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Preparation of conductive polyaniline grafted graphene hybrid composites *via* graft polymerization at room temperature

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Abstract: The graphene was covalently functionalized with phenol groups *via* 1,3-dipolar cycloaddition reaction without degrading its electronic properties. The most important thing is that two hydroxyl groups can be covalently attached to the graphene sides in a single step. Here, these phenols on the functionalized graphene have been further derivatized with γ -aminopropyltriethoxysilane to form a dense aminopropylsilane self assembled monolayer with active sites for the graft polymerization of aniline. Conductive polyaniline layer was chemically grafted on the surface of the self assembled monolayer coated graphene by in situ polymerization of aniline monomer in the presence of ammonium peroxydisulfate under acid conditions. This reaction was found to be extremely efficient in producing conductive polyaniline/graphene hybrid composites, even at room temperatures and short reaction times (24 h), which was usually done using graphene oxide. The chemical grafting of PANI was confirmed using fourier transform infrared spectroscopy. Thermogravimetric analysis indicated that the polymer functionalized graphene consisted of 24.5 wt% polymer. The morphology of the polyaniline grafted graphene hybrid composites and hydroxyl functionalized graphene were examined by scanning electron microscope and transmission electron microscope, showing relatively uniform polymer coatings present on the sides of graphene.

1. Introduction

Ever-increasing attention has been paid to the field of graphene-based materials since the graphene isolated by K.S.Novoselov et al. in 2004^[1] due to that it is a single-atom-thick, two-dimensional sheet of sp²-hybridized carbon atoms arranged in a honeycomb crystal structure with exceptionally high strength, surface area, thermal conductivity, and electronic conductivity.^[2, 3] These superior properties make graphene a very promising candidate in many potential applications, such as energy conversion and storage devices,^[4] catalysts,^[5] optoelectronic,^[6] chemical sensors, flash memory storage devices, transparent conductors, distributed ignition, and supercapacitors.^[7]

Laith Al-Mashat et al,^[8] synthesized a graphene/polyaniline (PANI) nanocomposites, which were applied in the development of a hydrogen (H₂) gas sensor and the sensing performance of the synthesized nanocomposites is much better than that of sensors based on only graphene sheets and PANI nanofibers. Recently, especially, in the wake of increasing air pollution, global warming and depletion of traditional energy resource, the development of renewable energy production and hybrid electric vehicles with low CO₂ emission have stimulated intense research on energy storage and use of alternative energy sources.^[9] The graphene has attracted much attention and been proved to be an outstanding candidate for preparation of graphene/conductive polymer based hybrids as Supercapacitor Electrode Material. Among the conducting polymers, PANI is considered to be the most promising electrode material for supercapacitors due to its excellent capacity for energy storage, easy synthesis, high conductivity and low cost.^[10]

For example, graphene/PANI composite films were synthesized *via* a electrochemical process, which could be directly used as the supercapacitor electrode.^[11] Wei Fan et

al. ^[12] used a solution-based coassembly process to prepare polyaniline hollow spheres (PANI-HS)@electrochemical reduced graphene oxide (ERGO) hybrids, which indicating a good cycling stability. Another supercapacitor devices based on self-assembled hierarchical graphene@polyaniline nanoworm composites also showed high electrochemical capacitance and effectively improved electrochemical stability and rate performances. ^[13] It must be pointed out that, in these composites, the interaction between graphene and the conductive polymer such as PANI is a Van der Waals force. It is well known that due to the large surface area of graphene and strong Van der Waals force among them would result in severe aggregation in the composites matrix. In order to obtain satisfied performance of the final graphene/polymer composites, the issues of the strong interfacial adhesion and compatibility between graphene and matrix, and well dispersion of graphene should be addressed. With the goal to solve these issues kept in mind, the graphene must be functionalized using both covalent and noncovalent approaches, However, the Van der Waals force and other noncovalent force are weaker than the covalent bond. ^[14]

Unfortunately, to date, polyaniline-graphene (PANI-G) hybrids connected by covalent bonds have rarely been reported. ^[15, 16] For example, a chemical bonded graphene-polyaniline hybrid in which a carboxylic acid ester group connects graphene and PANI was recently reported by Kumar.^[17] A novel graphene-polyaniline (GP) hybrid based on the PANI nanofiber grafted onto graphene electrochemical tests reveal that the GP hybrid has higher capacitance performances, which indicated superiority to materials interacted by Van der Waals force.^[16] Junwei An et al. ^[18] prepared a PANI-G hybrid connected by amide groups by grafting PANI nanofibers onto graphene and electrochemical tests show that the prepare PANI-G hybrid has a high capacitance, higher than that in G/PANI composites reported previously.

In this study, a novel route to prepare PANI/functionalized graphene hybrid composites in a three-step process using graphene and aniline as the starting materials is established. Our strategy involves covalently functionalization of graphene with phenol groups *via* 1,3-dipolar cycloaddition reaction, and these phenols on the functionalized graphene have been further derivatized with γ -aminopropyltriethoxysilane (APTES) to form a dense aminopropylsilane self assembled monolayer (SAM) with active sites for the graft polymerization of aniline. Conductive PANI layer was chemically grafted on the surface of the self assembled monolayer coated graphene by in situ polymerization of aniline monomer in the presence of ammonium peroxydisulfate (APS) under acid conditions at room temperature, resulting in conductive polyaniline/graphene hybrid composites. Since the graphene was covalently functionalized with PANI, strong interfacial adhesion and compatibility between graphene and matrix, and well dispersion of graphene are ensured, and hence phase separation is minimized. The chemical grafting of PANI and the morphology of the resulting materials were characterized using various analytical techniques.

2. Experimental

2.1. Materials

Natural flake graphite with an average particle size of 300 mesh and a purity of >99% was supplied by Qingdao Haida Graphite Co., Ltd, China. 3,4-dihydroxybenzaldehyde, *N*-methylglycine and γ -aminopropyltriethoxysilane were purchased from Aldrich and used without further purification. Dimethylformamide (DMF, 99%, Shanghai Chemical Industrial Co., Ltd., China) was purified by stirring over KOH for 48 h and then distilled under reduced pressure. All other reagents and solvents were purchased from commercial suppliers and used as received.

