Amino Terminated Polyethylene Glycol Functionalized Graphene and Its Water Solubility

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ABSTRACT

A chemical modification process was developed to functionalize graphene with specific groups. Graphene oxide (GO) was successfully functionalized with thionyl bromide which can be used as precursors for further functionalization. Amino terminated-polyethylene glycol (PEG-NH$_2$) molecules were linked to single-layer graphene sheets through covalent bond. FT-IR, SEM and UV-vis spectroscopy techniques were used to characterize PEG modified graphene oxide and PEG modified reduced graphene oxide (PEG-RG). PEG-RG could disperse in water, tetrahydrofuran and ethylene glycol, with individual, single-layer graphene sheets spontaneously. The dispersion behavior of PEG-RG in an aqueous solvent has been investigated. A series of solutions of PEG-RG with concentrations of 0.001% to 1.5% were prepared and the PEG-RG dispersions exhibited long-term stability. In addition, a PEG-RG film with layered structure and high conductivity has been successfully prepared by filtration.

INTRODUCTION

Graphene has shown various unique properties, including superior mechanical strength and low density and high heat conductance [1, 2]. Many potential applications of graphene are based on its unique mechanical and electrical properties. Graphene oxide (GO) is water soluble with low conductivity and the reduced graphene oxide (RG) is a good conductivity with poor solubility in water. Generally, the solubility of GO in aqueous solution is because of its rich oxygen containing and hydrophilic groups, such as hydroxyl, epoxide and carbonyl groups. Upon a reduction process, most of the oxygen containing groups, hydroxyl, epoxide and carbonyl, will be totally removed and GO is converted to a rich π-conjugation graphene. The restoration of π-conjugation in graphene sheet can recover the conductivity of graphene but will scarify the solubility of graphene. RG is not compatible with other materials, such as most polymer matrices and limits its applications. To solve these problems, several techniques have been developed to modify the surface properties of RG and enhance its compatibility with other matrices and the solubility in aqueous and organic solvents[3, 4]. Potential techniques include

physically absorbed functional molecules onto graphene sheets, chemical covalent linked functional groups onto graphene surface [5, 6]. To date, the dispersion of RG in aqueous solvents has been accomplished via physically absorbed, aqueous soluble groups functionalized molecules on RG sheets with different molecules and polymers, but the presence of such stabilizers is not desirable for most applications. The dispersion behavior of as-prepared graphene oxide has remained largely unexplored.

In this report, we propose a new protocol to functionalize RG with amino-terminated poly (ethylene glycol) (PEG-NH$_2$). The detailed processes are illustrated in Figure 1. Polyethylene glycol molecules were linked to single-layer graphene sheets through covalent bonding. The as-prepared PEG-RG can disperse into individual graphene sheets in water spontaneously, forming a suspension with long-term stability. A series of solutions of PEG-RG with concentrations of 0.001% to 1.5% were prepared. In addition, a PEG-RG film with layered structure and high conductivity has been successfully prepared.
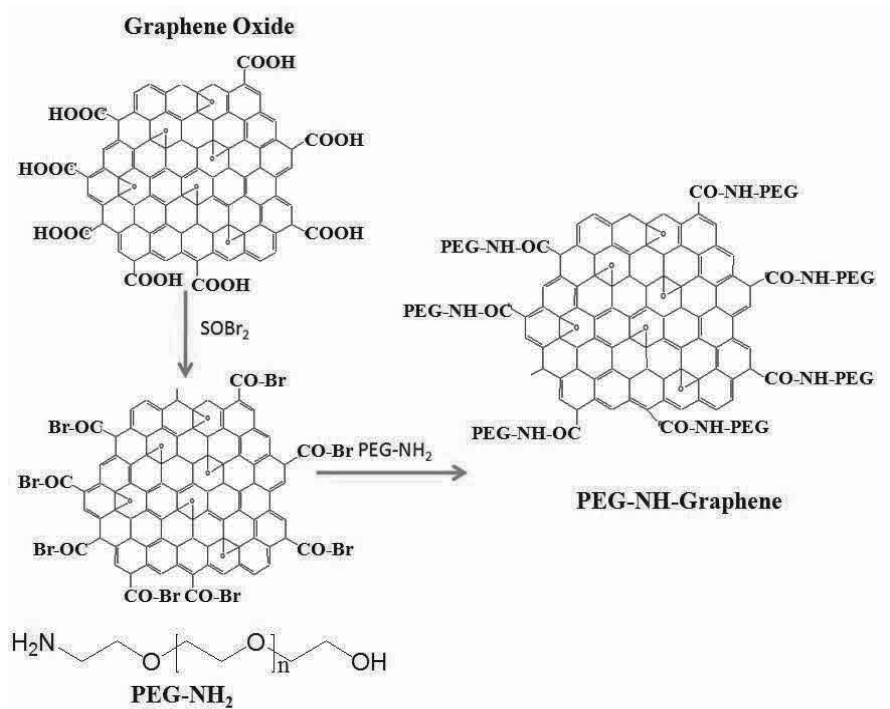

