile phones, electric vehicles, and renewable energy. ^[138] Energy storage and other applications LIBs are typically made up of a LiCoO₂ cathode, a graphite anode, a separator, and a saturated organic electrolyte. The round-trip intercalation and deintercalation of lithium ions between the two electrodes is the main mechanism for its power generation. The growth of flexible wearable devices has raised demand for flexible LIBs, necessitating not only less expensive functional materials and manufacturing technologies, but also environmentally benign components for long-term development.

Taking advantage of the mechanical flexibility of lightweight cellulose fibers and using paper as the substrate for LIBs, fully flexible electronics with higher areal energy densities can be fabricated. Liu et al. developed a simple and cost-effective method for the preparation of LIBs using multi-walled carbon nanotube (SWCNT)-supported cellulose paper as the anode ^[139]. The flexible SWCNT paper is synthesized by a simple filtration method without the use of metal substrates or binders, and thus has the advantages of light weight and high

electrical conductivity, but its performance is slightly lower than that of conventional electrodes. To further improve the electrochemical performance of paper electrodes. Yi Cui et al. fabricated highly conductive paper by coating common commercial paper with thin films of CNTs and silver nanowires ^[130]. The experimental results show that this method not only greatly improves the adhesion of the film, but also simplifies the coating process and reduces the cost, providing a high-quality lightweight current collector for LIBs. In conclusion, LIBs fabricated from paper are one of the most promising next-generation high-specific-capacity storage devices. However, some problems of LIB itself, such as Li dendrite growth easily causing short circuit, still need to be solved urgently.

2.5.4 Pressure Sensor

Recently, pressure sensors for wearable devices and electronic skin have attracted much attention due to their unique properties.

Paper-based pressure sensors are simple, low-cost, and scalable, do not require complex equipment, can detect dynamic forces in a wide range, and can detect a variety of complex forces (eg, pressure, torsion, and bending). These properties enable paper pressure sensors to monitor responses from breathing, wrist pulses and even acoustic vibrations in real time. Therefore, paper-based pressure sensors are expected to provide a promising avenue for the convenient integration of future smart wearable electronic devices.

2.5.5 Nanogenerator

Nanogenerators based on piezoelectric effect, triboelectric effect, pyroelectric effect and electrostatic induction effect have been shown to be a simple and inexpensive self-powered system. It can convert various environmental mechanical energy (such as human motion, sound waves), wind and water into electricity ^[140]. In 2011, Kim et al. developed the first paper-based mechanical

generator with high thermal stability ^[141].

Kima et al. demonstrated a paper-based triboelectric nanogenerator that is ultrasoft and tailorable ^[142]. The nanogenerator uses commercial toilet paper as a raw material and supports silver nanowires through a "dipping and drying" method. The fabricated triboelectric nanogenerator possesses extremely low surface sheet resistance ($6 \Omega \text{sq}^{-1}$), low cost ($\$3.00 \text{ m}^{-2}$) and light weight (87 gm^{-3}). Thanks to the flexibility and trimmability of toilet paper, the size and shape of the nanogenerator can be changed at will and still function properly. This method is similar with the one used in this paper and the samples produced in this paper performed equally well.

2.5.6 Optoelectronic devices

Paper-based optoelectronic devices generally include paper-based solar cells and paper-based organic light-emitting diodes.

Hu Liangbing et al. ^[143] first used nanopaper with 90% transparency as the substrate to build organic solar cells on it, but the light energy conversion efficiency of this solar cell was only 0.21%. In addition to nanocellulose (CNF), cellulose nanocrystals (CNCs) with shorter lengths can also be used as substrates for solar cells. Zhou Yinhua et al. developed a solar cell based on CNC transparent paper ^[144]. This CNC thin film-based solar cell not only has a light energy conversion efficiency of 2.7%, but also achieves the recyclability of solar cell materials. This solar cell exhibits excellent rectification behavior with smaller series resistance and larger parallel resistance.

Although the research on cellulose-based flexible materials has been in progress in recent years, there are still many problems that have not been solved. The two biggest problems are that the production process of some new technologies is more troublesome and takes a long time. Another part of the new technology

requires higher manufacturing costs. These two factors limit many technologies to the laboratory level, and cannot be put into practical production and applications on a large scale. Therefore, the development of a new type of paper-based flexible material with low cost and short production cycle has become one of the current research hotspots.

3. Methodology

This project investigates the various properties and influencing factors of PVDF/graphene aerogels and carbon paper, as follows:

- a. Synthesize PVDF/graphene aerogels using different synthetic routes and explore the differences in their properties.
- b. Synthesize different types of carbon paper and explore their properties.

The main goal is to Investigate the fabrication methods of novel electrodes for energy storage and the factors that affect electrode performance.

The main content of the experiment is shown in the figure 3-1:

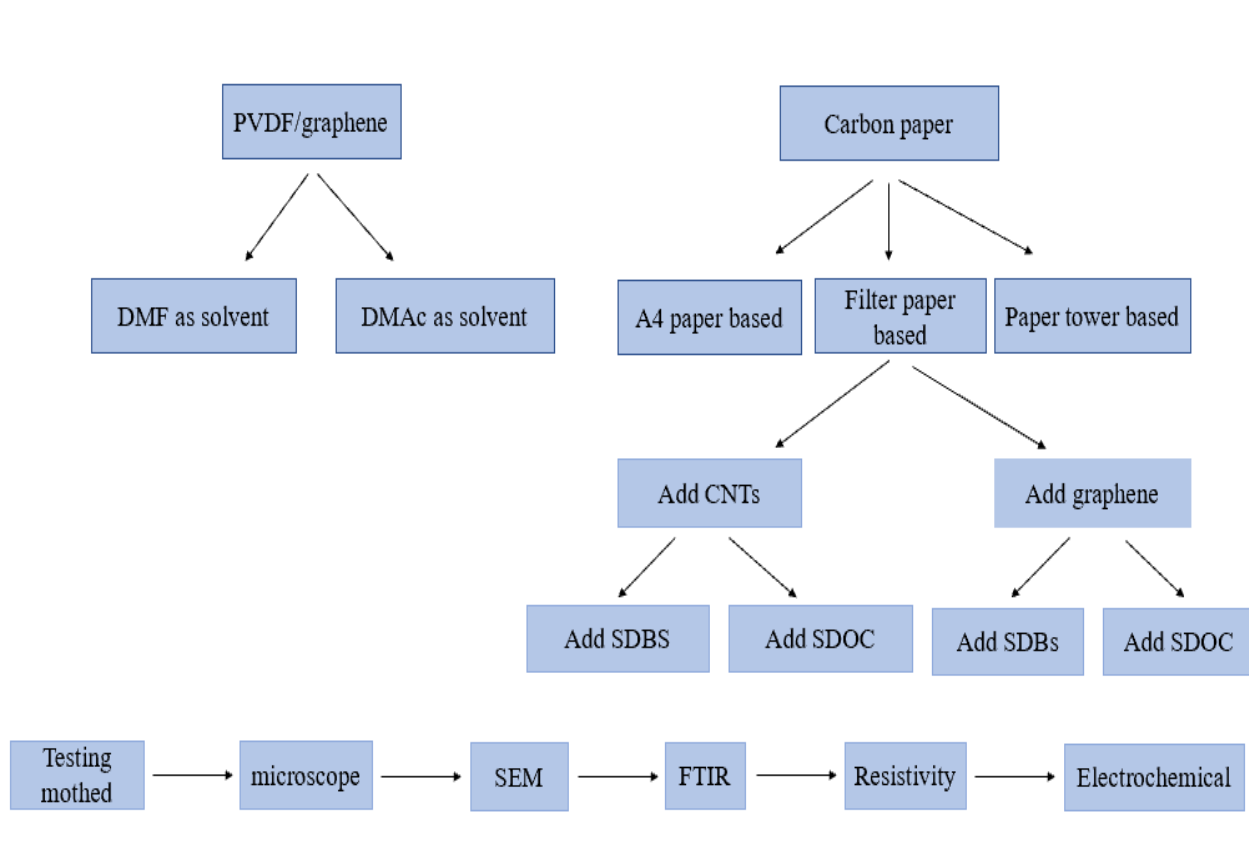


Figure 3-1 Project flow chart

3.1 Materials

Name	Characteristic	Company/Product code	CAS number
Polyvinylidene fluoride (PVDF)	Powder (Pure)	Sigma-Aldrich/182702	24937-79-9
Graphene	Nanoplatelets, few-layered graphene	NanoIntegris	7782-42-5
N, N-Dimethylformamide (DMF)	Anhydrous, 99.8%	Supelco/227056	68-12-2
N, N-Dimethylacetamide (DMAc)	Anhydrous, 99.8%	Sigma-Aldrich/271012	127-19-5
Carbon Nanotubes (CNTs)	Multi-walled, >95% carbon basis	Sigma-Aldrich/901019	308068-56-6
Sodium dodecylbenzenesulfonate (SDBS)	Solid (Pure)	Sigma-Aldrich/289957	25155-30-0
Sodium deoxycholate (SDOC)	Powder, >98%	Sigma-Aldrich/30970	302-95-4
Filter Paper	20µm	Whatman/1823-047	None
A4 paper	3*500 sheets, 80gsm	Oxford	None
Paper tower	None	Amazon Commercial	None
Sodium Sulfate Anhydrous (Na ₂ SO ₄)	Solid particles (pure)	Supelco/28225	7757-82-6
Deionized water	Liquid	Provided by the lab	None

Table 2 Materials used in the experiment

3.2 Sample preparation

3.2.1 Preparation of PVDF/graphene aerogels

This project investigated the effects of different solvents (DMF, DMAc), different graphene additions and different processes on the properties of PVDF/graphene aerogels. The experiments were divided into two main stages: 1. hydrogel preparation and 2. hydrogel to aerogel conversion process. And these two stages can be specifically divided into four experimental steps.

3.2.1.1 Preparation of PVDF/graphene aerogels (DMAc as solvent)

Referring to the preparation process of PVDF/graphene aerogel applied to adsorption by Zhang et al. ^[145]. The specific procedure can be seen in Figure 3-2 and Appendix 1. In this project, 1.2g PVDF powder was dissolved in 5ml DMAc at 90 °C. Graphene of different masses (30 mg, 60 mg, 90 mg) were weighed (see table 3), 15ml deionized water was added then ultrasonic dispersed (room temperature, 40kHz, 1.5hrs). The treatment using an ultrasonic bath was sufficient to disperse the small amounts of graphene. The PVDF solution and the graphene dispersion were then poured into 50 ml glass tubes for thorough mixing.

PVDF: Graphene	PVDF (g)	Graphene (mg)
40:1	1.2	30
20:1	1.2	60
40:3	1.2	90

Table 3 Amount of PVDF and Graphene

The mixed solution was degassed at 60 °C for 24 hours and then left to stand at room temperature for 12 hours for sol-gel reaction and degas. The samples were

soaked three times with ethanol (20ml) to remove DMAc. Finally, use a freeze dryer to dry the samples (-60 °C), and the optimal drying time is 24h through experiments (see the results and discussion section for data). This experiment mainly investigates the effect of changing the amount of graphene on the structure and electrochemical performance of the sample .

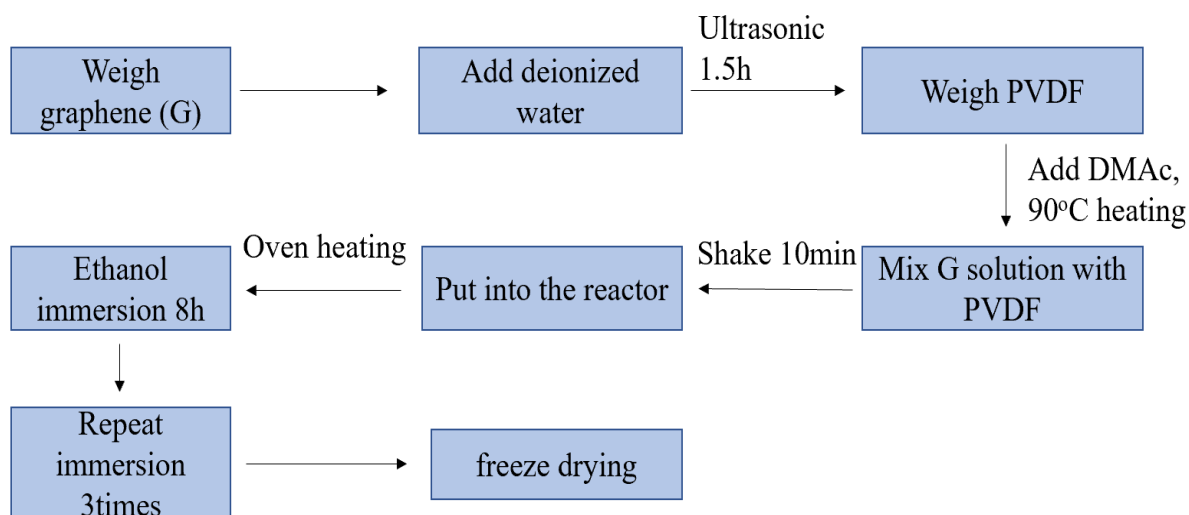


Figure 3-2 Experimental process with N, N-Dimethylacetamide (DMAc) as solvent

3.2.1.2 Preparation of PVDF aerogels (DMAc as solvent)

Add 10ml DMAc and 1.5ml deionized water to 1.2g PVDF powder, and dissolve at 90 °C (15min). The solution was then placed in an oven with a set temperature of 60 °C, degassed for 24 hours, and then allowed to stand at room temperature for 12 hours. Then the samples were soaked in ethanol three times, and then dried in a freeze dryer for 24 h. In this experiment, it will be investigated whether the addition of graphene has an effect on the structure of PVDF aerogels. For detailed steps, please refer to Appendix 2

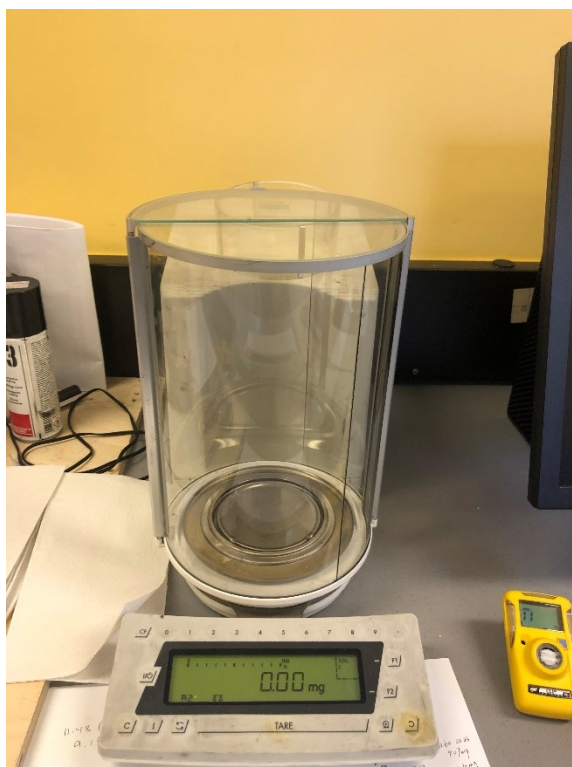


Figure 3-3 Electronic scale for weighing PVDF in experiments (Sartorius, BSA124S)

3.2.1.3 Preparation of PVDF/ graphene aerogels (DMF as solvent)

This project use a similar procedure to that used by Bidsorkhi et al. ^[146], the specific procedure can be found in appendix 3. In this project, (10mg, 20mg, 30mg) graphene was weighed and deionized water was added (see Table 4), and then ultrasonically dispersed (room temperature, 40kHz, 1.5hrs).

PVDF/ Graphene	PVDF (mg)	Graphene (mg)
5:1	50	10
5:2	50	20
5:3	50	30

Table 4 Amount of PVDF and Graphene

After adding 5 ml of DMF to 50 mg of PVDF and fully dissolving it, the PVDF solution and the graphene dispersion were mixed. The mixed solution was poured into a hydrothermal autoclave (50ml) and heated in an oven at 160 °C for 10 h. The hydrogel was then taken out and soaked in deionized water (20ml) for 8 h.

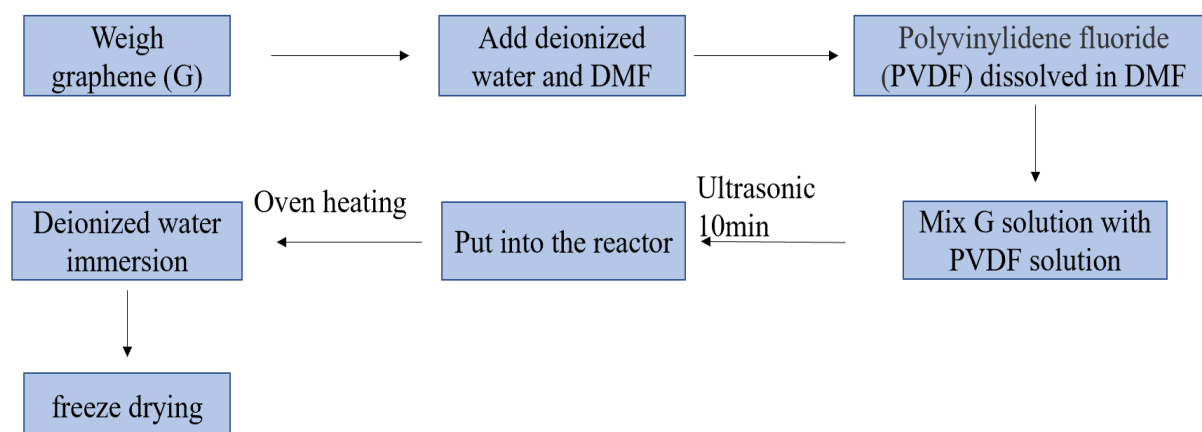


Figure 3-4 Experimental process with N, N-Dimethylformamide (DMF) as solvent

Repeat the soaking process 5 times. The samples were then freeze-dried (see the Results and Discussion section for the analysis of freeze-drying time). The detailed steps are shown in Figures 3-4 and Appendix 3. This experiment focuses on the effect of graphene addition on the properties of composite aerogels.



Figure 3-5 The oven used for heating in the experiment (Townson, F6010CN)

3.2.1.4 Freeze drying process



Figure 3-6 Freeze Dryer (Beijing Boyikang, Lab-50-1)

There are a lot of solvents in the pore structure of the PVDF/graphene hydrogel framework, and there is a process of converting the solid-liquid interface to the solid-gas interface during the conventional drying process. During this process,

the liquid expands and bends toward the interface, exerting a capillary pressure on the material walls. In order to avoid the damage to the gel structure caused by capillary pressure, freeze drying and supercritical drying have become the mainstream choices for drying gels. Shan et. al.^[147] used atmospheric pressure oven drying (APOD), supercritical drying (SD) and freeze drying (FD) to dry graphene composite hydrogels.

The degree of volume shrinkage is: $FD < SD < APOD$. Shen carried out BET tests on the dried samples, and the results are shown in Table 5.

Drying method	Drying condition	Time (hrs)	Specific surface area
Atmospheric pressure oven drying (APOD)	45°C, 7.5mPa	24	23 m ² /g
Supercritical drying (SD)	80°C	96	480 m ² /g
Freeze drying (FD)	-40°C, vacuum	48	457 m ² /g

Table 5 Effects of different drying methods on the specific surface area of aerogels ^[147]

From Shan's experimental data ^[147], we can see that although the volume shrinkage of the samples prepared by supercritical drying is smaller than that of the samples prepared by freeze drying, the specific surface areas of the samples prepared by them are relatively similar. Due to the small variation of the sample after freeze-drying and the large specific surface area. And the experimental process between the supercritical method is more complicated and the cost is higher, so in this project, we chose the freeze-drying method as the drying method of the hydrogel.

The freeze-drying used the Lab-50-1 freeze-drying machine of Beijing Boyikang Company, which is an external freeze-drying machine. Freeze-drying first places

the hydrogel in a freezer for freezing, the purpose is to convert the water in the hydrogel into a solid. After 24 hours of freezing, take it out and put it into the drying chamber of the freeze dryer, then close the chamber lid, turn on the vacuum pump, and run the drying program of the freeze dryer. After drying for 24 hours, the samples were taken out and drying was completed. For detailed steps, please refer to Appendix 4

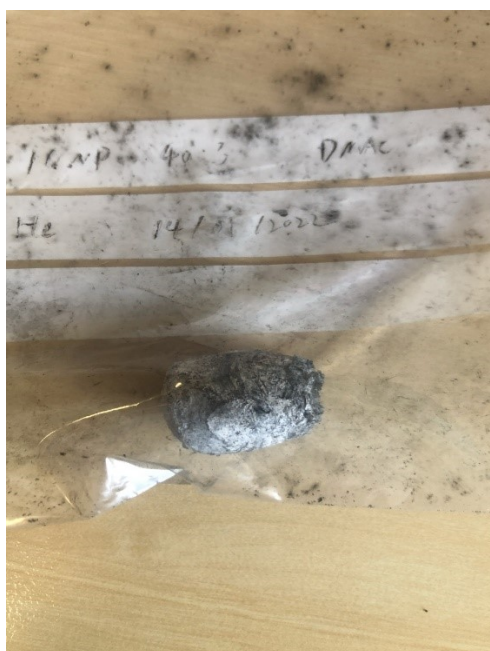


Figure 3-7 PVDF/graphene aerogel samples obtained by freeze-drying

3.2.2 Preparation of carbon paper

This project used dipping process to produce samples and investigated the effects of different conductive substances, different surfactants and different surfactant additions on the performance of the samples.

At the same time, three different substrate materials were selected in this experiment. All three substrate materials are cheap and easy to obtain, which can lay a good foundation for future large-scale commercial production. However, the internal and surface structures of the three substrate materials are slightly different. And the properties of different samples produced based on different substrate materials will also be studied and analyzed. This experiment will also investigate the effect of surfactant addition on sample performance. See Table 6 for specific sample descriptions and symbols.

3.2.2.1 Dipping process

The dipping process is a very common and is a widely used technology ^[155]. This technology does not require special equipment and complicated processes. The basic principle of the dipping method is, dipping brings the solid into contact with the liquid. Then capillary pressure causes the liquid to penetrate the pores (the paper absorbs the liquid). After the solution is immersed in the pore structure of the paper and then dried, the active substance contained in the solution can be supported on the paper. In order to increase the amount of loading or the depth of dipping, sometimes the air in the carrier can be evacuated in advance, and the vacuum dipping method is used; increasing the temperature of the dipping liquid (reducing its viscosity) and increasing the stirring have similar effects.

Although the dipping method is simple to operate, many complex problems are often encountered in the preparation process ^[156]. For example, when the surfactant is dried, sometimes the concentration of the active material on the

inner surface is reduced due to the movement of the catalytically active material to the outer surface, or even the carrier is not covered.

Considering that to improve the conductivity of the sample, it is necessary to fully disperse the conductive substance (graphene or CNT), so that the graphene and CNT will not form agglomerates on the surface of the carrier, so that it can be adsorbed more uniformly to increase the conductive area.

3.2.2.2 Dispersion of CNT/graphene

In order to better disperse graphene and CNT, in addition to using an ultrasonic machine to disperse it, it is also necessary to add some surfactants to the solution to keep graphene and CNT dispersed for a long time without re-agglomeration due to surface hydrophobicity. Two surfactants, SDBS and SDOC, were used in this experiment. These two surfactants will adsorb on the surface of graphene or CNT. They will isolate the hydrophobic surface of graphene and CNT from the solution, thereby reducing the surface tension of the particles. Thereby preventing the occurrence of particle agglomeration. For both surfactants, the critical micelle concentration (cmc) can be used as a reference point, because below the cmc, micelles do not begin to form structure around the particle. The cmc is equal to 1.6 mM (0.557 mg mL^{-1}) for SDBS and 2.6 mM (1 mg mL^{-1}) for SDOC. When preparing the solutions of SDBS and SDOC, the amount of both surfactants should be larger than their critical micelle points to achieve better dispersion effect. Whether the addition of more surfactant when the amount is greater than the critical micelle point will affect the conductivity of the sample is a point of this experimental study.

In this project two different conductive substances were used, graphene and CNT, to compare the dispersion performance of different surfactants on conductive substances.

3.2.2.3 Solutions preparation and dipping process

	SDOC/ G	SDBS/G			SDBS/CNT			SDBS/ G
Ratio	2:1	2:1			2:1	5:1	10:1	5:1
Adsorption substrate	Filter Paper	Filter Paper	A4 Paper	Paper Towel	Filter Paper	Filter Paper	Filter Paper	Filter Paper
Symbol	A	B	C	D	E	F	G	H

Table 6 Sample number

The specific experimental steps are as follows:

- Use an electronic scale to weigh a certain amount of graphene (5mg) or CNT (5mg).
- Use an electronic scale to weigh a certain amount of SDBS (10mg, 24mg, 50mg) or SDOC (10mg), The specific conductive substance mass to surfactant mass ratio can be found in Table 6.
- Pour the weighed SDBS or SDOC into the 50ml plastic sample tube.
- Put the weighed graphene or CNT into the sample tube and mix with SDBS or SDOC, and add 20ml of deionized water. In the experiment, the weight of the conductive material was kept unchanged, and only the weight of the surfactants was changed
- Use an ultrasonic machine to ultrasonically disperse the graphene or CNT for 2h. An ice bath must be used during sonication to prevent evaporation of the liquid.

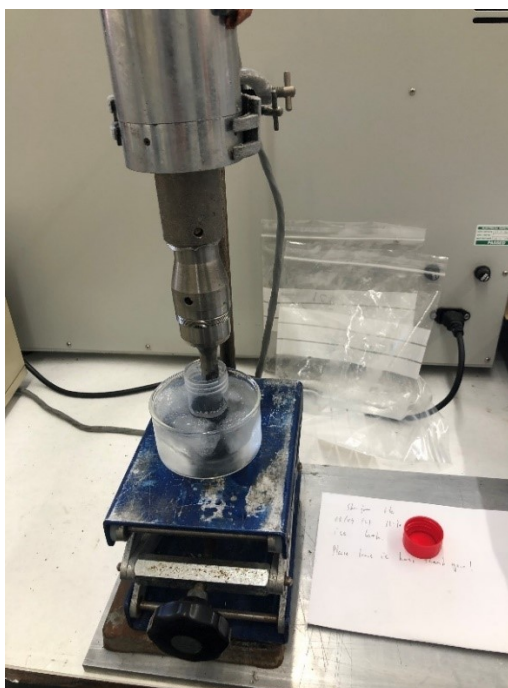


Figure 3-8 Ultrasound and ice bath process (Branson, digital sonifier and ultrasonic probe)

- f. Cut the prepared three kinds of paper into 3*3cm squares.
- g. Weigh each paper sample and label it
- h. Dip the cut paper into the well-dispersed solution for 5 seconds each time.



Figure 3-9 Prepared graphene or CNT solution

- i. To achieve better coating quality and reduce preparation time, the samples were dried on a heating plate for 15 minutes after each dipping to remove surface

moisture, and the dipping and drying operations were repeated ten times for each sample.



Figure 3-10 Drying process (IKA, C-MAG HS7)

j. After ten times, dry the sample at room temperature for 48h.

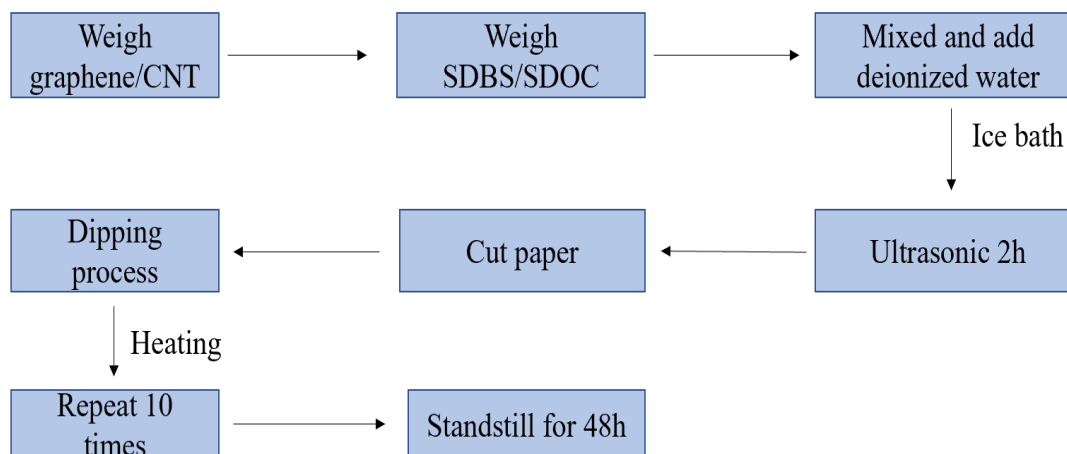


Figure 3-11 Dipping process

3.3 Optical microscope observation

3.3.1 Introduction of equipment used

Optical microscopes employ the magnifying imaging concept of convex lenses to magnify microscopic things that the human eye cannot differentiate to a size the human eye can discern, and the angular magnification M represents their magnification power. Because the opening angle of the same object to the eye is proportional to the distance of the object from the eye, it is generally agreed that the magnification of the instrument is the magnification of the image at a distance of 25 cm from the eye (photopic distance). Because a microscope's viewing angle is normally quite small, the ratio of viewing angles can be replaced by the ratio of its tangents.

