Preparation of nanocrystalline TiO_2 porous films from terpineol-ethanol-PEG system

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Nanocrystalline TiO_2 porous films were prepared by a sol-gel dip coating method from a solution using poly(ethylene glycol) as a template, ethanol as a solvent and terpineol as a highly viscous solvent. The thickness of films increases greatly by increasing the amount of terpineol. However, the overmuch incorporation of terpineol hinders the formation of porous structure and accelerates the crack creation. The crack-free film having a three-dimensionally extended porous structure was obtained at the ethanol/terpineol ratio of 8:1, the film thickness with three depositions being 2.5 μm.

Pretreatment of the precursor at an appropriate temperature also plays an important role in pore formation. Single-phase anatase TiO_2 porous films were obtained after calcinations at 550°C for 1 h, and the crystal size increases with an increase in the amount of terpineol. The pore formation mechanism is discussed primarily in relation to the phase separation in the system and self-assembly of PEG.

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1. Introduction

Crystalline titania (TiO_2) films, especially anatase, is of great interest in many scientific applications such as photoelectronic optical devices [1–3], gas sensors [4], photocatalysts [5–7] and even electrochromic films [8]. Increasing the surface area of film is a promising way to improve the desired functions because almost all of these applications utilize the chemical reactions on the surface [9, 10]. So porous TiO_2 thin films with large specific surface area have attracted more and more attention. The sol-gel process is generally recognized to be an efficient route for fabricating homogeneous porous films by incorporating organic polymer with precursor solution [11–13]. However these porous films are not thick enough to satisfy the needs of practical application.

To reach the required thickness of the films, the sol-gel and dip-coating process is often repeated a number of times. Another way is to increase the viscosity of the precursor solution to increase the film thickness through a single dip coating. However, the tensile stress induced by the shrinkage of the films during heat treatment may lead to peeling off or cracking of the films when the layer is thicker. Negishi *et al.* reported the preparation of crack-free TiO_2 dense thin films using a highly viscous solvent α-terpineol [14]. This solvent with a high boiling point is suitable for dip-coating since it does not react with metal alkoxide and has a good affinity to glass substrate. Kajihara *et al.* prepared thicker TiO_2 macroporous films from a system containing poly(ethylene glycol) (PEG) and poly(vinylpyrrolidone) (PVP), where PEG played the role of pore-forming reagent and PVP having higher molecular weight was used to increase the viscosity of the solution [15]. From this system, 1 μm-thicked TiO_2 porous thin film can be fabricated successfully by repeating the deposition five times. In the present paper, we report the preparation of porous TiO_2 films with various thickness by using PEG as a template and low-cost terpineol as a highly viscous solvent. The influence of the processing parameters, such as the temperature at which the solution was pretreated and the volume ratio of ethanol to terpineol in the solvent, on the porous structure and thickness of the films have been investigated. The mechanism for formation of the porous structure is also discussed in relation to the phase separation in the TiO_2-based sol-gel system and the self-assembly of PEG adsorbed onto TiO_2 oligomers[16, 17].

2. Experimental

2.1. Chemicals

For the preparation of more viscous titanium sol, the following materials were used: polyethylene glycol (M_{av} =