Figure 1 Chemical structure and scheme of the chemical modification process

EXPERIMENTAL DETAILES

Two types amino polyethylene glycols, O-(2-Aminoethyl) polyethylene glycol (MW~10000 and 5000) were purchased from Aldrich, and another type of O-(2-Aminoethyl) polyethylene glycol (MW: 3,000) from Fluka. The following reagents and solvents were used without further purification: hydrazine, thionyl bromide and triethylamino (Aldrich), sulfuric

acid, hydrogen chloride, sodium hydroxide, ethanol, methanol (Fisher). Graphene oxide and reduced graphene oxide were prepared by using Hummers method [5, 7].

The process to link PEG-NH2 onto graphene surface is demonstrated in Figure 1. Typically, 0.1g graphene was dissolved into 50ml SOBr$_2$, and this solution was refluxed at 80 °C for 24 hours under nitrogen atmosphere to yield GO-Br (Graphene-CO-Br). At the end of the reaction, excess SOBr$_2$ and solvent were removed by distillation and filtration, and GO-Br was mixed with 5ml of triethylamino, 0.2g of amino-PEG in 50ml DMF. The mixture was then refluxed at 130 °C for 36 hours. After the reaction finished, the solution was cooled and 300ml DMF was added to the above solution. Finally, the product was isolated by filtration on a polycarbonate membrane (0.2μm) and washed totally with DMS and DI water. The excess PEG-NH$_2$ were removed through five washing cycles, which included suspension, sonication, filtration, drying, and re-suspension of the solid in water. Finally, the PEG-GO were dried in a vacuum oven at 80 °C for 12 hours and then dispersed into 50ml DI water and reduced with hydrazine utilized by previous reports. Upon the reduction process, the color of the solution converts from a brown to black color. The product (PEG-RG) was obtained by filtration and washing with ethanol, water and HCl sequentially and dried in an oven for future use.

Nicolet 4700 Fourier transform infrared (FTIR) Spectrometers, (Thermo Fisher Scientific, USA), X-ray photoelectron spectroscopy (XPS, Surface analysis PHI5600, Physical Electronics, Inc.), Hitachi S-3400N SEM and Bruker X-flash x-ray microanalysis system, and UV-Vis spectrometry (Thermo Fisher Scientific, Evolution 300) were used to characterize the changes in chemical structure and surface morphology of the graphene after each surface treatment step. For the FT-IR (Perkin Elmer Spectrum One, USA) analysis, EDTA-RGO and EDTA-GO, along with GO and RGO, were separately pressed into a pellet together with potassium bromide and then scanned from 500 cm^{-1} to 4000 cm^{-1} at a resolution of 4cm^{-1}. The conductivity of EDTA-RGO film was tested with a Multi Height Microposition Probe with RM3-AR test unit (Bridge Technology).

RESULTS AND DISCUSSIONS

The FTIR spectra of the GO, Br-GO and PEG-RG are presented in Figure 2a, respectively. The presence of carboxyl groups was identified with the appearance of a peak at 3386cm^{-1}. This peak was observed in four graphenes. This evidence is also confirmed with the presence of peak at 1738cm^{-1}, the characteristic of C═O stretching vibrations from of the carboxylic and carbonyl group of graphene. It should be noted that this peak was observed from all four samples with almost the same intensity with minimal shift upon chemical modification process. This stable band also confirms that the carboxylic or carbonyl groups of graphene cannot be reduced to C-OH. The peak located at 1120 cm^{-1} could be ascribed to the epoxy group

on the graphene surface. Upon reduction with hydrazine, this peak disappeared, which confirms the reduction process can convert C-O-C on graphene oxide surface to π-conjugate. Upon modification with PEG, several new bands at 1090 cm^{-1}, 1440 cm^{-1}, 1700 cm^{-1} and 2917 cm^{-1} were observed. The presence of epoxy groups of PEG chain was confirmed by the appearance of a band at 1090 cm^{-1}. This band is observed on PEG-GO and PEG-RG samples only, with the same intensity and no shift upon chemical reduction process. The presence of two new bands at 2917 cm^{-1} and 1440 cm^{-1} are associated with the C-H symmetric and antisymmetric in CH_2 groups of PEG chains.