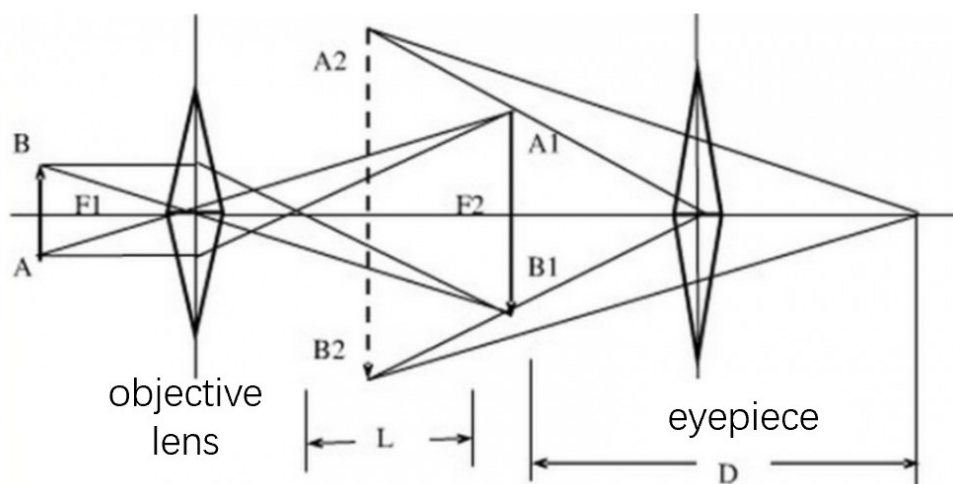


Figure 3-12 Optical microscope schematic

The optical microscope consists of two converging lenses, and the light path diagram is shown in the figure 3-12. The object AB is turned into a magnified and inverted real image A1B1 through the objective lens, and A1B1 is located inside the focal length of the object side of the eyepiece, and after passing through the eyepiece, it becomes an enlarged virtual image A2B2 at the photopic distance.

3.3.2 Testing procedure

Turn on the computer and microscope. Open the software, select the aperture, and adjust the mirror to make the field of view clear. Place the sample to be measured on the stage, adjust the coarse screw knob first and then the fine screw knob until the image on the computer becomes clear. Save the image. After all tests are done, clean the stage and turn it off. For detailed operation steps, please refer to Appendix 5.



Figure 3-13 Optical microscope used in experiments (Leica, S9E)

3.4 Scanning electron microscope (SEM)

3.4.1 Introduction of used equipment

A scanning electron microscope is a large-scale equipment used to examine the surface morphology of materials. When an incident electron beam of a certain energy bombards the surface of a sample, the electrons have one or more elastic

and inelastic collisions with the nuclei and outer electrons of the element; some electrons are reflected out of the sample surface, while the rest penetrate into the sample, gradually loses kinetic energy, and eventually stops moving and is absorbed by the sample. During this process, more than 99 percent of the incoming electron energy is transformed into thermal energy of the sample, while the remaining 1 percent stimulates different signals from the sample. ^[74] These signals primarily comprise secondary electrons, backscattered electrons, absorbed electrons, transmission electrons, Auger electrons, electron electromotive force, cathodoluminescence, X-rays, and so on, as seen in Figure 3-14. The information obtained from these signals is used to analyse the material via scanning electron microscopy equipment.

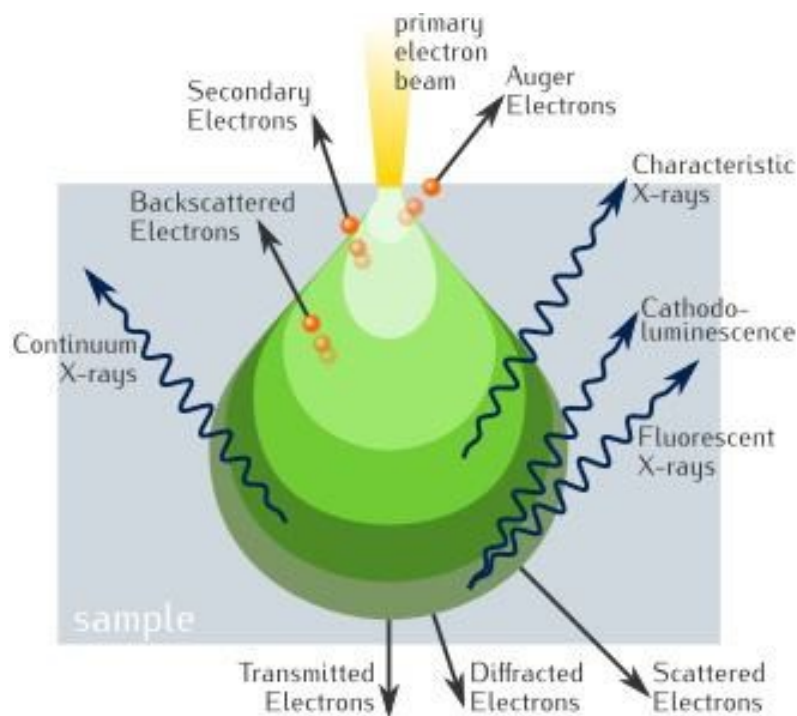


Figure 3-14 Various signals generated by the interaction of the electron beam with the sample and their corresponding effects ^[67]

Structurally, as shown in Figure 3-15, SEM is mainly composed of seven systems, namely electron optical system, detection, signal processing, display system, image recording system, sample chamber, vacuum system, cooling circulating

water system, Power supply system [53].

The thermionic electrons released by the filament are accelerated by a voltage of 2-30KV and focused by two condenser lenses and an objective lens to form an incoming electron beam with a certain energy, intensity, and spot diameter. The incident electron beam is raster scanned in a certain time and spatial order by the magnetic field created by the scanning coil. The secondary electrons produced from the sample are gathered by the collector as a result of the interaction between the incident electrons and the sample, and secondary electrons released in all directions can also be collected. These secondary electrons are accelerated and fired into the scintillator, where their information is turned into optical signals before entering the photomultiplier tube through the light guide tube, where the optical signals are translated into electrical signals [83]. This electrical signal is amplified by the video amplifier and sent into the picture tube's grid to adjust the brightness of the fluorescent screen, resulting in the appearance of the same image matching to the sample on the fluorescent screen.

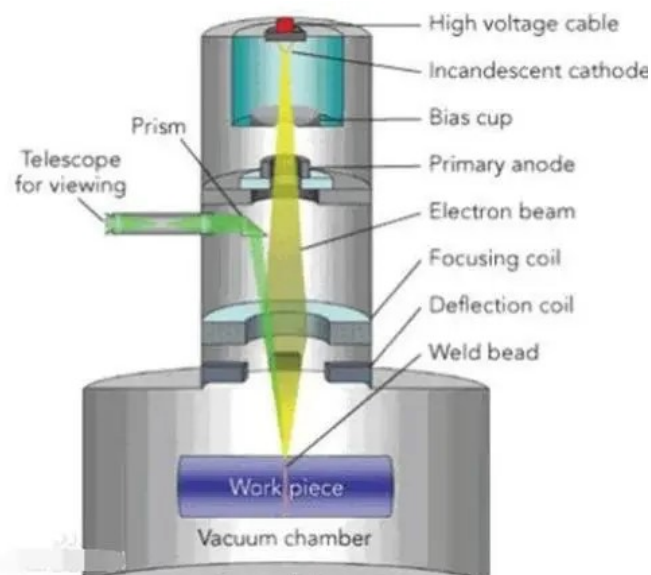


Figure 3-15 SEM structure diagram

3.4.2 Testing procedure

The sample to be tested is glued to the sample holder and coated with gold or palladium. Check vacuum and circulating water status. After placing the sample holder in the sample stage, exhaust and fix the sample stage. Choose the appropriate accelerating voltage and beam current. Use the scroll wheel to select a suitable area to take a photo. After the test, clean the sample holder and turn off the power. For detailed operation steps, please refer to Appendix 6.



Figure 3-16 SEM used in experiments (Hitachi, SU5000)

3.5 Fourier Transform infrared spectroscopy (FTIR)

3.5.1 Introduction of used equipment

Infrared absorption spectroscopy is mostly used to analyse functional groups in molecules, although it may also be used for quantitative analysis (less used, especially when there are difficulties in quantitative analysis of multiple components). Infrared spectroscopy may be used on a broad variety of substances. It can detect inorganic, organic, and polymer chemicals in solid,

liquid, or gaseous samples. When studying an unknown substance, infrared may often provide functional group information. It is useful in confirming the structure of the product when combined with additional methods such as mass spectrometry, nuclear magnetic resonance, single crystal diffraction, and so on (the most widely used). Please see Figure 3-17 for the construction diagram ^[64].

Interferometer: It is the heart part of the infrared spectrometer, consisting of a fixed mirror, a moving mirror, and a beam splitter (KBr).

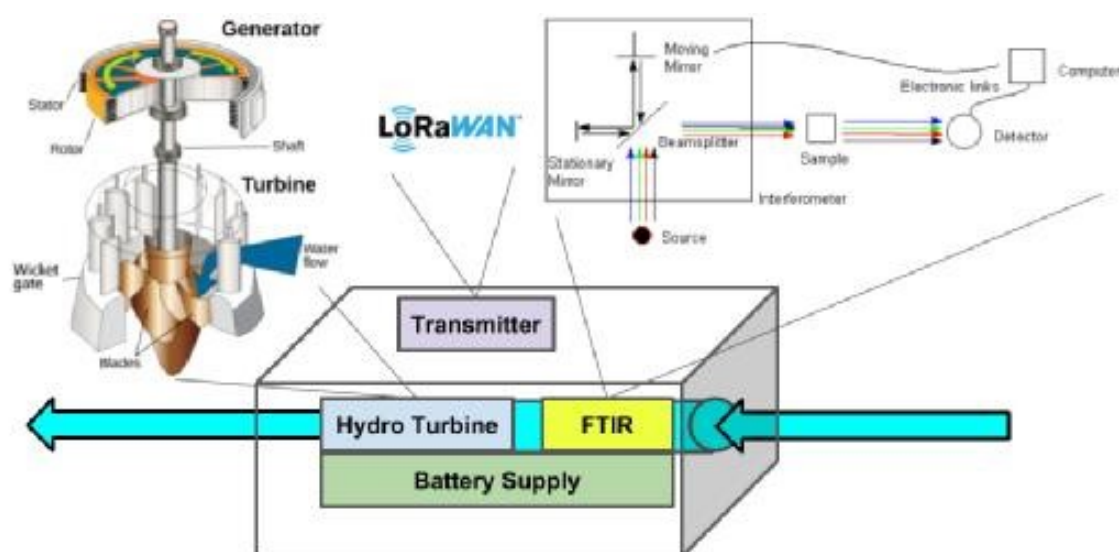


Figure 3-17 FTIR structure diagram ^[148]

At the exit of the interferometer, two beams of light with an optical path difference interfere and then reach the sample.

Fixed mirror: Reflects the light beam.

Moving mirror: The laser beam is used to control the moving rate of the scanner to modulate the beam, resulting in wading light.

Beam splitter: Transmitted beam.

Detector: The interference signal is amplified, filtered, digitized, and mathematically transformed (Fourier transform) into a spectrogram.

3.5.2 Testing procedure

Power on and open the test software, first calibrate the data with water as a calibrator, then clean the sample stage, place the sample to be measured on the sample stage, set the parameters and conduct the test. Clean the stage and turn off the power when the test is complete. For detailed operation steps, please refer to Appendix 7.



Figure 3-18 FTIR used in the experiment (Thermo Fisher, Nicolet iZ10)

3.6 Resistivity Testing

3.6.1 Specimen preparation

The samples should be dried in air under a fume hood for 48 hours before conducting the conductivity test to prevent the diffusion of graphene (since the surface of the dried sample is filled with graphene or CNT powder, while dry

graphene and CNTs are hazardous chemicals (see Appendix 10 and Appendix 11 for details). The length between the copper contact pins is 1 cm. In this case, the resistance value of copper is lower than 0.01Ω , and this small error is negligible in the experiment. Therefore, if the testing value of different regions of the same sample is different during the testing process, it is more likely It should be caused by the unevenness of the coating and the agglomeration of conductive substances. More research should be done to confirm the cause.

3.6.2 Introduction of used equipment

The basic principle of multimeter is to use a sensitive magneto DC ammeter (microammeter) as the meter head. When a small current passes through the head, a current is indicated. However, the meter head cannot pass large currents, so it must be connected in parallel and in series with some resistors for shunting or voltage reduction, so as to measure the current, voltage and resistance in the circuit.

3.6.3 Testing procedure



Figure 3-19 Photography of measuring resistance (RS PRO, RS-14)

Fix the sample on the measuring tool first. Turn on the multimeter, select the appropriate gear, perform zero adjustment, then connect two copper probes with test leads, read the data and record it, and then shut down. For detailed usage steps, see Figure 3-20 and Appendix 8. Because the resistance of the tested samples is very small, the results may be affected by the internal resistance of the copper wire in the fixed tool.

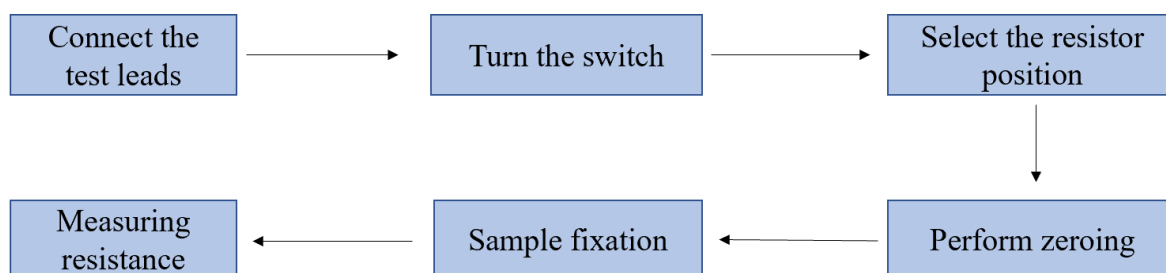


Figure 3-20 Schematic diagram of measuring resistance

3.6.4 Calculation of Resistivity

a. In order to ensure the accuracy of the experiment, two samples were prepared using each solution, and the resistance of different parts of each sample was measured to determine whether the prepared samples uniformly adsorbed conductive substances.

b. Since the calculation of resistivity needs to know the cross-sectional area of the sample, and the thickness of the sample paper is too thin, it is difficult to know the thickness of a single sheet of paper by measuring, so choose to use a vernier caliper to measure the thickness of ten pieces of sample paper, so as to calculate a single sheet of paper.

c. Resistivity is a physical quantity that describes the resistance properties of various substances. The resistivity of a substance is defined as the ratio of the product of resistance and cross-sectional area to the length of the original (20°C at room temperature) produced of the substance. The resistivity of a conductor

has nothing to do with its length or cross-sectional area. The electrical property of the conductor material itself is dictated by the conductor material. Equation 1 may be used to calculate the resistivity of each sample.

$$\rho = \frac{R \cdot S}{L} \quad \text{equation 1}$$

Where: ρ = material resistivity

R = material resistance

S = material cross-sectional area

L = material length

3.7 Electrochemical Testing

3.7.1 Introduction of equipment used for electrochemical analysis



Figure 3-21 The electrochemical workstation used in the experiment (Autolab, 302N)

The electrochemical workstation is essential in battery testing. It combines a

potentiostat, a galvanostat and an electrochemical AC impedance. It can not only run routine tests on three basic functions, but it can also run tests based on these three basic functions. Functionality testing that is stylized. It can detect not only the basic parameters such as battery voltage, current, and capacity during the test, but also the AC impedance parameters reflecting the battery reaction mechanism, completing the tracking and analysis of battery parameters in various states.

Electrodes are multiphase systems that consist of electronic conductors or semiconductors in contact with electrolyte solutions or electrolytes. Electrochemical systems use electrodes, which are places where reactions take place, to input or output electrical energy. Electrochemical systems are classified into two types: two-electrode systems and three-electrode systems, with three-electrode systems being the most common.

a. Three-electrode system (Figure 3-23)

Electrochemical reactions are based on the study of electron movement on electrodes. A three-electrode system is required to observe the reactions occurring at the cathode and anode of a battery or electrolytic cell, respectively.

The added electrode is referred to as the reference electrode, and it serves as a reference electrode for measuring the potential of the electrode that performs these reactions. The electrode to be measured is known as the working electrode, and the electrode opposite it is known as the auxiliary electrode.



Figure 3-22 The three-electrode system used in the experiment (Cranfield)

To measure the voltage between the research electrode and the reference electrode and arbitrarily adjust the potential of the research electrode in the three-electrode method, the most ideal equipment is a potentiostat with automatic adjustment function.

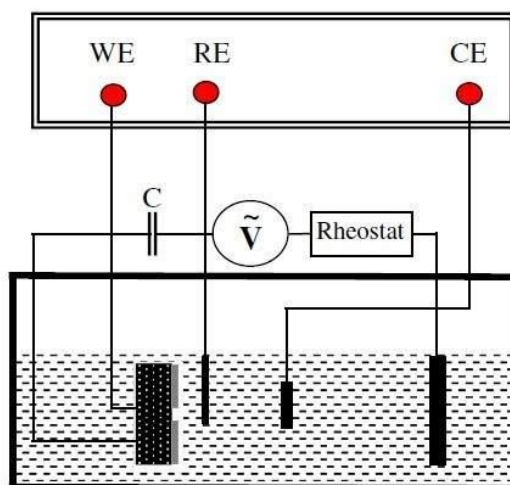


Figure 3-23 Schematic diagram of the structure of the three-electrode system (WE= work electrode, RE= reference electrode, CE= auxiliary/counter electrode)

b. Working electrode

The reaction under study occurs on the electrode, which is also known as a

research electrode. The fundamentals of working electrodes are, in general, as follows:

The electrochemical reactions under investigation are unaffected by the reactions occurring in the electrodes themselves, allowing them to be measured over a wide potential range.

Electrodes must not react with components of the solvent or electrolyte.

The electrode area should not be too large, the electrode surface should be uniform and smooth, and the surface should be easily purified.

c. Auxiliary electrode

Also known as the counter electrode, the auxiliary electrode, and the working electrode form a loop to ensure that the studied reaction occurs on the working electrode, but there must be no way to limit the battery's observed response. When the working electrode undergoes an oxidation or reduction reaction, the auxiliary electrode can be configured as a gas evolution reaction or a reverse reaction of the working electrode reaction, so that the electrolyte composition remains unchanged; that is, the performance of the auxiliary electrode does not generally have a significant impact on the reaction on the research electrode.

d. Reference electrode

A near-ideal unpolarized electrode with a known potential. The reference electrode, which is used to determine the electrode potential of the study electrode, conducts virtually no current (relative to the reference electrode).

3.7.2 Preparation of electrolyte

a. Wash the beaker and glass rod, then dry them with a paper towel.

b. Weigh 14.2g Na_2SO_4 using an electronic scale.

- c. Pour the weighed Na_2SO_4 into the beaker, add 100ml of deionized water, and stir with a glass rod, to prepare 1mol/L Na_2SO_4 solution.
- d. In order to completely dissolve the Na_2SO_4 particles, put the solution in a sonicator and sonicate for 30min (room temperature, 40kHz).
- e. Let the sonicated electrolyte stand at room temperature for electrochemical testing.
- f. Clean the glass rod and clean the electronic scale.

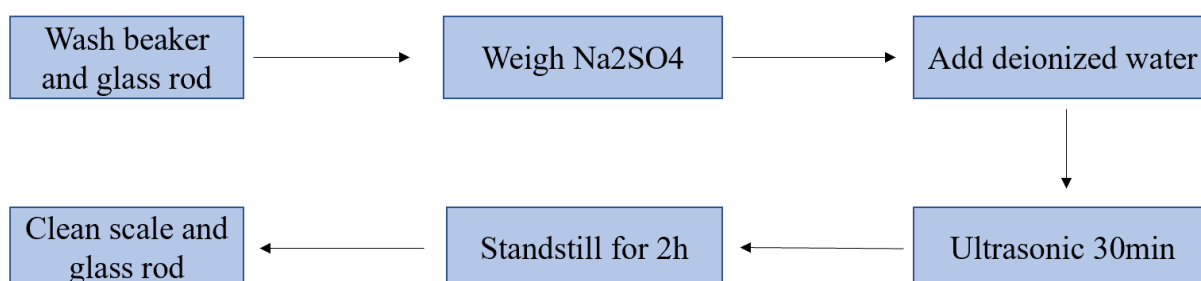


Figure 3-24 Schematic diagram of electrolyte preparation

3.7.3 Specimen preparation

- a. Take paper samples that have been dried at room temperature for 48 hours.
- b. Use an electronic scale to weigh each sample and subtract it from the weight before the dipping process to determine the mass of material adsorbed on each sample.
- c. By recording the weight change of each sample, calculate the mass of the conductive substance adsorbed on each sample according to the mass ratio of conductive substances and surfactants in different solutions immersed in each sample.
- d. Cut the sample into a 3*1cm rectangular strip.
- e. Affix 1*1cm insulation tape to the middle of each strip sample, so as to ensure

that only the 1*1cm area of the lower half of the sample is in contact with the electrolyte. In this way, the electrochemical performance of this part can be accurately measured.



Figure 3-25 Prepared electrode samples

f. Put the lower half of the paper sample with electrical tape into the electrolyte to soak for 8 hours, so that the electrolyte not only stays on the surface of the sample, but fully enters the inside of the sample. Thereby improving the detection accuracy.

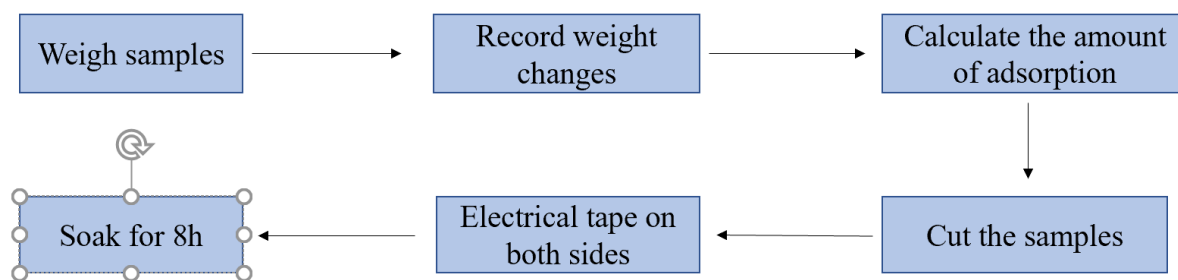


Figure 3-26 Electrode sample preparation process diagram

3.7.4 Testing procedure



Figure 3-27 The electromagnetic shielding box used in the experiment (Cranfield)

First assemble the three-electrode system. Turn on the electrochemical workstation, observe whether its working light flashes normally, and check whether it is connected to the computer normally. Move the three-electrode system into an electromagnetically shielded box. Select the item to be tested and set the parameters for pre-testing. After checking that the data is normal, start the formal test. After the test is completed, clean the laboratory utensils and turn off the machine. For specific experimental steps, please refer to Appendix 9

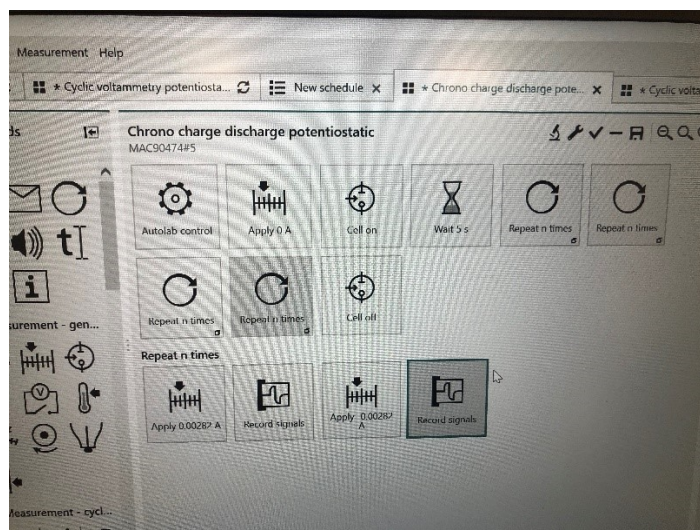


Figure 3-28 Test software used in the experiment (Cranfield)

3.7.5 Calculation of specific capacitance

Two different methods were used in this test: cyclic voltammetry and the Galvanostatic charge/discharge.

The technique of cyclic voltammetry (CV) is widely used in electrochemical research. In this approach, the electrode potential is adjusted to scan one or more times with a triangle waveform at varying speeds throughout time. The potential range is adjusted to allow for alternating reduction and oxidation processes on the electrode, and the current-potential curve is recorded. The shape of the curve can determine the degree of reversibility of the electrode reaction, the likelihood of intermediates, phase boundary adsorption or new phase development, and the nature of the coupling chemical reaction. It is widely used to establish electrode reaction parameters, control stages, and reaction mechanism, as well as to monitor which reactions may occur throughout the complete potential scanning range and what qualities they have.

One of the most important methods for studying the electrochemical properties of materials is the galvanostatic charge-discharge method (also known as chronopotentiometry and GCD). Its basic operation is as follows: charge and

discharge the tested electrode under constant current conditions, record the variation law of its potential with time, then study the electrode's charge and discharge performance, and calculate its actual specific capacity. The electrochemical response signal of the control current, when the control signal of the current is applied, the potential is the measured response signal, and the law of the potential change as a function of time is mainly studied in the process of charge and discharge experiments under constant current conditions.

Here we focus on how to calculate the specific capacitance of each sample from cyclic voltammetry (CV) data using Origin software.

The equation for specific capacitance is given by:

$$C_p = \frac{Q}{mV} \quad \text{equation 2}$$

Where: Q = charge stored in coulombs

m = mass of active material

V = potential

C_p = specific capacitance

As we know that:

$$I = \frac{Q}{t} \quad \text{equation 3}$$

Or

$$Q = I * t \quad \text{equation 4}$$

Where: Q = charge stored in coulombs

I = current

t = time

By putting equation 4 in equation 2 we got:

$$C_p = \frac{(I*t)}{mV} \quad \text{equation 5}$$

Dividing nominator and denominator by t:

$$C_p = \frac{(I*t)/t}{mV/t} \quad \text{equation 6}$$

Or:

$$C_p = \frac{I}{m \left(\frac{V}{t} \right)} \quad \text{equation 7}$$

In above equation, V/t is the scan rate of CV and we can represent it by k :

$$C_p = \frac{I}{m*k} \quad \text{equation 8}$$

Or:

$$I = C_p * m * k \quad \text{equation 9}$$

Now consider a CV curve:

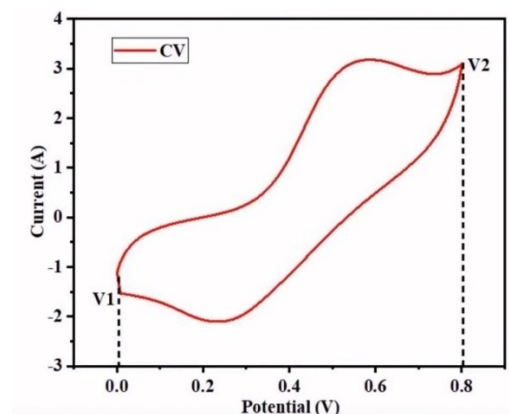


Figure 3-29 CV data schematic

In CV curve, the current changes by changing the potential from $V1$ to $V2$.

Therefore, equation 9 can be written in its integral form as:

$$\int_{V_1}^{V_2} I(v)dv = \int_{V_1}^{V_2} (C_p * m * k)dv \quad \text{equation 10}$$

If we look carefully to above equation, the integral on left hand side $[\int_{V_1}^{V_2} I(v)dv = \text{Area}]$ represent the area of the CV curve. $(I(v) * dv) = Y * X = \text{Area}$.

Therefore, equation 10 can be written as:

$$\text{Area} = \int_{V_1}^{V_2} (C_p * m * k)dv \quad \text{equation 11}$$

For a specific material, the value of C_p , m and k is constant. Therefore, the integral in equation 11 can be solved as:

$$\text{Area} = (V_2 - V_1)C_p * m * k \quad \text{equation 12}$$

In CV curve, we have three areas:

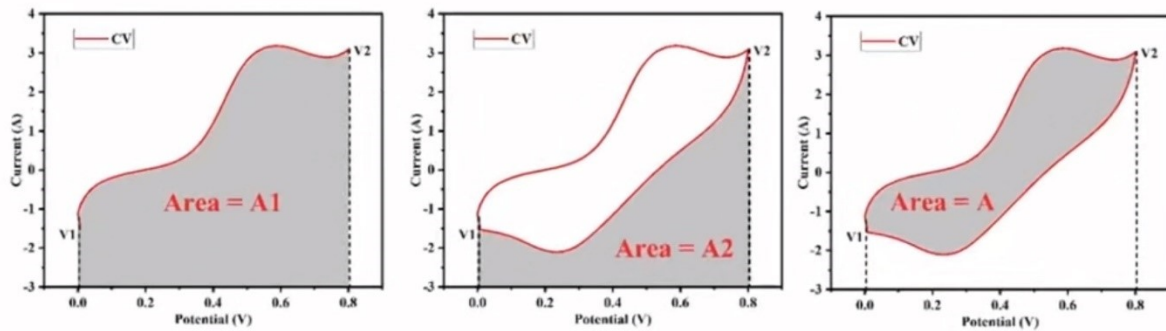


Figure 3-30 three CV data schematic

When capacitor is charging, then $\text{Area} = A1$ and equation 12 can be written as:

$$A1 = (V_2 - V_1)C_p * m * k \quad \text{equation 13}$$

Similarly, when capacitor is discharging, then $\text{Area} = A2$ and equation 12 can be written as:

$$A2 = (V_1 - V_2)C_p * m * k \quad \text{equation 14}$$

For the calculation of area (A) inside the CV curve, we have to subtract equation

14 from equation 13:

$$A = A_1 - A_2 = [(V_2 - V_1)C_p * m * k] - [(V_1 - V_2)C_p * m * k]$$

equation 15

Or:

$$A = [(V_2 - V_1)C_p * m * k] + [(V_2 - V_1)C_p * m * k]$$

equation 16

Or:

$$A = 2[(V_2 - V_1)]C_p * m * k)$$

equation 17

Or:

$$\frac{A}{2} = (V_2 - V_1)C_p * m * k$$

equation 18

Or:

$$\frac{A}{2(V_2 - V_1) * m * k} = C_p$$

equation 19

Or:

$$C_p = \frac{A}{2mk(V_2 - V_1)}$$

equation 20

Where: C_p = specific capacitance

A = area inside the CV curve

m = mass of active material

k = scan rate of CV

$V_2 - V_1$ = the potential window of CV

Equation 20 shows that to calculate the specific capacitance of the sample, the

amount of conductive materials loaded on the sample also needs to be measured. During the preparation of carbon paper samples, all paper substrates are weighed before the dipping process. After the dipping process, the samples are weighed again. The weight of the conductive substance and surfactant adsorbed on the paper substrate can be obtained. The weight of the conductive substance adsorbed on the sample can be calculated based on the ratio of conductive substance and surfactant added to the different solutions.

