

Synthesis and Characterization of Calcium Doped TiO₂/Poly (o-toluidine) Nanocomposite

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Abstract - Nanocomposites can be made with a variety of enhanced physical, thermal and other unique properties. The addition of small amount of nanoparticles to polymers has been able to enable new properties for the composite materials. In recent years, polymer nanocomposites have received significant attention because of their importance on both from academic and industrial point of view. This paper reports our findings on synthesis of calcium ion doped TiO₂/Poly o-(toluidine) nanocomposite by in-situ oxidative polymerization technique. The resultant nanocomposite was characterized by XRD, UV-Vis spectroscopy, SEM and TEM methods. From UV-Vis spectroscopy and by using Tauc plot the band gap energy of Ca²⁺ ion doped TiO₂/POT nano composite is calculated and is found to be 3.6 eV. From XRD data the crystalline particle size is determined and it is found to be 53.3 nm. SEM shows the microstructure of bulk specimens and phase arrangement of polymer nanocomposites of different constituent are also studied. The core-shell structure of the nanocomposite was confirmed by TEM analysis.

Key words - nanocomposite, dopant, TiO₂, POT, XRD.

I INTRODUCTION

In the recent years nanotechnology has become one of the promising tools for scientific innovations. In general Composite materials are solids and obtained from the combinations of two and more simple materials that develop a continuous phase and a dispersed phase.[1]. Conducting polymers have been extensively studied in the last 10 years and used for technological applications in electrochromics, batteries, biosensors, gas separation membranes, enzyme immobilization matrices and metal projection against corrosion [2]. They have an immense advantage of being simple to synthesis, with their chemical structure tailored to alter their physical properties, such as their band gap. Further to their ease of synthesis and with lower cost, they are known to have low poisoning effects [3,4]. They have attracted great attention in the field of active materials for applications such as in organic light emitting diodes (OLEDs) [5], field-effect transistors (OFETs) [6] and solar cells [7-10]. Polyaniline [PANI] and its derivatives are one of the most promising conducting polymers [11-14]. The most important feature that make Polyaniline [PANI] and Poly (o- toluidine) [POT] so interesting as sensitive p-n junction layer for the solar cell is the variation of its electrical and optical properties at room temperature [15,16].

One of the most promising and widely studied metal oxide is TiO₂ due to its unique physical, chemical, optical and electrical and photoelectric conversion efficiency properties.[17-18].We have also chosen TiO₂ because of its abundance in nature, stability at high electric field, wide gap, large surface area, non-toxicity, dielectric constant, easy synthesis and environmental friendliness. Doping of transition metals, rare earth and noble metal ions with TiO₂ have been reported on many papers. But the doping of Ca²⁺ ion i.e, an alkaline earth metal ion to TiO₂/POT composite have not yet been reported. Hence in this work we have synthesized and characterized the Ca²⁺ ion doped TiO₂/POT composite by using in-situ oxidative polymerization method.

II. EXPERIMENTAL

Synthesis of Ca²⁺ Ion Doped TiO₂/Pot Nanocomposite

All chemicals were of analytical grade and used as received, without further purification.

The synthesis of the Ca²⁺ ion doped TiO₂/POT nano composite was carried out by using the following procedure. The TiO₂/POT nanocomposite was prepared by in-situ oxidative polymerization [19] of o-toluidine monomer in the presence of TiO₂ using potassium peroxy disulphate as an oxidizing agent. 1g of TiO₂ is dispersed in 100ml of HCl (1M) aqueous solution. 2ml of o- toluidine is added to the above solution .Then about 5g of potassium peroxy disulphate as the oxidant is dissolved in 25ml of distilled water and added to the reaction mixture. The reaction mixture was allowed to polymerize under stirring for 3 hrs at room temperature. A light black coloured solution is immediately converted to greenish precipitate. The precipitate was then filtered, washed with double distilled water and methanol to remove the excess acid. 1g of CaCl₂ is dissolved in water and the resulted solution was added drop by drop to the above green precipitate under vigorous stirring. After the complete addition, the mixture was allowed to stir for 1 hr and aged 48 hrs. Later, it was calcined at 400°C for about 1 hr in muffle furnace and then cooled in a desiccator and ground to form homogenous powder.

Characterization of Nanocomposite

XRD spectra were recorded for 2θ from 20° to 80°, with model ultima IV, RI GAKU diffractometer using

monochromatized CuK α radiation ($\lambda = 1.54\text{\AA}$) with a germanium solid state detector. The size of the nanocomposite was confirmed with a TE CNAI FE12 TEM instrument operating at 120KV. UV-Visible absorption spectra of the sample were obtained by using Shimadzu 3600, and BaSO₄ as reference substance. The surface morphology was studied by using the LEO 435-VF, scanning electron microscopy tool.

