

A novel strategy for making poly(vinyl alcohol)/reduced graphite oxide nanocomposites by solvothermal reduction



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ABSTRACT

Poly(vinyl alcohol) (PVA)/reduced graphite oxide (rGO) nanocomposites were synthesized by solvothermal reduction of graphite oxide (GO) in the presence of PVA. The solvent, the mixed dimethyl sulfoxide (DMSO)-dimethylformamide (DMF), could act not only as a reducing agent but also as a good stabilizer, which achieved effectively reduction of GO in the PVA matrix and avoided the agglomeration of rGO during reduction. A 53.0% increase in tensile strength and 52.6% improvement of Young's modulus were achieved by addition of 3 wt% of rGO. Furthermore, a significant improvement of thermal stability was observed for the PVA/rGO nanocomposites.

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1. Introduction

Graphene, as a single layer of carbon atoms in a two-dimensional honeycomb crystal lattice, is predicted to have a range of unusual properties. Theoretical [1] and experimental [2] results show that single-layered two-dimensional graphene sheets are the strongest materials developed thus far. Graphene nanosheets also have high thermal conductivity and high specific surface area [3]. Owing to these outstanding properties, graphene and its derivatives (graphite oxide (GO)/reduced graphite oxide (rGO), functionalized graphene, etc.) have been widely studied in various fields including energy devices [4–9], conductive materials [10,11], drug delivery [12,13] and polymer nanocomposites [14–16].

In recent years, polymer/graphene nanocomposites have attracted a tremendous amount of attention to obtain high-performance light-weight materials. To achieve maximal mechanical enhancement, the manufacturing of such nanocomposites requires that the graphene is dispersed homogeneously or best at the molecular level in the matrix and the external load is efficiently transferred via a strong interaction at the interface between the graphene and the matrix. Unfortunately, graphene suffers from aggregation resulting from strong Van der Waals attractive forces, which makes dispersion and exfoliation difficult. In this respect, since GO can undergo exfoliation completely in water, dimethyl-sulfoxide (DMSO) and dimethylformamide (DMF), it is possible to achieve a truly molecular-level dispersion of graphene oxide in the polymer matrix if the

solvent could dissolve the polymer matrix. More important, exfoliated graphene oxide nanosheets can be readily reduced chemically to graphene nanosheets by a variety of common reagents [17–19]. On the other hand, these oxygen-containing groups impart GO sheets with the function of strong interaction with polar polymers, which makes hydroxyl-rich poly(vinyl alcohol) (PVA) become the most suitable matrix [20,21].

Nowadays, two typical strategies have been reported to address these issues for preparing PVA/graphene nanocomposites. In the first strategy, PVA/graphene nanocomposites were prepared by one-step reducing GO in PVA aqueous solution using toxic hydrazine as reducing reagent [22–24]. For example, Yang et al. [22] prepared PVA/rGO nanocomposites by this method with a 32% increase in tensile strength and a 16% improvement of Young's modulus at a loading of 3.5 wt% rGO. The result indicated that the rGO was dispersed well on a molecular level and aligned in the PVA matrix. While in the second strategy, PVA/graphene nanocomposites were obtained by two steps. PVA/GO films, as the precursor, were firstly obtained by dispersing GO in PVA aqueous solution due to the strong interaction between oxygen groups on GO sheets and hydroxyl group on PVA chains, then reduced by immersing the films into reductant solution (the mixed solution of NaOH and Na₂S₂O₄) at 60 °C for 1 h [25]. A 40% increase in tensile strength and 70% improvement in elongation at break have been obtained with only the addition of 0.7 wt% of rGO. Though this method had successfully prepared PVA/rGO nanocomposites, it was complicated and the reducing agent in PVA/GO films could not be removed completely. For the above reasons, it is highly desirable to develop a simple and efficient approach for preparing PVA/rGO nanocomposites.

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In this study, we reported a novel strategy for making well-dispersed PVA/rGO nanocomposites by solvothermal reduction of GO in the presence of PVA. rGO sheets could be prepared by solvothermal reduction of well-dispersed GO in solvent (DMF, DMSO and N-methyl-2-pyrrolidone) in previous work [26–28]. The PVA/rGO films were obtained by a simple one step: GO was dispersed in PVA solution (the mixed solvent DMSO-DMF), then reduced at 100 °C. Our method had several advanced features that made it particularly attractive for polymer/graphene nanocomposites: (1) it was simple and efficient, (2) the solvent acted not only as a reducing agent but also as a good stabilizer, which achieved effectively reduction of GO and avoided the agglomeration of rGO during reduction, (3) this method opened a new way to produce polymer/graphene nanocomposites.

2. Experimental details

2.1. Materials

Graphite powder was purchased from Nanjing XF Nano Material Tech Co., Ltd. PVA was 99% hydrolyzed with an average polymerization degree of 1700 (SINOPEC Sichuan vinylon works) and used as received. Potassium permanganate (KMnO_4), sulfuric acid (H_2SO_4 , 98%), hydrogen peroxide (H_2O_2), sodium nitrate (NaNO_3), DMF and DMSO were purchased from Aladdin Chemical Co., Ltd. The materials were directly used without further purification. All the water used was deionized.