3.7.6 Capacitance Retention

- a. Connect the electrochemical workstation, turn it on, check the connection status and open the test software.
- b. Use the electrochemical workstation to perform multiple chronopotentiometry tests on each sample. Since the electrode material has been immersed in the electrolyte during this process, a part of the conductive material will fall off from the base material, thereby affecting the specific capacitance of the sample.
- c. Record the data of each sample after one hundred, three hundred, five hundred and one thousand times of charging and discharging.
- d. Use the graphing software to graph the obtained data and use the formula derived in the previous section to calculate the specific capacitance value after different times of charge and discharge.
- e. Use the graphing software to compare the capacitance retention rate of each material, summarize the law of capacitance decay, to discover the principle, and find out the samples with better performance, and make a summary.
- f. Clean the instruments used in the experiment, check that the computer and electrochemical workstation are in good condition, and then turn off the power.

4. Result and discussion

4.1 Sample drying rate analysis

All the samples produced in this project, whether they are aerogel samples or carbon paper samples, need to be dried. Therefore, the selection of the drying time of the sample is also a problem to be studied in this project. This section mainly analyzes the drying rate of different samples. By weighing the sample every 6h during the drying process to explore the optimal drying time for different samples. This research has a non-negligible role in the application of further experiments and technologies in the future.

4.1.1 PVDF aerogel drying rate (DMAc as solvent)

Since all aerogel samples are PVDF composite aerogels, it is necessary to first explore the drying rate of pure PVDF aerogels. Based on this, it is possible to further explore whether the addition of graphene or the type of solvent will affect the drying rate of the composite aerogels. The drying rate curve of pure PVDF aerogel can be seen from Figure 4-1.

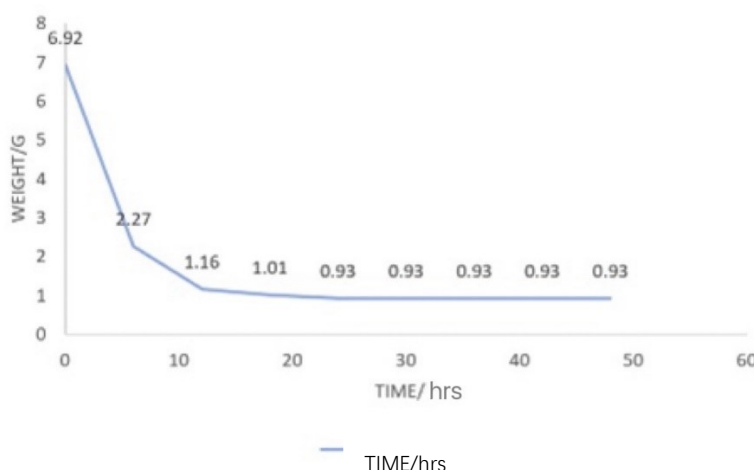


Figure 4-1 Drying rate curve of pure PVDF aerogel (Ethanol wash, -60°C, 24hrs)

It can be seen from Figure 4-1 that the drying rate of pure PVDF aerogel is not linear, which may be because most of the ethanol volatilized in the first stage of

drying exists on the surface of the hydrogel or closer to the surface part, and after the ethanol volatilization of the surface part, the internal ethanol volatilization becomes longer due to the path to be passed. Therefore, it is difficult to be volatilized, resulting in a decrease in the volatilization rate in the second stage. But it can be clearly found that the mass of the sample remains at 0.93 g after 24 h. Therefore, it can be inferred that the ethanol in the sample has been completely volatilized after 24 h.

4.1.2 PVDF/graphene aerogel drying rate (DMAc as solvent)

The drying rates of PVDF/graphene aerogels with different amounts of graphene added with DMAc as solvent are shown in Fig. 4-2

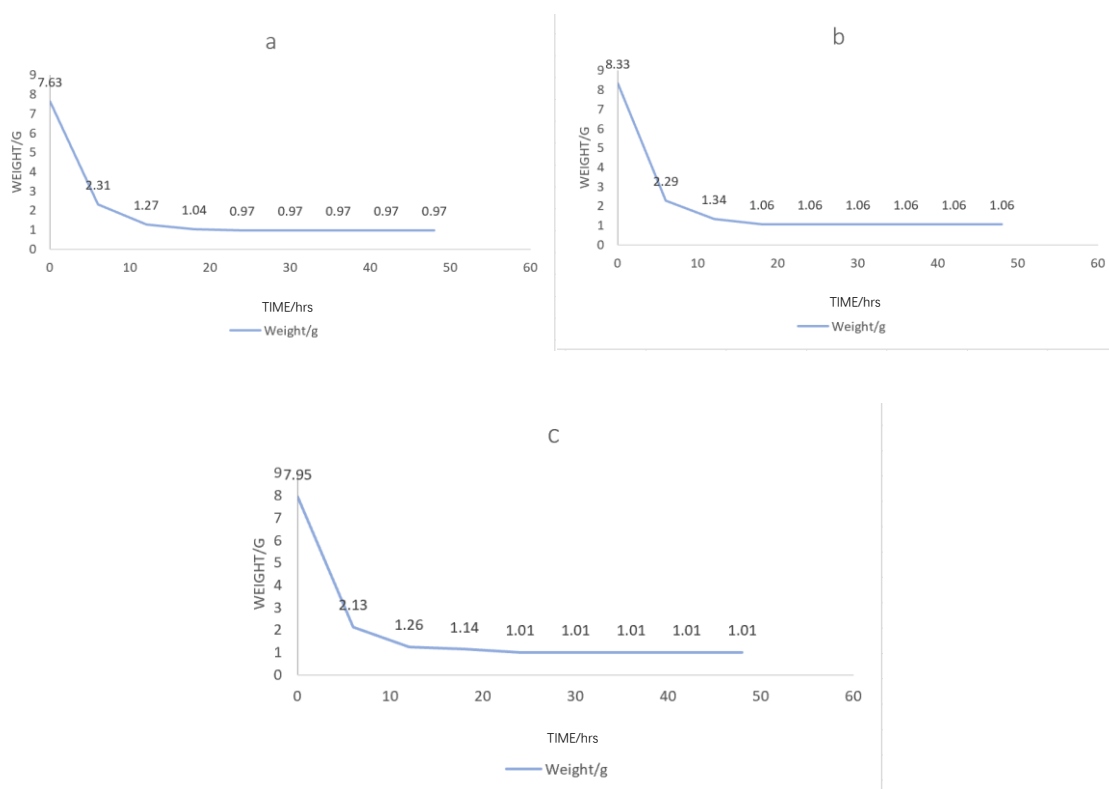


Figure 4-2 The drying rate curve of PVDF/graphene aerogel with DMAc as solvent (a, b, c are the graphene additions of 30 mg, 60 mg, and 90 mg, respectively, Ethanol wash, -60°C)

It can be seen from Figure 4-2 that the drying rate curve of the aerogel after adding graphene is basically consistent with the drying rate curve of pure PVDF

aerogel. By comparing the three graphs a, b, and c, it can be found that with the increase of graphene addition, the drying rate curve does not change. Therefore, the amount of graphene added has no effect on the drying rate of the composite aerogel. And after 24h, the weights of the three samples remained stable, so it can be seen that 24h is the best drying time for this type of composite aerogel.

4.1.3 PVDF/graphene aerogel drying rate (DMF as solvent)

The drying rates of PVDF/graphene aerogels with different amounts of graphene added with DMF as solvent are shown in Fig. 4-3

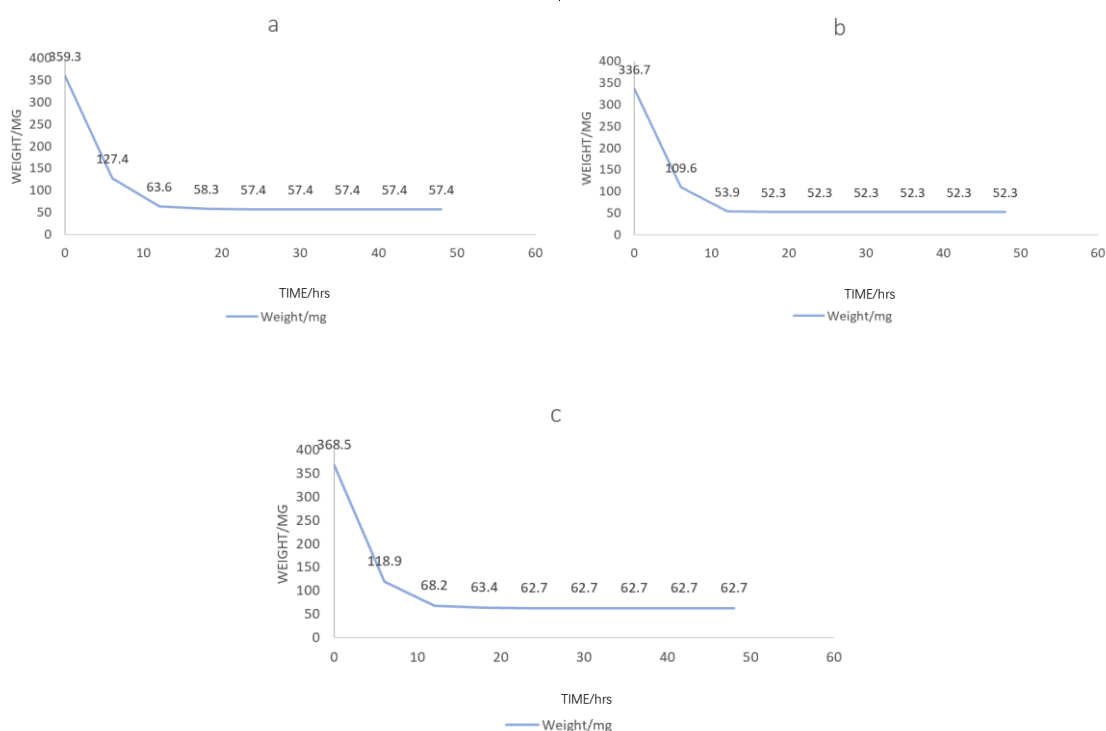


Figure 4-3 The drying rate curve of PVDF/graphene aerogel with DMF as solvent (a, b, c are the graphene additions of 10 mg, 20 mg, and 30 mg, water wash, -60°C)

It can be seen from Figure 4-3 that the drying rate curve of the composite aerogel with DMF as solvent is basically consistent with the drying rate curve of PVDF aerogel with DMAc as solvent, so it can be known that the type of solvent does not affect the drying rate. By comparing the three graphs a, b, and c, it can be found that with the increase of graphene addition, the drying rate curve does not

change. Therefore, the amount of graphene added has no effect on the drying rate of the composite aerogel. And after 24h, the weights of the three samples remained stable, so it can be seen that 24h is the best drying time for this type of composite aerogel.

4.1.4 Carbon paper drying rate

When making carbon paper samples, because there are many variables, there are many factors that need to be considered that affect the drying rate of the samples. Therefore, this section discusses from four aspects: base material, type of surfactant, amount of surfactant added and type of conductive substance. In order to explore the effect of different variables on the drying rate of samples, we can find the optimal drying time of samples that can be applied in future research and production.

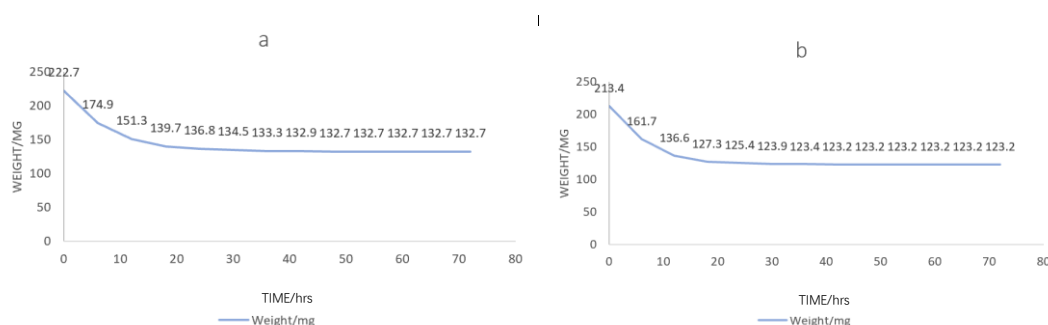


Figure 4-4 Carbon paper drying rate (a, b for graphene as conductive substance, filter paper as substrate material and equal amounts of SDBS and SDOC as surfactant, respectively, room temperature)

It can be seen from Figure 4-4 that when using the same base material and conductive substance, the drying rate curve of carbon paper with SDOC as surfactant is basically consistent with the drying rate curve of carbon paper with SDBS as surfactant. Therefore, it can be known that the type of surfactant does not affect the drying rate of carbon paper. By comparing the two graphs a and b, it can be found that the weight of the two samples remained stable after 48h, which shows that 48h is the best drying time for this type of carbon paper.

When controlling the surfactant type, conductive substance type and surfactant addition, the drying rates of carbon paper samples with different substrate materials are shown in Figures 4-5.

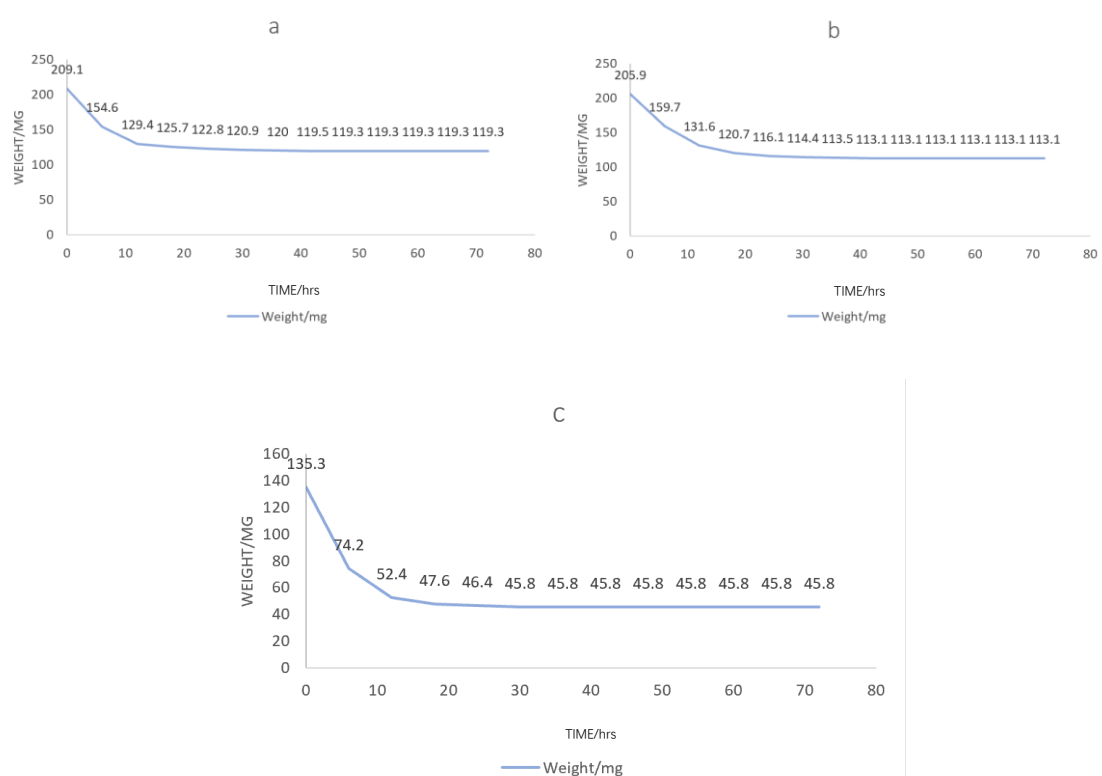


Figure 4-5 Drying rates of carbon paper when different substrate materials are selected (a, b and c are filter paper, A4 paper and tissue paper as substrate materials respectively, room temperature)

It can be seen from Figure 4-5 that when the same conductive substances and surfactants are used, the drying rate curve of carbon paper with filter paper as the base material is basically the same as the drying rate curve of carbon paper with A4 paper as the base material. However, their drying rate is slower than that of carbon paper based on paper towel, which may be because the thickness of paper towel is much thinner than that of filter paper and A4 paper. Therefore, it can be known that the type of base material will affect the drying rate of carbon paper. By comparing the two pictures a and b, it can be found that the weight of the two samples remains stable after 48h, while the weight of the c sample

remains stable after 30h. It can be seen that the filter paper and the A4 paper sample 48h are the same type of carbon paper. And for the paper towel sample the optimal drying time is 30h.

When controlling for surfactant type, substrate material and surfactant addition, the drying rates of carbon paper samples with different conductive materials added are shown in Figures 4-6.

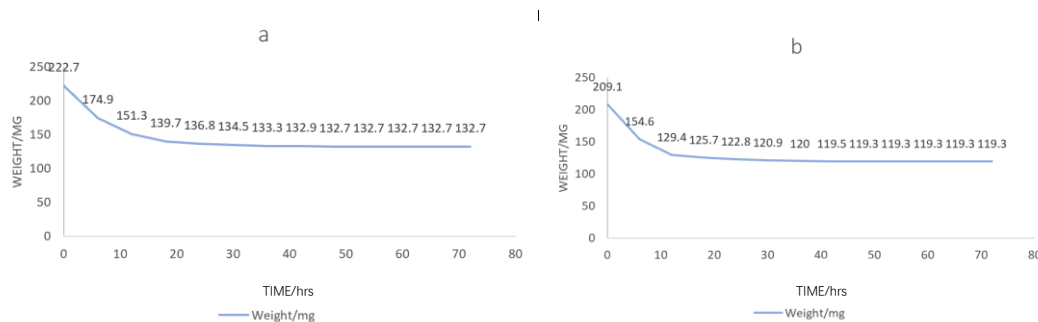


Figure 4-6 Drying rate curves of carbon paper samples with different conductive materials added (a, b with graphene and CNTs respectively, room temperature)

It can be seen from Figure 4-6 that when using the same base material and surfactant, the drying rate curve of the carbon paper with graphene as the conductive material is basically consistent with the drying rate curve of the carbon paper with CNTs as the conductive material. By comparing the two graphs a and b, it can be found that the weights of the two samples remained stable after 48h. It can be seen that the type of conductive material does not affect the drying rate of the carbon paper samples, and for the CNTs carbon paper samples and graphite 48h is the best drying time for the carbon paper sample.

The drying rates of the carbon paper samples produced by varying the surfactant addition when controlling for surfactant type, substrate material and conductive material are shown in Figure 4-7.

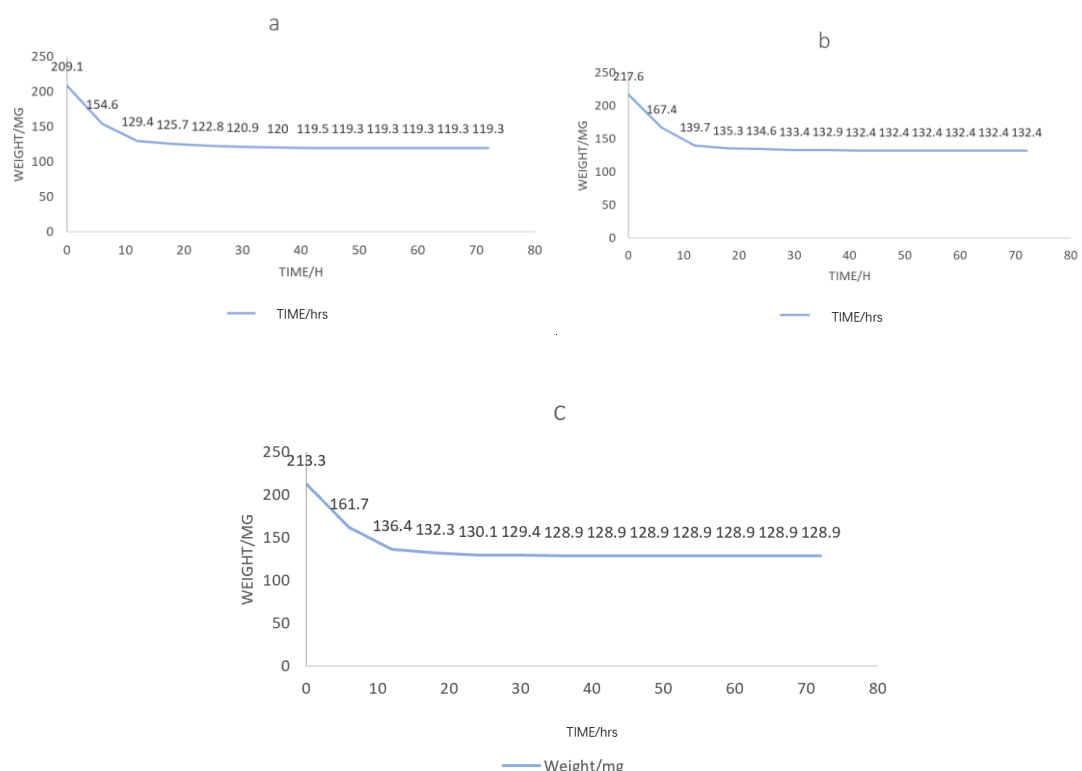


Figure 4-7 Drying rate curves of carbon paper samples with different surfactant additions (a, b, c are samples with SDBS to CNTs ratios of 2:1, 5:1, 10:1 respectively, room temperature)

It can be seen from Figure 4-7 that when the same base material, surfactant and conductive material are used, the drying rate curve of carbon paper obtained by only changing the amount of surfactant is basically the same. By comparing a, b, c it can be seen from the three graphs that the weights of the three samples remain stable after 48h. It can be seen that the amount of surfactant added will not affect the drying rate of the carbon paper samples, and 48h is the best for this type of carbon paper samples. drying time.

To sum up, the type of surfactant selected in this experiment, the amount of surfactant added and the type of conductive material will not have any effect on the drying rate of the sample, only the type of substrate material will affect the drying rate of the sample. But 48h is a generally optimal drying time.

4.2 PVDF/graphene aerogel (DMAc as solvent)

4.2.1 Sample structure analysis

In order to investigate the structure of the produced PVDF/graphene aerogel samples, optical microscopy was used.

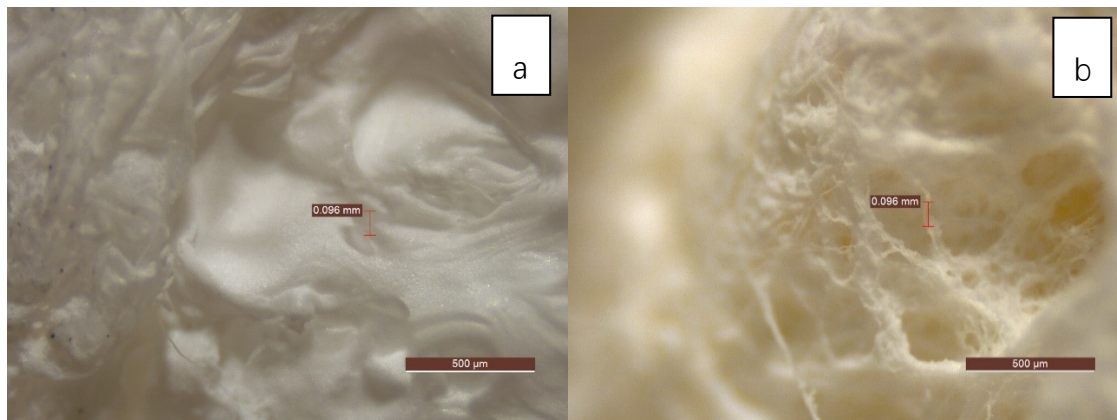


Figure 4-8 a, b are the surface structures and internal of pure PVDF aerogels with DMAc as solvent, respectively

It can be seen from Figure 4-8 that the interior of the pure PVDF aerogel has a pore structure, but the size and distribution of the pores are not uniform. This may be due to the disordered self-assembly of PVDF during the formation of the hydrogel, resulting in this disordered internal structure. Compared with the interior, the surface of pure PVDF aerogel appears slightly smoother and less porous. This may be due to the use of glassware with a smoother surface during the production process. During the disordered self-assembly process of PVDF, its assembly is restricted due to the blocking of the bottle wall, so the self-assembly reaction is more intensive near the bottle wall, resulting in a denser surface structure. The internal structure is more loose and porous because it is under normal temperature and pressure and receives less external barriers.

As no significant graphene desorption was observed during the hydrogel washing phase of the aerogel preparation, the graphene loss can be considered to be minimal. Thus the weight fraction of the sample with 30 mg of graphene added

is 2.5%, 60mg is 5% and 90mg is 7.5%.

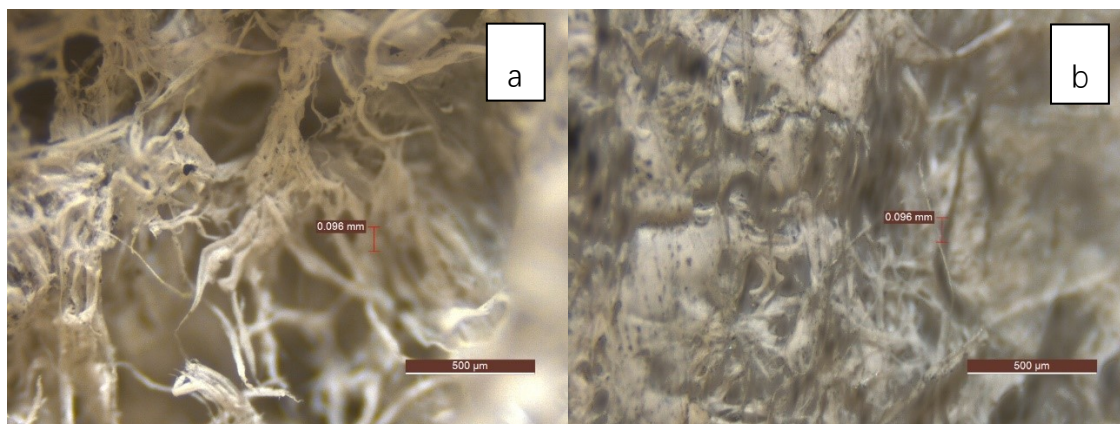
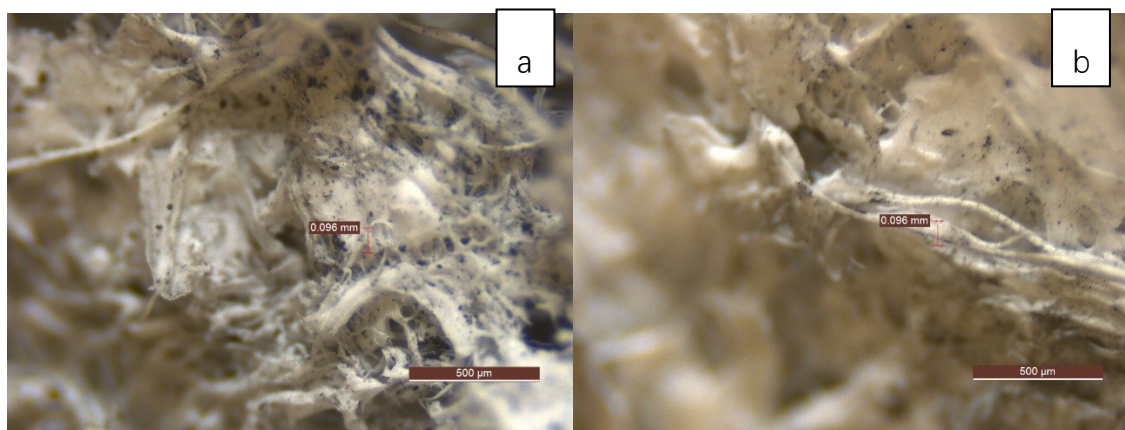


Figure 4-9 Structural images of PVDF/graphene aerogel with 30mg of graphene added (a, b show its internal and external structure respectively)

It can be seen from Figures 4-9 that the porous structure of pure PVDF aerogel is perfectly preserved inside the PVDF/graphene aerogel, the size and distribution of the pores are also not uniform. The reason for the formation of this phenomenon should be consistent with that of pure PVDF aerogels. It can be seen that the addition of graphene does not affect the structure of PVDF aerogels. Compared with the interior, the surface of the PVDF/graphene aerogel also appears slightly smoother and less porous. Such a smooth surface will seriously affect all aspects of the performance of the sample as an electrode, so it is possible to choose to use a larger reaction vessel in future experiments or to peel off the outer smooth surface during electrode application.



