

Electroactivity of few-layered graphene / polyaniline composites.

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Abstract

In this study, we used the dual functionality of anilinium dodecyl sulfate (DS-AN) both to exfoliate expanded graphite (EG) and to produce graphene / polyaniline composites, in a two-step method. On the one hand, DS-AN performs the common functions of a surfactant, and on the other hand, the salt is a monomer to propagate polyaniline; that is, DS-AN is a reactive surfactant (or surfmer). Electron microscopy clearly evidenced graphite exfoliation, where most layers were in the form of few-layer graphene (more than 4 layers). The electrochemical performance of composites was evaluated by cyclic voltammetry with three-electrode cell configuration (CV), where the capacitive responses between -0.20 and 1V (vs. Ag/AgCl) in concentrated acidic media are demonstrated. The composite electrode was carried out at different scan rates showing much higher specific capacitance than pure polyaniline and graphene electrodes under the same conditions.

Keywords: Graphene, Polyaniline, Surfmer

Sesión: Nanocompuestos y materiales poliméricos compuestos

1 INTRODUCTION

Graphene is a truly two-dimensional carbon nanomaterial comprised of layers of carbon atoms arranged in six-membered rings. Due to the unique properties of its electrons, graphene has attracted much attention from physical, chemical and materials scientists since its isolation in 2004 (Novoselov *et al.*, 2004).

Micromechanical exfoliation of highly oriented pyrolytic graphite (peeling with Scotch tape) was the first method to produce graphene. Nowadays, however, due to the great success of graphene, large amounts of it are required to satisfy research needs. Several ingenious strategies to produce graphene can be consulted in literature (Xin *et al.*, 2011). The use of surfactants assisted by sonication has been widely reported to obtain graphene nanosheets (Lotya *et al.*, 2010). However, this strategy has the drawback that the product is contaminated by surfactant itself, causing a negative effect on the conductive properties of the material.

Herein, we report the use of anilinium dodecylsulfate (DS-AN) as a surfmer; that is, on the one hand, the salt performs the common functions of a surfactant, and on the other hand, the salt is a monomer to synthesis polyaniline. With this strategy, further steps for cleaning surfactant are not required, since DS-AN was converted to polyaniline.

Conducting polymers can be used as electrode materials for redox capacitor. Polyaniline is one kind of them. Due to its properties, it has gained great interest in terms of several advantages for practical applications like intrinsic conductive, cheap, ease of polymerization in aqueous media, and good specific capacitance (Mastragostino *et al.*, 2002).

Recently, graphene is expected to be an excellent electrode material for supercapacitors due to its superior electrical conductivity, high specific surface area, and chemical stability (Liao *et al.*, 2011). Although, graphene can also be incorporated with conducting polymers (Wu *et al.*, 2010) to improve the electrochemical properties of composite by the synergistic effects of the double layer and the faradaic capacitance. The combination of graphene with polyaniline has been proved to be attractive to reinforce the stability of the polyaniline and maximize the capacitance value (Wang *et al.*, 2009).

Supercapacitors provide higher specific power than batteries, and higher energy than conventional dielectric capacitors because of the high capacitance of the electrode materials (Zhang *et al.*, 2010). There are two types of supercapacitor: the electric double layer capacitors and the redox supercapacitors, in each type the energy storage mechanism are different. The capacitance in double layer capacitor is electrostatic in origin. In the redox supercapacitor, fast faradaic charge transfer occurs at the electrode materials, as in battery, and then produces the pseudocapacitance (Park *et al.*, 2002).

2 MATERIALS Y METHODS

2.1 Materials

Expanded graphite (Grafoil), and anilinium dodecylsulfate as the surfmer. The oxidizing agent ammonium persulfate (Productos Químicos Sydney 2000) was recrystallized prior to use.

