

Effects of poly-ethylene glycol (PEG) template on structural and optical properties of nanocrystalline titanium dioxide (TiO₂) films

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Nanocrystalline TiO₂ films have been deposited onto glass slides by spin-coating technique using titanium chloride (TiCl₃) with content variation of poly-ethylene glycol (PEG) addition as a template. Precursors were prepared from 20 mL TiCl₃ solution with varied content of PEG addition (0.01 g, 0.1 g, and 1 g). Results of XRD analysis shows a transformation of crystal phase of TiO₂ with respect to PEG content. The film with 0.01 g PEG has a rutile phase, whereas the films with 0.1 g and 1 g PEG have an anatase phase. The SEM photographs show a highly porous of nanocrystalline TiO₂ films. Optical properties of TiO₂ films depend on the content of PEG. UV-Vis absorbance spectra show that the films have an absorption band within UV region with absorption edge shorter than 360 nm corresponding to wide optical bandgap of TiO₂. Optical bandgap of TiO₂ films were determined by using a plot of $(h\nu)^2$ vs. $h\nu$ based on absorbance spectra, that give a direct bandgap of 3.4 eV for rutile and 3.6 eV for anatase.

Key words: Porous, Nanocrystalline TiO₂, PEG template, Optical bandgap.

Introduction

TiO₂ is well known as a transition-metal oxide semiconductor that has been employed in many technical applications because of its unique physical, chemical and optical properties [1]. TiO₂ have three structure phases, e.g. anatase, rutile, and brookite. TiO₂ is a semiconductor material in *n*-type with optical bandgap of 3.2 eV for anatase and 3.0 eV for rutile phase, which allows the oxide to absorb lights with wavelengths shorter than 385 nm [2]. Therefore, TiO₂ have a most applicable in photocatalytic detoxification and disinfection of water and other environmental applications [3, 4].

In thin film form, TiO₂ have been studied most extensively for various electrical and optical applications and have attracted considerable attention in many application oriented fields like photoelectrocatalysis, gas sensor, optoelectronics devices and ceramic membranes [5, 6]. TiO₂ films can be directly synthesized by a wide variety of techniques such as chemical vapor deposition [7]), physical vapor deposition [8], pyrolysis [9, 10], electrodeposition [11], chemical deposition [12], and sol-gel processing [13–16].

On the other hand, porous TiO₂ films with large specific surface area are expected to have wide applications for optical cells, solar energy conversion and high efficient photocatalysts [17]. Nanocrystalline-

nanoporous TiO₂ thin films have been constructed for a high efficiency solar cell with dye sensitizer as electron donor, known as dye sensitized nanocrystalline solar cell. Porous TiO₂ films most applicable for photoelectrodes in a dye sensitized nanocrystalline solar cell, due to it have a more large active area for dye adsorption in TiO₂ particle surface to enhance photon absorption [18–20]. A large number of techniques have been used to prepare porous TiO₂ films, such as sol-gel method [13–15], direct deposition from aqueous solution [12] and spray pyrolysis [9].

In this research, we fabricated porous nanocrystalline TiO₂ films on slide glass substrates by using spin-coating technique via sol-gel process with poly-ethylene glycol (PEG) addition as a template. In the method, porous TiO₂ films were prepared from TiCl₃ solution with varied content of PEG addition. The pore size of TiO₂ films is to be controlled by changing the PEG content in the precursor for spin-coating solution. Addition of PEG as a template to obtain a porous TiO₂ film has carried out by some researchers [1, 5, 17, 21], but no more used TiCl₃ as titanium source. The polymer addition to the solution is usually utilized to adjust the viscosity of the solution. The aim of this research is to study the effect of PEG addition on structure, morphology and optical properties of porous TiO₂ films prepared using TiCl₃ solution as precursor.

Experimental Procedure

Nanocrystalline TiO₂ films were prepared in the following way: 20 ml of TiCl₃ was dissolved in the 16.6 ml 2-propanol and 100 ml distilled water. To

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investigate the effect of PEG addition, into the precursor solution was added PEG (MW = 2000) in three content variation, that are 0.01 g, 0.1 g and 1 g. A white suspension was obtained. Three drops of nitric acid was added while stirring with magnetic stirrer for 3 hrs at 80 °C with strong stirring to remove organic solvent. TiO₂ films were prepared on the slide glass substrates by spin coating technique utilizing above sol precursor at speed of 3500 rpm for 15 second, this process was carried out for four times. The sample films were annealed in furnace at 400 °C for 1 hr.

