Synthesis of Nanographite/Polyaniline Composites Using a Reactive Surfactant as Polyaniline Precursor

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Abstract - Nanographite/polyaniline nanocomposites were synthesized by using anilium dodecylsulphate (DS–AN) first, as the surfactant, to assist expanded graphite exfoliation, and then, as the monomer, to synthesize conductive polyaniline. Based on this double functionality, DS–AN is classified as a reactive surfactant. Raman spectroscopy showed a I(G)/I(2D) ratio of ca. 1.5 for the exfoliated graphite, which indicated graphite flakes in the range of 10 graphene layers (nanographite). Nanographite morphology, observed by electron microscopy, gave also evidence of graphite flakes consisting of few layers of graphene. Concerning composite morphology, electron microscopy evidenced the formation of a polyaniline film on the nanographite surface, which suggested direct DS–AN polymerization on the flake surface.

Keywords: Conducting polymer, Nanographite, Polyaniline, Reactive surfactant.

1. Introduction

Graphene has emerged as one of the most important materials for current and future research, due to its outstanding electronic, optical, and mechanical properties (Geim and Novoselov, 2007). On the search for the scale up production of graphene, the use of surfactants assisted by ultrasound has been widely reported. The products of this method are dispersions formed by mixtures of multilayered graphene (<10 layers). Surfactant function during graphite exfoliation are two: a) lowering liquid–vapor interfacial energy of the solution to an optimal range that corresponds to the energy required to separate the sheets beyond the range of the van der Waals forces, and b) adsorbing onto the graphene sheets, creating a repulsive surface preventing the reaggregation of the exfoliated sheets (Notley, 2012). On this respect, several surfactants have been used; for example, Loyta et al. (2009) took advantage of the methods that were reported to disperse carbon nanotubes in water and produced aqueous suspensions of multilayer graphene with the aid of sodium dodecylbenzenesulfonate. According to characterization, the product showed a low level of defects and anticipated that its properties could be improved by surfactant removal. However, surfactants are generally nonconductive, producing charge transfer blocking in the nanomaterial resulting in the deterioration of the graphene properties (Tölle et al., 2012). Therefore, before a subsequent application, further processing is required to remove the surfactant, which may be difficult because of the strong surface interaction between surfactants and carbon materials.

Herein, we report the use of anilinium dodecylsulfate (DS–AN) as a reactive surfactant (surfmer); that is, on the one hand, it performs the common functions of a surfactant, and on the other hand, it is the monomer of polyaniline. It is possible to obtain nanographite/polyaniline nanocomposites without further requirement of critical cleaning or chemical reduction by using DS–AN, as after exfoliation it is submitted to an oxidative polymerization to obtain conductive polyaniline. We have reported recently the use of this novel concept of surfmer, inverse surfmers, in the synthesis of polystyrene/polyaniline core–shell composites via a two–step methodology: emulsion polymerization–oxidative polymerization (Zaragoza-Contreras et al., 2012). Consequently, the aim of this paper is to demonstrate the versatility of DS–AN as reactive surfactant in the synthesis of nanographite/polyaniline composites.

2. Experimental Section
2.1 Composite Synthesis

In the first step, expanded graphite was treated as follow: 1.0 g of expanded graphite, DS–AN (variable concentration), and 150 mL of distilled water were mixed in a glass vessel. The mixture was heated at 50°C and left to mix for 24 h with gentle stirring. Afterwards, the mixture was left to cool at laboratory conditions and then put in refrigeration for 2 h. Finally, the mixture was sonicated using a sonic dismembrator programmed to apply pulses with 100% of amplitude every 2 s for 60 min. In the second step, DS–AN was submitted to an oxidative polymerization, by adding ammonium persulfate (APS) in molar ratio, APS:DS–AN, of 1.0:1.0. The polymerization was allowed for 48 h at −2 °C. After this time, the dark–green dispersion obtained was sonicated again under the same conditions as in step one. The solids were recovered by filtration and washed with distilled water to remove co–products.