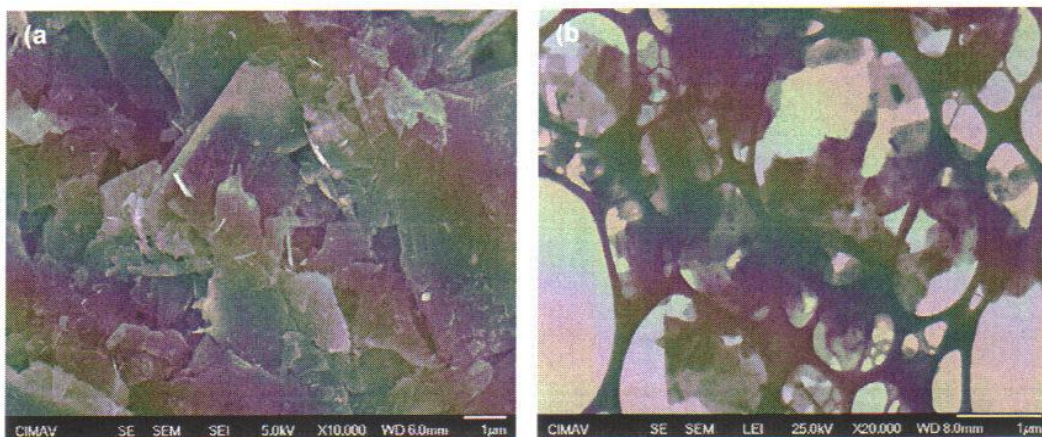


Fig. 1 (a) TEM image of EG and (b) TEM image of graphene / polyaniline composite.

2.2 Methods

2.2.1 Synthesis of graphene / polyaniline composites

In the first step, expanded graphite (EG) was treated as follows: 1.0 g of EG, 0.1 g of DS-AN, and 150 mL of distilled water were mixed together 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 to room temperature and then put in refrigeration for 2 h. Finally, the mixture was sonicated using a sonic dismembrator (Model 505, Fisher Scientific) programmed to apply pulses with 100% of amplitude for 10 min.

In the second step, the DS-AN used to treat EG was submitted to an oxidative polymerization, by adding ammonium persulfate (APS) in molar ratio, APS : DS-AN, of 1.2 : 1. The polymerization was allowed for 48 h at -2 °C. After that, the dark-green dispersion obtained was sonicated again for 10 min at 100% of amplitude. The solids were recovered by filtration and washed with distilled water to remove the co-products. Finally, the solids were re-dispersed in 200 mL of distilled water by applying sonication for 2 min. The final product was centrifuged at 4,000 rpm for 15 min, and kept as an aqueous suspension.

2.2.2 Preparation of electrodes and electrochemical measurement

The electrochemical performance was evaluated in a three-compartment cell equipped with the working electrode, an Ag/AgCl was used as the reference electrode, and a platinum wire was employed as the counter electrode.

The working electrode was prepared as follows: the composite suspension was dropped onto appropriated packed graphite-paste that was filled firmly into one end

of a plastic tube, with a copper wire inserted through the opposite end to establish an electrical contact. Cyclic voltammetry was carried out at different scan rates ranging from 10 to 50 mVs⁻¹ within potential range of -0.20 to 1 V in a 2 M H₂SO₄ aqueous electrolyte at room temperature.

3 RESULTS AND DISCUSSION

In this study, we used the dual functionality of DS-AN both to exfoliate EG and to produce graphene / polyaniline composites, in a two-step method. The exfoliation of the GE was based on the low solubility of DS-AN in water at room temperature (Krafft temperature of 32.5°C, and cmc of 2.99 mmol L⁻¹). In this way, when the graphite was exposed to DS-AN in aqueous solution at 50°C, it was expected the adsorption of the surfactant on the graphite surface and among the graphene layers, in the same way as reported in literature for other surfactants (Lotya, *et al.*, 2009). With temperature reduction, DS-AN precipitates from the aqueous phase; consequently, the expansion of the graphite layers is expected, and exfoliation would be made through ultrasound application. Subsequently, DS-AN was submitted to an oxidative polymerization by exposition with APS to produce the composites.

3.1 Microscopy

The product of the second stage was a dark-green fluid dispersion indicating the presence of polyaniline in the conductive form (emeraldine base salt). The images of the graphene / polyaniline composites using 10 mmol L⁻¹ of DS-AN are portrayed in Fig.1. As observed, the exfoliation of EG was evident.