III. RESULTS AND DISCUSSION

X-Ray Diffraction Analysis:

Fig.1 represents the XRD pattern of the Ca²⁺ ion doped TiO₂/POT nanocomposite. From the XRD data it is evident that doped nanocomposite exhibit diffraction peaks at $2\theta = 21.2^\circ, 25.1^\circ, 29.2^\circ$ and 47.5° which can indexed to the (101), (004), (200) and (112) crystal facets of anatase TiO₂ (JCPDS file no:21-1272). From XRD pattern it is evident that calcination at 400°C would result in anatase crystal phase transition. The size was calculated by using Debye-scherrer's formula [20]. From this the crystalline size was found to be 53.3nm.

$$D = \frac{0.9\lambda}{\beta \cos \theta} \text{ ----- 1}$$

Where D is the average crystallite size, λ is the wavelength of incident X-ray radiation ($\lambda = 1.54 \times 10^{-9} \text{ nm}$), β is the full width half maximum (FWHM) of the most intense peak expressed in radians and θ is the position of the diffraction peak in the diffractograms.

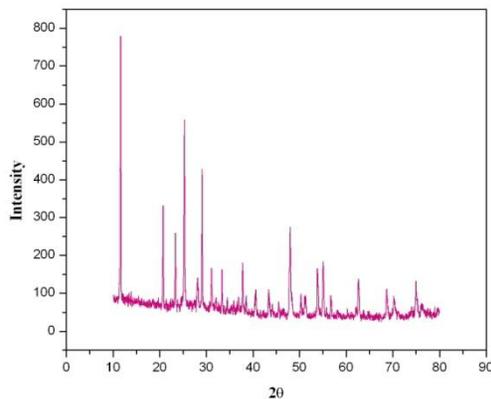


Fig.1 XRD patterns of Ca²⁺ ion doped TiO₂/POT

UV-VIS Absorption Analysis

The optical properties of Ca²⁺ ion doped TiO₂/POT nanocomposite were investigated by UV-Vis spectroscopy as shown in Fig.2 (a,b). From the UV-Vis analysis we can measure the band gap of the synthesized nanocomposite. The position of fundamental absorption edge of the nanocomposite was determined by using the following equation,

$$(\alpha h\nu)^2 = A (h\nu - E_g)^n \text{ ----- 2}$$

Where α, h, ν, E_g and A are the absorption coefficients, Plank constant, light frequency, band gap and a constant, respectively. The n value depends on the transition characteristics. The E_g value can be estimated by extrapolating the straight portion of the $(\alpha h\nu)^2 - (h\nu)$ plot [21]. The band gap for the prepared Ca²⁺ ion doped TiO₂/POT nanocomposite was 3.6 eV.

