Non-covalent functionalization of graphene sheets by sulfonated polyaniline†

Hua Bai, Yuxi Xu, Lu Zhao, Chun Li and Gaoquan Shi*

Received (in Cambridge, UK) 5th December 2008, Accepted 19th January 2009
First published as an Advance Article on the web 10th February 2009
DOI: 10.1039/b821805f

Graphene sheets were stably dispersed in water by functionalization with sulfonated polyaniline (SPANI), and the composite film of SPANI-functionalized graphene showed improved electrochemical stability and enhanced electrocatalytic activity. Functionalization and dispersion of graphene sheets are of crucial importance for their applications. Dispersion of graphene enables processing of this material by solvent-assisted techniques, such as layer-by-layer (LBL) assembly, spin coating and filtration. Soluble or dispersible graphene sheets are usually prepared by chemical modifications or non-covalent functionalizations. For example, reduction of graphene oxide modified by alkylamine produced stable dispersions of graphene sheets in organic solvents, and water-soluble graphenes were obtained by inducing carboxylic or sulfonate groups onto their basal planes. Non-covalent functionalization is considered to have less impact on the structure and properties of graphene. The reduction of graphene oxide in the presence of poly(sodium 4-styrenesulfonate) formed a stable aqueous dispersion of graphene sheets. We also found that pyrenebutyric acid could be used to non-covalently functionalize graphene sheets via strong π–π interactions between pyrenyl rings and basal planes of graphenes. Recently, it was reported that graphene nano-ribbons functionalized by conjugated polymer, potassium ions and 7,7,8,8-tetracyanoquinodimethane (TCNO) are also soluble in water or organic solvents.

In this communication, we report the non-covalent functionalization of graphene sheets by a conducting polymer, sulfonated polyaniline (SPANI, Scheme 1), to produce a water-soluble and electroactive composite. SPANI, with good air stability and electrochemical activity, is easily synthesized and has high water solubility. Furthermore, in neutral media, SPANI exhibits redox properties, while pristine polyaniline loses its electrochemical activity. Therefore, it is expected that SPANI can disperse graphene sheets via π–π interactions, and provide the resulting SPANI-modified graphene (SPANI/r-G) with unique electrochemical properties.

Graphene sheets were prepared by reducing exfoliated graphite oxide in the presence of SPANI. Typically, graphite oxide (GO) was synthesized from natural graphite through a modified Hummers method and SPANI was prepared by sulfonating polyaniline following a published procedure. To prepare SPANI/r-G, 36 mg SPANI was added into a 5 mL aqueous dispersion of graphite oxide (1 mg mL−1). Successively, 100 μL hydrazine was injected into the solution and the reaction was carried out at 90 °C for 24 h. Reduction of GO dispersion without any stabilizer led to the precipitation of graphite particles (Fig. 1, right), due to the rapid irreversible aggregation of graphene sheets. However, in the presence of SPANI, a homogeneous black dispersion was formed after the reduction (Fig. 1, left). The dispersion was stable and no obvious precipitates were observed after storing for two weeks or centrifuging at a speed of 8000 revolutions per minute (rpm) for 5 min. Furthermore, the dispersion remained stable when its pH was adjusted to 1–2 by adding 1.0 M hydrochloric acid. These results indicate that the reduced graphene oxide was well-dispersed by SPANI, mainly due to the strong π–π stacking between the backbones of SPANI and the graphene basal planes, and the electrostatic repulsion between the resulted negatively charged SPANI/r-G sheets.

The SPANI/r-G composites were characterized by scanning electron microscopy (Fig. S1†), Raman spectroscopy (Fig. S2†), X-ray diffraction (Fig. S3†) and X-ray photoelectron spectroscopy (XPS). Fig. 2 shows the C1s XPS spectra of GO and SPANI/r-G. The spectrum of GO (Fig. 2A) indicates the presence of 4 types of carbon bonds: C–C (284.8 eV), C–O (286.9 eV), C–O (288.1 eV), and O–C–O (289.3 eV). After reduction, the peaks associated with C–C or C–H (284.8 eV) became predominant, while the peaks related to the oxidized carbon species were greatly weakened. Furthermore, additional peaks assigned to C–S (285.5 eV) and C–N (286.1 eV) species of SPANI have appeared in the spectrum of SPANI/r-G. The successful reduction of GO was further confirmed by electric conductivity measurements. The conductivity of the composite film prepared by filtration was measured to be 0.3 S cm−1; and this value is close to those of the reduced GO sheets reported previously. It should be noted here that the content of SPANI in this film was fairly low because a large amount of SPANI was passed through the filtration membrane during filtration. The conductivity of SPANI/r-G composite film prepared by dropping casting was much lower (0.03 S cm−1) than that of the film obtained by filtration, because the SPANI component in the casting film was also

![Scheme 1](image-url)
reduced by hydrazine (the conductivity of hydrazine-reduced SPANI was measured to be only $3 \times 10^{-4} \text{ S cm}^{-1}$). However, the conductivity of this film was increased to around 0.2 \text{ S cm}^{-1} by oxidation with the aqueous solution of 1.0 M (NH$_4$)$_2$S$_2$O$_8$ and 1.0 M HCl. This phenomenon indicates that the SPANI component in the composite is electrochemically active.

