Effect of Process-Related Parameters on Band Gap of Electrophoretically Deposited TiO_2/Nb_2O_5 Composite Thin Films

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Abstract

Nano-crystalline composite thin films of titanium dioxide and niobium (v) oxide (TiO_2/Nb_2O_5) were successfully deposited on fluorine doped tin oxide (FTO) coated glass substrate using electrophoretic deposition (EPD) technique. The colloidal suspension utilized in EPD cell consisted of mixture of TiO_2 and Nb_2O_5 nanopowders and 2-propanol in a Pyrex glass. Values of potential difference (25 to 60V) were applied across the EPD electrodes placed in a parallel configuration 1.2cm apart and partially immersed in the suspension. The optimization of EPD parameters was achieved from transmittance measurements and band gap energy calculations. Both Nb_2O_5 and TiO_2 nanoparticles were seen in XRD graphs to be present in the composite films in the ratio 1 to 1.78 which confirmed that both type of nanoparticles suspended in 2-propanol developed positive surface charges and were moved towards and deposited on the cathode upon application of an electric field. The band gap energy was evaluated for films deposited from varied EPD process-related parameters namely, concentration, deposition times and applied potential. The maximum values of band gap were obtained for films electrophoretically deposited from particle concentration of 0.01g/40mL (or 0.25g/L), applied voltage of 35V, and deposition time of 90s. These values of EPD process-related parameters formed the optimum values for deposition of crack free films of good porosity. The changes in band gap values are attributed to either energy shift of conduction band or valence band energy levels. The TiO_2/Nb_2O_5 composite thin films, fabricated in this study from optimized parameters of EPD technique had smooth morphology as shown by SEM images. Further work is needed to evaluate the potential of TiO_2/Nb_2O_5 composite films deposited by EPD for dye – sensitized solar cell application.

Keywords: Electrophoretic deposition (EPD), TiO_2/Nb_2O_5 composite thin films, PV applications, Solar energy, Optical band gap

1. Introduction

Dye sensitized solar cell (DSSC) designs using titanium dioxide (TiO_2) and liquid electrolyte have continuously

Africa Journal of Physical Sciences ISSN: 2313-3317

in converting sunlight to electric energy depends on several factors among them the efficiency with which light is harvested, and transmitted through the photoelectrode, the number of electrons injected into the photoelectrode, and the ease with which electrons are transported through the photoelectrode (Zhang *et al.*, 2009). Therefore, the photoelectrode can be considered as an essential component that influences the performance of a solar cell. Inside a DSSC, light photons are converted into electric energy on the photoanode (photoelectrode) which consists of nanoporous network of TiO_2 particles sensitized with a layer of visible light absorbing dye. The key to efficient light harvesting is the high surface area of the nanoporous TiO_2 film which provides increased surface area for dye adsorption. It is highly desirable that

electrical, structural and optical properties of nanoporous TiO_2 films fabricated techniques like DC magnetron sputtering technique (Eguchi *et al.*, 2000, Suchea *et al.*, 2007), sol gel technique (Traversa *et al.*, 2001), screen-printing method (Chiba, *et al.*, 2006; *Ito et al.*, 2008), pulsed laser deposition (Tonooka *et al.*, 2009), doctor blade (Lee *et al* 2013) and electrophoretic deposition (EPD) technique (Miyasaka and Kijitori, 2004; Yum, *et al.*, 2005; Bandy *et al.*, 2011; and Narayan & Raturi, 2012) have been conducted.

Conventional techniques such as sputtering and pulsed laser require expensive and complicated

equipment. EPD method can overcome such drawbacks. However EPD technique has not been fully exploited in fabrication of composite electrodes for use in dye-sensitized solar cells despite being a simple, relatively cheap technique, that produces high porous films and which could be scaled up for mass production if successfully developed. In this study, the optimization of EPD process-related parameters to fabricate a nanocrystalline and nanoporous TiO_2/Nb_2O_5 composite electrode thin films for application in the dye-sensitized solar cells was explored. The deposition parameters such as deposition time, applied DC voltage and the concentration of the precursor material can alter the optical properties of the resulting thin film, in this work, effect on band gap when these parameters have been varied has been studied. This is an important parameter especially in photovoltaic application and other thin film application.

