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Preparation and Characterization of Polyaniline-Co_3O_4 Nanocomposites via Interfacial Polymerization

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Abstract Polyaniline (Pani) and Polyaniline-Co_3O_4 nanocomposites (PCO) were prepared by employing interfacial polymerization using ammonium persulphate as an oxidizing agent. The formations of regular nanocomposite materials were studied by Fourier transform infrared (FTIR) spectroscopy and XRD techniques. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were conducted to characterize the morphology. Thermo-gravimetric (TG) and differential thermal analysis (DTA) were carried out study the thermal stability of the resulting composites. The nanocomposites were weakly ferromagnetic at room temperature. Formation of conducting emeraldine salt form was concluded by electrical conductivity.

Keywords Interfacial Polymerization, Polyaniline, Co_3O_4 Nanocomposites, Conductivity

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1. Introduction

Magnetic nanoparticles (NPs) offer prodigious potential for applications not only as catalysts or energy storage devices, but also in biomedicine, as contrast enhancement agents for magnetic resonance imaging, or for drug delivery. The same characteristics that make cobalt-based nanoparticles highly attractive and stimulate the researchers to make cobalt based functional nanoparticles. In this context, we synthesized and characterized cobalt oxide nanoparticles. Believing that the characterization of nanoparticles is relevant for understanding their biological activity in future, we analyzed them using various instrumental techniques. It is reported that the biological effects could be due to a potential release of cobalt ions, we evaluated spontaneous dissolution in different media.

Conducting polymer composites is some suitable composition of a conducting polymer with one or more inorganic nanoparticles so that their desirable properties are combined successfully. Over the last few years, conducting polymer composites have been studied with growing interest because of their numerous applications in various electrical and electronic devices[1-3]. Materials based on cobalt oxides have attracted a great interest in view of their technological and fundamental scientific importance [4]. In this paper, we report the preparation and characterization of polymer-cobalt oxide nanocomposites synthesized by interfacial polymerization method. Unlike the previous reported methods the formation metal oxide nanocomposites without using any surfactants block copolymer templates[5-10], where the metal oxide is introduced during the polymer synthesis, where metal oxide is associated with the polymer chain during polymer synthesis. In this method, no further doping is required after polymer synthesis and uniform distribution of metal oxide within a polymer matrix without the aid of any surfactant.

Polyaniline is the only conducting polymer whose electrical properties can be controlled suitably by charge-transfer doping and/or protonation. Inorganic–organic composite materials are important due to their extraordinary properties, which arise from the synergism between the properties of the components. There are several routes to these materials, but probably the most prominent one is the incorporation of inorganic building blocks in organic polymers. These materials have gained much interest due to the remarkable change in properties such as mechanical[11], thermal[12-15], electrical[16], and magnetic[17] compared to pure organic polymers.

Most of the efforts are based on well-known macro- or micro composites between inorganic moieties and organic polymers, and expand ideas from this microcosm to a new class of materials, called nanocomposites[18]. Expressions like 'nanoparticles' and 'nanocomposites' seem to be very trendy, and are often misused in the literature in the sense of advertising for systems which do not properly fall under the label 'nano'. In view of inappropriate use of the term nano, there is a strong need to understand the mechanism of the formation of such materials. Important aspects of the chemistry involved in the formation of these systems are uniformity, phase continuity, domain sizes and the molecular

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mixing at the phase boundaries, which all have a direct influence on optical, physical, and mechanical properties[19].

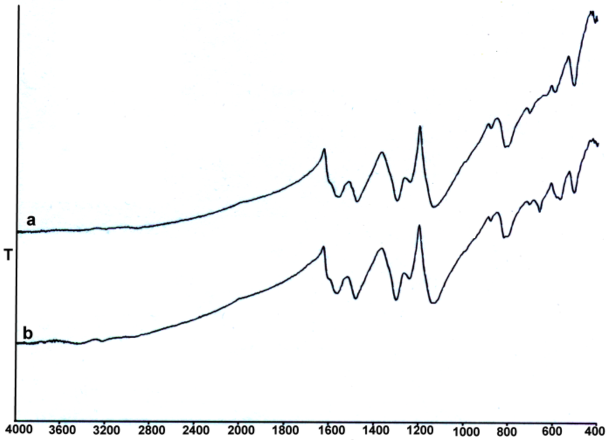

Figure 1. (a-b) FTIR Spectrum of Polyaniline-Cobalt oxide nanocomposites

Additionally, the properties of the composite materials depend on the morphology of the phases, which has to be controlled over several length scales. Therefore, the development of such materials is a 'land of multidisciplinary'[20], where chemists, physicists, material scientists and engineers have to work closely together. From a chemical point of view, one can distinguish between several ways to incorporate inorganic systems in organic polymers depending on the interactions between the moieties: materials with strong (covalent, coordination, ionic): weak (van-der-Waals, hydrogen-bonds, hydrophilic–hydrophobic balance); or without chemical interactions between the two components[20,21].

