Materials Science-Poland, Vol. 22, No. 2, 2004

Photoelectrochemical properties of sol-gel derived TiO_2 thin films in aqueous sodium oxalate solution

ZULKARNAIN ZAINAL[*], CHONG YONG LEE, MOHD ZOBIR HUSSEIN, ANUAR KASSIM

Department of Chemistry, Faculty of Science and Environmental Studies, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor Darul Ehsan,Malaysia

Photoelectrooxidation of aqueous sodium oxalate on TiO_2 thin films has been investigated. The films, prepared by sol-gel dip-coating, were characterised using Scanning Electron Microscopy and X-ray Diffractometry. Photosensitivity of samples was studied using Linear Sweep Voltammetry and Chronoamperometry techniques. The photoelectrochemical performance of thin film electrodes was evaluated in function of heat treatment, number of dip-coatings and applied potential. The percentage of oxalate degradation was determined by calculating the total charge from the photocurrent. The films heat-treated at 773 K were better fitted to indirect optical transition with $E_g = 3.21$ eV.

Key words*: photooxidation; TiO_2; sol-gel; sodium oxalate; titanium substrate*

1. Introduction

Sodium oxalate is a major toxic impurity in liquid alumina processing. It must be continuously removed, because it induces problems that lead to low-quality metallurgical alumina due to particle attrition [1]. Additionally, low solubility of sodium oxalate in liquid makes it easy to crystallize during alumina precipitation. This interference with agglomeration leads to an increased generation of unwanted fine alumina trihydrate [2].

Several techniques for the causticization of sodium oxalate have been reported, including physical separation, microbiological processes and other conventional thermal pathways using ambient temperature and pressure [3–5]. Among them, photocatalytic destruction of organic pollutants has emerged as the most attractive method during water purification, since it can lead to a complete mineralization of toxic compounds into unharmful products such as H_2O, CO_2, and other inorganic substances [6]. Many semiconductors, such as TiO_2, WO_3, SrO_2, ZrO_2, ZnO, Fe_2O_3, CeO_2, CdS and ZnS

---

[*] Corresponding author, email: zulkar@fsas.upm.edu.my.

[6,7], have been investigated in terms of their catalytic properties in photocatalytic degradation of a wide variety of environmental contaminants. Among these semiconductors, TiO_2 has been proven to be an excellent photocatalyst in this particular field [6,7].

Nevertheless, most of the studies on photocatalytic oxidation of sodium oxalate use TiO_2 slurry [1–2, 5, 8], while very few studies on thin film photocatalysts exist [9]. In this work, we studied TiO_2 thin films prepared by the sol-gel dip-coating method. This immobilization method is more preferable than the slurry or suspension systems, due to easy and convenient catalyst handling – the need of post-treating to separate the catalyst from the reaction mixture has been eliminated [10]. In addition, TiO_2 can be induced electrochemically when supported on electrically conducting substrates [11–13]. Thus, characteristics of the films under applied external bias potential could be investigated. The effects of various operational parameters such as heat-treatment temperature, number of dip-coating layers and applied potential were studied.

2. Experimental

2.1. Materials

All chemicals, namely sodium oxalate (Fisher, 99.5%), tetraisopropyl orthotitanate (>98% Ti, Merck-Schuchardt), ethanol (Analytical reagent grade, GmbH Chemical) and nitric acid (BDH, 69 %) were used without further purification. All solutions in this experiment were prepared using deionized water (Milipore Alpha Q system, 18.2 MΩ·cm).

2.2. Sample preparation

The sol-gel samples were prepared by adding 1 ml of concentrated nitric acid to 200 ml of water, followed by 28.1 g of tetraisopropyl orthotitanate in 10 ml of ethanol. The mixture was stirred with a magnetic stirrer for 5–6 days to obtain a thick hydrolyzate. The substrate – titanium plates (Aldrich Chemical Company, 0.25 mm thick, 99.7%) – were cut into discs 1.00 cm in diameter and polished with silicon carbide paper (a bioanalytical system PK-4 polishing kit). The plates were rinsed in an ethanol bath before use. TiO_2 films were obtained by manually dipping the titanium plates in the hydrolyzate for a few seconds and leaving them to dry at room temperature. Then the coated plates were heated at 373 K for 5 min in an oven, followed by the dip-coating procedure. This was repeated several times, until the desired number of coatings was obtained. Finally, the plates were heat-treated in a Thermolyne 21100 furnace at temperatures ranging from 373 K to 773 K for two hours to obtain titanium dioxide films.