Additional evidence that PEG-graphene exhibits PEG groups on RG surface can be found in XPS spectra (Figures 2b and 2c). As shown in Figure 2b, the high resolution Br_{3d} XPS spectrum confirms the presence of bromide in Br-GO with a single Br_{3d} peaks at 71.3eV. On the contrary, the bromine of Br-RG is expected to be replaced by amino groups from NH_2-PEG on PEG-RG sample, and no significant indication of the presence of carbon linked bromine was observed in the spectrum of PEG-RG. Through the high resolution of XPS of C_{1s} of PEG-RG and GO (data not shown here), a stronger signal of oxygenated carbon signal at 288.4eV was observed from GO, this signal is weaker at PEG-RG and shifted to 284.8eV. These results confirm that the reduced process can remove most of the epoxy and hydroxyl groups. In addition, the signal of C_{SP2} carbon atoms increased at 284.3eV. These results, combined with FT-IR and UV-vis data, indicate the reduction of PEG-GO to PEG-RG and reflect the restoration of π-conjugation of graphene.
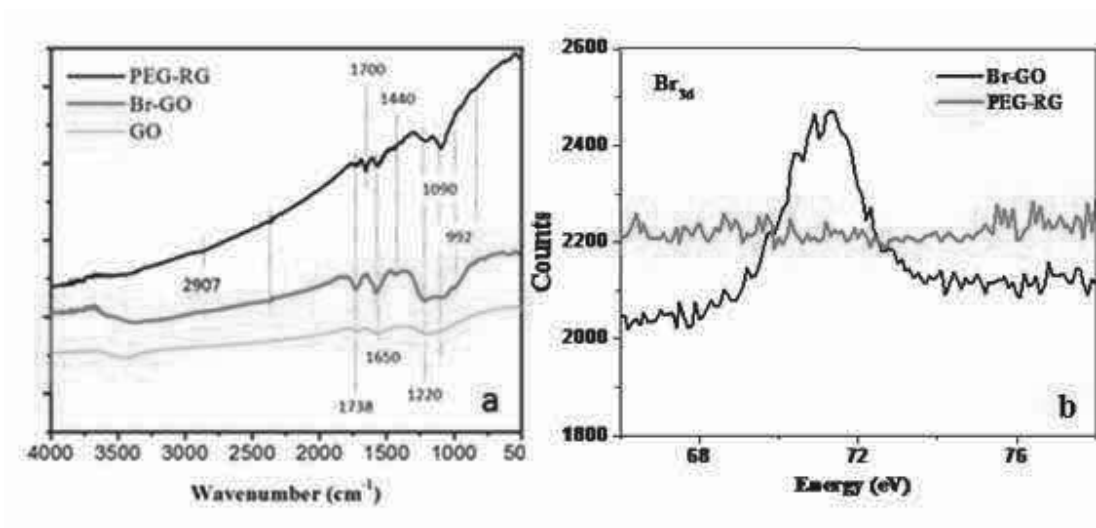

Figure 2 (a) FT-IR spectra of GO, PEG-GO and PEG-RG, (b) the high resolution of XPS spectra of Br_{3d} in Br-GO and PEG-RG

Figure 3a shows a typical SEM image of PEG-RG without sonication treatment, where the sample was prepared by drop-casting of 1% PEG-RG H_2O suspension (without sonication) on smooth gold surface. Figure 3b show a typical SEM image of single layer PEG-RG sheet on

an ultra-smooth gold surface, this sample was prepared by drop-casting of diluted PEG-RG H_2O suspension (with 1 hour sonication treatment). The dimensions of PEG-RG range from several hundred nanometers to several micrometers and graphene oxide sheets with lateral size up to 40μm were observed. PEG-RG appears transparent and is folded over on one edge, with isolated small fragments of graphene on its surface, and proves that water-soluble PEG-RG is similar to single graphene sheets peeled from pyrolytic graphite. Upon filtration, a PEG-RG dispersion through an anodic alumina or polycarbonate membrane, a flexible PEG-RG film with a well-packed layered structure and controllable thickness is fabricated. After peeling from the filter membrane, the electrical conductivity of the PEG-RG film, along with GO and PEG-GO films, were measured. As predicted, GO and PEG-GO films exhibit low electrical conductivity and can be attributed to the damage of π-electron conjugation system in graphene oxide sheets. On the contrary, the reduction process of GO had restored the π-electron conjugation system of graphene sheets and the electrical conductivity of PEG-RG film was recovered with an electrical conductivity up to 380 S/m. The measured electrical conductivity of PEG-RG film is lower than RG film but is higher than other chemical modified graphene.
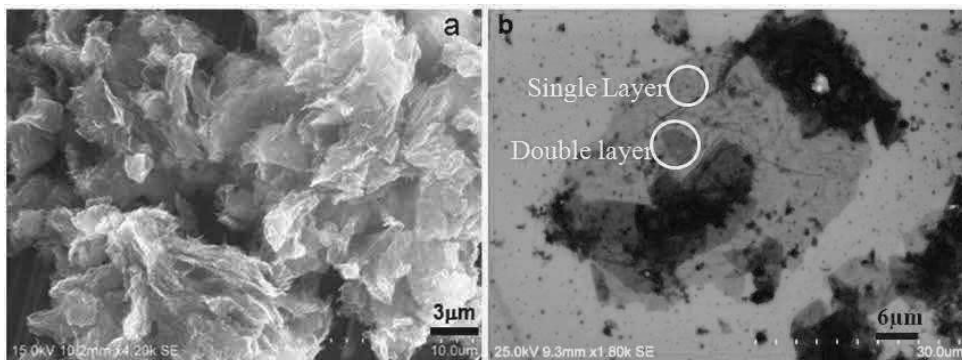