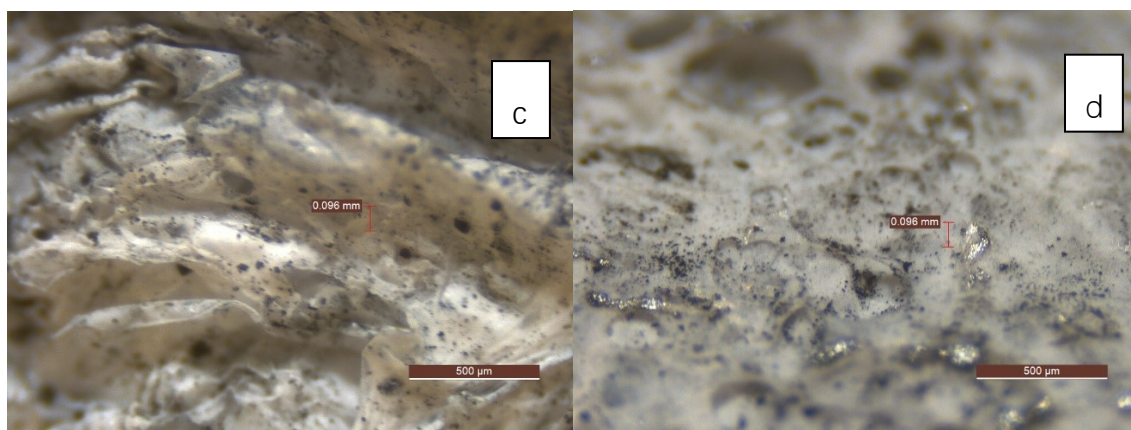


Figure 4-10 Structural images of PVDF/graphene aerogels with 60mg and 90mg of graphene added (a, b, interior and exterior of the sample with 60mg of graphene added, c, d, interior and exterior of the sample with 90mg of graphene added, respectively)

It can be seen in Figures 4-10 the increased addition of graphene does not result in a change in the aerogel structure. As the quantity increases, the external structure does not change. However, it can be seen that due to the hydrophobicity of graphene, the distribution of graphene in the sample is very uneven, and even agglomeration occurs in some places, which will affect the electrochemical performance of the sample. This may be due to the fact that graphene is inherently superhydrophobic and will be difficult to disperse fully in water without modification or the addition of surfactants. However, the porous structure inside the sample may greatly improve the active specific surface area for electrochemical reactions. The true current density of the sample as an electrode can be considerably lowered due to an increase in the number of active chemicals engaging in the discharge process, as well as an improvement in the porosity and specific surface of the electrode. As a result, the battery's energy loss (including voltage loss and capacity loss) is considerably decreased, and the battery's performance may be increased.

4.2.2 Sample micromorphology analysis

Using an optical microscope, only the macroscopic structure of the sample can

be observed. In order to investigate the microscopic morphology of the sample, it is necessary to use SEM to test the sample, so as to observe the microscopic structure of the sample and the distribution of conductive substances inside the sample.

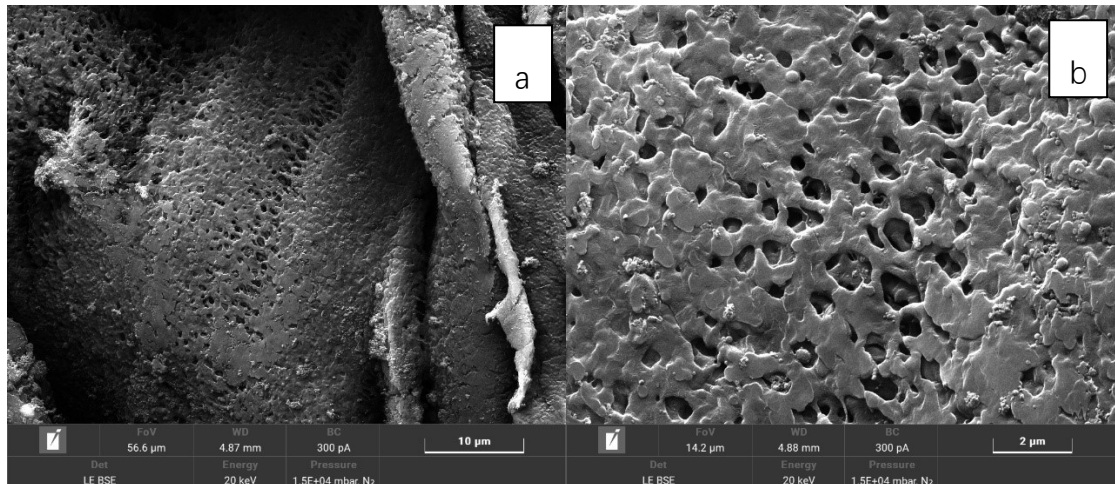


Figure 4-11 SEM image of pure PVDF aerogel (a, b are images magnified by 5k and 20k, respectively)

Figure 4-11 shows that the surface of pure PVDF aerogel still has some tiny pores, but the number of these pores is very small and most of the surface area is still smooth, these tiny pores can appropriately compensate for the loss of performance caused by the smooth surface, but will play a small role.

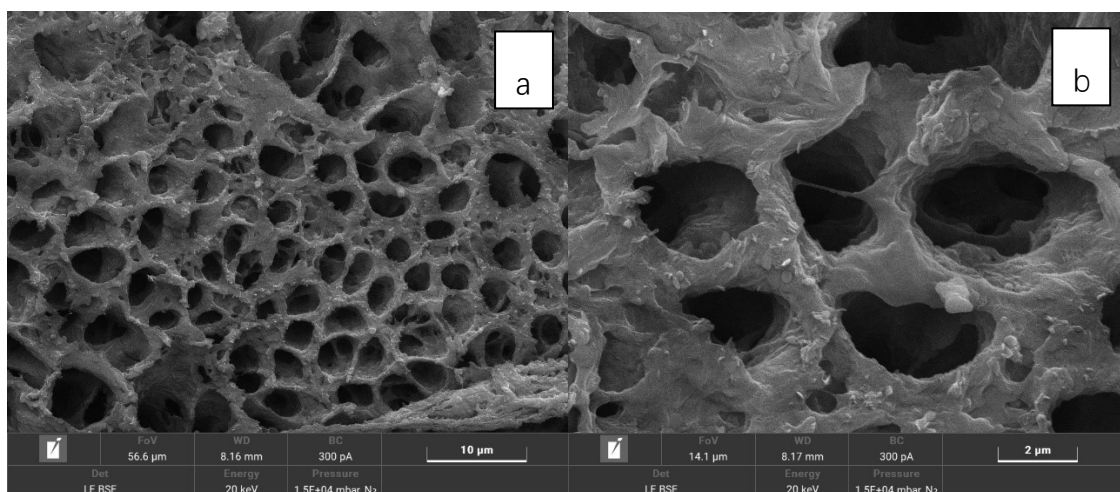


Figure 4-12 Internal SEM images of PVDF/graphene aerogel samples with 30mg of graphene added (a, b are images at 5k and 20k magnification respectively)

It can be seen from Figure 4-12 that the PVDF/graphene aerogel added with 30 mg of graphene has a large number of pores of uniform size inside, and the distribution of these pores is relatively uniform. The large number of homogeneous pores means that the sample has a large specific surface area, which facilitates the adsorption of more graphene. From Figure 4-12b, it can be seen that there are some fine flake structures on the surface of these pores, and these flakes may be graphene sheets. However, the number of these flakes is small and the distribution is very uneven. This may be related to the poor dispersion effect of graphene.

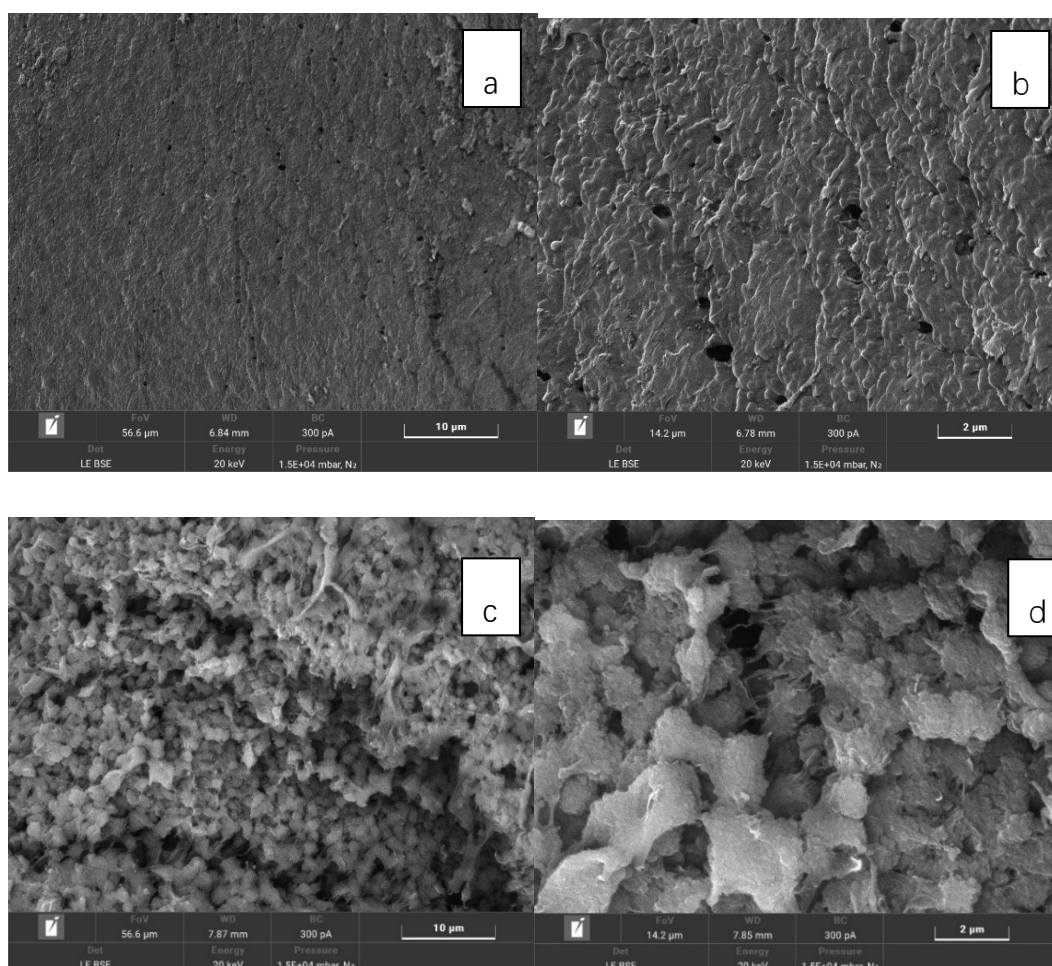


Figure 4-13 SEM images of PVDF/graphene aerogel samples with 60 mg and 90 mg of graphene added (a, b are respectively 5k and 20k magnified images of the sample with 60 mg graphene added, c, d are respectively 5k and 20k magnifications of the 90mg graphene sample)

It can be seen from Figure 4-13a that the surface of the PVDF/graphene aerogel with 60 mg of graphene added is very smooth and hardly has any pore structure, and only a few small pores can be seen from Figure 4-13b. Comparing with Fig. 4-11, it can be concluded that the synthesis process of PVDF and PVDF/G aerogel has a certain disorder, which leads to the inconsistency of the surface structure, and the selection of the size of the reaction vessel also has a great influence on the production of the sample. In this experiment, a 30ml glass test tube was chosen, and this size obviously limits the self-assembly of aerogels. From Figure 4-13c, d, it can be seen that a relatively dense interlayer is formed between the surface and internal structure of the PVDF/G aerogel, and many spherical structures are formed in this interlayer with only small voids. The formation of this structure may also be related to the self-assembly of PVDF and the small size of the reaction vessel. And it can be found that the change of amount of graphene added did not seem to have any effect on the microscopic morphology of the samples.

From the comparison between Fig. 4-13a and Fig. 4-13c, it can be seen that the structure of the samples is very different, which may be due to the selection of the surface SEM image of the sample with graphene content of 60mg and the internal SEM image of the sample with graphene content of 90mg. Therefore, this group of SEM images maybe not representative.

4.2.3 Analysis of sample components

FTIR is a common method for determining sample functional groups in chemistry and materials experiments to determine sample components, so FTIR is also used in this experiment to help determine whether there are new components created during the PVDF aerogels synthesis.

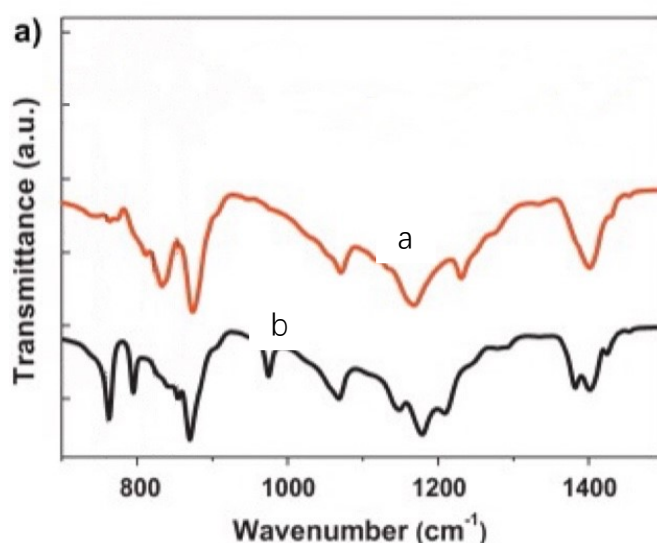


Figure 4-14 FTIR images (a, b are FTIR images of PVDF/graphene aerogel samples and FTIR images of pure PVDF aerogel samples, respectively)

The Fourier transform infrared (FTIR) spectra of pure PVDF aerogel samples and graphene-supported PVDF aerogel samples can be seen from Figures 4-14. Available from FTIR images of pure PVDF aerogel samples, 526 cm^{-1} (curved), 977 cm^{-1} (twisted), 1167 cm^{-1} (stretched) and the 1203 cm^{-1} band, which is assigned to the alpha phase of PVDF. By adding graphene, the band at 977 cm^{-1} almost disappeared, and the peak intensity after the addition was significantly lower than that before the addition, and the PVDF/graphene aerogel samples showed higher light absorption at 509 cm^{-1} and 840 cm^{-1} bring. It is known from the literature ^[146] that the last absorbance band (1400 cm^{-1}) is related to the β phase of PVDF.

Compared with the experimental data (Figure 4-15) in the article published by Bidsorkhi et al., although different preparation paths and solvents were used in this experiment and his experiment, the obtained results peaks and extensions were highly similar. There is no direct connection between the choice of solvent and the composition of PVDF/graphene aerogels. And since no new bonds are generated, it can be known that graphene and PVDF are mainly combined in a hydrogen bond and non-covalent manner.

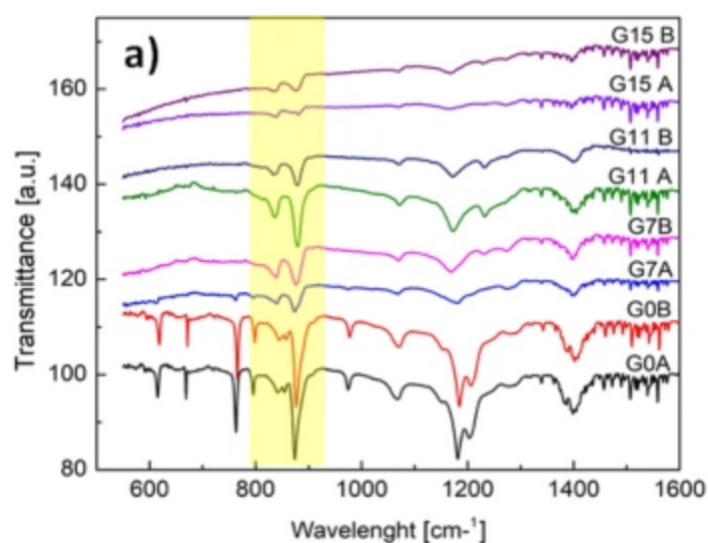


Figure 4-15 FTIR images of PVDF/graphene aerogels with different graphene contents [146]

4.2.4 Electrochemical testing

After characterization with multiple physical means, a lot of information about the structure and composition of the sample can be learned. However, if the samples are to be used in the field of energy storage, the electrochemical properties of the samples need to be tested. In this project, the Ag/AgCl electrode was selected as the reference electrode, the platinum sheet electrode was used as the counter electrode, and the 1 mol/L Na₂SO₄ solution was used as the electrolyte to explore the electrochemical performance of the sample in the aqueous battery system.

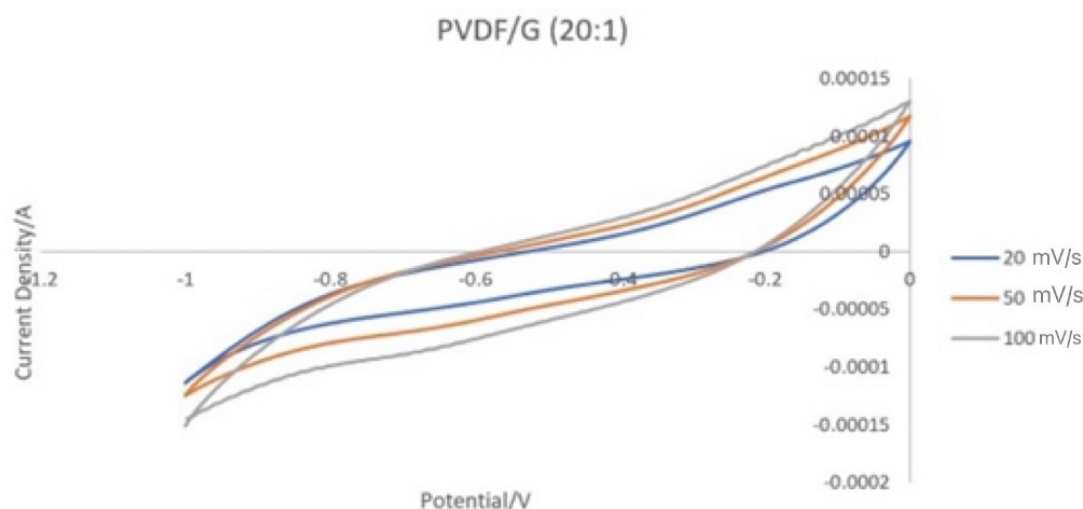


Figure 4-16 Cyclic voltammetry (CV) scan curves of PVDF/G aerogel samples with a ratio of 20:1 at different scan rates

It can be seen from Figure 4-16 that the scan curves of this sample at different scan rates all present a regular approximate rhomboid, which indicates that the sample has good electric double layer capacitance ^[35]. From Equation 20 (section 3.7.5), we can know the rhomboid formed by the curve. A larger value represents a larger specific capacitance. Therefore, it can be known that the specific capacitance of the sample is the largest when the scan rate is 100mV/s.

It can be seen from Figure 4-17 that the curves of the samples with different graphene contents at a scan rate of 100 mV/s all present a regular approximate rhomboid, which indicates that the three samples have good electric double layer capacitance. This proves that the PVDF/G aerogel fabricated in this experiment is indeed a material with good electrochemical performance. This has laid a solid foundation for the application of materials in the field of energy storage. It can be seen from the figure that with the increase of graphene content, the rhomboid keeps getting larger, which shows that the specific capacitance of the material is improved with the increase of graphene content, so it can be determined that the electrochemical performance of the material will improve with the amount of graphene added.

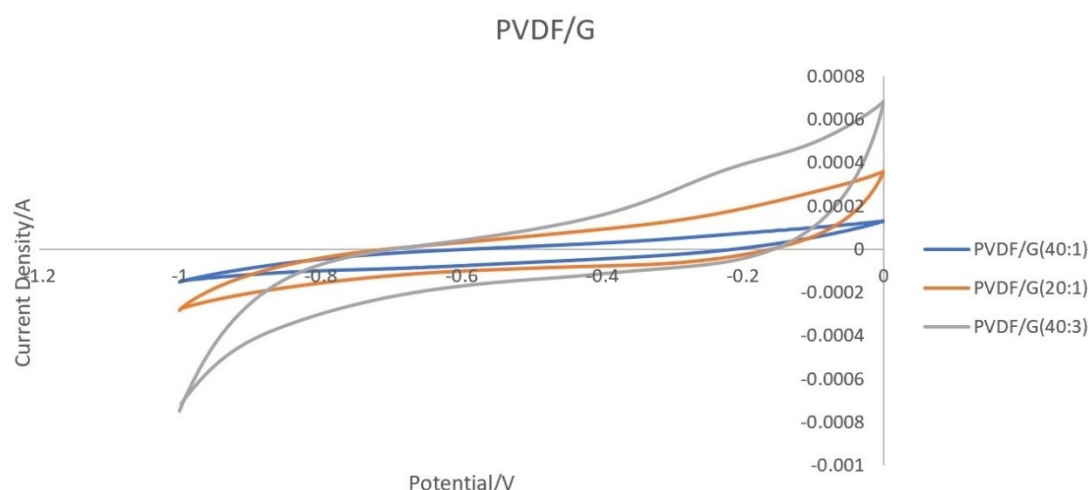


Figure 4-17 Cyclic voltammetry scan curves of PVDF/G aerogel samples with different graphene contents at a scan rate of 100mV/s

It can be seen that the shape of the curve changes somewhat when the ratio of PVDF to graphene is 40:3. Combining the structure of the material with the microscopic morphology, it can be judged that this may be due to the uneven distribution of graphene inside the sample, which affects the transport of electrons inside the electrode.

PVDF/G	Specific capacitance/ Fg^{-1}
40:1	8.43
20:1	19.26
40:3	31.66

Table 7 Specific capacitance of samples with different graphene contents

Table 7 shows the specific capacitance of the sample is not higher than that of some existing graphene aerogels [36], which may be related to the substrate material PVDF, but also to the non-uniform dispersion of graphene in the aerogel.

Based on the above comparison results, a sample with a 40:3 ratio of PVDF to graphene was selected as the best electrode sample for further electrochemical testing. From Figure 4-18, it can be found that this sample maintains a similarly

shaped rectangular curve at different scan rates, indicating the bilayer capacitance of this sample. The scan curve of this sample did not distort at a scan rate of 100mV/s, indicating that this sample has good performance and maintains the electrochemical stability of the sample even at high scan rates.

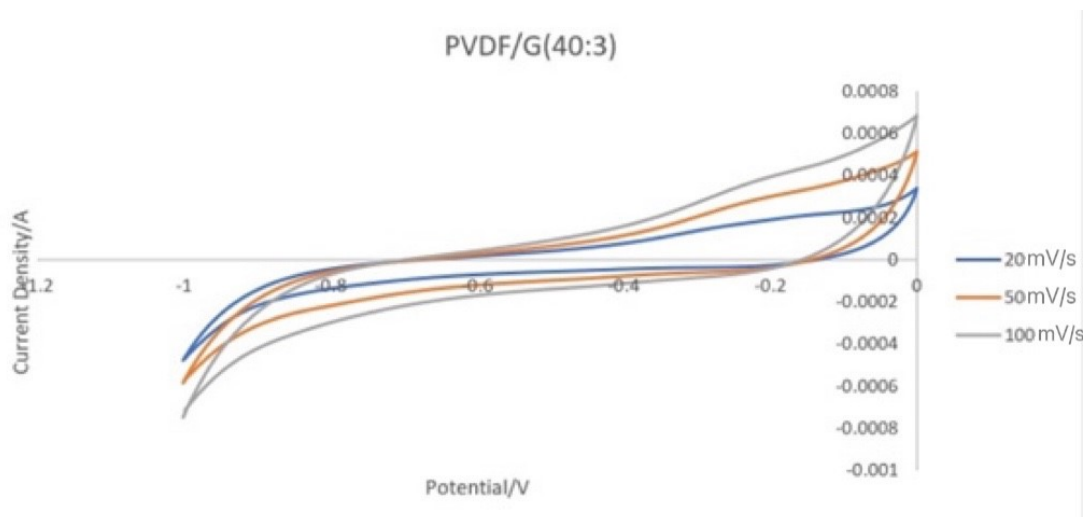


Figure 4-18 Cyclic voltammetry scan curves for aerogel samples with PVDF/G ratio of 40:3 at different scan rates

Combining the charging and discharging curves of the sample with a PVDF/G ratio of 40:3 at different current density in Figure 4-19 and Appendix 14, it can be seen that the charging and discharging curves of this sample can be combined to form a non-standard triangle, which indicates the reversibility of the charging and discharging of this sample ^[45]. However, the electrochemical properties of the material still need to be improved based on the fact that the charging time is generally greater than the discharging time.

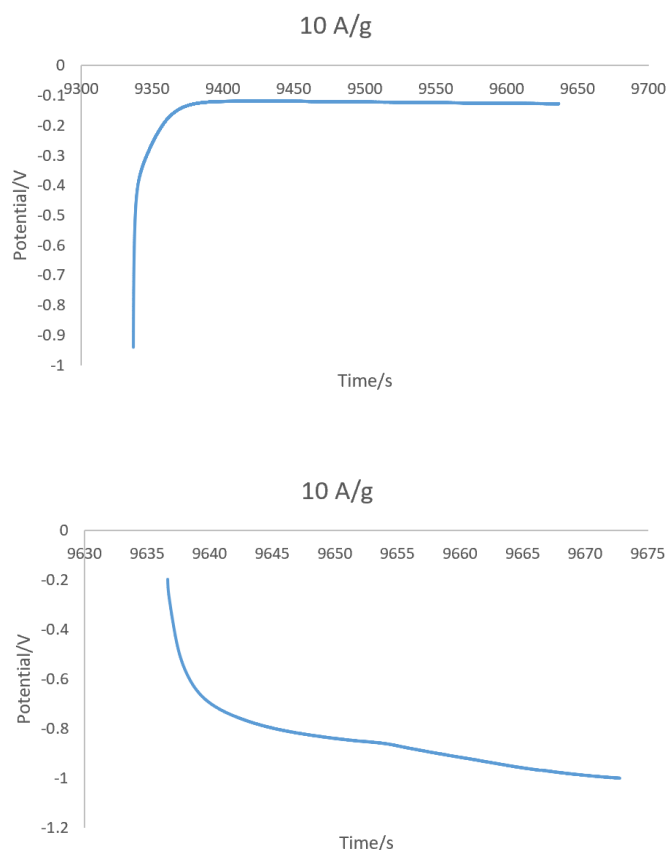


Figure 4-19 Charging (up) and discharging (down) curves for PVDF/G aerogel with a weight ratio of 40:3 at a current density of 10 A/g

By comparing Figure 4-19 with Appendix 14, it can also be noticed that the specific capacitance decreases with increasing current density, this is because under high current charging and discharging conditions, the charging and discharging times are too short for the sodium sulphate electrolyte ions to move quickly to the surface and inside the active material.

Figure 4-20 shows that the capacitance retention of the material remains at 94.3% after 100 cycles, which indicates that the material has good stability as an electrode material. As long as the specific capacitance of the sample is further improved by a certain method, combined with its own stability, the sample may be used in the field of energy storage.

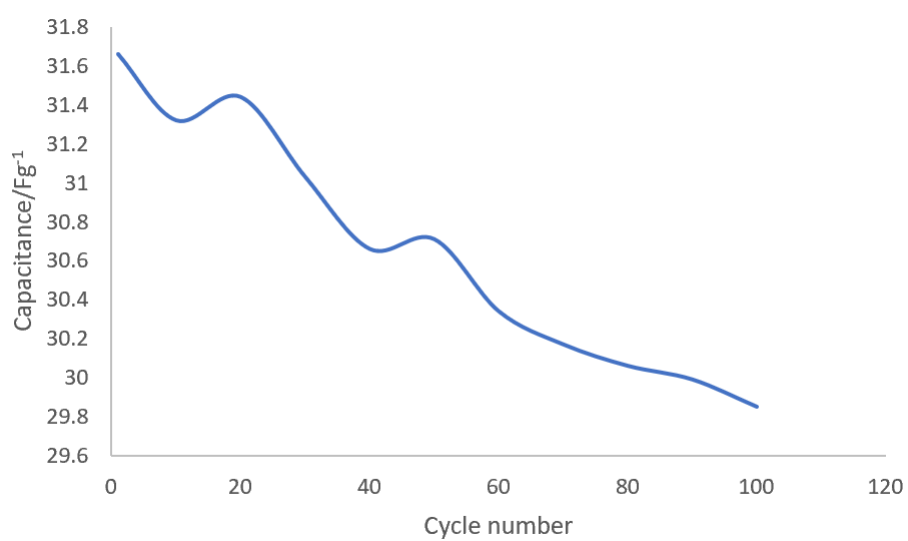


Figure 4-20 Capacitance retention of PVDF/G (40:3) aerogel after 100 charge/discharge cycles

4.3 PVDF/graphene aerogel (DMF as solvent)

4.3.1 Sample structure analysis

In order to investigate the structure of the produced PVDF/graphene aerogel samples and the factors influencing them, this experiment was carried out using an optical microscope.

As no significant graphene desorption was observed during the hydrogel washing stage. Therefore the weight fraction of the sample with 10mg of graphene added is 20%, 20mg is 40% and 30mg is 60%.

