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## Fabrication and characterisation of titania nanoporous thin film for photoelectrochemical (PEC) conversion of water

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### Abstract

In this paper, nanoporous titania thin films for PEC conversion of water were dip coated by using acetic acid as a stabiliser and poly(ethylene glycol) (PEG) as a pore former. The evolution of microstructure and morphology of the thin films at different conditions was investigated by XRD, SEM and AFM. Anatase was the primary crystalline phase of the as-obtained titania nanoporous thin film after heat treatment at 500°C/2h. A small amount of PEG, a low ratio of acetic acid/Titania butoxide (HoAC/TBOT) and a relatively low withdrawal speed facilitate the formation of TiO<sub>2</sub> nanoporous thin films with a homogeneous distributed nanostructure.

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*Key words* Titania, nanoporous, thin film, Sol-gel, photoelectrochemical conversion

### Introduction

Titania nanoporous thin films, as a fundament of potential applications in photoelectronic optical devices, dye sensitized solar cells, photocatalysts and biomaterials [1-4], have attracted considerable attention. In order to realise stable PEC conversion of water, we must have an appropriate band gap to utilise the majority of the solar spectrum, satisfactory quantum yield (photon-to-current efficiency), high transparency for incident light of the semiconductor layer. Moreover, the band edges of the

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semiconducting material must be compatible with the electrochemical potentials of the  $O_2$  and  $H_2$  evolution reactions. There must be sufficient conductivity and catalytic activity towards the gas producing reaction, and materials must be stable in contact with the electrolyte under solar irradiation. Typical photo-anodes for water splitting are metal oxide semiconductors e.g.,  $TiO_2$ ,  $WO_3$ , or  $\alpha-Fe_2O_3$ . Up to now,  $TiO_2$  thin film is still a promising candidate for photo-anode because of its low cost, chemical and physical stability and environment friendly features.

In order to obtain  $TiO_2$  thin film with high specific surface area of, different methods such as wet-chemical, sol-gel method and sol-polymer methods [8] have been used. Among the above methods, the sol-gel technique is one of the most promising methods, enabling preparation of materials at low temperature. Titania sols obtained by hydrolysing acetic acid or acetyl acetone stabilised titanium alkoxides are the most frequently used precursors for the titania thin film through sol-gel processing. The titania films can be prepared by immersing different substrates using dip-coating as well as spin coating method. Commonly used substrates for titania thin films are silica, alumina and silicon wafers [9-11]. Subsequent heat treatment is then carried out to remove the organic content from the species of titanium or the precursors to obtain crystalline phases.

Recently, titania porous films were realised by a sol-gel dip-coating method from a titanium tetraisopropoxide solution that contains poly(ethylene glycol) (PEG) [12]. The morphology of sol-gel-derived titania films can be catalogued as smooth and porous, depending on different experimental conditions. The morphology of nanoporous  $TiO_2$  thin films was controlled by varying the content and the molecular weight of PEG, the withdrawal speed, and the temperature of the dip coating solutions.

In order to realise the PEC conversion of water, nanoporous titania thin films were prepared by dip coating via sol-gel process in this paper. The evolution of microstructures of the thin film at different conditions was investigated by SEM and AFM.

## Experimental procedure

**Cleaning process** Prior to the dip coating process, the stainless steel plates were cleaned in acetone (5 min), distilled water (3 min), 0.1 M  $H_2SO_4$  (30 min), distilled water (3 min), and in 70°C washing liquid (20 g  $K_2Cr_2O_7$ + 40 ml  $H_2O$  + 350ml  $H_2SO_4$ ) (30 min), respectively. Subsequently, the plates were washed in distilled water (3 min), followed by drying at 80°C in an oven in air atmosphere. After being cleaned, the metal plates were immersed in different precursors (listed in Table 1) for several seconds. In order to compare the selection of different substrates on the surface morphologies of titania thin film, aluminium and silicon substrates were also used in the work after cleaning.