Figure 3. SEM image of PEG-RG sheets before (a) and after (b) sonication in water

Our main purpose is to investigate the solubility of graphene in various solvents via different modification techniques. Thus 1.0mg/ml water suspensions of GO, RG, PRG-GO and PEG-RG were prepared, respectively. Obviously, the GO water suspension was stable and the solubility of RG in water is very poor due to the agglomeration and poor hydrogen-bonding ability. A light brown color was observed from PEG-GO suspensions and this brown color was converted to a black color after PEG-GO was reduced to PEG-RG, confirming the restoration of the π-conjugation network within the graphene sheet structure. Both PEG-GO and PEG-RG exhibit good solubility in aqueous solutions and the solubility of PEG-GO is better than PEG-RG. Compared with RG, PEG-RG suspensions exhibit good solubility and stability and no phase separation or sedimentation occurs within three months. PEG-RG suspensions with concentrations varying from 0.01 % to 0.2% (wt/ml) were then prepared and the color of the solutions were found to increase linearly with concentration of PEG-RG (Figure 4a). All of above solutions were very stable and no sedimentation occurs up to several months. The stability

of PEG-RG solution enables us to investigate the UV-vis absorption properties of PEG-RG solutions. The solution of PEG-RG displayed a smooth curve with an absorption maximum at 260nm and tailed to 600nm (Figure 4b). The absorbance at 260nm is proportional to the concentrations of PEG-RG. In addition, a slight decrease of the solubility of PEG-RG compared with PEG-GO upon the reduction process was observed. This is understandable because of the poor solubility of RG in aqueous solutions. And we also find that the average molecular weight of amino-PEG had affected the solubility of PEG-RG.
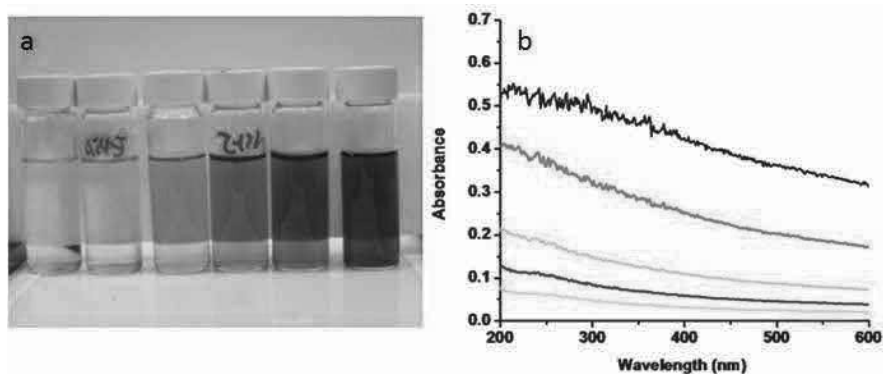

Figure 4. The photo images (a), and UV-vis absorption spectra (b) of a series of PEG-RG solution with different concentrations (0.01%, 0.02%, 0.05%, 0.1%, and 0.2%).

CONCLUSIONS

In conclusion, our results demonstrate the feasibility of combining conventional organic synthesis techniques with techniques for the modification of reduced graphene oxide. The technique developed here can be extended to synthesize various functionalized graphene by using other functional groups. The method also provides a general route for preparing solutions and conducting films based on functional graphene and seeks different applications of graphene-based materials. This result should facilitate the preparation of graphene derivatives or the development of graphene-based hybrid materials. We have further characterized the compatibility of PEG-RG with a series of polymer matrices.

ACKNOWLEDGMENT

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