2.2. Preparation of GO and rGO

GO was prepared according to Hummer's method [29]. Briefly, Graphite (2 g) was mixed with NaNO_3 (1 g) and H_2SO_4 (46 ml) at 0 °C, then KMnO_4 (6 g) was slowly added maintaining the temperature below 5 °C. The cooling bath was removed and the suspension was heated to 35 °C and maintained for 30 min. Then, 100 ml of water was slowly added and the temperature was controlled lower than 100 °C. After 1 h, the mixture was further diluted with 280 ml of water, treated with 50 ml of 5% H_2O_2 , filtered and washed with hot water. Finally, the GO was obtained after drying by vacuum.

rGO was obtained via solvothermal reduced from GO. GO was dispersed in the mixed solvent DMSO-DMF ($v\text{DMSO} : v\text{DMF} = 2:1$) in a concentration of about 0.6 mg ml^{-1} to create a yellow-brown dispersion by sonication for 30 min. Then the reduction was carried out at 100 °C for 24 h, rGO was finally obtained after filtered and dried at 60 °C for 24 h in a vacuum oven.

2.3. Preparation of PVA/rGO films

PVA/rGO nanocomposites were prepared as follows: GO was dispersed in 54 ml of the mixed solvent ($v\text{DMSO} : v\text{DMF} = 2:1$) upon sonication for 30 min. 3 g PVA was added into the GO dispersion, then heated at 100 °C for 24 h with mechanical agitation. The blending was cast into glass dishes and kept at 40 °C for film formation until its weight equilibrated. The weight contents of rGO in the nanocomposite films described above were controlled to be 0.5, 1, 2 and 3 wt%.

2.4. Characterization and measurements

UV spectra were measured by UV-1800 (Beijing Purkinje General Instrument Co., Ltd.). Transmission electron microscopy (TEM) was performed with a Tecnai G2 F20 S-TWIN electron microscope operating at an accelerating voltage of 100 kV. Fourier transform infrared spectra (FTIR) characterizations were performed at

ambient temperature with a spectrometer (Nicolet 6700), which is equipped with diffuse reflectance accessories. Wide-angle X-ray diffraction (XRD) pattern of the samples were obtained with X' Pert Pro X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$) under a voltage of 40 kV and a current of 40 mA. Samples were scanned over the range of diffraction angle $2\theta = 1\text{--}50^\circ$, with a scan speed of $0.5^\circ \text{ min}^{-1}$ at room temperature. Microscopic morphology observations were conducted on a JSM-7500 F scanning electron microscopy (SEM) under an acceleration voltage of 5 kV. The samples were fractured in liquid nitrogen and gold-sputtered prior to observation. The thermogravimetric analysis (TGA) was performed in a TA-2000 thermo-analyzer instrument (TA Co., USA). The samples were dried under vacuum before the experiments and then placed in a platinum pan. The loss of weight was monitored from 40 to 600 °C at a heating rate of $10^\circ \text{ C min}^{-1}$ under a nitrogen flow. The mechanical properties of PVA/rGO nanocomposite films were measured according to the standard of GB/T 1040.3-2006 [30] with a universal tensile testing machine (Instron 5567) at a crosshead speed of 50 mm min^{-1} . The reported values were calculated as averages over five specimens for each group of specimen.

3. Results and discussion

3.1. Solvothermal reduction of GO

Fig. 1 showed UV-vis absorption spectra of GO dispersions as a function of the reaction time upon heating at 100 °C. As seen in Fig. 1, the color of dispersion changed from yellow to black gradually over a period of 4 h and was maintained with a further increase of time. Meanwhile, the corresponding absorption of the dispersion increased rapidly with the reaction time and red shifted a little, signaling the conversion of graphene oxides into rGO sheets and the restoring of the electronic conjugation within the rGO sheets [31,26]. Nevertheless, little change in the absorption of the dispersion could be observed after 24 h, revealing that the reaction was completed within 24 h. In addition, no agglomerate could be observed for all of the dispersions (inset image in Fig. 1) during the heating process, suggesting that the mixed solvent could behave as an effective stabilizer for rGO sheets.

X-ray diffraction determined the changes of interlayer distance of nanosheets shown in Fig. 2. The characteristic XRD diffraction peak of pure GO sheets appeared at $2\theta = 10.4^\circ$ with a d-spacing of 0.78 nm. It was significantly larger than that of pristine graphite ($\sim 0.34 \text{ nm}$), due to the intercalating oxide functional groups, such

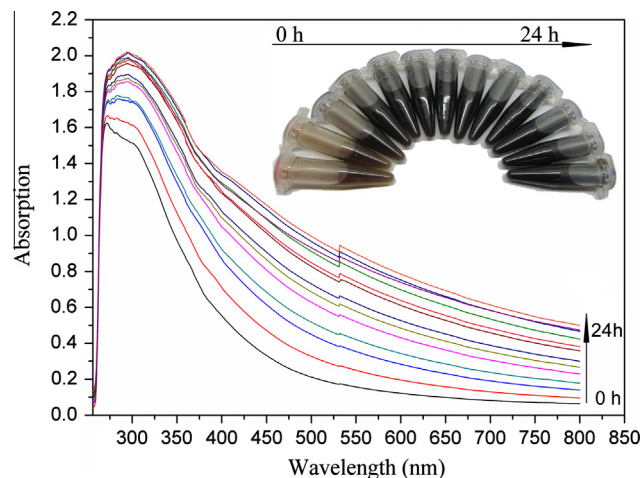


Fig. 1. UV-vis absorption spectra of GO dispersions in mixed solvent as a function of the reaction time upon heating at 100 °C (one assay per 2 h). Inset: the corresponding photographs.

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