2. Materials and methods

The substrate used were Fluorine doped tin oxide (FTO) glass having sheet resistances of 8Ω/square manufactured by Pilkington, Hartford Glass Co. Inc., USA. The substrate were cut into small pieces using a diamond glass cutter into dimension measuring 16mm×25mm×1mm. the substrate were cleaned using foam from mixture of soap detergent, acetone and sodium hydroxide to remove any greasy stains. The substrates were then sonicated for 10 minutes in distilled water and then rinsed. These glass were used as electrodes in EPD setup shown in figure 1.

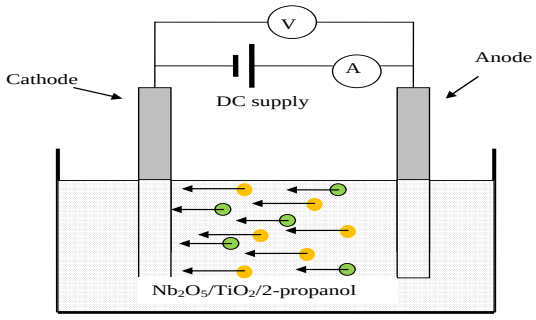


Figure 1 *A schematic setup of EPD cell setup (after Will, et al., 2001 and Sarkar et al., 2005)*

The colloidal suspension in EPD cell consisted of TiO_2 nanopowder (Cas No. 13463-67-7 Aldrich) and Nb_2O_5 nanopowder (Cas No. 1313-96-8 Acros Organics BVBA, Belgium) mixed with 40mL 2-propanol (Scharlau chemie) in a Pyrex glass. Magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$, 99.9%, Aldrich) pellets were added to suspension to provide magnesium ions to attach to semiconductors and thereby control the zeta potential of suspension (Bandy *et al.*, 2011 and Lee *et al.*, 2011). The electrodes were arranged in a parallel configuration and partially immersed in the suspension.

Various amounts of TiO_2 (0.01g to 0.3g) and Nb_2O_5 (0.01g to 0.3g) powder were mixed with 40 milliliters of 2-propanol in a glass beaker to form EPD suspension. The suspension was then stirred using Power Sonic 405 ultrasonic for 10 minutes. The color of the suspension turned milky white after sonication. The electrodes were arranged in parallel and partially immersed in suspension. Various values of DC voltage (25V to 60V) were applied across the electrodes. Electrophoretic deposition was seen to form on the cathode (cathodic deposition). In addition, deposition of the composite films was carried out for different times (60 s to 180s). Finally the deposited composite thin films were annealed at 400^0C for 30 minutes and gradually cooled to room temperature to avoid development of cracks.

3. Results and discussion

3.1 X-RD characterization

The crystal structure of TiO_2/Nb_2O_5 composite thin films were investigated using X-Ray Diffraction (X-RD) as shown in figure 2. The spectra confirmed presence of both titanium dioxide and niobium (v) oxide particles in film. Presence of both type of particles was critical in ensuring that both types of nanoparticles developed surface charges while in suspension, and were therefore moved towards and deposited on the oppositely charged electrode. It can be seen that the relative abundance of TiO_2 particles as indicated by the length of peaks correspond to higher degree of crystallinity than that of Nb_2O_5. Increase in crystallinity was due to annealing of the films at 400^0C for 30 min.

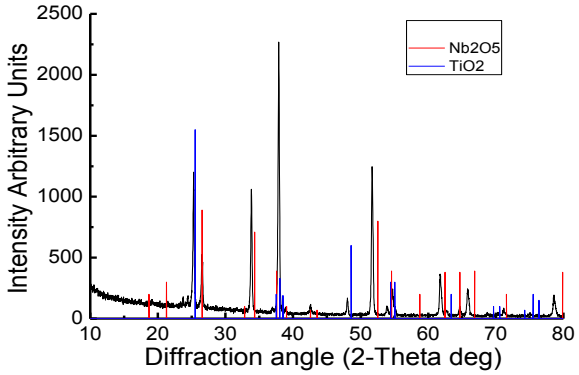


Figure 2*. XRD spectra of TiO_2/Nb_2O_5 composite thin films annealed at 400^0C for 30 minutes under atmospheric conditions.*

3.2 Morphological characterization of fabricated TiO_2/Nb_2O_5 composite thin films using scanning electron microscope (SEM)

The samples analyzed for morphological structure were composite TiO_2 and Nb_2O_5 thin films deposited by electrophoretic method for precursor prepared at 0.01g/40mL, and deposited using 35DCV for 90 s, the SEM micrographs (Figures 3& 4) scanned at EHT=10.00KV are shown in figure 3 and 4.