**Preparation of nanoporous  $TiO_2$  thin film.** In this experiment, the preparation of samples followed the method of Kajihara [12]. Titania butoxide (TBOT, Aldrich, Spain) was used as titanium resource, while PEG aqueous solution (Mw = 400 g/mol, Aldrich, Spain) was employed. Initially, titania butoxide was dissolved in absolute alcohol (Aldrich, Spain) and a small amount (0.0075 mol) of distilled water, followed by adding HoAC with vigorously stirring. After the stable sol was obtained, 0.5 to 2.0 g PEG and different amounts of HoAC (listed in Table 1) were added to the mixture and kept at 25°C at which the dip coating was performed. Different withdrawal speeds were chosen in the range from 0.64 to 3.31 mm/s. The as-prepared thin films were heat-treated at 500°C in air for 2 h.

**Characterisation techniques.** The sol after gelation was milled as powders for DTA/TG tests which were performed by thermogravimetry (SETARAM, Labsys<sup>TM</sup> TG-DTA16, France). The morphologies were examined by SEM (S-4100, Hitachi, Tokyo, Japan). The crystalline phase of the thin film was determined by XRD (D/MAX-C, Rigaku) and surface topography as well as thickness of nanoporous  $TiO_2$  thin films was observed by AFM (AFM, Digital – Instrument, Nanoscope III).

Table 1. Compositions of the precursors for dip coating

Compositions of the precursors					
H <sub>2</sub> O (mol)	Ti(C <sub>4</sub> H <sub>9</sub> O) <sub>4</sub> (mol)	EtOH (mol)	HoAC (mol)	PEG (g)	Withdrawal speed (mm/s)
0.0075	0.0075	0.25	0.0075	1.0	0.64
0.0075	0.0075	0.25	0.0075	1.0	1.19
0.0075	0.0075	0.25	0.0075	1.0	1.70
0.0075	0.0075	0.25	0.0075	1.0	3.31
0.0075	0.0075	0.25	0.0075	0.5	0.64
0.0075	0.0075	0.25	0.0075	1.0	0.64
0.0075	0.0075	0.25	0.0075	1.5	0.64
0.0075	0.0075	0.25	0.0075	2.0	0.64
0.0075	0.0075	0.25	0.0075	0.5	0.64
0.0075	0.0075	0.25	0.015	0.5	0.64
0.0075	0.0075	0.25	0.0375	0.5	0.64

## Results and Discussion

### Crystalline phase of the thin films and DTA/TG.

Fig. 1 presents the DTA/TG curve of the gelled powders containing 0.5 g PEG. It could be observed from DTA curve that there were three peaks during the heat treatment process. One endothermic peak around 100°C corresponded to evaporation of the physically adsorbed water, while the other two exothermic peaks were attributed to the burn out of organics (around 350°C) and the formation of anatase crystalline (around 400°C), respectively. Meanwhile, the weight loss of the sample became stable after 400°C as shown in TG curve. A heat treatment of 500°C for 2 h was therefore selected in this work to obtain TiO<sub>2</sub> thin film.

The crystalline phases in the metal plate and in the thin film containing 0.5 g PEG heat-treated at 500°C for 2 h were determined by XRD, which was showed in a previous work [13], in which the stronger peaks belong to the metallic substrate plate and the weaker one to the anatase phase. The predominance of the substrate peaks is due to the porous nature and relative thinner thickness of the films.

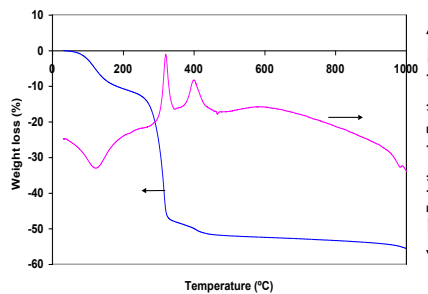


Figure 1. DTA/TG curve of the gelled powders containing 0.5 g PEG

**Morphologies of the thin films.** The preparation conditions, such as the amount of PEG and withdrawal speed, played significant roles in the morphologies of TiO<sub>2</sub> thin films, as shown in Figs. 2 and 3, respectively. It can be observed that at low PEG content (0.5 g), the morphology of titania thin films exhibits a homogenous distribution of fine pores. By further increasing the amount of stabilizer, the thin film became denser and the pores vanished in the presence of 1.0 g PEG (Fig. 2b). Increasing the PEG content to 1.5 g (Fig. 2c) resulted in macro-cracks, followed by an almost dense microstructure when the

amount of PEG is 2.0 g (Fig. 2d). Therefore, low PEG content promotes the formation of thin film with homogenous distributed pores.

