

Chapter 2

Synthesis, Separation, Transfer, and Structural Characterization of Graphene-Based Woven Fabric

2.1 Introduction

As the most widely used strategy, large-area graphene films are easily obtained by chemical vapor deposition (CVD) method. In the CVD process, metals are used as substrates, such as copper, nickel, platinum, iridium, and polonium, on whose surface the reactions take place, for example, acieration and catalysis. Using metal foils as substrates, two-dimensional graphene films are synthesized by CVD. However, the application of graphene film in macroscopic area is hindered by poor quality and lack of geometric stability.

To further explore the practical application of graphene in macroscopic area, in this chapter we obtain graphene-based woven fabrics (GWF) using copper mesh and nickel mesh as templates by CVD. The method is simple, abandoning substrates of metal foils. The surface of GWF shows continuous graphene film, while the network pipeline structure has stable self-adjustment, making the strength of GWF and its composite material increase by a large margin.

Three-dimensional GWF was synthesized using woven copper mesh as template. 2D network structure and 3D network pipeline structure were obtained through solution etching directly and PDMS protecting etching. The 2D network structure products possess membrane morphology. The products display good dimensional stability, transparency, and conductivity. The 3D network structure product has hollow conductive pipes. Using woven nickel mesh as template, composite films of graphene-based woven fabric and porous carbon (GWF/PC) are synthesized. The composite films possess all-carbon structures, which integrate the dual advantages of graphene and PC, having not only excellent electrical properties and flexibility of graphene but also the porous characteristics of amorphous carbon.

2.2 Synthesis Method and Characterization of GWF

2.2.1 Preparation Method

The most widely used templates are copper and nickel in the preparation of graphene by CVD, since the price is low and the product is of high quality. The growth mechanism of graphene on copper and nickel is different. When growing on nickel substrate, carbon atoms and nickel atoms interdiffuse to form solid solution. Supersaturated carbon atoms precipitate from nickel template surface to form graphene when cooling quickly, as shown in Fig. 2.1a. At a certain temperature, the concentration of acieration and speed of cooling have great influence on the quality and layer of graphene for such metal. The layer of product is thinner with lower concentration of carbon atoms and quicker cooling speed. The quality and layers of the obtained material have uncertainty since the concentration and cooling speed are difficult to control. When using another typical metal of copper as substrate, the formation mechanism of graphene is the surface catalysis of copper since carbon atoms and copper atoms almost cannot dissolve into each other, as shown in Fig. 2.1b. When several layers of graphene form and cover the surface of copper substrate, the subsequent deposition and growth of carbon atoms are hindered. In this circumstance, a few-layer and even single-layer graphene is easy to be obtained by controlling parameters in the preparation process.

GWF was prepared by CVD method. The heating installation is tube-like electric resistance furnace of horizontal style, as shown in Fig. 2.2. The CVD reaction area was a quartz tube of length 1700 mm, external diameter 50 mm, and internal diameter 48 mm. The constant temperature area in the furnace was as long as 200 mm, and the reaction temperature was monitored by the temperature controller. In the reaction process, methane cracked thermally at high temperature, resulting in interreaction of carbon atoms and woven substrates. After deposition for a while (normally 15–30 min), the woven substrate was moved out of the reaction area quickly. Mesh substrate with the surface covered by graphene was obtained by quick cooling.

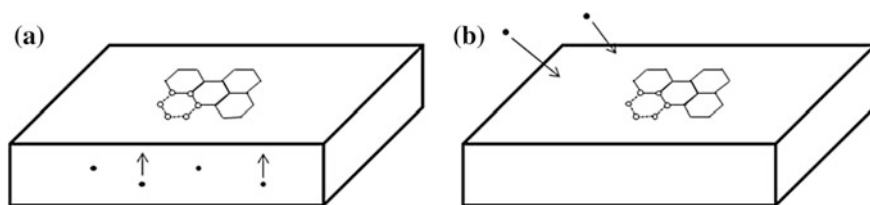


Fig. 2.1 Diagrams of the formation mechanism of graphene on different substrates. **a** Permeation and precipitation of carbon atoms on nickel substrate. **b** Surface catalysis mechanism on copper substrate

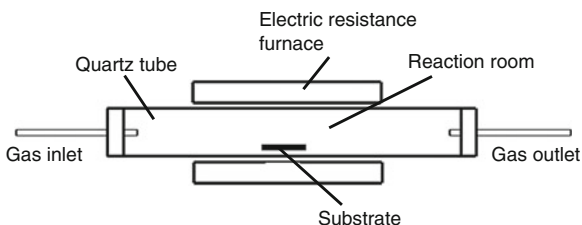


Fig. 2.2 Diagram sketch of the installation to prepare GWF by CVD method

2.2.2 Characterization of Graphene

Commonly used characterizations of graphene include optical microscopy, electron microscopy, Raman spectroscopy, and scanning scope.

Optical microscope (OM) is used to observe graphene on a silica substrate. Different color and contrast of graphene is observed due to interference and diffraction of light, to analyze information such as size, shape, and the layer number of graphene. Optical microscopy has become a commonly used method to test graphene layers [1, 2].

Scanning electron microscope (SEM) makes use of secondary electron imaging to observe the shape of an object. The ability to emit secondary electron of graphene is low, and the thickness as well as the up and down on the surface is at nanometer level, so it is difficult to observe SEM images of graphene. However, wrinkles of graphene form after sedimentation on substrates. The wrinkles can be clearly observed. Therefore, SEM is often used to characterize graphene films of large area [3].

Transmission electron microscopy (TEM) mainly observes focused and magnified images by making electron beam pass through thin film samples. Due to easy absorption and scattering by samples, the penetration of electron beam is low, so the samples must be thin slices. Graphene film itself is ultrathin, can be directly detected by TEM. High-resolution TEM can directly characterize graphene in atomic scale. The electron diffraction can characterize the crystal structure of graphene to judge the graphene layers [4] (Fig. 2.3).

Raman spectroscopy (Raman) is a nondestructive testing and characterization method using light scattering effect. The incident light and the sample interact with each other. The frequency of the scattering light changes with the rotation and vibration of the molecules, thus the molecular structure of the material can be analyzed. Under laser wavelength of 514 nm, graphene has two characteristic peaks, respectively, G peak at 1580 cm^{-1} and 2D peak at 2700 cm^{-1} . G peak is near the characteristic peak of carbon atoms of sp^2 structure, mainly reflecting the degree of crystallization and the symmetry of graphene, while 2D peak at 2700 cm^{-1} originates from inelastic scattering of a pair of two-phonons. The peak shape and

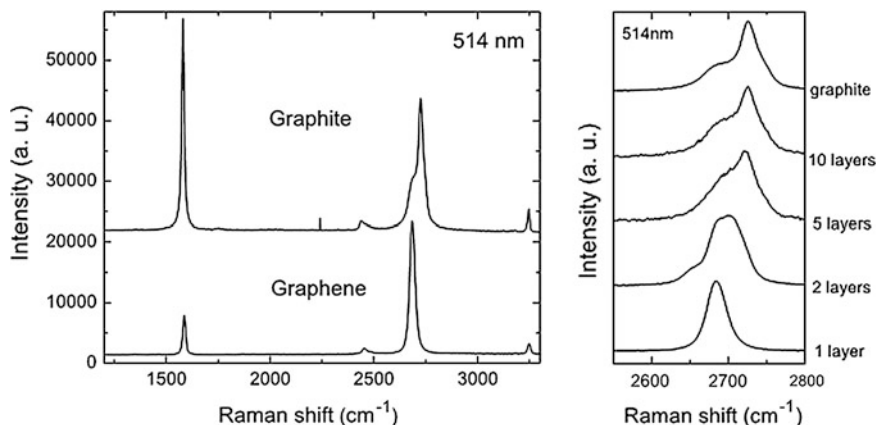


Fig. 2.3 Raman spectrum of graphene. Reprinted with permission from Ref. [5]. Copyright 2006 by, American Physical Society

strength are both different for G peak and 2D peak. D peak near 1350 cm^{-1} mainly reflects the disorders of graphene, due to defects, wrinkles, edge effect, etc. [5, 6].

Atomic force microscope (AFM) makes use of the atomic force between microcantilever and the sample, and can directly observe the three-dimensional atomic structure on the surface of the samples. The surface morphology of graphene could be observed and the thickness of graphene can be measured. The original samples are required to be clean and smooth to reduce unnecessary errors [7, 8].

2.2.3 Main Detection Instruments

(1) Optical microscope (OM)

It is used to observe the morphology of the samples. The instrument model is Axio scope A₁, with the largest magnification of 1000.

(2) Scanning electron microscope (SEM)

It is used to observe the microstructure of samples. The instrument model is Leo 1530, with secondary electron resolution of 1 nm.

(3) High resolution transmission electron microscope (HRTEM) and selected area diffraction

It is used to observe the microstructure of samples and analyze the sample lattice. The instrument model is JEOL—2011, with resolution at 0.18 nm.

(4) Raman spectroscopy (Raman)

It is used to test the structural characteristics of samples. The instrument model is Renishaw System 2000, with laser wavelength at 514 nm, minimum beam spot at $1\text{ }\mu\text{m}$ in diameter, and spectral resolution of 1 cm^{-1} .

(5) X-ray diffractometer (XRD)

It is used to detect the crystalline structure of the samples, with angle ranging from 5° to 140° , and the maximum output power as 3 kW.