2.2 Characterization

Exfoliated graphite and nanographite/polyaniline composites were characterized using a field emission electron microscope (JSM–7401F, JEOL Ltd.) and a transmission electron microscope (JEM 2200SS, JEOL Ltd.). Surface area of expanded graphite, exfoliated graphite (treated graphite), and nanographite/polyaniline composites were determined by Brunauer–Emmett–Teller method (BET) (Autosorb 1 Analizer, Quantachrome Instruments). Expanded graphite and the exfoliated graphite were analyzed using a Micro–Raman spectrometer (LabRAM UV–VIS, Horiba Jobin–Yvon), at the excitation wavelength of 632.8 nm and 1800 mm^{-1} filter. The nanographite/polyaniline composites were characterized by thermogravimetric analysis (TGA Q500, TA Instruments). Measurements were achieved using 10 mg of sample and heated from laboratory temperature to 950 °C, at a heating rate of 10 °C min^{-1}.

3. Results and Discussion

In this study, DS–AN was used first, to exfoliate expanded graphite performing as a surfactant, and second, to obtain nanographite/polyaniline composites performing as the monomer of polyaniline. During exfoliation DS–AN performed in the same way as the common surfactants; that is, adsorbing on the surface of the graphite flakes creating a repulsive ionic layer avoiding reaggregation. Micrographs of expanded graphite and graphite treated with 10 wt% DS–AN are portrayed in Figure 1(a,b). As noted, treated graphite and expanded graphite can be clearly contrasted; on the one hand, expanded graphite consists of planar micrometric thick flakes. On the other hand, after treatment, wrinkled nanometric flakes of graphite are obtained. To analyze flake intimate structure, high–resolution (HR) TEM characterization was performed (Figure 1(c)). The analysis showed that the flakes consist of a mixture of some few nanometric orderly arranged stacks that may be classified as few–layer–graphene (flakes with less than 10 individual layers of graphene). However, as the thickness of the flakes is highly variable we preferred to designate the material as nanographite.
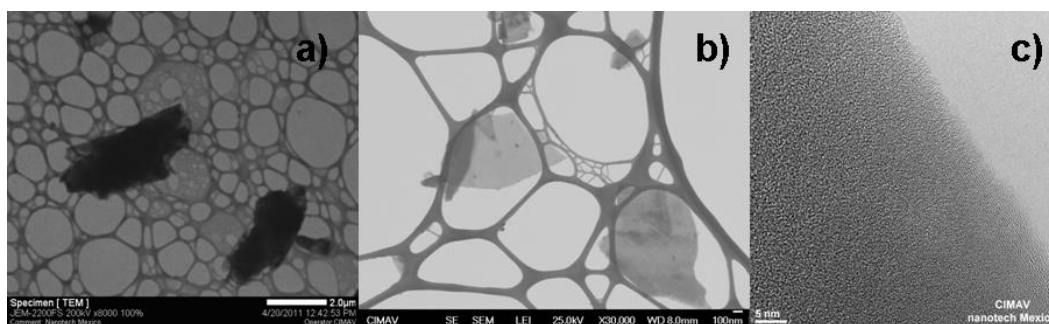

Fig. 1. (a) STEM micrographs of pristine expanded graphite. (b) STEM micrograph of nanographite. (c) HR-TEM of nanographite.

After exfoliation, DS–AN was submitted to an oxidative polymerization using ammonium persulfate (APS) as the oxidizing agent to produce nanographite/polyaniline composites. The products of the second stage were dark–green fluid dispersions, showing the presence of polyaniline in the conductive form (emeraldine base salt). Morphology of pure polyaniline and nanographite/polyaniline composites was observed by scanning electron microscopy in STEM mode, Figure 2. As observed, PAni particles obtained from the chemical polymerization of DS–AN are in the range of 10 to 30 nm, lots of them of elongated shape. In the case of the composites, the exfoliation gained in the first step was kept; that is, flake reagglomeration was not evident. Here, the dark regions indicate that PAni is regularly distributed on the flake surface.

Fig. 3(a) shows Raman spectra of expanded graphite and treated graphite with 10 wt% DS–AN. In both spectra, the three typical peaks of graphite at 1350, 1600, and 2700 cm^{-1} are present. These bands correspond, respectively, to D, G, and 2D bands. The D band is associated to defects or impurities in the sample; the G band corresponds to zone center phonons of E_{2g} symmetry. The significant change in intensity of the 2D peak of the treated graphite compared to the same peak in expanded graphite, were considered an evidence of graphite exfoliation (Ferrari, 2007). An important factor is the ratio between the intensity of G and 2D line, I(G)/I(2D). The increase in this ratio is related to the increment in the number of graphene layers. Concerning this, our results indicated a I(G)/I(2D) ratio of ca. 1.5 for the exfoliated graphite, which suggested graphite flakes of less than 10 graphene layers, corresponding to the so called few–layer–graphene, which is in accordance with microscopy observations.