2.2. Preparation of graphite oxide and graphene

Graphite oxide, a pseudo-two-dimensional solid in bulk form, was prepared from natural graphite powder by oxidation with KMnO_4 in concentrated H_2SO_4 according to Hummers' method.^[19] Concentrated H_2SO_4 (46 mL) was poured into the 250 mL three neck flask and stirred in an ice bath until the temperature dropped to 0-3°C. Natural graphite (2.0 g) and NaNO_3 (1.0 g) were added and stirred uniformly. KMnO_4 (6.0 g) was gradually added with stirring and cooling in order to keep the temperature below 20°C. The solution was heated to 35±3°C and maintained for 30 min. Then, distilled water was slowly added, and the temperature was controlled lower than 100°C. After 15 min, this reaction was terminated by addition of a large amount of distilled water and 30% H_2O_2 solution (5 mL). The mixture was filtered and washed with 5% HCl aqueous solution and water. The sample of graphite oxide was obtained after drying. To prepare graphene, 100 mg graphite oxide was dispersed in 100 mL of water to create a yellow-brown dispersion, and the exfoliation of graphite oxide to graphene oxide was achieved by sonication with a cylindrical tip for 30 min. Then the resulting homogeneous solution was mixed with 80 μL of hydrazine solution as a reducing agent, and 350 μL of ammonia solution was added to adjust pH to around 10. After stirred for a few minutes, the mixed solution was heated at about 95°C for 1 h. The reduced product was isolated by filtration through polytetrafluoroethylene (PTFE) membrane (0.22 μm), washed with water and methanol, and dried for 24 h in vacuum oven. Then graphene, that is, the reduced graphene oxide, was obtained.

2.3. Functionalization of graphene with phenol (Graphene-*f*-OH, 1)

Twenty milligrams of graphene, 200 mg of 3,4-dihydroxybenzaldehyde, and 200 mg of *N*-methylglycine were suspended in 50 mL of DMF and heated at 120°C for 5 days. The mixture was then filtered through Millipore filters (0.45 μm) and washed

thoroughly with DMF. The filtrate was sonicated in DMF for 1 h and then removed; the resulting suspension was filtered again through Millipore filters (0.45 μm). This procedure was repeated three additional times with sonication in (1) DMF, (2) 1:1 (v/v) $\text{C}_2\text{H}_5\text{OH}/\text{CHCl}_3$, and (3) diethylether. The remaining black solid was dried under vacuum (10^{-2} bar) for 3 days.

2.4. Functionalization of graphene with phenol (Graphene-*f*-NH₂, 2)

One hundred milligrams of graphene-*f*-OH were dispersed into a solution of APTES in ethanol (50 mL, about 10 mmol/L) under a nitrogen atmosphere, sonicated for 15~20 min, held at room temperature for 24 h, and then washed with ethanol in an ultrasonic bath to remove the unreacted APTES. The resulting amine-functionalized graphene (Graphene-*f*-NH₂, 2) was removed from the nitrogen atmosphere, collected by filtration, rinsed successively with ethanol, and finally dried.

2.5. Preparation of polyaniline/functionalized graphene hybrid composites

Polyaniline/functionalized graphene (PANI/*f*-G) hybrid composites were prepared by in situ polymerization of aniline in a suspension of amine-functionalized graphene (Graphene-*f*-NH₂, 2) in acidic solution. In a typical polymerization, the purified aniline was dissolved in 1 M HCl at a concentration of 0.3 M. Graphene-*f*-NH₂ was dispersed in the resulting solution by bath-sonicating for 1 h. While maintaining vigorous stirring at room temperature, another solution of ammonium peroxydisulfate, with a mole ratio to aniline of 1:4, in 1 M HCl was rapidly poured to the mixture. Polymerization of aniline started after about 5 min, while the color of the mixture changed into green. The mixture was allowed to stir at room temperature overnight resulting in PANI in its emeraldine (EM) salt state. The EM salt grafted graphene was rinsed with distilled water, and was subsequently washed several times in *N*-methylpyrrolidinone (NMP) in order to remove any physically adsorbed EM base,

then, the solution was centrifuged and the PANI/*f*-G hybrid was obtained by filtration. The PANI/*f*-G hybrid was washed with alcohol, followed by washing with distilled water to remove any residual NMP and then by drying under reduced pressure. The yield of PANI grafted graphene (G-g-PANI) is 26%.

2.6. Preparation of pure polyaniline

Pure polyaniline was synthesized by a rapid mixing reaction.^[20] Aniline was first distilled under vacuum to remove the oxidation impurities. The purified aniline (0.3 g, 3.2 mmol) was dissolved in 10 mL of 1 M HCl aqueous solution. While maintaining vigorous stirring at room temperature, ammonium peroxydisulfate (0.18 g, 0.8 mmol) in 10 mL of 1 M HCl aqueous solution was rapidly poured into the aniline solution. Polymerization was observed in about 5 min when the characteristic green color of polyaniline emeraldine salt appeared. The mixture was allowed to stir at room temperature overnight. At the end, the mixture was diluted by 100 mL of water. The precipitated polymer was collected by filtration and repetitively washed with water, ethanol until the filtrate became colorless. After having been dried under vacuum at 60°C, the pure PANI sample (0.09 g) was collected as a deep blue powder in 30 % yield.