X-ray diffraction analysis was employed to investigate the crystallinity of TiO₂ deposited on the glass substrates. This analysis was used to derive information about crystal phase and crystallite size of the films. The analysis were performed using Cu K α X-rays (wavelength: 0.154 nm) at 30 kV and 30 mA in the region of $2\theta = 20-50^\circ$. To investigate the surface morphology or microstructure, the TiO₂ films were observed by scanning electron microscopy (SEM). The SEM images can derive any information about granularity and porosity of the films. The films thickness is determined using a film micrometer. Optical properties of porous TiO₂ films were observed by using UV-Visible spectrophotometer. From the absorbance spectra, optical bandgap (E_g) of the films will be determined.

Results and Discussion

Fig. 1 shows the x-ray diffraction pattern of the TiO₂ films, which were prepared by spin coating on slide glass substrates with different content of PEG addition in the precursor. The XRD patterns of TiO₂ films show the presence of very broad peak that indicate the TiO₂ particles of very small crystalline size. Difference of PEG content in the precursor solution affects the crystal phase of the grown films. Fig. 1(a) shows a rutile phase of TiO₂ film prepared from precursor with 0.01 g PEG as identified from the most intense of diffraction peak at 27.4° corresponding to (110) diffraction plane. The other peaks appear at 35.5° corresponding to (101) plane and at 41° for (111) plane. There are no others phases appear in the film, so that the film can be concluded as single phase of rutile TiO₂. While both films which were prepared from precursor with 0.1 g and 1 g of PEG content exhibit a similar XRD pattern as given at Fig. 1b and 1c. The both films were identified as anatase phase of TiO₂ as indicated by the most intense of diffraction peak at 25.2° corresponding to anatase (101) plane. There are no others significant peaks appear in the diffraction pattern that indicate the films have a single phase of anatase. The films have a low crystallinity due to addition of PEG in the precursor.

It is well known that TiO₂ has three polymorph or crystal phase (anatase, rutile and brookite). Anatase phase can be transformed to other phase (rutile and

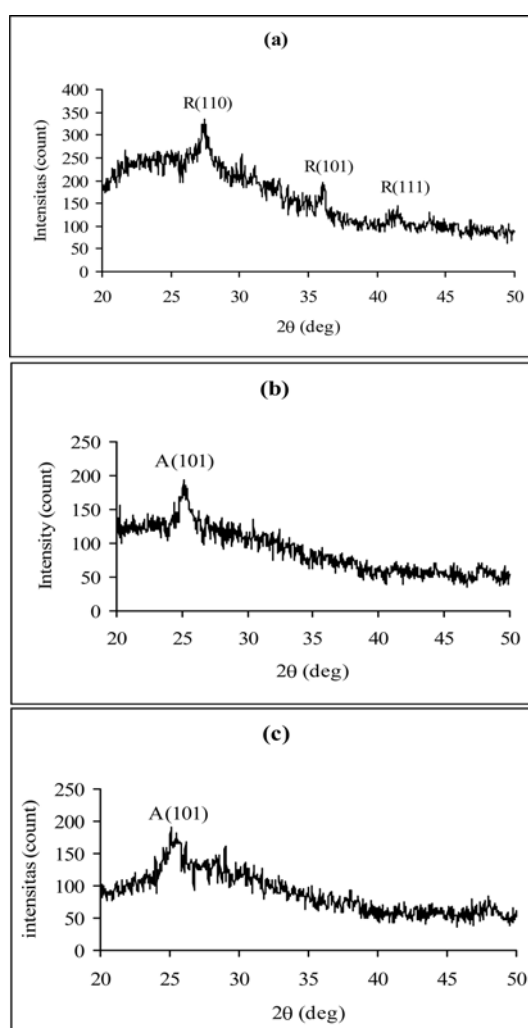


Fig. 1. X-ray diffraction patterns of TiO₂ films with (a) 0.01 g PEG, (b) 0.1 g PEG, (c) 1 g PEG.

brookite) via several manners including heat treatment at a relative higher temperature. In this research, it found that the template also affect the crystallinity and phase transformation of TiO₂ grown. All films are synthesized just in different amount of PEG in the precursor solution. TiO₂ which has a rutile phase was prepared from TiCl₃ with smallest PEG content. Increasing the amount of PEG addition resulted in anatase phase of TiO₂. It probably caused by the excess content of PEG to prevent the formation of rutile phase when the films heated at a relative high temperature (400 °C).

The broadening of XRD patterns indicate the TiO₂ particles of very small crystalline size. The crystallite size of the films were determined from broadening of XRD pattern of rutile [110] and anatase [101] peaks by using the Scherrer equation,

$$\sigma = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

where σ is the crystallite size, $\lambda = 1.5604 \text{ \AA}$ is the

wavelength of X-ray using Cu K α source, β , the full-width at half-maximum (FWHM) of the diffraction peak, and θ the diffraction angle.