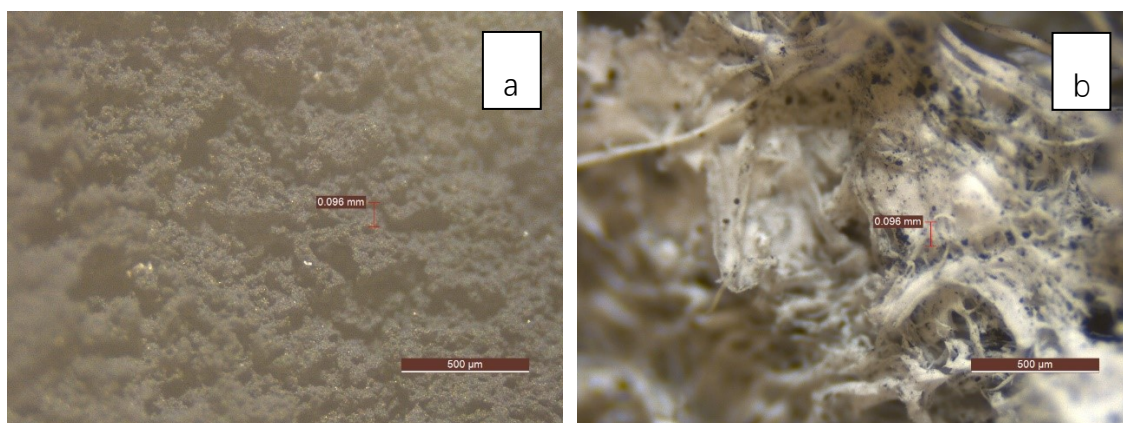


Figure 4 –21 a. image of PVDF/graphene aerogel structure with DMF as solvent and graphene addition at 10mg b. Image of the structure of a composite aerogel with DMAc as solvent

From Figure 4-21 it can be seen that the PVDF/graphene aerogel with DMF as the solvent has a relatively loose and porous structure, but the size of its pore structure is much smaller than that of the PVDF/graphene aerogel with DMAc as the solvent. This may be due to the fact that the reaction process of the composite aerogel with DMF as a solvent is carried out under high pressure, while the reaction of the composite aerogel with DMAc as a solvent is carried out under normal pressure. High pressure will cause PVDF to react more densely during the self-assembly process, resulting in a small and dense pore structure. However, the degree of graphene dispersion in this sample is obviously better

than that of the sample with DMAc as solvent, which may be because the graphene dispersion and PVDF solution are mixed more uniformly during the mixing process. It is also possible that under high temperature and high pressure, the graphene is dispersed more uniformly in the solution. At the same time, it can be found that the internal and external structures of the PVDF/graphene aerogel using DMF as the solvent are consistent, and a smooth and dense film is not formed on the surface. By observation, the hydrogel did not contact the inner wall of the autoclave in the autoclave. This also proves that the limitation of the size of the reaction vessel leads to the generation of the aerogel surface film structure.

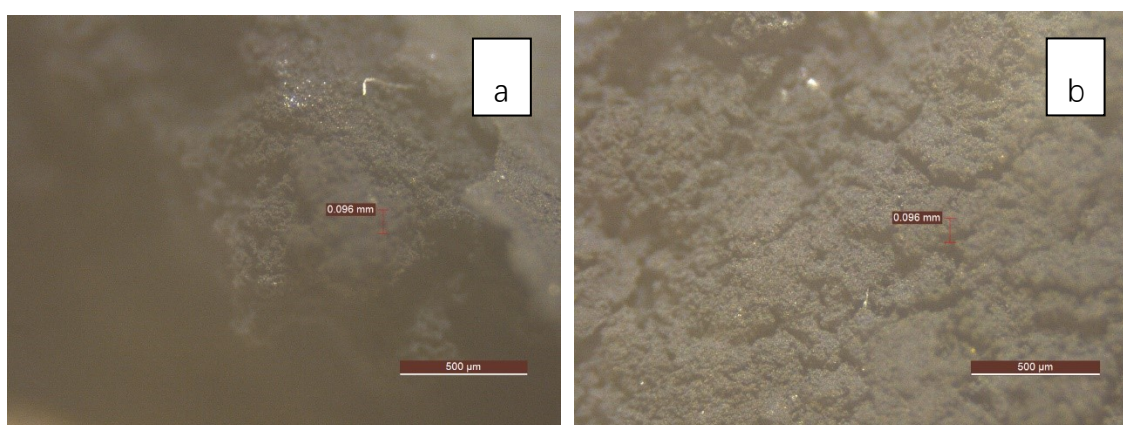


Figure 4 -22 Images of PVDF/graphene aerogel structure with DMF as solvent (a, b for 20mg and 30mg of graphene addition respectively)

It can be seen from Figure 4-22 that the structure of PVDF/graphene aerogel does not change significantly with the increase of graphene addition, and the size of pores is highly consistent with the degree of densification. Therefore, it can be seen that the internal and external structures of PVDF/graphene aerogel are not directly related to the amount of graphene added. However, its relatively dense structure may limit its electrochemical performance. In future experiments, it may be possible to investigate the effects of reaction temperature and reaction pressure on the structure of PVDF/graphene aerogels by changing the reaction conditions during the reaction.

4.3.2 Sample micromorphology analysis

In order to study the microscopic morphology of the produced PVDF/graphene aerogel samples and the factors affecting them, this experiment uses SEM to observe the produced samples. The SEM images were also combined with images from optical microscopy for analysis.

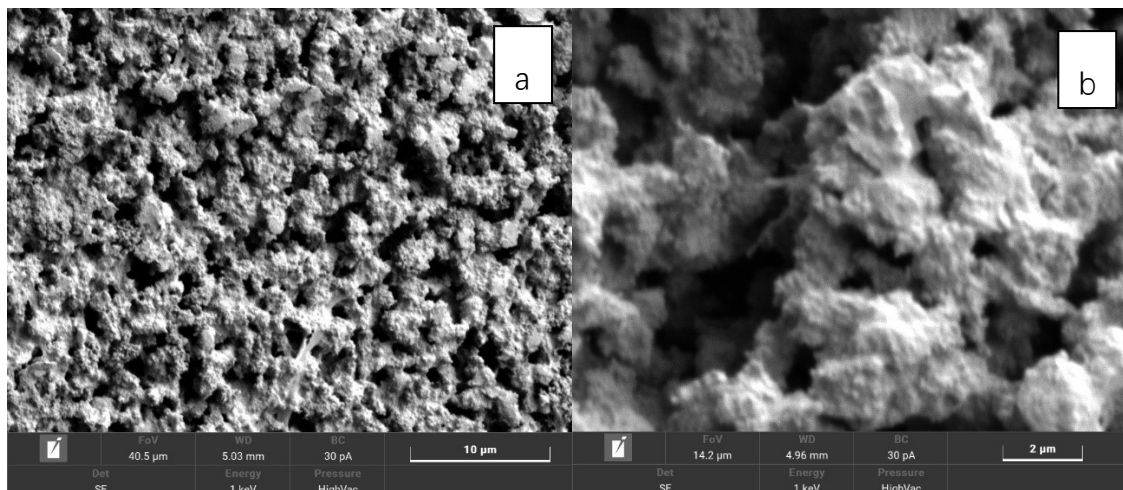


Figure 4-23 SEM images of PVDF/graphene aerogel (a, b are images of the sample with 10mg of graphene added magnified by 7k and 20k times respectively)

From Figure 4-23 a, it can be seen that the PVDF/graphene aerogel with 10 mg of graphene has abundant pore structures inside, and PVDF self-assembles to form many spherical structures. The pore size formed by these spherical structures is only as small as 2-5 microns or even smaller. It can be seen from Figure 4-23 b that these pore walls are frameworks produced by stacking PVDF spherical structures, but the presence of graphene sheets greatly increases their specific surface area. During the freeze-drying process, the formation of ice crystals pushes the movement of PVDF spherical structures and graphene sheets; the PVDF spherical structures are reassembled around the ice crystals to form such small-sized aerogel pore walls ^[154]. In further observation, it was found that the edge positions between these small spherical structures were interconnected and cross-linked to form a three-dimensional overall network structure.

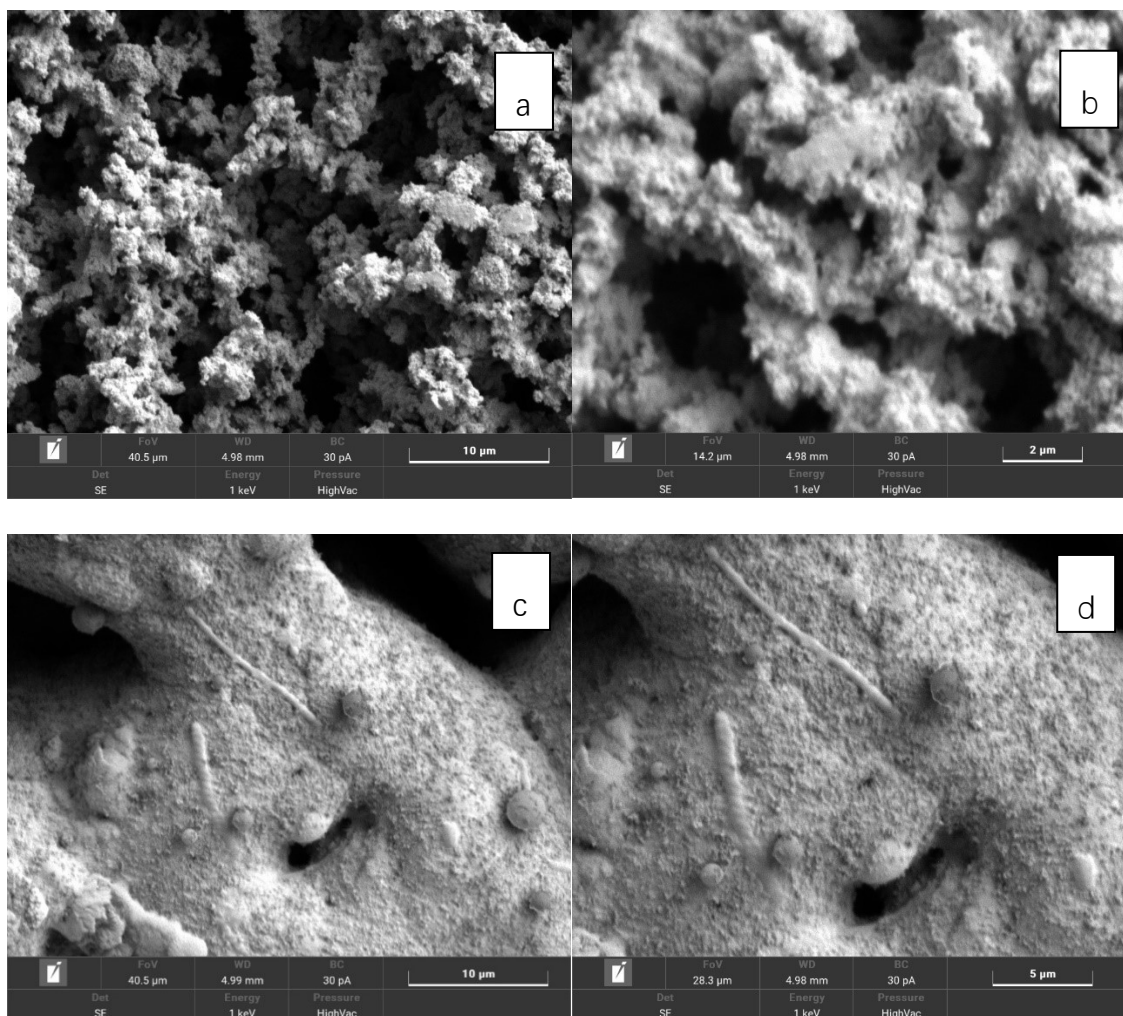


Figure 4 -24 SEM images of samples with 20mg and 30mg of graphene added (a, b are images of samples with 20mg of graphene added at 7k and 20k magnification respectively, c, d are images of samples with 30mg of graphene added at 7k and 10k magnification respectively)

It can be seen from Fig. 4-24 a, b that the internal structure of the PVDF/G aerogel with 20mg graphene added is no different from that of the sample with 10mg graphene added. It can be seen from Fig. 4-24 c, d that the surface of this sample shows a larger spherical structure that is inconsistent with the interior, but some graphene sheets can be seen attached to the spherical wall. The change of amount of graphene added did not appear to have a large effect on the microscopic morphology of the samples.

4.3.3 Analysis of sample components

Although the experimental data have been compared with the data in the literature ^[146] in the previous chapter, it was found that the type of solvent and the experimental reaction path have no direct relationship to the composition of the final PVDF/graphene aerogel. However, for the accuracy of the data, in this section, the PVDF/graphene aerogel samples with DMF as solvent were still tested by FTIR.

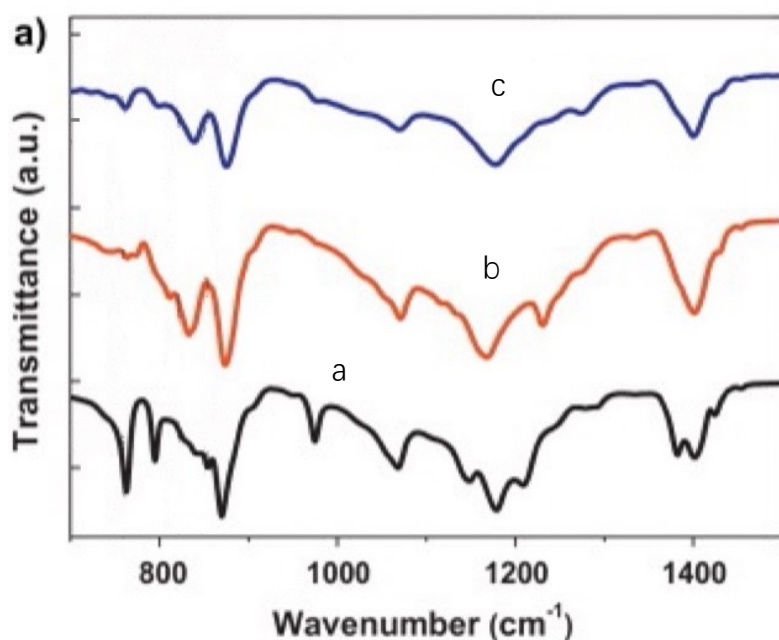


Figure 4-25 FTIR curves of three aerogels (a, b, c for pure PVDF aerogel, PVDF/graphene aerogel with DMAc as solvent and PVDF/graphene aerogel with DMF as solvent respectively)

From Figure 4-25 it is not difficult to see that the peaks and stretch heights of the infrared spectra of the two PVDF/G aerogels using DMF and DMAc as solvents overlap, and even the absorption bands are in roughly the same range. This further confirms that the solvent has no effect on the composition of the sample, and the fabrication process of PVDF/graphene aerogel is highly reproducible.

4.3.4 Electrochemical testing

In this experiment the PVDF/G aerogel produced with DMF as the solvent was too brittle and therefore not suitable as a flexible electrode material. Furthermore, the brittle nature of the material caused the electrode clamp of the electrochemical workstation to keep breaking the sample when it was tested electrochemically using the electrochemical workstation. This results in the sample could not be tested. In summary, this range of aerogel samples is not suitable for use as an electrode material, as a certain level of strength or toughness is generally required. However, the structure and microscopic morphology of the samples indicate that they have a good pore loading structure, which would be beneficial for other applications such as the adsorption of liquid organic waste. Moreover, due to the lipophilic and hydrophobic properties of graphene, this aerogel may be used as a good material for oil-water separation [145].

4.4 Carbon paper

4.4.1 Sample structure analysis

To investigate the structure of the produced carbon paper samples and the factors that affect them, the samples produced under different conditions in a series of experiments were observed using an optical microscope at room temperature.

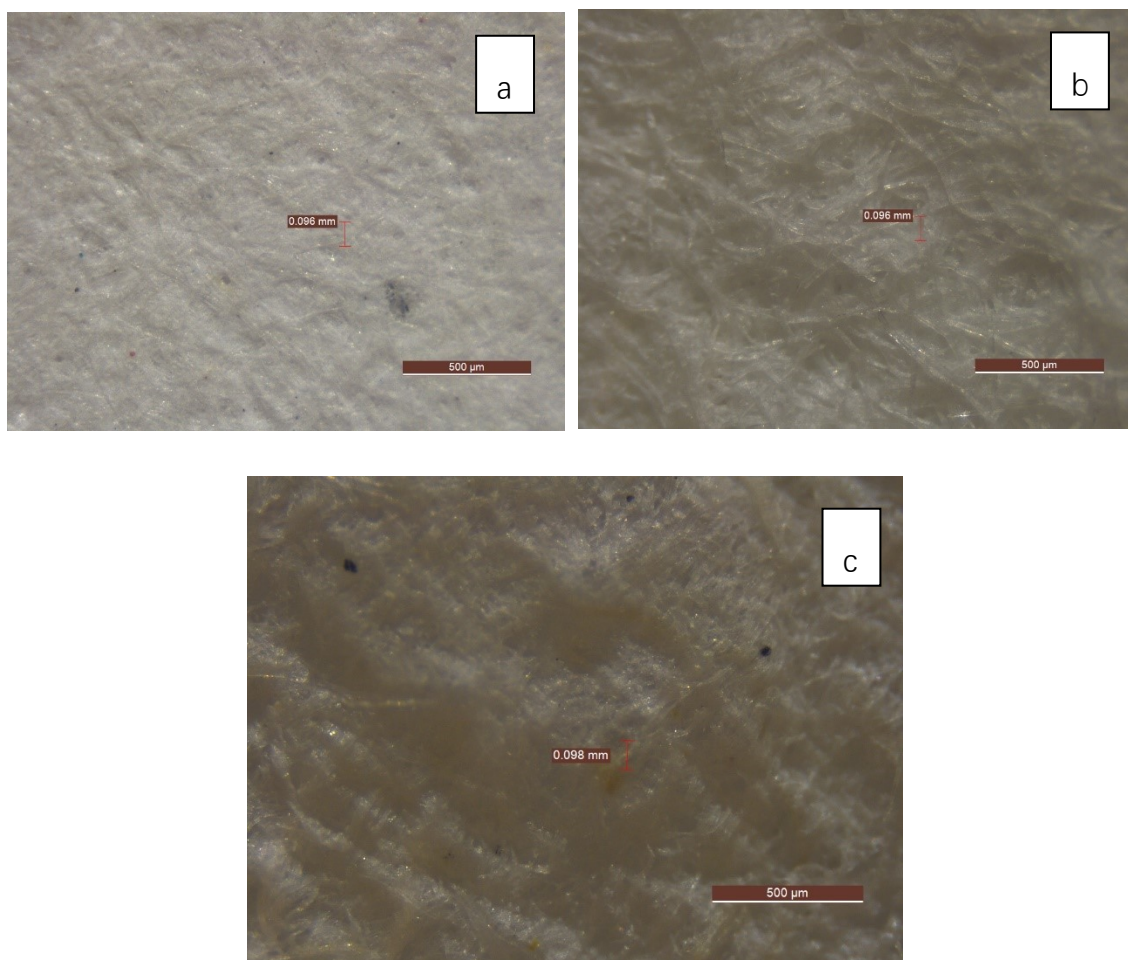


Figure 4 -26 Structural images of three different base materials (a, b, c are A4 paper, filter paper and paper towel, respectively)

From Figure 4-26 it can be found that A4 paper has the smoothest surface structure among the three different substrate materials, and the fibers on its surface are relatively dense, which will greatly affect its ability to load conductive materials, thereby affecting its electrochemical performance. Compared with A4 paper, both filter paper and paper towel have a rougher surface structure, which

provides a good foundation for loading more conductive substances. Comparatively, the surface porosity of paper towel is larger, which may also be one of the reasons for the faster drying rate of the samples based on it. Larger pores are more convenient for water evaporation.

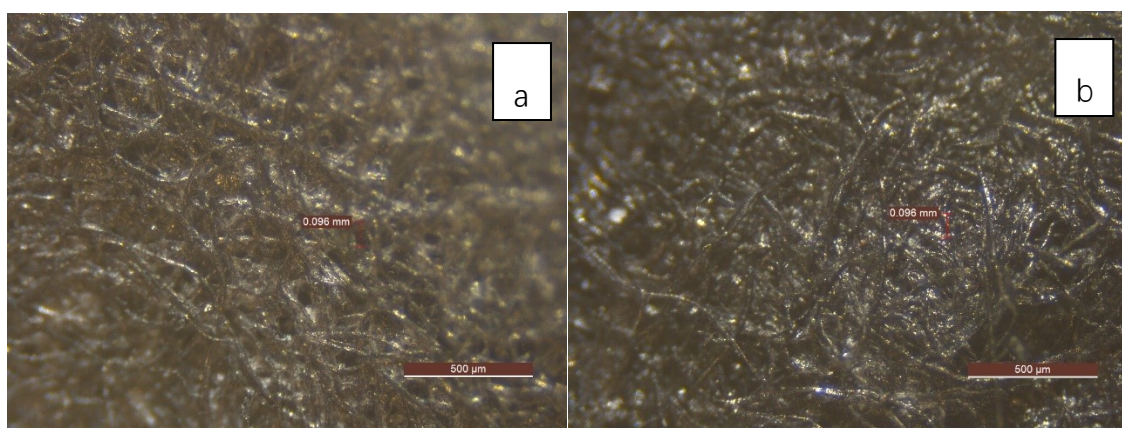


Figure 4 -27 Structure of carbon paper with different surfactants (a, b for samples with SDBS and SDOC respectively)

From Figure 4-27 it can be seen that the surface structure of the samples with SDBS or SDOC as the surfactant will not change, and it can be judged from the color of the fiber surface that the conductive substances in the two samples are well adsorbed on the paper. Not only is the distribution very uniform, but there is also no obvious agglomeration, and the degree of loading of the conductive material is very high. It can be seen that the use of these two surfactants can make the conductive substances well dispersed in the solution and well supported on the substrate material. Therefore, it is impossible to judge the difference in performance of the samples with SDBS and SDOC as surfactants from the macroscopic point of view.

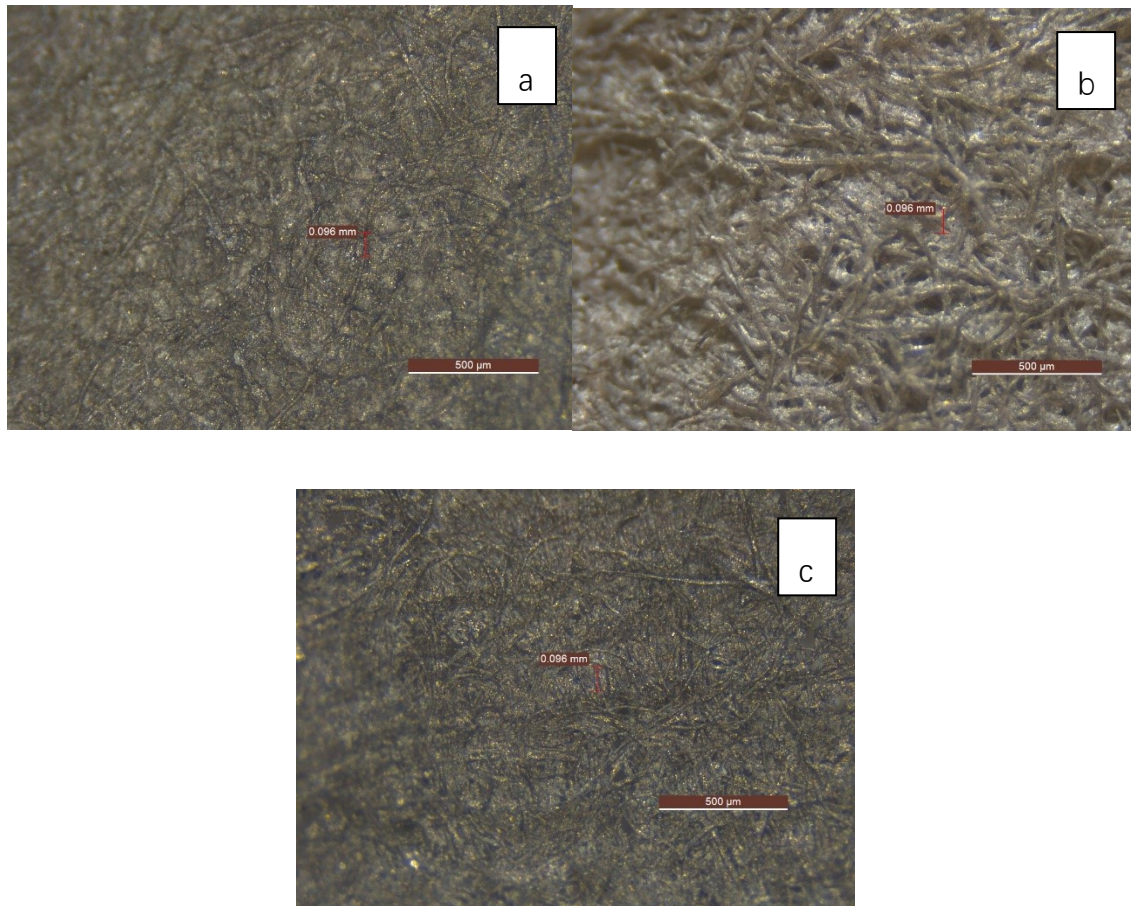


Figure 4 -28 Carbon paper samples prepared using different papers (a, b, c are A4 paper samples, filter paper samples and tissue paper samples respectively)

From Figure 4-28 it can be found that the surfaces of the three paper samples are loaded with very uniform conductive substances, and no obvious agglomeration is found, but the surface of the A4 paper sample is relatively smooth, with only a small amount of protrusions and pores, which will affect its performance of loading capacity of conductive substances. Both filter paper and paper towel have obvious pores and fibrous structures on the surface, which can carry more conductive substances, but the fiber of filter paper is obviously thicker than that of paper towel, and the effect of fiber thickness on the performance of the sample needs to be further tested.

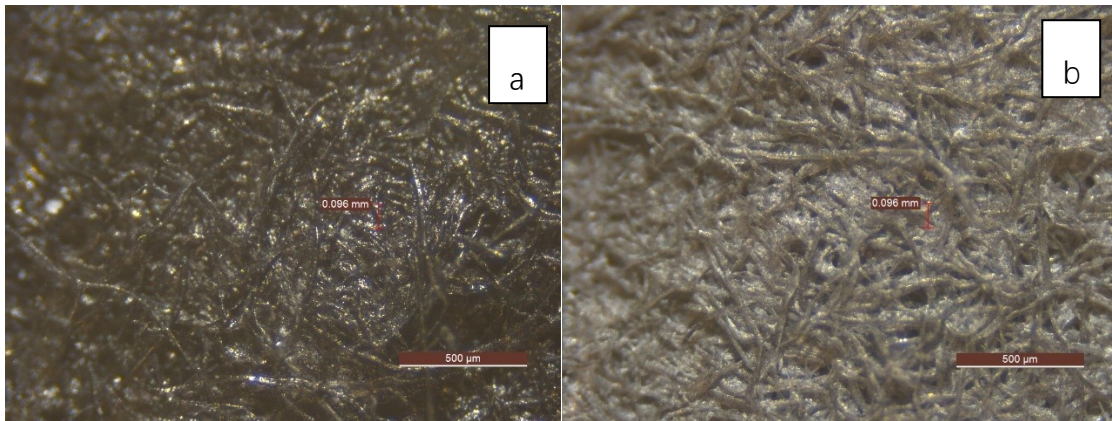
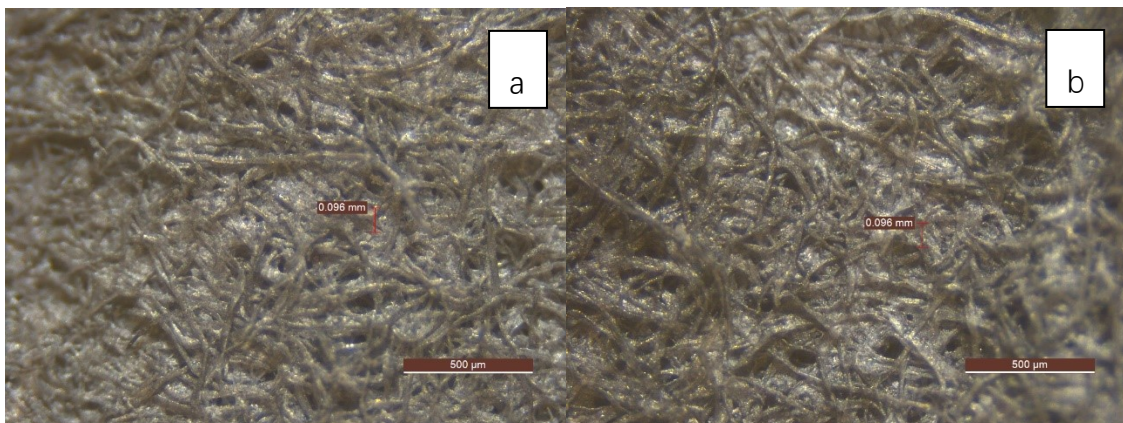


Figure 4 -29 Carbon paper samples prepared using different conductive substances (a, b for graphene samples, CNTs samples respectively)

From Figure 4-29 it is observed that the surfaces of the two paper samples are loaded with very uniform conductive substances, and no obvious agglomeration is found, but the surface of the graphene sample is darker and seems to be loaded with more conductive substances. The specific performance also needs to be measured.



