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Effect of loading titanium dioxide on structural, electrical and mechanical properties of polyaniline nanocomposites

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ABSTRACT

Nanocomposites based on Polyaniline Titanium dioxide (PANI-TiO_2) were prepared by in situ chemical polymerization. The structure was confirmed by X-rays diffraction studies. The interesting behavior of the XRD pattern around 10% TiO_2 content was marked as critical concentration of the dopant. The crystallite size was found to increase for PANI-TiO_2 nanocomposites. Charge transport mechanism was investigated by temperature dependent dc electrical conductivity measurements in the temperature range of 293 K–353 K. An increase in dc conductivity was found on addition of TiO_2 at all temperatures and three dimensional variable range hopping (3D VRH) model was the most probable model of charge transport. Activation energy, density of states and hopping length were calculated and found to be influenced by TiO_2 incorporation. Structural morphology was studied by scanning electron microscopy (SEM). The granular structure and grain size increased and was confirmed by Transmission Electron Micrographs. The tensile modulus as a function of TiO_2 loading in PANI showed enhancement in mechanical properties.

1. Introduction

The conjugated conducting polymers provide an opportunity to address fundamental issues in condensed matter physics [1]. Among them Polyaniline is also a promising candidate in organic solar cells, printing electronics circuits, electromagnetic shielding, organic LEDs, biosensors, actuators, artificial muscles chemical sensors, super capacitors, gate oxide and electrochromism [2–6]. The interest in conjugated polymers is due to the substantial π-electron delocalization along their backbones which gives rise to interesting optical [7] and nonlinear optical properties [8–10] and allows them to become good electrical conductors typically when oxidized or reduced [11]. Titanium dioxide (TiO_2) is widely used in welding-rod coatings, specific paints, inks, acid-resistant vitreous enamel etc, owing to its high refractive index, durability, dispersion, tinting, strength, chemically inert nature and non toxicity [12,13]. TiO_2 composite with conducting polymer, such as poly (3-methylthiophene) supported on TiO_2 was formed for solid-state photo electrochemical device [14,15].

The present study investigates the difference in charge transport mechanism in pristine Polyaniline (PANI) and its nanocomposites with TiO_2 to find out the cause of increased electrical conductivity in these nanocomposites when compared with pristine PANI. The Mott's parameters were calculated and were found to be influenced by adding TiO_2 in Polyaniline. Structural, mechanical and morphological properties were investigated and hence the formation of PANI-TiO_2 nanocomposite was confirmed (Table 2).

2. Experimental

2.1. Materials

Aniline and TiO_2 were purchased from Riedel-de-Haen. Ammonium persulphate (APS) was provided by Merck and Hydrochloric acid (HCl) was provided by Sacharlu. All other materials were used as provided without any further purification.

2.2. Synthesis of polyaniline (PANI)

Polyaniline was synthesized by polymerization of aniline in the presence of hydrochloric acid as a catalyst and ammonium

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Table 1
2θ and corresponding d-values of TiO_2 composite.

2θ (degree)	25.3	36.97	37.75	38.55	48	53.87	55.06	62.69	68.75	70.23	75.02
d-values (nm)	3.52	2.30	2.34	1.90	1.70	1.67	1.48	1.37	1.36	1.34	1.26

persulphate as an oxidant by chemical oxidative polymerization method. For synthesis, 5 ml HCl and 5 ml aniline were added in 30 ml of distilled water in a 250 ml beaker equipped with magnetic stirrer and stirred for 30 min and then 6.125 g of $(NH_4)_2S_2O_8$ was dropped slowly in the suspension at 27 °C for 5 h to complete the reaction. The molar ratio of monomer to oxidant was 1:2. The suspension was left for 24 h to complete the polymerization. Finally the suspension was filtered, washed with distilled water several times to remove HCl and other adhering substances. Greenish black powder of polyaniline was obtained and dried at 70 °C for 24 h in a vacuum oven [16].

2.3. Synthesis of polyaniline-TiO_2 composites

TiO_2 doped polyaniline was prepared with TiO_2 contents of 10 and 30 wt% in aniline. Stoichiometric amounts TiO_2 were mixed in 100 ml of distilled water and 5 ml aniline and stirred for 30 min. 5 ml HCl was added drop wise to the solution and the mixture was stirred for 1 h. Further steps were similar to those of the synthesis of polyaniline.

