



Preparation and Characterization of Polyaniline/Fe₂O₃ Nanocomposite using Surfactant

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(Received: 27 September 2010;

Accepted: 11 May 2011)

AJC-9937

Nanocomposites of polyaniline containing ferric oxide were synthesized by a chemical method using sodium dodecylbenzenesulfonate as a surfactant. Characteristics of the products such as morphology, particle size and chemical structure were studied. The results indicated that these properties were dependent on the surfactant and metallic oxide were used.

Key Words: Nanocomposite, Polyaniline, Morphology, Fe₂O₃.

INTRODUCTION

Electronically conducting polymers are the novel class of synthetic metals with wide spread application in number of technological devices like EMI shielding and electrostatic charge dissipation¹⁻⁵, sensors⁶⁻⁸, organic light emitting diodes⁹⁻¹¹ and polymer solar cells^{12,13}.

Polyaniline (PAn) is one of the most technologically important materials because of its environmental stability in a conducting form, unique redox properties and high conductivity¹⁴. Polyaniline composite materials possess the potential of a multitude of applications, such as in gas sensitivity, sensors and inductors¹⁵⁻¹⁷.

Although the simplest method for the synthesis of bulk polyaniline is chemical oxidative precipitation polymerization of aniline using a chemical oxidant such as ammonium peroxy disulfate. The resulting polyaniline is highly aggregated and therefore unsatisfactory for most applications. Industrial demand has led to the development of several strategies to overcome such problems. The synthesis of polyaniline in colloidal form is one of the attractive alternatives to overcome its poor processability due to its insolubility in common organic solvents and water¹⁸⁻²⁵.

Conducting polymer-metal nanocomposites provide exciting systems to investigate the possibility of designing device functionality²⁶⁻³⁰ and exhibit enhanced sensing and catalytic capabilities compared to the pure conducting polymer³¹⁻³⁵. In the synthesis of polyaniline-metal nanocomposites, metal ions are often reduced in the presence of preformed polyaniline and metal nanoparticles deposited on the surface of the polymer where the metal ions and polyaniline contact³⁶. Polymerization of aniline in the presence of preformed metal nanoparticles

also leads to the formation of polyaniline-metal nanocomposites³⁷.

In this study, polyaniline nanocomposite was prepared in the aqueous solution using (NH₄)₂S₂O₈ as an oxidant in the presence of Fe₂O₃ as an additive and sodium dodecylbenzenesulfonate as a surfactant.

EXPERIMENTAL

A magnetic mixer model MK20, digital scale model FR200, scanning electron microscope (SEM) model XL30, fourier transform infrared (FTIR) spectrometer model Shimadzu 4100 and X-ray diffraction (XRD) were employed.

Materials used in this work were aniline (extra pure > 99 %, d = 1.02 g/mL), ammonium peroxy disulfate, sulfuric acid and sodium dodecylbenzenesulfonate from Merck. All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation.

Preparation of polyaniline nanocomposite: 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid (1 M) containing 2.5 g of (NH₄)₂S₂O₈. After 5 h, the polymer was filtered and in order to separate the oligomers and impurities, the product was washed several times with deionized water. It was then dried at room temperature.

Preparation of polyaniline/Fe₂O₃ nanocomposite: 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid (1 M) containing 2.5 g (NH₄)₂S₂O₈. After 2 h, 0.2 g of Fe₂O₃ was added to stirred aqueous solution. The reaction was carried out in aqueous media at room temperature. After 3 h, the polymer was filtered and in order to separate

the oligomers and impurities, the product was washed several times with deionized water. It was then dried at room temperature.

Preparation of polyaniline/sodium dodecylbenzenesulfonate nanocomposite: 1 mL aniline monomer was added to stirred aqueous solution (100 mL) of sulfuric acid (1 M) containing 2.5 g of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and 0.4 g of sodium dodecylbenzenesulfonate. After 5 h, the polymer was filtered and in order to separate the oligomers and impurities, the product was washed several times with deionized water. It was then dried at room temperature.