2. Experimental

2.1. Materials

All the chemicals and reagents used were of analytical grade. Double distilled water was used throughout the work. Prepared Cobalt oxide is used for the preparation of polymer composites[22] and ammonium persulphate was purchased from Qualigens; Aniline was double distilled before use and Hydrochloric acid was purchased from Aldrich chemicals. Polyaniline (Pani) and polyaniline-Cobalt oxide nanocomposites of different compositions (Pani-Co_3O_4) have been synthesized by employing interfacial polymerization method using ammonium persulphate as an oxidizing agent.

2.2. Preparation of Methods

Pani-Co_3O_4 nanocomposites were prepared with different weights of Co_3O_4 (0.1, 0.2 and 0.3 g here after called as PCO_1, PCO_2 and PCO_3 respectively.) The details of the method are as follows: 0.5 g of aniline is dissolved in 20 ml of $CHCl_3$. 0.1 M ammonium persulphate is dissolved in 1.0 M HCl & the Co_3O_4 same is slowly added to the above mixture of aqueous and organic phase. After 5 min, dark-green formed slowly at the interface and then gradually diffused into the aqueous phase. After 24 hr, the entire aqueous phase was filled homogenously with dark-green color film, organic layer observed shows orange color due to the formation of aniline oligomers. The aqueous phase was then collected, and washed with ethanol and water to remove the unreacted aniline. The residue of polymer thus obtained is purified and dried in a vacuum oven at 40℃ for 36 hr. The dried polymer composite sample is used for the structural characterization. The same is further used for thermal and conductivity studies.

2.3. Characterization Techniques

The powder X-ray diffraction patterns were recorded on a JEOL JDX-8P diffractometer using CuKα radiation (1.54 Å) at 30 kV. The Fourier transform infrared (FTIR) spectra of the samples were recorded on a Perkin-Elmer FT-IR (Model No. 1000) in the range 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Bright field transmission electron microscopy image was obtained from JOEL 100 CX operated at 190 KeV. Thermo gravimetric (TG) and differential thermal analysis (DTA) experiments were performed using NETZSC H STA 409 PC. TG and DTA data were obtained at a heating rate of 10℃/min up to 900℃ under Argon atmosphere. Two probe D.C. electrical conductivity measurements were carried out using a Keithely high precision multimeter on pressed pellets of 1 c m thickness and 1 c m diameter.

3. Results and Discussion

3.1. FTIR Spectroscopy Studies

Figure 1 (a-b) shows FTIR spectra of the polymer nanocomposite samples. The bands at 1563 and 1481 cm^{1} are attributed to C=N and C=C stretching mode of vibration for the quinonoid and benzenoid units of Pani. The peaks at 1300 and 1236 cm^{-1} are assigned to C– N stretching mode of benzenoid ring. The peak at 1239 cm^{-1} is the characteristic of the conducting protonated form of Pani[23,24]. The bands in the region 1000– 1110 cm^{-1} are due to in plane bending vibration of C– H mode. The band at 820 cm^{-1} originates out of plane C– H bending vibration. FTIR spectrum of the polymer composites shows two peaks at 665 and 703cm^{-1}; which are attributed to the presence of cobalt oxide in the polymer nanocomposite (Figure 1.b). These two peaks closely match the reported values of the optical vibration modes of Co_3O_4[25].

For the Pani-Co_3O_4 composites its IR spectrum is almost identical to that of the pure pani but all bands shift slightly towards red (lower frequency side), and the intensity ratio of quinonoid band has also changed. These results indicate that some interactions (kind of weak Vander Waals force of attraction) exist between pani and nano Co_3O_4.