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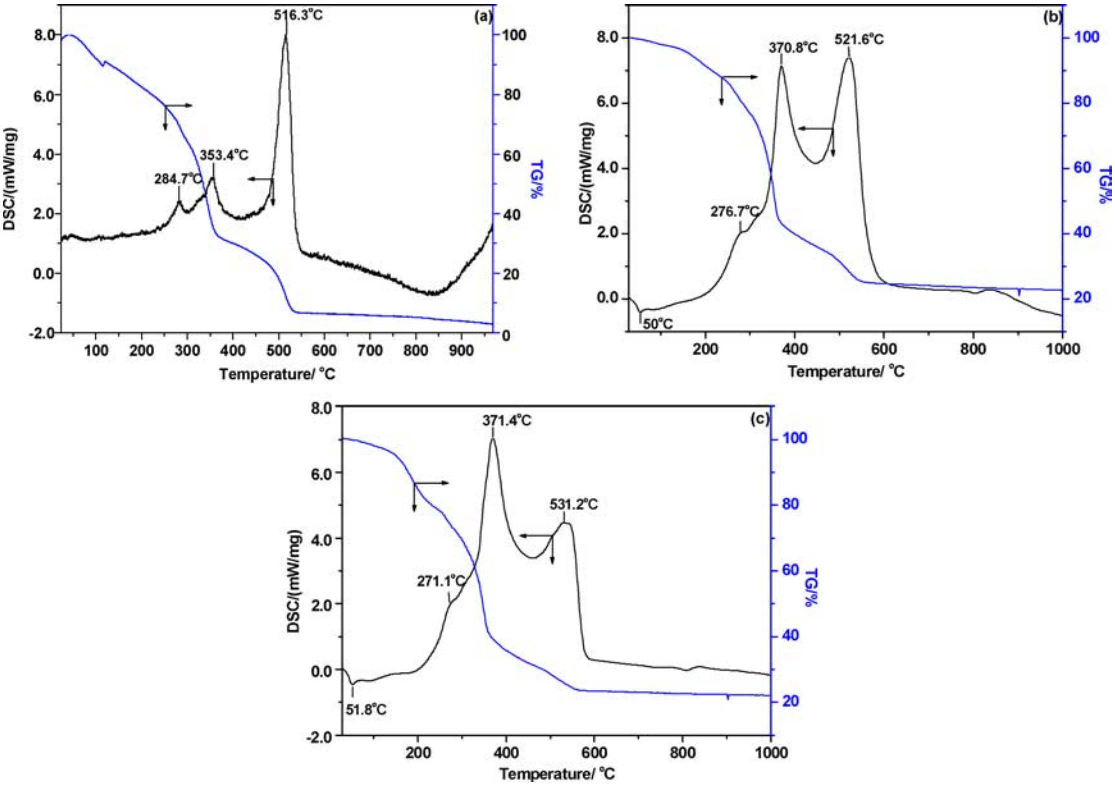

Figure 1 TG-DTA curves of TiO_2 xerogels with varied amounts of terpineol in the solvent: (a) terpineol free system (designated as T_0); (b) $V_{\text{terpineol}}/V_{\text{ethanol}} = 1:1$ (designated as T_1); (c) $V_{\text{terpineol}}/V_{\text{ethanol}} = 8:1$ (designated as T_2).

2000, $H(OCH_2CH_2)_nOH$; PEG), tetrabutylorthotitanate ($M = 340.35$, $Ti(OC_4H_9)_4$; $Ti(OBu)_4$), diethanolamine ($M = 105.14$, $NH(CH_2CH_2OH)_2$; DEA), ethanol ($M = 46.07$, CH_3CH_2OH; EtOH), terpineol ($M = 154.25$, $C_{10}H_{18}O$).

2.2. Synthesis

The precursor solution for the thicker TiO_2 porous film deposition was prepared by dissolving 8.68 mL of $Ti(OBu)_4$ in 40 mL of a mixture solution of terpineol and ethanol, the volume ratio of ethanol to terpineol being varied in the range of 1:8–8:1. To suppress the high reactivity of titanium alkoxide towards hydrolysis, 5 mL of DEA was added as a complexing reagent for $Ti(OBu)_4$. After magnetic stirring for 2 h, the obtained solution was hydrolyzed by the addition of a mixture of water and EtOH dropwisely under stirring for another 2 h. Then, 2.0 g of PEG was added into the resultant solution. The container was sealed and maintained at various temperature (25°C, 50°C or 70°C) for 1 h.

The above solution was deposited on slide glasses ($75 \times 25 \times 1$ mm) by dip-coating at the withdrawing speed of 15 mm/min. The deposited films were dried at 100°C for 30 min, and then heated in air up to 550°C and left at the maximum temperature for 1 h.

