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ARTICLE TYPE

Leveling graphene sheet through electrospinning and its conductivity

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Abstract: This study provided a strategy to extend and level easily-curvated graphene sheets through electrospinning. The suspension of graphene oxide (GO) sheets in polar polymers, such as polyacrylonitrile (PAN) and polyvinyl pyrrolidone (PVP) were firstly electrospun into a composite network in which GO sheets were sandwiched and leveled under the drag force of electrospun nanofibers at the surface and around the edge of GO sheets. Then, the leveled GO sheets were reduced under the vapor of reducing agents and then become graphene sheets. The scanning electron micrographical results confirm the extended and leveled shape of graphene. With this strategy, the easy curvature problem of graphene sheets can thoroughly be dissolved. Very importantly, the pressed multilayer samples have the high conductivity of 10^3 S/m. This indicates that the wide potential applications in photo- and electro-devices of graphene materials from natural graphite will be developed.

1. Introduction

In recent years, graphene has become a very useful material, due to its unique features, such as extraordinary electronic properties [1] , mechanical strength [2] , and ultrahigh thermal conductivity [3]. Two-dimensional crystalline arrays of carbon atoms arranged in a honeycomb lattice in graphene, generate small-band-gap semi-metals with unusual electronic and optical properties, including extremely high carrier mobility [4,5]. Currently, graphene is typically produced from graphite by a “topdown” process—either physical exfoliation [6] or liquid phase exfoliation[7]. The interlayer space of graphene (d002) is ~3.4 Å, which is slightly larger than that of the graphite (002) facet (3.348–3.36 Å). This may be due to the turbostratic AB-stacked structure and nanocurvature distortion in graphene [8,9] . Furthermore, the reduced graphene sheets from graphite oxide (GO) will produce curvated morphological structure and form powdery materials via its natural layer-by-layer stacking of basal graphene sheets[9]. Based on this powder structure, graphene can be applied for paints, coatings, composites, films, adhesives, lubricants and functional fluids, where graphene nanopowders act as a multifunctional additives[10]. However, some of the applications of graphene require its leveling shape in plane, especially for electric- and photo- devices like solar cells or light-emission diodes, where there is the limitation in thickness (for example, less than 200 nm) structured in devices[11]. This study provided a strategy to extend and level easily-curvated graphene sheets through electrospinning. Our experimental results indicated that several popular polymers can act as ideal hosts for graphene extension.

2. Experimental

GO was prepared by modified Hummers' method. The GO slurry thus produced was dried in a vacuum oven at 45 °C for 24 h. The chemical reduction of GO were carried by reducing agents, such as hydrazine hydrate, phenylhydrazine, glucose and so on. As a typical example, a 4%-GO slurry was diluted by 1-L deionized water and sonicated for 40 min. Then the mixture was reduced by a single or mixing reducing agent mentioned above. The reaction details were described in supporting information section. The reduced products (black precipitations) are normally powdery agglomerates.

Electrospinning method was used in this research. The dried grapheme oxide(1 g) was added into N,N-dimethyl formamide (DMF)(50 ml) solvent and the suspension was sonicated for 40 min. Then, polyacrylonitrile (PAN) was added into the suspension according to the set ratio of DMF:PAN=22:3 in weight, and the sonication was continued for 8 h to obtain the spinning solution. Electrospinning was proceeded under the set voltage (20kV) and current (0-3mA). Then, the spun fiber composite was stifled under the vapor of hydrazine monohydrate for 6 h. Similarly, ethylene alcohol was as solvent to dissolve GO and PVP (8wt% in ethylene alcohol). All the dissolving and electrospinning conditions for the GO-PVP suspension were the same as mentioned above.

The conductivity measurements were done on a four-probe conductive tester, (TS-8, Probes Tech. Guangzhou,China). The samples were prepared through the hot-pressing method on a pressing machine (TH-6009, Test Machine Co. Ltd, Tianhui, China). After peeling away the reduced graphene-polymer nanofiber composite pieces from the aluminum paper substrate, we multilayered up 5 pieces of this composites and then hot-pressed them to form the samples for conductive measurement.

A scanning electron microscope (JEOL JSM-6390LV), a Fourier transform infrared spectroscope (Nicolet, USA MAGNA-IR 550), and an X-ray diffraction (XRD) spectrometer (Bruke German D-8 Advance diffractometer) were used for the measurements. The elemental analyses of GO and graphene were performed on a PE2400 (Perkin Elmer, USA). Also, Raman spectroscope was applied for the measurement of graphene or GO crystalline structures.

