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Superhydrophilic porous TiO_2 film prepared by phase separation through two stabilizers

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ABSTRACT

A novel method was developed to produce a TiO_2 film with circular pores on its surface. The pores aroused from the precursor solution using both acetylacetone (AcAc) and diethanolamine (DEA) as stabilizers. The appearance of interconnected or isolated pores for the films was discussed in relation to the phase separation in the sol–gel process with the presence of Acac and DEA. Macropore size, together with connectivity of pores and gel skeleton, can be controlled by selecting an appropriate composition for preparation at DEA amount or regulating a time scale of the sol–gel transition. Finally, wetting behavior of the resulting films was characterized by using contact angle measurements. The TiO_2 films with interconnected or relatively isolated pores exhibit superhydrophilic characteristic, although it is not exposed to ultraviolet irradiation. Deducing from the Wenzel–Cassie regimes' transition criterion, the existence of Cassie impregnating wetting regime rather than Wenzel one upon these porosity-driven superhydrophilic surfaces can be obtained.

1. Introduction

TiO_2 is a widely used photocatalytic and hydrophilic material, which has been employed in many industrial applications for its fine optical, chemical and hydrophilic properties. As we known, the fabrication of porous and nanostructured TiO_2 films that introduces special surface topography and large surface area has attracted considerable attention for its enhanced photocatalytic activity, photoinduced hydrophilicity and other potential applications [1–4]. A variety of methodologies have been developed to create micro-nanoporous TiO_2 thin film including the sol–gel method [5], sputtering techniques [6], chemical vapor deposition (CVD) [7], ultrasonic spray pyrolysis [8], and hydrothermal synthesis [9]. In particular, the sol–gel process is one of the most wisely used techniques for fabrication of porous structures of thin oxide films since its many attractive advantages, i.e., easy to control structure with different additives. It has been reported porous TiO_2 films have been prepared via surface modification with several templates including SiO_2, polystyrene, poly(methyl methacrylate), and surfactant in sol–gel route [10–15].

In sol–gel method, the complexing agent or stabilizer is a well-known additive to control the rate of hydrolysis of the metal alkoxides and improve the adherence, transparency and the quality of the corresponding films. The stabilizing action of complexing agents is an outcome of its chelate forming ability with the alkoxides. It has been reported that the stable and water-resistant precursor solution could been obtained by some type of stabilizers (e.g., diethanolamine [16], acetylacetone [17], or acetic acid [18]) that complexing with the alkoxides and convert into the chelate forming. Additionally, acetylacetone and diethanolamine are usually used as inhibitors for controlling the rate of hydrolysis and precipitation of the metal alkoxides. Therefore, the template and complexing agent are often used for the fabrication of porous TiO_2 thin films in sol–gel approach, but a few porous films have been reported by the sol–gel method with template-free method [4,13,19–21].

In this paper, we report for the first time on the studies of surface microstructures of porous TiO_2 thin films prepared by using two stabilizers in sol–gel route. A comparison of porous TiO_2 films with conventionally prepared TiO_2 films will show the significance of the preparation method. Here we present an possible formation mechanism for this circular-macropores based on generation of micelles in the bulk of the solution and discuss the characteristics of the porous films.

2. Experimental

2.1. Chemicals

For the preparation of TiO_2 films, the following materials were used: tetrabutyl titanate (M = 340.35, $Ti(OC_4H_9)_4$; $Ti(OBu)_4$), acetylacetone (M = 100.12, $CH_3(CO)CH_2(CO)CH_3$; AcAc),

