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Synthesis, characterization and dc conductivity studies of polyaniline / chromium oxide composites

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ABSTRACT

Conducting polyaniline/Chromium oxide (PANI/Cr₂O₃) composites have been synthesized by insitu deposition technique by placing fine graded Cr₂O₃ in polymerization mixture of aniline. The composites are characterized by employing X-ray diffractometry (XRD) and Infrared (IR) spectroscopy. It is observed from the XRD studies that Cr₂O₃ has retained its structure even though it is dispersed in PANI during polymerization reaction. By observation of IR spectra, it is seen that some of the characteristic stretching frequencies are considerably shifted towards higher frequency side. The surface morphology of these composites was studied by Scanning electron microscope (SEM). High magnification SEM image reveals the presence of Cr₂O₃ particles (cenospheres) in PANI, which are homogeneously distributed through out the composite sample. The dc conductivity was studied in the temperature range from 40-150 °C. It can be seen that the value of conductivity increases up to 30 wt% of Cr₂O₃ in PANI and then decreases thereafter. The dimensions of Cr₂O₃ particles in the matrix have greater influence on the conductivity value.

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KEYWORDS

Conductivity;
Polyaniline composites;
Cr₂O₃.

INTRODUCTION

Conducting polymers have become the foci of interest in materials science because of their specific electronic properties, which can be tailored via synthetic organic chemistry. The resulting electronic system has in general either quasi-one or two dimensional character, resulting in a specific electronic conduction ranging from insulating semi conducting to highly conducting phase. The multiplicity of intra and intermolecular vibrational modes in conjugated polymers are the key for

the many exciting properties, leading to numerous technological applications, such as active electrode materials in energy storage^[1]. Optoelectronic devices^[2,3], display devices^[4,5], corrosion inhibitors^[6,7], controller of electromagnetic radiations and electrostatic charge^[8,11].

The electrical transport in polymeric materials^[12,13] has become an area of increasing interest in research because of the fact that these materials have great potential for solid state devices. Similarly, conducting polymer composites attracted considerable interest in recent years because of their numerous applications in

variety of electric and electronic devices. Conducting polymer composites with some suitable compositions of one or more insulating materials led to desirable properties^[14]. These materials are especially important owing to their bridging role between the world of conducting polymers and that of nanoparticles. For applications of conducting polymers, knowing how these conducting polymer composite will effect the behavior in an electric field is a long-standing problem and is of great importance. The discovery of doping in conducting polymers has led to further dramatic increase in the conductivity of such conjugated polymers to values as high as 10^5 Scm⁻¹.

Among all conducting polymers, polyaniline (PANI) achieved widespread importance because of its unique conduction mechanism and environment stability. The survey of literature reveals that the detailed conductivity studies on PANI/Cr₂O₃ are scarce. In the present study, PANI and PANI/Cr₂O₃ composite (with varying weight percentage of chromium oxide in polyaniline) have been synthesized. These samples are characterized by the various techniques such as XRD, IR, SEM and the dc conductivity of these samples are measured and studied.

EXPERIMENTAL

Synthesis of PANI/Cr₂O₃ composites

Aniline (AR grade) was purified by distillation before use and ammonium per sulphate [(NH₄)₂S₂O₈]₂, HCl were used as received.. 0.1 mole aniline monomer is dissolved in 1 mole hydrochloric acid to form polyaniline. Fine graded pre-sintered yttrium oxide (AR grade, SD-Fine Chem.) powder in the weight percentages (wt %) of 10, 20, 30, 40 and 50 is added to the polymerization mixture with vigorous stirring in order to keep the chromium oxide powder suspended in the solution. To this reaction mixture, [(NH₄)₂S₂O₈]₂ which is used as an oxidant is added slowly drop-wise with continuous vigorous stirring for the period of 4-6 hours at temperature 0-5° C. Polymerization of aniline takes place over fine grade chromium oxide particles. The resulting precipitate is filtered under suction and washed with distilled water until the filtrate becomes colorless. Acetone is used to dissolve any unreacted aniline. After washing, the precipitate is dried under dynamic vacuum

at 60-80°C for 24 hrs to get resulting composites. In this way five different polyaniline chromium oxide composites with different weight percentage of chromium oxide (10, 20, 30, 40 and 50) in polyaniline have been synthesized. All the composites are crushed into fine powder in an agate mortar in the presence of acetone medium. The composite powder is pressed to form pellets of 10mm diameter and thickness which varies from 2 to 2.75 mm. The electrical measurements on these samples were made using the silver paint as electrodes on both sides.