3. Measurements

Pellets of PANI-TiO_2 composites were formed by using a press machine at 10 ton pressure in stainless steel dye of 13 mm diameter and 1 mm thickness. DC conductivity was measured by Keithley 2400 source meter using two probe method within temperature range of 300 K–355 K. In two points probe method two ohmic contacts were made to measure the voltage drop that developed across the probes when known value of current passed through the samples. The temperature was controlled by cryostat and measured by digital bimetallic thermometer. The conductivity and reproducibility of all samples were checked. X-ray powder diffraction analysis was carried out using an automated diffractometer, PANalytical X'Pert PRO equipped with Cu Kα radiations (λ = 1.54 Å). The instrument was operated at 40 kV and 30 mA and samples of doped and undoped polyaniline were mounted on a standard holder. The diffracted patterns were recorded over the range of 10°–80° with counting time 0.5 s and the step size 0.02. Scanning electron microscopy was carried out by using an EVO50 ZEISS instrument. TEM was carried out with Philips CM12 microscope at accelerating voltage of 80 kV. Micrographs were obtained on a very thin film obtained by dropping the solution on the surface of water and then fishing it on a grid. The grid was kept under vacuum to evaporate solvent for 24 h at room temperature. Instron mechanical tester was used for the measurement of mechanical properties of the materials.

4. Results and discussion

In XRD spectrum of TiO_2 (Fig. 1) seven sharp peaks at 2θ values of 25.3°, 36.97°, 37.75°, 38.55°, 48°, 53.87°, 55.06°, 62.69° and 68.75° were observed which showed its crystalline structure [17,31].

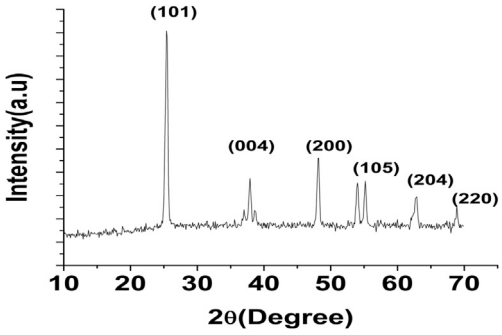

Fig. 1. X-ray diffraction pattern of TiO_2.

X-ray diffraction pattern of the PANI (Fig. 2a) exhibits no sharp peak except a broad peak in the range of 15°–25° which shows that the synthesized PANI is amorphous in nature. It may be noted that sharp peaks around 22° in the XRD pattern of PANI indicate the crystallinity of the synthesized material (Fig. 2a) [17]. Fig. 2b and c shows the XRD patterns of PANI-TiO_2 composites, which contain the characteristic diffraction peaks of TiO_2 and amorphous PANI. The peak intensity of TiO_2 in the composites is weaker than that of the pure sample and decreases with increase of PANI content, which reveals that the PANI coating layer has an effect on the peak intensity of TiO_2. It is evident, then, that PANI-TiO_2 composites were formed.

The average crystallite size of PANI + 10%TiO_2 composite calculated by Scherrer formula is 0.99 nm whereas the average crystallite size of PANI + 30%TiO_2 composite is 1.47 nm, which is in good agreement with SEM and conductivity results.

The SEM image of pure PANI exhibits complete amorphous regions as shown in (Fig. 3a). This image clearly reveals that surface of PANI is not smooth. Uneven lumps and holes visible in PANI are suitable for adsorption. It is found that the doping of TiO_2 has a strong affect on morphology of the resulting PANI-TiO_2 composites (Fig. 3b, c). In case of PANI-TiO_2 composites, the SEM micrographs revealed a honeycomb structure with an interlocking arrangement of granular particles. This suggests that most of TiO_2 nanoparticles coated with PANI and have formed a network during the polymerization process. A close investigation of the surface revealed that PANI-TiO_2 composites exhibited a porous open structure and high surface area. It has been pointed out that such porous structures significantly enhance the rapid diffusion due to larger exposure area.

Fig. 4 (a, b) shows typical TEM micrographs of pure TiO_2 and PANI-TiO_2 nanocomposite. It can be seen that the pure TiO_2 and PANI-TiO_2 nanoparticles were spherical in shape with the size in the range of 30–40 nm.

The relation between DC conductivity and temperature in polymer samples gives important information concerning the nature of phenomena related to the charge transport in a polymer system [18,19]. Fig. 5 gives the linear plots of ln (σ) versus reciprocal of the temperature, where the Arrhenius behavior is observed. These are the best linear fits to the data.

Table 2
Mott's parameters for PANI, PANI-10%TiO_2 and PANI-30%TiO_2 at 303 K.

Samples	T_O (K)	Density of states N (E_f) (eV^{-1} cm^{-3})	Hopping length R at 293 K (cm)	Activation energy W at 293 K (eV)	σ_{dc} (S/cm)
PANI pure	1.18×10^9	6.59×10^{18}	5×10^{-7}	0.29	3.02×10^{-5}
PANI-10%TiO_2 composite	3.87×10^8	2×10^{19}	3.79×10^{-7}	0.22	5.7×10^{-5}
PANI-30%TiO_2 composite	1.78×10^{10}	4.4×10^{17}	9.8×10^{-7}	0.58	8.67×10^{-6}