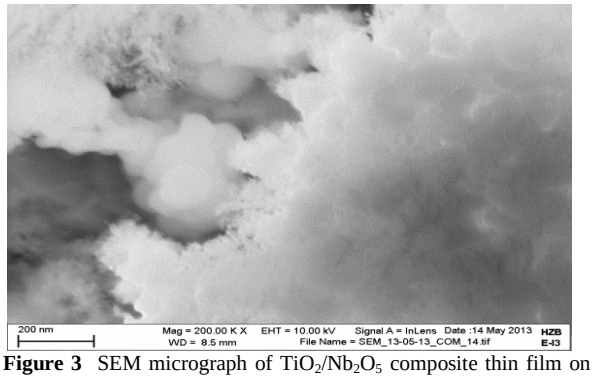


Figure 3 SEM micrograph of TiO_2/Nb_2O_5 composite thin film on a $F:SnO_2$ (mag × 200K)

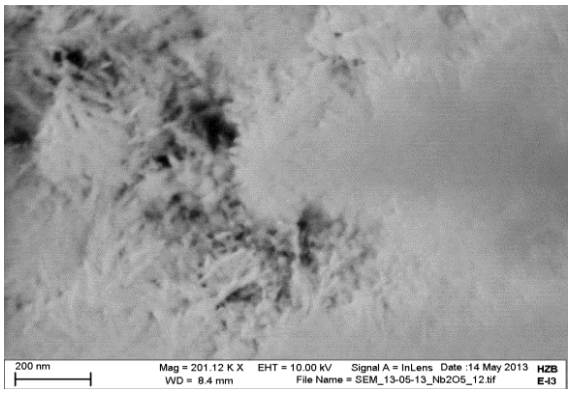


Figure 4 SEM micrograph of micrograph of Nb_2O_5 semiconductor thin film on a $F:SnO_2$ (mag ×201.12K)

The SEM images of TiO_2/Nb_2O_5 composite thin films, reveal that TiO_2 and Nb_2O_5 nanoparticles in the composite films are of near uniform distribution with a small fraction of the thin film which looks porous. The surface coating appears to adhere well to the glass surface. It can be seen from SEM micrographs that the TiO_2/Nb_2O_5 composite thin films electrophoretically deposited on FTO coated substrates possesses a high degree of porosity which is the key factor in obtaining efficient dye-sensitized solar cells.

3.3 Optimization of EPD process parameters

According to the Hamaker's equation (Besra and Liu, 2007), the mass (m) of film formed through electrophoretic deposition is related to EPD process-related parameters of concentration (c), electric field (E=V/L), and deposition time (t) as indicated in equation (1).

$$m \propto cEt \qquad (1)$$

Here we report results of variation of band gap with concentration, voltage (fixed L) and deposition time. The assessment of quality of the electrophoretically deposited TiO_2/Nb_2O_5 composite electrode thin films was carried out using visual inspection (digital photographs) and UV-Vis-NIR spectrophotometer (transmission spectra). The morphology of films was determined using Scanning electron microscope (SEM).

The optimum EPD process-related parameters for depositing TiO_2/Nb_2O_5 composite thin films were determined from graphs of band gap versus applied voltage, deposition time, and concentration as shown in Figs 4, 5, & 6. The optical band gap (E_g) for direct transition in a semiconductor is calculated from following equation (2) proposed by Tauc (1974);

$$(\alpha h\nu)^2 = B(h\nu - Eg) \qquad (2)$$

Where α(λ) is absorption coefficient and is a function of wavelength, h is Planck's constant, ν is frequency, and B is a proportionality constant. The values of the film optical energy gap (E_g) were determined by extrapolating to the hv-axis, the linear part of the $(\alpha h\nu)^2$ versus hv curve (Narayan & Raturi, 2012 ; Swanepoel, 1983).

Absorption coefficient α(λ) values were derived from transmittance (%T) using Equation (3); (Tepantlan *et al.*, 2008).

$$\alpha(\lambda) = \frac{1}{z}\ln\left(\frac{100}{\%T(\lambda)}\right) \qquad (3)$$

Where z is film thickness.

The theoretical direct band gap values of TiO_2 is E_g = 3.25eV (Nowotny, *et al.*, 2008) and for Nb_2O_5 is E_g = 3.49eV (Jose *et al.*, 2009). However, the band gap energy values obtained in this work were relatively high > 3.7eV (Figs 5, 6 & 7). Other researchers have also reported relatively high band gap values of pure TiO_2 and Nb_2O_5 as shown in table 1.

