**Polyaniline/MnTiO₃ Nanocomposites: Fabrication, Characterization and Optical band gap**

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**ABSTRACT**

Polarized polyaniline-manganesetitanate nano composites (NCs) with two contents loading of MnTiO₃ were successfully synthesized via sol–gel process using Manganese acetyl acetonate, tetra-n-butyltitanate, stearic acid, potassium iodate and sulfuric acid. The prepared PANI/MnTiO₃NCs were characterized by energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), UV-vis diffuse reflectance spectra (DRS), Particle Size Distribution (PSD) and Zeta Potential. The results indicated that MnTiO₃NPs with particle size between 22 and 30nm were distributed in PANI matrix. The value of direct band gap for MnTiO₃ and the PANI/MnTiO₃NCs with 10 and 20wt% of MnTiO₃NPs loading using the Tauc model came out to be 1.15 Ev, 1.35 and 1.25. Band gap analysis indicates semiconducting behavior of the NCs.

**Keywords**: nanocomposite, MnTiO₃, Zeta Potential, EDX, PSD, DRS

**INTRODUCTION**

PANI as a typical conducting polymer has recently received a great deal of attention. PANI is one of the most promising electrically conducting polymers due to its unique electrical and electrochemical properties, easy polymerization, high environmental stability and low cost of monomer⁴⁻⁸, and its wide applications in microelectronic devices, diodes, light weight batteries, sensors, super capacitors, microwave absorption, corrosion inhibition⁹⁻⁸, etc. The properties of PANI can be tailored by changing its oxidation states, dopants or through blending it with other organic, polymeric or inorganic nanosized semiconducting particles. To obtain materials with synergetic advantage between PANI and inorganic NPs, various composites of PANI with inorganic NPs such as CeO₂, TiO₂, ZrO₂, Fe₂O₃, and Fe₃O₄ are reported. The titanium-based oxides, such as barium titanate ⁹, cadmium titanate ¹⁰, bismuth titanate ¹¹, cobalt titanate ¹² and lead titanate
can be referred to as a 'smart' family owing to their excellent dielectric, piezoelectric, pyroelectric and photostrictive properties. Manganese ion in oxides is a well-known activator used mainly for producing tunable solid-state laser media, holographic recording and optical data storage as well as thermoluminescent detectors. Recently, manganese titanate (MnTiO$_3$) has attracted much attention for its strong absorption in the visible region which may be propitious to the utilisation of solar energy and photocatalysis. Manganese titanate, pyrophanite MnTiO$_3$, is a humidity sensing material with excellent sensitivity, good selectivity, low temperature coefficient near zero and good stability. The pyrophanite MnTiO$_3$ has also been studied for magnetic and photoelectrochemical properties. Physical properties (mechanical, thermal, etc.) of polymers can be improved by adding inorganic materials to polymer matrices. In this study, PANI/MnTiO$_3$ NCs with two (10, 20 wt%) contents loading of MnTiO$_3$ were prepared, and the whole procedure and structural characterization of PANI/MnTiO$_3$ NCs phases have been investigated by SEM, EDX, DRS, and Zeta Potential.

**MATERIALS AND METHODS**

Manganese acetylacetonate, tetra-n-butyltitanate, stearic acid, potassium iodate and sulfuric acid used in experiments were all of analytical grade reagents. The composition of the sample was estimated using a model Oxford of Energy dispersive analysis of X-rays (EDX). The UV-vis diffused reflectance spectra (DRS) were obtained from UV-vis Scincom 4100 spectrometer. The SEM pictures were recorded with KYKY Model EM 3200 instrument at the accelerating voltage of 25kV. Streaming zeta potential measurements were carried out on a ZetaCAD instrument (France).

**Synthesis of MnTiO$_3$ nanoparticles**

PANI/MnTiO$_3$ composites were prepared along a synthetic procedure. MnTiO$_3$ NPs were prepared through a modified wet-chemistry synthesis method which is described in the literature. In this procedure, a fixed amount of manganese acetylacetonate was added to the melted stearic acid and dissolved. Then, stoichiometric tetra-n-butyltitanate was added to the solution, stirred to form sol, naturally cooled down to room temperature, and was dried to obtain dried gel. Finally, the gel was calcined at 900°C in air to obtain MnTiO$_3$ NPs.

**Synthesis of PANI/MnTiO$_3$ nanocomposite**

In order to prepare oF PANI/MnTiO$_3$ NCs, the essential substances for preparation of PANI were initially added. To prepare PANI, 1g potassium iodate was added to 100 ml of sulfuric acid (1 M) and then a uniform solution was resulted by using magnetic mixer. After 30 min, the sufficient amount of ultrasonicated MnTiO$_3$ NPs was added to solution to prepare 10 and 20 percent of PANI/MnTiO$_3$ NCs and after 20 min, 1 ml fresh distilled aniline monomer was added to stirred aqueous solution. The reaction was carried out for 5h at room temperature. Then the obtained product was dried at temperature about 60°C in oven for 24h. Finally, after heat-treatment from 60°C to 300°C for 2h, the PANI/MnTiO$_3$ NCs were obtained. The whole procedure and structural characterization of PANI/MnTiO$_3$ NCs phases have been investigated by SEM, EDX, PSD, DRS, and Zeta Potential.

