



Synthesis and Characterization of Poly Ortho Toluidine doped with Commercial TiO₂ Nanoparticle

V. Gayathri, R. Balan *

Department of Physics, Chikkanna Government Arts College, Tiruppur, TN, India

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*balanphy@yahoo.co.in

ABSTRACT

This work was aimed at the study of the change in the properties of commercial TiO₂ with conducting polymer such as Poly ortho toluidine (POT) synthesized by Oxidative chemical polymerization. The metastable anatase phase of TiO₂ and POT+TiO₂ composites were characterized by using X-Ray Diffraction analysis, Scanning Electron Microscopy and Fourier Infrared Spectroscopy. The bandgaps of the samples were found by UV-Visible spectroscopy.

Keywords: Commercial TiO₂; FT-IR, Poly ortho toluidine; SRD; UV-Vis.

1. INTRODUCTION

Conducting polymers such as polyaniline is considered to be unique due to its excellent electrical and optical properties. Poly aniline have been used in a variety of applications such as corrosion protection, catalysis and sensors because of its non-redox doping, good environmental and thermal stabilities, high conductivity and economic feasibility. The properties of conducting polymer composites depends upon the doping concentration of nanoparticles (Tieli Zhou *et al.* 2015; Kiran Kumari *et al.* 2011). Among conducting polymers poly ortho toluidine (POT) is highly promising and it has better solubility and higher processability by steric hindrance π -electron effects (Gigliola Lusvardi *et al.* 2017). TiO₂ nanoparticles are semiconducting in nature with good photocatalytic activity and they have wide range of applications like cosmetics and air purification. The three types of crystallographic structures of TiO₂ are anatase, rutile and brookite. Among all these phases, rutile is the most stable one where anatase and brookite correspond to metastable and unstable states (Bin Wang *et al.* 2015).

The aim of this work was to study the changed properties of TiO₂ in the presence of POT in the composites. Chemical oxidative polymerization method was used to synthesize POT. The synthesis as well as structural and optical properties of POT doped with TiO₂ nanoparticles were reported. The functional groups of samples were examined by FTIR spectroscopy. The morphological, structural and bandgap analyses of TiO₂ and POT/TiO₂ composites were carried out by SEM-EDX, XRD and UV-Vis. spectroscopy.

2. EXPERIMENTAL DETAILS

2.1 Materials and Method

O-toluidine (99% AR grade, Lobal Chemie Laboratory Reagents and Fine Chemicals), H₂SO₄, Ammonium peroxy disulfate (>98%, Merck), Commercial TiO₂ (98%, Fisher Scientific) and Millipore-Q water were used as received.

POT-TiO₂ composites has been synthesized by chemical oxidative polymerization at room temperature. In this process, an appropriate amount of size reduced TiO₂ was dispersed in 0.2 M of H₂SO₄ by ultrasonication. Then the dispersed TiO₂ solution was added slowly to 0.1 M aqueous solution of O-toluidine with continuous stirring for 30 minutes. 0.1 M aqueous solution of ammonium peroxy disulfate was added dropwise to polymerization bath to initiate the polymerization and the solution was left for 4 hours with continuous stirring; then the solution was kept overnight. The resultant precipitate was filtered and washed several times with acetone followed by water and to be dried at 80 °C in an oven. Finally, dark green colour powder form of POT/TiO₂ composite can be obtained.

3. MATERIAL CHARACTERIZATION

X-ray diffraction data of samples were recorded using an XPERT Diffractometer. The surface morphology and elemental compositions have been investigated by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). Absorption spectra of the anatase phase of TiO₂ and composites were recorded using UV-Visible Spectrometer (DRS, Analytek Jena, Germany). The

functional groups of samples were found by ATR-FTIR, Bruker, Germany.

4. RESULTS AND DISCUSSION

4.1 X-ray diffraction analysis

The XRD characteristic peaks at 25° , 31° and 37° , as shown in Fig. 1 (a), represented the anatase phase of TiO_2 corresponding to (101), (004) and (200) planes. The XRD spectra of POT+ TiO_2 , shown in Fig. 1 (b), was similar to that of pure TiO_2 , revealing that the crystalline phase of TiO_2 was not altered by POT. The only difference observed was the intensity of diffraction peaks of POT+ TiO_2 composites was slightly

lesser than that of pure TiO_2 due to the amorphous nature of POT in the composites.

4.2 Morphological analysis

The morphology of pure TiO_2 and POT+ TiO_2 were examined by SEM. From the SEM micrographs of TiO_2 nanoparticles shown in Fig. 2 (a), it was evident that they were spherical in shape whereas, Fig. 2 (b) revealed the flake-like feature with globular structure of POT interlinked with TiO_2 nanoparticles which confirmed the formation of composites. Fig. 3 (a and b) shows the elements corresponding to TiO_2 and POT+ TiO_2 composites, respectively.