Table 1. Values of direct and indirect band gaps of TiO_2 and Nb_2O_5 reported by various authors

Type of Thin film	Eg (eV) (direct)	Eg (eV) (indirect)	Reference
TiO_2	3.88	NA	Narayan & Raturi (2012)
	4.14	3.4	Ghrairi & Bouaicha (2012)
	3.5-3.9	2.1-3.0	Oommen *et al.*, 2012
Nb_2O_5	3.9	NA	Parakh & Garg (1985)

NA ≡Not available

It can be interpreted that these changes in energy band gap values results reflect energy shift of either the valence band or conduction band levels (Kim and Jeong, 2007). The straight-line behaviour in the high frequency region supports the existence of direct band gap.

3.4 Optimization of applied voltage

Figures 5(a) shows a photo-graph of TiO_2/Nb_2O_5 composite thin films electrophoretically deposited when applied voltage was varied from 25 to 60V. For each voltage, the electrodes were separated by 1.2cm, suspension concentration was 0.01g/40ml, and deposition time was maintained at 90s. Band gap values from optical transmittance data and plots of eqn. (2) were then plotted as shown in figure 5b.

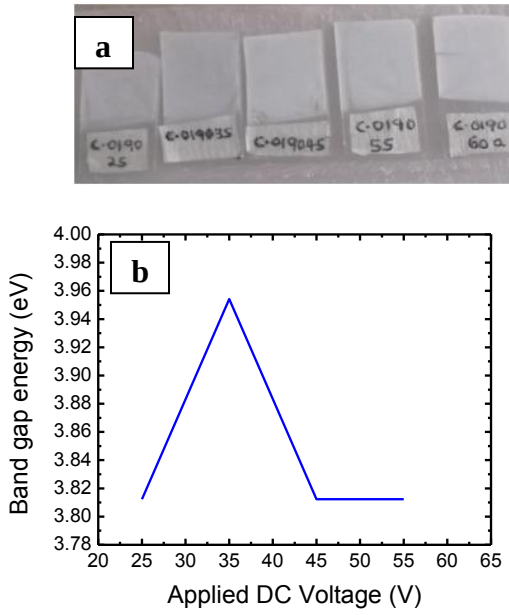


Figure 5 *(a) Photographs of TiO_2/Nb_2O_5 composite electrode thin films electrophoretically deposited for 90 s from 0.01g/40mL, and for varying voltages (b) variation of band gap energies of the films with applied voltage.*

The deposition condition of the composite thin films were the same as for the samples used in making the SEM The increase of band gap energy to maximum of 3.95eV and subsequent decrease of band gap with applied voltage could be interpreted as resulting from either energy shift of conduction band or valence band levels. micrographs.As can be seen in figure 5(b), the value of band gap was maximum (3.96eV) at 35V. This is the value corresponding to highest value of transmittance (eqn 3). Higher voltages (<35V) produced relatively thick films which yielded low band gap energies corresponding to low transmittance. Typically, thick films hinder transmission of light rays through them resulting to low transmittance values. The thick films resulting from deposition at high voltages were non-porous and unsuitable for dye absorption. In addition, thick films decrease the electron diffusion which result in low conversion efficiency. It follows, that optimum applied DC voltage for deposition of TiO_2/Nb_2O_5 composite thin films is 35V.

3.5 Optimization of deposition time

Figure 6(a) shows the images of the TiO_2/Nb_2O_5 composite electrode thin films electrophoretically deposited at 60 to 180 seconds. For each deposition time, the TiO_2/Nb_2O_5 composite thin films were deposited by application of 35V to a 0.01g/40ml concentration of nanopowders. Band gap values from optical transmittance data and graphs based on eqn. (2) and were plotted as shown in figure 6b.

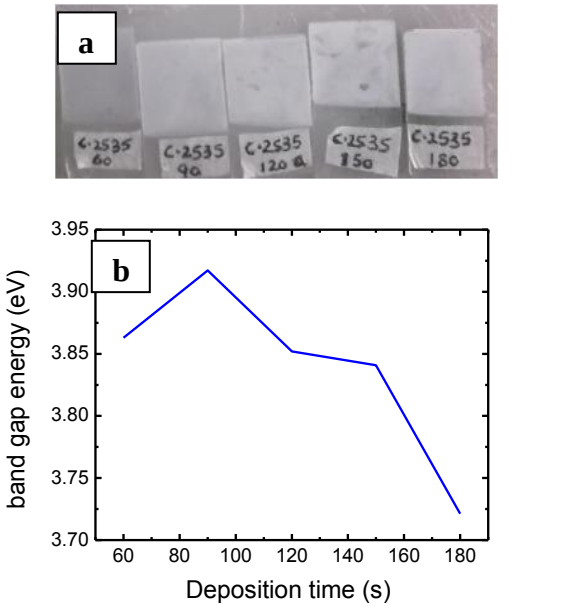


Figure 6 *(a) Photographs of TiO_2/Nb_2O_5 composite electrode thin films electrophoretically deposited from 0.01 g/40mL, at 35DCV for varying deposition time and (b) variation of band gap energy of the films with deposition time*