2.3. Analytical measurements

A potentiostat EG&G Princeton Applied Research (PAR) VersaStat, driven by a model 270 electrochemical Analysis System Software, was used in the electrochemical and photoelectrochemical measurements. These measurements were carried out in a standard electrochemical cell. The working electrode was made by mounting the TiO_2 coated titanium plates onto a Teflon electrode holder. The exposed area was about 0.64 cm^2. The other electrodes were: Ag/AgCl (0.222V vs. NHE) as a reference electrode, and platinum as a counter electrode. All the experiments were carried out using 0.01 M sodium oxalate as the electrolyte. Two light sources were used to excite the TiO_2 electrode: a tungsten halogen projector lamp (Osram, 300 W and 120 V) and a UV light beam (BlackRay model 100AP, PAR38 mercury lamp 100 W). The light source was placed 15 cm from the sample. All measurements were carried out at room temperature, approximately 298 K.

Scanning electron microscope measurements (SEM) were performed with a SEM JSM 6400 JEOL Scanning Microscope. The morphology and surface characteristics of the coated TiO_2 on the substrate were analyzed. Gold coatings were applied to the samples before running the SEM experiments by using a BIO-RAS sputter coater. X-ray diffractometry (XRD) analysis was employed to study the structure of TiO_2 layers coated on titanium surfaces. These measurements were performed using a Shimadzu XRD 6000 diffractometer or a Siemens D-5000 Diffractometer for 2θ ranging from 5° to 60°, with an Ni-filter and CuK_α beam (λ = 1.54056 Å). Optical absorption studies were carried out using a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The coated ITO glass plates were placed across the radiation pathway while an uncoated ITO glass plate was put across the reference channel. The band gap energy E_g was determined from an analysis of the absorption spectra.

3. Results and discussion

3.1. Morphology of the TiO_2 electrode

Figure 1 shows scanning electron micrographs of the heat-treated films. Cracks appeared on the surface of the film after treatment at 373 K. The occurrence of cracks during the gel drying process was due to large differential evaporation, large stress and variation in gel pore size [14]. Upon heating at 473 K and 573 K, the thermal gradients result in breaking the particles further into inhomogeneous forms. This occurred accompanying dehydration and decomposition of organic compounds [15]. Heat treatment at 673 K resulted in the formation of aggregates. These aggregates were transformed into a well formed and better covered layer at 773 K.