2.7. Physical measurements

Fourier transform infrared (FTIR) spectra were measured with a PE Spectrum One B instrument. Atomic force microscopy (AFM) measurements were conducted on a Veeco Nanoman VS AFM system operated in a tapping mode. The hydroxyl-functionalized graphene (Graphene-*f*-OH) samples were prepared by dispensing a small amount of Graphene-*f*-OH in DMF. Then, a drop of the suspension was dropped on a freshly cleaved mica surface. High resolution transmission electron microscopy (HRTEM) measurements were conducted on a JEM-2100F TEM

microscope. The HRTEM samples were prepared by dispensing a small amount of dry powder in ethanol. Then, a drop of the suspension was dropped on 300 mesh copper TEM grids covered with thin amorphous carbon films. Field emission scanning electron microscope (FESEM) measurements were carried out on a Nova NanoSEM 230 field emission scanning electron microanalyzer. The FESEM samples were prepared as following; firstly, the phenol-functionalized graphene (Graphene-*f*-OH) and polyaniline grafted graphene (Graphene-*g*-PANI) samples were dispersed in ethanol, respectively. And then a drop of dilute as-prepared dispersion of the resulting products was placed onto a copper plate attached to an aluminum sample holder, and the solvent was allowed to evaporate at room temperature. Thermogravimetric analysis (TGA) was carried out on a TA Instrumen 2960 at a heating rate of 10°C/min under nitrogen flow. The X-ray Photoelectron Spectroscopy (XPS) was carried out on a K-Alpha 1063 system. The Bulk DC conductivity measurements of the hybrid composites were made on pressed pellets (1.3 cm diameter, <1 mm thickness) with an Alessi four-probe-point conductivity probe.

3. Results and Discussion

3.1. Preparation of polyaniline/graphene hybrid composites

Our strategy to prepare PANI/*f*-graphene hybrid composites (G-*g*-PANI) consisted of three major steps, which is illustrated in Figure 1.

Figure 1. Schematic diagram illustrating the three-step process of preparation of graphene grafted PANI (G-*g*-PANI).

Initially, as shown in Figure 1, the graphene was functionalized with with phenol *via* the 1,3-dipolar cycloaddition reaction carried out using *N*-methylglycine and

3,4-dihydroxybenzaldehyde according to the method we developed and reported previously.^[14] After this reaction, most of the physically adsorbed organic materials were removed by filtration. The most important thing is that two hydroxyl groups can be attached to the graphene sides by a single reaction without degrading its electronic properties, which benefits the higher grafting density of polymer and the wider application especially in conductive nanocomposites. In this preparation strategy, γ -aminopropyltriethoxysilane was selected as a coupling agent, which has two functions from its functional groups. The phenol-functionalized graphene (**1** in Figure 1) could then be treated with APTES in ethanol at room temperature to introduce the attachment of amine group to the sides of the graphene (**2** in Figure 1), which was used as active sites for the graft polymerization of aniline. That is, a dense self assembled monolayer was formed when it reacted with surface —OH groups on the phenol-functionalized graphene hybrids. Because the attached silane chains possess a reactive end —NH₂ group, PANI chains can be grafted chemically on functionalized graphene easily in the third step as illustrated in Figure 1. Polyaniline/functionalized-graphene (PANI/*f*-G) hybrid composites were prepared by in situ polymerization of aniline in a suspension of amine-functionalized graphene (Graphene-*f*-NH₂, **2**) in acidic solution. FTIR spectroscopic analysis of the resulting products has made the functionalization process clear, as illustrated in Figure 1. Figure 2, Figure 3 and Figure 4 show the FTIR spectra of graphene, G-*f*-OH, G-*f*-NH₂, pure PANI, as well as the PANI grafted graphene (G-*g*-PANI) hybrid.

Figure 2. FTIR spectra of (a) graphene, and (b) phenol-functionalized graphene.

Figure 3. FTIR spectra of (a) graphene, and (b) amino-functionalized graphene (Graphene-*f*-NH₂).

Figure 4. FTIR spectra of (a) pure PANI, and (b) PANI grafted graphene (G-g-PANI).

Figure 4. FTIR spectra of (a) pure PANI, and (b) PANI grafted graphene (G-g-PANI).

Figure 2 shows the FTIR spectra of pristine graphene and phenol-functionalized graphene (Graphene-*f*-OH, **1** in Figure 1). As illustrated in Figure 2, the FTIR spectrum of graphene-*f*-OH (curve b in Figure 2) shows C—H stretch features at 2950, 2922 and 2852 cm^{-1} that do not appear in the spectrum of pristine graphene (curve a in Figure 2). Also, apparent C—C stretch bands and a weak aromatic C—H band are observed at 1100-1700, 618 and 3040 cm^{-1} , respectively. The C—O stretch band at 1120 cm^{-1} and the O—H stretch band at 3600-3700 cm^{-1} , both of which are characteristic of phenols. The FTIR spectra analysis provides support for successful functionalization as proceeds as illustrated in Figure 1 *via* 1,3 dipolar cycloaddition reaction using 3,4-dihydroxybenzaldehyde, which were discussed in detail in our in our published paper.^[14] The FTIR spectrum of amino-functionalized graphene (G-*f*-NH₂) is shown in Figure 3 (Curve b), the appearance of the peaks at 3020 and 2930 cm^{-1} , can be assigned to the stretching vibrations of —CH₂— in the amino-functionalized graphene, is also indicative of the formation of a well-defined SAM layer. The new bands at 1600 (as a shoulder of the 1647 peak) and 1452 cm^{-1} are attributed to the bending vibration of —CH₂—,^[21] and the new bands at 1385 and 1200 cm^{-1} are assigned to the stretching vibrations of N—H and C—N respectively, which appear in the spectrum of the amino-functionalized graphene. These results clearly confirmed that the γ -aminopropyltriethoxysilane molecules were covalently linked to graphene, suggesting successful surface functionalization of the graphene with amino group. The FTIR spectra of pure PANI (curve a) and G-g-PANI (curve b) are shown in Figure 4. The main characteristic peaks are assigned as

follows: the band at 3420 cm^{-1} is attributable to N—H stretching mode, C=N and C=C stretching mode for the quinonoid and benzenoid units occur at 1640 and 1500 cm^{-1} , the band at 1400 cm^{-1} have been attributed to C—N stretching mode for benzenoid unit, while the peak at 1123 cm^{-1} is assigned to the in-plane bending vibration of C—H (mode of N=Q=N, Q=N=H⁺—B and B—N⁺H—B), which is formed during protonation. In additionally, it also can be found that the incorporation of graphene leads to the shift of some bands of PANI. For example, the bands at 1600 cm^{-1} in FTIR spectrum of pure PANI (curve a in Figure 4) corresponding to the stretching mode of C=N, is shifted to 1640 cm^{-1} in the spectrum of G-g-PANI sample. The FTIR spectra of the pure PANI and grafted PANI to nanoparticle were discussed in detail in our in our published paper.^[20] All these indicated that there were strong interaction between graphene hybrid and PANI and restricted modes of vibrations in PANI grown in the presence of graphene.