2.3. Characterization

The viscosity of the precursor solution was measured with a Brookfield viscometer ($\varphi = 1.0$ mm, Yatai Co. Ltd., China). Thermal analysis (TG-DTA) was carried out using a STA 449C thermal analyzer (Netzsch Co. Ltd., Germany). The TG-DTA samples were prepared by drying the dip-coating solutions in an oven at 60°C for 12 h. The morphology of the films was examined using a XL-30 environment scanning electron microscopy (ESEM) (Philips Co. Ltd., Netherlands). Both ESEM and a DEKTAK6M surface profile meter (Veeco Co. Ltd., America) were employed for the determination of film thickness. UV-VIS spectra were recorded on a DU-8B UV-VIS spectrometer (Beckman Co. Ltd., America). X-ray diffraction (XRD) patterns of the TiO_2 film were obtained with a D/max-2500 X-ray diffractometer (Rigaku Co. Ltd., Japan) using Cu Kα radiation ($\lambda = 0.154059$ nm).

3. Results and discussion

3.1. Preparation of thicker TiO_2 porous films

To obtain porous pure TiO_2, the organic template and solvent have to be removed by calcination. TG-DTA results of TiO_2 xerogels (Fig. 1) show that organic substance in the gels can be removed by heating up to 550°C. At approximately 50°C, a small endothermic peak which represents the removal of residual and adsorbed water is observed in both b and c of Fig. 1.

The intensity of the exothermic peaks between 270 and 280°C, which correspond to combustion of the residual ethanol, decreases with decreasing the ethanol amount. The exothermic peaks at approximately 350 or 370°C are

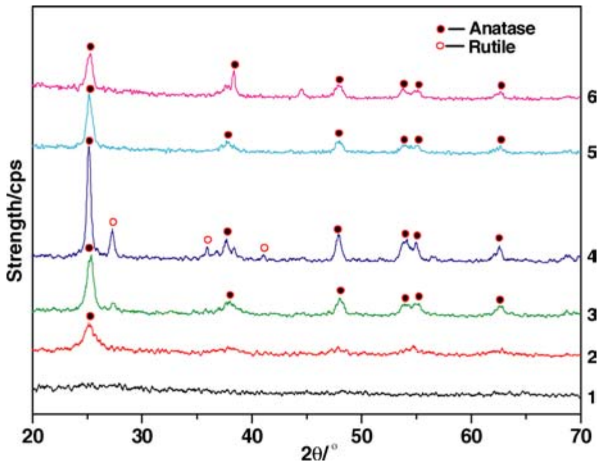

Figure 2 XRD patterns for the calcined samples: 1–xerogel calcined at 300°C; 2–xerogel calcined at 400°C; 3–T_0 calcined at 500°C; 4–T_0 calcined at 550°C; 5–T_1 calcined at 550°C; 6–T_2 calcined at 550°C.

attributed to not only combustion of organic compounds such as terpineol, DEA and PEG, but also the amorphous-anatase transition of TiO_2. It is clearly proven by the results of XRD measurements, which show that the samples calcined at temperature up to 300°C are amorphous, while diffraction peaks of anatase are found in samples calcined at 400°C(seen in trace 1 and 2 of Fig. 2). Increasing the volume ratio of terpineol in the solvent leads to a slight shift of this peak to higher temperature and increase in the intensity. Trace 3 and 4 of Fig. 2 show that while only ethanol is used as the solvent, the intensity of the anatase peaks increases and weak peaks of rutile appear when the heat treatment temperature of the samples was enhanced from 500 to 550°C. These results indicate that the exothermic peak at approximately 516°C in a of Fig. 1 most likely can be assigned to the further amorphous-anatase transition of TiO_2 and the transition of a fraction of anatase to rutile. However, after terpineol is added into the sol, the samples calcined at 550°C are single-phase anatase (seen in trace 5 and 6 of Fig. 2), suggesting that the TGA peaks at approximately 520°C in (b) or 530°C in (c) of Fig. 1 only correspond to the amorphous-anatase transition. It is considered that terpineol shift the anatase-rutile phase transition to higher temperature, favoring the formation of pure phase anatase which is well known to have higher activity [18]. The reason for this may be that the great steric hindrance of terpineol inhibits the interface contact between the colloidal particles due to its higher molecular weight, and as a result, the interfacial diffusion and solid state reaction of TiO_2 are impeded.

