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Fabrication, optical and electrical properties of solvethermal reduced graphene oxide/polyimide composites by *in situ* polymerization

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ABSTRACT

Solvothermal reduced graphene oxide (SRGO) suspensions in dimethylacetamide (DMAC) are facilely prepared by a solvothermal process. Then, SRGO/polyimide (PI) composites are efficiently prepared by *in situ* polymerization and finally cured at 300 °C for 2 h. Optical, dielectric and electrical properties are carefully evaluated by the optical transmission, dielectric constants (ε) and dielectric loss factors, conductivity, etc. The SRGO/PI composite film with 0.5 wt% SRGO sheets exhibits the obvious optical absorption in region of 0.5–2.4 μm and the higher emissivity in region of 6–24 μm. Moreover, the dielectric constants and resistivity of SRGO/PI composites display an obvious decrease from $\varepsilon = 4.0$ to $\varepsilon = 3.0$ and from 10^{14} to $10^{6}\ \Omega$ cm, respectively. This approach would supply a potential revolution to improve optical and electrical properties of SRGO/PI composites.

1. Introduction

Graphene sheets usually exhibit the excellent mechanical strength, optical and electric conductivities, due to the two-dimensional carbon atomic structure, which have been wildly applied in photonic devices, electric materials and ultra-high strength films [1]. Up to now, a large number of methods have been reported to prepare the graphene based composites, such as solution and melt mixtures [2], layer-by-layer assembly [3], and *in situ* polymerization [4].

Recently, preparation and properties of the high performance graphene based polyimide (PI) composites have been attracted the more and more attentions [5–11]. Wang et al. used amino (-NH_2) functionalized graphene oxide (NGO) sheets as the enhanced materials to prepared the ultrahigh strength and low dielectric constant NGO/PI composites by *in situ* polymerization [12]. Furthermore, a two-stage process, which was a solution blending of CMG and oligomers under the compression moulding, was also utilized to fabricate the chemically modified graphene (CMG)/PI composites [13]. These GO/PI composites exhibited the good interactions between functionalized graphene oxide (GO) sheets and PI molecules.

However, reduced graphene oxide (RGO) sheets are hard to directly disperse in the optimal solvents of polyamic acid (PAA) and PI resin, i.e. dimethylacetamide (DMAC), *N*-methylpyrrolidone (NMP) [14–16]. Meanwhile, the chemically reduced GO sheets only present the weaker interactions with PI molecules and exhibit the seriously aggregated tendency in PI matrix, which would be limited to obtain the high performance RGO/PI composites and develop their applications [17].

In this paper, we design an effective route to prepare the high performance **s**olvothermal reduced graphene oxide (SRGO)/PI composites. Firstly, graphite oxide is effectively prepared by a modified Hummers method. GO sheets could be homogeneously dispersed in DMAC by ultrasonic treatment with a frequency of 40 kHz for 1 h. Then, we prepare SRGO sheets suspensions in DMAC under a solvothermal treatment at 180 °C for 24 h. SRGO/PI composites could be fabricated by *in situ* polymerization and thermal treatment at 300 °C for 2 h. In this route, the transformation from GO to SRGO sheets is more effective and the dispersity of SRGO sheets in PI matrix is more homogenous. Finally, the optical and electric properties of SRGO/PI composites are carefully investigated by dielectric analyzer and optoelectronic measurements. We believe this route is a promising preparation method of SRGO based composites, which would be intensively applied in the solar cells, absorbing light films, electric devices and transistors [18,19].

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2. Experimental sections

2.1. Preparation of graphite oxide

Graphite oxide was prepared by modified Hummer's method as reported [20]. Firstly, 5 g natural graphite powders were put into a three neck flash under the ice-water bath condition. We submersed a mixture of 100 mL H_2SO_4 and 1.5 g $NaNO_3$ into the three neck flash. While stirring for 30 min, we put $KMnO_4$ to this mixture solution and rose the temperature to 35 °C. When the stirring was completed of the hybrid mixture, we added 150 mL of de-ionized water into the three neck flash and heated it to 98 °C. The reaction of the mixture took 1 h; whereas, this solution was cooled to approximately 40–50 °C in which dissolved most of the Mn^{2+}. We added 14 mL of H_2O_2 (30%) into the solution, expelling the impurity component. We washed the solution three times and naturally dried at normal temperature and pressure allowing the graphite oxide to be prepared. All the reagents were bought from Chinese Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation of SRGO suspensions in DMAC by solvothermal process

The homogeneous SRGO suspension in DMAC was prepared by a facile solvothermal route, which was described as this process: 0.4 g graphite oxide was added to the flask containing 100 mL of DMAC. We kept mechanically stirring for 10 min, where GO sheets were steadily dispersed in DMAC after sonication for 120 min; whereas, the transform GO suspension was transferred into a Teflon-lined autoclave. The autoclave was sealed and treated at 180 °C for 24 h and naturally cooled until the autoclave reached room temperature. Finally, the well-dispersed SRGO suspensions was obtained.