3. Results and Discussion

Figure 1a shows the SEM image of the sample reduced by hydrazine hydrate, which was spinning-coated on a transparent tape substrate, but the samples for Figure 1b and 1c were reduced by phenylhydrazine, which were spinning-coated on a monocrystalline silicon substrate and a transparent tape substrate respectively. One can find that the morphology in Figure 1a shows a continuous and well-distributed spread. However, the morphologies in Figure 1b and 1c are uncontinuous and GO sheets were seriously curvated. The XRD patterns of graphene samples show the broad peaks at $2\theta=24.70$ for samples A, B and C, in which A was reduced by hydrazine hydrate (1ml hydrazine hydrate for 1g graphene in 1000 ml water), B and C were reduced by phenylhydrazine with different concentrations (B: 5 ml phenylhydrazine for 1g GO and C: 10 ml phenylhydrazine for 1g GO in 1000 ml water). The corresponding interlayer space (d002) is 3.432 Å that is similar to the literature[12]. However, the sample D reduced by glucose (2 ml glucose for 1g GO in 1000 ml water) has a large interlayer space d002>7.000 Å for the (002) peak at $2\theta=10.26°$ because of the lower reducing degree of GO. At this case, the intercalated H_2O molecules and various oxide groups are existed [12], [13]. Therefore, the interlayer spaces of the graphene sheets confirm that the hydrazine hydrate and phenylhydrazine are better reducing agents to obtain the graphene coatings.

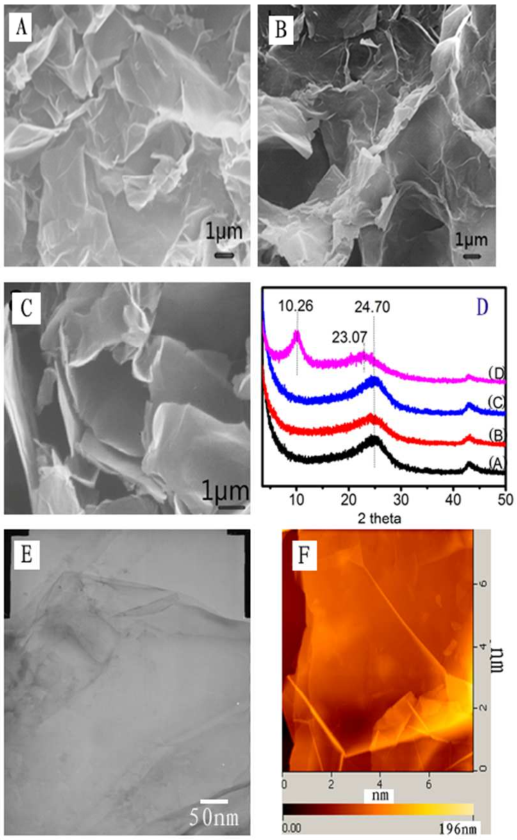


Figure 1. SEM images of graphene reduced by different reducing agents and coated on different substrates [A. hydrazine hydrate, transparent tape substrate; B. phenylhydrazine, monocrystalline silicon substrate; C. phenylhydrazine, transparent tape substrate]; D. XRD patterns of graphene reduced by different reducing agents [D(A): hydrazine hydrate, D(B) (5 ml phenylhydrazine)； D(C) (10 ml phenylhydrazine)； D(D) (glucose)]; E. TEM image of graphene sheet (reduced by hydrazine hydrate); F. AFM image of graphene sheet (hydrazine hydrate).

Figure 1E and 1F are images of TEM and AFM of graphene sheets reduced by hydrazine hydrate, in which we can find that (1) both of them show the curved structures of graphene sheet, and (2) the size of graphene sheet from natural graphite is bigger than 6 μm (but normally less than 10 μm). The paper published on Nature Nanotechnology[14] shows the size of grahene sheet is abut 1 μm. In deed, the actual size is much depending on the places where the original graphites as a starting materials of graphene were mined out. In Figure 1E, the image shows the graphene sheet is very thin and with slight wrinkle.

FT-IR spectra indicate that there are the characteristic absorbance bands of O-H at 3402 and 1612 cm^{-1}, which correspond to the hydroxyl groups at GO and small intercalated H_2O molecules between GO sheets (Figure 2A). After reduced by phenylhydrazine and glucose as reducing agents, these characteristic bands largely decrease (Figure 2B and C), which means the graphene oxide is partly reduced. Moreover, these characteristic bands almost disappear (Figure 2D) when graphene oxide sample was reduced by hydrazine hydrate. However, the spectrum shows C=C stretching band at 1652 cm^{-1} in Figure 2D. Obviously, this band was overlapped by broad 1162 cm^{-1} band in

Figure 2B and C, although C=C covalent bonds exist in these samples. This means that the carbon atoms that link hydroxyl oxide groups in graphene oxide sheet change from sp3 into sp2 hybridized orbital.

