THE MORPHOLOGY OF PANI/GRAPHENE COMPOSITES PREPARED UNDER ISOTHERMAL CONDITIONS

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Abstract

This article investigates the morphology of polyaniline/electrochemically exfoliated graphene composites prepared by oxidative polymerization with ammonium persulfate at a constant temperature (15 °C). During the polymerization, the pH of the reaction mixture decreases, which was used to monitor the rate of the reaction. A granular morphology with the presence of large sheet-like structures is found to be predominant for the composite prepared without added acid, while rod-shaped and tubular morphology is characteristic for the composite prepared with the addition of glacial acetic acid. The nanotubular and nanorod morphology of the sample prepared with the addition of glacial acetic acid was also confirmed by the presence of prominent phenazine structural units in Raman spectra. The composite prepared with the addition of HCl has granular morphology with a small amount of rod-like structures.

Introduction

Polyaniline (PANI), as a member of the intrinsically conducting polymers family, is one of the most studied polymers because of its facile synthesis, environmental stability, low cost, and reversible acid-base doping-dedoping process which influences its electrical conductivity [1, 2]. Due to its electrical, optical, and electrochemical properties, PANI is considered a suitable material for various applications such as counter electrodes in dye-sensitized solar cells [3], electrode material for supercapacitors [4], sensors [5], and corrosion protection films [6] among others. Among the three forms of PANI (leucoemeraldine, emeraldine, and pernigraniline) only the emeraldine salt is conductive due to the conjugated p-electron system. Numerous studies have shown that doping PANI with various dopants could significantly improve the conductivity of PANI [7-9]. Recently, composites of PANI and graphite, graphene oxide (GO), or reduced graphene oxide (rGO) are extensively studied for boosting the capacitance of supercapacitor devices [10], enhancing the dispersive and crystalline performance of corrosion protection films [11, 12], and improving the thermal stability of the nanocomposite [13].

Graphite has a layered structure composed of sp^2 hybridized carbon atoms arranged in a honeycomb structure. Individual layers of graphite known as graphene have attracted considerable interest as a filler in polymers due to its electrical, mechanical, and thermal properties [14-16]. However, graphene as a filler is mostly present in its highly oxidized form as a GO with a diminished electrical conductivity. One way to overcome this issue is to partially restore graphene's structure by reduction to obtain rGO, but its conductivity remains incomparable to the graphene's. An alternative pathway is electrochemical exfoliation of graphite to obtain graphene with preserved structure and electrical properties [17-19]. During the process, produced hydroxyl ions weaken van der Waals forces between graphite layers which allows the intercalation of electrolyte ions that form gas bubbles upon reduction which are responsible for graphene exfoliation. In this way it is possible to obtain single- and fewlayer graphene with a large flake size and well-preserved structure, but with a sufficient amount of polar groups attached to graphene to make it water dispersible [20].

The goal of the present work was to investigate the morphology of PANI/graphene composites. The samples were prepared under isothermal conditions in the presence of electrochemically exfoliated graphene. The change of pH during polymerization was monitored and the samples were characterized by SEM and Raman spectroscopy.

Experimental

Electrochemically exfoliated Highly Oriented Pyrolytic Graphite (eHOPG) was prepared as described previously [17]. Solution 1 was prepared by mixing 10 mg of eHOPG and 1 ml of aniline (Sigma Aldrich) in 49 ml of DI water until well homogenized. Solution 2 was prepared by dissolving 2.85 g of ammonium persulfate (Fluka) in 50 ml of DI water. The polymerization reaction was conducted in EasyMax 102 Basic Thermostat System by mixing solutions 1 and 2 at a constant temperature of 15 °C under stirring (100 rpm). The change in pH was monitored during the reaction (Mettler Toledo pH meter). The obtained product was centrifuged three times at 2575 ×g for 30 minutes and the supernatant was discarded. Finally, the precipitate was dried in a vacuum oven at 60 °C overnight. Samples PANI-HCl and PANI-CH_3COOH were prepared following the same procedure with the addition of 2 ml 0.2 M HCl (Sigma Aldrich) or 2.3 ml of glacial acetic acid (Merck) in the reaction mixture, respectively.

SEM analysis was performed on a Zeiss Supra 35 VP field-emission electron microscope at an accelerating voltage of 1 kV. Small amount of each sample was mounted on aluminum studs using adhesive graphite tape. Raman spectra were recorded by confocal Raman microscope (alpha 300 R+, WiTec, Ulm, Germany). The excitation laser of the 532 nm wavelength and 0.22 mW power was focused using 100 × (NA = 0.9) objective onto the sample surface. The confocal pinhole diameter was 50 μm and the accumulation time for a single Raman spectrum was set to 40 s. Constant background was subtracted from all measured Raman spectra.

Results and discussion

Polymerization of aniline was performed in the presence of electrochemically exfoliated graphene under a constant temperature of 15 °C. It was shown that under lower temperatures the synthesized PANI shows better physicochemical characteristics [21], however, if the temperature is too low the polymerization takes a longer time to complete. During the polymerization the change of pH of the reaction mixture was monitored (Figure 1).

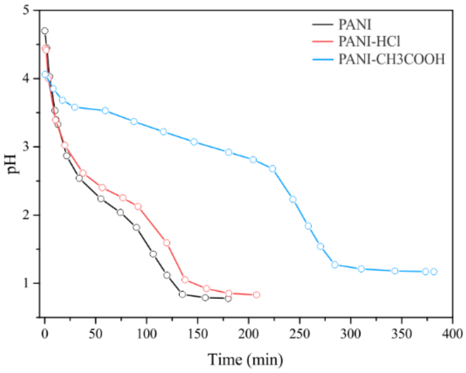

Figure 1. The changes of pH of the reaction mixture during time for PANI/ graphene composites.

