Electroactivity in Nanographite/Polyaniline Composites Using Anilinium Dodecylbenzenesulfonate as Polyaniline Precursor

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Abstract - Nanographite/polyaniline nanocomposites were synthesized by using anilium dodecylbenzenesulphate (DBS–AN) first, as the surfactant, to assist expanded graphite exfoliation, and then, as the monomer, to synthesize conductive polyaniline. Based on this double functionality, DBS–AN is classified as a reactive surfactant. Cyclic volammetry analyses showed nanocomposites electroactivity. Effect of polyaniline concentration, electrolite concentration and scan rate were studied.

Keywords: Cyclic voltammetry, Nanographite, Polyaniline, Reactive surfactant

1. Introduction

Herein, we report the use of anilinium dodecylbenzenesulfate (DBS–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 DBS–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*). Thus, the aim of this paper is to demonstrate the use of DBS–AN as reactive surfactant in the synthesis of nanographite/polyaniline composites and its application in electrode design.

2. Experimental Section
2.1 Composite Synthesis

Expanded graphite was treated as follow: 1.0 g of expanded graphite, DBS–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, DBS–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 the 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.). Nanographite/polyaniline composites were characterized by cyclic voltammetry (CV) using a potentiostate analyzer (model 1260 plus 1287, Solartron). The software CorrView 2 was used to visualize the graphics. Electrochemical measurements were performed in a standard three-electrode cell at room temperature, using Pt wire (area=0.03 cm^2) as the counter electrode, and Ag/AgCl/saturated KCl as the reference electrode. The working electrode was a polyethylene cylinder packed with carbon paste, with a copper wire inserted through one end of the cylinder. The sample of dried composite was deposited on the opposite end to the copper wire. Sulfuric acid (H_2SO_4) molar solutions were used as the electrolyte.

3. Results and Discussion

In this study, DBS–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 DBS–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 Pure polyaniline, treated with 10 wt% DBS–AN, and nanographite/PAni composite synthesized with 30 wt% DBS–AN are portrayed in Fig. 1. As noted, pure PAni particles obtained from the chemical polymerization of DBS–AN are in the range of 50 nm, lots of them of elongated shape. 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. The image indicates 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. After exfoliation, DBS–AN was submitted to an oxidative polymerization using ammonium persulfate (APS) as the oxidizing agent. The products of the second stage were dark–green fluid dispersions, showing the presence of polyaniline in the form of emeraldine base salt. 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. 2a) shows the cyclic voltammograms (CVs) of the composites, in 0.5 M H_2SO_4, at a scan rate of 50 mV s^{-1}. In the potential region between -1 and 1V, it is observed that by increasing PAni content, the response of current density and integrated charge also increases, demonstrating, in all cases, electroactivity. Clear redox peak of PAni is observed in all plots. When the potential difference of electrodes is 0 V, corresponds approximately to the half-oxidized or half-doped state of PAni. During cycling, the positive range will be swept from the half-doped state called emeraldine to fully-doped state called pernigraniline, while negative range will be swept from half-doped state to fully-dedoped state called leucoemeraldine. Both leucoemeraldine and pernigraniline states are highly non-conducting in nature, and offer higher electronic resistance. At a high voltage of the cell, PAni does not have sufficient ion exchange sites to get doped. To continue characterization, sample NG/DBS67 (composite containing 67 wt% PAni) was selected because it presented the best electroactive response.

Series of CVs, with different electrolyte concentrations were carried out at a scan rate of 50 mV s^{-1}, are shown in Fig. 3b). In these assays, four sulfuric acid solutions were used as electrolytes because PAni shows electroactivity only at low pH (*Zhao et al., 2009*). As observed, the shape of the CVs changed as function acid concentration. The current peak became wider and increased. Such behavior is maintained up to a saturation level of 3 M H_2SO_4, where the acid saturation decreased the current density of the sample. Moreover, the oxidation peaks shifted to a more positive value, while reduction peak shifted to a more negative value, as the acid concentration increased. The observed trend is due to the increased concentration of the sulphate groups with increase of acid content (*Zhou, et al., 2010*). The oxidation peak is characteristic of the state in which maximum ion transport to the surface of the electrode material