3.2. Influence of pretreatment temperature of the precursor solution

Kajihara *et al*. have reported that the morphology of TiO_2 film is determined mainly by the competition between the polycondensation of hydrolyzed titanium alkoxide and the phase separation between the titania oligomers adsorbed by PEG and the solvent mixture [11]. Porous films can be obtained when the rate of phase separation is relatively fast. Since the phase separation and the reactivity of titanium precursor strongly depend on the temperature, the solution was pretreated at three temperatures (25°C, 50°C, 70°C) for 1 h to investigate the effect of temperature on the formation of porous structure. Fig. 3 shows the surface morphologies of TiO_2 films as synthesized (dried at 100°C) and calcined at 550°C. As discussed in the

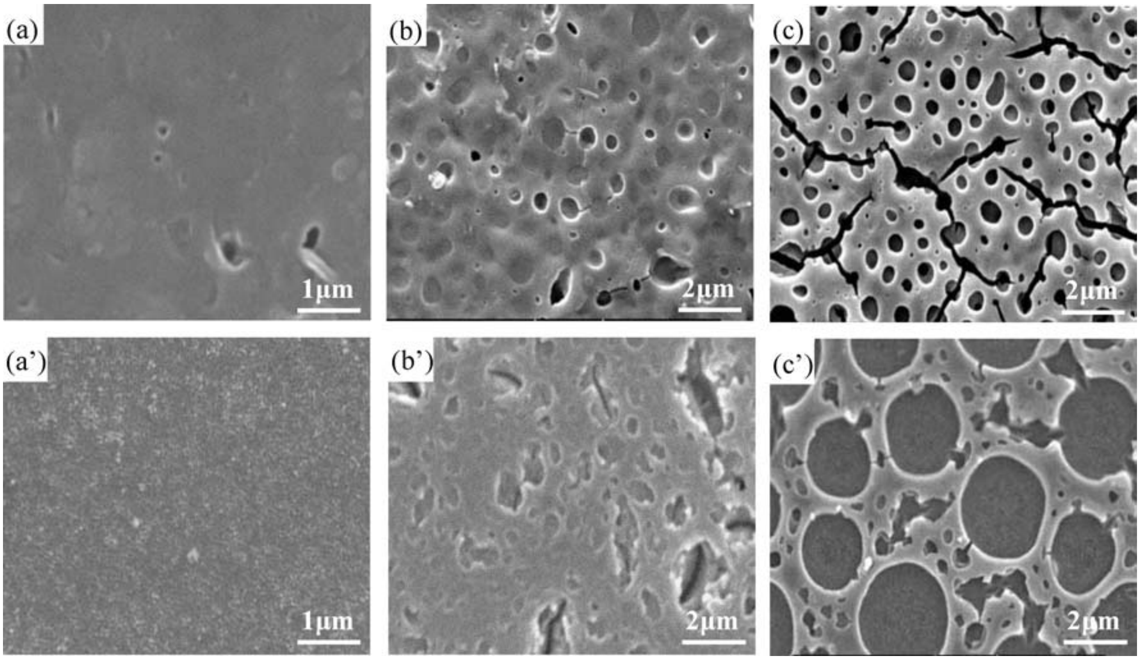

Figure 3 SEM photographs of the TiO_2 films comparing by pretreatment temperature of the precursor solution at the ethanol/terpineol volume ratio of 8:1: (a) 25°C, as synthesized; (a′) 25°C, calcined; (b) 50°C, as synthesized; (b′) 50°C, calcined; (c) 70°C, as synthesized; (c′) 70°C, calcined.

previous paper [13], the solvent removed during drying and PEG removed during calcining play a role of double-templates in the formation of TiO_2 porous films. However in the present system, terpineol can not be removed by drying due to its high boiling point (about 220°C). So it is supposed that in the precursor solution, ethanol, terpineol and PEG cooperate with each other to direct the microphase separation and self-assembly of PEG [13]. After the evaporation of ethanol during drying, the original porous structure appears in the films (Fig. 3a–c). Based on it, the remained two components terpineol and PEG adsorbed on titanium oligomers are assumed to re-cooperate before the combustion, and the removal of them upon thermal treatment lead to the reformation of the final porous films seen in Fig. ′–c′3a. It can be seen that the porous structure in the gel films induced by the phase separation becomes more and more distinct along with an increase in the pretreatment temperature of the precursor. A similar trend is observed in the calcined TiO_2 films. These results suggest that pretreatment of the precursor at an appropriate temperature does play an important role in forming well-defined TiO_2 porous structure, because both the phase separation and the self-assembly motion of PEG molecules are more enhanced than the polycondensation when the pretreatment temperature increases. The solution maintained at 25°C does not afford the formation of porous structure because no phase separation takes place at this lower temperature.

