Research Paper

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Synthesis And Characterisation Of TiO_2/ Poly (O- Toluidine) Nanocomposite

Chemistry

KEYWORDS : Nano composites, POT, XRD, UV- Vis analysis, TiO_2

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ABSTRACT

The present study involves the synthesis of TiO2/Poly (o-toluidine) [POT] nano composites by chemical oxidative polymerization method. X-ray diffraction (XRD), UV- Visible spectroscopy (UV- Vis), Scanning electron microscopy (SEM) , Atomic force microscopy (AFM) and Transmission electron microscopy (TEM) techniques were used to characterize the particle size, structure and surface morphology of the nanocomposite. The mean crystallite sizes of the pure TiO2 and the TiO2 /POT were 54.5 nm and 59.9 nm respectively. The band gap energy value was also calculated for the nanocomposite. The particles of the nanocomposite were found to be spherical in shape. The nanocomposites have a core-shell structure.

1. INTRODUCTION

Nano materials, defined as the particles ranging from 1- 100 nm in diameter, have become widely utilized, because of their unique physico-chemical properties. In recent years, the development of inorganic/polymer hybrid materials on nanometer scale have been receiving significant attention due to their wide range of potential applications in optoelectronic devices and in field effect transistors [1-2]. The inorganic fillers at nano scale exhibit high surface- to-volume ratio and are thus expected to modify drastically the electrical, optical and microscopic properties of polymer. In general, the synthesis of inorganic /polymer hybrid materials have the goal of obtaining new composite materials with synergetic or complementary behaviours between the polymer and inorganic material [3].

Nano TiO_2 is a very well known and well researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties [4]. A number of different metallic and metal oxide particles have been encapsulated into the shell of conducting polymers giving rise to a host of nanocomposites [5]. Polyaniline has been at the centre of investigations due to its applications in multidiscipilinary areas such as electrical, electronic, electrochemical, electromagnetic, electro-luminescence, chemical, membrane and sensors [6-10]. Poly (o-toluidine) [POT] is a derivative of polyaniline which contains methyl group in its ortho position. Recently, POT was also found to have additional advantage with respect to polyaniline due to its faster switching time between the reduced and oxidized states [11-13]. Poly (o-toluidine) doped with Camphor sulphonic acid is synthesized by Dhanavel et. al [14]. The aim of this work is to prepare TiO_2/POT using chemical oxidative polymerization method and characterize the obtained nanocomposite by using some analytical techniques. The particle size, optical band gap energy value and the structure of the composite were determined.

2. EXPERIMENTAL:

2.1. MATERIALS:

The monomer o-toluidine (99%) was distilled under reduced pressure prior to use. Potassium peroxydisulphate (98%), pure TiO_2 (anatase) were all of AR grade and used without further purification.

2.2. Synthesis of TiO_2/POT nanocomposite:

TiO_2/POT nano composite was prepared as follows: TiO_2 (1g) is dispersed in 100 ml of HCl aqueous solution (1M). 2 ml of o-toluidine is added to the above solution. Then about 5 g of potassium peroxydisulphate as the oxidant is disoloved 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. The obtained precipitate was filtered and washed with ethanol followed by water and then dried at 110˚C for 3 hrs to get TiO_2 / POT nano composite

3. RESULTS AND DISCUSSION:

3.1. XRD Analysis:

Figures 1a and 1b show XRD patterns of pure TiO_2 and TiO_2 / POT nanocomposite. Both the figures show sharp and well defined peaks which indicating the crystallinity of the materials. The observed 2θ values are consistent with the standard JCPDS data. It could be seen that TiO_2 is formed in a tetragonal anatase phase (figure 1(b)) with a= 3.7837Å and c=9.05087Å. The intensity of diffraction peaks for TiO_2/POT composite is lower than that of TiO_2. The presence of poorly crystalline POT and the reduction of volume fraction of TiO_2 weaken the diffraction peaks of TiO_2 in the composite. The crystallite sizes of pure TiO_2 and TiO_2/POT nano composite were calculated as 54.5 nm and 59.9 nm respectively according to the Debye-scherrer formula [15],

$$D = \frac{0.89\lambda}{(\beta cos\theta)} \quad \text{---------- 1}$$

Where D is the average crystallite size, λ is the wavelength of incident X-ray, β is the full width half maximum (FWHM) of X-ray diffraction expressed in radian and θ is the position of the diffraction peak in the diffractograms.