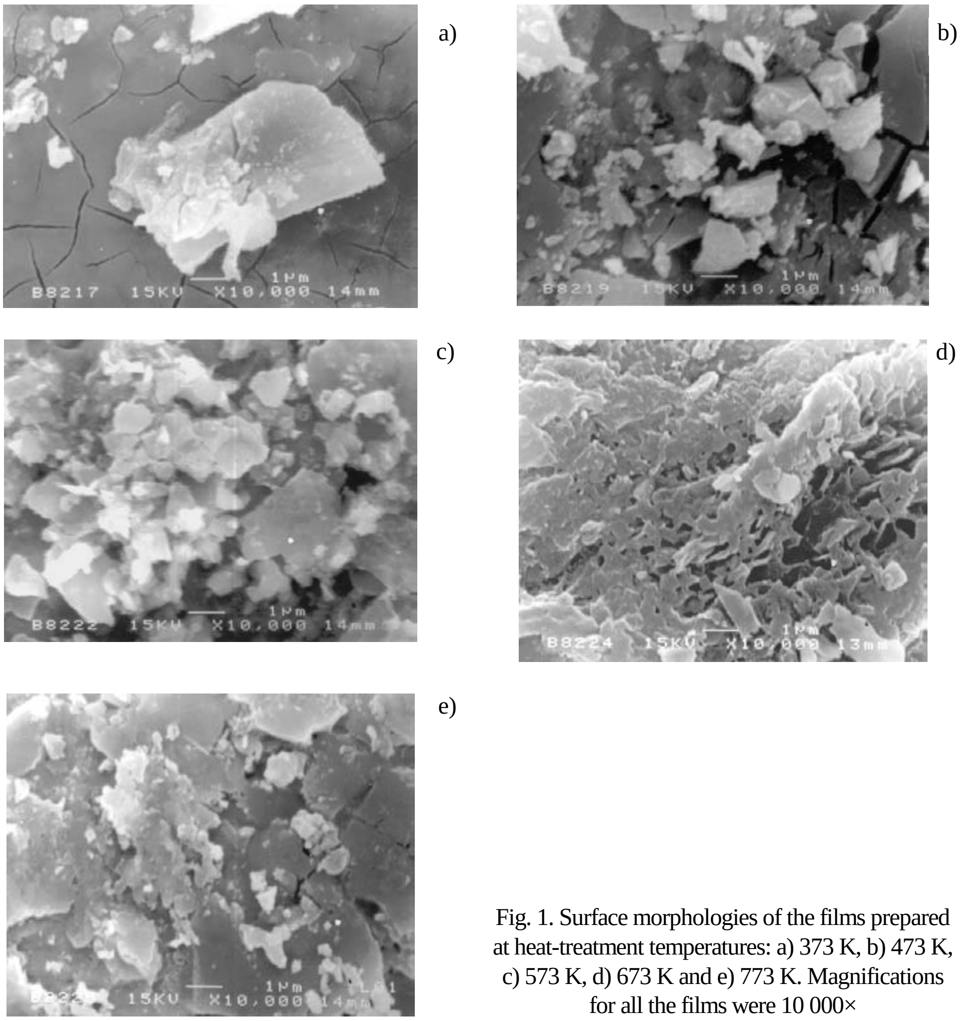

Fig. 1. Surface morphologies of the films prepared at heat-treatment temperatures: a) 373 K, b) 473 K, c) 573 K, d) 673 K and e) 773 K. Magnifications for all the films were 10 000×

3.2. X-ray Diffraction measurements

XRD data for films heat-treated at various temperatures are shown in Fig. 2. Apart from substrate (Ti) peaks, no other peaks were obtained at 573 K and below. Even though the intensity of the sample peaks is rather weak due to the nature of the thin films, the peaks belonging to TiO_2 existed when the samples were heated at 673 K and higher temperatures. The typical peak at d = 3.52 Å, which corresponds to the (101) plane of anatase TiO_2, was detected for samples heated at 673 K and 773 K. Heat treatment at 773 K improved film crystallinity and resulted in the appearance of another peak at d = 3.25 Å, which corresponds to the (110) plane of rutile TiO_2.

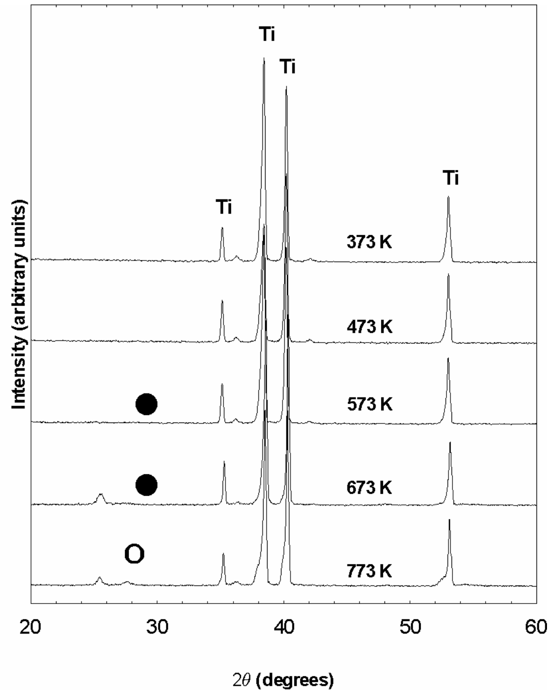

Fig. 2. The XRD pattern of films heat-treated at temperature of 373 K to 773 K (● = Anatase, ○ = Rutile, Ti = Titanium)

3.3. Effect of heat treatment

The photocurrent behaviour of the heat-treated samples was investigated by irradiation with a halogen and near-UV lamp. The photocurrents are dependent on the heat treatment temperature, as shown in Fig. 3a and b. Very strong photocurrents were observed for the electrode heated at 773 K as compared to the samples heated at 673 K and below. This indicates that more photoactive samples were obtained by heat-treating.

The photocurrent of thin-film electrodes is affected by several factors, including crystallinity, film resistance and electrode area [16]. It seems that the crystallinity contributes significantly to the photocurrent efficiency. X-ray diffraction results show that TiO_2 signals were only detected after the films were heat-treated at 673 K. The sample heated at 773 K which showed the presence of the anatase and rutile phases was found to be more photoactive compared to the sample heated at 673 K, which contained the anatase phase only.