3.3. Influence of ethanol to terpineol ratio

3.3.1. Porous structure

Because the water-immiscibility of terpineol gives a poor dispersion of TiO_2 sol in the hydrolysis process, ethanol is used to improve the hydrolysis of titanium alkoxide. It has been found that the volume ratio of ethanol to terpineol significantly affects the structure of the films produced. Fig. 4 shows the SEM photographs of TiO_2 films with varied ethanol/terpineol volume ratio in the range of 1:8 to 8:1. It can be seen from the low-magnification images (Fig. 4a–f) that the cracks formation becomes less evident and crack-free porous film can be obtained when the ethanol/terpineol volume ratio is as high as 8:1. The high resolution image (Fig. ′4a) shows that no pores can be detected in the system at lower ethanol/terpineol ratio. It is supposed that the high viscosity of terpineol interferes with the phase separation and self-assembly of PEG due to the suppressed molecular motion. When this ratio is increased to 1:4, irregular-shaped pores and some cracks appears in the film (Fig. ′4b). However, the porous structure becomes less distinct at the ratio of 1:1, seen in Fig. ′4c. With a further increase in the ethanol/terpineol ratio, the porous structure formation becomes more and more significant, meanwhile the pore diameter increasing. In other words, with decreasing the volume ratio of terpineol, the phase separation and the self-assembly of PEG proceed more readily because of the less hindrance coming from terpineol, leading to the formation of the porous structure with a more regular pattern and better arrangement. On the other hand, the enhanced self-assembly of PEG also results in the increase of the pore diameter. The TiO_2 porous film obtained at the ethanol/terpineol volume ratio of 8:1 exhibits two different pore sizes, i.e., about 200 nm and 2 μm. It is suggested that the phase separation probably takes place not only between PEG and the solvent mixture, but also between ethanol and terpineol. Furthermore, the ethanol/terpineol volume ratio is supposed to affect the phase separation between them. When the amount of ethanol and terpineol is equivalent, the compatibility between them is relatively high and the phase separation is not obvious (seen in Fig. ′4c). By increasing the disparity between the amount of ethanol and terpineol, the phase separation tendency gets more significant, producing the two domains in the system: one is ethanol-rich and the other is terpineol-rich. In the ethanol-rich domains, the phase separated pattern (small pores) is stable during drying and can be reserved after calcination. While in the terpineol-rich domains, the phase separated pattern (large pores) is unstable and reformed through the mobility of terpineol liquid at higher temperature but below its boiling point when the films are calcined. Under the function of the surface tension of terpineol, the reformed pores become rounder and shrink to form large pores.

3.3.2. Film thickness

The film thickness depends significantly on the volume ratio of ethanol to terpineol because terpineol greatly increases the solution viscosity, as shown in Fig. 5. Accordingly the enhanced crack formation of TiO_2 films at lower ethanol/terpineol ratio (shown in Fig. 4) may be attributed to the larger tensile stress in thicker films created by film shrinkage during the drying and heating stages. In the present system, crack-free TiO_2 film having three-dimensionally extended network porous structure as thick as 0.66 μm has been prepared with a single dipping and heat treatment, as shown in Fig. 6a. By repeating the deposition process three times, the film thickness can be increased to 2.5 μm, seen in Fig. 6b. However in the terpineol free system (Fig. 6c), at least 10 dip-coating times is needed to obtain a 0.2 μm-thick film. So the deposition times to obtain sufficient film thickness can be reduced greatly by using terpineol as a highly viscous solvent.