**RESULTS AND DISCUSSION**

**DRS study**

The absorption coefficient and optical band gap of a material are two important parameters by which the optical characteristics and its practical applications in various fields are judged. Fig. 1 shows the DRS patterns of pure MnTiO$_3$ and the PANI/MnTiO$_3$ NCs with 10 and 20 wt% of MnTiO$_3$ NPs loading. In fig. 1a, a sharp absorption peak is observed around 325 nm, which indicates the optical band gap attributed to the O$^{2-}$→Ti$^{4+}$ charge transfer interaction. Also, in the PANI/MnTiO$_3$ NCs with 10 and 20 wt% of MnTiO$_3$ NPs loading a sharp absorption peak is observed around 345 and 350 nm. Fordirectband gap determination, plot of $(a h\nu)^2$ versus $h\nu$ is presented in Fig. 2. Band gap value was obtained by extrapolating the straight portion of the graph on $h\nu$ axis at $a = 0$, as indicated by the solid line in Fig. 2. The value of direct band gap for MnTiO$_3$ and the PANI/MnTiO$_3$ NCs with 10 and 20 wt% of MnTiO$_3$ NPs loading using the Tauc model came out to be 1.15 E, 1.35 and 1.25. Band gap analysis indicates semiconducting behavior of the NCs.
Morphology of samples

Fig. 3 shows the scanning electron micrograph of pure MnTiO$_3$ (Fig. 3a.) and the PANI/ MnTiO$_3$ NCs with 10 and 20wt% of MnTiO$_3$ NPs loading, respectively (Fig. 3b–c.). The particles have agglomerated grain structure. In the scanning electron micrograph of the NCs, with the increase of MnTiO$_3$ content, the agglomeration becomes more appreciable and displays some connections in some regions. SEM images reveal a homogeneous dispersion of MnTiO$_3$ NPs in the PANI matrix. EDX patterns of pure MnTiO$_3$ (Fig. 4a.) and the PANI/MnTiO$_3$ NCs with 10 and 20wt% of MnTiO$_3$ NPs loading, respectively are shown in Fig. 4b. EDX patterns of pure MnTiO$_3$ (Fig. 4a.) shows...
separate peaks of Manganese(Mn), Titanium (Ti), and Oxygen, which compositional analysis by EDX confirms that the MnTiO₃ nanopowders were obtained. EDX pattern of PANI/MnTiO₃ NCs with 10 and 20 wt% of MnTiO₃ NPs loading are displayed in Fig. 4b, which shows separate peaks of Manganese(Mn), Titanium (Ti), Oxygen, Carbon and Nitrogen (N), confirm that the sample is of desired composition having both the PANI and MnTiO₃ nanoparticles. The results show that as the MnTiO₃ content increases in 10 and 20 weight fractions, the intensity of MnTiO₃ crystalline peaks gradually increases.

**Particle Size Distribution (PSD)**

Particle size distribution analysis (PSD) is a measurement designed to determine information about the size and range of a set of particles in a representative material. Particle size was determined using dynamic light scattering measurements. Fig. 5 shows the size distribution histogram of pure MnTiO₃. The Zetasizer software uses algorithms to extract the decay rates for a number of size classes to produce a size distribution. The X-axis shows a distribution of size classes, whereas the Y-axis shows the relative intensity of the scattered light. The particle size distribution of the pure MnTiO₃ had a wide distribution (three peaks); therefore, its distribution is very heterogeneous. The particle size distribution of MnTiO₃ for 88.2% of the particles were 85 nm, 6.4% were 250 nm, and 5.4% were 1088 nm.

**Zeta potential measurements**

Fig. 6 shows the zeta potential measurements obtained for pure MnTiO₃ (Fig. 6(a)) and the PANI/MnTiO₃ NCs with 10 and 20 wt% of MnTiO₃ NPs loading. Initially, MnTiO₃ had an average ζ of -9.75 mV and the PANI/MnTiO₃ NCs with 10 and 20 wt% of MnTiO₃ NPs loading had an average ζ of -20 and -50.81 mV. With respect to Fig. 6, Zeta potential indicated that the fabricated PANI/MnTiO₃ NCs with 10 and 20 wt% of MnTiO₃ NPs were increased with 34 and 67% efficiency respectively.

**CONCLUSION**

We have successfully synthesized PANI/MnTiO₃ NCs with two (10, 20 wt%) contents loading of MnTiO₃ using wet chemical method. The whole procedure and structural characterization of PANI/MnTiO₃ NCs phases have been investigated by SEM, EDX, DRS, and Zeta Potential. The particle size distribution of MnTiO₃ for 88.2% of the particles were 85 nm, 6.4% were 250 nm, and 5.4% were 1088 nm. Zeta potential indicated that the fabricated PANI/MnTiO₃ NCs with 10 and 20 wt% of MnTiO₃ NPs were increased with 34 and 67% efficiency respectively.

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