occurs. From these results, 2 M H$_2$SO$_4$ solution was selected as the electrolyte for the further experimentation. Fig. 2c) shows the CVs in 2 M H$_2$SO$_4$ at a scan rate of 50 m Vs^{-1} for different values of the inferior limit of potential. As shown, the voltammetric response corresponding to each redox couple was different for each inferior limit of potential. The current density and integrated charge increased slightly at the beginning of the more positive potential sweeps, indicating that at these potentials the polymer is completely reduced (*Kanungo, et al., 2002*). According to literature, voltammetric response of polyaniline in acidic medium has two couplings redox potential in the range of -0.2 V < V < 1 V (*Gómez, et al., 2011*). Consequently, a potential window from -0.2 to 1 V was selected in the following electrochemical tests.
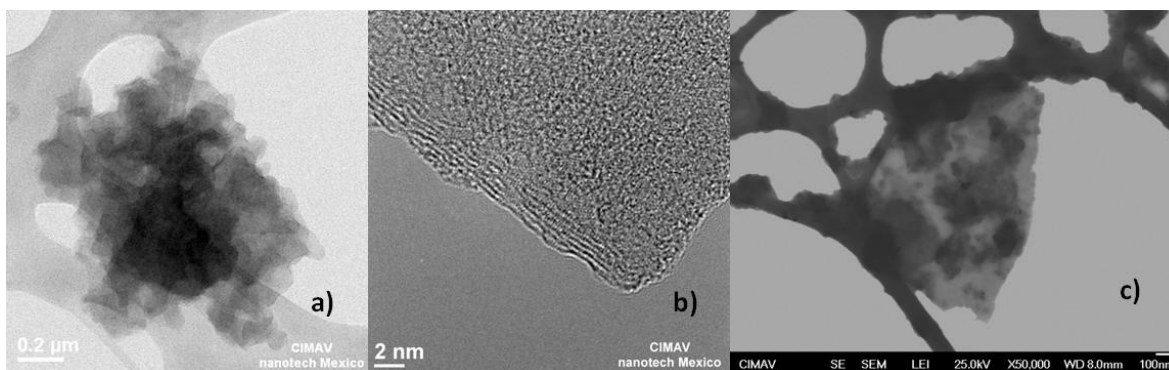

Fig. 1. (a) HRTEM of pure PAni. (b) HRTEM of nanographite treated with 10 wt% DBS−AN. (c) STEM of nanographite/PAni composite with 30 wt% DBS−AN.
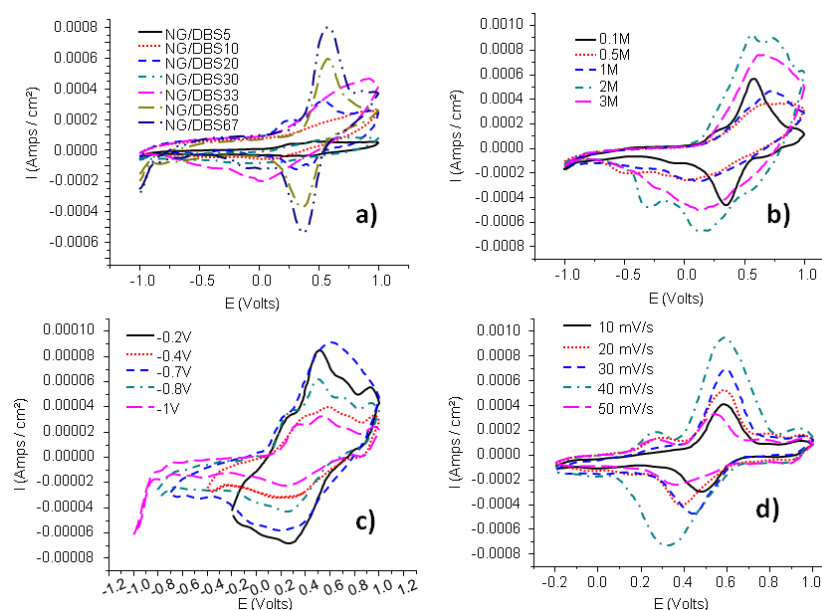

Fig. 2. Cyclic voltammetry as function of: a) DBS−AN concentration, b) Electrolyte concentration, c) Inferior limit of potential, and d) Scan rate.

Fig. 3d) shows the variation of the peak parameters with the scan rate in the range 10–50 mVs^{-1} for each composite in 2 M H$_2$SO$_4$ electrolyte. In the potential range between -0.2 and 1V, the compounds show a redox couple that is manifested as two voltammetric peaks. These peaks are not symmetric with respect to either shape or position on the potentials axis. The cathodic peak is always wider and appears at inferior potential values. As shown in this figure, voltammogram shape practically does not change when

varying the scan rate. The cathodic peak current was always lower than the anodic one, and both of them increased proportionally to a straight line with the scan rate, which corresponds to a reversible electrochemical reaction (*Zhao L. et al., 2009*). Literature describes that the CV current densities of oxidation waves increase linearly with potential scan rates in the region of 0–50 mV s⁻¹, indicating that redox processes are controlled by counter ion insertion-deinsertion processes (*Malta et al., 2002*). However, the current densities start to deviate from the lines as the scan rates are higher than 50 m Vs⁻¹, implying the redox processes tend to be limited by ion diffusion from the electrolyte solutions to the electrode surfaces

4. Conclusion

We have demonstrated the application of anilinium doedecylsulfate (DBS–AN) as a new route towards the production of nanographite/polyaniline composites, taking advantage of the double functionality surfactant–monomer of DBS–AN. Thanks to this property, the possible negative effect of DBS–AN against the electrical conductivity of the composites was minimized as it is converted to polyaniline. Nanographite/polyaniline electrodes showed electrochemical response, which was improved with respect to nanographite or pure polyaniline electrodes. The nanographite exhibited an improvement effect, which makes the composites to have more active sites for faradaic reaction and larger specific capacitance by combining the electrical double layer and the redox reaction in comparison to the pure polyaniline. According to composites performance supercapacitors design is possible based on the synergetic effects between capacitive charging of the double layer combined with the PAni faradaic effect.

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