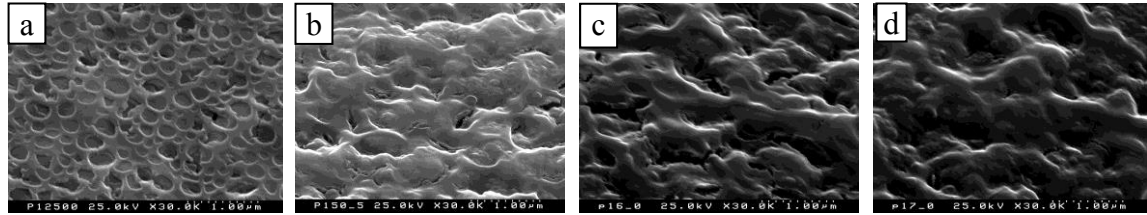


Figure 2. SEM morphology of the samples prepared with different amounts of PEG:  
(a) PEG=0.5 g, (b) PEG=1.0 g, (c) PEG=1.5 g, (d) PEG=2.0 g.

In addition, the morphology of nanoporous TiO<sub>2</sub> thin film is greatly dependent on the withdrawal speed as shown in Fig. 3. The morphology of titania films shows a homogeneous distribution of pore size and pore shape for a withdrawal speed of about 0.64 mm/s (Fig. 3a). With gradually increasing speeds, the pores became more irregular in shape and less well distributed (Figs. 3b, 3c), and almost disappeared at the higher withdrawal speed of 3.31 mm/s (Fig. 3d), where few pores were observed.

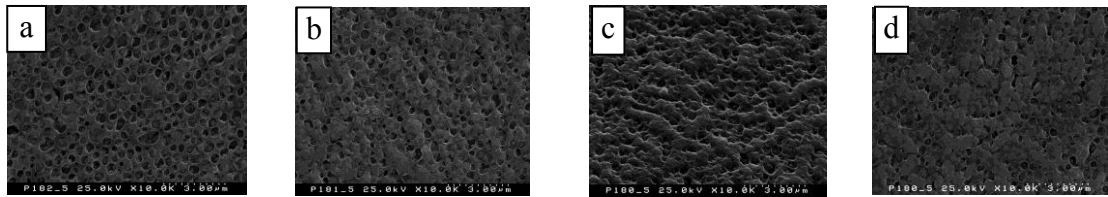


Figure 3. SEM morphology of the nanoporous TiO<sub>2</sub> thin film containing 1.0 g PEG at different withdrawal speeds: (a) 0.64 mm/s; (b) 1.19 mm/s; (c) 1.70 mm/s; (d) 3.31 mm/s.

Furthermore, the morphology of nanoporous TiO<sub>2</sub> thin film is also affected by the amount of HoAc as shown in Fig. 4. The morphology of titania films shows a homogeneous distribution of pore size and pore shape for samples with low amount of HoAc (Fig. 4a). As the amount gradually increased, fewer pores could be observed until the ratio of HoAc/TBOT reached 5:1 (Figs. 4b, 4c). In this case, the hydrolysis role originated from HoAc as catalyst suppressed the role of PEG as pore former. Therefore, no pores could be observed once the ratio was above 5:1.

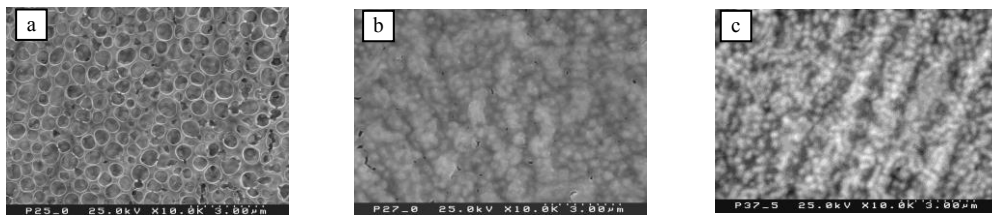


Figure 4. SEM morphology of the sample with different HoAc/HBOT ratios.  
(a). HoAc/TBOT=1:1; (b) HoAc/TBOT=2:1; (c) HoAc/TBOT=5:1

### Topography of the thin films

In order to compare the effect of different electrodes on the microstructure of obtained titania thin film, AFM topography of porous TiO<sub>2</sub> thin films containing 0.5 g PEG after heat treatment at 500°C/2 h onto different electrodes is showed in Fig. 5 (a) aluminium (b) the stainless steel and (c) silicon substrate.