3.2. Morphology and structure

Figure 5 gives typical AFM images of the resulting hydroxyl-functionalized graphene (Graphene-*f*-OH) and amino-functionalized graphene dispersion in DMF after their deposition on a freshly cleaved mica surface. It can be found from Figure 5 that the average thickness of the as-prepared hydroxyl-functionalized graphene is about 0.78 nm , compared with the theoretical value of 0.78 nm for single-layer graphene, which corresponds to a single layer graphene. This results show that the functionalization of graphene with phenol did impart significantly enhanced solubility to the Graphene-*f*-OH in DMF and resulted in good separation and no agglomeration of graphene that functionalized with hydroxyl. In addition, it can be found from Figure 5 that there are slightly increase in the topological height for the amino-functionalized graphene.

Figure 5. AFM images of (a) exfoliated graphene-*f*-OH sheets, and (b) amino-functionalized graphene on mica surface with height profile.

Figure 6. (a) XPS spectra of amino-functionalized graphene, and (b) content of various element of amino-functionalized graphene determined by XPS.

The XPS spectra G-*f*-NH₂ hybrid and the content of various element of the amino-functionalized graphene determined by XPS are shown in Figure 6. Spectral analysis further verifies the presence of amino groups in the G-*f*-NH₂ hybrid. Figure 6b reveals that the amount ratio of O:N:C:Si in G-*f*-NH₂ hybrid is 30.18:3:58.68:8.13. This finding is attributed to the successful functionalization of graphene with amino groups. The morphology and structure of the pure PANI, graphene and PANI/functionalized graphene (G-*g*-PANI) hybrid composites were characterized using scanning electron microscope (SEM) and transmission electron microscope (TEM). The results are shown in Figure 7 and Figure 8, respectively.

Figure 7. Representative SEM images of (a) pure PANI, (b) graphene-*f*-OH, and (c) G-*g*-PANI hybrid.

Figure 8. Representative TEM images of (a) pure PANI, (b) G-*f*-NH₂, and (c) G-*g*-PANI hybrid. Inserts are the selected area electron diffraction patterns of some materials.

The selected area electron diffraction (SAED) patterns from the pure polyaniline prepared by the rapid mixing method disclose that the pure PANI materials are a lack

of obvious crystalline character (Figure 8). The graphene prepared here has a typically curved, layerlike structure with the size of tens of micrometers. For PANI/functionalized-graphene composites, SEM and TEM images show that all the graphene sheets are homogeneously surrounded with PANI. For the G-g-PANI hybrid composites with a amount of the PANI component grafted at the surface of graphene sheets. The morphology of G-g-PANI hybrid composites is very different from the pure graphene, i.e., the graphene sheets in the G-g-PANI hybrid composites mainly exist in wrinkled form with PANI distributed on the graphene sheets. Such morphology is supposed to stabilize the three-dimensional bulky structure of the composites during the charge-discharge process, which may lead to higher capacitance and longer cycling life. A comparison of the SAED patterns of pure PANI and G-g-PANI hybrid composites discloses that with the incorporation of graphene, the composites also show an increasing of crystalline character, indicating that higher conductivity could be obtained in the composites with the incorporation of graphene. The thermal properties of the PANI/functionalized graphene hybrid composites were further studied by thermogravimetric analysis (TGA).

Figure 9. TGA curves of (a) graphene, (b) G-*f*-OH, (c) G-*f*-NH₂, (d) G-g-PANI hybrid, and (e) PANI. (heating rate =10°C/min under a nitrogen atmosphere).

As shown in Figure 9, all the materials show a little mass loss around 100°C due to the deintercalation of H₂O. The obtained graphene that was reduced by hydrazine, only shows 15% mass loss from 30°C to 600°C, indicating that most of the oxygen-containing groups were removed during the chemical reduction process.

Compared with graphene, a mass loss of 9.5% can be observed for G-*f*-OH sample from 30°C to 600°C (see Figure 9b), which is attributed to the decomposition of the grafted hydroxyl groups. It can be also found from Figure 9c that there is a mass loss of 5.5%, which is reasonably attributed to the decomposition of the grafted amino hybrid. Compared with graphene, a mass loss of 30.5% can be observed for G-*g*-PANI hybrid composites from 30°C to 600°C. The relatively larger mass loss of G-*g*-PANI hybrid composites than the G-*f*-NH₂ hybrid should be contributed to the decomposition of the grafted PANI in the hybrid composites. The amount of the grafted PANI is 24.5 wt% calculated from the data of TGA, which is much higher than that of the samples prepared with the TiO₂ nanoparticle pretreated by silane coupling agent.^[22] At the same time, the pure PANI sample displays a 87.3% mass loss from 100 to 600 °C, which is reasonably attributed to the decomposition of the pure PANI. The level of chlorine doping in PANI is 3.6%, which was determined by ion chromatography.

3.3. Electrical conductivity of the composites

The electrical conductivities (σ) of G-*f*-OH, G-*f*-NH₂, pure PANI, graphene and G-*g*-PANI hybrid composites were determined on pressed pellets from powder by using an Alessi four-probe resistivity measurement system, and the average conductivities are collected in Table 1.

Table 1 List of the conductivities of G-*f*-OH, G-*f*-NH₂, pure PANI, graphene and G-*g*-PANI hybrid composites

The pure PANI sample is conducting with the conductivity of 10.8 S/m. The graphene exhibits a much higher conductivity of 277.4 S/m which is close to that of pristine graphite. [23] As discussed above, the hybrid composites prepared *via* the in situ polymerization have a graphene-like layered structure with PANI grafted on the sides of the graphene sheets. The homogeneously distributed PANI among graphene sheets would affect greatly on the electrical properties of the hybrid composites. The conductivity of G-g-PANI hybrid composites is enhanced dramatically to 235.6 S/m compared with the pure PANI sample.