Preparation of polyaniline-sodium dodecylbenzenesulfonate/ Fe_2O_3 nanocompo-site: 0.2 g of Fe_2O_3 was added to stirred aqueous solution (100 mL) of sulfuric acid (1 M) containing 0.4 g of sodium dodecylbenzenesulfonate. After 1 h, 2.5 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$ was added to stirred aqueous solution. After 0.5 h, 1 mL aniline was added to stirred solution. The reaction was carried out in aqueous media at room temperature for 3 h. After 3 h, the polymer was filtered and in order to separate the oligomers and impurities, the product was washed several times with deionized water. It was then dried at room temperature. Similarly, different composition of polyaniline-sodium dodecylbenzenesulfonate/ Fe_2O_3 nanocomposite containing metallic oxide and surfactant were prepared (Table-1).

TABLE-1
EFFECT OF METALLIC OXIDE AND SURFACTANT
ON THE PARTICLE SIZE OF POLYANILINE NANOCOMPOSITE

Type of composite	Conc. of Fe_2O_3 (g/L)	Conc. of DBSNa (g/L)	Particle size (average) (nm)
Pure polyaniline	–	–	160
Polyaniline and DBSNa	–	4	115
Polyaniline and Fe_2O_3	2	–	100
Polyaniline + DBSNa + Fe_2O_3	2	4	90

RESULTS AND DISCUSSION

The chemical method can be a general and useful procedure to prepare conductive polymer and its composites. It is well established that the charge transport properties of conjugated polymers strongly depend on the processing parameters³⁸. Polyaniline has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a high chemical flexibility. It undergoes protonation and deprotonation in addition to adsorption through nitrogen, which, having a lone pair of electrons, is responsible for the technologically interesting chemistry and physics.

The surface morphology of polymers was studied, using scanning electron microscope. As shown in Figs. 1-4, the size and homogeneity of particles are dependent on the presence of surfactant and metallic oxide. This is presumably due to the amount of adsorbed chemically surfactant (grafting copolymer) to the polyaniline particles. Surface active agents affect the physical and chemical properties of the solutions. The type of surfactant is known to influence the rate of polymer formation, particle size, size distribution, morphology and homogeneity³⁹⁻⁴⁴.

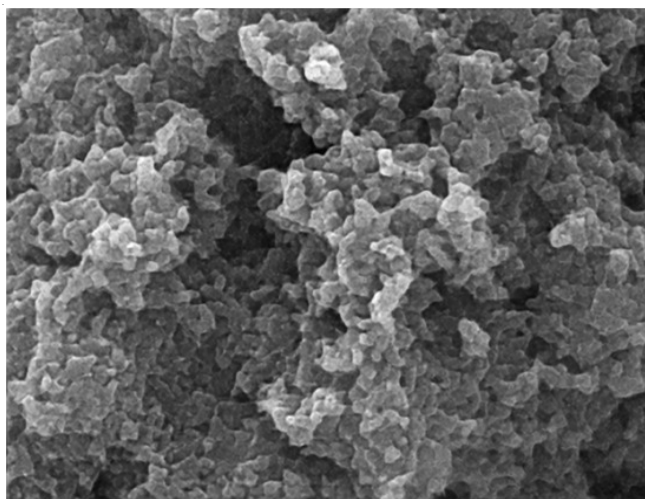


Fig. 1. Scanning electron micrograph of polyaniline without surfactant

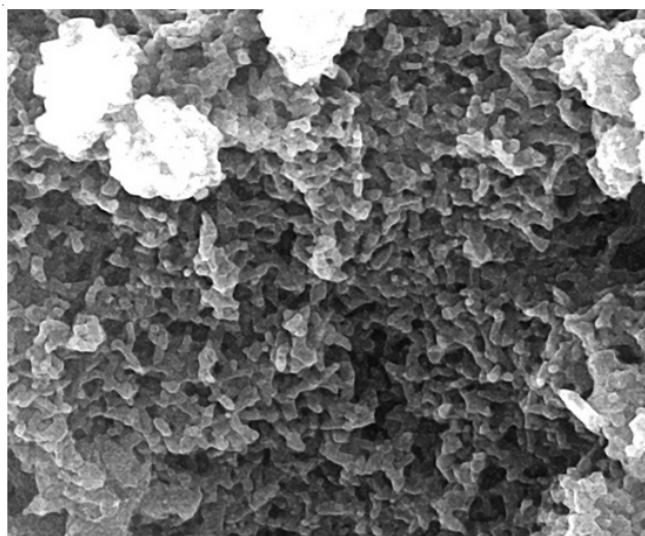


Fig. 2. Scanning electron micrograph of polyaniline using sodium dodecylbenzenesulfonate as a surfactant