The maximum value of band gap energy was obtained for deposition time of 90s, which according to eqn. (3) corresponds to maximum transmittance. For short deposition times (<90s), the band gap decreased since time was too short for formation of appreciable layer of film from the low level of concentration. For longer deposition times (>90s), the band gap decreased due to formation of thick films (> 100nm). Decrease in band gap with increased deposition time could be attributed to shift in either conduction or valence bands leading to narrower energy band gaps in composite thin films. Thick films, which in general are non-porous, do not absorb sufficient amount of dye and are undesirable in solar cells applications. The best quality films from visual inspection and values of band gap energies correspond to deposition time of 90 seconds.

3.6 Optimization of concentration

Figure 7(a) shows the photo-graph (images) of the TiO_2/Nb_2O_5 composite electrode thin films electrophoretically deposited from powder concentration ranging from 0.01g/40mL to 0.03g/40mL. For each concentration, the TiO_2/Nb_2O_5 composite thin films were deposited by application of 35V for 90s. Visual inspection showed that the films corresponding to 0.01g/40ml concentration had the best quality films.

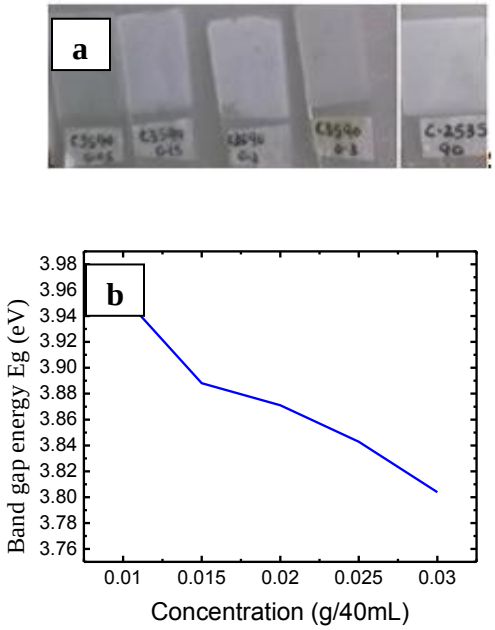


Figure 7 *(a) Photographs of TiO_2/Nb_2O_5 composite electrode thin films electrophoretically deposited for 90 s, at 35V, and for varying voltages (b) variation of band gap energies of the films with concentration.*

The decrease in band gap energies with increased concentration (fig 7b) resulted from development of thick films which limit transmittance of light rays. This decrease in band gap could also be attributed to shift of either conduction or valence bands leading to narrower band gaps in composite semiconductor. It was difficult however, to determine the minimum concentration of suspension from band gap energy values since the metal oxide particles barely coated on the glass slides for concentration less than 0.01g/40ml. Powder concentration of 0.01 g/40mL was therefore chosen as optimum EPD concentration value for fabrication of TiO_2/Nb_2O_5 composite electrode thin films.

4. Conclusions

In this research work TiO_2/Nb_2O_5 composite thin films were successfully deposited by electrophoretic technique after optimization of EPD process related parameters namely, deposition time, concentration and applied electric field. The optimum concentration, voltage and deposition time were 0.01g/40mL, 35DCV, and 90s respectively. Both Nb_2O_5 and TiO_2 nanoparticles were shown, by XRD graphs, to be present in the composite films in the ratio 1 to 1.78. The changes in band gap values with process-related parameters are attributed to either energy shift of conduction band or valence band levels. The deposited films were seen to be crack free and of good porosity. The TiO_2/Nb_2O_5 composite thin films, fabricated in this study from optimized parameters of EPD technique were of good-quality and smooth morphology as shown by SEM images. Further studies are required to test the suitability of TiO_2/Nb_2O_5 composite films deposited by electrophoretic deposition technique for application in dye-sensitized solar cell.

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