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The effects of dopant on morphology formation in polyaniline graphite nanoplatelet composite

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ABSTRACT

In this study, a nanocomposite (SELA-PANi/GNP) consisting of selenious acid (SELA) doped polyaniline (PANi) and graphite nanoplatelet (GNP) was prepared, and its structure and properties – in particular, morphology formation, as well as interaction between the two phases – were investigated using scanning electron microscopy (SEM), UV–vis spectroscopy, FTIR spectroscopy, X-ray diffraction, and electrical conductivity measurement. A PANi/GNP nanocomposite prepared in aqueous HCl solution (HCl-PANi/GNP) was also prepared for comparison with SELA-PANi/GNP. The results reveal that the dopant plays an important role in morphology formation in PANi/GNP nanocomposites. When HCl was used as the dopant, PANi coated GNPs were formed and no phase separation between PANi and GNP was seen. In contrast, when SELA was used as the dopant, the morphology of PANi remained unchanged in the composite, owing to the formation of rod or sphere micelle PANi structure during *in situ* polymerization; no interaction was observed between the two phases. The crystalline structure of PANi was not affected by the incorporation of GNP. The electrical conductivity of PANi/GNP increased with increasing GNP content, because of the electrical bridge effect of GNP in the PANi matrix.

1. Introduction

Graphite, which is naturally abundant, has been widely used in the last decade as an electrically conducting filler in the preparation of conducting polymer composites [1]. Recently, graphite nanoplatelet (GNP), composed of one or more layers of graphene planes with a thickness of 0.34–100 nm, has attracted significant research interest. GNP promises a cost effective high quality alternative to carbon nanotubes (CNT) and carbon nanofibres (CNF) [2–4]. A GNP can be viewed as a flattened sheet of CNT, with similar mechanical and electrical properties; however, single-sheet GNP demonstrates much higher thermal conductivity and twice the specific surface area, as compared to single-walled CNT [4]. Several studies of polymer nanocomposites based on GNP, including PPy/GNP [5,6], PEDOT/GNP [7], epoxy/GNP [8], and PS/GNP [9], have been performed. In general, incorporation of GNP in the polymer matrix can lead to improvements in mechanical and thermal properties of materials and especially to enhanced electrical conductivity. For example, the percolation threshold for PS/GNP composite is 1 wt%, whereas the composite filled with 7500 mesh graphite has a higher percolation threshold of ca. 6 wt% [9].

Among conducting polymers, polyaniline (PANi) has attracted much research interest because of its ease of synthesis and the low cost of its monomer, as well as its adequate electrical conductivity and good environmental and thermal stability [10,11]. To improve the thermo-mechanical and electrical properties of PANi, with the aim of exploitation of the resulting materials in a wide range of fields, including electromagnetic interference shielding, radar evasion, rechargeable batteries, and electrodes for supercapacitors, PANi/CNT [12–14] and PANi/GNP [15–17] nanocomposites have been prepared and investigated. In these polymer composites, morphology formation and interaction between phases may play an important role in determining material properties [18]. In particular, PANi-coated CNT and GNP morphology in PANi/CNT [13,19] and PANi/GNP [20] nanocomposites prepared with HCl dopant have been observed. In our previous paper [21], we described a simple, template-free process for synthesis of large quantities of uniform PANi nanostructure by using selenious acid (SELA) as dopant and ammonium persulfate (APS) as oxidant. By varying the molar ratio of dopant to monomer (D/M ratio), different PANi morphologies, ranging from flake to nanorod and nanosphere, were formed, with average diameters of 1 μm, 150 nm, and 150 nm respectively. During the study of SELA doped PANi, SELA doped PANi/GNP nanocomposites were prepared, and morphology formation and phase interaction in this system were investigated and discussed. For the sake of comparison, conventional PANi and

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PANi/GNP composites prepared in 0.5 M HCl aqueous solution were also prepared and their morphologies were examined.

2. Experimental

2.1. Materials

ACS-grade aniline, selenious acid, nitric acid, and natural graphite flakes with average diameter 500 μm were purchased from Aldrich. Ammonium persulfate (APS), hydrochloric acid, and sulfuric acid were purchased from SAMCHUN Chemical. All chemicals were used as received.

2.2. Preparation of graphite nanoplatelets

Graphite nanoplatelets were prepared according to the literature reports [22]. A 30-ml solution of concentrated H_2SO_4 and HNO_3 (4:1, v/v) was added to a reaction flask containing 0.5 g graphite flakes. The mixture was stirred at ambient temperature for 24 h and then filtered and washed with excess distilled water. The acid-intercalated graphite flakes were dried at 100 °C for 24 h. Thermal treatment was performed in a muffle furnace at 900 °C for 60 s. Afterwards, the worm-like expanded graphite flakes were sonicated in ethanol solution (ethanol:water = 2:1, v/v) for 10 h. The product was filtered and washed with distilled water and then dried in a vacuum oven for 24 h. The resulting graphite nanoplatelets had an average diameter of 25 μm and thicknesses ranging from 50 nm to 140 nm.

