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Morphological and crystalline structural characteristics of PEDOT™/TiO_2 nanocomposites for applications towards technology in electronic devices

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ABSTRACT

Nanocomposites of Poly(3,4-ethylenedioxythiophene), Tetra Methacrylate (PEDOT™)/TiO_2 were prepared and characterized by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. Scanning electron microscopy indicated highly dense surface morphology of the prepared samples. Transmission electron microscopy images indicated that the prepared samples have particle size comparable with those obtained by X-ray diffraction results. The crystallite sizes, lattice strain and other related physical parameters were calculated by using X-ray peak broadening analysis. Optical constants such as extinction coefficient and refractive index as well as dielectric constants were calculated for PEDOT™/TiO_2 nanocomposite film using spectrophotometric measurements of both transmittance and reflectance in the wavelength range of 300–2400 nm. PEDOT™/TiO_2 nanocomposite films/n-Si diodes were prepared by spin coating method. The electrical properties of the diodes were investigated at different temperatures in the range 300–375 K. The prepared diode showed a rectification characteristics and the rectification ratio was studied as a function of voltage at different temperatures. Temperature dependence of both ideality factor and barrier height was also investigated. High values of ideality factor confirmed the abnormality characteristics of the prepared diodes as compared to the conventional behavior of ideal diode.

1. Introduction

Recently, titanium dioxide (TiO_2) focused much attention due to its multifunctional and promising semiconductor characteristics such as physical and chemical photochemical stability and non-toxicity optoelectronic applications [1,2]. This material is suitable for medical and biomedical technology, gas sensors, wear protection, photochemical, electrical applications [2,3]. In addition, TiO_2 is near to a perfect semiconductor for photocatalysis due to its low cost, high stability and safety against both humans and the environment [4].

Conducting polymers have been achieved by either blending conductive filler or additives into insulating polymer matrix [5]. Among the well-known used conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) has attracted much attention in recent years due to its huge properties such as long-term stability, outstanding flexibility, better film forming, easy coating, high conductivity, good thermal stability, optical transparency, high conductivity, enhanced optical transparency for doped case, low-band gap energy, and sensitivity to the composition of environment [6–8]. With the rapid development of nano-science and nanotechnology, various methods to provide functional optical polymers have been revealed. It has recently been that a nano-hybridization of nanopolymers such as PEDOT™ with nanoparticles of metallic or inorganic such as TiO_2 is favorable methodology to prevail that obstacle without lowering their potential advantages [9]. Herein, we report a sol gel as a simple and effective

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method to fabricate PEDOT™/TiO_2 nanocomposite films. Various characterization techniques were applied to characterize the crystalline and morphology properties by X-ray diffraction, Transmission and scanning electron microscopy. Absorption and dispersion characteristics in a wide wavelength range is studied. Moreover, heterojunction characterization of the PEDOT™/TiO_2 nanocomposite/n-Si are also investigated.

2. Experimental details

2.1. Synthesis of TiO_2 and PEDOT™/TiO_2 nanocomposite

Titanium dioxide (TiO_2) nanoparticles were prepared from 10 mL titanium tertbutoxide (Merck, Darmstadt, Germany). This nanoparticles was added into a flask containing 15 mL ethanol (99.5%, J.T. Baker, Phillipsburg, NJ, USA). The mixture was refluxed at 105 °C, and during the reflux procedure ethanol, water and HCl mixture (12.5 mL+ 0.5 mL+ 0.25 mL) were added. The mixture was stirred for 3 h at about 100 °C then, the mixture was dried for 24 h at 100 °C.The obtained solid material was ground in a ball mill for about 10 min. The powder material was taken in a porcelain crucible and heated at about 400 °C in a furnace and white colored powder was obtained. The flow chart of the procedure for preparing TiO_2 nanopowder is shown in Fig. 1.

For obtaining PEDOT™/TiO_2 nanocomposite, a direct mixing of TiO_2 nanoparticles and PEDOT™ can be carried out in solution phase and the mixture was stirred for 20 min and ultrasonicated with a tip sonicator for 20 min to obtain a well-dispersed solution. The flow chart of the detailed procedure for preparing PEDOT™/TiO_2 nanocomposite is also shown in Fig. 1.