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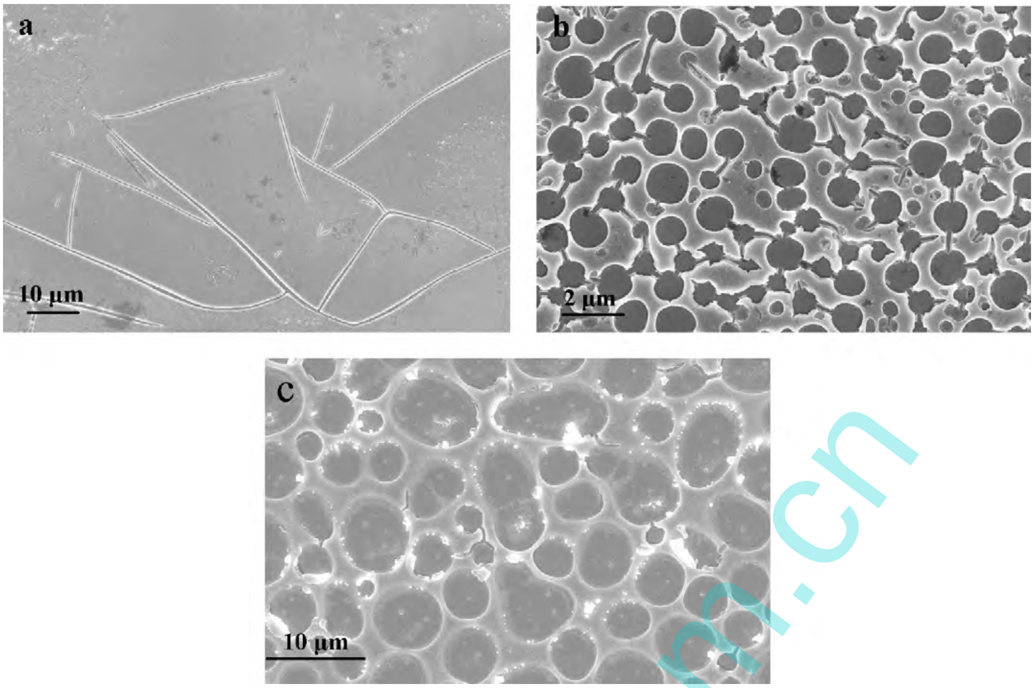


Fig. 1. SEM micrographs of TiO_2 thin films at three different volume ratio of AcAc:DEA:$Ti(OBu)_4$ (a) A1—AcAc:DEA = 2:1; (b) A2—AcAc:DEA = 1:1; (c) A3—AcAc:DEA = 2:3.

diethanolamine (M = 105.14, $NH(CH_2CH_2OH)_2$; DEA), ethanol (M = 46.07, CH_3CH_2OH; EtOH), and HNO_3.

2.2. Preparation of precursor sols

The starting solution was prepared by mixing 10 ml tetrabutyl titanate of ethanol (C_2H_5OH) followed by the addition of AcAc and DEA. To further research the forming mechanism of porous surface, different amounts of DEA (1, 2 and 3 ml), which were named A1, A2 and A3 respectively. After stirring this solution for 30 min, the mixture of 10 ml ethanol, 10 ml deionized water and 1 HNO_3 was added and the stirring was continued for 3 h at room temperature. The relative volume ratio of each chemical in the precursor sol was $Ti(OC_4H_9)_4$:AcAc:C_2H_5OH = 1:0.2:10. All sols were aged for 3 h.

2.3. Preparation of TiO_2 thin films

Acetone washed and dried transparent glass substrates and microglass slides were spin coated by precursor sols with the rotation speed of 800 rpm for 20 s and 3000 rpm for 30 s in succession. The process above was repeated 3–4 times so as to obtain the required thickness of the films. The coatings were dried at 100 °C for 0.5 h and calcined in air at 500 °C at heating rate of 5 °C/min and kept at 500 °C for 1 h.

2.4. Characterizations

Morphologies of the TiO_2 films were investigated by a LEO 1530 VP field emission scanning electrons microscope (SEM). Atomic force microscopy (AFM) measurement was performed using a instrument (CSPM 2003) with 3 μm × 3 μm scanned area and images were acquired under ambient conditions in contact mode using a Nanoprobe cantilever. Contact angles for water (WCA) were measured with an OCA40 contact angle goniometer from Dataphysics Co. Germany. Typically, the average value of five measurements, made at different positions of the film surface was adopted as the value of WCA.