Measurements

X-ray diffraction patterns of PANI/Cr₂O₃ were obtained with Philips X-ray diffractometer using CuK α ($\lambda = 1.5404\text{\AA}$). The infrared (IR) spectra of the composites were recorded on Perkin Elmer (model 783) IR spectrometer in KBr medium at room temperature, in the region 4000 – 450 Cm⁻¹. The powder morphology of PANI and PANI/Cr₂O₃ samples in the form of pellets was investigated using Philips XL 30 ESEM scanning electron microscope (SEM). The dc conductivity of the PANI/Cr₂O₃ composites were measured by two probe technique using a laboratory made setup in the temperature range 40 – 150 °C.

RESULTS AND DISCUSSION

Figure 1 shows XRD patterns for PANI/Cr₂O₃ composite with 50 wt% of Cr₂O₃ in PANI. It is seen from Figure 1, that the rhombohedral peak of Cr₂O₃ indicates the crystalline nature of the composite. By comparing the XRD pattern of the composite with that of Cr₂O₃, the prominent peaks corresponding to $2\theta = 25.1$, 34.22, 36.83, 50.85 and 55.49 are due to (0 1

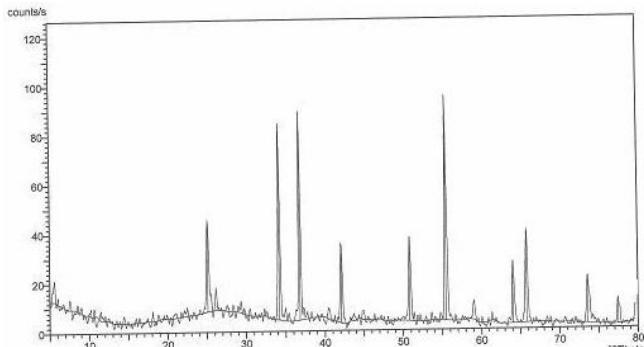


Figure 1 : X-ray diffraction pattern of PANI with 50 wt% of Cr₂O₃

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2), (1 0 4), (1 1 0), (0 2 4) and (1 1 6) planes of Cr_2O_3 [JCPDS file no. 38 -1479] By comparing the XRD pattern of the composite and Cr_2O_3 , it is confirmed that Cr_2O_3 has retained its structure even though it is dispersed in PANI during polymerization reaction.

Infrared spectrum (IR)

Figure 2 shows the IR spectra of PANI/ Cr_2O_3 composite (50% wt of Cr_2O_3 in PANI). The IR transmission spectra of powder using KBr pellets having different weight percentage of Cr_2O_3 in PANI were recorded in the range 450 – 4000 Cm^{-1} to confirm polymerization of polyaniline. The spectra for all the samples showed strong bands in the region 470 – 1600 Cm^{-1} that are the characteristics of PANI^[14]. Similar stretching frequencies can also be found in other composites but intensity of metal oxygen peak increases as the weight present of Cr_2O_3 is increased. The important peaks that are observed in this composite in IR spectra are observed at 1567 Cm^{-1} , 1482 Cm^{-1} , 1304 Cm^{-1} , 1248 Cm^{-1} , 1143 Cm^{-1} , 869 Cm^{-1} , 804 Cm^{-1} 623 Cm^{-1} , 575 Cm^{-1} and 511 Cm^{-1} . It is found from the IR spectra that some of the characteristic stretching frequencies are considerably shifted towards higher frequency side. The typical peaks observed are at 1567 Cm^{-1} , 1482 Cm^{-1} , 1304 Cm^{-1} , 1143 Cm^{-1} , 804 Cm^{-1} and 511 Cm^{-1} which may be attributed due to the Vander walls kind of interaction between Cr_2O_3 and PANI chain^[15].