(6) X-ray photoelectron spectroscopy (XPS)

It is used to test the composition and element valence of samples. The detected concentration limit is % at 0.1, with microanalysis at 10 μm , and depth resolution ranging from 1 to 3 nm.

(7) Thermogravimetric analyzer (TGA)

It is utilized to analysis the thermal performance of samples. The temperature ranges from room temperature to 1000 $^\circ\text{C}$, and the heating rate is 0.1–50 $^\circ\text{C}/\text{min}$.

(8) Specific surface area analyzer

It is utilized to test the specific surface area, porosity, pore size distribution, etc. The temperature ranges from room temperature to 450 $^\circ\text{C}$. The measurable specific surface area is up to 0.001 cm^2/g , with the holes volume below 0.0001 cm^3/g . The hole diameter is 3.5–2000 $\text{\AA}$ (N_2).

9) uv-vis—near infrared spectrophotometer

It is used to detect light reflection and absorption, etc. The instrument model is Lambda 950. The accuracy of near infrared measurement is ± 0.30 nm, while the accuracy of uv/visible light is ± 0.08 nm.

(10) Mechanical test system

It is used to test the mechanical properties. The instrument model is Instron 5843. The speed ranges from 0.05 to 1000 mm/min, and the collecting rate of synchronous data is 5000 Hz.

(11) Solar cell testing system

It is used to test I - V characteristic curve of solar cells. The simulator model is Newport 91195. The source meter model is Keithley 2601.

(12) Electrochemical workstation

It is used to test the electrochemical performance of samples. The instrument model is CHI 660D. Potential range is from -10 to 10 V, with current range at ± 250 mA.

2.3 Preparation of GWF Using Copper Meshes as Templates and the Influence Factors

2.3.1 Preparation Technology

Using copper mesh as template, the preparation and transfer of GWF include the selection of the substrate, CVD etching of the substrate, and transfer to the target substrate. The process is shown in Fig. 2.4.

Raw materials in the experiment include copper mesh substrate with high purity (content of copper > 99.99 wt%), brass mesh substrate (the content of copper is 64 wt%),

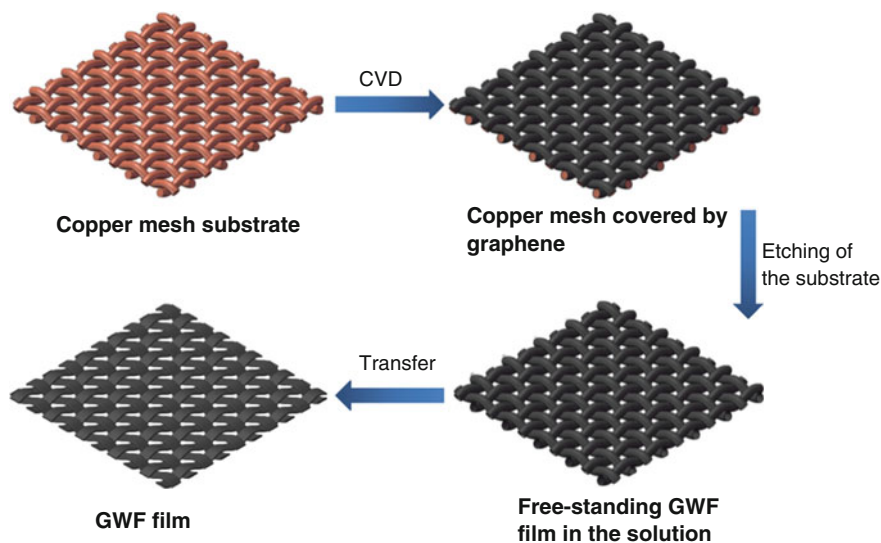


Fig. 2.4 Illustration of the preparation and transfer of GWF

argon with high purity (purity > 99.999 vol%), hydrogen (purity > 99.999 vol%), methane (purity > 99.99 vol%), ferric chloride (pure), hydrochloric acid (1 mol/L).

The specific process is as follows:

- (1) Clean the copper mesh in hydrochloric acid (1 mol/L) with ultrasonic.
- (2) Wash the copper mesh with deionized water with ultrasonic cleaning for 3 min. Repeat the steps 2–3 times, and then dry it with nitrogen.
- (3) Put the clean copper mesh into the reaction chamber, then seal the quartz tube.
- (4) The chamber is replenished with argon with the rate of flow as 1000 mL/min for 30 min to carry out exhaust processing.
- (5) Argon with the rate of flow as 600–1000 ml/min and hydrogen with the rate of flow as 50–200 ml/min are provided in the temperature rising process. The rising rate is 10 °C /min. The reaction temperature is 1000 °C, keeping 30–60 min.
- (6) Adjust the flow rate of argon to 100–200 ml/min. Close the hydrogen and then methane with flow rate of 15–30 ml/min is provided. The reaction time is 15–30 min.
- (7) After the reaction, remove the copper mesh from the chamber quickly. Then fill the chamber with argon with flow rate of 100 ml/min and close the methane. Stop heating. Close the argon and take out the product when the temperature cools to room temperature.

Figure 2.5 shows the optical image microscopes and SEM images of the copper mesh substrate before (a, b) and after reaction (c, d). After reaction, there is a thin layer of graphene on the substrate, making the sample slightly dark.

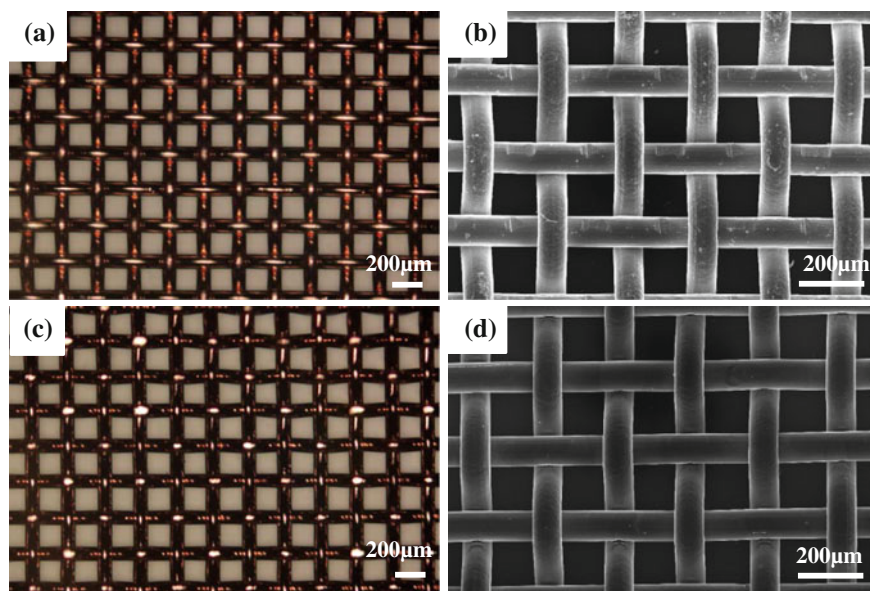


Fig. 2.5 Optical microscopies (OM) and SEM imaged of the samples before and after the reaction. **a** OM before the reaction; **b** SEM image before the reaction; **c** OM after the reaction; **d** SEM image after the reaction

2.3.2 Influencing Factors

2.3.2.1 The Selection of the Substrate

The selection of the substrate is the first step in the preparation of GWF. The copper mesh is made of copper wires of different diameters. The macro profile of GWF is directly determined by the substrate. According to the practical need, copper mesh substrates could be selected or prepared. The two most important parameters are the diameter of copper wires and the mesh grid (the number of sieve pores in a square mesh of width 25.4 mm).

Different GWFs were prepared using copper meshes with different parameters as substrates. The diameter of the copper wire is 100 μm , and the grid is 80, 100, 120, respectively. After etching the substrates, the optical microscopies and SEM images are shown in Fig. 2.6. The finally obtained GWF shows the same size as the copper mesh substrates, revealing good spatial uniformity and low defect features. Large-area GWFs could be prepared to meet the requirement by selecting large substrates and chambers.

The selected substrate could be copper mesh of high purity (copper content > 99.99 wt%), pure copper mesh (copper content > 99.3 wt%), or brass mesh (copper content as 60–70 wt%). In general, it is easier to prepare GWF with less

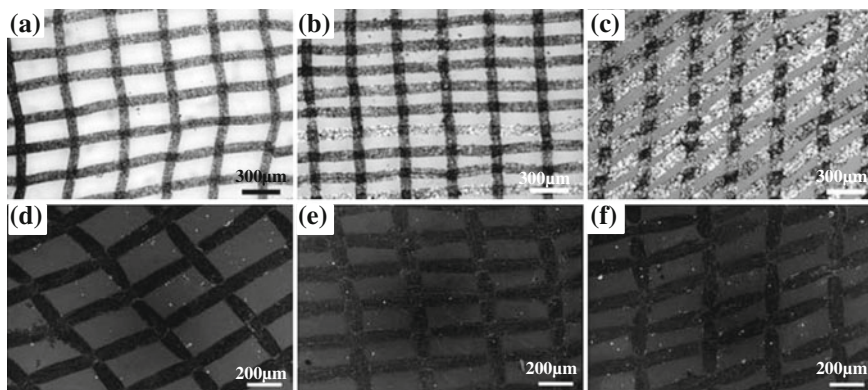


Fig. 2.6 Optical microscopies (OM) and SEM images of GWF with the grid of substrates as 80, 100, 120, respectively. **a–c** OM for 80, 100, 120, respectively. **d–f** SEM images for 80, 100, 120, respectively

layers of graphene and high purity of substrates. This dissertation mainly used pure copper meshes and brass meshes as substrates.