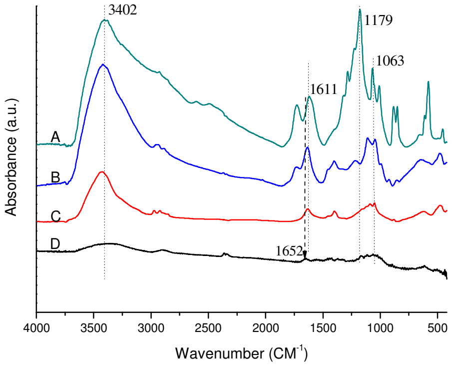
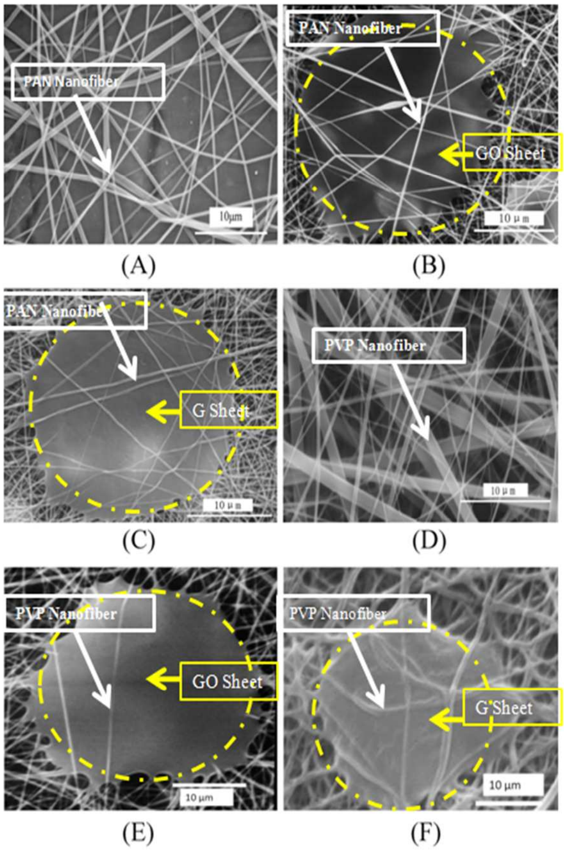


Figure 2. FT-IR spectra of (A) GO, (B) reduced by glucose and (C) reduced by phenylhydrazine and (D) reduced by hydrazine hydrate.

The proposed structure for graphene confirmed in Figure 1A and Figure 2D is very useful to prepare photo- /electric- devices [15]. However, there are two factors to prohibit the applications of graphene: (1) the large ratio of plane size (i.e., ~5 μm) to thickness (i.e., 0.34 nm) generates the curvature nature; (2) the reduced raphene sheets do not dissolve in any solvents. Figure 3 shows the SEM photographs of PAN electrospun nanofiber, GO-PAN electrospun nanofiber composite, and graphene-PAN nanofiber composite getting from reduced GO-PAN. The electrospun PAN nanofibers with the diameter of less than 100 nanometers (Figure 3A) form smooth nanofiber network. Whereas, GO sheet was sandwiched among nanofibers and show the joints around the edge of GO sheet where nanofibers attach on tightly (Figure 3B). After GO-PAN sample was reduced by hydrazine hydrate, the sample show similar situation that electrospun nanofibers attach around and on graphene sheet in Figure 3C. This image indicates that graphene extends because of the nanofibers' drag effect. The concentration of polymer-GO, electrospinning voltage, and solution temperature affect the formation. As comparison, PVP is also available polymer for electorspinning (Figure 3D). When it was used as polymer matrix, the extended GO sheet can also be obtained (Figure 3E). After it was reduced under vapor of hydrazine hydrate, the level graphene sheet was kept (Figure 3F). The extension include two steps: (1) the triple conjugate bonds in –CN groups and hydrogen atom in HO- groups form –CN:-HO- hydrogen bond at the GO surface; (2) after reduction of GO-PAN electrospun nanofiber composite, the HO- group lost and thus the hydrogen bonds do not exist anymore, the hydrogen bond is alternated by the π – π interaction between triple conjugate bonds in –CN groups and huge 2D conjugate structure of graphene sheet (Figure 4A). Thus, the nanofiber-attached graphene sheet structure is kept well. Similarly, the polar groups (O=C and N) in pyrrolidone ring in polyvinyl pyrrolidone have strong interaction with graphene oxide and graphene sheet too, through the same interaction principle (Figure 4B). Therefore, the PVP can play the similar role as PAN.