2.3. Preparation of SRGO/PI composites

In order to prepare SRGO/PI composites, polyamic acid (PAA) was synthesized in the as-prepared SRGO suspensions by *in situ* polymerization from the monomers of 4,4′-oxydiphenylamine (ODA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA). All monomers were purified by recrystallization and thermal treatment at 150 °C for 3 h under the vacuum condition. Using nitrogen (N_2) as a protecting gas, 6.40 g of ODA and 4 g of BTDA were added into a three-necked flask. The uniform SRGO/PAA solutions with different SRGO contents, i.e. 0.25 wt%, 0.5 wt%, 1 wt %, 1.5 wt%, 2 wt and 3 wt%, were achieved by sonication and stirring for 5 h. To fabricate SRGO/PI composites, the complex solutions were coated on a clean glass plate and treated in 60 °C for 3 h and 100 °C for 1 h, for removing the DMAC solvent. Then, the products were cured at 200 °C for 2 h and 300 °C for 2 h. The high performance SRGO/PI composites were obtained after these two stages.

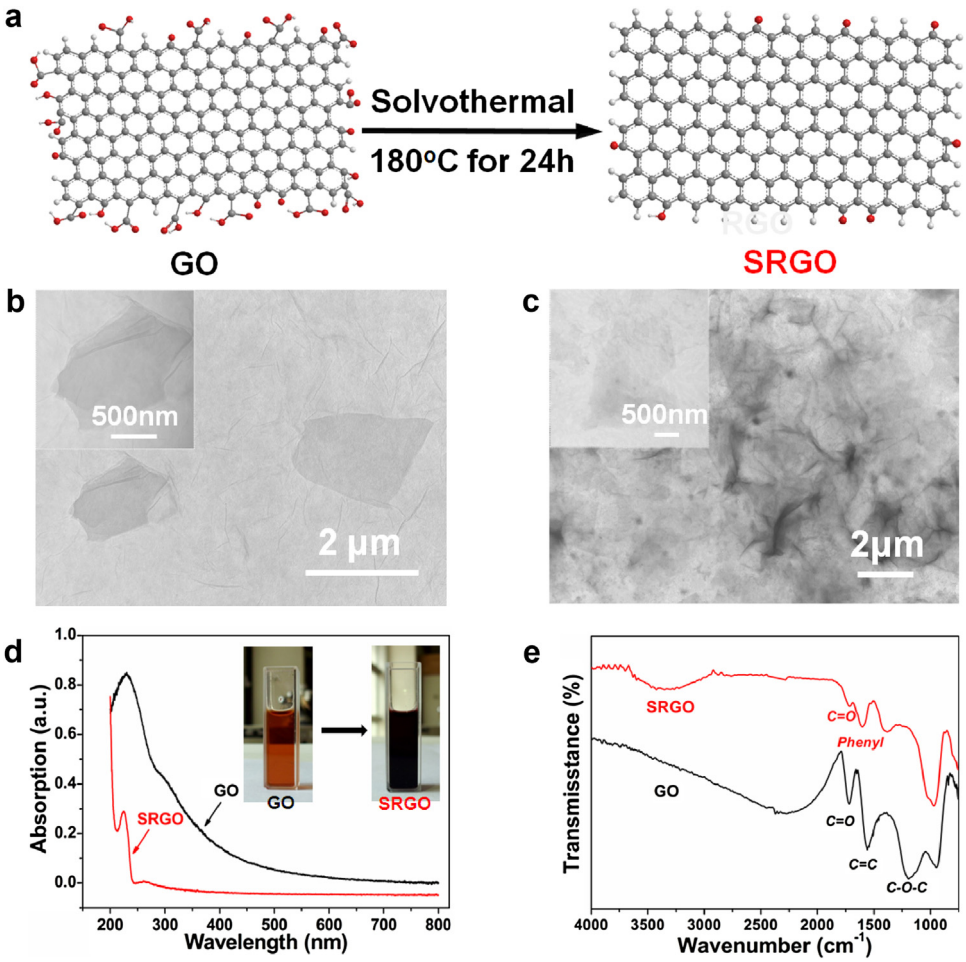

Fig. 1. (a) Schematic illustration to fabricate the SRGO sheets by solvothermal treatment, (b) and (c) the TEM photographs of the GO and SRGO sheets, the inserts are respectively their high-magnified photographs, (d) UV–vis spectra of GO and SRGO sheets, the inserts are digital photographs of the GO and SRGO samples, (e) FT-IR spectra of the GO and SRGO sheets.