Fig. 3 compares the AFM images of GO and SPANI/r-G nanosheets. The samples were prepared by depositing the corresponding dispersions on new cleaved mica surfaces and drying in air. As shown in Fig. 3A, the GO nanosheets have characteristic thickness of $\sim 1.2$ nm, indicating the full exfoliation of graphite oxide.$^5$ The thickness of a SPANI/r-G sheet was measured to be $\sim 2.6$ nm, which is much larger than the interplanar space of the natural graphite. Considering there exist unreacted functional groups in reduced GO,$^5$ possible multilayer adsorption of SPANI chains onto the graphene surface,$^6$ and the overestimate of sheet thickness in AFM measurements,$^6$ one may expect that these sheets (Fig. 3B) are uniformly graphene monolayers.

Polyaniline was reported to have good electrochemical catalytic activity towards various substrates, and a lot of work has been devoted to the electrochemistry of polyaniline-modified electrodes.$^{17}$ However, the electroactivity of polyaniline is strongly dependent on the pH value of electrolyte solution, and is greatly weakened in neutral solution. In contrast, SPANI can maintain its electroactivity in neutral or even basic media because of the self-doping effect.$^{18}$ Thus, it is expected that the composite material obtained would be applicable to the electrocatalytic reactions of biologically important molecules in neutral media.$^{19}$ To examine the viability of SPANI/r-G for electrocatalysis, the electrochemical properties of SPANI/r-G were studied using cyclic voltammetry. The SPANI/r-G- and SPANI-modified electrodes were prepared by dropcasting certain amounts of the corresponding dispersion or solution on glassy carbon (GC) electrodes (dried at 50 $^\circ$C), and the cyclic voltammograms (CVs) of these electrodes were recorded in 1.0 M H$_2$SO$_4$ and 0.1 M phosphate buffered solution (PBS, pH = 6.8), respectively. As shown in Fig. 4A, the CVs of both SPANI- and SPANI/r-G-modified electrodes in acidic electrolyte exhibited two pairs of redox waves, which are characteristic of polyaniline and related to the conversions between its different doping states. However, in the neutral media, only one pair of waves in the potential range of $-0.1$ to 0.1 V were observed in each CV, which was attributed to the oxidation of SPANI from insulating leucoemeraldine to conductive emeraldine (Fig. 4B).$^{18}$ The CV curves of SPANI/r-G in PBS were stable during repeated voltammetric scans. These results indicated that SPANI/r-G has good electroactivity in both acidic and neutral media.

It should be noted here that the CV wave current densities of SPANI/r-G composite modified electrode are much higher than those of SPANI-modified electrode in either acidic or neutral aqueous medium. This is mainly due to the loss of SPANI from the latter electrode surface. The dissolution and diffusion process of green SPANI near the electrode surface can be clearly observed when the electrode was immersed in PBS. It was also reported that SPANI-modified electrode was unstable and had to be stabilized by electrochemical copolymerization or by layer-by-layer deposition.$^{18,20,21}$ In this work, we found that the addition of graphene sheets could greatly improve the film-forming ability and the water resistance of SPANI. The dropcast film of SPANI/r-G is stable.
Fig. 5  Cyclic voltammograms of 10 mM ascorbic acid at SPANI (dashed line), SPANI/r-G (solid line) modified and bare GC electrode (dotted line) in 0.1 M PBS (pH = 6.8). Potential scan rate = 50 mV s⁻¹.

in aqueous media, possibly due to the strong interactions between SPANI chains and the basal planes of graphene and also the aggregation of graphene sheets, which resulted in the formation of a crosslinked 3-dimensional network. This property enables us to modify electrodes by simply dropcasting the SPANI/r-G aqueous dispersion.

The improved water resistance of the SPANI/r-G composite film makes it more suitable for the electrode modification with respect to pure SPANI. Fig. 5 shows the CVs of 10 mM ascorbic acid at SPANI, SPANI/r-G modified and GC electrodes in 0.1 M PBS (pH = 6.8). A relatively narrow anodic wave (E_p - E_{p/2} = 0.095 V) was observed on the CV of SPANI/r-G modified electrode at around 0.10 V (E_p, E_{p/2} is the half-wave potential). In comparison, the anodic wave of ascorbic acid at bare GC electrode is broader (E_p - E_{p/2} = 0.168 V) and at a much higher potential (0.44 V). These results indicated that the SPANI/r-G film increased the electron transfer rate and improved the reversibility of the ascorbic acid oxidizing reaction. The decrease of oxidation potential of ascorbic acid in neutral media is very important for biosensing in real sample solution, because the oxidations of other oxidizable species at high potentials can be avoided. A weak anodic wave around 0.10 V was also observed from the CV of the SPANI-modified electrode, indicating the electrocatalytic activity of the composite material is attributed to its SPANI component. The weak wave current originates from the dissolution of the polymer.

In summary, non-covalent functionalization of graphene sheets by SPANI makes the SPANI/r-G soluble in water at high concentration (>1 mg mL⁻¹). The composite film of SPANI/r-G exhibits high conductivity, good electrocatalytic activity and stability. This composite material has potential applications in electrocatalysis and electrochemical sensing.

This work was supported by the National Natural Science Foundation of China (50533030, 50873052, 20774056 and 20604013).

Notes and references