3.3.3. Optical properties

Fig. 7 shows the UV-Vis transmitted spectra of the TiO_2 porous films by repeating the deposition cycle only one time and calcining at 550°C, in the wavelength range 300–900 nm. The absorption edges of each film are about 320 nm. It can be noted that the transmittance of the films decreases with an increase in ethanol/terpineol ratio, due to scattering of light from the porous structure in the film. On the other hand, the decrease in the number of interference waves, which is related to the film thickness

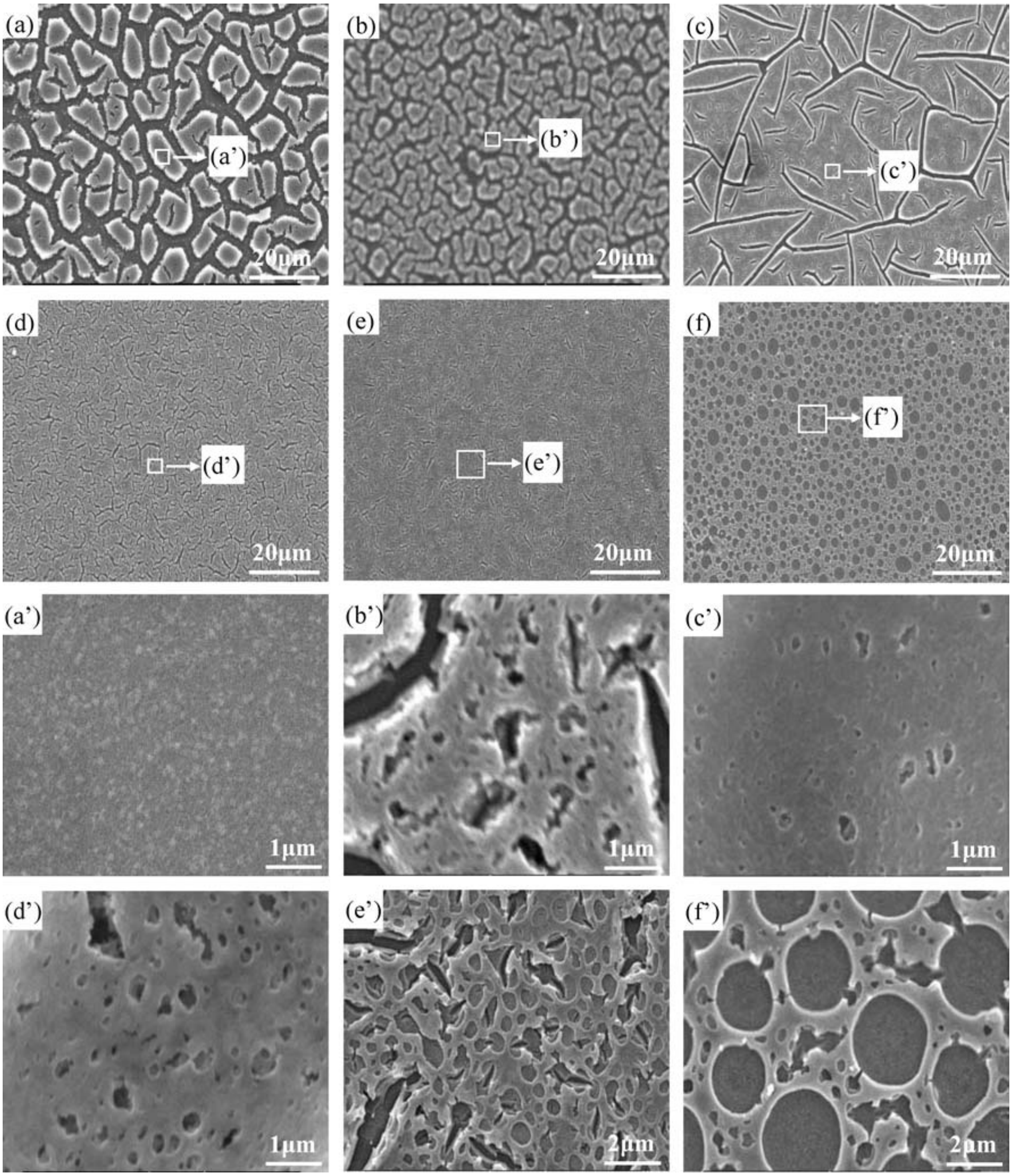

Figure 4 SEM photographs of the TiO_2 films prepared from the solutions pretreated at 70°C, at the ethanol/terpineol volume ratio of: (a, a′) 1:8; (b, b′) 1:2; (c, c′) 1:1; (d, d′) 2:1; (e, e′) 4:1; (f, f′) 8:1.