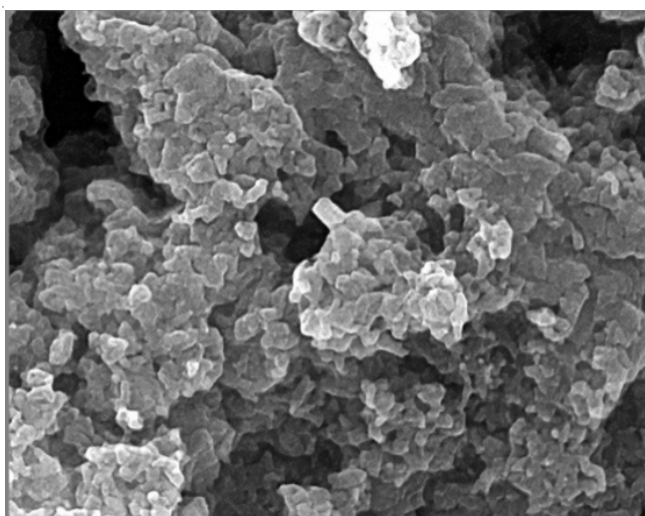


Fig. 3. Scanning electron micrograph of polyaniline/ Fe_2O_3 nanocomposite

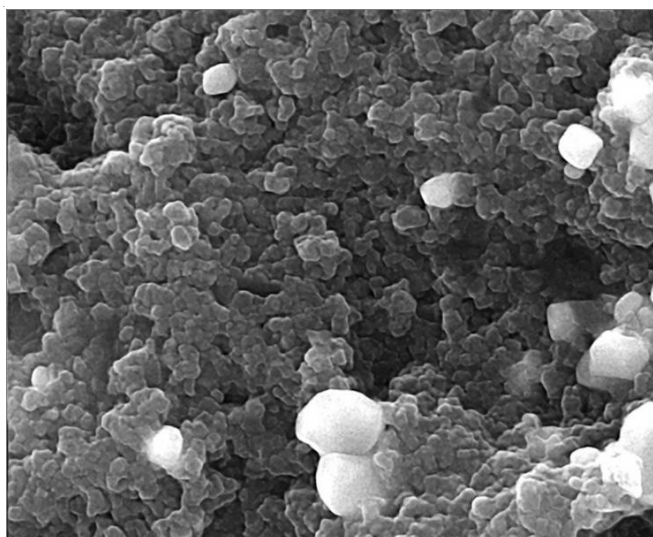


Fig. 4. Scanning electron micrograph of polyaniline-sodium dodecylbenzenesulfonate/Fe₂O₃ nanocomposite using sodium dodecylbenzenesulfonate as a surfactant

FTIR spectra in the 4000-450 cm⁻¹ region, for polyaniline in aqueous media are shown in Fig. 5. As can be seen in Fig. 5a, polyaniline polymer shows the presence of characteristic absorption bands at 1562 cm⁻¹ (C=C stretching vibration of the quinoid ring), 1475 cm⁻¹ (stretching vibration of C=C of the benzenoid ring), 1302 cm⁻¹ (C-N stretching vibration), 1137 cm⁻¹ (C-H in-plane deformation) and 804 cm⁻¹ (C-H out-of-plane deformation).

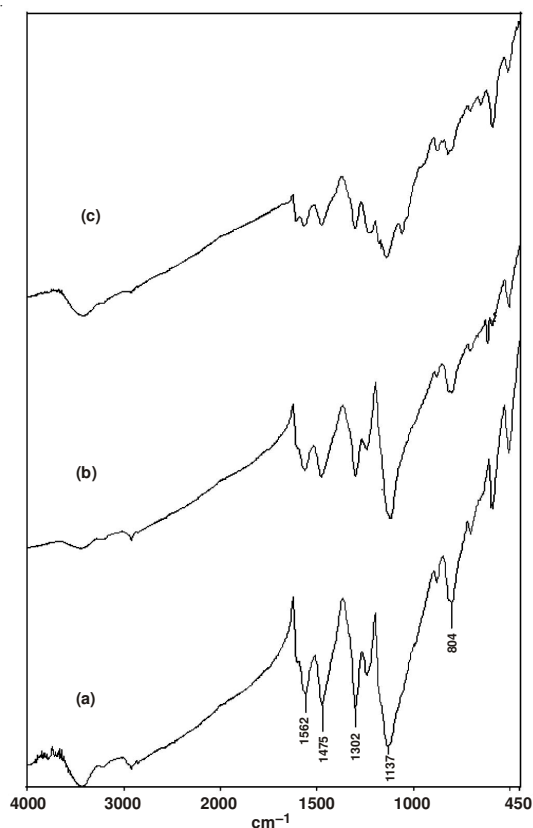


Fig. 5. FTIR spectra of (a) pure polyaniline, (b) polyaniline-sodium dodecylbenzenesulfonate and (c) polyaniline-sodium dodecylbenzenesulfonate/Fe₂O₃ nanocomposite