2.3.2.2 Influence of Temperature

As the most important step in the preparation process, CVD can determine the quality of the finally obtained product. The key parameters in the process are preheating and heating, reaction temperature, provision of argon and hydrogen, import of carbon source, and the cooling process.

There are some cracks and holes on the surface of copper wire during the rolling process, some of which are even in the size of several microns. Nucleation and growth of graphene films on the crude copper surface is difficult, since the thickness of single-layer graphene is only 0.34 nm. To obtain continuous graphene films, we performed exhaust process, heating, and preheating before reaction. Exhaust is to reduce the influence of residual oxygen on the surface of the copper mesh. In the heating process, the temperature reaches 1000 °C within 30–90 min. Preheating means to maintain the temperature for a period of time (about 30–60 min) till it reaches reaction temperature of 1000 °C. The crystals in the copper mesh substrates recrystallize and regenerate in the preheating process at 1000 °C, resulting in larger crystal grains and smoother surface. The long heat treatment makes the copper atoms rearrange to form lattices with consistent orientation. It also leads the atoms to be of higher energy condition and thus contribute to the deposition of carbon atoms and the formation of continuous graphene films.

The reaction temperature depends on the requirements of heat treatment and the choosing of carbon source. The copper base is easy to melt when the temperature is too high, while recrystallization and growth of copper is slow at low temperature.

The pyrolysis temperature is different for different carbon sources, and the reaction is difficult to react below pyrolysis temperature. For example, the pyrolysis of methane at atmospheric pressure is generally 800–900 °C. The carbon atoms tend to reunite as nanoparticles on the copper substrate at temperature below 900 °C, and they distribute more uniformly on the substrate with higher temperature to form continuous films with less impurities. 1000 °C is the proper reaction temperature for methane. When using ethylene as carbon source, the reaction temperature can decrease to realize low temperature preparation. In addition to alkane gas, other liquids like ethanol can also be used as carbon source, which needs an ethanol gasification unit in the preparation process. However, the O atom in ethanol has oxidation etching effect to the copper substrate, so using ethanol as carbon source is less appropriate than methane in CVD process.

2.3.2.3 Influence of Feeding of Gas

The feeding of hydrogen and argon in the process of reaction will impact the products. Hydrogen is a reducing gas, protecting the copper substrate from oxidation by providing a reducing environment for the reaction process. To a certain extent, hydrogen will inhibit the nucleation of carbon atoms, and thus limit the growth of graphene. The hydrogen can be always provided in the reaction process to prepare graphene with a few layers. Stopping providing hydrogen after pre-heat-treatment can obtain graphene with more layers. However, a great amount of hydrogen is bad for the growth of graphene films, since the hydrogen atoms react with copper atoms at high temperature, making the copper crystals change irregularly, leading to some defects in the substrate, such as out-of-flatness and holes. At the same time, amorphous carbon is easy to deposit on the substrate during pyrolysis of carbon source in the atmosphere of high hydrogen, inhibiting the growth of graphene.

Argon can control the airflow and carry carbon source. Carbon atoms can be carried out of the reaction chamber before depositing on the substrate at high rate of flow, benefiting the growth of graphene films with few layers. By contrast, graphene films with more layers are easy to obtain. Except the flow rate, the purity of hydrogen and argon also has influence on the products since oxygen atoms can destroy the environment for the deposition of carbon atoms on copper substrate. Using gas with high purity (purity ~99.99 vol%) can improve the quality of the products greatly than ordinary gas.

Another factor that affects the quality of products is the feeding of carbon source gas. The products are thick when the carbon source is provided with high flow rate for a long time. At high flow rate, carbon atoms tend to reunite to form big amorphous carbon particles on the copper substrate. By contrast, low flow rate and short providing time can make poor disposition of carbon atoms, making thin or even discontinuous products. Since the copper mesh has more defects than the copper foil, it needs higher flow rate and longer providing time of carbon source gas at the same condition to get continuous products.

2.3.2.4 Influence of Cooling Process

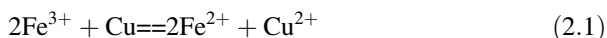
The control of cooling is important to the thickness and purity of the products. When cooling with the furnace at a slow rate, there are always some tiny amorphous carbon particles on the products. In addition, the film becomes thicker with the enrichment of carbon atoms. Continuous, even graphene films with few layers and less purity can be obtained through rapid cooling.

2.4 Separation and Transfer of GWF

The prepared GWF couples with the copper substrate tightly. It cannot be used directly except for separation and transfer from the substrate. In this dissertation, we adopt two strategies, i.e., solution etching directly and transfer with the protection of PDMS (poly(dimethyl siloxane)). In the former process, the three-dimensional graphene woven fabrics collapse into a flat structure, while keeping the 3D structure with the protection of PDMS using the latter method.

2.4.1 Solution Etching Directly

In the solution etching directly method, the chosen solution can react with the substrate material, but cannot react with graphene. We use the mixed solution of FeCl_3 (0.5 mol/L) and HCl (0.5 mol/L) to etch the substrate. The reaction principle is as follows:



Steps for separation and transfer:

- (1) Make the mixed solution of 0.5 mol/L FeCl_3 and 0.5 mol/L HCl , and put it into a petri dish;
- (2) Cut the prepared product into appropriate sizes and put it on the surface of etching solution. The product can float on the surface due to surface tension;
- (3) The copper substrate can be etched in 2 h and the three-dimensional graphene mesh collapse into flat structure slowly in the etching process. Finally, the obtained GWF floats on the surface of the etching solution;
- (4) Transfer the GWF on the surface of DI water using a yarn mesh to clean the attached ions, such as Fe^{3+} , Fe^{2+} , Cu^{2+} , and Cl^- . Repeat this step 2–3 times and move the membrane on the surface of DI water for subsequent transfer and application.

The process of direct solution etching is shown in Fig. 2.7a. The dissolution of copper mesh substrate comes from the part immersed into the solution. When the

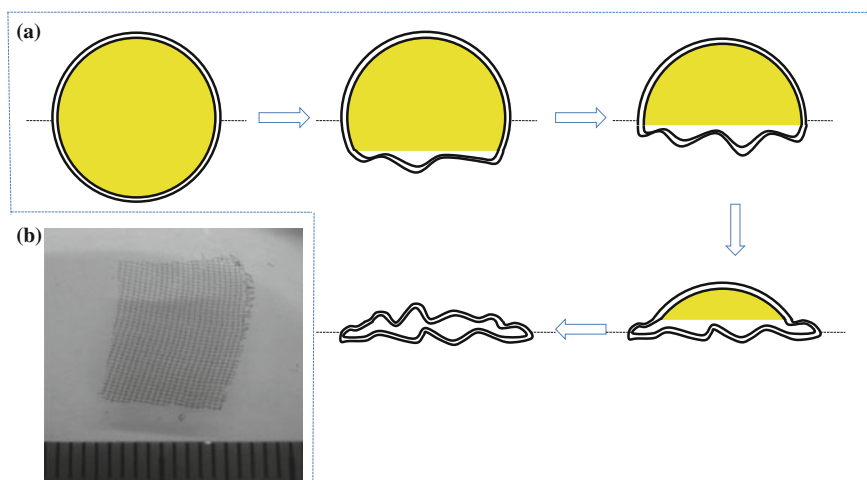


Fig. 2.7 Schematic diagram and photograph of GWF in the process of solution directly etching. **a** Schematic diagram; **b** GWF floating on the surface of the solution

skeleton of copper mesh is etched, graphene covering the surface floats on the surface of the solution, with some wrinkles on it. The copper mesh substrate keeps sinking under gravity until it is completely etched by the etching solution. Due to the dragging force of graphene, the width of graphene stripes after etching is appropriate for the diameter of copper wires of the copper mesh substrate. After transfer and cleaning, GWF floats on the surface of DI water, as shown in Fig. 2.7b. It is clear that the structure of woven fabric is preserved, as knitted by transverse and vertical graphene strips. Graphene strips come from the collapse of graphene tubes on the surface of copper wires in the process of etching, with their size determined by the copper mesh substrate. The selection of copper mesh substrate can control the specification and dimension of GWF exactly.

GWF after cleaned by DI water can be transferred on other substrates for subsequent tests and applications. It is easy to transfer on substrates with hydrophilic surface. While for those with hydrophobic surface, hydrophilic treatment is needed to make the transfer process easier. GWF combines with the substrate well after the transfer process. After it is totally dried, it is hard to fall off when immersed in DI water.

Subsequent substrate in the transfer process can be either flexible or rigid. Due to the flexibility of graphene, when it is transferred on flexible substrate, it can keep the woven structure during flexible deformation. In Fig. 2.8, GWFs were transferred on different flexible substrates (slides, silica gel, plastic polyethylene terephthalate (PET)), changing according to the flexible deformation of the flexible substrates.

