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Influence of Polyethylene Glycol on the Properties of TiO_2 Films by Squeegee Method

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Abstract

An extremely easy method is presented for producing TiO_2 nanoparticles (NPs) films as photoanode in dye-sensitized solar cell applications. This paper presents the study on the effect of Polyethylene glycol 20000 (PEG 20000) on the properties of TiO_2 NPs films. The amount of PEG 20000 were varied between 0.1 and 0.5 g. Sonication and stirring of commercial TiO_2 NPs Degussa P25 and PEG 20000 in ethanol results in highly homogeneous dispersions which are used to prepare TiO_2 films. The use of optimum amount of PEG 20000 will increase the light absorption due to the increment of the surface area within the film. The films were characterised using ultraviolet-visible-near infrared spectrometer, field emission scanning electron microscopy and current-voltage measurement.

Keywords titanium dioxide, TiO_2, nanoparticles

INTRODUCTION

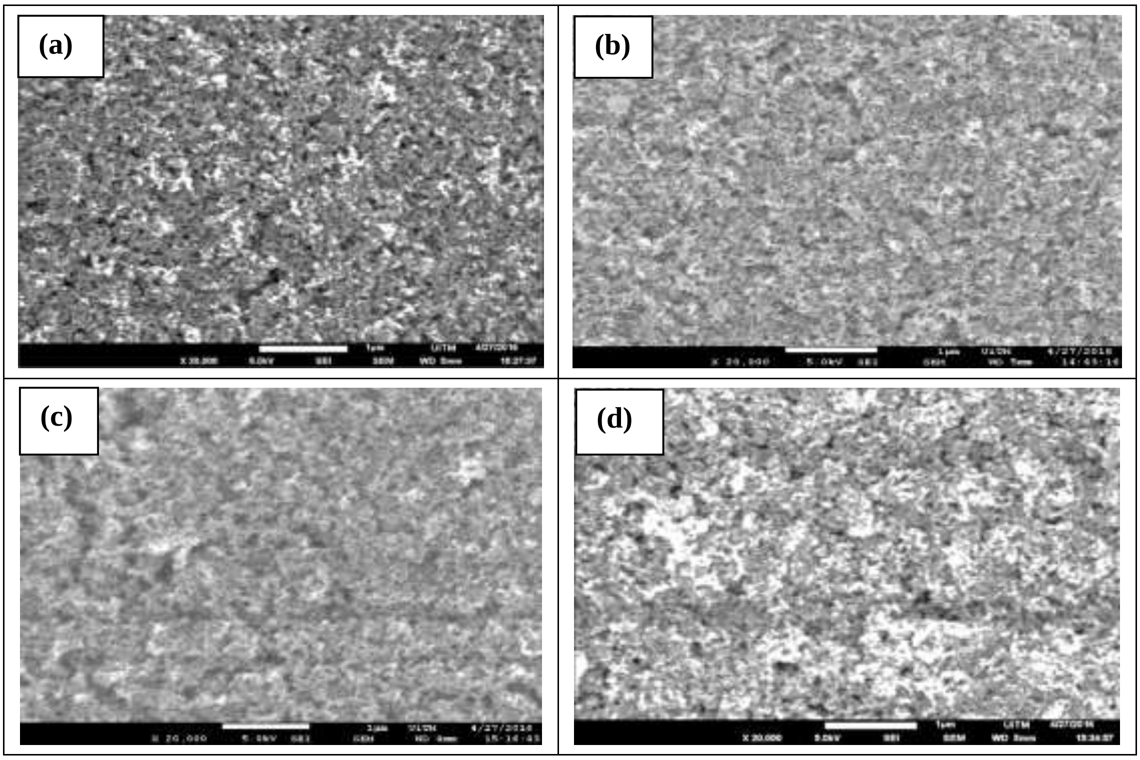
Titanium dioxide (TiO_2) also known as titanium IV oxide is a versatile transition-metal oxide and has been recently studied extensively due to its wide range of applications such as solar cells [1], sensors [2], luminescent materials [3], dielectric layers [4] and etc. TiO_2-based materials were widely used in various fields such as anti-bacterial applications, water purification, decomposition of various organic pollutants and solar cell applications due to its high photocatalytic activity, bio-compatibility, non-toxicity, wide bandgap, high refractive index, good transmittance invisible range, outstanding electrical properties and ease of mass production [5]. There are three recognisable phases exist in pure titanium dioxide polymorphs: rutile (tetragonal structure, $P4_2$/mnm), anatase (tetragonal structure, $I4_1$/amd) and brookite (orthorhombic structure, *Pbca*) phases having bandgap 3.03, 3.20 and 2.96 eV respectively at ambient pressure [6]. Normally, only anatase and rutile structures were observed in the formation of thin film while amorphous TiO_2 is often observed when the deposition temperature is very low [7]. Almost all viable physical and chemical deposition techniques have been adopted to prepare TiO_2 thin films. TiO_2 thin films can be prepared by a variety of methods such as sol-gel method [8], pulsed laser deposition [9], chemical vapor deposition [10], spray pyrolysis [11] and sputtering techniques [12]. The choice of deposition technique is crucial depending on specific application. In this work, the squeegee method was chosen for the thin film preparation which offers the advantage of depositing films on a large scale area [13]. The aim of this work is to investigate the effect of the polyethylene glycol 20000 amount on the quality of the TiO_2 films.