3. Results and discussion

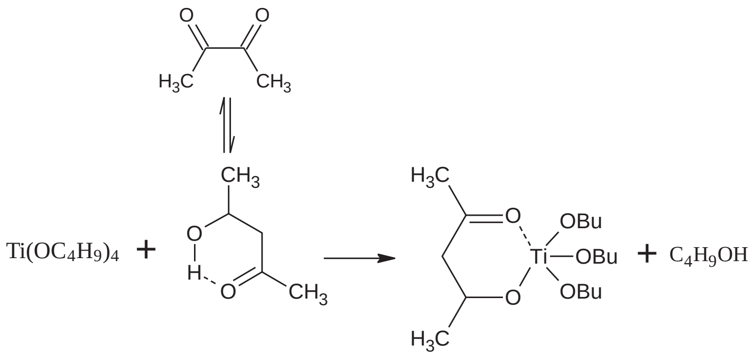
3.1. Morphology of TiO_2 thin films

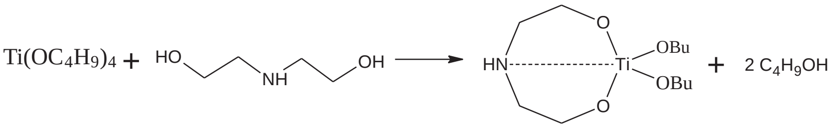
Fig. 1 shows the topography images of TiO_2 thin films heated at 500 °C with different amount of stabilizers after the same aging time of 3 h ((A1) AcAc 2 ml and DEA 1 ml, (A2) with AcAc 2 ml and DEA 2 ml, (A3) with AcAc 2 ml and DEA 3 ml). The proportion of each component solution system is given in Table 1. Depending on the addition amount, admixtures significantly changed the surface morphology of TiO_2 thin films. In the diagrams, clear cracks appeared on the TiO_2-A1 film. Interconnect macropores, however, extraordinarily formed when the amount of DEA increased to 2 ml and the TiO_2 surface turned to much higher isolated pores when the DEA was enhanced to 3 ml. TiO_2-A2 gave the normally numerous pores with average size around 1 μm on the surface, a little smaller than the porous size measured on TiO_2-A3 sample, which had the 8 μm average size after sintering.

Using AcAc or DEA exclusively as a stabilizer in experiments, a flat and thin TiO_2 film will appear in the virtual of the fact that AcAc or DEA serves only as an inhibitor which complexes with $Ti(OBu)_4$ so that the rate of hydrolysis and precipitation of the metal alkoxides can be controlled [22,23]. Other agents such template agents and surfactants are necessary if fabricating porous structure [22,24,25]. The complexing reactions taking place are presumed as follows:

Table 1
Component ratio of double complexing agents system.

Samples	Complexing agents/ml	Water/ml	HNO_3/ml	pH
A1	AcAc 2, DEA 1	10	1	2.12
A2	AcAc 2, DEA 2	10	1	6.57
A3	AcAc 2, DEA 3	10	1	7.75





Complexing resultants Ti(OBu)$_{4-x}$(acac)$_x$ and Ti(OBu)$_{4-x}$(DEA)$_x$ will be produced during the complexing reactions when both AcAc and DEA are mixed with Ti(OBu)$_4$ precursor. And the hydrolysis process of Ti(OBu)$_4$ precursor takes place after adding water into sols. The reaction results in the formation of Ti(OBu)$_{4-x-y}$(acac)$_x$(OH)$_y$ and Ti(OBu)$_{4-x-y}$(DEA)$_x$(OH)$_y$ which are polar solvents with hydrogen bonding. They would lead to the further condensation reactions, including dehydration and debutanation, as well as a relatively narrow distribution of growing oligomers [22,26].

The situation, however, has entirely changed when both AcAc and DEA were used as complexing agents. With the slow dropping of mixture that consists of ethanol, water and HNO_3, the alkoxide of titanium complexed with DEA exhibits the much higher reactivity toward hydrolysis and polycondensation that that complexed with Acac since the ability to complex of ACAC is stronger than that of DEA [22]. On the other hand, the DEA which is a weak base neutralizes with HNO_3 and generates additional water which enables the acceleration of the polycondensation rate, impelling the development of phase separation for TiO_2 sols. Debutanation polycondensation and dehydration polycondensation, which rapidly occur in the presence of excessive water gradually decreases the polarity of gel phase by consuming the hydroxyl groups, while the polarity of the solvent remains high. In the course of polycondensation, therefore, the phase separation is driven by the reduction of miscibility between the polar solvent and polycondensed inorganic species.

In these series of experiments, we also operated a similar experiment which using only DEA with the same amount of water. The sol, however, showed a heavy precipitation. The reason lies in the amount of water which is too much for the DEA-complexing system to sustain. From this phenomenon, it can be found that excessive Acac added in other sols played a crucial role, mainly due to the fact that it displays stronger chelate forming ability with the alkoxides preferentially and therefore reduce the rate of hydrolysis and precipitation of metal alkoxides, which is unfavorable for the development of phase separation. Comparatively, DEA here exhibits the ability of being incorporated for an adjustment of phase separation dynamics to obtain better defined macroporous structures.

