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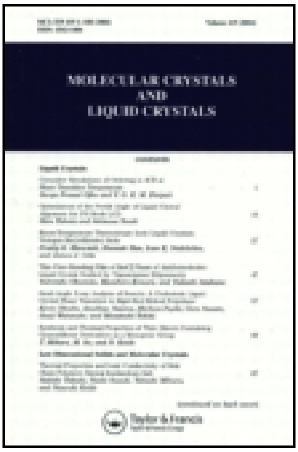

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Synthesis of Reduced Graphene Oxide Functionalized with Poly (o-anisidine) through in-situ Oxidative Polymerization

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The reduced graphene oxide functionalized with poly (o-anisidine) (RGO/POA) nanohybrids were synthesized through an in-situ oxidative polymerization in the presence of RGO. The formation of the graphene and its composites were confirmed by Fourier transform infrared spectroscopy, X-ray diffraction, thermogravimetric analysis and ultraviolet–visible spectroscopy techniques. Scanning electron microscopy was used to characterize the morphology of the nanocomposites which showed the uniform distribution of RGO sheets within the POA matrix. Furthermore, the X-ray photoelectron microscopy results showed the reduced oxygen content and N1s peak of the composites which confirmed the reduction reaction and presence of adsorbed POA chains on the surface of the RGO. The incorporation of RGO exhibited profound effect on the thermal stability of the POA chains. The enhanced thermal stability implies a synergistic effect between two components.

Keywords Chemical reduction; conducting polymer composites; oxidative polymerization; poly (o-anisidine); reduced graphene oxide

Introduction

Conducting polymers (CPs) have attracted a great deal of interest owing to their unique morphologies, excellent conducting and electrochemical properties [1]. These unique properties of CPs have been used in wide range of applications including light emitting diodes, photovoltaic devices, biosensors, transparent and conductive films [2–5]. Especially, CPs have been regarded as promising pseudocapacitive materials in energy storage devices [6,7]. A number of CPs such as polypyrrole (PPy), poly (3,4-ethylenedioxthiophene) (PEDOT), and polyaniline (PANI) have been synthesized and widely studied [8,9]. Among various CPs, PANI derivatives are one of the most extensively investigated polymers due to their good electrical conductivity, high environmental stability, and ease of synthesis through chemical and electrochemical methods [10]. However, the poor solubility in aqueous and organic solvents which further limits their use in many potential applications [11]. To circumvent this problem, numerous substituted derivatives such as alkyl, alkoxy and other substituents along with the polymer backbones have been developed.

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On the other hand, the composite materials based on coupling of CPs and carbon nanostructures such as graphite, carbon black/nanofiber/nanotube, have shown that they possess properties of the individual components with a synergistic effect [12,13]. In particular, graphene, a new carbonaceous material with two-dimensional (2D) nanostructure, has attracted great attention both in fundamental science and applied research [14]. Owing to its exceptional thermal stability, optimal mechanical stiffness, excellent electronic properties and electrical conductivity, graphene can be widely used in the applications of solar cells, lithium batteries, supercapacitors, biosensors and transparent conductive electrodes [15]. By far, numbers of materials, consisting graphene and CPs such as graphene/PPy, graphene/PANI, graphene/PEDOT etc. have been prepared.

In this paper, we report a simple method for the fabrication of poly (o-anisidine) functionlized reduced graphene oxide (RGO/POA) composites by in-situ chemical oxidative polymerization using ammonium persulfate as oxidant. The structure, morphology and thermal property of the composites were discussed in detail based on the results from FTIR, FESEM, XPS and TGA. The main objective of the present work is to prepare conducting graphene/poly (o-anisidine) composites as a high performance electrode material for energy storages devices.

Experimental

Materials

Pristine graphite was purchased from Sigma Aldrich. o-Anisidine (99%, Aldrich) was distilled twice under vacuum, stored in the dark and at low temperature prior to use. All other chemicals (analytical grade) were obtained from Junsei chemicals and used without further purification.