Fig. 3(b) shows TGA traces of expanded graphite, nanographite, polyaniline, and the composites. As observed, nanographite was stable up to 637 °C to then degrade continuously until 800 °C. This behavior has been attributed to carbon oxidation to carbon dioxide. On the other hand, in the case of the expanded graphite, no weight loss is observed until 706 °C; that is, the expanded graphite is 70 °C more thermally stable than the nanographite. Such difference has been explained in terms; for example, of decreased van der Waals interaction (Viculis, et al., 2005). Concerning polyaniline, a mass loss at ca. 230 °C is observed, which was associated to degradation of the doping agent. Subsequently, another transition at ca. 350 °C is observed; this transition was attributed to the decomposition of the polyaniline backbone (Arenas et al., 2010).
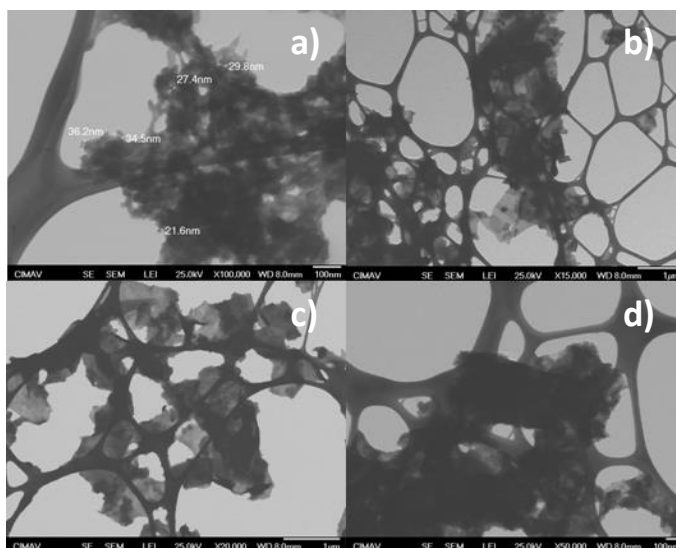

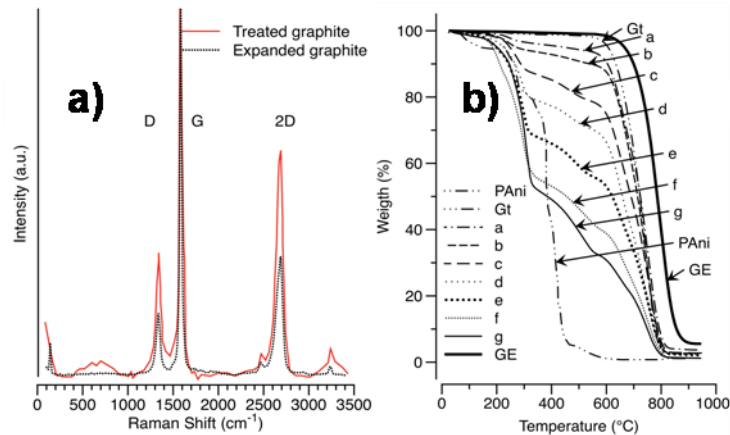Fig. 2. STEM images. a) PAni, and b) to d) composites synthesized with 10, 30, 67 wt% DS–AN, respectively.

Fig. 3. (a) Raman spectroscopy of expanded graphite and treated graphite (nanographite). (b) TGA traces of expanded graphite (GE), treated graphite (Gt), PAni, and a) to g) composites with 3, 5.1, 11.3, 19.5, 28.2, 43.2, 46.7 wt% Pani, respectively.

4. Conclusion

We have demonstrated the application of anilinium doedecylsulfate (DS–AN) as a new route towards the production of nanographite/polyaniline composites, taking advantage of the double functionality, surfactant–monomer, of DS–AN. Thanks to this property, the possible negative effect of DS–AN against the electrical conductivity of the composites was minimized as it is converted to polyaniline. Because of the strong interaction between DS–AN and nanographite flakes, it was assumed that DS–AN polymerization occurred directly on the flakes surface. Finally, it can be mentioned that based on the composite properties applications, for instance, in sensor design or electrochemical supercapacitors are evident.

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