The generation of protons during the polymerization leads to the decrease of pH of the reaction mixture. An initial fast decrease in pH is induced by the fast oligomerization of aniline molecules, which is followed by a slower pH decrease due to the prevalence of less-oxidizable anilinium cations and the decrease of the concentration of ammonium persulfate [22]. The next step is characterized by the rapid pH decrease caused by polymer propagation. In this phase, pernigraniline-like oligoaniline units have sufficient power to oxidize both anilinium cations and leucoemeraldine- and protoemeraldine-like oligoanilines, and parallel to this pernigraniline-like oligoanilines become oxidized by remaining peroxydisulfate. These polymerization steps are clearly distinguished for all three samples, however, the rate of the polymerization is much slower for the PANI-CH_3COOH sample compared to PANI and PANI-HCl samples. Also, the final pH value for PANI-CH_3COOH sample is slightly higher than the final pH value of PANI and PANI-HCl samples (1.18 compared to 0.78 and 0.85, respectively).

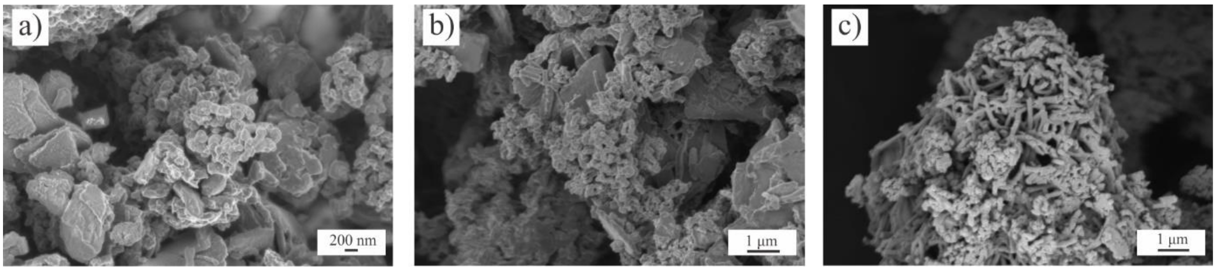

Figure 2. SEM images of PANI/graphene samples: a) PANI, b) PANI-HCl, and c) PANI-CH_3COOH.

According to SEM images (Figure 2), PANI/graphene composite synthesized without added acid has granular morphology with the presence of large sheet-like structures. Sample PANI-HCl is morphologically similar to sample PANI, but a certain amount of rod-like shapes can be detected. On the other hand, sample PANI-CH_3COOH is dominated by rod- and tube-like structures with diameters between 100 and 150 nm and lengths of up to 1 µm. Besides, a small amount of irregular shapes and granular particles can also be detected.

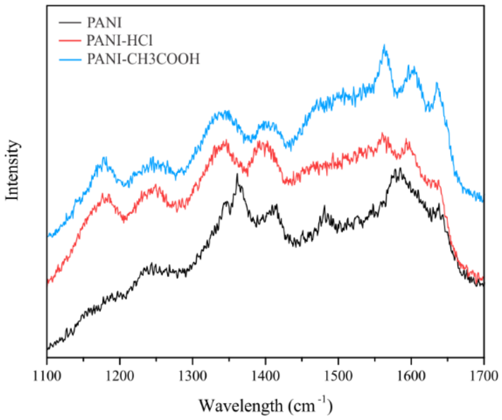

Figure 3. Raman spectra of PANI/graphene composites.

In Figure 3 Raman spectra of PANI/graphene composites are shown. Typical D and G Raman bands of graphene that appear at 1351 and 1591 cm^{-1} are strongly overlapped by bands that are associated with PANI structural units: band at 1586 cm^{-1} originates from the C=C and C-C stretching vibrations of the quinoid rings, while the band at 1344 cm^{-1} stems from the C-N$^{+\cdot}$

stretching vibrations of delocalized polaronic structure [23]. Besides, in the spectrum of PANI/graphene prepared in the absence of acid, bands at 1410 and 1394 cm^{-1} that arise from the substituted phenazine structural units in polymer structure are also observed. Except for the aforementioned bands that stem from PANI units, spectra of PANI-HCl and PANI-CH_3COOH contain bands at 1180 cm^{-1} (the C-H bending in-plane vibration of semiquinonoid rings), 1234 and 1249 cm^{-1} (the C-N stretching in benzenoid units), 1561 and 1392 cm^{-1} (stretching of substituted phenazine structural units), and 1631 cm^{-1} (C-C/C=C stretching vibrations of benzenoid units with a contribution of the substituted phenazine units). Phenazine structural units indicate the presence of nanotubular and nanorod PANI morphology [24]. As expected, the bands that correspond to phenazine units are most prominent in PANI-CH_3COOH spectra.

Conclusion

PANI/graphene composites were prepared by oxidative polymerization of aniline with ammonium persulfate at a constant temperature (15 °C). Additional samples were prepared with the addition of 0.2 M HCl, or glacial acetic acid. Polymerization rate was monitored by the change of pH of the reaction mixture. Comparable polymerization rates were measured for PANI and PANI-HCl samples, while the reaction with added acetic acid takes longer to complete. Granular morphology with large sheet-like structures was found for PANI sample. PANI-HCl sample has similar morphology as PANI, but with a presence of a certain amount of rod-like shapes. Sample PANI-CH_3COOH is dominated by rod- and tube-like structures with diameters between 100 and 150 nm and lengths of up to 1 μm. Nanotubular and nanorod morphology of PANI-CH_3COOH sample was confirmed by the presence of prominent phenazine structural units in Raman spectra.

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