Compared with ordinary graphene films, due to the geometric quadrilateral instability of GWF, there can be shear and wavy deformation (Fig. 2.9), having effects on morphology and properties of graphene to a certain extent. These

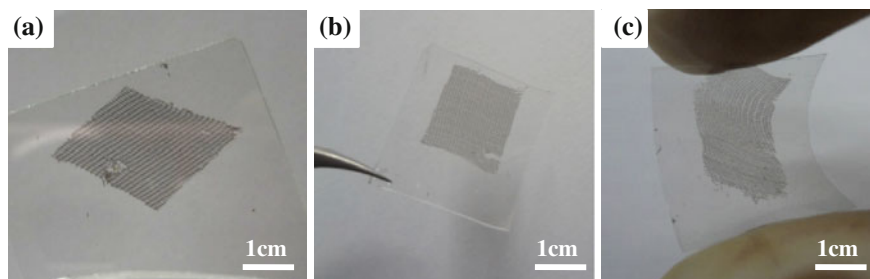


Fig. 2.8 GWF transferred on different subsequent substrates. **a** Glass slide; **b** silica gel; **c** PET

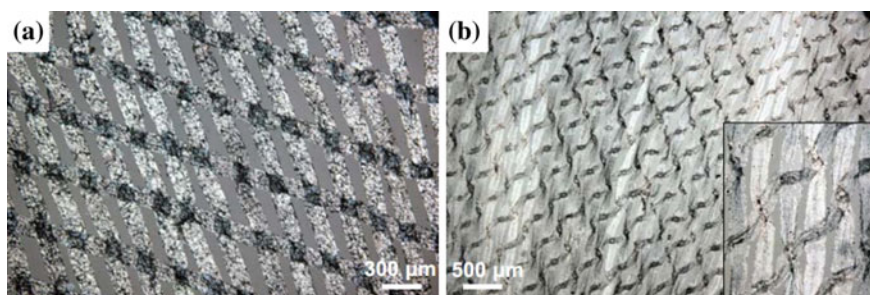


Fig. 2.9 Optical images of the shear and wavy deformation of GWF in the process of etching and transfer. **a** Shear deformation, **b** wave deformation. The *inset* shows wave deformation at high magnification

deformations can absorb and offset some effect of external force in the process of transfer, avoiding the cracks formed on the entire film and guaranteeing the continuity of the thin film in the etching and transfer process.

2.4.2 Transfer with the Protection of PDMS

PDMS (poly(dimethyl siloxane), also called organic silicon) is a kind of macromolecule organic silicon compound. Liquid PDMS is viscous, colorless, tasteless, nontoxic, and nonvolatile. Solid PDMS is a kind of silica gel. It is nontoxic, hydrophobic, inert, nonflammable, and transparent. The preparation and curing process of PDMS is simple, being used in areas like packaging, microelectromechanical, etc.

Using copper mesh substrate to prepare GWF, directly etching process in the solution of FeCl_3 causes the collapse of original structure, and it is easy to break in

the process of transfer. To a certain extent, the protection of PDMS to transfer can solve the above problems. The method can be divided into PDMS surface protection and PDMS block protection based on the way and dosage of PDMS.

2.4.2.1 PDMS Surface Protection

- (1) Mix PDMS prepolymer and the cross-linking agents (vulcanizing agent) in the proportion of 10:1 evenly and let it stand for 1 h;
- (2) Drop liquid PDMS on the surface of graphene with copper mesh as substrate. Repeat the process in both the positive and negative surfaces of the samples, making PDMS coating everywhere;
- (3) Impend the sample to stand for 24 h. After curing, the structure of vertical and horizontal weaving of the original copper mesh substrates remains. The curing time could be reduced at appropriate temperature;
- (4) Put the prepared samples with PDMS coating into the mixed etching solution of 0.5 mol/L FeCl_3 and 0.5 mol/L HCl . After about 4 h, the substrate is etched completely, leaving GWF with PDMS coating on the surface.

The finally obtained products can be divided into PDMS filled style and PDMS coated style based on the dosage of PDMS. Due to the flowing property of liquid PDMS, that existing in the space of copper mesh substrate can flow away when the dosage is small, forming samples with PDMS coated style. While if the dosage is big, it can remain in the space, forming PDMS filled samples.

The composite material of GWF and PDMS obtained after etching can protect the structure of GWF well, with good flexibility as PDMS substrate and excellent optical and electrical properties. Figure 2.10 shows the samples after transfer with the protection of PDMS, with PDMS filled in (a) and coated in (b). The layer of PDMS in the filled style is thick, with PDMS filling in the space of copper mesh substrate. The flexibility of the samples is good, while for the PDMS coated samples, the layer is thin, with poor flexibility. Figure 2.10c shows the SEM image of the cross section of samples with the protection of PDMS. Due to the support of PDMS as the skeleton, GWF remained the original three-dimensional woven structure after etching the substrate, showing hollow tubes. In Fig. 2.10d, the inner wall of the tubes is coated with graphene films evenly, with the original wrinkles formed in the preparation process, providing the electrical property of composite material. Figure 2.10e shows good strength and flexibility of GWF/PDMS composite. GWF cannot be freely operated without the protection of PDMS. Proper stretching and turn of the composite cannot cause irreversible changes, making it a new and promising composite material with good electrical property and photopermeability.

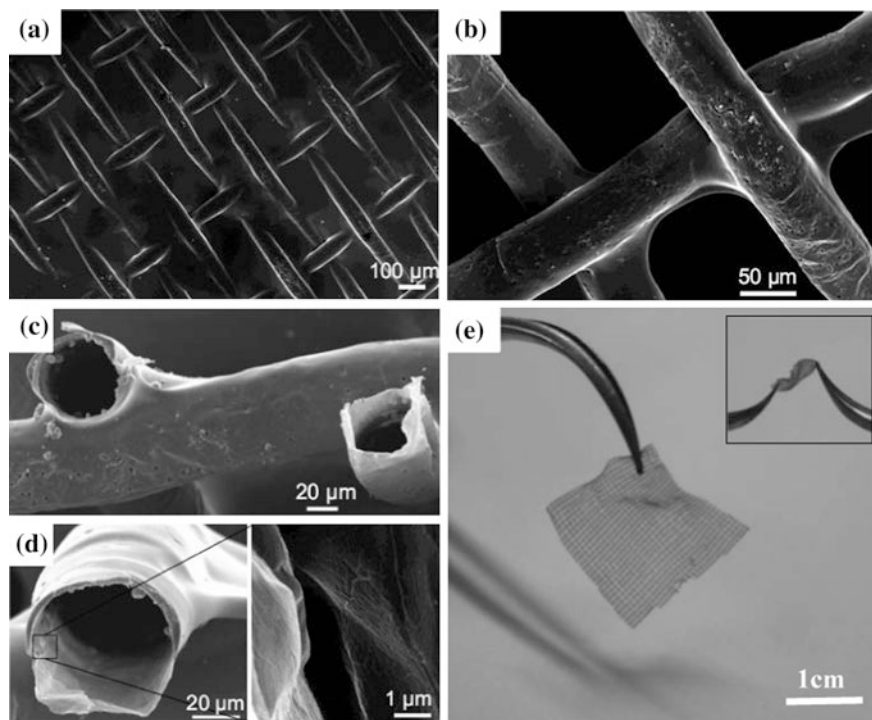
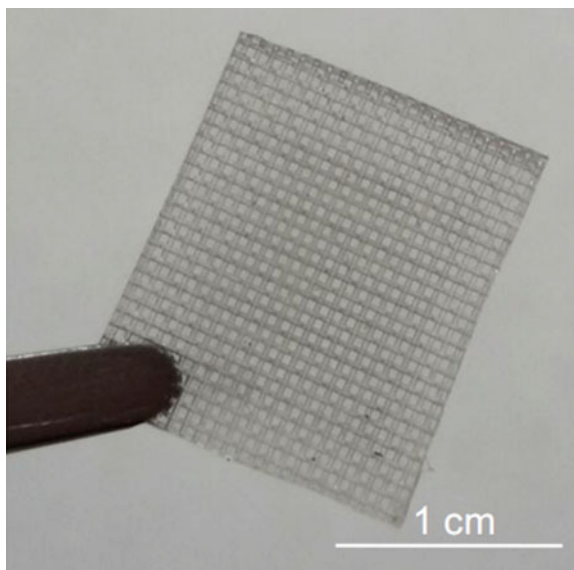


Fig. 2.10 Products transferred with the protection of PDMS on the surface. **a** SEM image of a sample with PDMS filled style; **b** SEM image of a sample with PDMS coated style; **c** SEM image of a typical hollow tube structure; **d** SEM image of graphene film on the inner wall; **e** The GWF/PDMS composite materials can be directly moved and turned

2.4.2.2 PDMS Block Protection

- (1) Mix PDMS prepolymer and the cross-linking agents (vulcanizing agent) in the proportion of 10:1 evenly and let it stand for 1 h;
- (2) Put the CVD-prepared samples into PDMS a height of 2 cm. The samples are totally immersed into PDMS;
- (3) Impend the samples to stand for 24 h. After curing, they are coated with PDMS. The curing time could be reduced at appropriate temperature;
- (4) Cut the samples along the edges of the copper mesh until the copper wire is exposed. Put the samples into the mixed etching solution of 0.5 mol/L FeCl_3 and 0.5 mol/L HCl . The etching direction is along the axial direction of the copper wire. The etching time is determined by the size of the samples and the diameter of the copper wires. Appropriate mixing can reduce the etching time.
- (5) Use DI water to clean the pre-etched samples several times, and PDMS filled GWFs are obtained.

Fig. 2.11 Three-dimensional graphene structure with hollow electrical tubes etched with the protection of PDMS



Compared with transfer to PDMS surface protection, samples prepared with PDMS block protection can preserve the 3D woven structure of copper mesh. After the etching of copper mesh substrate, GWF (graphene woven fabric) composed of electrical graphene microtubes can be obtained with the support of PDMS, as shown in Fig. 2.11.