[19, 20], indicates the thickness of the films decreases with decreasing the amount of terpineol, being consistent with the above results shown in Fig. 5.

3.3.4. Crystal structure

Fig. 8 shows the X-ray diffraction patterns for the TiO_2 porous thin films calcined at 550°C. The broad amorphous peaks between 15° and 38° correspond to the glass substrate. The patterns show that the porous titania framework is well crystallized and consists only of anatase, being in agreement with the XRD results of TiO_2 powders shown in Fig. 2. Moreover, the peaks appear more intense by increasing the amount of terpineol owing to the increase in the film thickness. Meanwhile, the width at the half height of the main peak of the anatase structure becomes narrower, indicating the formation of greater crystallites in the films. The average crystal size of TiO_2 was calculated from the (101) peak of anatase in Fig. 8, using

$$r = K\lambda/b\cos\theta \tag{1}$$

where K is a constant of which the value is 0.89 [21], λ is the wavelength of the X-ray (0.15409 nm), b is the

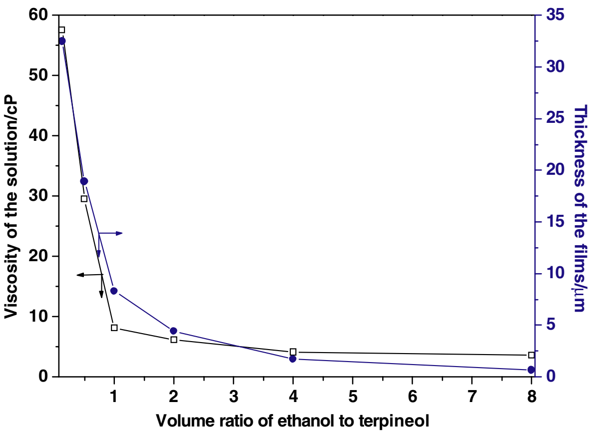

Figure 5 Dependence of the solution viscosity and film thickness on ethanol/terpineol volume ratio.

halfwidth, and θ is the diffraction angle. The results are shown in Table I. It can be seen from Table I that the crystallite size of TiO_2 increases with an increase in the amount of terpineol. As discussed in Part 3.2, the high viscosity of terpineol hinders the formation of porous structure, which may prevent the growth of TiO_2 single crystals [14], as a result of the suppressed phase separation and self-assembly of PEG. Consequently, the larger size of TiO_2 particles was obtained. Optimization of the preparation conditions and research of other organic reagents as solvents, smaller pore macro-mesoporous TiO_2 films as well as their photocatalytic and photoelectrochemical activities are in progress.

TABLE I The thickness and crystallite size of the TiO_2 films at varied amount of terpineol

Ethanol/terpineol volumn ratio	Film thickness/μm	Phase structure	Crystalline size/nm
8:1	0.66	Anatase	10.3
4:1	1.7	Anatase	12.5
2:1	4.4	Anatase	16.7
1:1	8.3	Anatase	20.0
1:2	18.9	Anatase	23.4
1:8	32.5	Anatase	28.9

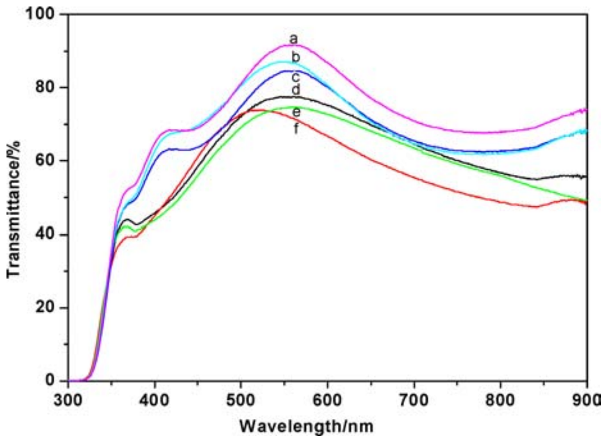

Figure 7 Effect of ethanol/terpineol volume ratio on the UV-Vis transmittance of TiO_2 films: (a) 1:8; (b) 1:2; (c) 1:1; (d) 2:1; (e) 4:1; (f) 8:1.