MATERIALS AND METHOD

The TiO_2 NPs films were grown on 2x2 cm^2 glass substrates by squeegee technique. The TiO_2 paste was based on 3.5 g of commercial P25-TiO_2 nanopowder (Sigma Aldrich, USA, BET surface area 45-55 m^2g^{-1}, particle size < 25 nm), 0.5 ml titanium tetraisopropoxide (TTIP) and 15 ml ethanol were mixed with a molar ratio of [n(P25):n(TTIP):n(EtOH) = 1:0.036:5.92] to form a light yellow solution. The use of P25 in the preparation of TiO_2 paste is intended to prevent the film from cracking. Then, the prepared paste was was subjected to ultrasonic irradiation using ultrasonic water bath (Hwasin Technology Powersonic 405, 40 kHz) at 50 ºC for 30 min. After the sonication process, the TiO_2 paste was smoothed out by glass rod on the glass substrate. The ethanol evaporated in air at room temperature after a few minutes. The coated TiO_2 paste was dried in air at 150 ºC for 10 min and sintered at 450 ºC for 1h. The formed films were homogenous and strongly attached to the photoanode substrate. The resulting film thickness was controlled by the adhesive Kapton Polyimide tape thickness. The topography of TiO_2 NPs films were characterised by a field emission scanning electron microscope (FESEM, model: ZEISS Supra 40VP) with an electron beam energy accelerating voltage of 0.2 and 30 kV. The optical properties of the sample were characterised by ultraviolet-visible-near infrared spectrophotometer (UV-Vis-NIR, model: Varian Cary 5000) within the range from 300 to 2200 nm. The sheet resistance was performed by the two-point probe using a Keithley 2400 computer-controlled current-voltage source meter. For that purpose, gold metal contact with a thickness of 60 nm was deposited onto the samples as an electrode for current-voltage (I-V) measurement by sputter coater (model: EMITECH K550X) at a deposition pressure of $1x10^{-1}$ mbar.

RESULTS AND DISCUSSION

In this study, the morphological properties of the TiO_2 NPs films were investigated via field emission scanning electron microscopy (FESEM) at 20 k magnification and 5 kV applied voltage. Figure 1 shows the FESEM images of the produced TiO_2 NPs films with various amount of PEG 20000 by squeegee method. It is clearly seen from Figure 1 that the morphology have a more smooth and porous film structure for 0.1 g amount of PEG. However, the structure become less homogenous with agglomerated particles at higher PEG amount.



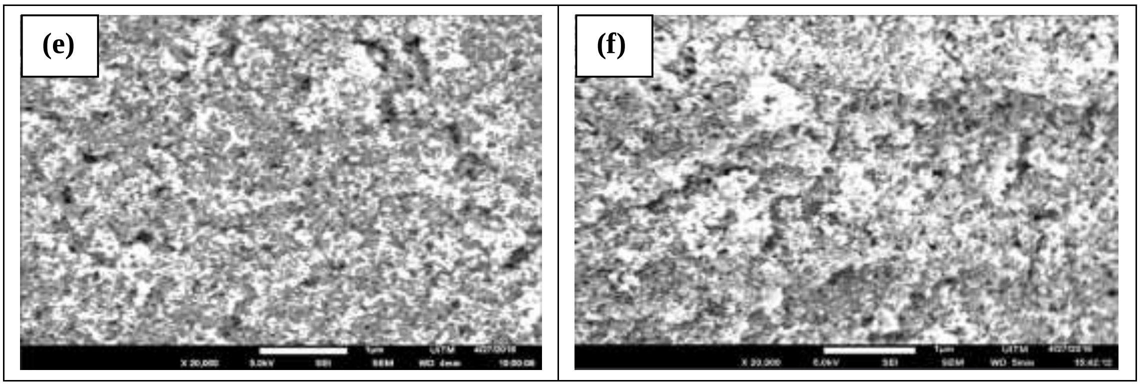


Figure 1 FESEM images of TiO_2 NPs films at different amount of PEG (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4 and (f) 0.5 g.