3.2. X-ray Diffraction Studies

The crystallinity and chain packing of the synthesized polymer-composites were examined by X-ray diffraction analysis. The Figure 2 (a-b) shows the characteristic peak of Pani[26] with other four main peaks at 2θ= 31.95^0, 38.3^0, 45.5^0 and 65.5^0 correspond to (220), (222) (400) & (440) matching with the JCPDS pattern of Co_3O_4 nanoparticles (**JCPDS-78-1970**).

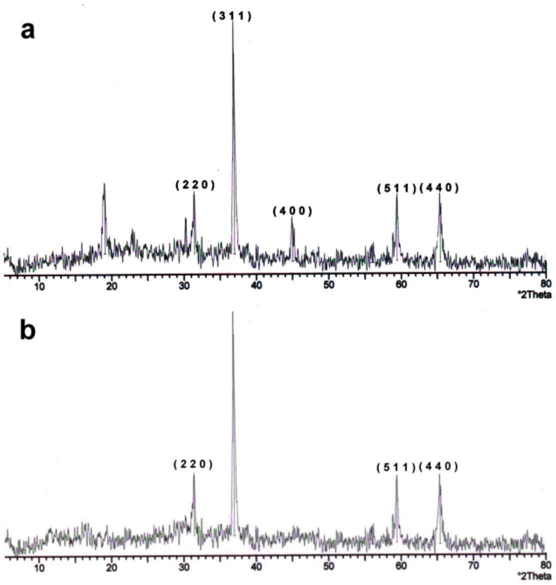

Figure 2(a-b). XRD pattern of Polyaniline-Cobalt oxide nanocomposites

3.3. Scanning Electron Microscopy

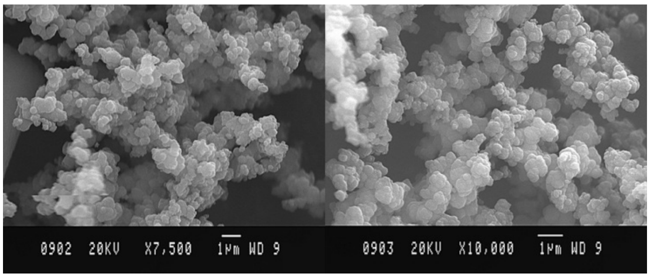

Figure 3. (a-b): SEM images of Polyaniline Cobalt oxide at low and high magnifications

The scanning electron micrograph (SEM) of the nano-composite samples at low ad high magnifications are shown in Figure 3(a-b). The Co_3O_4 particles are well dispersed and are of spherical shape with uniform diameter lying in the range from 1µm to 100 nm. A uniform morphology and chemical homogeneity observed.

3.4. Transmission Electron Microscopy

Transmission electron micrograph (TEM) images for the representative Pani-Co_3O_4 composite (Pani-CO_1) is shown in Figure.4. Which shows the typical dark filed TEM image of the as synthesized Pani-Co_3O_4 nanocomposites. The TEM image clearly shows agglomerated irregular dark cloudy shaped to be nearly 100 nm in diameter sized Pani-Co_3O_4 nanocomposites.