Increase of the photocurrent may be due to a decrease in the film resistance. If the bulk resistance is too high, the quantum efficiency will become lower due to a decrease of the electrical gradient across the depletion and thin space charge layer [16, 17]. When a higher temperature was applied, a strong adhesion between the film and substrate was achieved, successfully reducing the bulk resistance. The reduction of Ti^{4+} to Ti^{3+} in the film by decomposed organic matter or unburned free carbons during the heating process is also believed to contribute to the decrease of film resistance. The presence of Ti^{3+} ions would dominate both the photoelectrochemical reaction at the surface and bulk electrical conductivity by forming donor levels in the conduction band of TiO_2 [16, 18].

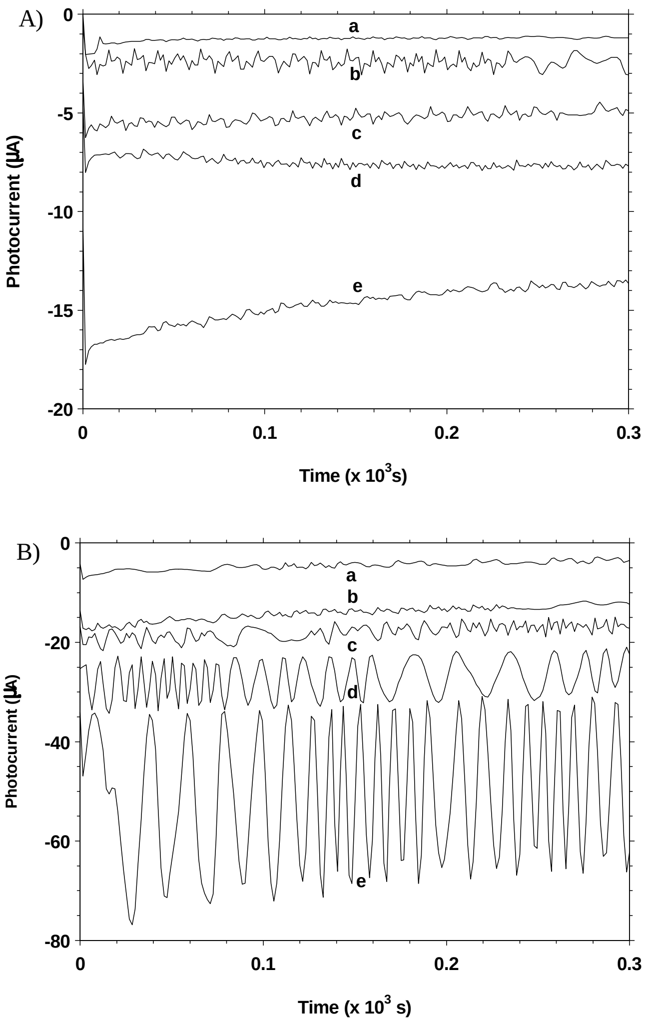

Fig. 3. Comparison of the photocurrent values for electrodes prepared at different heat-treatment temperatures under illumination of halogen lamp (A) and UV lamp (B): a) 373 K, b) 473 K, c) 573 K, d) 673 K and e) 773 K, potential fixed at 0.8 V

The results presented in Fig. 3 also compare the efficiency of generating the photocurrent with halogen and UV lamp sources. The value of photocurrent for films illuminated with the UV lamp is much higher than that observed for the halogen lamp. Light from the halogen lamp is less efficient in promoting charge carrier activity in the films compared to UV light. This is related with the number of photons with the energy exceeding the band gap energy of TiO_2 ($E_g > 3.2$ eV) for each light source. Light from the near UV lamp contains more of these, and thus can better excite TiO_2 [19]. Although UV lamps are appropriate light sources for activating TiO_2 films, other light sources such as halogen lamps should also be considered to avoid the hazardous effects of UV radiation.

3.4. Effect of potential applied

The effect of the applied bias potential on the behaviour of electrodes heat treated at 773 K is shown in Fig. 4. Photocurrent values were obtained by measuring the difference between the current under illumination (I_p) and without illumination (I_d). The results show that the photocurrent increases with the applied potential when the samples are illuminated with a UV lamp.