The transmission spectra of the films in the range between 350 and 2200 nm are shown in Figure 2. It was found that all the samples attained a reasonably low transmission due to thick layer of the films. The optical transmittance spectra are used to determine the band gap of the semiconductors. Basically, absorption determines the electron excitation from valance band to conduction band, which can be used for calculation of the band gap. The relationship between absorption coefficient, α and incident photon energy, hv in fact is given by following equation for allowed indirect transitions.

$$\alpha hv = B(hv - E_g)^n \qquad (1)$$

where B is a constant, E_g is the band gap of the material, α is the optical absorption coefficient, v is the frequency of the photons and h is the Planck's constant and the exponent n characterizes the nature of the electron transition. The exponent n depends on band gap type of the semiconductor. For a direct gap n = 1/2. In this case, the graph $(\alpha hv)^2$ versus the photon energy, hv is linear over a certain energy range. The intercept of the straight line with x-axis is precisely the value of the optical gap. For indirect band gap n = 2, the value of the gap is obtained similarly from the x-intercept of the extrapolated linear part of the graph $(\alpha hv)^{1/2}$ versus the photon energy, hv [14,15]. We have adopted the second method which is widely used in the literature for TiO_2 [16].

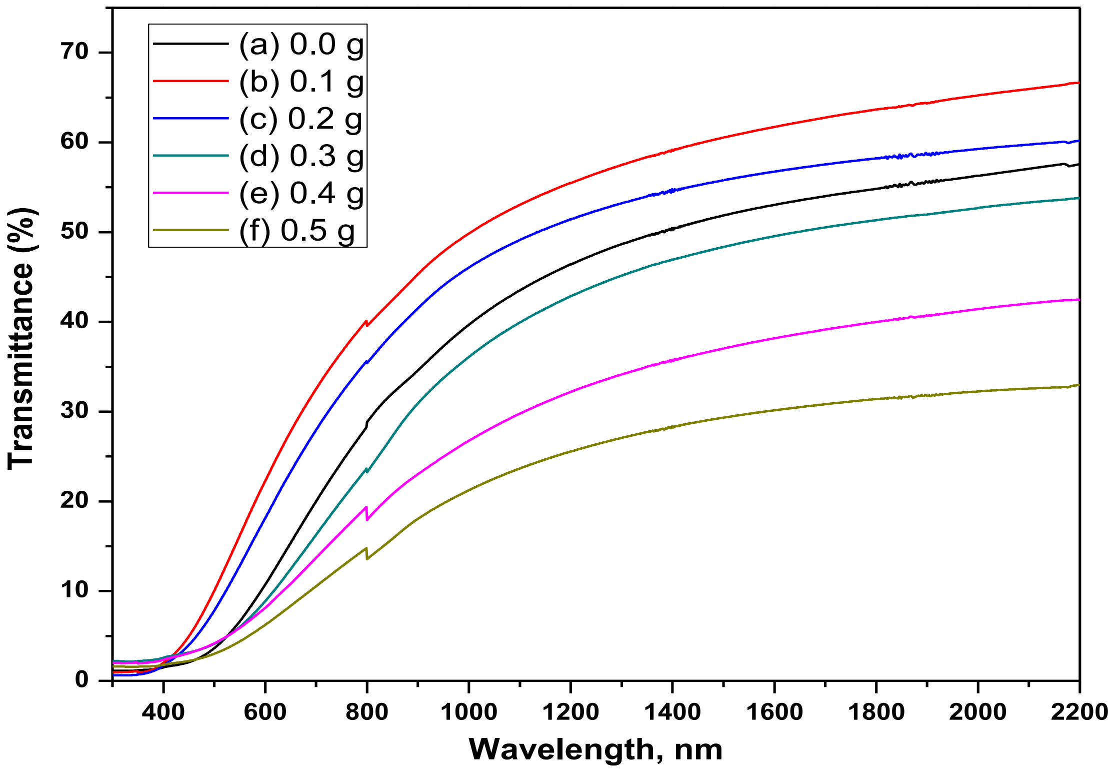


Figure 2 Transmittance of TiO_2 NPs thin films at different amount of PEG (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4 and (f) 0.5 g.

Table 1 Thicknesses, average transmittance and optical band gap energy of TiO_2 NPs films deposited at various amount of PEG.