Compare direct solution etching with PDMS protected transfer. The former is the etching-based method, with the obtained GWF floating on the surface of the etching solution. GWFs can be transferred on other substrates for subsequent tests and application. Since there is no skeleton to support in the etching process, the 3D woven fabrics can collapse to flat structure. While in the transfer with PDMS protection, the 3D characteristics of copper mesh substrate can be preserved. The obtained GWF/PDMS composites have excellent strength, and can be moved, stretched, and reversed freely. However, the operation is relatively complex, and the etching time is longer. In addition, the testing and related application are more complex due to graphene on the surface of the copper mesh covered by PDMS.

2.5 Structural Characterizations of GWF

2.5.1 Morphology Characterization

GWF is woven by graphene microtubes in vertical and horizontal directions, preserving the woven structure of copper mesh substrate. GWF obtained from direct solution etching is flat structure due to the collapse of graphene tubes during the

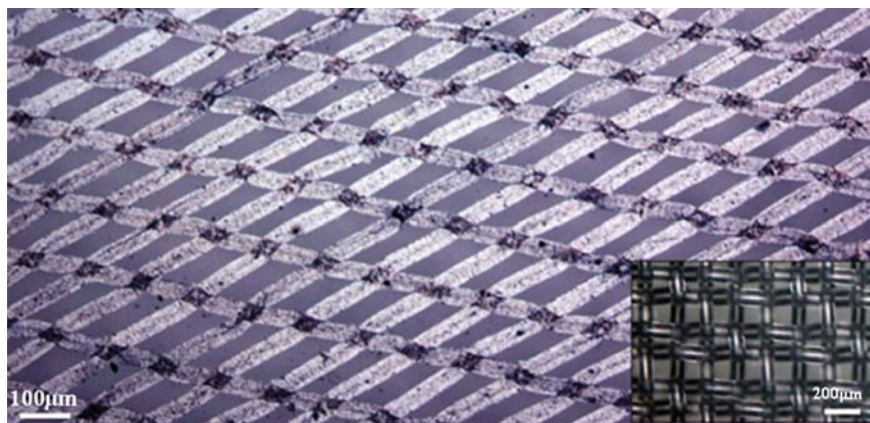


Fig. 2.12 The OM photo of GWF. The *inset* shows the OM photo of nylon woven structure

etching process. The flat graphene strips overlap to form a self-locking plane fiber system, as shown in Fig. 2.12. There are light color parts and dark color parts of GWF. The former is collapsed graphene strips, and the latter are two overlapping graphene strips. A typical GWF is shown in Fig. 2.12.

In the transfer process, GWF obtained by direct etching method has many irregular ravines and grains due to the unfolded walls, attributed to the pulling of its own weight and the influence of the target substrate. Figure 2.13 shows the testing result of white light interference of the reticular graphene surface. Figure 2.13a reveals the white light interference of the surface morphology of GWF. The thickness of the graphene film is not big, with the thickness of few-layer graphene generally not more than 10 nm. However, after etching and transfer, the thickness of GWF is bigger than that of the ordinary graphene thin film prepared under the same conditions. Figure 2.13b shows the net thickness of GWF. A separate graphene strip with a lot of ups and downs is shown as line B, with thickness of 50–100 nm. A line represents the thickness of the overlapping strips at the intersection point, commonly in the size range of 200–300 nm.

2.5.2 Microstructure

As shown in Fig. 2.14a, the copper mesh used in the experiment is in woven plain manner. Warp wires are woven on and down weft wires at an angle of 90° mechanically. After the preparation process by CVD method, SEM images of the intersection point are shown in Fig. 2.14b, c. Figure 2.14d reveals the structure diagram. We can see that there is not only mechanical contact between the warp graphene channels and the weft ones, but also connection of materials. The newly added parts are composed of single-layer and multilayer graphene, as well as

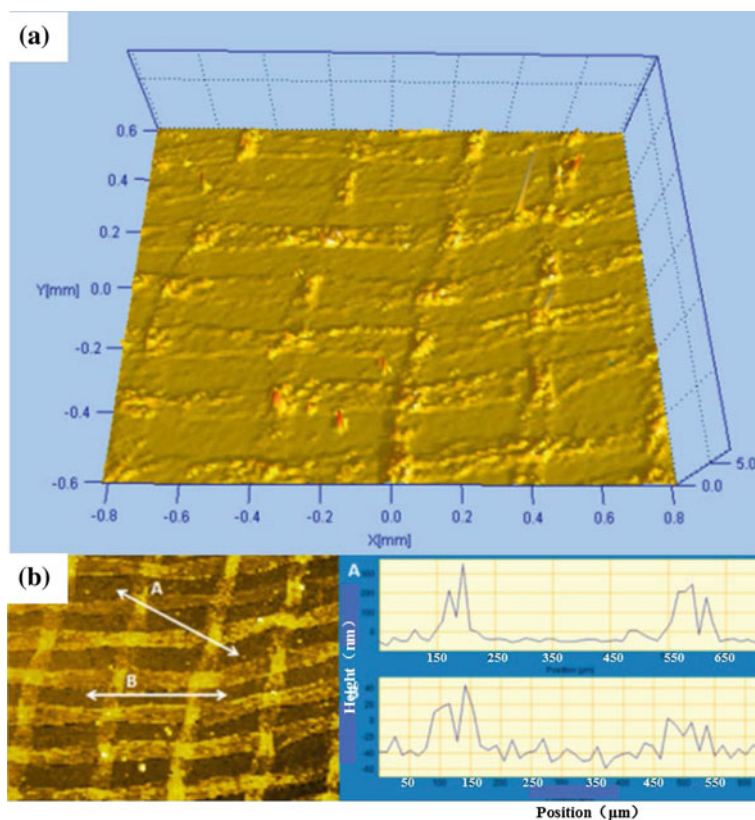


Fig. 2.13 The white light interference of GWF. **a** 3D morphology, **b** the test of the thickness

amorphous carbon films. These films grow from the walls of original graphene channels and connect graphene channels in two directions by way of folding and overlapping. Due to the connection, the prepared GWF can preserve the woven morphology of the original copper mesh substrate, making current conduct in the vertical and horizontal directions freely.

The external morphology of the connection can be observed by SEM, while the internal morphology needs to be observed with the protection of PDMS in the etching process of copper mesh substrate. The internal structure and its schematic diagram are shown in Fig. 2.15.

Figure 2.15a shows the internal surface of GWF, with the diagram of the structure in Fig. 2.15b of two vertical and horizontal weaving copper wires melting and recrystallizing at the high temperature of 1000 °C, making the original mechanical connected parts integrate to form new connection characteristics. Carbon atoms can crystallize and grow on the surface of copper, but cannot get into the new connected parts, forming two weaving graphene hollow pipes with connected internal space. Due to the irregular shape of the copper substrate in the

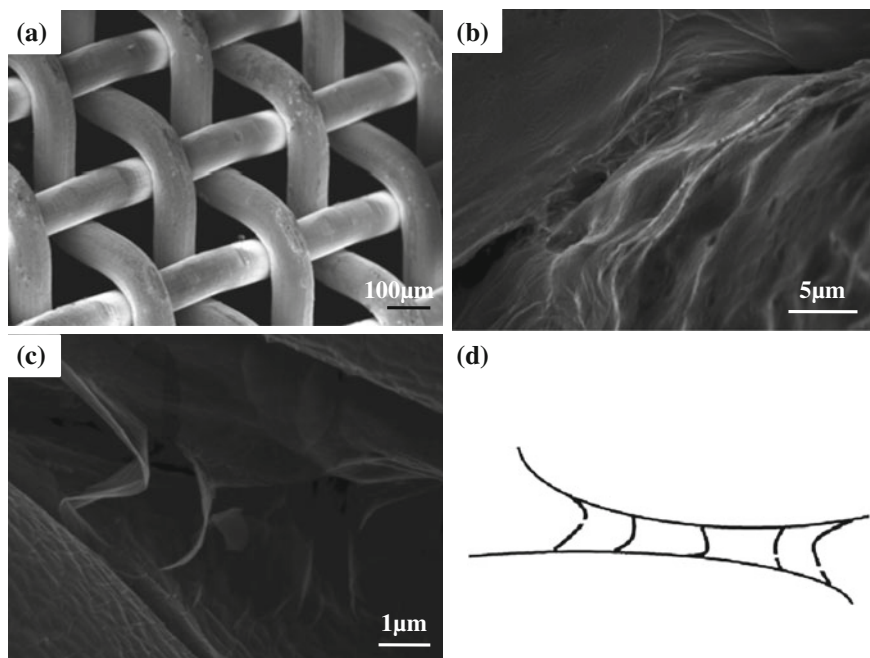


Fig. 2.14 The external morphology and its schematic diagram. **a** SEM image of copper mesh woven in plain manner; **b** SEM image of the connection at low magnification; **c** SEM image of the connection at high magnification; **d** schematic diagram of the external connection interface

molten part and its unstable structure, graphene film formed in this state is disordered. While in other parts, the film is of high quality, continuous, and uniform. The internal structural details like wrinkles can be observed by SEM.

Graphene channels would collapse when using the direct solution etching method. Due to the connection of graphene films at the intersection points, GWFs can preserve the mesh characteristics to a great extent. After the collapse, except the connection at the intersection points, there is also increased surface mechanical contact on the external surface of the two overlapping pipes and the internal surface of the hollow pipes, improving the electrical conductivity of GWFs. Due to the relatively complex structure of the junction, which contains two graphene hollow pipes, the thickness of the intersection is thicker than ordinary pipe after the collapse. The results accord with the testing result of the white light interference of thickness. The schematic diagram of the collapse process and the OM image of intersection after collapse can be seen in Fig. 2.15c, d.