4. Conclusions

Graphene was successfully grafted with PANI through the self-assembled aminopropylsilane monolayer and chemical oxidative graft polymerization. The successful grafting of PANI macromolecules onto the sides of graphene was confirmed by the analysis results of FTIR and TGA. The morphology and structure of the pure polyaniline, graphene and G-g-PANI hybrid composites are characterized by SEM and TEM. It is clear that the PANI functionalized graphene formed a homogeneous composite at the nanometer scale with the PANI distributed on the surface of graphene sheets. The amount of grafted PANI with 24.5 wt% was achieved. The graphene-g-PANI hybrid composites show high electrical conductivities which are essential for their applications as electrode materials for supercapacitors. It is expected to be used as supercapacitors, biosensors, corrosion protections, and antistatic packaging materials.

Acknowledgment

This work was financially supported by Hunan Provincial Natural Science Foundation of China (Project No.13JJA004), Foundation of State Key Laboratory of Powder Metallurgy, and the fund of National Natural Science foundation (Project No.

51302080), People's Republic of China.

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Figure and table captions

Figure 1 Schematic diagram illustrating the three-step process of preparation of graphene grafted PANI (G-g-PANI).

Figure 2. FTIR spectra of (a) graphene, and (b) phenol-functionalized graphene.

Figure 3. FTIR spectra of (a) graphene, and (b) amino-functionalized graphene (Graphene-*f*-NH₂).

Figure 4. FTIR spectra of (a) pure PANI, and (b) PANI grafted graphene (G-g-PANI).

Figure 5. AFM images of (a) exfoliated graphene-*f*-OH sheets, and (b) amino-functionalized graphene on mica surface with height profile.

Figure 6. (a) XPS spectra of amino-functionalized graphene, and (b) content of various element of amino-functionalized graphene determined by XPS.

Figure 7. Representative SEM images of (a) pure PANI, (b) graphene-*f*-OH, and (c) G-g-PANI hybrid.

Figure 8. Representative TEM images of (a) pure PANI, (b) G-*f*-NH₂, and (c) G-g-PANI hybrid. Inserts are the selected area electron diffraction patterns of some materials.

Figure 9. TGA curves of (a) graphene, (b) G-*f*-OH, (c) G-*f*-NH₂, (d) G-g-PANI hybrid, and (e) PANI. (heating rate =10°C/min under a nitrogen atmosphere).

Table 1 List of the conductivities of G-*f*-OH, G-*f*-NH₂, pure PANI, graphene and G-g-PANI hybrid composites

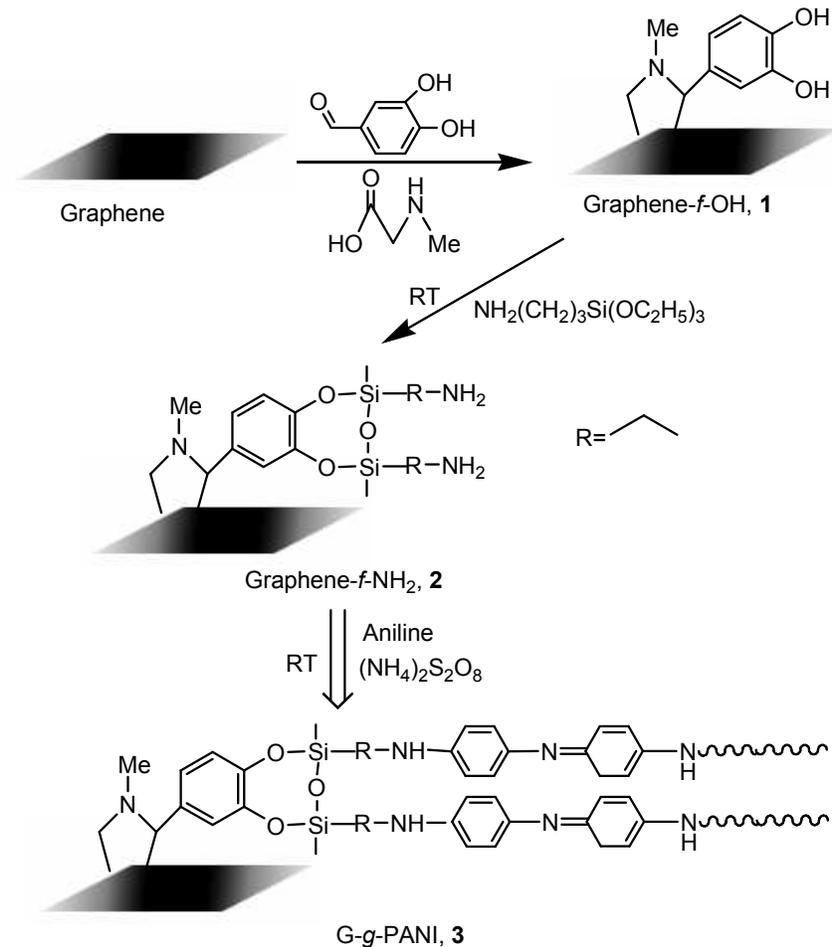


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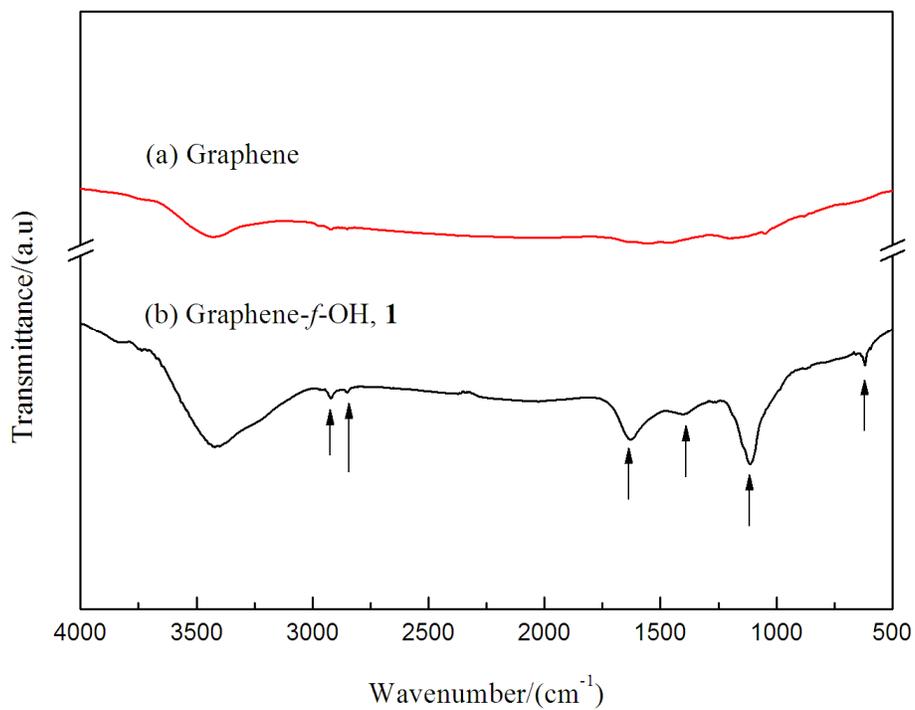