2.3. Synthesis of PANi/GNP nanocomposites

The synthesis procedures for PANi/GNP nanocomposites were based on the procedures for preparation of SELA doped PANi as reported in our previous paper [21]. In the case of SELA doped PANi/GNP nanocomposite (SELA-PANi/GNP), the monomer-to-oxidant molar ratio is 1. The dopant–monomer (D/M) molar ratio was chosen at 0.5 and 2, and the ratio of GNP to monomer (w/w, %) was varied. The HCl doped PANi/GNP (HCl-PANi/GNP) was prepared in 0.5 M HCl aqueous solution. In a typical experiment, GNP was dispersed in 3 ml ethanol solution (ethanol:water = 2:1, v/v) and then sonicated for 1 h. This suspension was added to 25 ml 0.5 M HCl solution containing 0.9313 g aniline for preparation of HCl doped PANi/GNP nanocomposite, or 25 ml aqueous solution containing 0.9313 g aniline and selenious acid. The mixture was stirred at room temperature for 30 min, after which 25 ml 0.5 M HCl solution containing 1.14 g APS, or 25 ml aqueous solution containing 1.14 g APS, was added dropwise to the mixture. The reaction mixture was kept under static conditions for 6 h at 0–5 °C. Following this reaction time, the product was filtered, washed with distilled water followed by acetone, and dried in an oven at 50 °C for 6 h.

The doped PANi and PANi/GNP nanocomposites were dedoped by stirring in aqueous 1 M NaOH solution for 24 h. After filtering, washing with distilled water, and drying at 50° C for 24 h, the dedoped form of PANi and the composite were obtained.

2.4. Characterization

The surface morphology of PANi/GNP nanocomposites was observed by scanning electron microscopy (SEM) (JEOL, JSM-840A). X-ray diffraction analyses were performed on a Bruker-AXS D8 instrument using Cu Ka radiation (λ = 1.5406 Å) at 40 kV and 40 mA. FTIR spectra were collected on an ABB-FTLA 2000 instrument using KBr pellets mixed with PANi/GNP nanocomposite powder. UV–vis absorption spectra of the samples were recorded on an Agilent 8453 instrument at ambient temperature. To characterize the electrical conductivity of the materials, PANi/GNP nanocomposite powders were compressed under high pressure (7.5 ton/cm^2, 30 s) into pellets with a thickness of approximately 300 μm and diameter of 13 mm. The electrical conductivity of PANi/GNP nanocomposite was then measured by the four-probe method using CMT-Series Jandel instruments at room temperature.

3. Results and discussion

3.1. Analysis of morphology formation in PANi/GNP nanocomposite

The morphology and properties – especially the electrical conductivity – of SELA-doped PANi depend strongly on the D/M ratio. By varying the D/M ratio, not only the morphology but also the oxidation level and doping state of PANi were significantly changed [21,23]. Fig. 1 shows typical SEM images of neat PANi and PANi/GNP nanocomposite prepared with HCl dopant and SELA dopant. In the case of the SELA dopant, the D/M ratios were 0.5 and 2.

It is clear that the use of HCl as dopant produced rod-like PANi structure with the diameters ranging from 100 nm to 170 nm (Fig. 1(a)). Significant changes in morphology are seen in the PANi/GNP composite prepared with HCl dopant: instead of the rod-like shapes, PANi particles with an average diameter of 230 nm were formed (Fig. 1(b)). In addition, the GNP was almost completely coated by PANi particles. This result is in good agreement with other reports [20]. In the SELA doped PANi, nanorods (average diameter 150 nm, Fig. 1(c)) and nanospheres (average diameter 150 nm, Fig. 1(e)) were formed, at D/M ratios of 0.5 and 2, respectively [21]. In the PANi/GNP nanocomposite, the morphology of PANi was the same as that of neat PANi. Rod and sphere morphologies were observed in PANi within PANi/GNP nanocomposites, with D/M ratios of 0.5 and 2 respectively (Fig. 1(d and f)). Furthermore, the respective average diameters of rod and sphere PANi structures in the polymer nanocomposite are almost identical to those in neat PANi. Moreover, GNP is only partly attached to PANi; that is, the PANi phase and GNP phase exist mainly separately. This result clearly indicates that there are significant differences in morphology formation in PANi/GNP nanocomposite when prepared with HCl and SELA dopants.

To explain the difference in morphology formation in HCl and SELA doped PANi/GNP nanocomposite (D/M = 0.5), we propose a mechanism for morphology formation, as shown in Scheme 1.

It is well known that the graphitic structure of fullerene C60 or CNT can react with aromatic amines, as described in Sun et al. [24]. Because of the structural similarity of GNP and CNT, GNP should be a good electron acceptor, while aniline is a fairly good electron donor. Thus, GNP and aniline may form a weak charge-transfer complex [20,24]. When GNP is added to an aniline/HCl solution, aniline monomers can immediately absorb onto the surface of the GNP owing to electrostatic attraction. During *in situ* polymerization, GNP acting as a support material can supply a large number of active sites for nucleation of PANi, thus inducing the coating of GNP by PANi particles [20].

In contrast, the morphology formation in SELA-doped PANi is via the mechanism of rod- and sphere-shaped micelles, as proposed by Amarnath et al. [21]. When aniline is mixed with selenious acid, selenious acid–aniline salt is formed through an acid/base reaction. In this salt, the phenyl ring is the hydrophobic end and $HSeO_3$ is the hydrophilic. At D/M ratios of 0.5 and 2, respectively, rod-shaped micelles and spherical micelles filled with free aniline are formed. Under *in situ* polymerization with GNP, the hydrophilic outer layer of the rod-shaped micelle may prevent the formation of a charge-transfer complex between the aniline monomer and GNP; thus, no absorption of aniline monomer onto the GNP surface occurs. The rod-shaped and spherical micelles will remain their form via *in situ*