2.2. Characterization tools

The crystal structure and lattice constants were characterized by X-ray diffraction (XRD, Philips X'Pert Pro MRD) using Cu K_α radiation ($\lambda = 1.5418$ Å), with a step 0.02°.The morphology of the prepared TiO_2 samples were investigated by scanning electron microscopy (SEM) type JEOL- JAX-840A, with accelerating voltage 30 kV.Transmission electron microscopy (TEM) study includes transmission electron micrographsstudytypeJEOL JEM-1230, with maximum resolving power 0.2 nm, energy 40–120 kV on steps, maximum magnification power 600,000 X and computerized with Ultra Scan 1000 2k × 2k CCD. The thickness of the films was determined with Mettler Toledo MX5 microbalance. The UV–Vis spectra of the films were recorded from 200 nm to 1000 nm wavelength using SHIMADZU UV-3600 UV–Vis–NIR spectrophotometer at room temperature (~300 K). The current–voltage (I–V) measurements were performed by the use of a high impedance Keithley 617 programmable constant current source electrometer.

2.3. Optical constants calculation

The optical constants such as refractive index, n, absorption index, k, and absorption coefficient, α, can be estimated from the experimental values of transmittance, T, reflection, R, and the film thickness, d, by using the following expressions [10,11]:

$$\alpha = \frac{1}{d}\ln\left[\frac{(1-R)^2}{2T} + \sqrt{R^2 + \frac{(1-R)^4}{4T^2}}\right] \quad (1)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (2)$$

$$n = \left(\frac{1+R}{1-R} + \sqrt{\frac{4R^2}{(1-R)^2} - k^2}\right. \quad (3)$$

3. Results and discussion

3.1. Crystalline and morphological characteristics

The crystal structure and orientation of the PEDOT™/TiO_2 nanocomposite was investigated by XRD measurement. The XRD pattern is shown in Fig. 2 which reveals a broad characteristic of small particle size. Stronger and sharper peaks are observed which characterizes the best crystalline nature of the powder. All the observed peaks are attributed to tetragonal anatase TiO_2 (JCPDF 84–1285) with the lattice parameters of a = 0.3784 nm and c = 0.9512 nm and space group 141/amd. The reason for the absence of PEDOT™ peaks is the amorphous nature of this polymer. The only influence of PEDOT™ in the crystalline structural characteristics by X-ray is the broadening and intensity of TiO_2 peaks in the composite. The diffraction of the sample showed Bragg's reflection at about (101), (112), and (200) planes. Other orientations like (105), (211), (213), (116) and (215) are also observed with comparatively lower intensities [12].

Moreover, the diffracted peaks are found to be broad at half maximum. These broadening are mainly attributed to some reasons such as lattice micro-strain and smaller crystallite size. Average crystallite size, D, can be calculated by using the following Scherrer's equation [13]:

$$D = K\lambda(\beta\cos\theta)^{-1} \quad (4)$$

Where K is the shape factor (~0.95), λ is the X-ray wavelength of Cu k_α radiation (0.15418 nm), $\beta = \sqrt{\beta_1^2 - \beta_2^2}$ where β_1 and β_2 are respectively the width at half maxima of the broadened peaks of the sample and a standard silicon crystal. Using a silicon defect free crystal can benefits for measuring the instrumental broadening. Low scanning rate of the 2θ and neglecting the micro-strain of the non-thermal stressed films enabled us to determine the mean crystallite size using Eq. (4). Fig. 3 depicts the Gaussian fit of the peaks of XRD for PEDOT™/TiO_2 . As a result, the mean crystallite size can be calculated and found to be ~11 nm. The micro-strain induced in powders due to the imperfection of crystal and distortion can be calculated using the following expression:

$$\varepsilon = \frac{\beta}{4\tan\theta} \quad (5)$$

Using the above two Eqs. (4) and (5), one can obtain the following expression

$$\beta\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta \quad (6)$$

The above equation is the Williamson–Hall (W–H) equation. A plot of β cosθ vs. 4sinθ is shown in Fig. 4. The mean crystallite size, D as well as the lattice strain can easily be obtained and found to be 17 nm and 2.7×10^{-3}, respectively. The difference in the value of the mean crystallite size by Scherrer's and Williamson–Hall (W–H) equations can be due the different in the accuracy of the two equations. The mean crystallite size value obtained by Williamson–Hall (W–H) equation result is in consistent with those