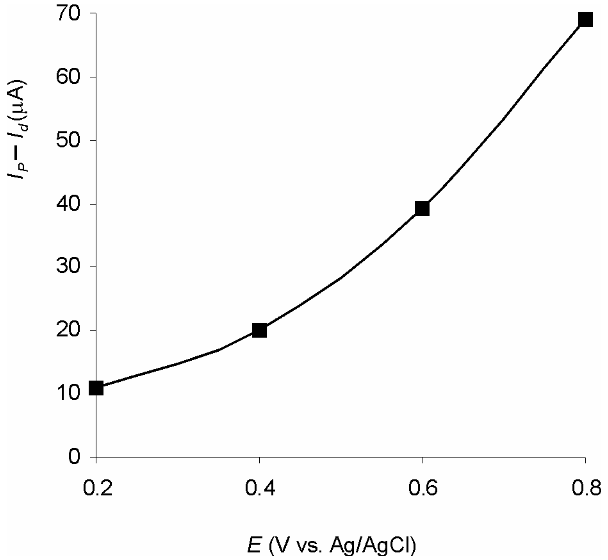

Fig. 4. Comparison of the photocurrent values of the films at potentials of 0.2–0.8 V under UV illumination

The photoactivity of the film increased when a higher potential was applied. This is because application of the anodic bias provides a potential gradient within the film, which drives the photogenerated holes and electrons in different directions [20, 21]. This can reduce the charge recombination of electrons and holes, stimulating the photooxidation process. Here, we propose the following mechanism for the photocatalytic oxidation of sodium oxalate in this electrochemical system.

In solution:

$$Na_2C_2O_4 \rightarrow 2Na^+ + C_2O_4^{2-} \tag{1}$$

At the working electrode:

$$TiO_2/Ti + h\nu \rightarrow TiO_2/Ti\left(e_{cb}^- ... h_{vb}^-\right) \tag{2}$$

$$(h^+)_{surf} + H_2O \rightarrow OH^\bullet + H^+ \tag{3}$$

$$(h^+)_{surf} + C_2O_4^{2-} \rightarrow C_2O_4^- \tag{4}$$

$$OH^\bullet + C_2O_4^- \rightarrow HCO_3^- + CO_2 \tag{5}$$

$$(h^+)_{surf} + HCO_3^- \rightarrow CO_2 + OH^- \tag{6}$$

$$TiO_2/Ti\left(e_{cb}^- ... h_{vb}^-\right) \rightarrow TiO_2/Ti + \text{heat} \tag{7}$$

At the counter electrode:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{8}$$

Equation (1) shows the homogenous dissociation process of oxalate in water. The electron–hole recombination step (Eq. (8)) was suppressed by electron drive from the TiO_2 thin film electrode to the counter electrode (Eq. (7)). In consequence, more reactive holes are made available for the photooxidation of oxalate.

3.5. Effect of the number of dip-coatings

The photocurrent behaviour of the samples under UV lamp illumination with different numbers of dip-coated layers is shown in Fig. 5. The maximum number of layers was 7, because the catalyst began to peel off from the substrate after heat-treating of samples with a larger number of layers. As shown in Fig. 5, the photocurrent increased with the number of layers and reached 20 μA for 7 layers. This result suggests that the photocurrent strongly depends on the thickness of the film. An increase of thickness provides more active sites for the oxidation of oxalate.

In addition, the film thickness greatly affected the effectiveness of the bias potential applied to the film. This is due to the creation of the space-charge region as a region of potential variation, which makes electron movement in semiconductors easier. When the thickness of the film is low (e.g., only 1 layer), the density of carriers in the film is not large enough to generate a high electrical field at the space charge region,