TEM and Raman spectrum analysis (Raman) are the two most commonly used methods in the detection of graphene microstructure. Figure 2.16a, b reveals the TEM and electron diffraction result of GWFs. Graphene pipes collapse into graphene strips with two layers after the etching process. The information about the layers can be observed in the figures. The film is uniform and continuous, with few

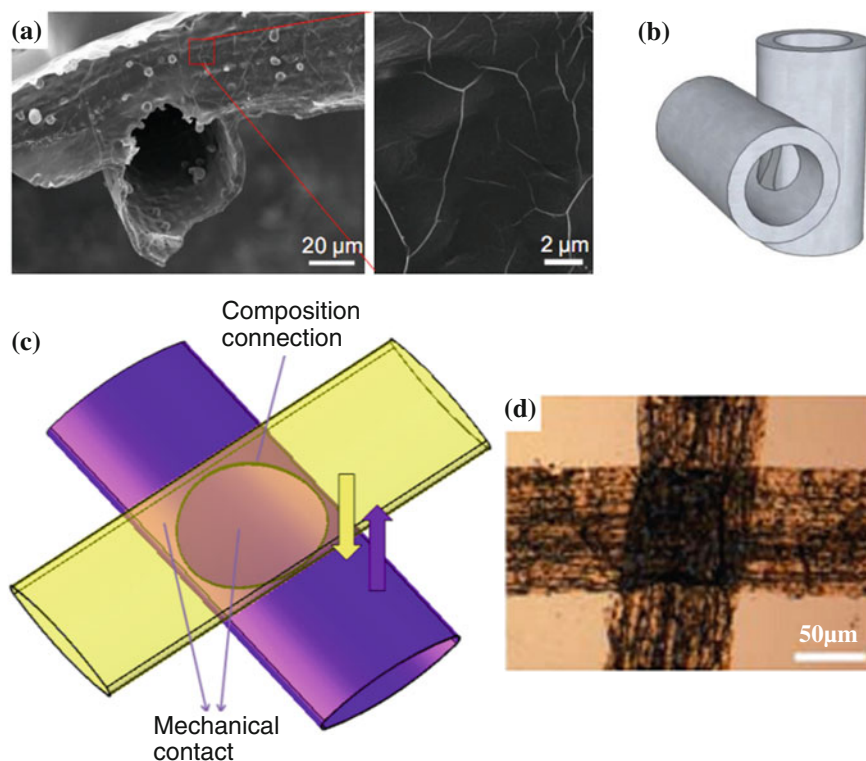


Fig. 2.15 The internal structure morphology and its diagram of GWF. **a** SEM image of the internal morphology; **b** Schematic diagram of the connection; **c** diagram of the collapse process of the connection; **d** optical microscope image of the connection

defects. The high resolution image shows that the edge is of four layers. Selected area electron diffraction test also shows the expected hexagon diffraction pattern of graphene. The diffraction diagram contains two sets of diffraction patterns, with the angle between the two groups at 26° , due to the electron beam going through the two up and down walls at the same time after the collapse of graphene pipes, obtaining two sets of regular diffraction. Considering light intensity, $I_{\{1-210\}}/I_{\{0-110\}}$ is appropriate 0.5–0.7, suggesting that each wall is made of few-layer graphene.

Figure 2.1c shows the Raman spectrum of the intersection of GWF (A area), the edge of the graphene strip (B area), and the middle of the graphene strip (C area). The right figure is based on OM image. The half-width of 2D peak at 2700 cm^{-1} is about $40\text{--}60\text{ cm}^{-1}$. The 2D peak to G peak ratio is 0.6–1.6, showing that GWFs are made of single-layer graphene. The existence of D peak reveals that there are some defects in GWFs. 2D peak becomes wider at the middle of the strips (area C), edge of the strips (area B), and the intersection joint (area A) in sequence. At the same time, the intensity of D peak is higher, showing that the middle part of the graphene

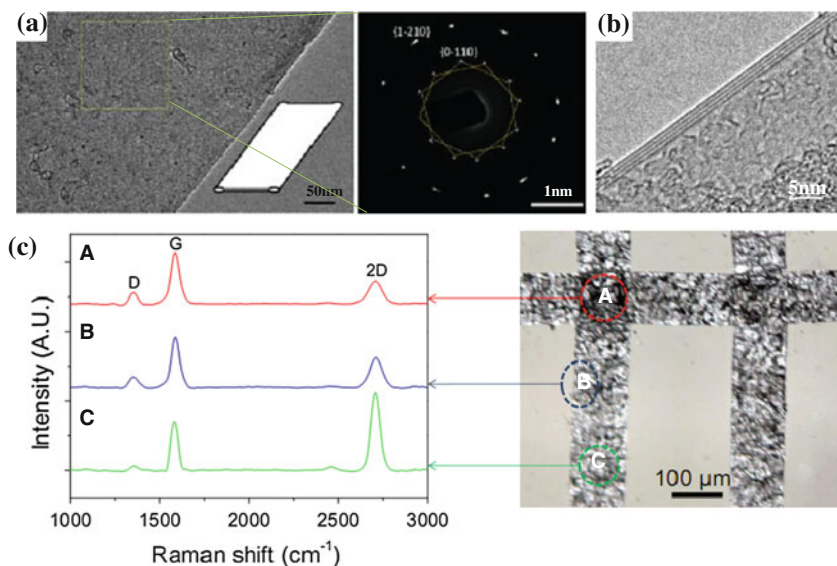


Fig. 2.16 TEM, Raman characterization of GWFs. **a** TEM image at low magnification and selected area electron diffraction; **b** TEM image at high magnification; **c** Raman spectrum of the feature district

strips is uniform, with few defects. There are more defects at the edge of the strips due to wrinkles. In addition, there are the most defects at the joint with the most layers.

2.6 Preparation and Structural Characterization of GWF/Amorphous Composite Using Nickel Mesh as Substrate

2.6.1 Preparation, Separation, and Transfer Process

The preparation process on nickel mesh substrate is the same as that on copper mesh substrate, including the selection of substrate, preparation by CVD method, the etching of substrate, and transfer, as shown in Fig. 2.17. Due to the different forming mechanisms, GWF/amorphous composite can be obtained by controlling the related parameters, different from the product by using the copper mesh as substrate.

The equipment is the same as that in the experiments using copper mesh substrates. Raw materials are as follows: high purity nickel mesh substrate (nickel content > 99.99 wt%), high purity argon (purity > 99.999 vol%), hydrogen (purity > 99.999 vol%), methane (purity > 99.99 vol%), ferric chloride (pure), hydrochloric acid (1 mol/L).

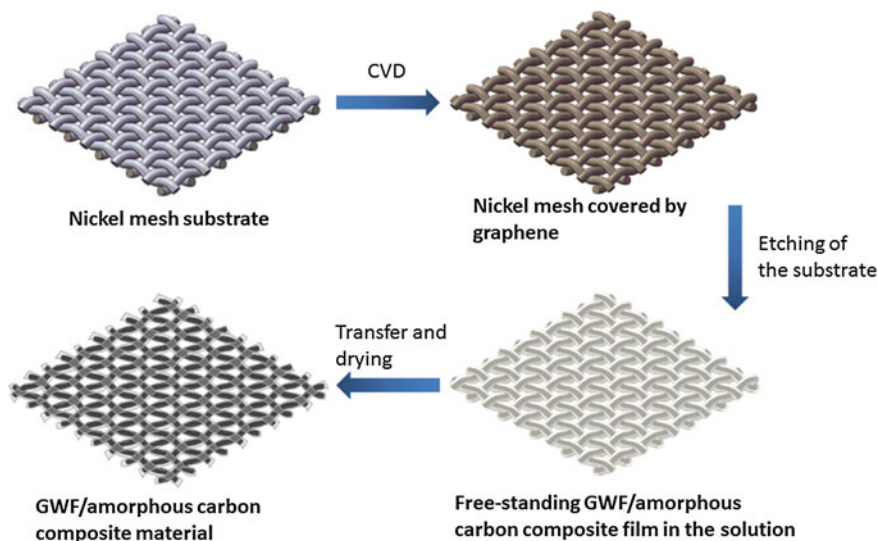


Fig. 2.17 Flowchart of the preparation and transfer of GWF with nickel mesh as substrate

The specific process is as follows:

- (1) Wash the nickel mesh with deionized water with ultrasonic cleaning for 5 min, and then dry it with nitrogen.
- (2) Put the clean nickel mesh into the reaction chamber, then seal the quartz tube.
- (3) The chamber is replenished with argon with the rate of flow as 1000 mL/min for 30 min to carry out exhaust processing.
- (4) Argon at flow rate 600–1000 ml/min and hydrogen at flow rate of 50–200 ml/min are provided. The temperature rising rate is 10 °C/min. The reaction temperature is 1000 °C.
- (5) Adjust the flow rate of argon to 100–200 ml/min. Close the hydrogen and then methane at flow rate of 20–50 ml/min is provided. The reaction time is 20–30 min.
- (6) After the reaction, remove the nickel mesh from the chamber quickly. Then fill the chamber with argon at flow rate of 100 ml/min and close the methane. Stop heating. Close the argon and take out the product when the temperature cools to room temperature.

The OM images of the nickel mesh substrate before and after the reaction are shown in Fig. 2.18a, b. After the reaction, the nickel mesh substrate is covered uniformly with a layer of graphene film, making the surface dim.

