

## Synthesis and Characterization of Fe<sub>3</sub>O<sub>4</sub>/polyaniline Core-shell Composites

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**Abstract** – Magnetite (Fe<sub>3</sub>O<sub>4</sub>)/polyaniline core-shell composites were synthesized using a reactive surfactant to improve magnetite dispersion and as the monomer of conducting polyaniline. Reduction of magnetic particle aggregation and core-shell morphology were evidenced by electron microscopy. Additionally, the decrement in magnetization ( $\sigma_r$ ) and (hysteresis)  $H_c$  observed in the core-shell composite was attributed to the increment in dipolar magnetic interaction due to the increased separation among the Fe<sub>3</sub>O<sub>4</sub> nanoparticles because of the PANi shell formation.

**Keywords:** Conducting polymer, Core-shell composite, Magnetite, Polyaniline, Reactive surfactant

### 1. Introduction

The main idea in a composite is to integrate several component materials and their properties in a single material. Magnetic polymer nano-composites represent a class of functional materials, where magnetic nanoparticles are embedded in polymer matrices. These nano-composites hold immense potential for applications in cell separations, enzyme immunoassay, drug targeting, electromagnetic device application, and electromagnetic interference suppression (Pyun, 2007). Conducting polymers have received special attention because of their excellent electronic properties and tunable conductivities in addition to their superior polymer properties. In particular, polyaniline (PANi) has been the subject of intense study during the past two decades because of its excellent electronic and chemical properties. PANi displays many novel and interesting properties such as special doping mechanisms, high environmental stability, and easy processing (Negi and Adhyapak, 2002). The PANi composites containing nanoparticles are usually investigated due to their unique magnetic and electrical characteristics. Metal oxides with the spinel structure constitute an important class of materials exhibiting a wide variety of interesting electrical, magnetic, and optical properties. Magnetite or Fe<sub>3</sub>O<sub>4</sub> is a common ferrite-possessing material with a cubic inverse spinel structure. Stable Fe<sub>3</sub>O<sub>4</sub> with high crystallinity and magnetic responses can be easily manufactured. A number of articles have been published on the magnetic properties, and it has

been observed that the magnetic properties of ferrites are influenced by coatings of a conducting polymer (Yang et al., 2009).

Herein, we report the use of anilinium dodecylbenzenesulfate (DBS-AN) as a reactive surfactant (surfmmer); 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. Thus, the synthesis of magnetite ( $\text{Fe}_3\text{O}_4$ )/polyaniline nanocomposites without further requirement of critical cleaning is possible.

## 2. Experimental Section

### 2.1 Synthesis of $\text{Fe}_3\text{O}_4$ and Core-shell Composites

Magnetite ( $\text{Fe}_3\text{O}_4$ ) was synthesized as reported by Vergés et al. (2008). This method used the  $\text{FeSO}_4$  salt precipitation in the presence of a base (NaOH) and a mild oxidant ( $\text{KNO}_3$ ). Optimal conditions for this synthesis were at concentrations of: a) ferrous solution containing 0.1M  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and 0.01M  $\text{H}_2\text{SO}_4$ ; b) oxidation solution containing 0.07 M NaOH and 0.1 M  $\text{KNO}_3$ . The two solutions were mixed by adding ferrous solution to the first solution at a constant rate of  $60 \text{ mL min}^{-1}$ , under stirring and inert atmosphere ( $\text{N}_2$ ) reaching  $\text{pH} > 11$  during the reaction; a green phase of iron salt was obtained in the solution. After, the solution was thermally aged at  $90 \text{ }^\circ\text{C}$  during 24 h in a water bath in order to obtain a magnetite stable phase. Then, the solution was cooled down at room temperature; the precipitate obtained was magnetically decanted, washed, and dried.

Magnetite/polyaniline core-shell composites were synthesized as follows: First, an aqueous dispersion of magnetite was prepared by sonication in the presence of anilinium dodecylbenzenesulfonate (DBS-AN). Afterwards, to synthesize the polyaniline shell, ammonium persulfate (APS) was used as the oxidizing agent at a molar ratio of 1.2:1.0 (APS:DBS-AN). The oxidative polymerization was performed at  $-2 \text{ }^\circ\text{C}$ .

### 2.2 Characterization

Scanning electron microscopy in transmission mode (STEM) was performed in a field emission electron microscope (JSM-7401F; JEOL) at 30 KV. To prepare the samples, a drop of aqueous dispersion, of magnetite or magnetite/polyaniline composite, was dispersed by sonication for 5 min in 30 mL of distilled water. Subsequently, a drop of dispersion was placed and left dry on a holey-carbon-cooper grid. XRD pattern of the pure magnetite was obtained at room temperature using an X-ray diffractometer (Expert Pro, PANALytical) with  $\text{Cu-}\alpha$  radiation. All peaks were identified with the magnetite cubic crystalline phase (PDF-3 01-075-0449). Magnetic measurements were run at room temperature using a magnetometer (Versalab Crio Free VSM, Quantum Design) with maximum applied field  $H_{\text{max}} = 20 \text{ kOe}$ .