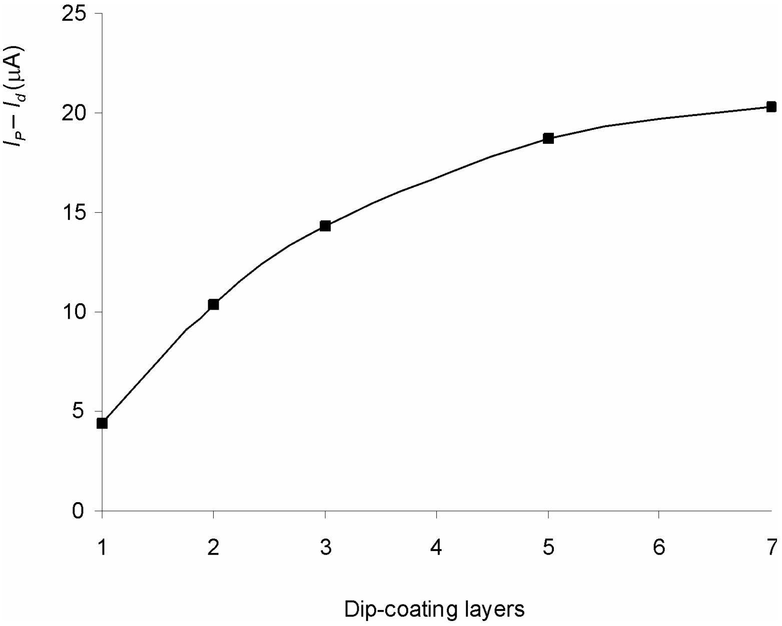

Fig. 5. The photocurrent values of the electrodes prepared with different number of dip-coating layers. Potential was fixed at 0.4 V and the illumination source is UV lamp

which results in a low photocurrent [17]. Contrary to this, an increase of the carrier density with the increase in film thickness would generate a high electrical field in the space charge layer. The photocurrent almost reaches saturation for films coated 5 and 7 times. This limitation could be overcome by applying higher light intensities and higher bias potentials.

3.6. Percentage of oxalate ions oxidised

The efficiency of oxalate oxidising during 5 min was studied under the illumination of a UV lamp using electrodes heat-treated at different temperatures. The efficiency of oxalate oxidation was calculated based on the total amount of charge produced during the experiment. The oxidation of an oxalate ion $C_2O_4^{2-}$ producing CO_2 gas is a well known two-electron process. The photocatalytic oxidation of oxalate is not complicated by the production of an intermediate species [9]. The oxidation process is:

$$^{-}OOC–COO^{-} \rightarrow 2CO_2 + 2e^{-} \quad (9)$$

Table 1 shows that the amount of oxalate ions oxidized increases with the electrode heat-treatment temperature.

Table 1. The percentage of oxalate ions oxidised during 5 min under irradiation of UV lamp on heat-treated electrodes

Light source	Heating temperature/K	Amount of charge/C	Amount of oxalate oxidised/μmol	Oxidised percentage/%
UV lamp	373	1.423	7.37	0.92
	473	4.420	22.90	2.86
	573	5.625	29.15	3.64
	673	8.554	44.32	5.54
	773	15.970	82.75	10.32

3.7. Band-gap study

The UV-Vis spectrum was obtained from TiO_2 deposited on ITO glass, which was heat-treated at 737 K. Data obtained from the optical absorbance vs. wavelength were introduced into the following relationship for near-edge absorption:

$$A = \frac{k\,(hv - E_g)^{n/2}}{hv}$$

where v is frequency, h is the Planck constant, k is a constant, while n has the value of either 1 or 4. The bandgap energy E_g could be obtained from a straight line plot of $(Ahv)^{2/n}$ as a function of hv. An extrapolation of the value of $(Ahv)^{2/n}$ to zero gives E_g. A straight line obtained for $n = 1$ indicates a direct electron transition between the states of the semiconductor. The transition is indirect if a straight line is obtained for $n = 4$.

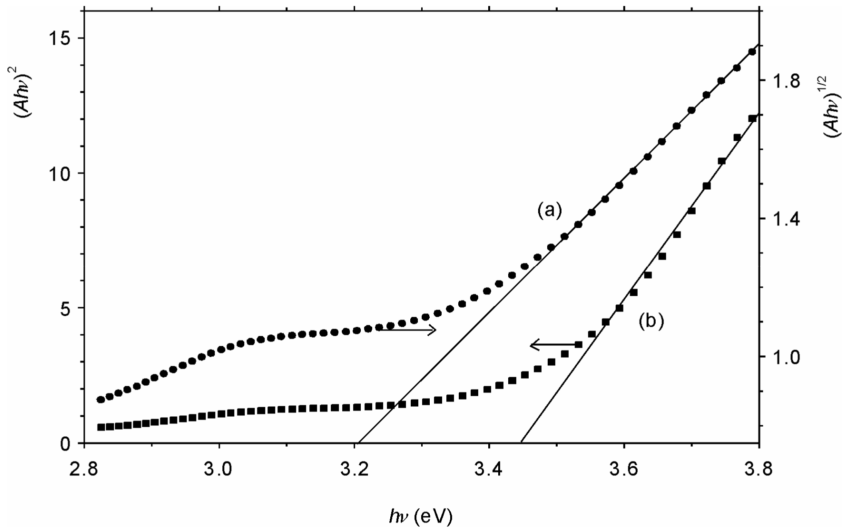

Fig. 6. Plot of $(Ahv)^{2/n}$ vs. hv for the film prepared at temperature of 773 K with: a) $n = 4$, b) $n = 1$

As is seen in Fig. 6, the data plotted in coordinates expected of direct and indirect transitions yielded bandgap values of 3.45 and 3.21 eV, respectively. The linear relationship is better fitted for the indirect than direct transition. Therefore, it could be concluded that the indirect transition model is more appropriate. Similar results were also reported elsewhere [17, 22].