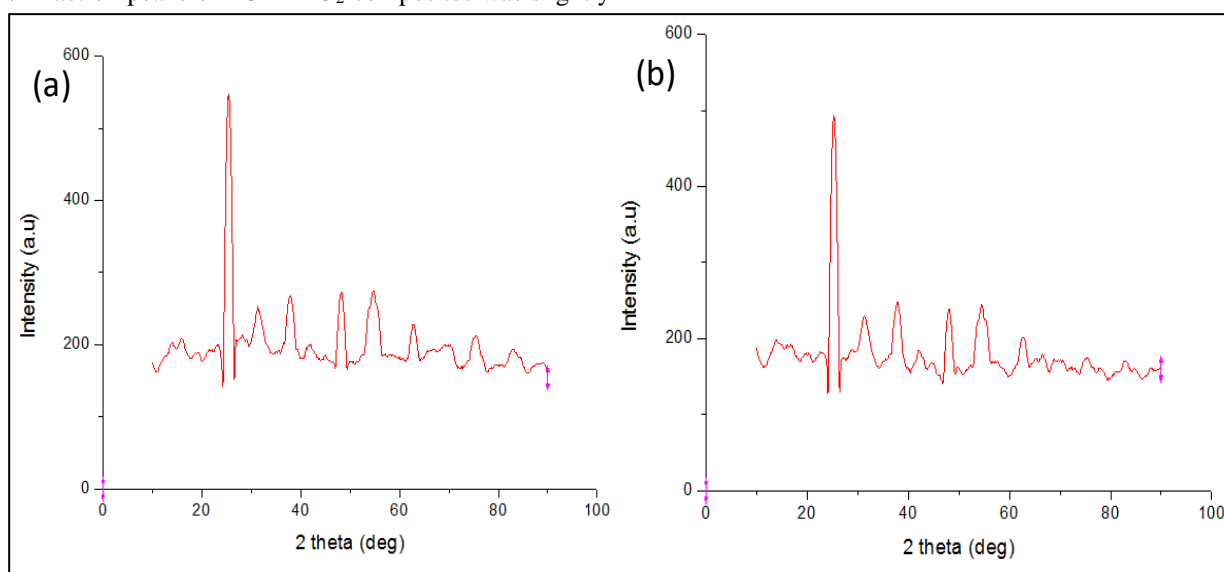


Fig. 1: XRD spectra of (a) TiO_2 nanoparticle and (b) POT + TiO_2 composites

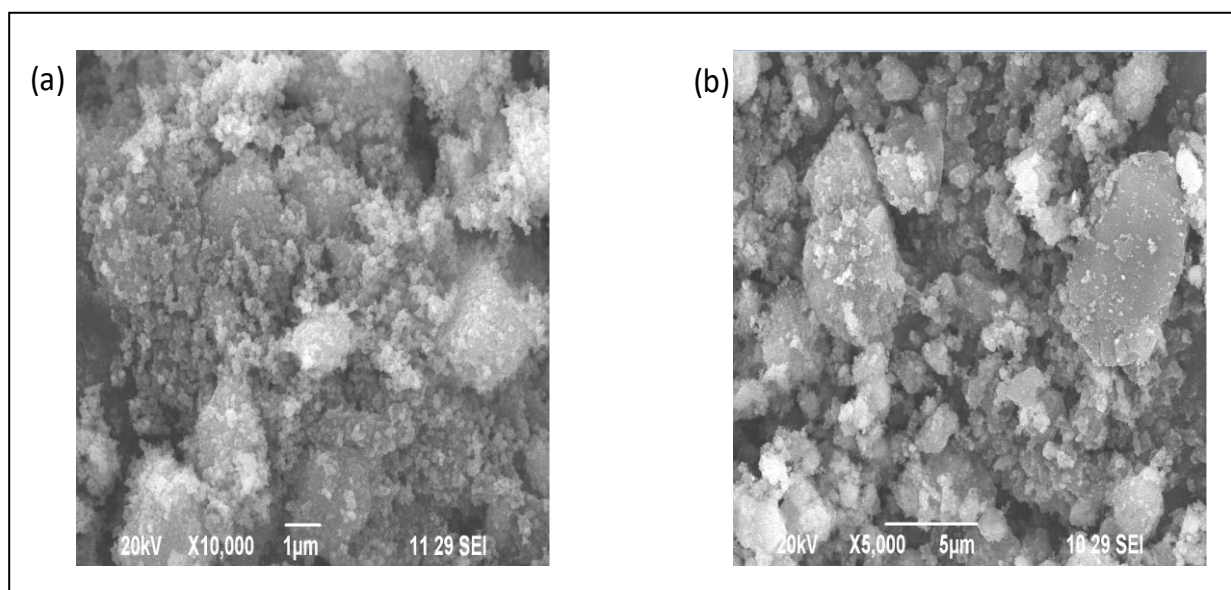


Fig. 2: SEM images of (a) TiO_2 nanoparticles and (b) POT + TiO_2 composites

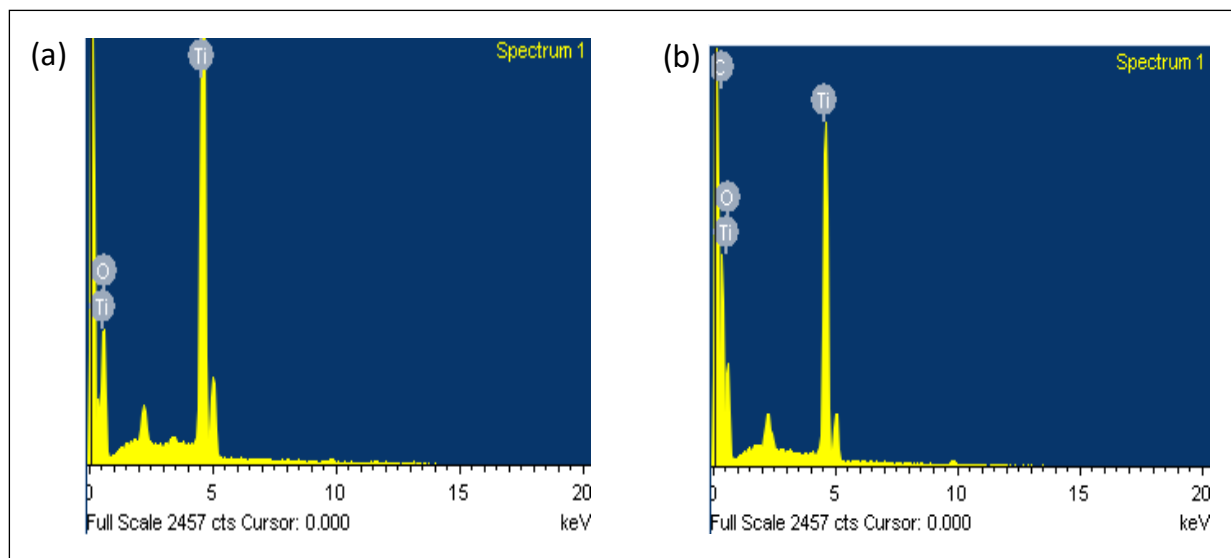


Fig. 3: EDX spectra of (a) TiO_2 nanoparticles and (b) POT + TiO_2 composites

4.3 UV-Vis. Spectroscopy

From UV-Vis. spectra shown in Fig. 4 (a and b), the absorbance of TiO_2 and POT+ TiO_2 composites were about 344 nm and 334 nm, respectively. The absorbance of composites was slightly shifted to a lower wavelength indicating the dispersion of TiO_2 in the composites. The bandgap of pure TiO_2 and POT+ TiO_2 can be calculated by using the formula $E = h\gamma$. The bandgap value of composites is 3.7 eV which is greater than pure TiO_2 (3.6 eV).

4.4 FOURIER INFRARED SPECTROSCOPY

In Fig. 5 (a and b) shows the FTIR spectra of pure TiO_2 and POT+ TiO_2 composites. The characteristic peaks at 3749 cm^{-1} and 604 cm^{-1} indicated the Ti-O-Ti and O-H stretching frequencies (Asha *et al.* 2014). The intensity of characteristic peaks corresponding to composites were somewhat similar to that of pure TiO_2 with additional peaks at 3619 cm^{-1} corresponding to the N-H stretching of an aromatic amine, confirming the formation of POT in the composites (Borriello *et al.* 2011). The peaks observed at 1494 cm^{-1} in composites corresponded to C-N stretching vibrations of quinoid and benzenoid rings (Canon Uchoyuk *et al.* 2012).