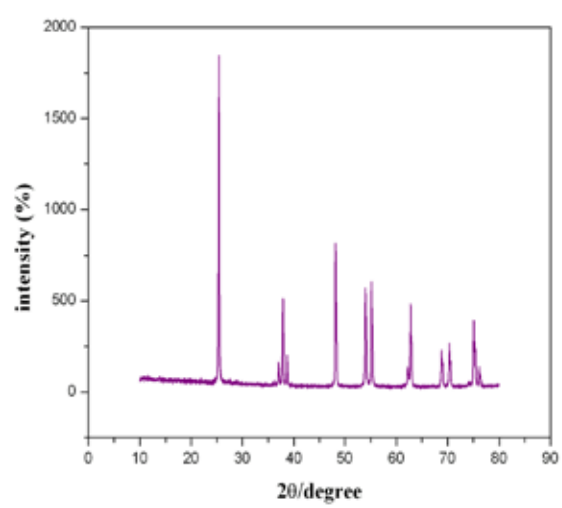

Figure.1.a. XRD pattern of pure TiO_2

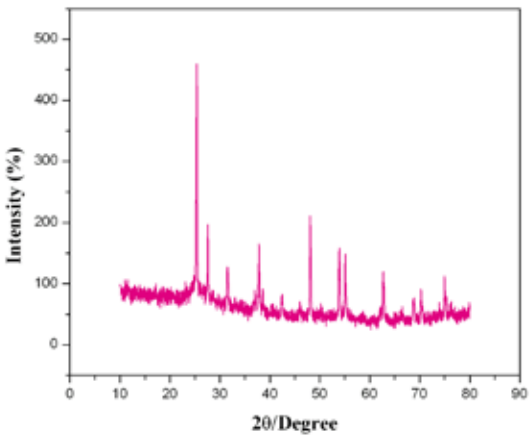

Figure.1.b. XRD pattern of TiO_2/POT nano composite

3.2 .UV- Vis absorption spectroscopy:

UV – Vis absorption spectrum of the nanocomposite was studied at room temperature in the wavelength 200-800 nm. It is useful to analyze the band gap energy value. Figure (2) shows the absorption spectrum of the TiO_2/POT nanocomposite. For pure TiO_2 and for TiO_2 /POT nano composite the peaks absorb at 350 nm and 332 nm respectively.The optical band gap energy (E_g) can be determined from the absorption co-efficient (α), which can be calculated from the transmittance of TiO_2 / POT nanocomposite and it is expressed as [16]

$$\alpha - \frac{1}{d}\ln(1/T) \text{ ---------- } 2$$

Where d is the thickness and T is the transmittance. The optical absorption co-eficient (α) is close to the band edge and it can be expressed by the following equation,

$$\alpha = \frac{A(h\upsilon - E_g)^n}{h\upsilon} \text{ ---------- } 3$$

Where hυ is the photon energy. A and n are constants; where n is 2 for a direct energy gap and ½ for an indirect energy gap. Figure (2) shows the absorption edge shifted towards lower wavelength side, indicating an increase of the energy band gap in the TiO_2/POT nanocomposite and the corresponding band gap value is 3.4ev which is shown in the figure (3).