Figure 2.18c, d shows the SEM images of the surface of the nickel mesh after the reaction, from which the wrinkles of the graphene film can be obviously seen. There are some white particles on the surface of the film, which are amorphous carbon

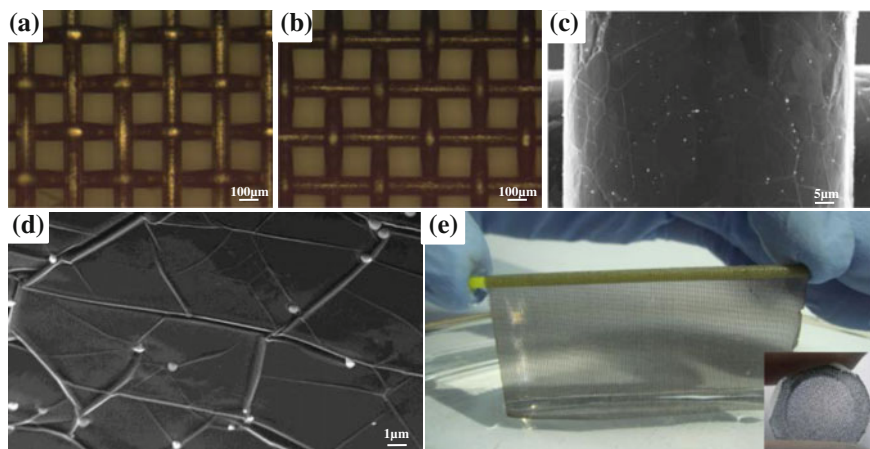
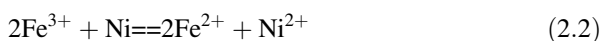


Fig. 2.18 Optical microscope (OM) images and SEM images. OM images of the nickel mesh substrate before (a) and after (b) the reaction; SEM images of the surface of the nickel mesh after the reaction with low magnification (c) and high magnification (d); e photograph of GWF after the etching process

particles due to the deposition of a large amount of carbon atoms in the pyrolysis process of carbon source.

We use the mixed solution of FeCl_3 (0.5 mol/L) and HCl (0.5 mol/L) to etch the substrate directly. The reaction principle is as follows:



Steps for separation and transfer:

- (1) Make the mixed solution of 0.5 mol/L FeCl_3 and 0.5 mol/L HCl , and put it into a petri dish;
- (2) Cut the prepared product into appropriate size (generally 1–10 cm^2), and put it in the etching solution;
- (3) The nickel mesh substrate can be etched in 5 h slowly to obtain GWF;
- (4) Transfer the GWF on the surface of DI water using a yarn mesh to clean the attached ions, such as Fe^{3+} , Fe^{2+} , Cu^{2+} , and Cl^- . Repeat this step for 2–3 times;
- (5) Move the membrane in DI water to another vessel for subsequent transfer and application.

The sample after etching is shown in Fig. 2.18e. Compared with that obtained using copper mesh as the substrate, this sample is darker and thicker, with higher strength. It can be operated by tweezers and other tools in the solution, and be drawn out of the solution directly. Using the annular tool as shown in the inset of Fig. 2.18e, we can collect the sample directly. GWFs can support itself on this

collection tool, while with the volatilizing of the moisture, the film has contraction deformation, not as smooth as just leaving the liquid.

2.6.2 Structural Characteristics

The principle of using nickel meshes as substrates in the preparation of GWFs is solid solution and precipitation of carbon atoms in nickel. At a certain temperature, the more the carbon source provided in a short time, the more the carbon atoms solubilize in the nickel. In the subsequent cooling process, carbon atoms do not precipitate on the surface of the nickel will remain in the nickel substrate, forming as amorphous carbon after the etching of nickel. The schematic diagram of the intermediate in the etching process is shown in Fig. 2.19a. The exposed carbon material cannot diffuse in the solution due to the coating and bounding of graphene film on its surface, as well as the drawing of itself, forming GWF/amorphous carbon composite finally. Its SEM image is shown in Fig. 2.19b. GWF/amorphous carbon composite materials are divided into GWF shell and kernel of amorphous carbon. The GWF shell is determined by the nickel mesh substrate, serving as the main skeleton to support the structure, and excellent conductive pathways; while for

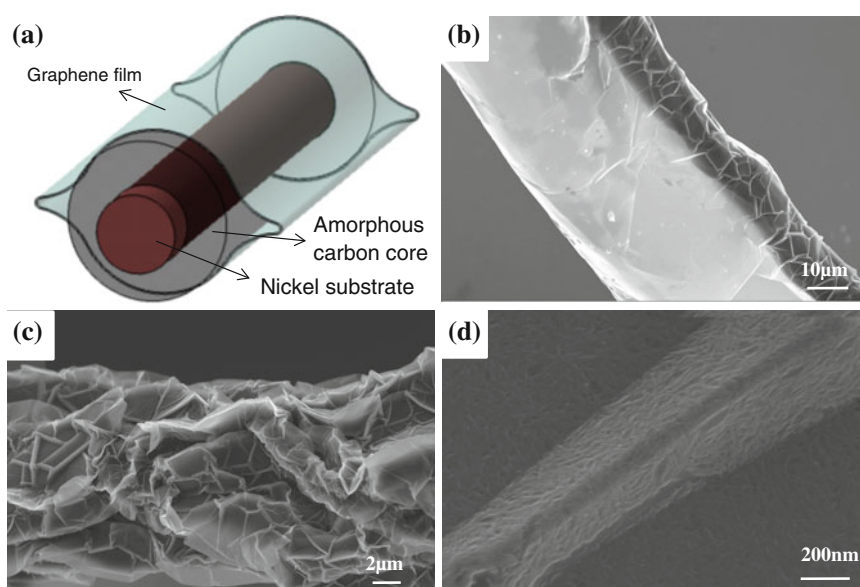


Fig. 2.19 Schematic diagram of the etching process of GWF/amorphous carbon composite material and typical SEM images. **a** Diagram of the etching process; **b** SEM image of GWF/amorphous carbon composite; SEM image of the amorphous carbon core at low magnification (**c**) and high magnification (**d**)

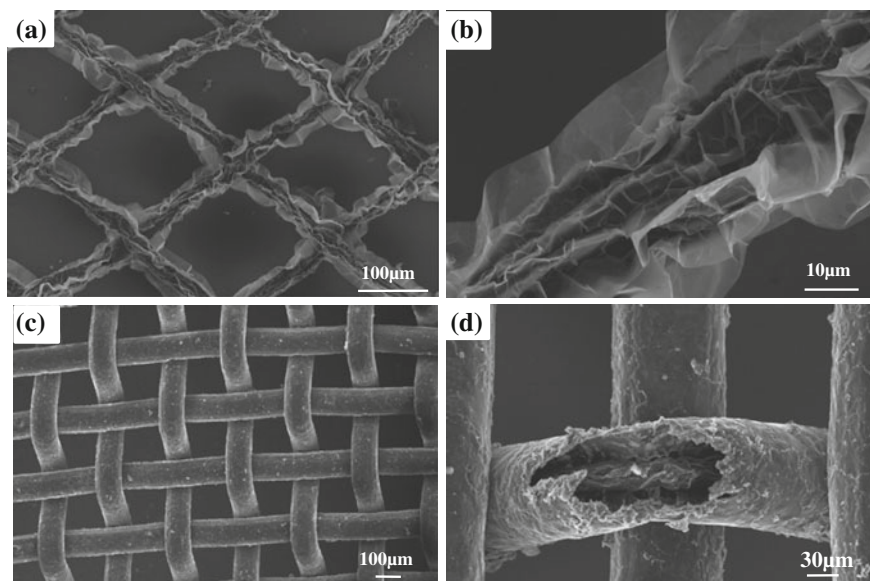


Fig. 2.20 SEM images of GWF/amorphous carbon composite material with soft type and hard type. SEM images of soft-type composite material at low magnification (a) and high magnification (b). SEM images of hard-type composite material before (c) and after (d) the grinding

the core, amorphous carbon arranges uniformly along the graphene pipelines. The surface of the core presents clear ravines and stripes, which is mainly due to the shrinking of the internal carbon nuclear in the process of etching. The entire carbon core is porous, full of holes in nanometer scale, presenting excellent porous characteristics. SEM images in Fig. 2.19c, d show the details of the composite structure.

The morphology and the proportion of the GWF shell and the amorphous carbon core can be changed by controlling the preparation technology and parameters. The shell can be divided into soft type and hard type according to the thickness of GWF. Soft GWF/amorphous carbon composite material cannot support itself due to the thin outer graphene film, which is easy to collapse, stick, or attach on the carbon core in the process of transfer and drying. The transparency of the soft type is better, with slightly weak strength, high proportion of amorphous carbon, and higher specific surface area. SEM images of the soft type can be seen in Fig. 2.20a, b. The composite structure could be clearly observed through the transparent outer graphene film. Hard-type GWF/amorphous carbon material has thick outer graphene film with high strength, which will preserve the skeleton structure of the nickel mesh substrate instead of collapsing in the process of transfer and drying. The strength of the hard-type material is higher than the soft type, with less transparency. At the same time, it can be used as the carrier or skeleton of other functional materials due to its stable structure. SEM images of the hard type are shown in Fig. 2.20c. Due to its thick outer membrane, the core cannot be directly observed

through the outer shell. Using abrasive paper to grind the surface of membrane attached on the nickel mesh substrate, the inner carbon core of the hard-type composite material could be observed after subsequent etching and transfer. The observed SEM image is shown in Fig. 2.20d. At a certain temperature, it is easy to get soft-type material when the feeding of carbon source is small and the cooling rate is big. In this condition, carbon atoms in the solid solution have not enough time to precipitate, mostly retaining in the substrate, obtaining soft-type material with thin outer shell. While it is easy to get hard-type material when the feeding of carbon source is big and the cooling rate is slow, in which condition the time is long enough for the carbon atoms to precipitate on the nickel surface to form thick outer shell, forming hard-type materials.