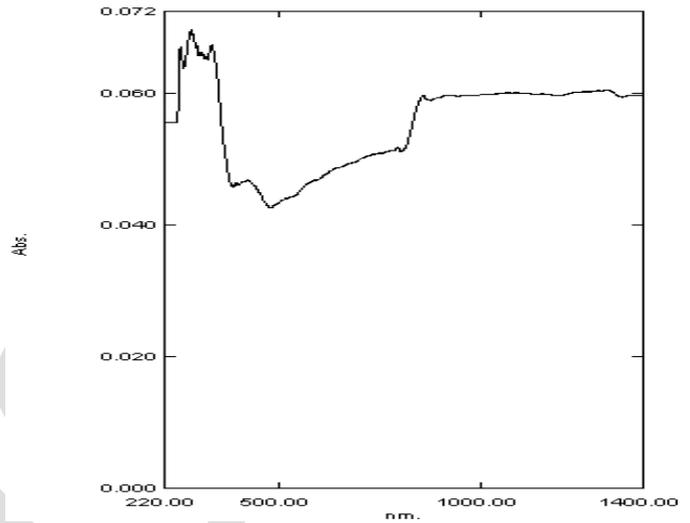


Fig.2a UV-Vis absorption spectrum of Ca²⁺ ion doped TiO₂/POT nanocomposite

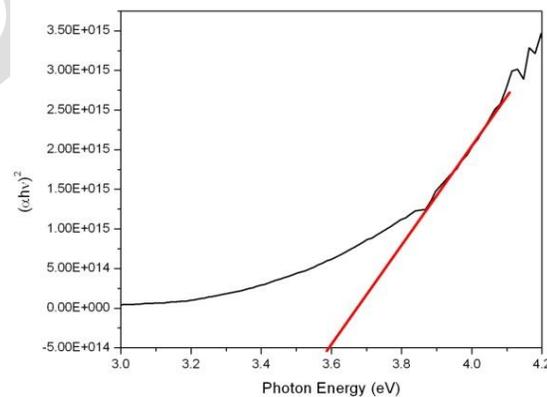


Fig.2b Band gap energy of Ca²⁺ ion doped TiO₂/POT nanocomposite

Scanning Electron Microscope Analysis

Scanning electron microscope is used to examine the surface morphology such as rectangle, triangle, radial, hexagonal, rod and spherical shapes of the nanocomposites. The Ca²⁺ ion doped TiO₂/POT nanocomposite has spherical shape as shown in Fig.3. The doping of Ca²⁺ ion developed a strong interaction with POT which forms a secondary phase. Fig. 3 clearly reveals that incorporation of Ca²⁺ ion with the TiO₂/ POT matrix, and the total structure of the nanocomposite has been completely transformed to core shell structure, thereby

minimizing the agglomeration of TiO₂ nanoparticles [22, 23]. SEM image shows that, the TiO₂ nanoparticles act as condensation nuclei for the growth of POT to form core shell structure with average diameter between 50–60 nm which was in good agreement with XRD results.

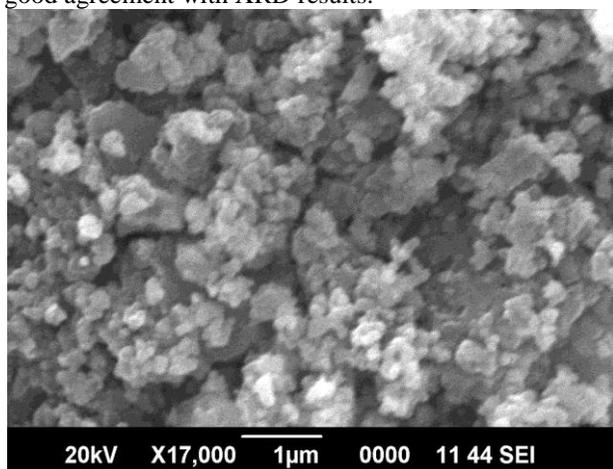


Fig.3 SEM image of Ca²⁺ ion doped TiO₂/POT nanocomposite

Transmission Electron Microscope Analysis

The obtained nano composites are observed to have a spherical shape and exhibit a narrow size distribution. The average particle size is approximately 53.3nm. Fig.4 shows the high resolution TEM micrograph of Ca²⁺ ion doped TiO₂/POT nanocomposite evidencing the highly crystalline nature of nanocomposite. It indicates that our composite have core-shell structure in which Ca²⁺ ions were uniformly on them.

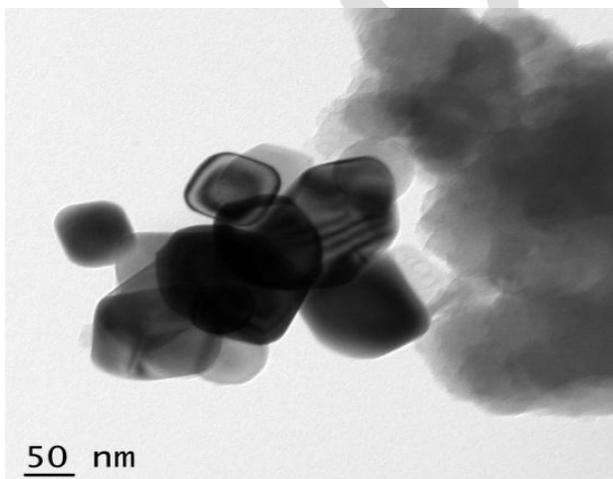


Fig.5 TEM image of Ca²⁺ ion doped TiO₂/POT nanocomposite

IV. CONCLUSION

In this study, the Ca²⁺ ion doped TiO₂/POT nanocomposite was successively synthesized by in-situ oxidative polymerization method. The particle size was found to be 53.3nm by XRD analysis. From UV-Vis absorption

spectroscopy the band gap energy value is calculated and it is found to be 3.6eV. This value is higher than nano TiO₂ material. The SEM and TEM results showed the calcium ions were uniformly distributed on the surface of the TiO₂/POT polymer matrix and the core-shell structure of the nanocomposite is confirmed.

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