The crystallite size calculated using Scherer equation was estimated smaller than 10 nm based on their FWHM value of all sample. The relative small of crystallite size indicate that the TiO₂ films grown on a glass substrate were nanostructures. Crystallite size of TiO₂ film with 0.01 g PEG calculated from intense rutile peak at 27.4° (110) gives a crystallite size of 2.1 nm. Increasing the PEG content in the solution will increase the crystallite size of TiO₂. TiO₂ Film with 0.1 g PEG have a crystallite size of 6.6 nm and sample with 1 g PEG gives a crystallite size of 3.9 nm calculated from anatase peak at 25.2° (101). Increasing the PEG content cause the particles have more space to expand after the PEG template vaporized when the films were heated at 400 °C for 1 hr. But the calculation results not show a linear relationship of crystallite size to PEG content.

Fig. 2 shows the surface morphology of the TiO₂ films on glass substrates by scanning electron microscopy (SEM). Highly porous nanostructures in the TiO₂ films, clearly seems on the surface micrograph. Formation of pores in the films due to evaporation of PEG when a heat treatment (calcination) of as prepared films at 400 °C for 1 hr. Therefore, PEG in the inorganic/PEG composites acts as a template to form the porous films. The grain or particle size of the TiO₂ could not be determined clearly, because the TiO₂ particles were interconnected inside the film, especially for TiO₂ film smallest PEG content in the precursor.

The porosity of the films and interconnectivity of TiO₂ particles prepared from the TiCl₃ precursor solution strongly depend on the content of PEG added into the precursor. Fig. 2 show that the porosity of the films changes with the PEG content in the precursor. The size and density of the pores increase with an increase of PEG content. On the other hand, interconnectivity of the TiO₂ particles decrease with an increase of PEG content in the precursor, which the best interconnectivity in TiO₂ film with a smallest content of PEG. In the TiO₂ film containing largest content of PEG not seems clearly interconnection between TiO₂ particles. These results indicate that the morphology of the TiO₂ films depend on the composition of precursor solution, primarily on the PEG content. It can be observed that an increase of PEG content in the precursor solution cause an increase of total volume of pores of the nanostructures TiO₂ films. High porous and interconnectivity resulted in a large active surface area of TiO₂ particles that mostly needs for a high efficient dye-sensitized solar cell and photocatalysis [18, 19].

Study of optical properties of a semiconductor thin film is fundamentally based on absorbance (A), transmittance (T) and reflectance (R) data that obtained from UV-Visible spectrophotometer. Absorbance or transmittance spectra

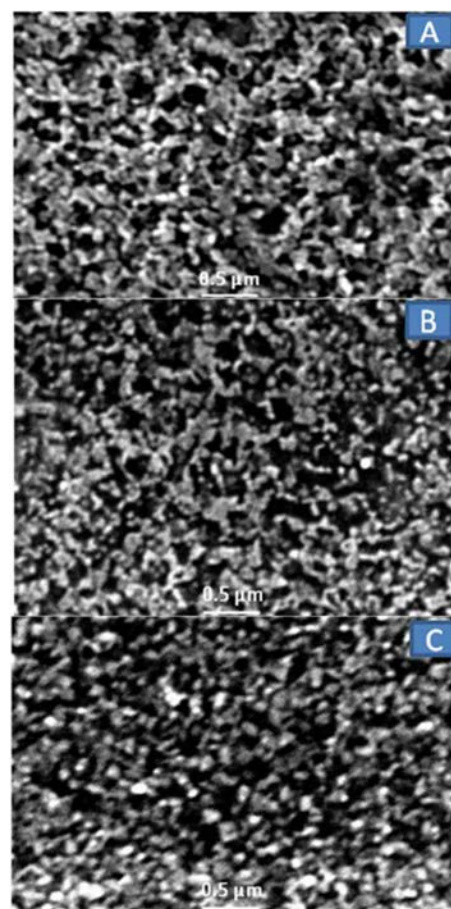


Fig. 2. SEM images of porous TiO₂ films; (a) 0.01 g PEG, (b) 0.1 g PEG, (c) 1 g PEG.

give any optical characteristics of the semiconductor thin films, including their optical bandgap.