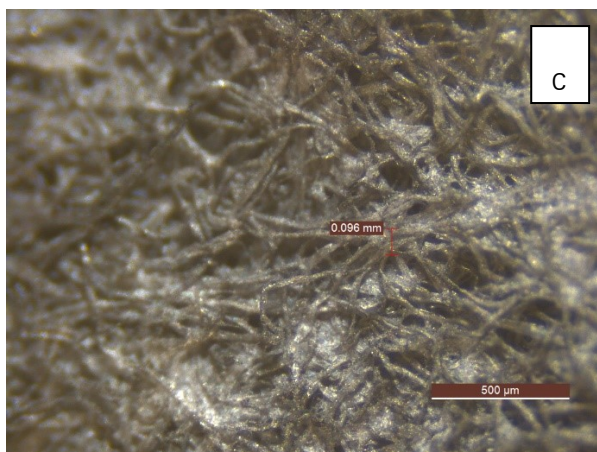
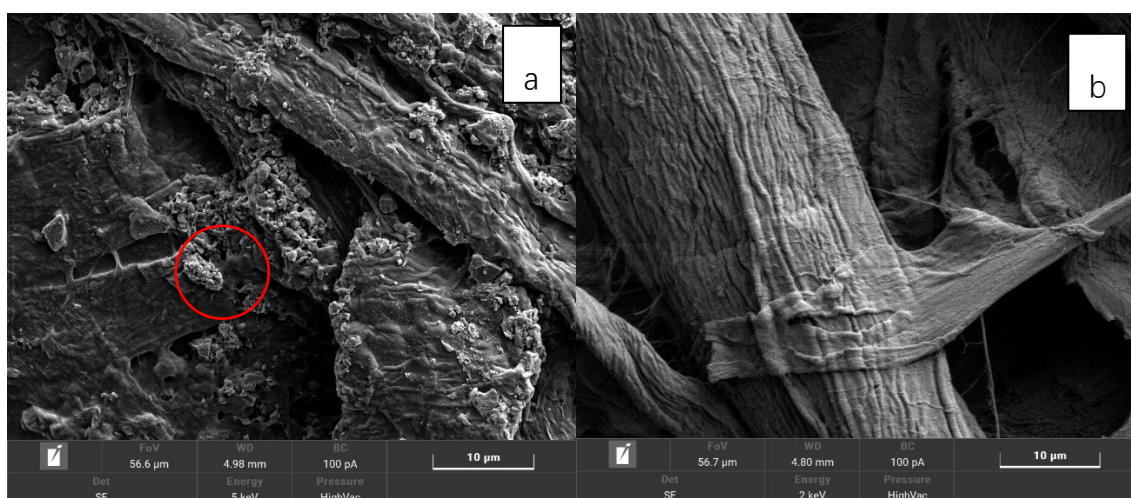


Figure 4- 30 Sample of carbon paper prepared using different amounts of surfactant (a, b, c are samples with SDBS to CNTs ratios of 2:1, 5:1, 10:1 respectively)

From Figure 4- 30 it can be found that the surfaces of the three paper samples are loaded with very uniform conductive substances, no obvious agglomeration is found, and the surface colors are highly consistent. Therefore, it can be concluded that the amount of conductive species has no direct relationship with the surface structure of the sample. It is not possible to directly judge the change of the addition amount of the conductive material through the optical microscope image. Therefore, the effect of the amount of conductive material added on the performance of the sample needs to be proved by other tests.

4.4.2 Sample micromorphology analysis (SEM)



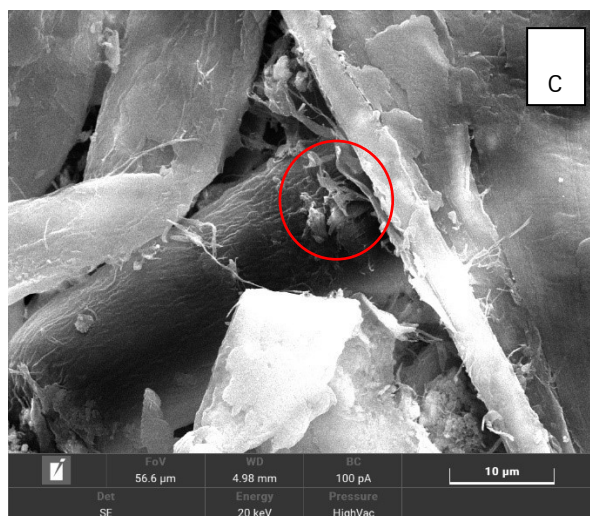


Figure 4- 31 SEM images of three kinds of paper at 5k magnification (a, b, c are A4 paper, filter paper and paper towel respectively)

It can be seen from Figure 4- 31 a that there are some small groups on the fiber surface of A4 paper, these small groups make the surface rougher, which may be due to the addition of some bleaching agent in the production process of A4 paper caused. It has some pores, which form a good basis for carrying conductive substances. It can be seen from Figure 4- 31 b that the surface of the fiber of the filter paper is smoother and has larger pores. It can be seen from Figure 4-31 c, there are groups on the fiber surface of the paper towel which are presumed to be bleach residues as bleach is often used in the industrial production of paper towel, and the fiber of the paper towel is thinner than the fiber of A4 paper and the fiber of the filter paper, which could indicate the paper towel will have more fibres per unit volume. Many fibers can carry conductive substances. And there are many pores between the fibers of the paper towel.

From Figure 4-32 it can be seen that a layer of non-uniform graphene sheets is stacked on the surface of the smooth filter paper fiber after adding graphene, but there seems to be no difference in the morphology of graphene loading for the samples with different surfactants. (See Appendices 12 and 13 for images with larger magnifications)

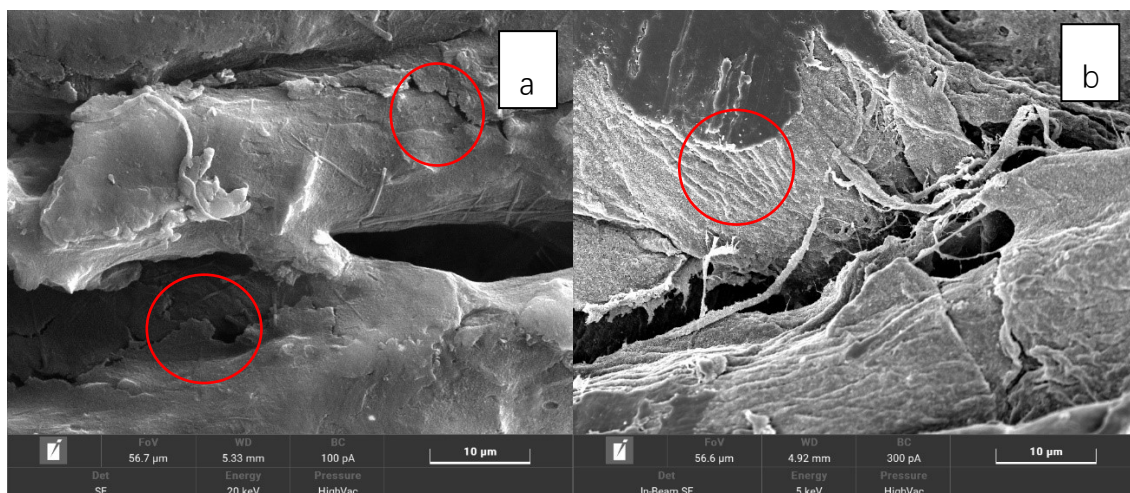


Figure 4-32 SEM images of samples with different surfactants added at 5k magnification (a, b are images of samples with SDOS and SDBS added respectively)

From Figure 4-33 it can be clearly seen the difference in the microscopic morphology of the samples added with different conductive substances. For the samples added with graphene, the graphene is stacked on the surface of the filter paper fiber to form a two-dimensional layered structure. For the sample with CNTs added, it can be seen that the three-dimensional structure is stacked on the surface of the filter paper fiber. This may be related to the structure of graphene and CNTs themselves. But obviously the three-dimensional structure can provide more active specific surface area for electrochemical reactions.

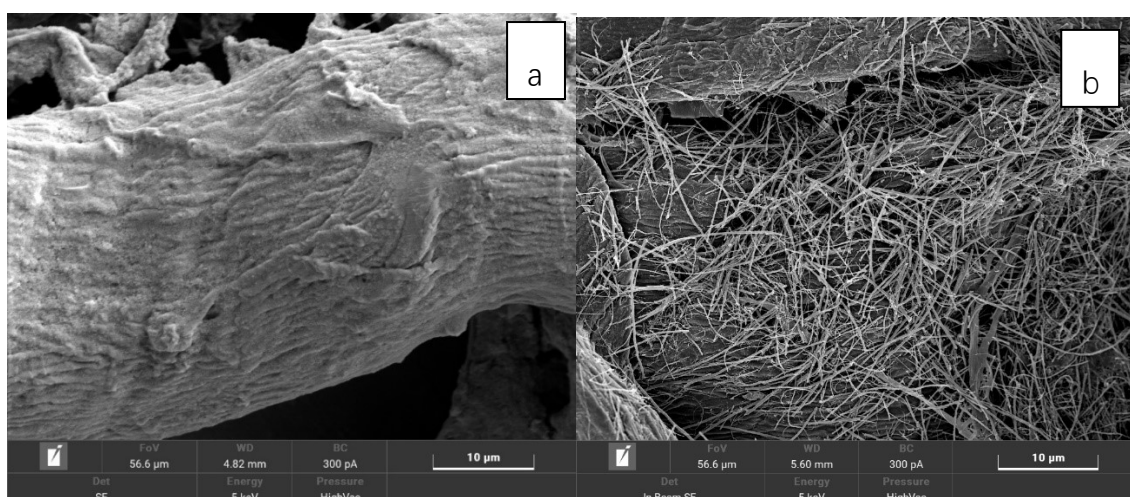


Figure 4 -33 SEM images of samples with different conductive substances (a, b for samples with added graphene and CNTs respectively)

By observing Figure 4-32, Figure 4-31b and Appendix 15, it can be found that with the addition of graphene, the pores between the filter paper fibers become smaller and the distance between them becomes closer, and the paper surface is smoother at this time. The addition of surfactant can act as a binder to make graphene and CNTs more easily adsorbed on the fiber surface ^[149]. The surface hydrogen-bonded graphene and CNTs provide more hydrogen bonding for the fibers, which enhances the bonding force between fibers ^[149].

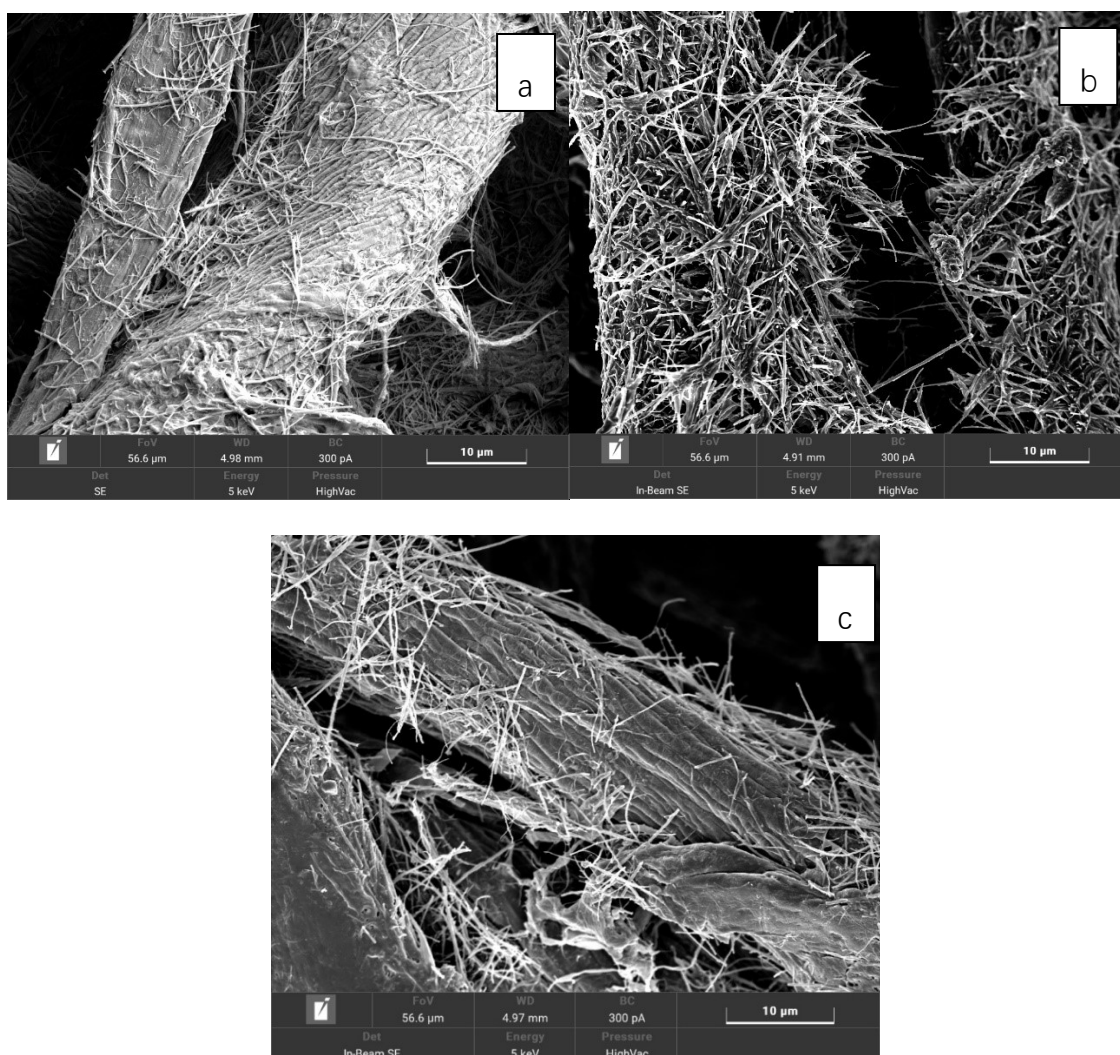


Figure 4-34 SEM images of samples with different surfactant additions (a, b, c are samples with SDBS to CNTs ratios of 2:1, 5:1, 10:1 respectively)

From the observation of Figure 4-34, it can be found that with the increase of SDBS addition, the number of carbon nanotubes supported on the filter paper

fibers first increases and then decreases. So a certain amount of surfactant can promote the dispersion and loading of CNTs, but Too much surfactant may affect the binding of CNTs and filter paper fibers. Moreover, the structure of the fiber surface itself did not change after adding the surfactant, so it can be known that the addition of the surfactant will not affect the structure of the filter paper fiber itself.

Of course, the area shown in the SEM image has a certain randomness, so it can not completely prove that the CNTs content in the sample increases first and then decreases with the addition of surfactant. These observations are also supported by the resistivity results presented in section 4.4.4.

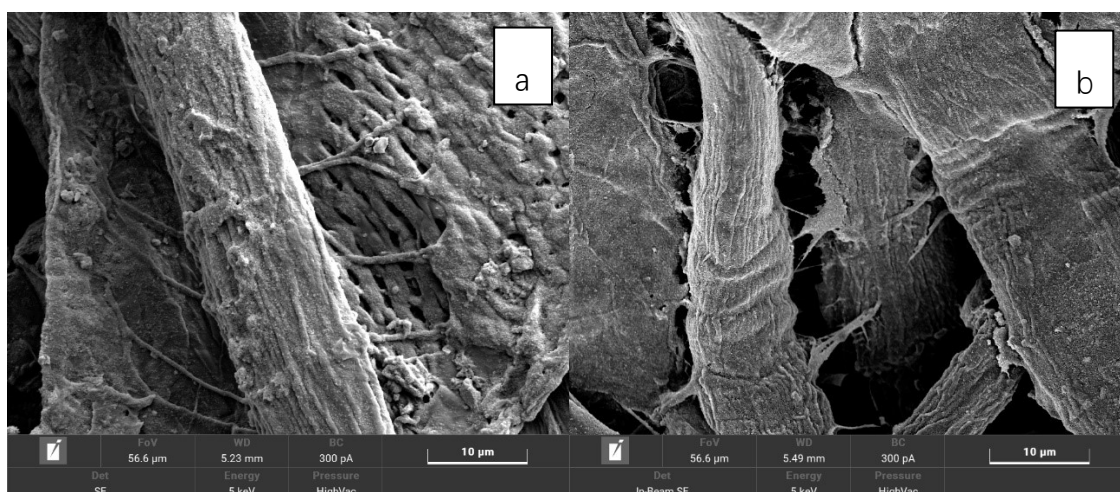


Figure 4-35 a, b for A4 paper sample and paper towel sample respectively

Combining Figure 4-35 and Figure 4-33a, it can be found that no matter which paper is used as the substrate material, graphene can form dense layered stacks on its fiber surface. Therefore, additional tests are required to further verify the effect of different papers on the performance of the samples.

4.4.3 Analysis of sample components

In this experiment, it is necessary to use FTIR to determine the changes of sample components during the reaction, and based on this, the mechanism of the binding of conductive substances to paper-based materials can also be

judged. Since the main components of the three different papers are considered to be fibers, and the changes in the concentration of surfactants will not lead to the generation of new components, only the effects of the types of conductive substances and surfactants on the samples are considered here.

Due to the limitations of laboratory conditions, this project cannot conduct infrared tests on pure graphene or pure CNTs, so the research on surfactants and conductive substances can only refer to the relevant experimental data of other researchers.

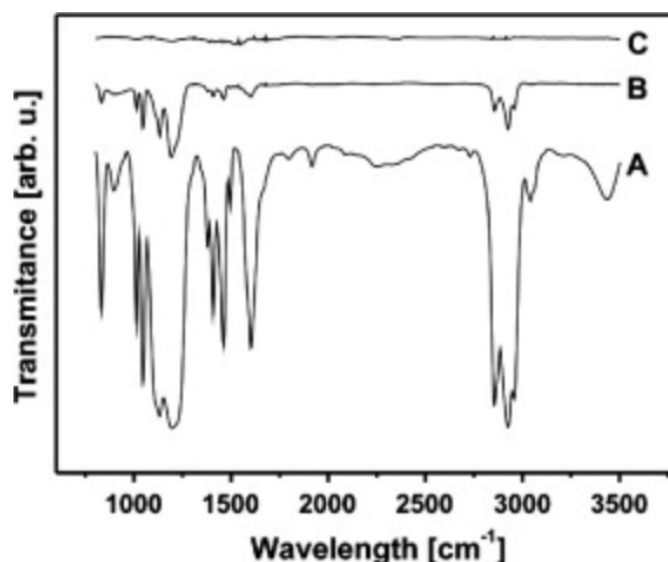


Figure 4-36 A. Infrared spectra of pure SDBS Infrared spectra of pure SDBS, B. Infrared spectra of SDBS-coated CNTs, C. Infrared spectra of pure CNTs ^[150]

Since the solution preparation method used by Bystrzejewski et al ^[150] is the same as in this experiment, the infrared spectrum in their study can be referred to. From the infrared spectra in Fig. 4-36, it can be found that, taking the FTIR spectra of pure CNTs as a reference, the spectra of SDBS-wrapped CNTs produced some peaks and stretch features similar to those of pure SDBS, but no new peaks appear. This clearly shows that surfactant molecules are adsorbed on the surface of CNTs.

By comparing the infrared spectrum of pure SDOC in Figure 4-37 with the infrared

spectrum of SDOC-coated CNTs, we can draw a conclusion similar to the above conclusion, that is, SDOC molecules are well adsorbed on CNTs.

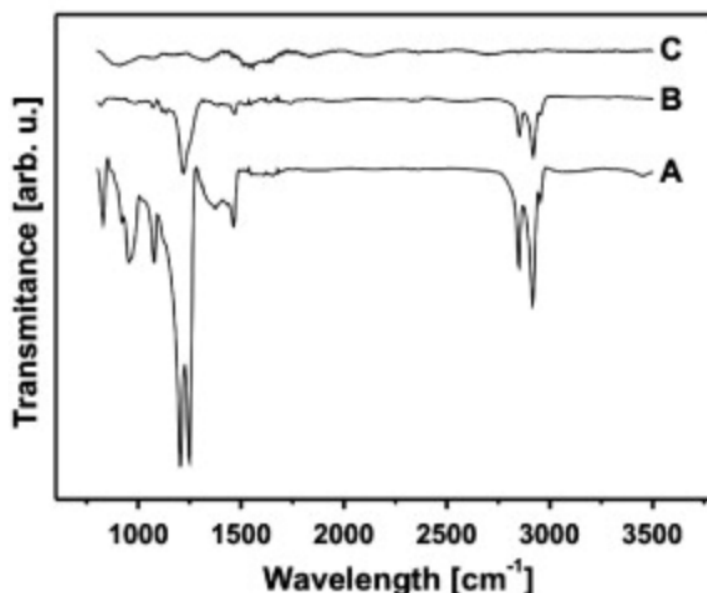


Figure 4-37 a. Infrared spectra of pure CNTs, b. Infrared spectra of SDOC-coated CNTs, c. Infrared spectra of pure SDOC ^[150]

Due to the hydrophobicity of CNT and graphene itself, the addition of surfactants such as SDBS will cause the hydrophobic end of the surfactant to be adsorbed on the surface of graphene in a non-covalent manner ^[151], while the hydrophilic end of SDBS will be in contact with water, it will be distributed as evenly as possible on the surface of graphene and CNT, reducing the contact between the hydrophobic surface of graphene and CNT and water, and reducing the force between graphene and CNT molecules. Therefore, the dispersion effect of graphene and CNT will be better as the amount of SDBS increases. This can explain why the loading of CNTs becomes larger as the SDBS amount increases from 2:1 to 5:1, because a more uniform dispersion can make more CNT molecules more uniformly adsorbed on the surface of each fiber of the paper and thus increase adsorption capacity (this part is detailed in the next section.) However, there is no change in the loading of CNTs from 5:1 to 10:1, which may be because CNTs have reached the maximum equilibrium concentration at 5:1.

Therefore, increasing the amount of surfactant cannot make more CNTs dispersed in water.

In summary, since no new chemical bonds are generated, SDBS and SDOC are adsorbed on CNTs and graphene in a non-covalent manner, while graphene and CNTs are adsorbed on the fibers of paper-based materials by hydrogen bonds and van der Waals forces. Therefore, neither the type of conductive material nor the type of surfactant will affect the composition of the sample, but the amount of surfactant added will affect the load of conductive material in the sample.

4.4.4 Conductive substance loading analysis

There are four variables in this experiment: a. The type of conductive material, b. The type of paper, c. The type of surfactant, d. The amount of surfactant added. It is therefore necessary to investigate the effect of different variables on the loading of conductive species in the samples, because the loading of conductive substances will directly affect the conductivity and electrochemical performance of the sample.

Each sample would be dipped in the solution for five seconds, then dried on a heating plate for 15min (the dipping and drying process would be repeated ten times), finally the samples would be dried at room temperature for 48hrs.

	SDOC/ G	SDBS/G			SDBS/CNT			SDBS/G
Ratio	2:1	2:1			2:1	5:1	10:1	5:1
Adsorption substrate	Filter Paper	Filter Paper	A4 Paper	Paper Towel	Filter Paper	Filter Paper	Filter Paper	Filter Paper
Symbol	A	B	C	D	E	F	G	H

Table 8 Sample number

Considering the large number of experimental samples, the samples are numbered in this experiment as shown in Table 8. Taking into account the accuracy and reproducibility of the experiment, two samples were prepared by the impregnation process using each solution in this experiment.

	Graphene loading mg/cm ²
A1	0.078
A2	0.071
B1	0.076
B2	0.083

Table-9 Graphene loading of samples using different surfactants

It can be seen from Table-9 that samples using different surfactants have similar loadings of conductive active substances. Therefore, the choice of these two surfactants has no effect on the loading of conductive substances. However, considering that the price of SDOC is much higher than that of SDBS, the use of SDBS is more conducive to the large-scale production and application of samples.

	CNT loading mg/cm ²
E1	0.134
E2	0.118
F1	0.263
F2	0.288
G1	0.269
G2	0.274

Table-10 Loadings of conductive substances for samples with different surfactant

contents

It can be seen from Table-10 that samples using different amounts of surfactants have great differences in the loading of conductive active substances. When the mass ratio of surfactant to conductive substance is 2:1, the amount of conductive substance loaded by the sample is significantly smaller than when the mass ratio is 5:1 and 10:1. Therefore, it can be seen that in the case of the same weight of the conductive material, more surfactant are conducive to better dispersion of the conductive material in the solution, thereby enabling more conductive material to be loaded on the paper. However, it can be seen from the loadings of conductive substances of the samples with mass ratios of 5:1 and 10:1 that the loadings of conductive substances of these two samples are similar. This may be because the dissolved amount of the conductive substance in the water has reached the maximum or the conductive substance has been completely dispersed in the water, so even if the amount of surfactant is increased, a larger loading cannot be obtained. In general, the loading of conductive substances is directly related to the amount of surfactant added.

	Graphene loading mg/cm ²
B1	0.076
B2	0.083
C1	0.037
C2	0.045
D1	0.064
D2	0.053

Table-11 Loadings of conductive substances for samples using different papers

From Table-11, it can be seen that the loading amount of conductive active

material of the samples using different papers is quite different. Among them, the filter paper sample has the most conductive material loading, which is benefited from its rough surface and larger pores in the fiber. The conductive material loading of the paper towel sample is slightly smaller than that of the filter paper sample. This may be due to the fact that the paper towel is so thin that the number of fibers inside it is less than that of the filter paper, so it can carry less conductive substances. The A4 paper sample has the smallest loading of conductive substances, which is due to the smooth and less porous surface of the A4 paper combined with its surface structure and microscopic morphology.

	Graphene or CNTs loading mg/cm ²
B1	0.076
B2	0.083
E1	0.134
E2	0.118

Table-12 Loadings of conductive substances for samples using different conductive substances

It can be seen from Table-12 that samples using different conductive substances have great differences in the loading of conductive substances. The loading of the samples using CNTs is significantly larger than that of the samples using graphene. However, due to the different conductive materials, it is not yet clear how the difference in loadings affects the performance of the samples. Therefore, further experiments are needed to verify the differences of samples with different conductive substances. At the same time, the loading of graphene and CNT is

different and it may be related to the structure of graphene and CNT. Since the specific surface area of CNT is larger than that of multi-layer graphene, more SDBS can be adsorbed on the surface of CNT, so that the dispersion effect of CNTs in water is better than that of graphene, resulting in more CNTs being uniformly adsorbed on the surface of the paper. But after the review, no researcher has done the comparison of SDBS on the adsorption effect of CNT and graphene on paper. Therefore, it cannot be verified

4.4.5 Resistivity analysis of samples

By observing the structure and microscopic morphology of the sample, the basic properties of the sample have been preliminarily understood. However, due to the limitations of optical microscope, SEM, FTIR and loading test, the performance of the sample cannot be displayed intuitively. Therefore, resistivity testing was also required to investigate the effect of four different variables on the conductivity of the samples. To ensure the accuracy and reproducibility of experimental data, each sample was prepared in duplicate for reference. And each sample will be selected three areas for testing. The average of the three area measurements for each sample will also be calculated.

b

SDBS/G	2: 1	Ω/m		Average
B1	1.94×10^{-3}	2.04×10^{-3}	2.16×10^{-3}	2.05×10^{-3}
B2	1.66×10^{-3}	1.78×10^{-3}	1.74×10^{-3}	1.72×10^{-3}

a

SDOC/G	2: 1	Ω/m		Average
A1	1.88×10^{-3}	1.82×10^{-3}	1.86×10^{-3}	1.85×10^{-3}
A2	2.12×10^{-3}	2.06×10^{-3}	2.18×10^{-3}	2.12×10^{-3}

Table-13 Resistivity of samples with different surfactants (a, b are resistivities of samples with SDOC and SDBS respectively)

From Table-13 and Figure 4-38, it can be found that the resistivities of the two groups of samples using different surfactants are very similar. And from the two sets of samples produced for each surfactant, it can be found that there are still some differences in resistivity between the samples using the same surfactant. This may be related to the production process, but these differences are small and almost negligible. This also shows that the samples produced by this dipping process have good reproducibility.

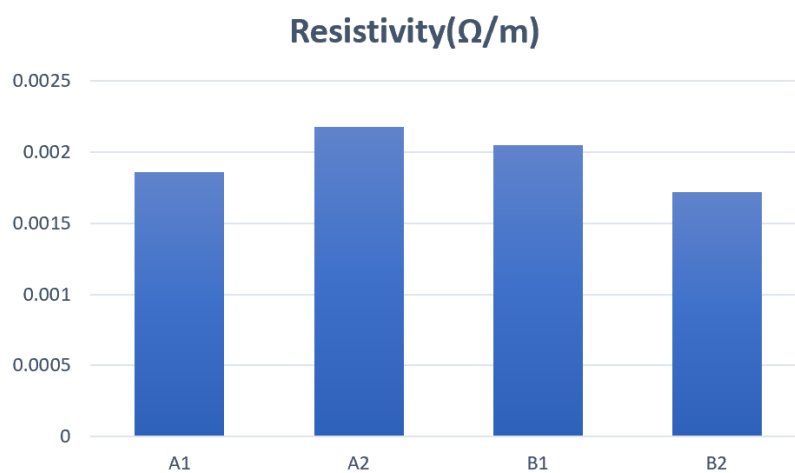


Figure 4-38 Images of resistivity data for samples using different surfactants

This will facilitate the large-scale production use of this process. At the same time, combined with the content of the previous section, it can be found that these two different surfactants have negligible effects on the loading and resistivity of conductive substances, so SDBS is more dominant because of its lower price.

a

SDBS/G	2: 1	Filter Paper	Ω/m		Average
B1		1.94×10^{-3}	2.04×10^{-3}	2.16×10^{-3}	2.05×10^{-3}
B2		1.66×10^{-3}	1.78×10^{-3}	1.74×10^{-3}	1.72×10^{-3}

b

SDBS/G	2: 1	A4 Paper	Ω/m		Average
C1		9.88×10^{-3}	10.42×10^{-3}	9.48×10^{-3}	9.93×10^{-3}
C2		9.40×10^{-3}	8.12×10^{-3}	8.16×10^{-3}	8.56×10^{-3}

c

SDBS/G	2: 1	Paper Towel	Ω/m		Average
D1		4.72×10^{-3}	4.20×10^{-3}	4.46×10^{-3}	4.46×10^{-3}
D2		5.18×10^{-3}	5.04×10^{-3}	4.86×10^{-3}	5.03×10^{-3}

Table-14 Resistivity of samples using different papers (a, b are resistivity of samples using filter paper, A4 paper and paper towel respectively)

From Table-14, it can be found that the resistivity differences of the three groups of samples using different papers are very large. And from the two sets of materials produced for each paper, there is still some difference in resistivity between samples using the same paper. This further confirms that this phenomenon is related to the production process and is unavoidable in production, but these differences are small and almost negligible. It also proves the repeatability of the production process. Combining Table-14 and Figure 4-39, it can be clearly found that the resistivity of the filter paper sample is the smallest, and the resistivity of the A4 paper sample is the largest. Combined with the conclusions in the previous section, it can be known that the reason for this result is related to the loading of conductive substances. Because a lot of uniform conductive substances are attached to the surface of the fiber, the filter paper sample can increase the current transmission area, thereby reducing the resistivity of the sample. However, the A4 paper sample and the paper towel

sample have a weaker charge passing ability due to less conductive material loading, resulting in a larger resistivity. The resistivity data here can be mutually corroborated with the previous analysis.