Preparation of RGO

First, the graphite oxide (GO) was prepared from natural graphite using a modified Hummer's method [16]. 1 g of graphite powder was mixed with 1 g of $NaNO_3$ in 48 mL of 98% H_2SO_4. 6 g of $KMnO_4$ was slowly added into the mixture under stirring. The mixture was stirred in an ice bath for 90 min and subsequently in a water bath of 35°C for 2 h. Then, 40 mL of DI water was slowly dropped into the mixture over a period of 30 min. The temperature of the mixture rose to around 90°C during the water addition. Finally, 100 mL of DI water was added into the mixture, followed by the addition of 10 mL of 30% H_2O_2 solution. The sediment in the mixture was collected by centrifugation. It was repeatedly rinsed with 5% HCl solution and successively with DI water. Finally, the as-obtained GO was dried in a vacuum oven at 50°C for 24 h. The reduction of GO was carried out as follows. 0.5 g of GO was dispersed in 100 mL of DI water and ultrasonicated for 1 h. Then, 5 mL of hydrazine monohydrate was added and the solution was heated in an oil bath at 100°C for 24 h. The reduced GO was gradually precipitated out as a black solid. This product was isolated by filtration and washing copiously with water. The obtained RGO was dried in a vacuum oven at 50°C for 24 h.

Synthesis of RGO/POA Composites

Briefly, 0.2 g of RGO was dispersed in 20 mL of 1.0 M HCl containing 0.5 g of o-Anisidine and ultrasonicated for 30 min. Then, 2.49 g of APS in 20 mL of 1.0 M HCl solution was slowly added dropwise to the above suspension and the reaction mixture was stirred at

0–5°C for another 24 h. The product was collected by filtering and washing the precipitate with methanol and deionized water, and dried in a vacuum at 60°C for 24 h. For comparison, pure POA was synthesized following the same procedure without RGO.

Characterization

Fourier transform infrared (FTIR) spectra were obtained on a Perkin–Elmer FTIR spectrometer in the range from 4000 to 400 cm^{-1} using KBr pellets. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a ESCA 2000 XPS (Thermo VG Scientific) XPS spectrometer with a Mg (Kα) X-ray source. Thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer Pyris 1 TGA at a heating rate of 10°C/min under nitrogen flow. Field emission scanning electron microscopy (FESEM) images were obtained with a Hitachi, JOEL JAM-6700F microscope (Japan). X-ray diffractograms (XRD) patterns were obtained on a Rigaku diffractometer using Ni-filtered Cu Kα radiation ($\lambda = 0.15406$ nm) operating under a voltage of 40 kV and a current of 40 mA. UV–Vis absorption spectra were recorded on a Shimadzu UV-2550 double-beam spectrophotometer in the range of 200–800 nm.

Results and Discussion

The molecular structures of the resulting RGO/POA composites were characterized by using XRD and FTIR spectroscopy. The XRD patterns of the pristine graphite, GO, RGO/POA composites and neat POA are displayed in Fig. 1. The neat GO exhibits a diffraction peak at $2\theta = 10.9°$, corresponds to the diffraction of its (0 0 2) planes with the basal spacing of 0.959 nm. After reduction, the original diffraction peak of GO disappears and a small peak is detected at $2\theta = 26°$, suggesting the reduction of GO. The XRD pattern of neat POA displays the broad diffraction peaks at 2θ values of 7.9° and 24.6°, which are ascribed to the periodicity perpendicular to the polymer chains of POA. However, in the case of RGO/POA composites, the diffraction pattern shows the broad band in the range from 15–27°, which may be attributed to the characteristic peaks of POA and RGO sheets.

As shown in Fig. 2, the FTIR spectrum of GO displays a strong band at 3410 cm^{-1} is assigned to the O—H stretching vibration. In addition, the characteristic bands at 1730,

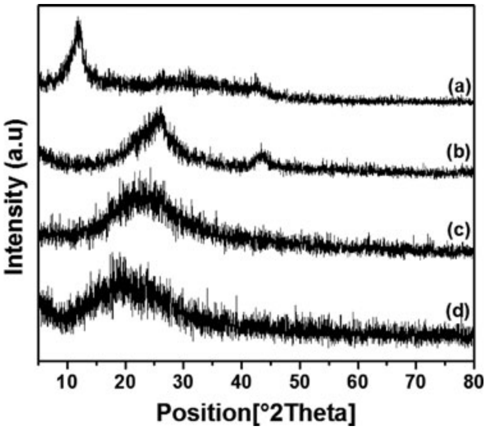

Figure 1. XRD patterns of (a) GO, (b) RGO, (c) RGO/POA composites, and (d) POA.