Fig. 3 shows the absorbance spectra of TiO₂ films in the wavelength range of 280-600 nm. There are no significant distinctions of the absorbance spectra between each film. The films strongly absorb UV range of electromagnetic spectrum corresponding to wide optical bandgap of TiO₂ films. TiO₂ film with 1 g PEG in the precursor shows more high absorption intensity in the UV region than others due to its thicker film (19 μm) than the others, where the film with 0.1 g PEG is 7 μm thickness and film with 0.01 g PEG is 4 μm thickness.

Determination of optical bandgap (E_g) is often necessary to develop the electronic band structure of a thin film of semiconductor material. Optical bandgap of a semiconductor thin film can be directly founded from absorbance spectra. For the high absorption region, absorption coefficient (α) of semiconductor materials can be expressed as follows [13];

$$\alpha = \frac{2.3026A}{d} \quad (2)$$

where A is absorbance (arbitrary unit) and d is thickness of the semiconductor film. Relation between

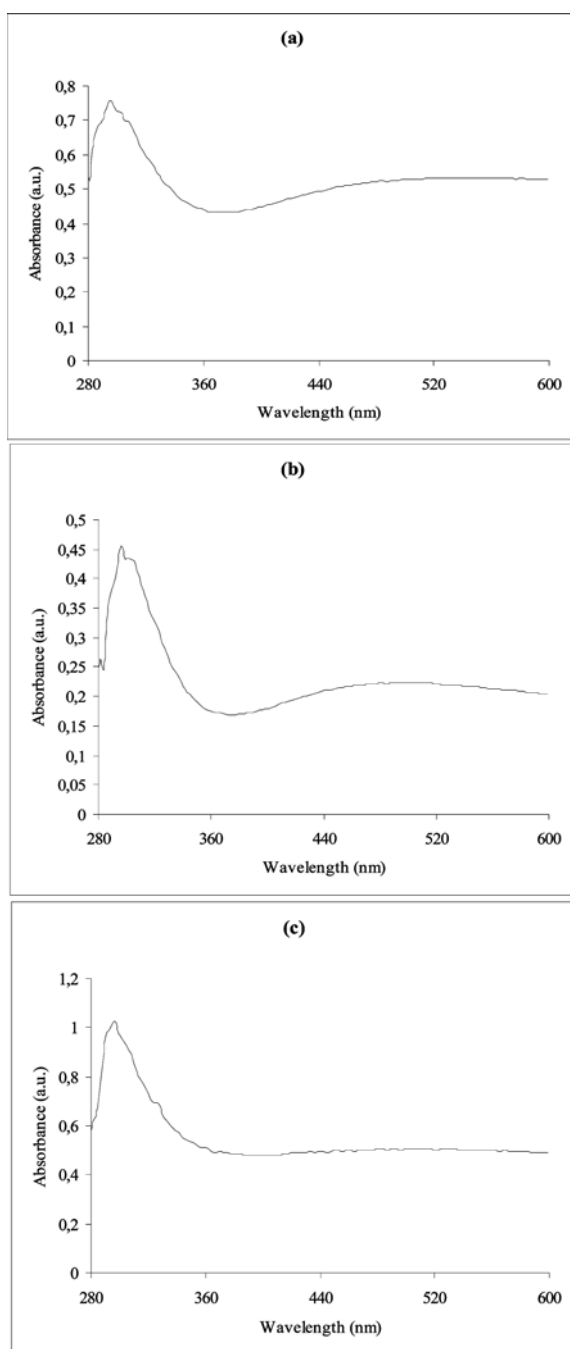


Fig. 3. Absorbance spectra of the porous TiO₂ films, 0.01 g PEG, (b) 0.1 g PEG, (c) 1 g PEG.

absorption coefficient (α) and incident photon energy ($h\nu$) can be written as follows (for direct transition) [13]

$$(\alpha h\nu) = C(h\nu - E_g) \quad (3)$$

where C is a constant and E_g is the optical bandgap of thin films. To determine the E_g value of the semiconductor films, we have to make a plot of $(\alpha h\nu)^2$ vs. $h\nu$ based on the absorbance data of the films, that well known as Tauc plot. The E_g value is determined