X-ray scattering patterns of pure Fe₂O₃ nanoparticle is shown in Fig. 6a. The main peaks are at $2\theta = 33.22, 40.95, 54.1, 57.65, 64.05$. According to Scherrer's equation⁴⁵:

$$\beta = k\lambda / D\cos\theta$$

where λ is the X-ray wavelength, k , the shape factor, D , the average diameter of the crystals in Å, θ , the Bragg angle in degree and β is the line broadening measured by half-height in radians. The value of k depends on several factors, including the miller index of the reflection plane and the shape of the crystal. If the shape is unknown k is often assigned a value of 0.89. When the reflecting peak at $2\theta = 33.22$ is chosen to calculate the average diameter, the average size of the Fe₂O₃ particles is 40 nm.

Fig. 6b shows the X-ray pattern of polyaniline/Fe₂O₃ nanocomposite. It can be seen that the polyaniline/Fe₂O₃ X-ray pattern is very much similar to that of Fe₂O₃. This indicates that polyaniline deposited on the surface of Fe₂O₃ has no effect on the crystalline structure of Fe₂O₃.

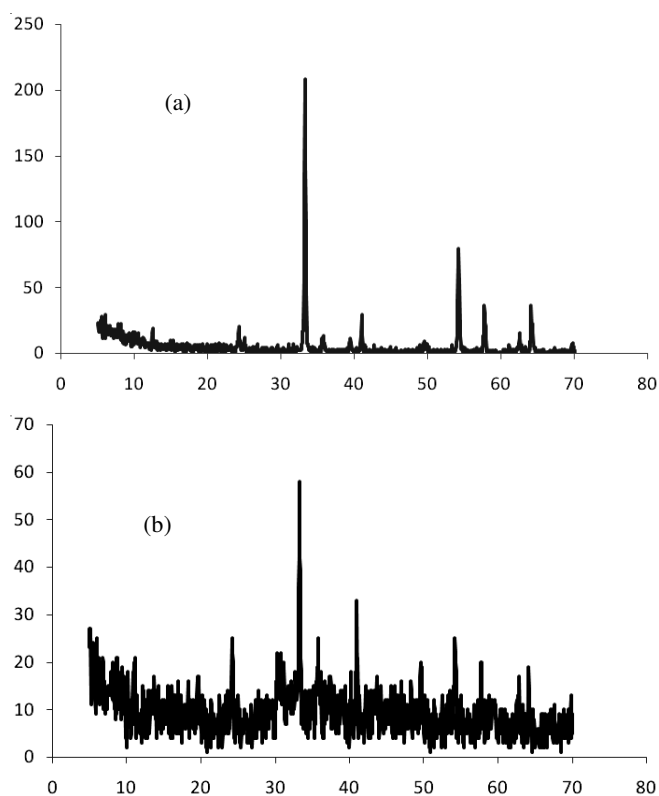


Fig. 6. X-ray scattering patterns of (a) pure Fe₂O₃ and (b) polyaniline/Fe₂O₃ nanocomposite

Conclusion

In this study the characteristics of polyaniline nanocomposites such as morphology and particle size were investigated using sodium dodecylbenzenesulfonate as a surfactant in the presence of metallic oxide as an additive. The SEM micrographs show that the surfactant plays a major role on the surface morphology of products, because, emulsifiers decrease the tendency to form agglomerate which leads to more homogeneous distribution in the particles. The surfactant has a considerable effect on the size and homogeneity of particles because surfactant adsorbed chemically to the polyaniline (grafting

copolymer). The FTIR spectra of polyaniline/Fe₂O₃ and polyaniline/sodium dodecylbenzenesulfonate are similar to that of polyaniline. The X-ray pattern shown that the polyaniline has no effect on the crystalline behaviour of Fe₂O₃.

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