Figure 2. FTIR spectra of (a) graphene, and (b) phenol-functionalized graphene.

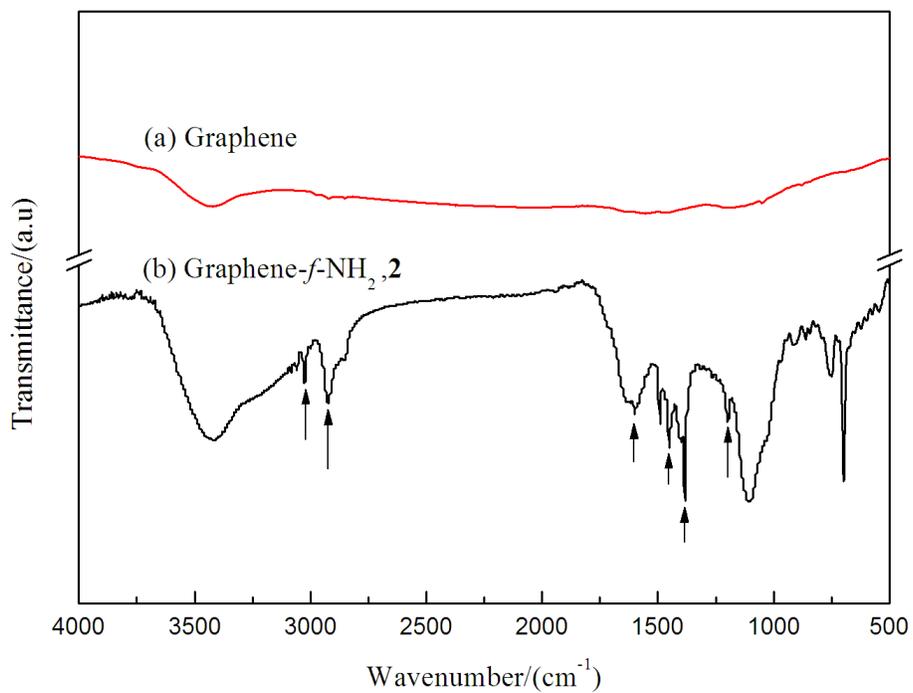


Figure 3. FTIR spectra of (a) graphene, and (b) amino-functionalized graphene (Graphene-f-NH₂).

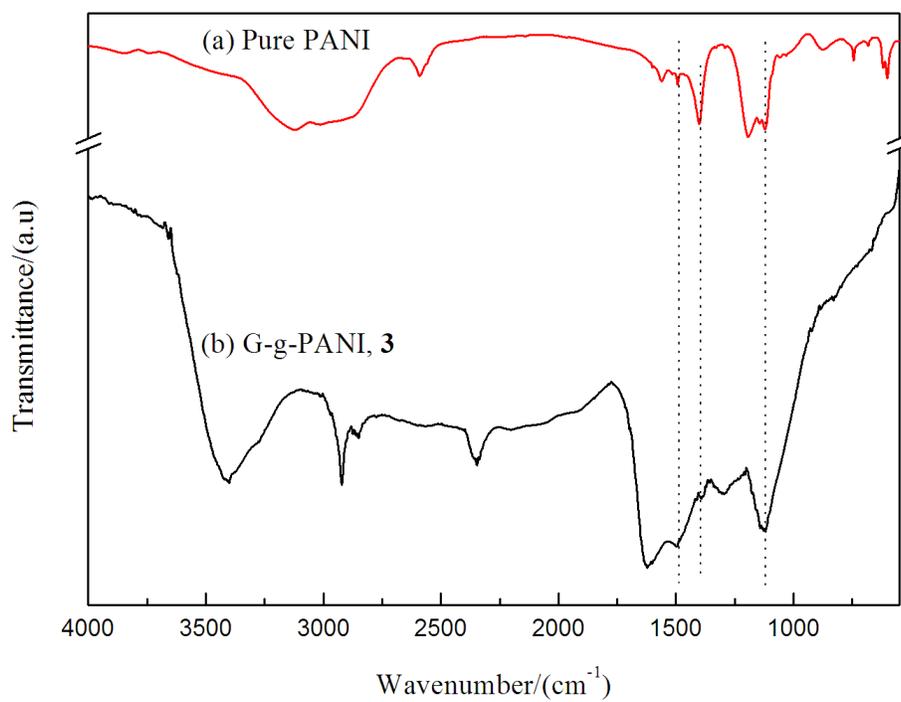


Figure 4. FTIR spectra of (a) pure PANI, and (b) PANI grafted graphene (G-g-PANI).