Amount of PEG (g)	Thickness, *t* (mm)	Average transmittance, *T* (%)	Optical band gap Energy, E_g (eV)
0.0	0.03	12.19	3.00-3.20
0.1		21.43	
0.2		18.09	
0.3		10.49	
0.4		9.16	
0.5		6.97	

The optical band gap, E_g range of the TiO_2 films with various amount of PEG is shown plotted in Table 1. It is observed that E_g was ranged between 3.00 and 3.20 eV with the increasing in PEG amount. The various change in the optical band gap of the TiO_2 films with the amount of PEG might be the result of the change in film density and grain size. Figure 3 depicts typical I–V curves at room temperature for all TiO_2 NPs films. The I–V characteristics measured between two contacts are linear indicating Ohmic contacts are formed. Sample with 0.1 g PEG shows maximum current values compared to other samples. This might indicates fewer amounts of carrier traps present in sample (b) while other samples suggest an increase numbers of traps which may reduce the conductivity value.

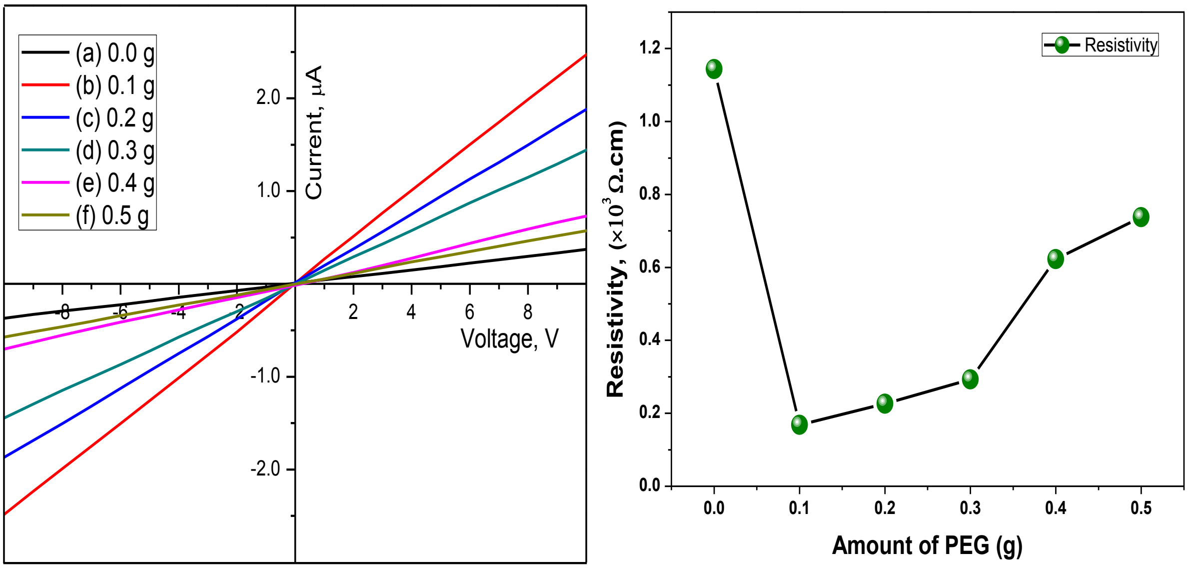


Figure 3 I-V and resistivity of TiO_2 NPs films at different amount of PEG (a) 0.0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4 and (f) 0.5 g.

The obtained results indicate that the resistivity of the samples increases with the increase in PEG amount. The minimum value of 0.168×10^3 Ω.cm was achieved for film with PEG content of 0.1g. The decrease in resistivity behaviour at the beginning might be due to the increase in the regular sites of the Ti atoms in the films network. Since TiO_2 is an *n*-type semiconductor, the concentration of Ti^{4+} in TiO_2 films forms a donor level between the band gap of TiO_2 which results in the reduction of recombination of electrons and holes [17,18].

CONCLUSION

TiO_2 NPs were successfully deposited on glass substrates by squeegee method. Effect of the PEG content on the structural, optical and electrical properties of TiO_2 NPs films was investigated. The morphology of the films became less homogenous as the PEG content being increased. The indirect band gap was ranged between 3.00 and 3.20 eV. The films had a lower transmittance which might be due to the porous structure within the film that increase the optical scattering within the films. Finally, based on the result of the experiment, the 0.1g of PEG of TiO_2 NPs had the lowest resistivity of 0.168×10^3 Ω.cm. Therefore, future development research must be done to improve the properties of the film for better performance.

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