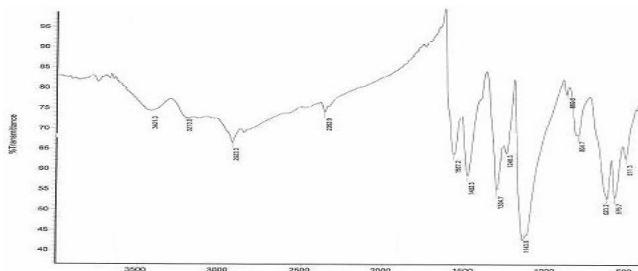


Figure 2 : Infrared spectroscopy of PANI with 50 wt% of Cr_2O_3

Scanning electron micrograph (SEM)

SEM of PANI/ Cr_2O_3 composites with 50 wt% of Cr_2O_3 in PANI is shown in Figure 3. High magnification SEM image reveals the presence of Cr_2O_3 particles (cenospheres) in PANI, which are homogeneously distributed through out the composite sample. It is for the first time, to best of my knowledge, such a beautiful distribution of cenospheres is observed which looks as if

the beads are floating over the water surface. These cenospheres show a large variation in their dimensions. The lowest diameter of cenospheres recorded was 250 nm and highest was with diameter 750 nm. Such large variation in the dimensions of cenospheres has a strong influence on the various electrical properties of the composites. The contrast in this image is due to the difference in scattering from different surface areas as a result of geometrical difference between PANI and Cr_2O_3 .

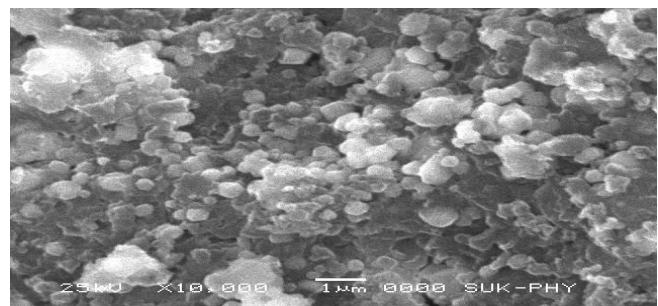


Figure 3 : SEM micrograph of PANI with 50 wt% of Cr_2O_3

Dc conductivity

Figure 4 shows the variations of dc conductivity as a function of temperature for all composites and Figure 5 shows the variation of dc conductivity as a function of wt% of Cr_2O_3 in PANI at different temperatures. It can be observed that in all the composites the conductivity increase with respect to temperature forming multiple phases of conductivity. It can be seen that the value of conductivity increases up to 30 wt% of Cr_2O_3 in PANI and then decreases there after. This may be due to the extended chain length of PANI which facilitates the hopping of charge carriers when the content of Cr_2O_3 is up to 30 wt%. This point is a percolation threshold and the composites obey percolation theory. Further the decrease in conductivity is observed after 30 wt% which may be attributed due to the distribution of Cr_2O_3

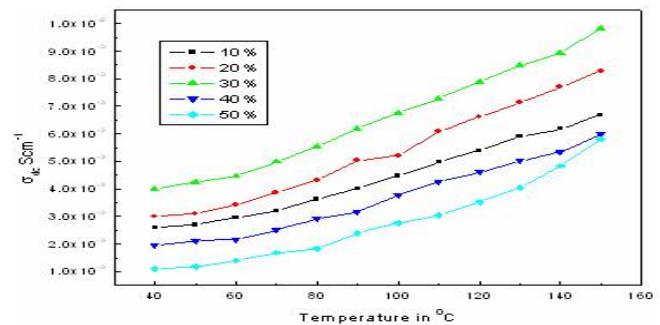


Figure 4 : Variation of σ_{dc} as a function of temperature for PANI/ Cr_2O_3 composites

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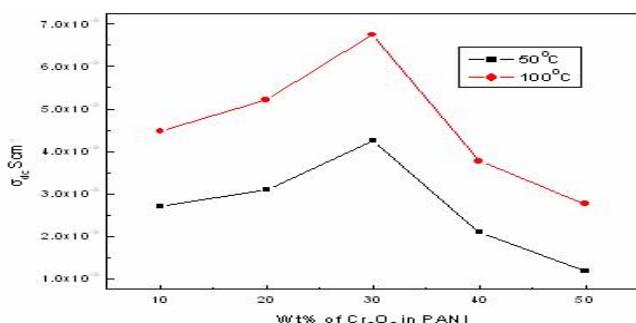


Figure 5 : Variation of σ_{dc} as a function of wt% of Cr_2O_3 in PANI at different temperatures.

particles of larger grain size, which are partially blocking the hopping of charge carriers, since charge trapping in PANI and its blends is a general universal feature of these materials^[16,17].

CONCLUSION

Efforts have been made to synthesize PANI/ Cr_2O_3 composites to tailor make their properties. Detailed characterizations of the composites were carried out using XRD, IR and SEM techniques. The results of dc conductivity show a strong dependence on the weight percent of Cr_2O_3 in PANI.

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