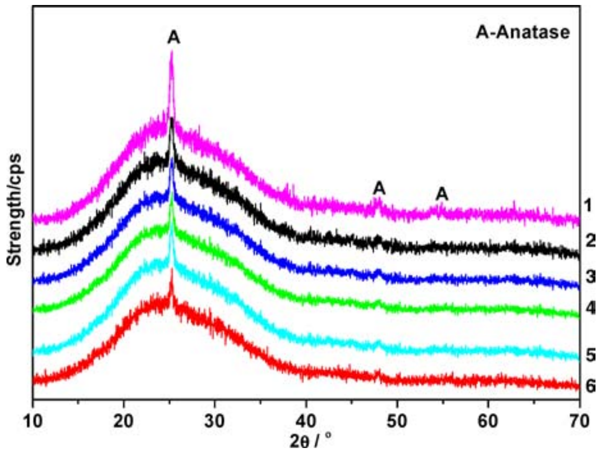

Figure 8 XRD patterns for the TiO_2 thin films at the ethanol/terpineol volume ratio of: 1—1:8; 2—1:2; 3—1:1; 4—2:1; 5—4:1; 6—8:1.

4. Conclusions

(1). Crystalline TiO_2 porous films were prepared from titanium alkoxide solutions containing polyethylene glycol (PEG), with terpineol as a highly viscous solvent.

(2). The mechanism for formation of the porous films is interpreted based on the phase separation and self-assembly of PEG in the system comprising four components: ethanol, terpineol, PEG and TiO_2 oligomers.

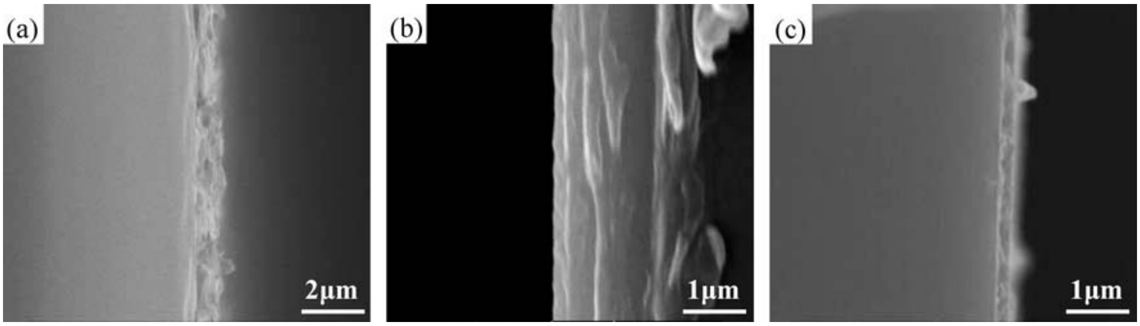

Figure 6 Cross-sectional SEM photographs of the porous TiO_2 films: (a, b) at the ethanol/terpineol volume ratio of 8:1, number of deposition is (a) one, (b) three; (c) terpineol free system, number of deposition is ten.

(3). Film thickness is increased greatly by incorporating terpineol to increase the viscosity of the dipping solution. However, excess addition of terpineol hinders the formation of porous structure and enhances crack formation due to the increased shrinkage stress in the case of dipping a thicker layer per cycle.

(4). The porous structure of TiO_2 films is also found to greatly depend on the pretreatment temperature of the precursor solution, because both the phase separation and the self-assembly motion of PEG can be accelerated by enhancing the solution temperature.

(5). It has been found that the addition of terpineol shift the anatase-rutile phase transition to higher temperature. TiO_2 porous films in single-phase anatase can be obtained after calcination at 550°C. The crystallite size of TiO_2 increases by increasing the amount of terpineol.

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