Trace of pores could be observed when titania thin film was coated onto the surface of aluminium substrate (Fig. 5a), while obvious and homogenous distributed pores could be observed both on the stainless steel and silicon substrates (Fig. 5b and Fig. 5c). Furthermore, the microstructure of pores onto silicon substrate became more perfect due to its intrinsic surface feature. Further investigation will be performed in the future to select electrode for PEC conversion of water splitting.

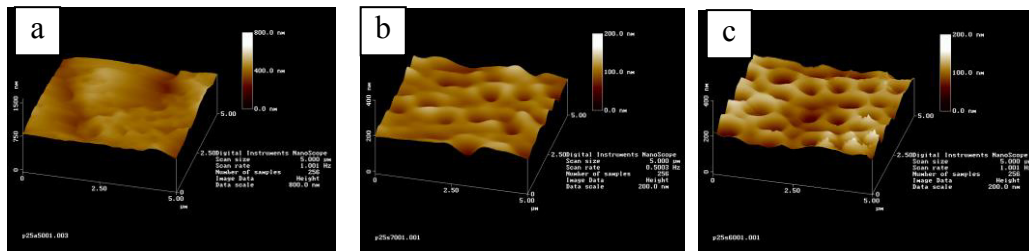


Figure 5. AFM topography of porous TiO<sub>2</sub> thin film containing 0.5 g PEG after heat treatment at 500°C/2 h on (a) aluminium, (b) the stainless steel and (c) silicon substrates

AFM morphological features of the cleaned stainless steel substrate before and after coating with TiO<sub>2</sub> thin film are presented in Fig. 6a and Fig. 6b, respectively. It could be observed that while the substrate surface presents a relatively flat topography, the deposited TiO<sub>2</sub> thin film containing 0.5 g PEG after 500°C/2 h exhibits homogeneously distributed pores along the entire coated area with mean pores diameters within the range of 300 to 500 nm.

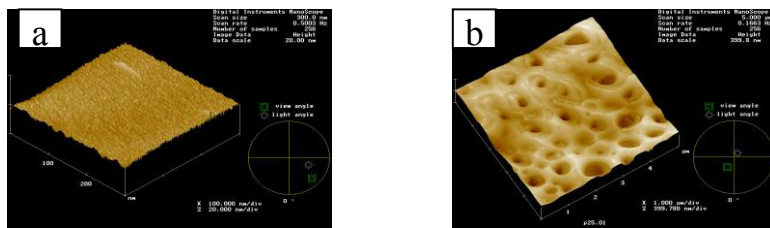


Figure 6. AFM topography of (a) the stainless steel substrate and (b) porous TiO<sub>2</sub> thin film containing 0.5 g PEG after 500°C/2 h

The thickness of the thin film was determined by section analysis via AFM. The morphology of the thin film from a precursor containing 0.5 g PEG (0.64 mm/s) with 10 layers heat-treated at 500°C is shown in Fig. 7 (cross section). The thin film thickness was measured to be approximately 30 nm.

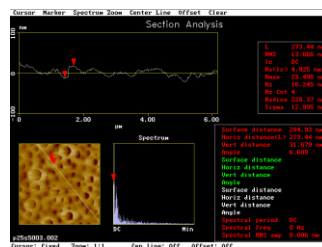


Figure 7. AFM section analysis of the monolayer of thin film containing 0.5 g PEG (0.64 mm/s)

## Conclusions

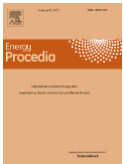
Nanoporous titania thin film were successfully prepared onto different substrates through sol gel method. Low PEG contents, low withdrawal speeds and low amount of HoAC promoted the formation of TiO<sub>2</sub> thin film with homogeneous distributed pores. The observed average pore size was about 300 to 500 nm and the thickness of thin film was about 30 nm. The obtained nanoporous titania thin film will be fundamental to be used as photo anode for PEC conversion of water splitting.

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## Biography

Dr. Sen Mei got his Ph.D of Material in University of Aveiro, Portugal on 2002. After that, he was an Alexander fellow in Germany before becoming a lead scientist at General Electric (GE). In 2007, he was employed as a research scientist in SINTEF, Norway. His research interests are focused on photocatalysis, PEC conversion and solar cells.