As seen in Fig. 2, sol–gel systems undergo a phase separation to generate micrometer-range heterogeneity composed of gel and fluid phases. A bicontinuous structure, in which both the separated

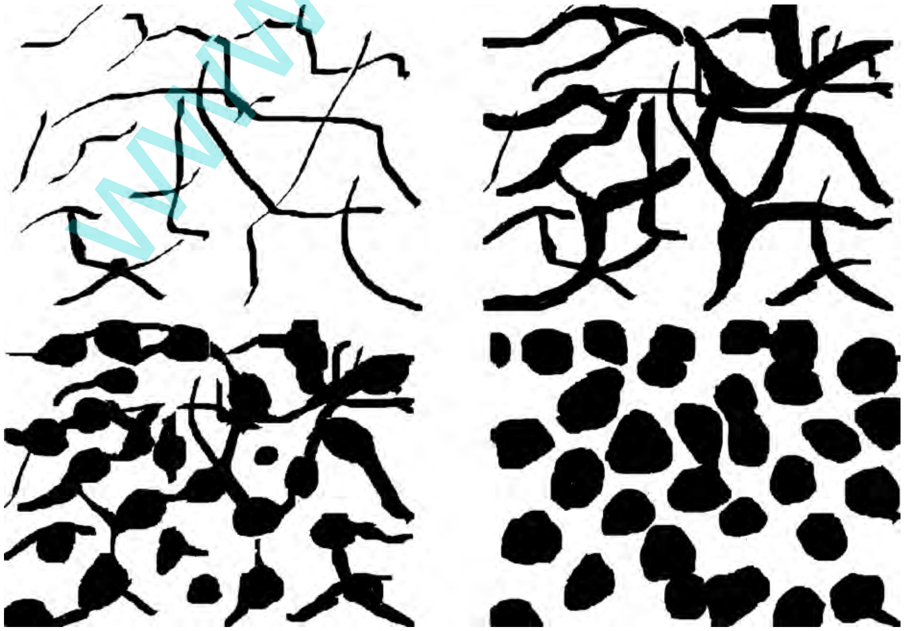


Fig. 2. Time evolution in a sol–gel system of developing phase separation.

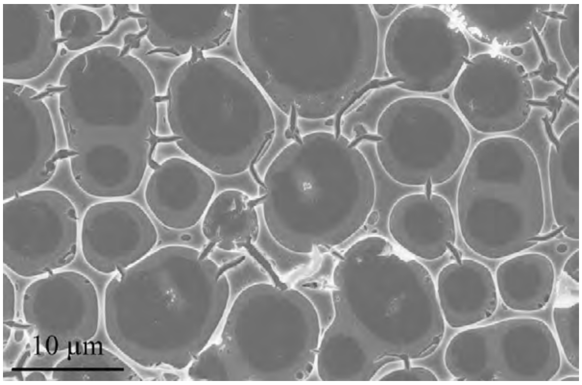


Fig. 3. FE-SEM image of sample A2′ aged after 48 h.

phases are highly continuous and interconnected, is obtained when the phase separation is induced parallel to the aging time, that is, the process of sol–gel transition. The phase-formation time here would be shortened according the adding amount of DEA which triggers the process of hydrolysis. In another word, the more aging time, the higher separated phase would be. As mentioned in Fig. 1, at the addition amount of 2 ml and 1 ml AcAc and DEA did not show any significant effect on fabricating porous surface within the same aging time but, this aging time was slightly decreased with the rising amount of DEA. Noticeably, DEA influenced the aging time obviously. After 48 h aging time, the TiO_2 sol turned to be a more complicated phase separation (sample-A2′), which was reflected on the surface in Fig. 3.

What is more, another factor which slows down the development of phase separation is the pH. Since the solution pH of TiO_2-A1 is 2.12 that is much lower than the isoelectric point of TiO_2, or pH = 5.5–6.0. Under this circumstance, alkoxy-derived oligomers positively charged and stabilized by the electrostatic repulsion in the acid condition have grown in broader distribution by successive condensation, posing an obstacle to the phase separation.

Depending on the addition rate, the admixture-DEA significantly accelerates the process of hydrolysis and polycondensation and therefore retarded the aging time. Among the three admixtures DEA of different amount showed more and more marked effect on surface morphology through influencing the rate of hydrolysis and polycondensation. On drying, the fluid phase of solvent mixture could oxidize and decompose to carbon dioxide which leaves numerous pores on the surface. And the gel phase becomes the porous skeleton.