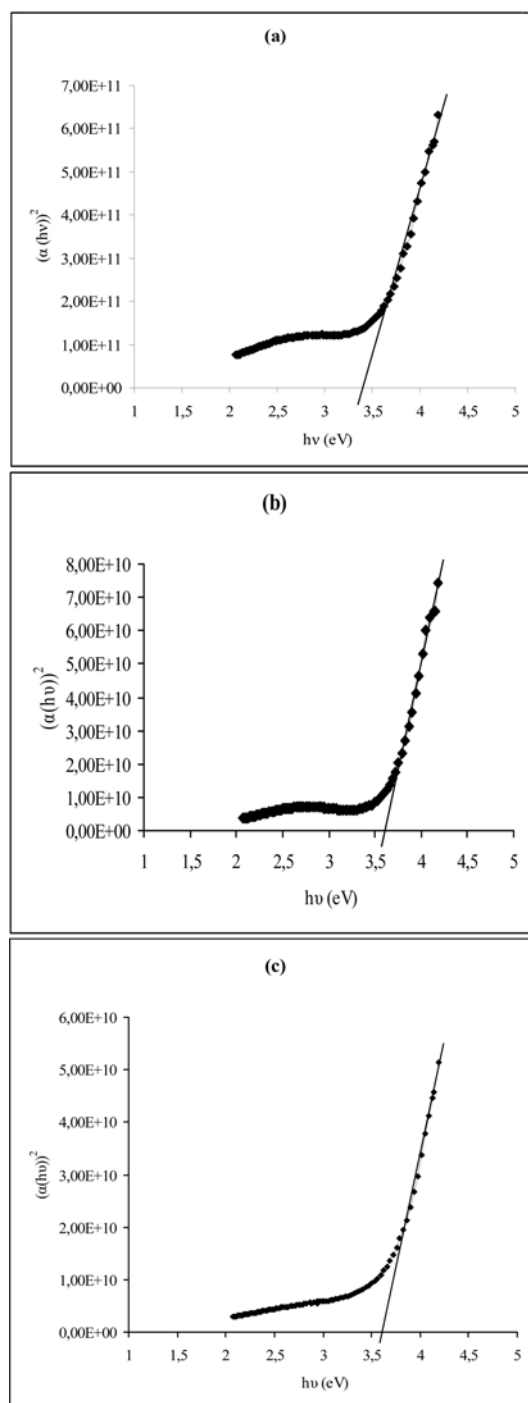


Fig. 4. $(\alpha h\nu)^2$ vs. $(h\nu)$ plots for E_g value of TiO₂ film with (a) 0.01 g PEG, (b) 0.1 g PEG, (c) 1 g PEG.

from interception of extrapolated linear region of curve to $h\nu$ axis.

Fig. 4 show a plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for each film prepared with different PEG content in the precursor solution. The plot curves show two specific regions with a step that notify an optical transition corresponding to absorption edge. The linear regions of the curves were extrapolated, where interception of the line with energy ($h\nu$) axis gives an optical bandgap (E_g) value of the each

film. Fig. 4(a) shows a bandgap of 3.4 eV for the sample prepared with 0.01 g PEG content in the precursor, which be a rutile phase regarding to XRD analysis. This value mostly larger than the bulk rutile film for direct transition, it is about of 3.0 eV [2]. Figs. 4(b) and 4(c) show a same optical bandgap for anatase phase of TiO_2 , it about of 3.6 eV. These bandgap values also higher than the bulk anatase films, it about 3.2 eV for direct transition [2, 6]. A relative large optical bandgap of all films compared to bulk one was sure due to small crystallite size of TiO_2 particles in several nanometer sizes, as calculated using Scherrer equation.

A low crystallinity of the films indicated by broadening of x-ray diffraction peaks due to PEG addition in the precursor, also affects to a relative large optical bandgap of TiO_2 films. Addition of PEG template into the precursor resulted in considerable defect levels inside the band gap make optical absorption of porous films so broad. Broadening the absorption spectrum of the films was caused by formation of defect levels inside the film structures that also cause slightly larger optical band gap. PEG content most affects to the optical properties of the films, attributed to the formation of porous structure in the films when the film prepared.

Conclusions

Porous nanocrystalline TiO_2 films could be prepared on glass substrates by spin coating using suspension precursor from TiCl_3 solution with PEG addition as a template. XRD analysis shows a transformation of crystal phase as PEG addition, the sample with addition of 0.01 g PEG has a rutile phase, whereas the samples with addition of 0.1 g and 1 g PEG have an anatase phase. The SEM photographs show highly porous nanocrystalline TiO_2 films varied to PEG content. The size and density of the pores increased with an increase of PEG content. Interconnectivity of the nano- TiO_2 particles decreased with an increase of PEG content. Optical properties of porous TiO_2 films also highly depend on the amount of PEG. Broadening the optical

absorption was caused by formation of defect levels inside the film structures that also caused slightly larger optical band gap. Optical bandgap (E_g) is determined from the absorbance spectra by using a plot of $(\alpha h\nu)^2$ vs. $(h\nu)$, that give an direct bandgap value (E_g) of 3.4 eV for rutile phase and 3.6 eV for anatase phase.

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