4. Conclusions

The results showed that the photoelectrochemical properties of TiO_2 thin film electrodes prepared by sol-gel dip-coating depend on heat-treatment temperature, on the number of dip-coated layers and on the potential applied. The largest photocurrent was achieved for films heat-treated at a temperature of 773 K. Higher percentages of oxalate oxidation were achieved when using such films with UV lamp illumination. These results indicate the significance of electrode preparation and the light source for the generation of the photocurrent. The film heat-treated at 773 K was found to be better fitted by an indirect optical transition, with bandgap energy of 3.21 eV.

Acknowledgements

We gratefully acknowledge the financial support from the Malaysian Government through the IRPA programme no: 09-02-04-0255-EA001 and 09-02-04-0369-EA001.

References

[1] WANG H., ADESINA A.A., Appl. Catal. B: Environ., 14 (1997), 241.
[2] BANGUN J., ADESINA A.A., Appl. Catal. A: General., 175 (1997), 221.
[3] OLLIS D.F., PELIZZETTI E., SERPONE N., Environ. Sci. Technol., 25 (1991), 1523.
[4] PELIZZETTI E., SERPONE N. (Eds), *Photocatalyst: Fundamental and Applications*, Wiley, New York, 1991.
[5] PAREEK V., BRUNGS M.P., ADESINA A.A., Adv. Env. Res., 7 (2002), 411.
[6] HOFFMAN M.R., MARTIN S.T., CHOI W.Y., BAHNEMANN D.W., Chem. Rev., 95 (1995), 69.
[7] NEPPOLIAN B., CHOI H.C., SAKTHIVEL S., ARABINDOO B., MURUGESAN V., J. Hazardous Materials, B89 (2002), 303.
[8] LEA J., ADESINA A.A., Chem. Eng. Sci., 54 (1999), 2209.
[9] BRYNE J.A., EGGINS B.R., J. Electroanal. Chem., 457 (1998), 61.
[10] BRYNE J.A., EGGINS B.R., BROWN N.M.D., MCKINNEY B., ROUSE M., Appl. Catal. B: Environ., 17 (1998), 25.
[11] LI X.Z., LI F.B., FAN C.M., SUN Y.P., Water. Res., 36 (2002), 2215.
[12] HIDAKA H., SHIMURA T., AJISAKA K., HORIKOSHI S., ZHAO J., SERPONE N., J. Photochem. Photobiol. A: Chem., 109 (1997), 165.
[13] VINODGOPAL K., KAMAT P.V., Sol. Energy Mater. Sol. Cells, 38 (1995), 401.
[14] ULRICH D.R., Chemtech (1988) April 242.
[15] COLOMER M.T., JURADO J.R., Chem. Materials, 12 (2000), 923.
[16] YOKO T., YUASA A., KAMIYA K., SAKKA. S., J. Electrochem. Soc., 138 (1991), 2279.
[17] YOKO T., HU L., KOZUKA H., SAKKA S., Thin Solid Films, 283 (1996), 188.

[18] MIZUSHIMA K., TANAKA M., ASAI A., IIDA S., GOODENOUGH J.B., J. Phys. Chem. Solids, 40 (1979), 1129.
[19] MIKULA M., BLEACHA J., CEPPAN M., J. Electrochem. Soc., 139 (1992), 3470.
[20] VINODGOPAL K., HOTCHANDANI S., KAMAT P.V., J. Phys. Chem., 97 (1993), 9040.
[21] VINODGOPAL K., STAFFORD U., GRAY K.A., KAMAT P.V., J. Phys. Chem., 98 (1994), 6797.
[22] POZNYAK S.K., TALAPIN D.V., KULAK, A.I., J. Phys. Chem. B, 105 (2001), 4816.

Received 25 February 2004
Revised 16 April 2004