Further structural characteristics for GWF/amorphous carbon composite are shown in Fig. 2.22. Raman testing in Fig. 2.22a shows the result of the shell and the core, revealing G peak at 1580 cm^{-1} and 2D peak at 2725 cm^{-1} . The shape of the peak and the ratio of the peak intensity show typical multilayer graphene. There is no obvious D peak, showing that the shell has few defects and good crystal structure. Raman testing of the carbon core shows three obvious peaks located in 1379 , 1580 , and 2930 cm^{-1} , respectively. D peak located at 1379 cm^{-1} reveals the disorder structure of the material; while G peak reflecting the crystallization degree of graphite (1580 cm^{-1}) and the broad 2D peak (2930 cm^{-1}) show that the carbon core is made of amorphous carbon.

X-ray diffraction (XRD) analysis is a commonly used method to research the internal atomic structure and the form. The crystal phase and structure of GWF shell and the carbon core can be analyzed by XRD. To study the core of GWF/amorphous carbon composite materials by XRD, the samples are grinded before etching to remove the graphene membrane on the surface of the core. Figure 2.21b shows XRD testing results of the shell and the core, respectively. There are characteristic peaks of graphene shell and carbon core at 26.6° and 26.2° , respectively, which is corresponding to the (002) crystal plane of graphite structure. The peak of the shell

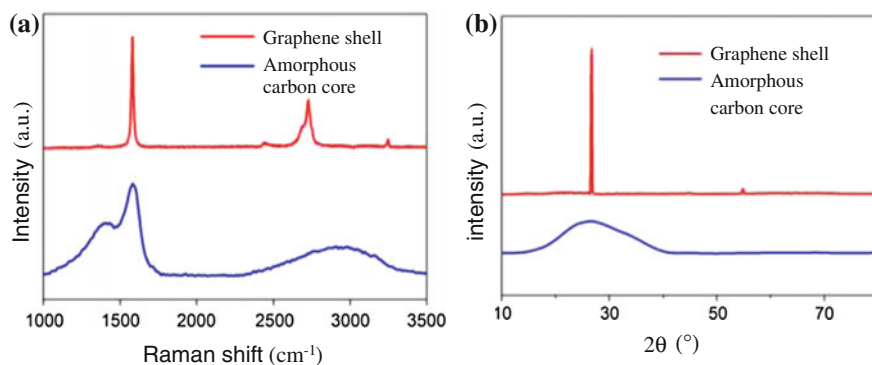


Fig. 2.21 Raman and XRD characterization of the shell and the core. **a** Raman spectrum; **b** XRD characterization

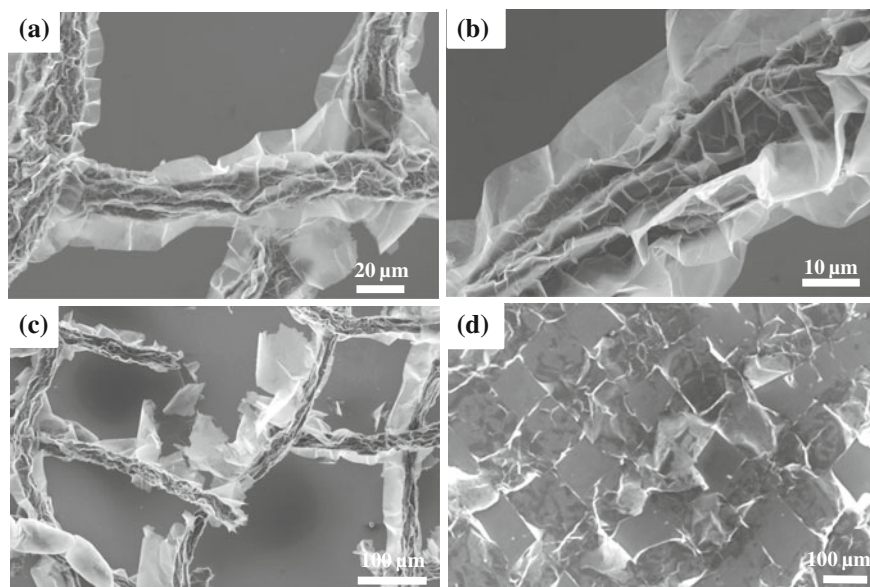


Fig. 2.22 SEM images after the treatment with acids and hydrogen peroxide solution. **a** nitric acid; **b** sulfuric acid; **c** hydrogen peroxide with high concentration; **d** hydrogen peroxide with low concentration

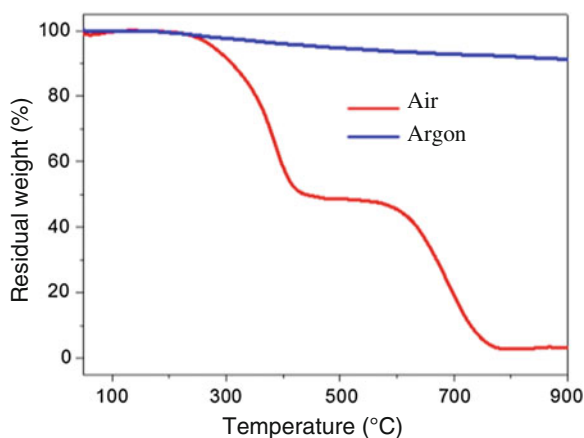
is very sharp and the signal intensity is high. While the peak of the carbon core decreases significantly, and the peak width increases, showing that the shell mainly consists of highly ordered graphite layers. The carbon core contains a large number of amorphous carbon, containing a large number of pores, which is consistent with the SEM observation.

2.6.3 Stability Test

The chemical stability of the GWF/amorphous carbon composite material is tested by putting the material in strong corrosive solution of nitric acid, sulfuric acid, and hydrogen peroxide. Figure 2.22a, b shows SEM images after treatment with nitric acid (1 mol/L) (a) and sulfuric acid (1 mol/L) (b) for 5 h. The morphology scarcely changes, keeping excellent chemical stability in nitric acid and sulfuric acid solution.

There are two different ways to carry out the treatment with hydrogen peroxide. First, using hydrogen peroxide at concentration higher than 1 mol/L. The internal carbon core reacts violently with the oxidation of hydrogen peroxide, producing

Fig. 2.23 TGA curve of GWF/amorphous carbon composite



carbon dioxide gas, which leads to the fracture of the external graphene layers when it discharges from internal to external. After reaction time of less than 10 min, the internal carbon core is not completely etched. The carbon core exposes more without the graphene coating on the surface, while the residual graphene shell on the core presents a “tree” structure, looking like torn clothes, as shown in Fig. 2.22c. The second way is putting the composite material into the hydrogen peroxide solution at concentration lower than 0.1 mol/L. In this condition, the internal carbon core can still react with the hydrogen peroxide, with slower reaction rate than the former method. The produced gas can discharge from the gap in the surface graphene, having little influence on the surface. After reaction for more than 4 h, the internal carbon core is completely oxidated, leaving the surface graphene, as shown in Fig. 2.22d.

The thermal stability of GWF/amorphous carbon composite material in air and argon environment can be studied by TGA analysis. The results are shown in Fig. 2.23.

The graphene shell and the amorphous carbon core have different heat-resisting ability in the air. The weight of the sample does not change under 250 °C. The first weight loss occurred between 250 and 450 °C with a weight loss of about 50–70 % due to burning of the carbon core with increase in temperature. The second weight loss occurred between 600 and 750 °C, with slow oxidation of graphene shell in the air. Compared with the carbon core, the graphene shell possesses better heat-resisting ability, based on the good crystal structure; while the weight of the composite changed little in the argon, with a weight loss of about 10 % when temperature rises to 900 °C. At the same time, the original woven structure and morphology remained during the heating process, showing excellent thermal stability.

2.7 Conclusion

In this chapter, GWF and its composite were prepared using copper mesh or nickel mesh as substrate by CVD method. Three-dimensional woven pipe structure and two-dimensional woven fabrics can be obtained through different etching strategies. The strength of GWFs can be obtained by improving the structure. A promising comprehensive platform was built by synthesizing the structural characteristics. The main conclusions are as follows:

- (1) GWF was prepared using copper mesh substrate. The influence of the selection of the substrate, the reaction temperature, the control of gas source, and the cooling process to GWFs are also studied.
- (2) The copper mesh substrates were removed by direct solution etching or PDMS protection etching, obtaining 2D woven fabric and 3D electrical hollow woven pipes, respectively.
- (3) The morphology and structure of GWF are characterized by methods of OM, SEM, TEM, XRD, Raman spectrum, and white light interference. The structural characteristics of the connected joint were discussed particularly.
- (4) GWF/amorphous carbon composite materials are prepared using nickel meshes as substrates. The all-carbon composite materials contain shell and core. Different preparation techniques have influence on the products. The structural characteristics and stability of the materials are studied by different detecting approaches.

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Synthesis, Properties and Application of Graphene
Woven Fabrics

Li, X.

2015, XII, 125 p. 103 illus., 77 illus. in color., Hardcover

ISBN: 978-3-662-47202-6