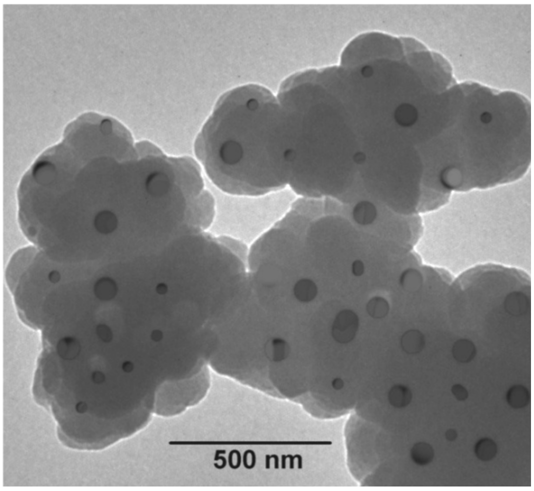

Figure 4. TEM image of Polyaniline-Cobalt oxide nanocomposite

3.5. Thermal Analysis

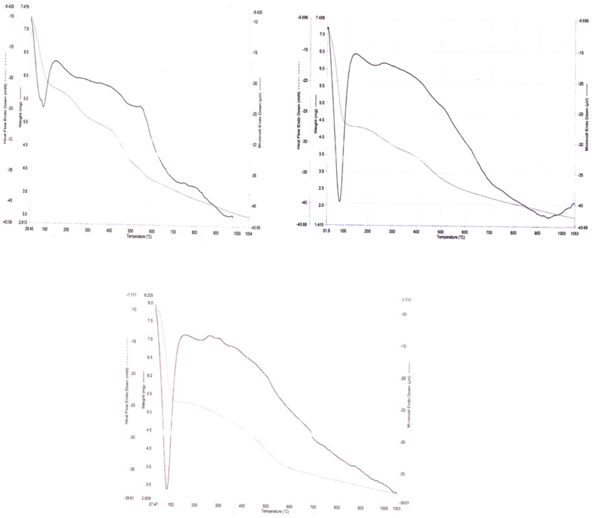

Figure 5. (a-c) TGA of Polyaniline-Cobalt oxide nanocomposites

The thermal decomposition of Pani-Co_3O_4 composites shows a two step weight loss for all the samples (Figure 5(a-c)). For PCO1, the first weight loss of 22.39% from 40 ℃ to 200 ℃ is due to the loss of water molecules present in the composite. A second weight loss of 31.95% ranging 300 to 400 ℃, indicates the loss of low fragment molecular weight present in the composites. No weight loss is observed up to 1054 ℃, which indicates the increase in thermal stability of the polymer composites compared to pure Pani[27].

DTA trace shows (Figure) an endothermic peak at 90℃ due to the loss of water molecule. An exothermic peak at 120℃ is due to the decomposition of polymer composites. Similarly for other two samples, viz., PCO2 & PCO3 is given in table.

Sample	Step	Tg/℃	DTG/℃	Loss %
PCO1 Figure 5 (a)	1	200℃	90℃	22.39
	2	400℃	140 ℃	31.95
PCO2 Figure 5 (b)	1	200℃	90℃	31.86
	2	400℃	150 ℃	51.58
PCO3 Figure 5 (c)	1	210℃	90 ℃	34.05
	2	400℃	120 ℃	42.21

Electrical Conductivity

Figure 6 (a-c) shows the variation of electrical conductivity of the Pani-Co_3O_4 samples of different concentrations. The room temperature conductivity value is of the order of 10^{-3} S/cm, which is comparable to that of pure Pani synthesized by other methods. The conductivity of our sample increased with rise in temperature.

There is a very slow increase in the conductivity from room temperature in all the three samples of 0.1, 0.2, & 0.3 M concentration of composites which are in the range of 10^{-3} to 10^{-2} S/cm and next from 180 to 200 °C the conductivity increased due to the doping of Co_3O_4.

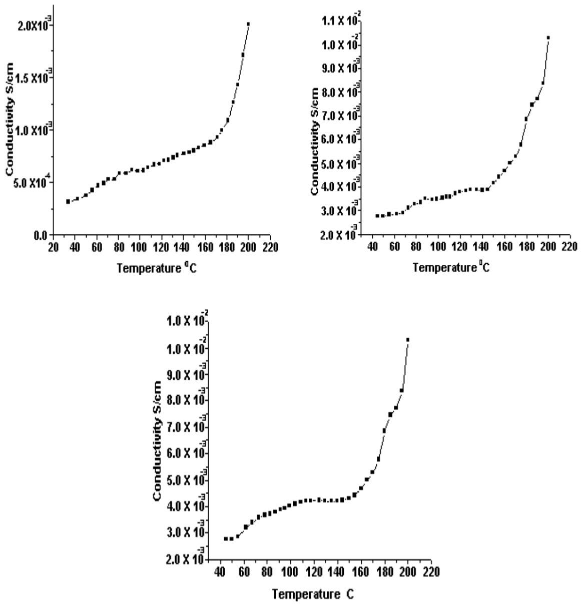

Figure 6. (a-c) D.C Conductivities of Polyaniline-Cobalt oxide nanocomposites

4. Conclusions

The synthesis of Pani-Co_3O_4 composites (about 100 nm in diameter) were achieved by interfacial polymerization of aniline. SEM shows the formation of clusters and TEM shows the incorporation of Co_3O_4 into the polymer. The evidences from FTIR and XRD indicate that there is some interaction between Pani and cobalt oxide (weak Vander Waals force of attraction). TG analysis suggests that the thermal stability of Pani-Co_3O_4 composites is higher than that of pure Pani is ascribed to the interaction between Pani and metal oxide. The nanocomposites were weakly ferromagnetic at room temperature which has many advantages as optical and electrical nanodevices and nanosensors, bio-medical and optoelectronic devices etc.

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