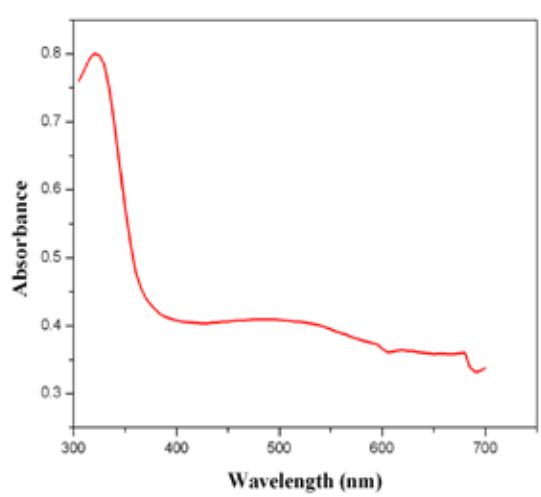

Figure.2. UV-Vis absorption spectrum of TiO_2 / POT nanocomposite

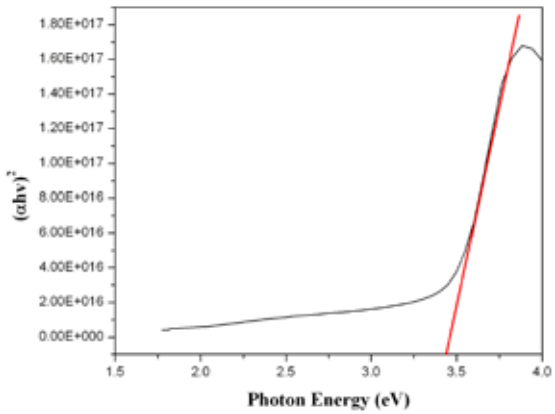

Figure.3. Band gap energy of TiO_2/POT nanocomposite

3.3 SEM ANALYSIS:

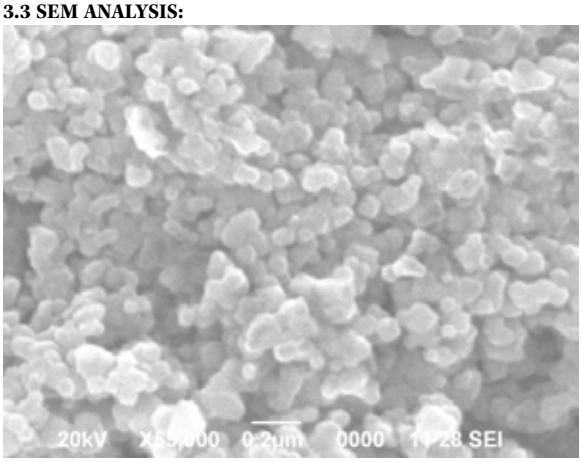

Figure.4. SEM image of TiO_2/POT nano composite

The shape of the sample is investigated using SEM analysis. Figure 4 shows SEM image of TiO_2 / POT nanocomposite. In the previous work, olhman et.al [17] has reported that the Poly-o-toluidine Zr(IV) tungstate composite shows granular type of morphology. Our TiO_2 /POT nano composite particles have spherical shape which is well seen in the Figure 4.

3.4 AFM ANALYSIS:

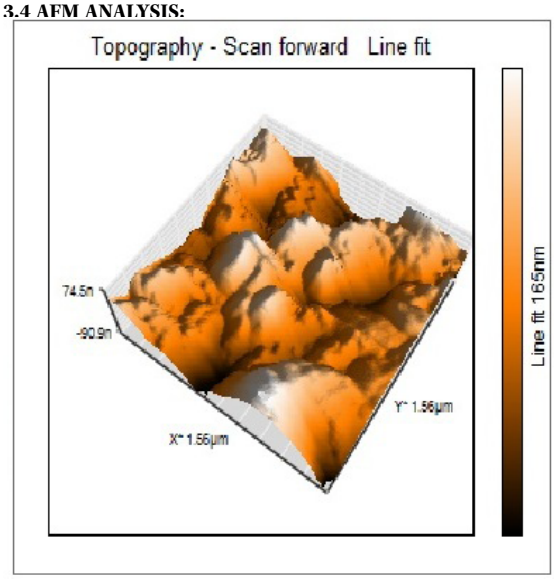

Figure.5. AFM 3D image of TiO_2/POT nanocomposite

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Atomic microscopy is an important tool to absorb the surface morphology. It provides 2 and 3 dimensional images of the sample surface. Surface topology features of TiO_2/POT nanocomposite as observed under AFM 3D is shown in figure 5. The sample exhibits an uniform surface with cone like grains covering the TiO_2 surface. The surface roughness was found to be in the range of 1.06 µm. The average crystallite of the sample was 60 nm which has in good agreement with the XRD results.

3.5 TEM Analysis:

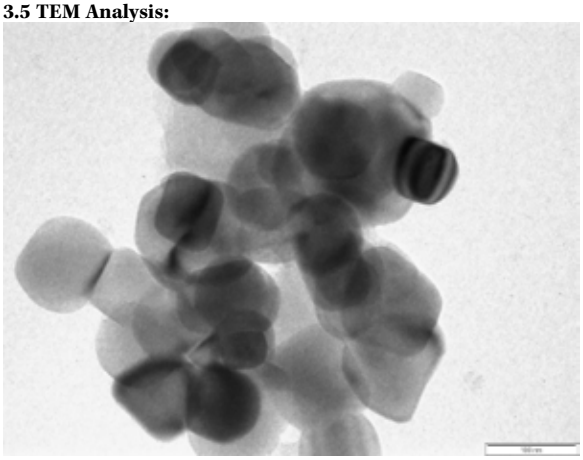

Figure.6. TEM image of TiO_2/POT nano composite

TEM micrograph of TiO_2/POT nanocomposite is shown in figure (6). Pawar et. al [18] showed that TiO_2 particles are embedded within the netlike structure built by polyaniline chains. But our TiO_2 /POT nanocomposite possess a core-shell structure. A core-shell structure has been formed by the polymerization of o-toluidine on the surface of TiO_2 nanoparticles which is well observed in Figure 6.

4. CONCLUSION:

In conclusion, the TiO_2/POT nano composite have been successfully synthesized by using chemical oxidative polymerization method. The material is characterized by using XRD, UV-Vis, SEM, AFM and TEM. XRD results show the tetragonal anatase phase of the particles of the TiO_2/POT nano composite. The average crystallite size of the nanocomposite is 59.9 nm which was calculated using Debye-scherrer equation. The band gap energy of the composite was found to be 3.4 ev.SEM analysis revealed the spherically shaped particles of the nanocomposite. AFM images showed that the average particle size of TiO_2 /POT nanocomposite was 60 nm. TEM analysis confirmed the core-shell structure of the nanocomposite. Thus, on the basis of our fundamental materials characterization a suitable nanocomposite is being suggested for the various fields of applications like optoectronics, solar cells and sensors.

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