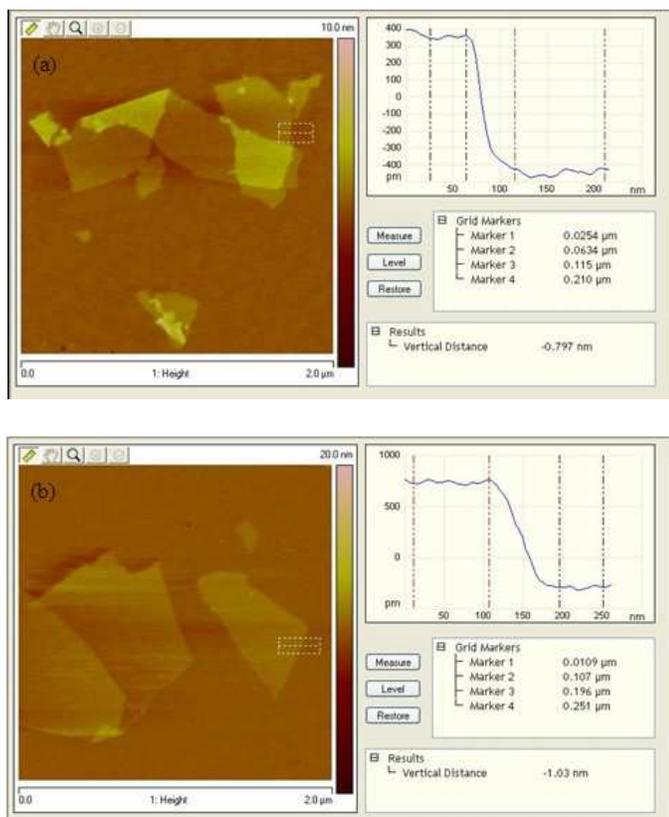


Figure 5. AFM images of (a) exfoliated graphene-*f*-OH sheets, and (b) amino-functionalized graphene on mica surface with height profile.

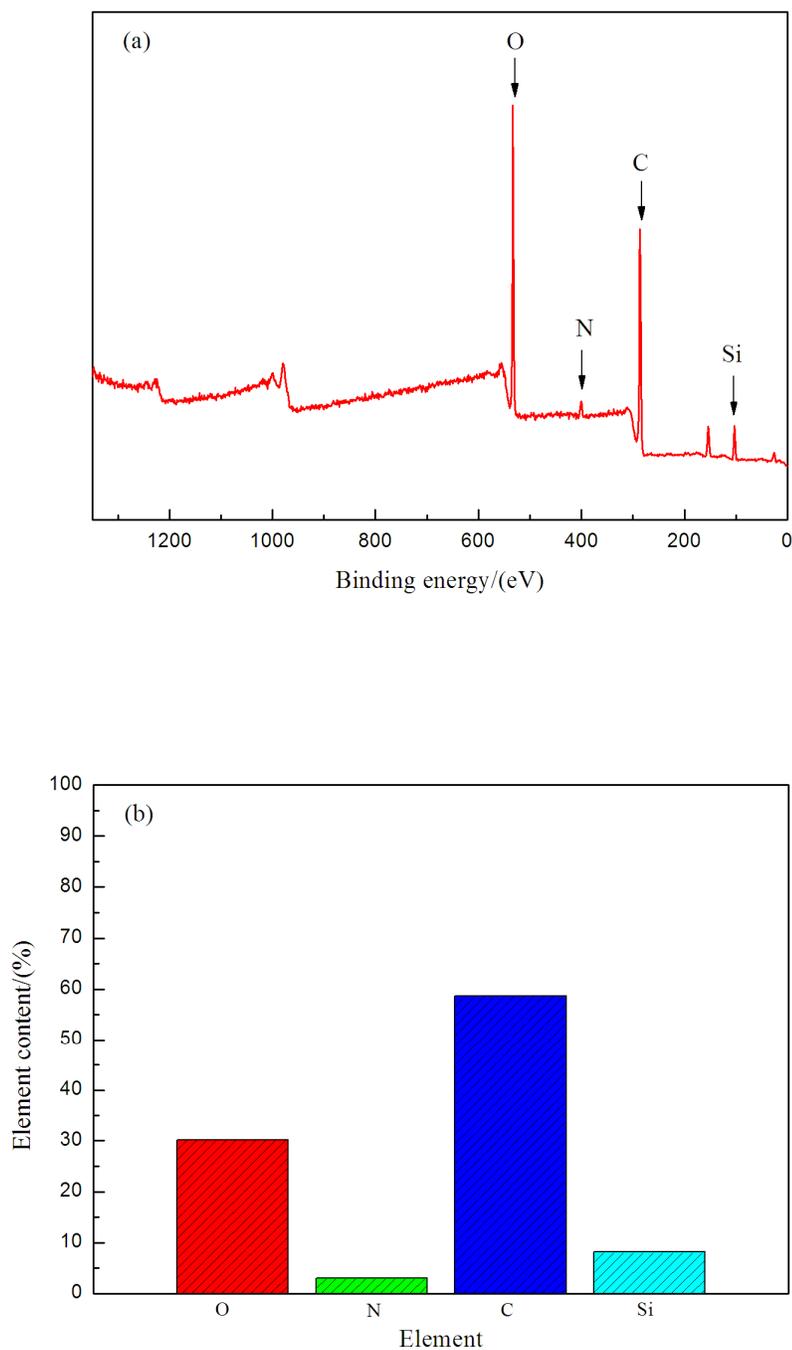


Figure 6. (a) XPS spectra of amino-functionalized graphene, and (b) content of various element of amino-functionalized graphene determined by XPS.