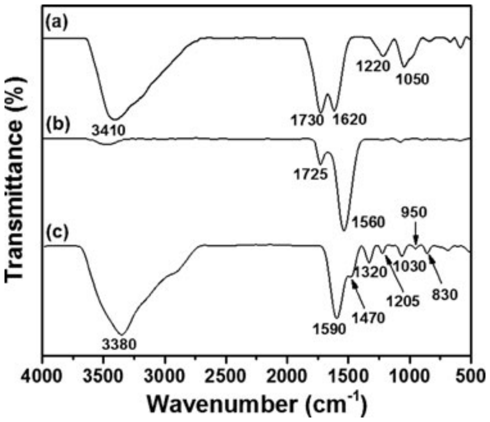

Figure 2. FT-IR spectra of (a) GO, (b) RGO, and (c) RGO/POA composites.

1620, 1220 and 1050 cm^{-1} are attributed to the C=O, C=C, C—O—C and C—O stretching vibrations, respectively. The reduction of GO is evidenced by the dramatic decrease in peaks intensity at 1730 and 1220 cm^{-1} and the formation of new peak at 1560 cm^{-1}, which corresponds to the skeletal vibration of graphene sheets. Furthermore, the spectrum of the RGO/POA composites exhibits the POA features at 3380 cm^{-1} (N—H stretching mode), 1590 cm^{-1} (C=C stretching modes of the quinoid ring), 1470 cm^{-1} (C=C stretching modes of the benzenoid rings), 1205 and 1030 cm^{-1} (stretching vibration of ortho-methoxy group), 950 cm^{-1} (in-plane CH vibration of quinoid ring) and 830 cm^{-1} (o-substituted benzene ring). Thus, the stretching vibration —OCH_3 band in the RGO/POA composites clearly indicates the presence of the o-Anisidine units in the composites. However, the characteristic band of graphene sheets at 1560 cm^{-1} cannot be identified in the spectrum of composites because of its overlapping with the characteristic peaks of POA.

The FESEM micrographs provide evidence supporting the differences between RGO and RGO/POA composites, as presented in Fig. 3. It can be clearly seen that the RGO sheets are homogeneously distributed in the POA matrix.

Figure 4 shows the XPS survey spectra of graphite, GO and RGO/POA composites. All the spectra exhibit the strong peaks at 284.5 and 531.5 eV, correspond to the C1s and

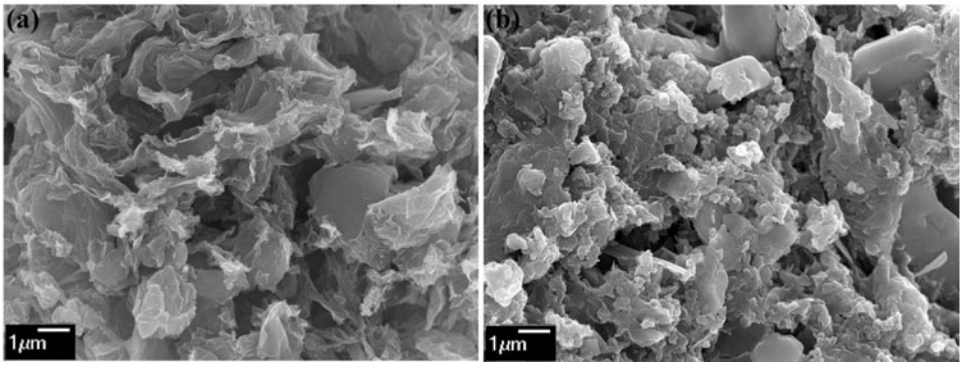

Figure 3. FESEM images (a) RGO and (b) RGO/POA composites.