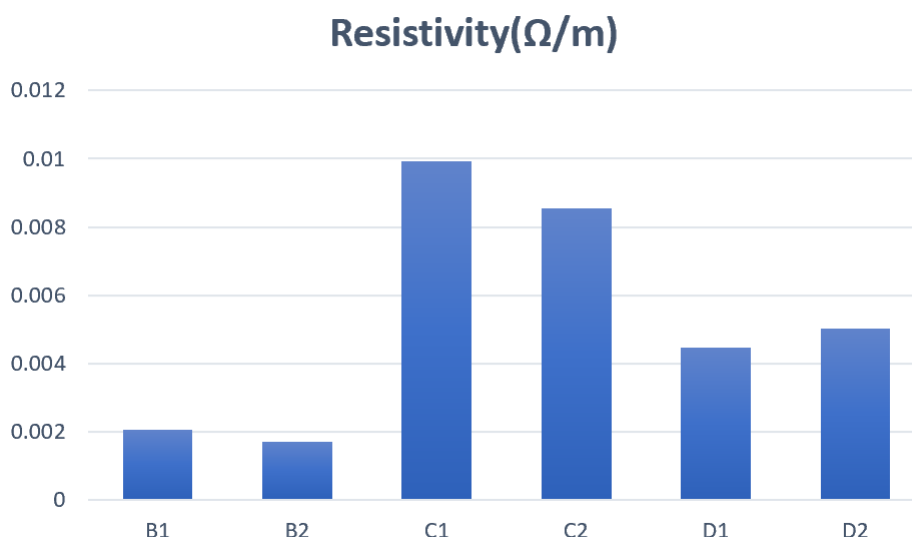


Figure 4-39 Resistivity images of samples using different papers

a

SDBS/G	2: 1	Ω/m		Average
B1	1.94×10^{-3}	2.04×10^{-3}	2.16×10^{-3}	2.05×10^{-3}
B2	1.66×10^{-3}	1.78×10^{-3}	1.74×10^{-3}	1.72×10^{-3}

b

SDBS/CNT	2: 1	Ω/m		Average
E1	1.54×10^{-3}	1.60×10^{-3}	1.58×10^{-3}	1.57×10^{-3}
E2	1.56×10^{-3}	1.52×10^{-3}	1.64×10^{-3}	1.57×10^{-3}

Table-15 Resistivity of samples using different conductive substances (a, b are resistivity data for samples using graphene and CNTs respectively)

From Table-15 and Figure 4-40, it can be found that the resistivity of the two groups of samples using different conductive substances have a little difference. The samples using CNTs have lower resistivity than the samples using graphene.

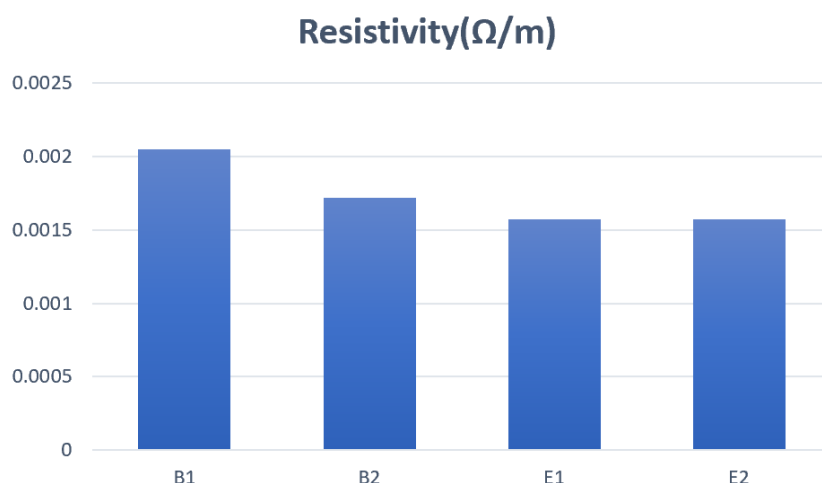


Figure 4 -40 Images of resistivity data for samples using different conductive substances

Combined with the content of the previous section, it can be known that this is due to the less conductive material loading in the graphene sample. However, graphene is a two-dimensional structure, while CNTs are three-dimensional, so the reason for this phenomenon may also be due to the different microstructures of the two.

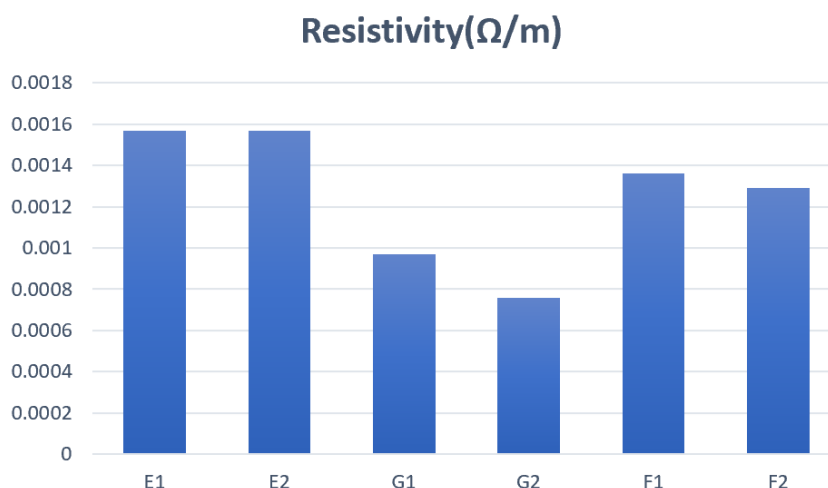


Figure 4 -41 Images of resistivity data for samples with different surfactant concentrations

a

SDBS/CNT	2: 1	Ω/m		Average
E1	1.54×10^{-3}	1.60×10^{-3}	1.58×10^{-3}	1.57×10^{-3}
E2	1.56×10^{-3}	1.52×10^{-3}	1.64×10^{-3}	1.57×10^{-3}

b

SDBS/CNT	5: 1	Ω/m		Average
G1	9.72×10^{-4}	9.18×10^{-4}	1.02×10^{-3}	9.70×10^{-4}
G2	7.38×10^{-4}	6.66×10^{-4}	8.64×10^{-4}	7.56×10^{-4}

c

SDBS/CNT	10: 1	Ω/m		Average
F1	1.32×10^{-3}	1.30×10^{-3}	1.46×10^{-3}	1.36×10^{-3}
F2	1.22×10^{-3}	1.36×10^{-3}	1.28×10^{-3}	1.29×10^{-3}

Table-16 Resistivity of samples with different amounts of surfactant added

From Table- 16 and Figure 4-41, it can be found that the resistivity differences of the three groups of samples added with different amounts of surfactants are relatively large. The sample with a weight ratio of surfactant to CNTs of 5:1 has the smallest resistivity, which can be attributed to its larger loading of conductive materials from the data in the previous section. However, when the weight ratio of surfactant and CNTs is 10:1, the resistivity of the sample increases instead. It can be seen from the reference ^[152] that this phenomenon is due to excessive SDBS will block the connection between CNT molecules, forming an obstacle. Since SDBS is non-conductive, it will increase the resistivity of the sample. Moreover, excessive addition of surfactant will increase production cost and cause waste of resources. At present, it seems that the weight ratio of surfactant to conductive substance is 5:1 is the best choice.

4.4.6 Electrochemical testing

The surface structure, microstructure and resistivity results for the carbon paper samples have been presented earlier. However, if the experimentally prepared carbon paper samples are to be used in the field of energy storage, the electrochemical properties are important and need assessing. In this section, Ag/AgCl electrodes were selected as reference electrodes, platinum sheet electrodes as counter electrodes and 1 mol/L Na₂SO₄ solution as electrolyte to test the electrochemical performance of carbon paper samples in aqueous energy storage devices.

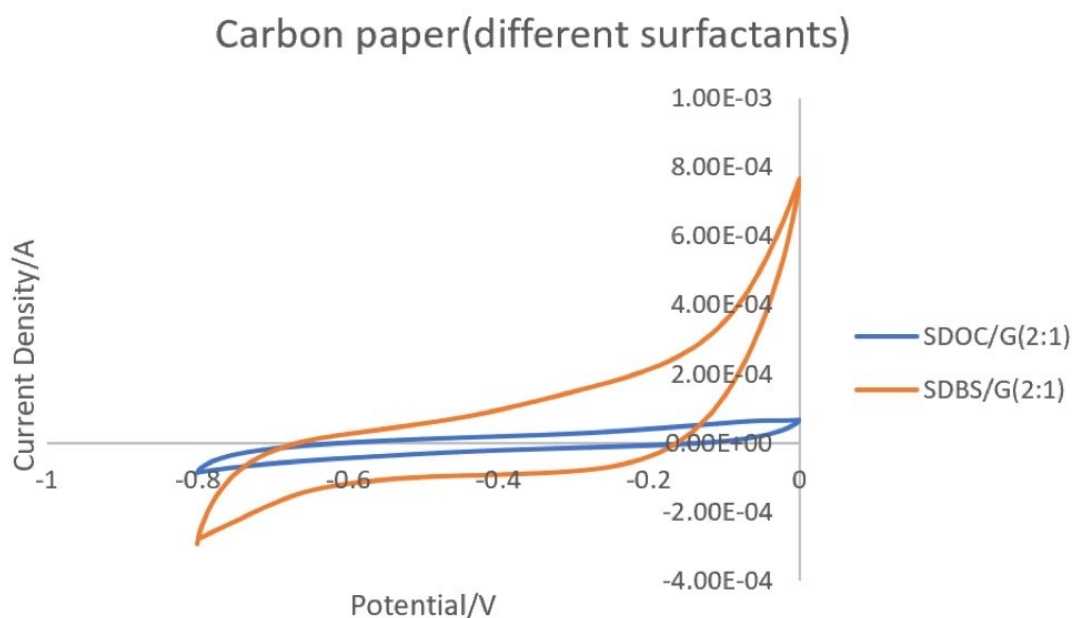


Figure 4-42 Cyclic voltammetry (CV) curves for carbon paper samples with different surfactants

It can be seen from Figures 4-42 that the CV curves of the samples using different surfactants at a scan rate of 100 mV/s are both approximately rectangular, which indicates that both samples have good electric double layer capacitance. This proves that the carbon paper sample produced in this experiment is indeed a material with good electrochemical performance. This result is similar to that in

the previous literature available ^[153]. This lays a solid foundation for the application of this material in the field of energy storage. It can be seen from the figure that the rectangular area of the SDBS-added sample is significantly larger than that of the SDOC-added sample. Combined with Equation 20, it can be known that the specific capacitance of the SDBS-added sample is greater than that of the SDOC-added sample. At the same time, it can be seen from the resistivity test that the resistivity of the two samples is similar, but SDBS is much cheaper than SDOC, so SDBS was selected as the surfactant in the subsequent experiments.

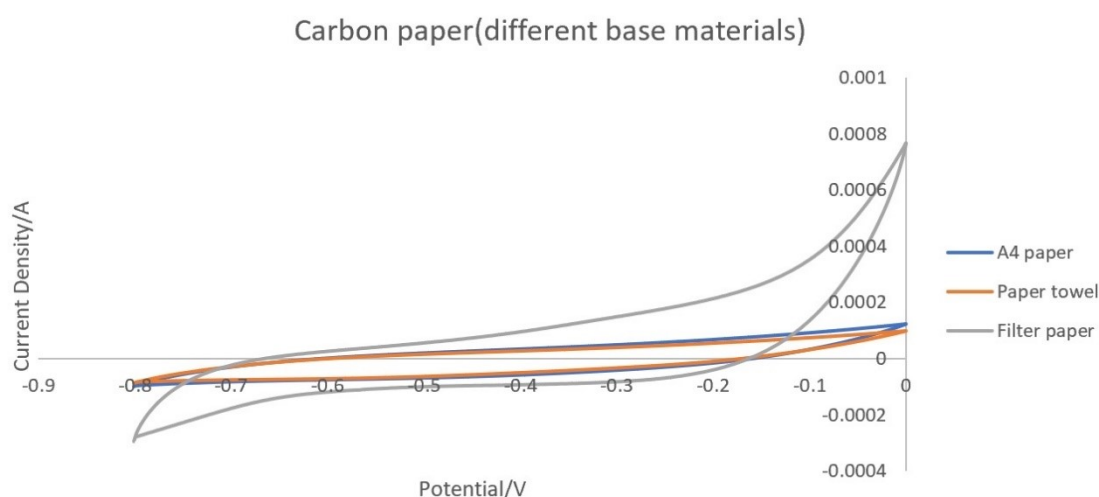


Figure 4-43 CV curves for samples using different base materials at a scan rate of 100mV/s

It can be seen from Figures 4-43 that the CV curves of the samples using different substrate materials at a scan rate of 100 mV/s all present an approximate rhomboid, which indicates that the three samples have good electric double layer capacitance. It can be easily seen from the figure that the rectangular area of the sample using filter paper is significantly larger than the rectangular area of the other two samples, but the rectangular area of the other two samples cannot be easily compared from the figure, so use Equation 20 to calculate the specific capacitances of the two samples and the results are shown in Table 17. It can be

seen from Table 17 that the specific capacitance of the sample using A4 paper is slightly larger than that of the sample using paper towel, but the difference is not very large.

Base material	Specific capacitance/ Fg^{-1}
Filter paper	28.53
A4 paper	15.17
Paper towel	14.83

Table 18 Specific capacitance of samples with different substrate materials

However, considering the loading rate and surface structure, the electrochemical performance of the paper towel sample is theoretically better than that of the A4 sample, but the obtained data are very close to the electrochemical performance of the two. The reason for this phenomenon may be that, because the paper towel is too thin, a large amount of conductive material will be lost during the wetting process of the tested sample before the electrochemical test (a part of the dispersed conductive material can be observed in the electrolyte in the experiment). Since the resistivity test results and electrochemical test results of the filter paper samples were good, subsequent tests will be done with filter paper only.

Conductive material	Specific capacitance/ Fg^{-1}
Graphene	28.53
CNTs	24.74

Table 19 Specific capacitance of samples with different conductive materials

Carbon paper(different conductive substances)

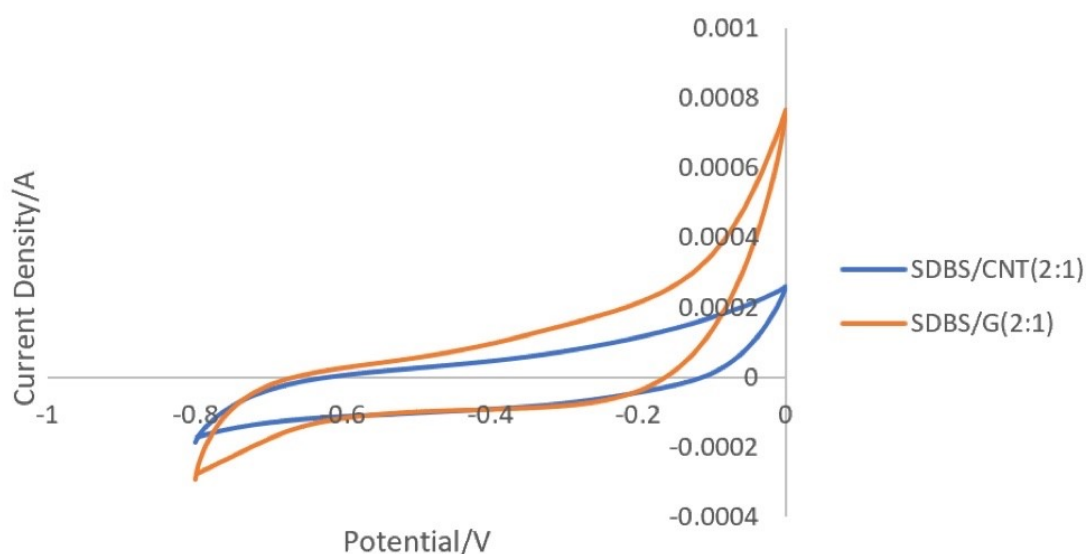


Figure 4-44 CV curves for samples using different conductive substances at a scan rate of 100mV/s

It can be seen from Figure 4-44 that the CV curves of the samples using different conductive substances at a scan rate of 100 mV/s all present an approximate rhomboid, which indicates that both samples have good electric double layer capacitance. However, the area of the rectangular area cannot be easily compared from the figure, so using Equation 20 to calculate the specific capacitance of the two samples is shown in Table 18. It can be seen from Table 18 that the specific capacitance of the graphene-added sample is slightly larger than that of the CNT-added sample, but the difference is not very large, so the graphene sample has no obvious electrochemical advantage over the CNT sample. Combined with the resistivity test, since the resistivity of the two samples is similar, but CNT is cheaper than graphene, CNT is selected as the conductive material in subsequent experiments.

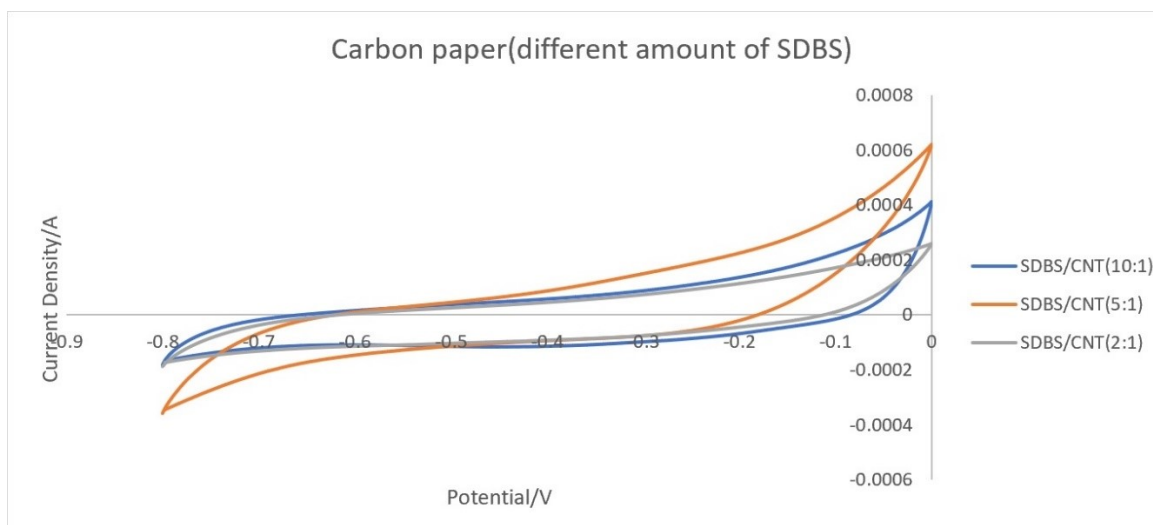


Figure 4-45 Specific capacitance of samples with different SDBS additions

It can be seen from Figure 4-45 that the CV curves of the samples with different SDBS addition amounts at a scan rate of 100 mV/s all present an approximate rhomboid, which indicates that the three samples have good electric double layer capacitance. Since it is not easy to see the size of the rectangular area of these three samples from the figure, it is necessary to use Equation 20 to calculate the specific capacitance of the three samples, as shown in Table 19.

Weight ratio	Specific capacitance/ Fg^{-1}
10:1	28.16
5:1	30.29
2:1	24.74

Table 20 Specific capacitance of samples with different SDBS additions

It can be seen from Table 19 that the specific capacitances of the two samples with SDBS to CNT weight ratios of 10:1 and 5:1 are very close, and significantly larger than those of the samples with SDBS to CNT weight ratio of 2:1. Combining the loading rate and resistivity test results, the data trend of the electrochemical test results can be found, which is consistent with the conclusions drawn from the first two tests. Since the samples with more surfactants did not show better

electrochemical performance and resistivity, and considering the high price of SDBS, excessive addition would lead to the expansion of cost and waste of resources. Therefore, in this experiment, it can be found that the most cost-effective carbon paper sample is the sample that uses filter paper as the base material, CNT as the conductive material, SDBS as the surfactant, and the mass ratio of SDBS to CNT is 5:1. In view of its various advantages, it will be further tested to explore its electrochemical stability.

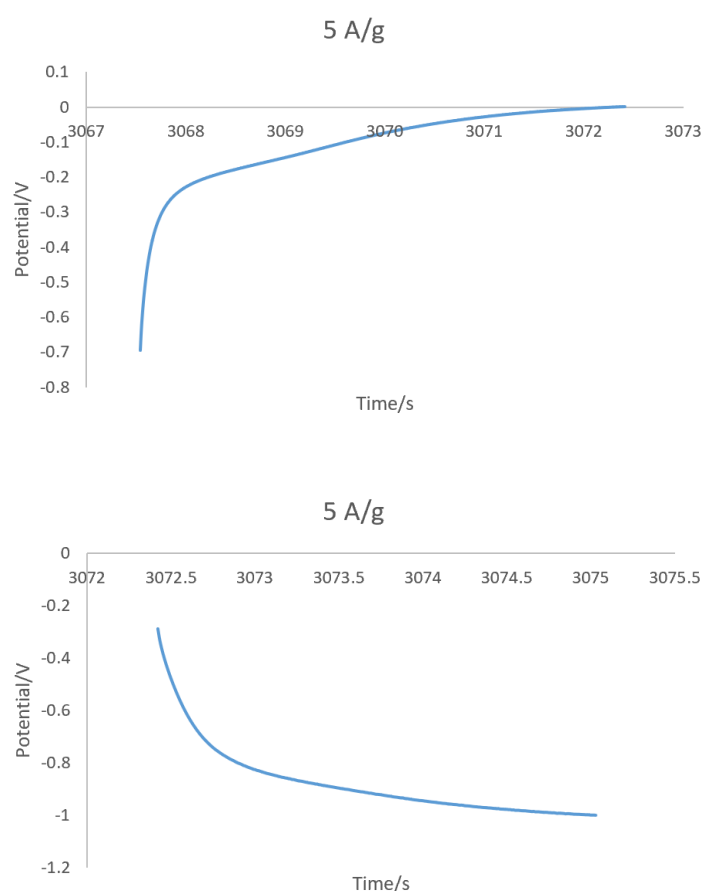


Figure 4-46 Charging and discharging curves of the optimum carbon paper sample at a current density of 5 A/g

From Figure 4-46 and Appendix 16, the charge-discharge curves of the optimal sample at different current densities, it can be seen that the charge-discharge curves of the sample can be combined into a non-standard triangle. This indicates that the charge and discharge of this sample are reversible.

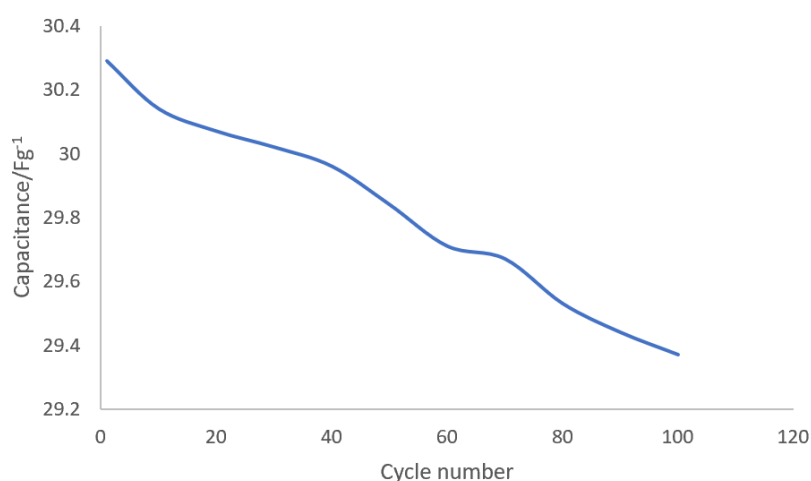


Figure 4-47 Cycling stability of optimal carbon paper samples

Figure 4-47 shows that the capacitance retention of this sample is still 97% after 100 cycles, which indicates that the material has good cycling stability as an electrode material. Such performance shows that this material has great potential for application in the field of energy storage.

In this section, through the analysis of experimental data, it can be concluded that the electrochemical performance of carbon paper is closely related to the type of substrate material, the type of surfactant, and the weight ratio of surfactant to conductive material. The type of conductive material has little effect on the performance of the sample. Finally, it can be found that the obtained optimal sample has great potential for industrial application.

5. Conclusion

The aim of this project is to investigate the fabrication methods of novel electrodes for energy storage and the factors that affect electrode performance. Therefore, in this project three different production processes were used to prepare a series of aerogel and carbon paper samples, and the samples were systematically tested. The structure and micromorphology of the samples were analyzed by optical microscopy and SEM. The components of the samples were analyzed by FTIR. The resistivity and electrochemical properties of the samples were analyzed with a multimeter and electrochemical workstation. According to these test results, it can be found that many factors affect the process and results of sample production. The specific conclusions are as follows:

1. A large number of irregular pore structures can be found in the PVDF/G aerogels synthesised with DMAc as solvent, which increases the active area for electrochemical reactions. The amount of graphene added in the PVDF/G samples with DMAc as the solvent will greatly affect the electrochemical performance of the samples. This is probably because the graphene content in the sample is improved with the increase of graphene addition, and the sample with more graphene will have a larger specific capacitance. But it is not clear whether there is a maximum addition amount. The aerogel samples prepared by this process have good cycling stability.
2. The PVDF/G aerogel sample with DMF as solvent has a good pore structure, but due to the high air pressure in its production process, its pore structure is very small and dense. Due to its low strength, it is not suitable for use as an electrode material, but its rich pore structure and good lipophilicity of graphene make it possible to be applied in the fields of oily waste adsorption and environmental protection. Considering the influence of high pressure on the structure and properties of the sample, the production process at high

temperature and low pressure (oven heating, normal pressure) is obviously more suitable for the production of PVDF/G aerogels for electrodes.

3. It can be found that different surfactant additions do not change the structure of the carbon paper samples. But it will affect the loading of conductive substances in the sample, and therefore the resistivity and electrochemical performance of the sample. It can be seen from the composition analysis that this is because the surfactant is adsorbed on the surface of the conductive material in a non-covalent manner, which can make CNT or graphene better disperse in the water, so that more conductive material can be loaded on the paper and can be loaded more uniformly. However, there is a saturated concentration of conductive substances dissolved in water. After reaching the saturated concentration, adding more surfactants will not make more conductive substances dispersed in water. Moreover, since surfactants are not conductive, excessive addition will also lead to clogging of conductive substances and affect the electrochemical performance of the samples. In this experiment, comprehensive consideration of resistivity results, electrochemical experiment results and cost, it can be found that the optimal weight ratio of surfactant (SDBS) and conductive material (CNT) is 5:1. Excessive addition of surfactant will also lead to increased cost and waste of resources.
4. According to the analysis of experimental data, it can be found that when the filter paper is used as the substrate, CNT is used as the conductive material, SDBS is used as the surfactant, and the weight ratio of SDBS to CNT is 5:1, the prepared sample has the best resistivity and specific capacitance. This is due to the large number of micro-pores between the fibers of the filter paper and the optimal loading of CNTs at this weight ratio. At the same time, the sample also has a rich pore structure, good charge-discharge performance,

and high electrical charge/discharge cycle stability, which is suitable for use as an electrode material.

5. The specific capacitance of the best carbon paper sample was recorded as 30.29 F/g, which is slightly higher than the specific capacitance of the existing CNT/paper composite of 22 F/g ^[153], but there is no obvious advantage in performance. However, simpler fabrication steps, shorter fabrication time, and lower fabrication cost make the fabrication process used in this experiment more suitable for large-scale industrial production compared to existing fabrication methods.

At the same time in this experiment, some observations can also be obtained as follows:

Due to the different fiber structures and thicknesses of different types of paper, the type of paper can have an impact on the resistivity and electrochemical performance of the samples. Moreover, using different papers as base materials has an impact on the drying time of carbon paper samples, and choosing the right paper will help to save energy during mass production. The best drying time at room temperature for most carbon paper samples is 48hrs. Different types of conductive substances do not have much effect on the performance of carbon paper, but considering that the price of CNTs is slightly lower than that of graphene, using CNTs in mass production will reduce production costs.

6. Recommendations/Further works

According to the obtained results, it can be known that PVDF/G aerogel with DMAc as solvent has good structure and electrochemical cycle stability, but its internal graphene distribution is uneven and the surface structure is smooth. These factors cause the reduced performance of the samples. Therefore, it can be considered to improve these disadvantages through certain methods. The specific methods are as follows:

1. Use larger reaction vessels for experiments.
2. Add surfactants when dispersing the graphene in the water to make it disperse more evenly.
3. Use longer sonication times when mixing graphene solutions with PVDF solutions to mix the two well.
4. Modify graphene with nitrogen and sulphur or add transition metals to aerogels to enhance the pseudocapacitance of the material and thus increase the specific capacitance of the material.
5. Further experiments to determine the optimal amount of graphene to add

The sample with DMF as solvent is too brittle, so it cannot be used as electrode material, but its porous structure can make it used in other fields, such as adsorbing oily substances as an adsorbent material, but the following tests are required for this purpose:

1. Test the hydrophobicity and contact angle of the sample
2. Test the adsorption capacity of the samples for different oily substances
3. Measure the adsorption capacity of the sample for the specified oily substance

The research results of carbon paper show that an electrode material which is

easy to produce and has high cycle stability was obtained in this experiment, but its specific capacitance is low. Combined with the current demand for environmental protection, the future research on carbon paper can focus on the following two points: a. How to improve the electrochemical performance of such samples while maintaining a simple production process and low cost; b. Exploring the use of recyclable resources to prepare carbon paper, and the purpose of protecting the environment and saving costs will be achieved. c. Explore experimental pathways for the preparation of graphene or carbon nanotubes from recyclable carbon materials to achieve further cost savings and reduce pollution.