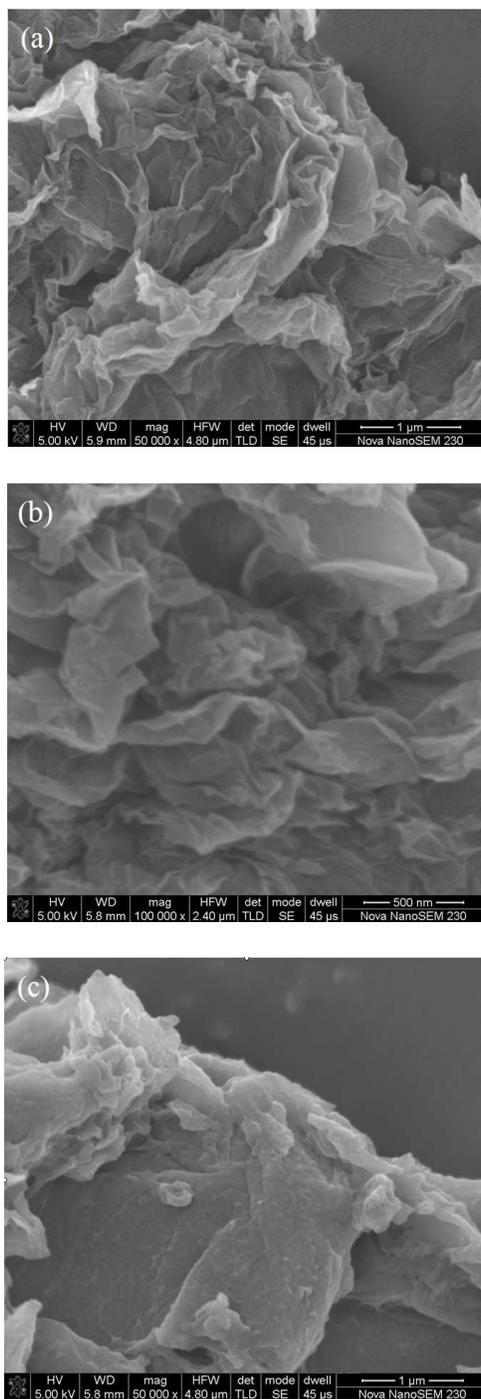


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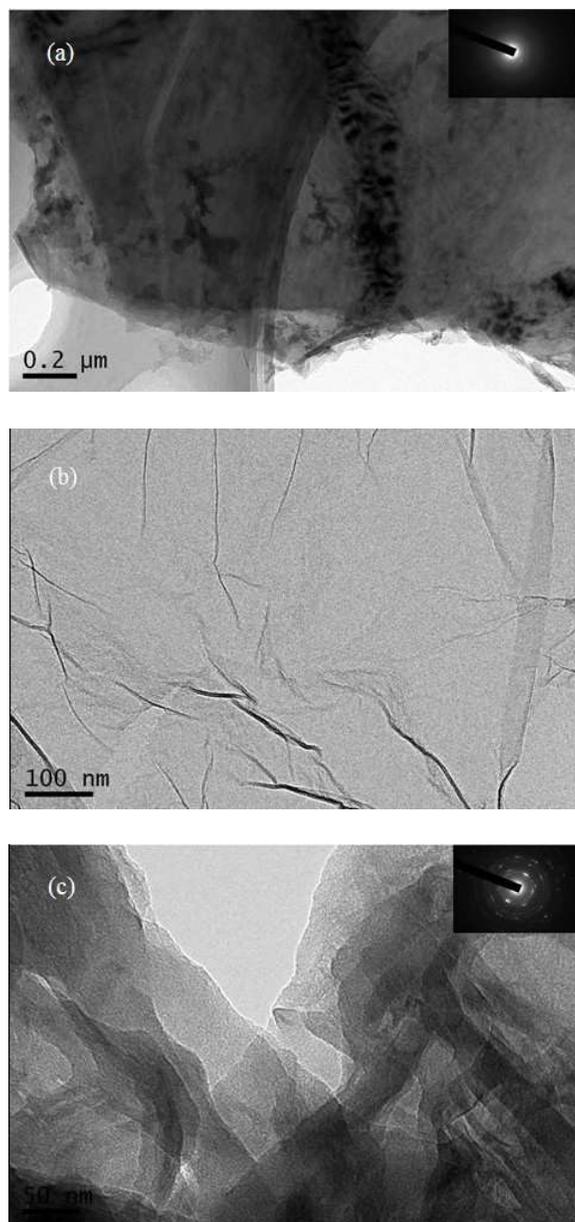


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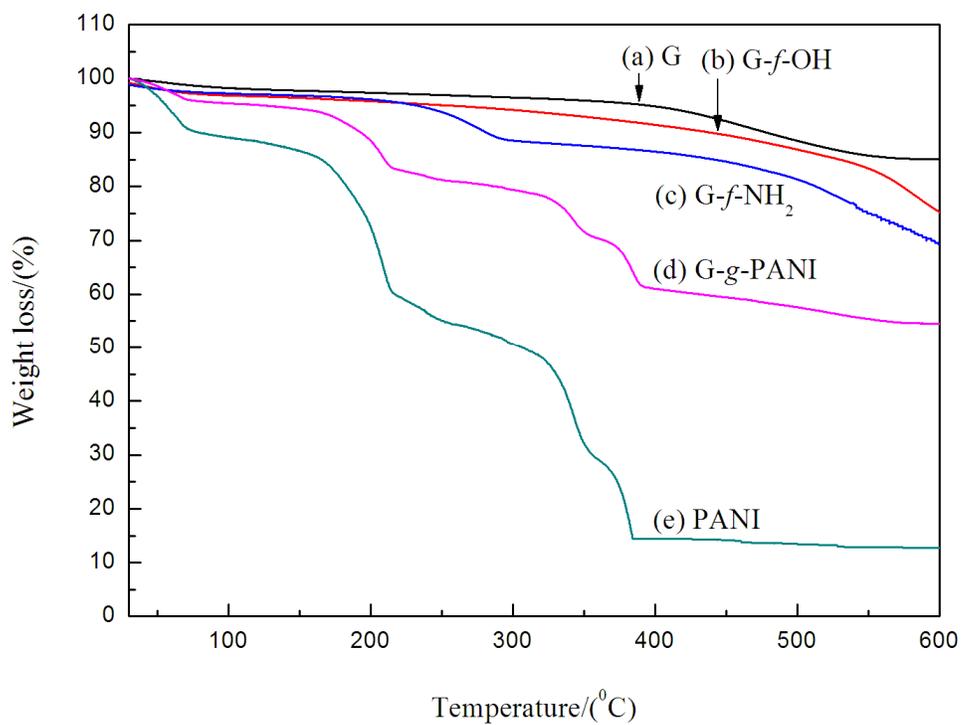


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Table 1 List of the conductivities of G-*f*-OH, G-*f*-NH₂, pure PANI, graphene and G-*g*-PANI hybrid composites

Materials	G- <i>f</i> -OH	G- <i>f</i> -NH ₂	Pure PANI	Graphene	G- <i>g</i> -PANI
Conductivity (S/m)	4.6	4.1	10.8	277.4	235.6