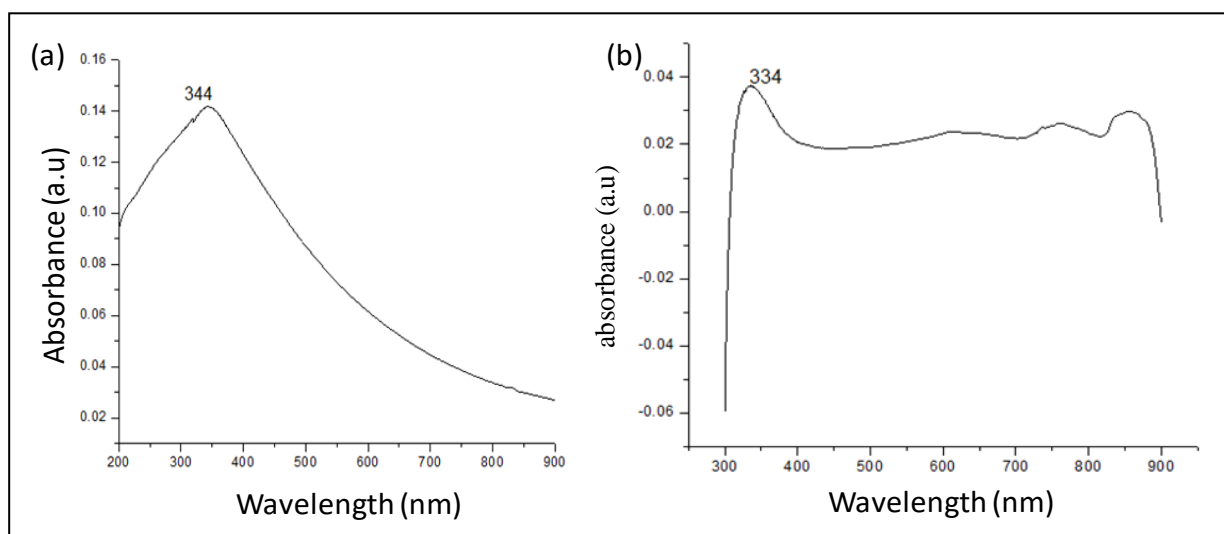


Fig. 4: UV-Visible spectra of (a) TiO_2 nanoparticles and (b) POT + TiO_2 composites.

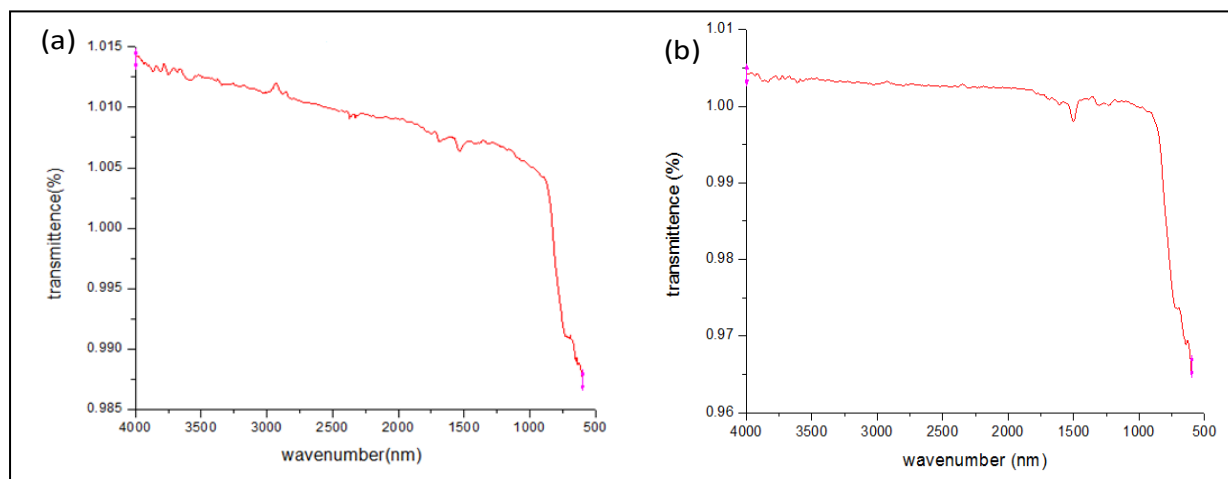


Fig. 5: FT-IR spectra of (a) TiO₂ nanoparticles and (b) POT + TiO₂ composites

5. CONCLUSION

The change in properties of TiO₂ due to poly ortho toluidine, synthesized by the chemical oxidative polymerization method was examined. XRD studies have shown that the crystalline structure of anatase TiO₂ with the amorphous nature of poly ortho toluidine confirmed the formation of composites with lesser intensity. The functional groups and spherical morphology of TiO₂ interlinked with poly ortho toluidine were examined by FT-IR and SEM-EDX. UV-Visible spectroscopic results have shown that POT+TiO₂ composites exhibited a higher bandgap when compared to pure TiO₂.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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