## 3. Results and Discussion

STEM image of the magnetite particles is portrayed in Fig. 1(a). As observed, the sample consists of nanometric-spherical particles ( $< 100 \text{ nm}$ ) with wide polydispersity. In the case of the core-shell composites, Fig. 1(b) the presence of the polyaniline shell is observed as the grey cloud where the magnetite particles are immersed. Reduction of magnetite particle agglomeration is also evident.

Fig. 2 shows the XRD pattern of the magnetite. As noted, no peaks of any secondary phase were observed. Average crystallite size was calculated using Scherrer's formula using the FWHM of the most intense peak (Cullity and Stock, 2001), giving values of  $\langle D \rangle = 36 \pm 1 \text{ nm}$ . UNITCELL software was used to calculate the lattice parameters. Values of  $a = 8.370(1) \text{ \AA}$  resulted, which indicates that lattice parameter is not affected by synthesis process (Holland and Redfern, 1997).

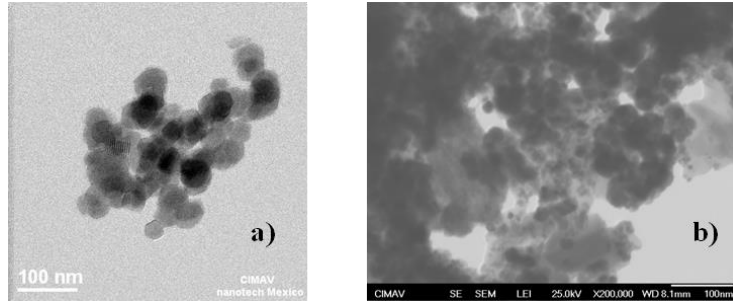


Fig 1. STEM micrographs of a) pure Magnetite, and b) magnetite/polyaniline composite.

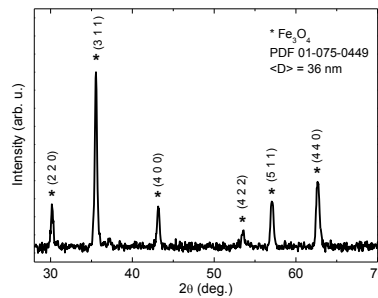


Fig. 2. Figure 1 shows the XRD pattern obtained at room temperature.

Fig. 3 shows the hysteresis loop measured at room temperature with a  $H_{\text{max}}$  of 20 kOe for  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{PAni}$  core-shell composite. The saturation magnetization values,  $\sigma_s$ , observed for  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4/\text{PAni}$  core-shell composite were 58 and 50  $\text{emu g}^{-1}$ , respectively. These values are much lower to the reported theoretical saturation magnetization in magnetite (92  $\text{emu g}^{-1}$ ), and to the value of commercial magnetite fine powder (84.5  $\text{emu g}^{-1}$ ) (Thapa et al., 2004). For the  $\text{Fe}_3\text{O}_4$  nanoparticles, the lowering on the saturation magnetization could be attributable to morphology and superficial effects such as oxidation differences. Another reason could be a lack of symmetry at the surface, which yields to broken ligands. This caused a deficiency of superexchange interaction between close-to-surface iron atoms. In addition, if a superficial oxygen layer is formed, the linked electrons cannot participate in superexchange anymore, resulting in a decrease of net magnetization (Kodama, et al., 1997).

Meanwhile, for the  $\text{Fe}_3\text{O}_4/\text{PAni}$  core-shell composite, the reduction in  $\sigma_s$  is attributed to the reduction on magnetic mass, as PAni is not contributing to magnetization values. Since the critical diameter for superparamagnetic behavior in  $\text{Fe}_3\text{O}_4$  is 20 nm, and because the average crystallite size reached for our  $\text{Fe}_3\text{O}_4$  nanoparticles, 36 nm, a ferrimagnetic behavior has to be expected in both samples (Lu et al., 1997), which is exposed by the remnant magnetization between 8 and 4  $\text{emu g}^{-1}$  and coercivity between 100 and 60 Oe. The lower values for  $\sigma_r$  and  $H_c$  observed in  $\text{Fe}_3\text{O}_4/\text{PAni}$  core-shell composite can be attributed to the increment in dipolar magnetic interaction due to a larger separation between the  $\text{Fe}_3\text{O}_4$  nanoparticles because the PAni shell.

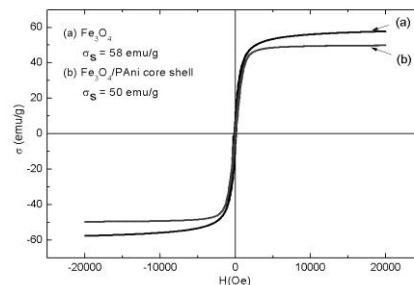


Fig. 3. Hysteresis loop measured at room temperature with a  $H_{\text{max}}$  of 20 kOe.

#### 4. Conclusion

The Fe<sub>3</sub>O<sub>4</sub> nanoparticles with 36 nm exposed a ferrimagnetic behavior, with a saturation magnetization of 58 emu g<sup>-1</sup>. After the PANi shell is formed, the magnetic properties goes to lower values due to magnetic mass reduction and the enhanced magnetic dipolar interactions because of the largest separation between Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

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