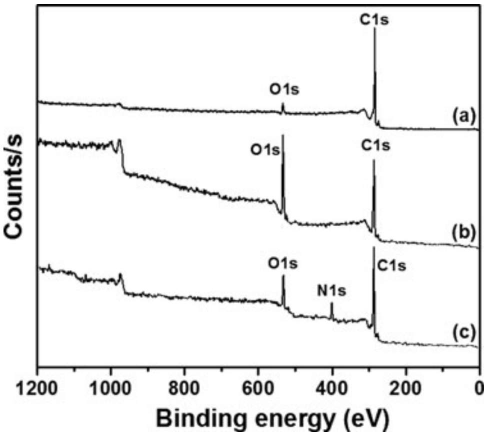

Figure 4. XPS spectra of (a) pristine graphite, (b) GO, and (c) RGO/POA composites.

O1s signals, respectively. The strong O1s signal in the spectrum of GO arises from the oxygen-containing functionalities such as C=O, O—H and C—O—C groups. In addition, the spectrum of RGO/POA composites reveals a presence of N1s peak at 399 eV, which supports the successful attachment of POA chains on the RGO surfaces.

The thermal property of the composites was elucidated by TGA analysis under nitrogen atmosphere. The TGA curve of the GO (Fig. 5a) shows an initial weight loss around 5% in the temperature range up to 80°C, which is related to the removal of physisorbed water. In addition, a major weight loss occurs at around 200°C, which can be ascribed to the decomposition of the different oxygen containing functional groups. For RGO, a total weight loss of 5% is observed in the temperature range 50 to 800°C due to the desorption of bound water molecules. On the other hand, the neat POA shows the weight loss at around 300°C corresponds to the structural decomposition of the POA backbone. In the case of the composites, the onset decomposition temperature is slightly higher (350°C) than that of neat POA, which may be attributed to the strong interfacial interaction between RGO and POA matrix.

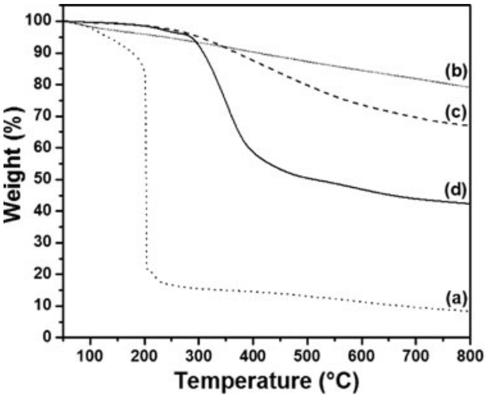

Figure 5. TGA curves of (a) GO, (b) RGO, (c) RGO/POA, and (d) POA.

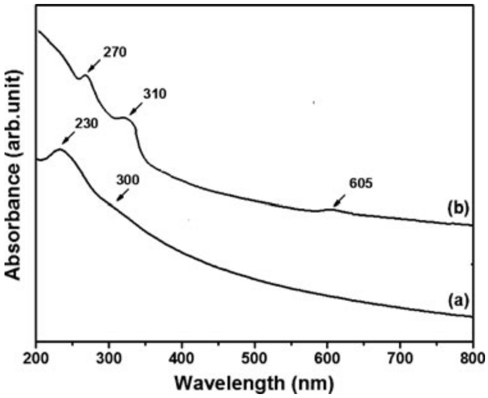

Figure 6. UV-Vis spectra of (a) GO and (b) RGO/POA composites.

UV–Vis spectroscopy is an effective tool to characterize the interfacial interaction between polymers and nanofillers. Figure 6 illustrates the UV–Vis spectra of neat GO and POA/ RGO composites. The GO exhibits an absorption maximum at 230 nm and a tiny shoulder at about 300 nm, corresponding to π–π^* transitions of the aromatic C—C bonds and n–π^* transitions of C=O bonds. For the composites, the strong peak at 310 nm corresponds to the π-π^* transition of the benzenoid ring, while the weak band at around 610 nm is attributed to the n-π^* transition within the quinoid structure. However, the GO peak is blue-shifted in the composites; indicating the presence of the RGO structure in the composites.

Conclusions

Poly (o-anisidine) wrapped reduced graphene oxide composites were successfully synthesized through oxidative chemical polymerization. The structure and morphology of the composites were characterized by FTIR, XRD, XPD, FESEM and TGA. FTIR study confirmed the formation of POA nanostructure in presence of RGO. Scanning electron microscopy results revealed a homogeneous dispersion and distribution of RGO sheets into the polymer matrix. Thus, the in-situ polymerization can be easily applied for the preparation of numerous composites.

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