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Appendix 1 Preparation of PVDF/graphene aerogels (DMAc as solvent)

- a. 1.2g of PVDF powder was placed in a beaker with 10ml of DMAc, and it was placed in an oven set to 90 °C to speed up its dissolution.
- b. Weigh 30mg graphene (the procedure was repeated with 60mg and 90mg graphene to produce a range of PVDF/graphene aerogels), pour 6ml deionized water into the weighed graphene and stir it by using an ultrasonic bath for 1.5h. Then slowly pour the dispersed graphene dispersion into the PVDF solution and shake it fully to mix it evenly (Directly mixing, according to the data, DMAc has good water solubility and will not react when mixed with water).
- c. The PVDF solution was left at 60°C for 24h to degasify. Then, it was placed under room temperature (20°C) for 12h to form wet gel via phase inversion induced sol-gel process.
- d. The sample was soaked in 20 ml of ethanol for 8h, then pour off the ethanol (during soaking, the container shall be sealed with fresh-keeping film to prevent the volatilization of ethanol). Repeat three times to remove the residual DMAc in the sample, then the corresponding hydrogel was freeze-dried at -60 C (<10 Pa) for 24 h to produce the porous aerogel.
- e. In this experiment, the effect of changing the amount of graphene on the structure and electrochemical performance of the sample will be investigated.

Appendix 2 Preparation of PVDF aerogels (DMAc as solvent)

- a. 1.2g PVDF powder was dissolved in 10mL DMAc, ultrasonic dispersion at 90 °C for 15 minutes in an ultrasonic cleaning machine. Subsequently, 1.5mL DI water was slowly dropped into the solution to form a PVDF solution (Directly mixing, according to the data, DMAc has good water solubility and will not react when mixed with water).
- b. The PVDF solution was left at 60°C for 24h to degasify. Then, it was placed under room temperature (20°C) for 12h to form wet gel via phase inversion induced sol-gel process.
- c. The sample was soaked in 15 ml of ethanol for 8h (During soaking, the container shall be sealed with fresh-keeping film to prevent the volatilization of ethanol). Repeat three times to remove the residual DMAc in the sample, then the corresponding hydrogel was freeze-dried at -60 C (<10 Pa) for 24 h to produce the porous aerogel.
- d. This experiment investigated whether the addition of graphene would have an effect on the structure of PVDF aerogels.

Appendix 3 Preparation of PVDF/ graphene aerogels (DMF as solvent)

- a. Graphene (10mg, 20mg, 30mg) was dispersed in 5 ml of the mixed solvents (3 ml deionized water and 2 ml DMF) under sonication for 1.5 h.
- b. 50 mg PVDF was dissolved in 5 ml of DMF to form a homogeneous solution. Then a stable suspension was obtained by mixing the G dispersion and PVDF solution (Directly mixing, according to the data, DMF has good water solubility and will not react when mixed with water) under sonication for 10 min.
- c. The mixture was sealed in a 25 ml Teflon-lined autoclave and heated at 160 C for 10 h. After the autoclave was cooled to room temperature, the as-prepared hydrogels was taken out with tweezers and then washed with deionized water several times to remove the residual DMF.
- d. Subsequently, it was immersed in additional deionized water and then taken out at an interval of 8 h. These operations were repeated five times. The corresponding hydrogel was freeze-dried at -60 C (<10 Pa) for 24 h to produce the porous aerogel.
- e. In this experiment, the effect of changing the amount of graphene on the structure and electrochemical performance of the sample will be investigated.

Appendix 4 Freeze drying process

- a. Turn on the main power switch on the left side of the vacuum freeze dryer chassis, and the air pressure digital display is atmospheric pressure 110kPa;
- b. Press and hold the main switch key on the control panel of the vacuum freeze dryer for more than three seconds, the temperature digital display shows the actual temperature of the cold trap;
- c. Start the freeze dryer refrigerator and pre-cool for more than 30 minutes;
- d. Put the sample into the sample holder, cover the plexiglass cover, and start the vacuum pump;
- e. After the air pressure digital display of the vacuum freeze dryer is stable, record the temperature and air pressure values;
- f. Record the temperature and air pressure values before shutdown;
- g. Press and hold the inflation valve on the control panel of the vacuum freeze dryer and immediately turn off the vacuum pump;
- h. When the pressure digital display is atmospheric pressure, open the plexiglass cover and take out the sample;
- i. Turn off the refrigerator of the vacuum freeze dryer, press and hold the main switch for more than three seconds, and finally turn off the main power switch;
- j. After the ice in the cold trap is completely turned into water, open the water outlet valve on the left side of the chassis to release the water, clean the inner wall of the cold trap with a dry cloth, and cover with a large piece of filter paper to prevent dust.

Appendix 5 Optical microscope operation steps

- a. Turn on the computer and enter the optical microscope imaging software.
- b. Rotate the converter to align the low magnification objective lens with the light aperture, and keep a distance of 2 cm between the front end of the objective lens and the stage.
- c. Then align a larger aperture with the light aperture, this is to make the light source better contact with the object, facilitate imaging, and make the image clearer. Observe the image on the computer. Rotate the mirror so that the light is reflected into the lens barrel through the light hole, and stop when you see a brighter field of view.
- d. Place the specimen of the slide to be observed on the stage, and the specimen should be in the center of the clear hole, which can make the image clearer.
- e. Rotate the coarse focusing screw to slowly lower the lens barrel and watch from the side until the objective lens is close to the sample, so as to prevent the objective lens from touching the sample.
- f. Observe the image on the computer, and turn the coarse focusing screw in the opposite direction to make the lens barrel rise slowly until the object image is clearly seen. Then turn the fine focus screw slightly to make the image seen more clearly.
- g. Save the clear image and name it.
- h. Turn off the computer and microscope, and turn off the power.

Appendix 6 SEM operation steps

- a. Preparation of bulk sample: stick the sample on the sample holder with conductive glue, coated with gold or palladium to ensure it is conductive and then put it into SEM observation.
- b. Power on, check the vacuum, circulating water status, and turn on the "Display" power
- c. Secure the sample holder according to the height specification.
- d. Press the "Air" button on the exchange compartment to release air, put the sample stage in after the buzzer sounds, rotate the sample rod to the "Lock" position, close the exchange compartment, press the "Evac" button to exhale, and the buzzer sounds Then, press the "Open" button to open the sample compartment door, push in the sample stage, rotate the sample rod to the "Unlock" position, and then pull it out, and press the "Close" button.
- e. Select the appropriate acceleration voltage and beam current on the operation panel, and press the "On" button to increase the voltage.
- f. Use the roller to position the sample stage to the observation point, and adjust the height of the sample stage in the operation interface.
- g. Select the appropriate magnification, click the "Align" button, adjust the knob, and gradually adjust the electron beam position and the astigmatism reference.
- h. Locate the observation area in the "TV" or "Fast" scan mode, focus and eliminate the astigmatism in the "Red" scan mode, and take a picture in the "Slow" or "Cssc" scan mode.
- i. Select the appropriate image size and shooting method, press "Capture" to take a picture, and name the picture.

j. Adjust the sample stage back to 8mm, and press the "Home" button to return the sample stage to the initial state.

k. After the "Home" indicator stops flashing, withdraw the sample stage and close the sample compartment. Exit the program, shut down the computer, turn off the power.

Appendix 7 FTIR operation steps

- a. Power on and start the testing software.
- b. Clean the sample stage, first take the reference for limit calibration.
- c. Clean the sample stage, and then take the sample for testing.
- d. Click baseline calibration, click calculate, and then click OK.
- e. Then click connect, click calculate, and then click OK to remove the spurious peaks caused by CO₂.
- f. Click Normalize again, click calculate, and then click OK.
- g. If desired, tap peak detection again.
- h. After the test, you need to select the file and export it before exporting the data.
- i. After the test is completed, clean the sample stage and turn off the power.

Appendix 8 Multimeter operation steps

- a. First, you need to connect the test leads of the multimeter. Generally, the red test leads should be placed in resistor option and the black test leads should be inserted into the COM port, so as to ensure the normal use of the multimeter.
- b. Rotate selector switch of the multimeter. If you need to measure the resistance, you must adjust it to the resistance setting, but you may not know the resistance value at the beginning. We can rotate it to the range of the estimated value, for example, in the 100 ohms in the middle.
- c. Connect the two ends of the resistor, the black test lead and the red test lead can be connected at this time, there is no difference between positive and negative, but it must be ensured that the contact cannot be loose.
- d. Place the paper sample to be tested in the measuring tool and tighten the upper and lower splints. Use the test leads to touch the two copper probes on the measuring tool.
- e. At this time, there will be data displayed on the display screen of the multimeter. If there is no data display, it is possible that the resistor is damaged, or the range setting is not enough. You can adjust the range, for example, to 200 ohms. After the range is increased, if the value is displayed, the resistance value of the sample can be directly measured at this time.

Appendix 9 Electrochemical workstation operation steps

- a. Connect the electrochemical workstation to the computer, turn on the power and the computer.
- b. Check whether the signal light of the electrochemical workstation flashes normally.
- c. Connect the soaked sample to the electrochemical workstation as the working electrode, and also connect the reference electrode and the counter electrode to the electrochemical workstation, and soak all three electrodes into the electrolyte to form a three-electrode system.
- d. Move the assembled three-electrode system into the electromagnetic shielding box, in order to avoid the external electromagnetic interference of the three-electrode system during the test, resulting in deviation of the measurement results.
- e. Open the test software, select the item to be tested, input parameters, and perform pre-test first.
- f. Examine the pre-test results to see if the test results match the sample characteristics.
- g. After checking, the formal test will be carried out.
- h. After the test is completed, save the test data, take out the three-electrode system, and properly clean and save all electrodes.
- i. Shut down the software and power.
- j. Use graphing software to analyze the resulting data. And using the obtained data to calculate the specific capacitance of each sample.

Appendix 10 Graphene nanoplatelets safety data sheet

SAFETY DATA SHEET

Product: Graphene Nanoplatelets

RAYMOR
NanoIntegris

(1) PRODUCT AND COMPANY IDENTIFICATION

Identification of the substance or preparation

TRADE/MATERIAL NAME: Graphene Nanoplatelets
CHEMICAL NAME: Graphene
SYNONYMS: Few-layered graphene

This SDS is valid for the following Graphene Grades:

PureWave Graphene, PureSheets MONO, PureSheets QUATTRO

Use of the substance/Preparation:

For laboratory research purposes only.

Supplier:

Raymor Industries Inc.
3765 La Vérendrye
Boisbriand, Quebec, J7H 1R8
CANADA
Phone No.: +1 450.434.6266

Emergency Telephone:

US: CHEMTREC 1-800-424-9300 or 1-703-527-3887
Canada: CANUTEC 1-613-996-6666 (24 hour transportation emergency)

(2) HAZARDS IDENTIFICATION (EC)

GHS Classification

Not available

GHS Label elements, including precautionary statements



Signal Word:

Warning

Hazard Statements:

May form combustible dust concentrations in air.

WHMIS Classification

Not available

SAFETY DATA SHEET

Product: Graphene Nanoplatelets

RAYMOR
NanoIntegris

OSHA/HCS Status:

This material is considered hazardous by the OSHA Hazard Communication Standard (29 CFR 1910.1200).

Classification of the substance or mixture: COMBUSTIBLE DUSTS

Precautionary statement(s):

Keep container tightly closed. Keep away from heat, sparks, open flames and hot surfaces. - No smoking. Sanding and grinding dusts may be harmful if inhaled. Prevent dust accumulation. Emits toxic fumes when heated.

HMIS Classification

Health hazard: 2

Flammability: 0

Physical hazards: 0

Potential Health Effects:

Inhalation May be harmful if inhaled.
Causes respiratory tract irritation.
Skin May be harmful if absorbed through skin.
Causes skin irritation.
Eyes Causes eye irritation.
Ingestion May be harmful if swallowed.

Hazard codes: Xi

Risk Statements: R36/37/38

(3) COMPOSITION/INFORMATION ON INGREDIENTS

<u>INGREDIENT NAME</u>	<u>CAS NUMBER</u>	<u>PERCENT</u>	<u>EC NUMBER</u>	<u>EC CLASSIFICATION</u>
Synthetic Graphite	7782-42-5	90-100	231-955-3	Xi R36/37/38
Trace impurities	Not available	0-1	Not available	Not available

Appendix 11 Carbon nanotubes safety data sheet

ThermoFisher
SCIENTIFIC

SAFETY DATA SHEET

Revision Date 21-Feb-2020

Revision Number 2

1. Identification

Product Name Fullerene, carbon nanotube, multi-walled

Cat No. : 44945

CAS-No 308068-56-6

Synonyms No information available

Recommended Use Laboratory chemicals.

Uses advised against Food, drug, pesticide or biocidal product use.

Details of the supplier of the safety data sheet

Company

Alfa Aesar
Thermo Fisher Scientific Chemicals, Inc.
30 Bond Street
Ward Hill, MA 01835-8099
Tel: 800-343-0660
Fax: 800-322-4757
Email: tech@alfa.com
www.alfa.com

Emergency Telephone Number

During normal business hours (Monday-Friday, 8am-7pm EST), call (800) 343-0660.
After normal business hours, call Carechem 24 at (866) 928-0789.

2. Hazard(s) identification

Classification

This chemical is considered hazardous by the 2012 OSHA Hazard Communication Standard (29 CFR 1910.1200)

Flammable solids	Category 2
Skin Corrosion/Irritation	Category 2
Serious Eye Damage/Eye Irritation	Category 2
Specific target organ toxicity (single exposure)	Category 3
Target Organs - Respiratory system.	

Label Elements

Signal Word

Warning

Hazard Statements

Flammable solid
Causes skin irritation
Causes serious eye irritation
May cause respiratory irritation



Precautionary Statements

Prevention

Wash face, hands and any exposed skin thoroughly after handling
Wear protective gloves/protective clothing/eye protection/face protection
Avoid breathing dust/fume/gas/mist/vapors/spray
Use only outdoors or in a well-ventilated area
Keep away from heat/sparks/open flames/hot surfaces. - No smoking
Ground/bond container and receiving equipment
Use explosion-proof electrical/ventilating/lighting/equipment

Inhalation

IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing
Call a POISON CENTER or doctor/physician if you feel unwell

Skin

IF ON SKIN: Wash with plenty of soap and water
If skin irritation occurs: Get medical advice/attention
Take off contaminated clothing and wash before reuse

Eyes

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing
If eye irritation persists: Get medical advice/attention

Fire

In case of fire: Use CO₂, dry chemical, or foam for extinction

Storage

Store in a well-ventilated place. Keep container tightly closed
Store locked up

Disposal

Dispose of contents/container to an approved waste disposal plant

Hazards not otherwise classified (HNOC)

None identified

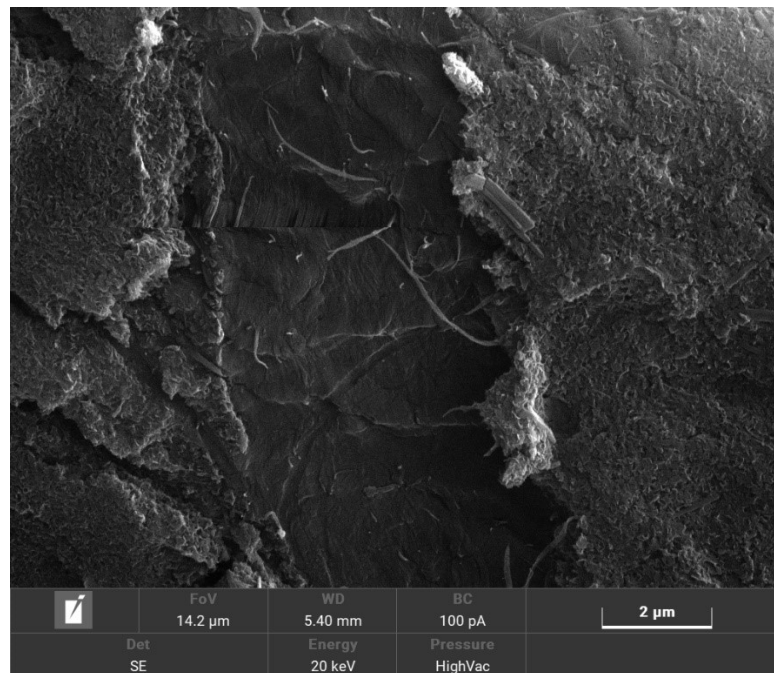
3. Composition/Information on Ingredients

Component	CAS-No	Weight %
Fullerene, buckytube/nanotube, single walled, as-produced	308068-56-6	<=100

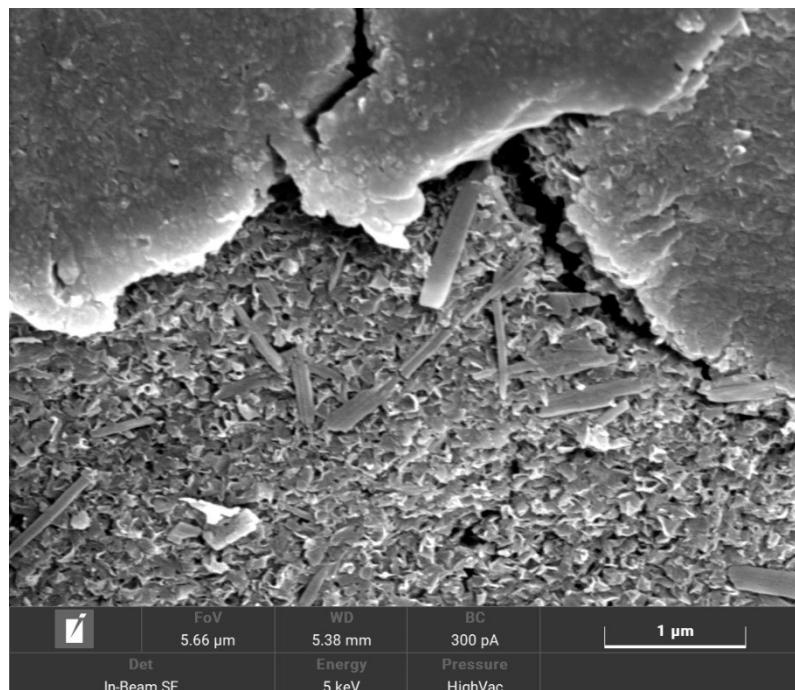
4. First-aid measures

General Advice	If symptoms persist, call a physician.
Eye Contact	Rinse immediately with plenty of water, also under the eyelids, for at least 15 minutes. Get medical attention.
Skin Contact	Wash off immediately with plenty of water for at least 15 minutes. If skin irritation persists, call a physician.
Inhalation	Remove to fresh air. If not breathing, give artificial respiration. Get medical attention if symptoms occur.

Appendix 12 SEM image of sample using SDOC as surfactant.

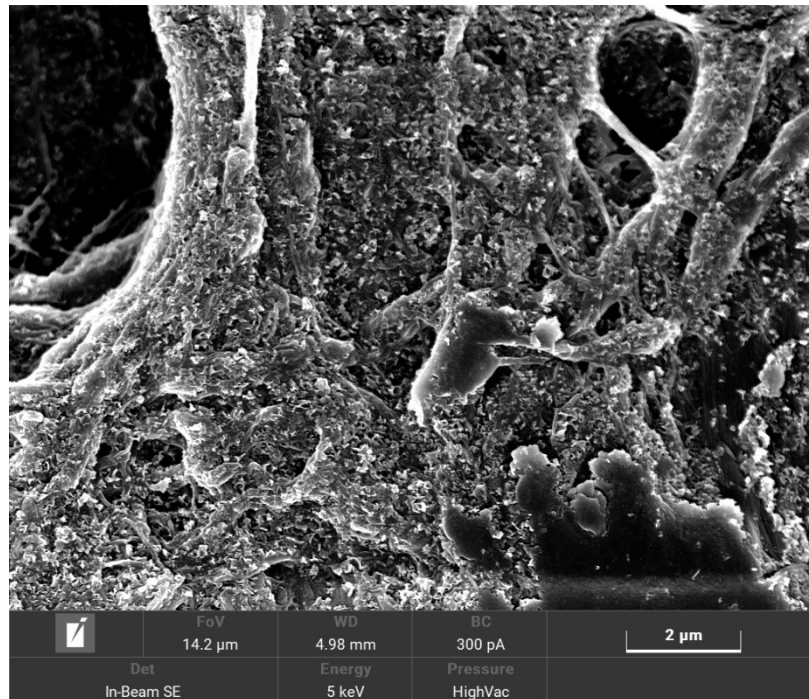


SEM image magnified 20k times

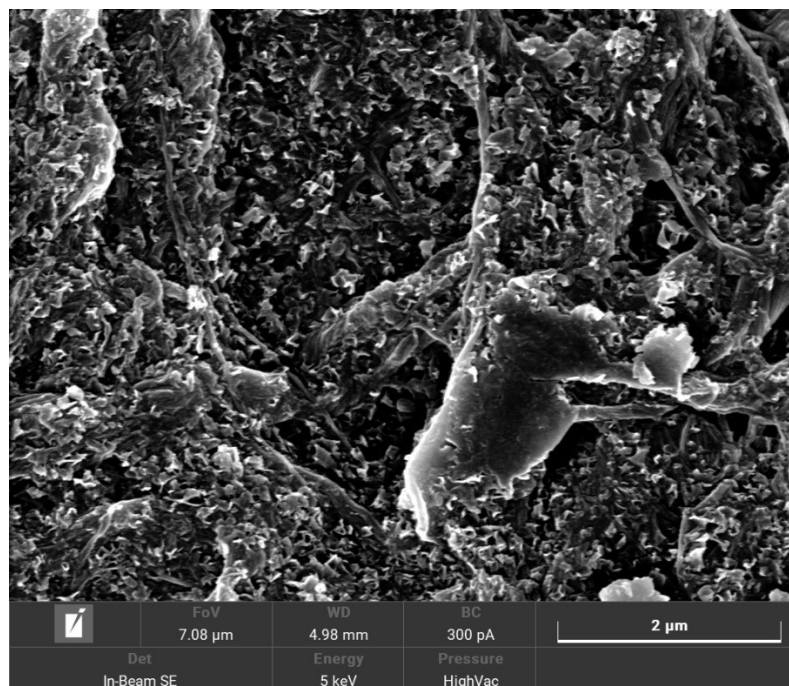


SEM image magnified 50k times

Appendix 13 SEM image of sample using SDBS as surfactant.

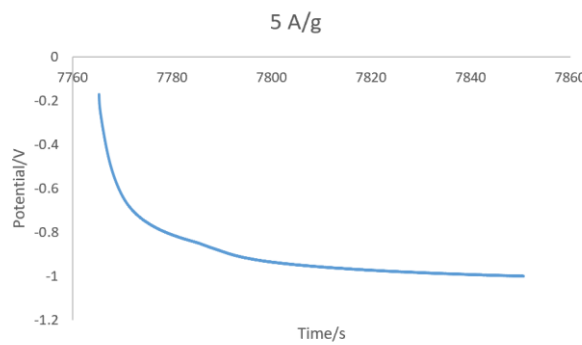
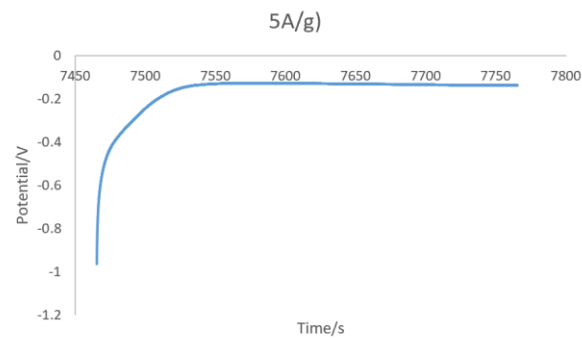
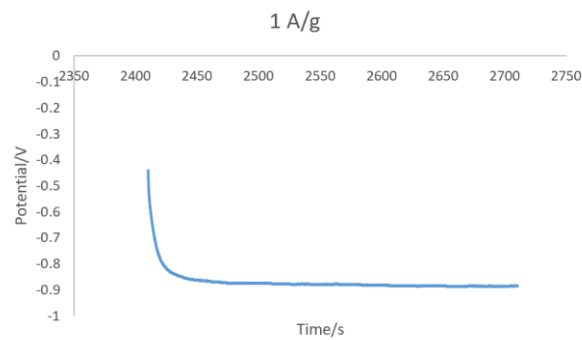
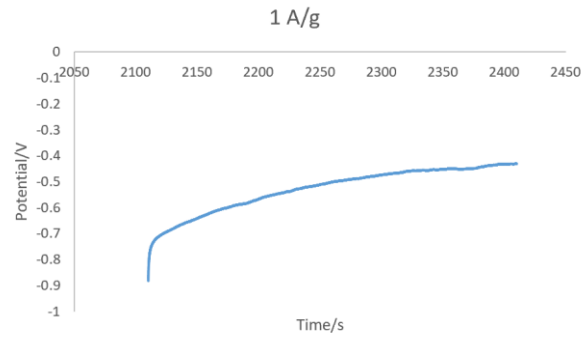


SEM image magnified 20k times

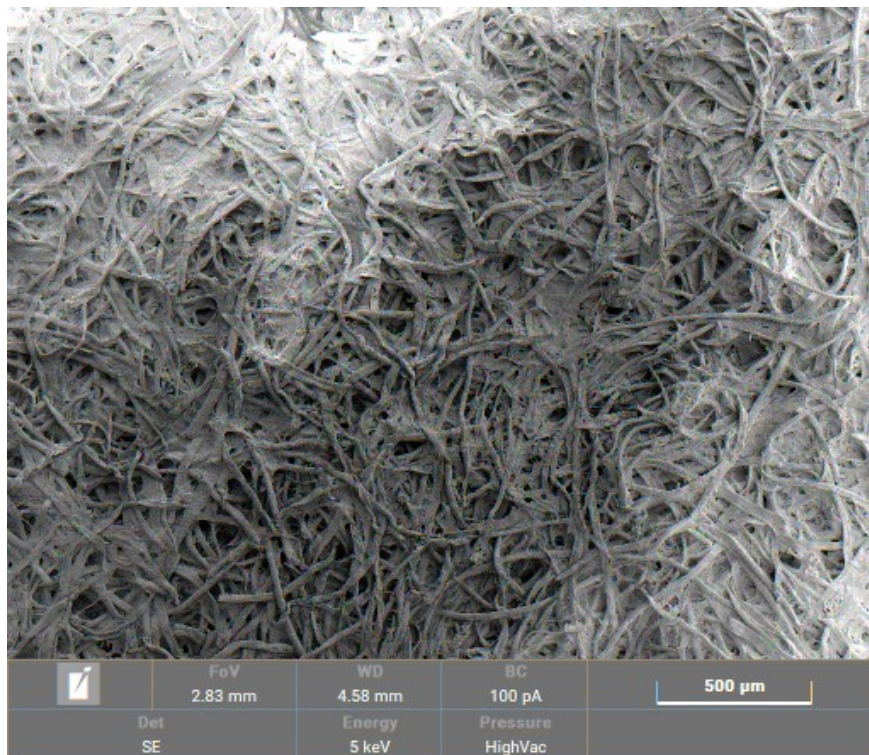
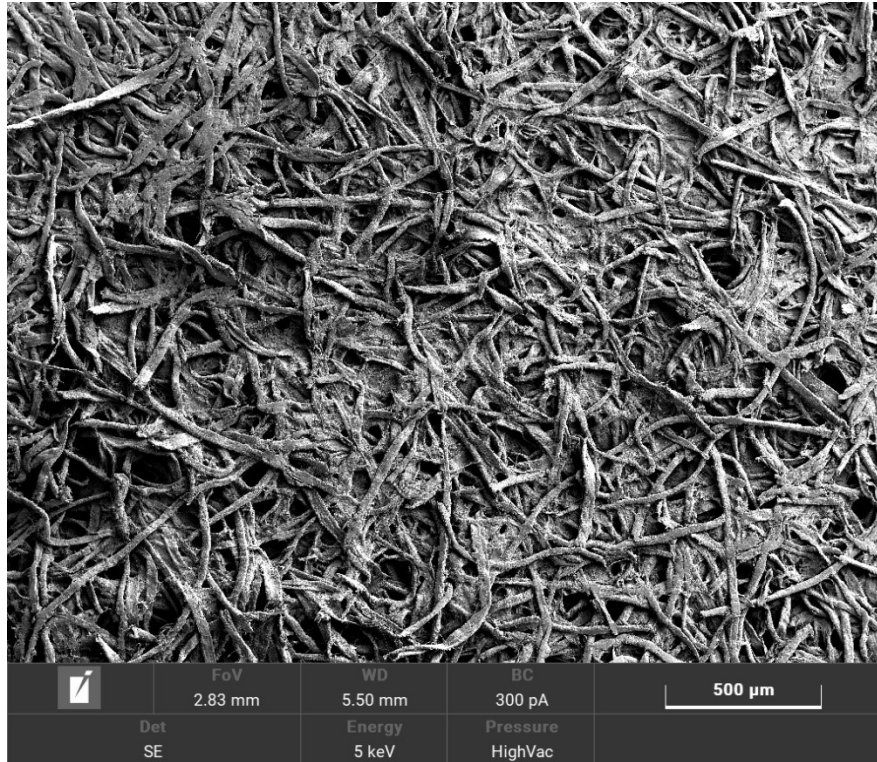


SEM image magnified 50k times

Appendix 14 Charge and discharge curves of PVDF/G (40:3) aerogels at different current densities



Appendix 15 Pure filter paper (above) and graphene-loaded filter paper (below)



Appendix 16 Charge and discharge curves of optimum carbon paper sample at different current densities