(A) (B)

(C) (D)

(E) (F)

Figure 3 SEM photographs of electrospun nanofibers and the corresponding GO or graphene nanocomposites. (A) PAN electrospun nanofibers, (B) GO-PAN electrospun nanofiber composite, (C) graphene-PAN nanofiber composite, (D) PVP electrospun nanofibers, (E) GO-PVP electrospun nanofiber composite, and (F) graphene-PVP nanofiber composite. (Notes: GO Sheet- graphene oxide sheet, G sheet- graphene sheet)

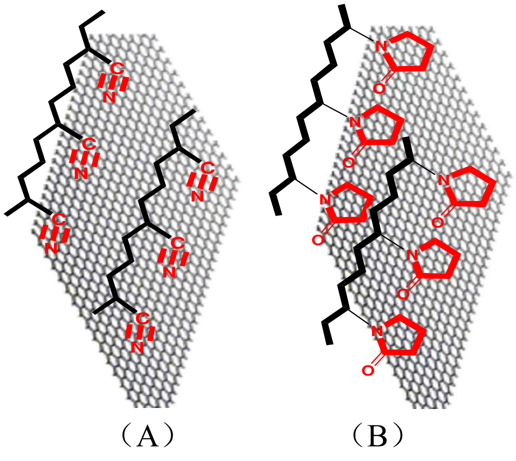
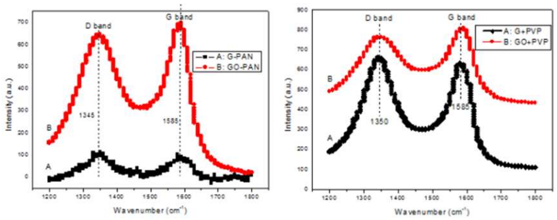


Figure 4 Indications of the interactions of granphene sheets with PAN (A) and PVP (B) respectively.

The characterization of samples of GO/Graphene-PAN electrospun nanofiber composites and GO/Graphene-PVP electrospun nanofiber composites by means of Raman scattering is shown in Fig. 5(1) and (2). In Figure 5(1), the comparison with the G-band intensity of GO-PAN electrospun nanonfiber composite indicates that the G-band intensity of the graphene-PAN nanofiber composite decreases, with a ratio (R) the G band to the D-band (R= I_G/I_D) of 0.84, which is lower than that of GO-PAN nanofiber composite (1.10). Whereas, when the nanofiber-forming polymer was changed into PVP, the ratio of R=I_G/I_D of graphene-PVP nanofiber composite is 0.95 and that of R=I_G/I_D of GO-PVP nanofiber composite is 1.14. Referring to the publications of L. Zhou[16, 17], these data regarding G- and D-bands concern about the crystalline structures of GO and graphene. Therefore, we can find (1) graphene sheets in nanofiber composite have lower degree of crystalline structure than that of GO in nanofiber composites, either PAN or PVP as host polymer; (2) difference of polymer hosts has influence on crystalline structures of GO/graphene in nanofiber composites.



(1) **(2)**

Figure 5 The spectra of Raman Scattering on (1) GO/Graphene-PAN electrospun nanofiber composites and (2) GO/Graphene-PVP electrospun nanofiber composites

Table 1 listed the conductivity data. The samples for conductivity measurement were pressed by pressing machine at 100℃. We can know that these composite sheets have good conductivity at 10^3 S/m. As compassion, the conductivities of pure PAN nanofiber and PVP nanofiber are 2.3×10^{-11} and 4.3×10^{-7} S/m, based on the reference [18]. With this method, we can obtain thin conductive film with the thickness of 200-300 nm.

Table 1 The conductivity of multi-layered graphene-polymer nanofiber composite sheets

Samples	Conductivity (S/m)
graphene-PAN nanofiber composite	7.5×10^3
graphene-PVP nanofiber composite	2.5×10^3

4. Conclusions

In summary, through the investigation of the morphological structures of graphene reduced by different reducing agents, we confirmed that the curvated feature of graphene sheets can not be prevented from the GO-coating reduction strategy, even though the sample was better from hydrazine hydrate reduction on a transparent tape. However, the novel strategy to extend single grraphene sheets by electrospinning is exceedingly effective. PAN and PVP herein we used are as the examples of polar polymers to be as nanofiber matrices. Successfully the gained level graphene sheets ware developed and they have good conductivity at 10^3 S/m order. Thus, we have dissolved the two key prohibitions in graphene applications for photo- / electro-devices: the curveted shape and the dissolvable problem of graphene sheets.

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Notes

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