Fig. 4 shows the surface morphology of calcined TiO_2 films (calcined at 85 °C/1 h) prepared from the same ethanol precursor solution containing admixtures (AcAc 2 ml and DEA 3 ml) within the same aging time. It offers an advantageous proof about the phase separation mechanism of this system mentioned in above. It can be observed that isolated pores appeared after the evaporation of the ethanol solvent (the boiling point of ethanol is 78.3 °C). Furthermore, a porous network structure can be obtained, as seen in the figure, when the ethanol in the solvent phase is removed by heat treatment.

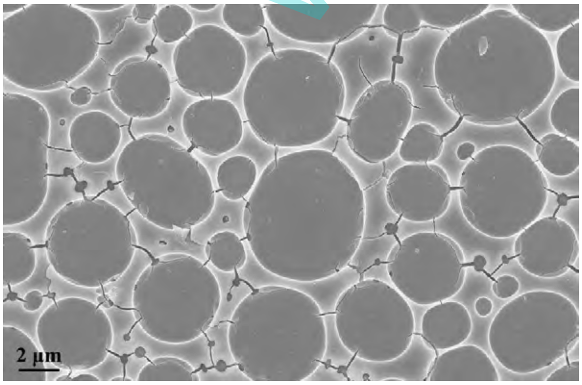


Fig. 4. TiO_2-A3 film sintering after 85 °C.

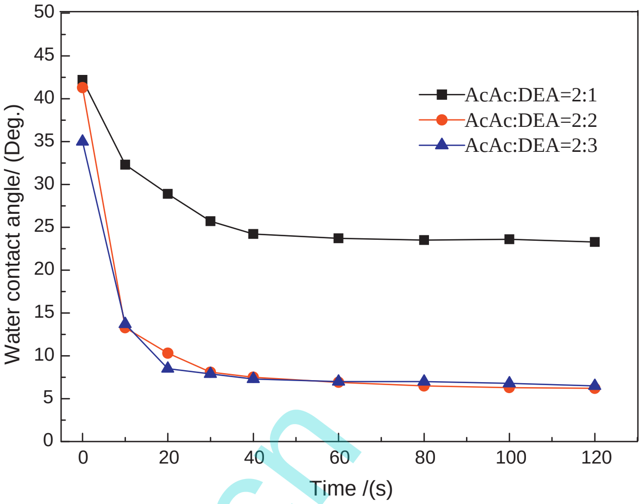


Fig. 5. Water contact angle of the TiO_2 films without UV illumination.

3.2. *Superhydrophilicity of TiO_2 porous films*

Superhydrophilic surfaces have considerably technological applications due to their special properties such as self-cleaning [27,28]. Fig. 5 shows the transient contact angle of 1 μl water on TiO_2 film. Combining with results on porous films, the hydrophilicity for TiO_2-A1 thin film with cracks has a small contact angle with water (23.3°) in ambient air. In pervious experiments, the hydrophilicity of TiO_2 thin film without holes can be attributed to the TiO_2 thin film with a narrower band gap and the best for anatase phase in the TiO_2 films as well as the formation of oxygen defects of TiO_2 films under lights [24,29]. It deserves to be mentioned that the sample prepared from sol A2′ and A3 displays superhydrophilicity even without UV irradiation and the WCA become 6.2° and 6.5° respectively within 120 s, while the substrate covered by sol A1 had an average WCA of 23.3° in 120 s. It is evident that the high surface roughness decreases the water contact angle on the porous films. Here, the intrinsically high level of wettability of the nanoparticles coupled with the roughness and porous nature of the coating established ideal conditions for superhydrophilicity.

It is important to discuss the root mechanism involved in the observed superhydrophilicity. It has been reported that rough surface may change the contact angle, and that microtextured topography can also influence [15,16]. Therefore, the appearance of pores on experiments turns to be the key factor affecting the topography of testing surfaces.

Two wetting regimes can be used to explain this superhydrophilic phenomenon, either the Wenzel or the Cassie regime [30,31]. In Wenzel regime, it is well established, for example, that for a given chemical composition, the increasing roughness of a surface can render it more hydrophobic or more hydrophilic. The Wenzel model describes homogeneous wetting by the equation [30]:

$$\cos\theta_w = r\cos\theta_0 \quad (1)$$

where θ_w and θ_0 are Wenzel contact angle and the Young's CA of a flat surface, respectively and r is the roughness factor, defined

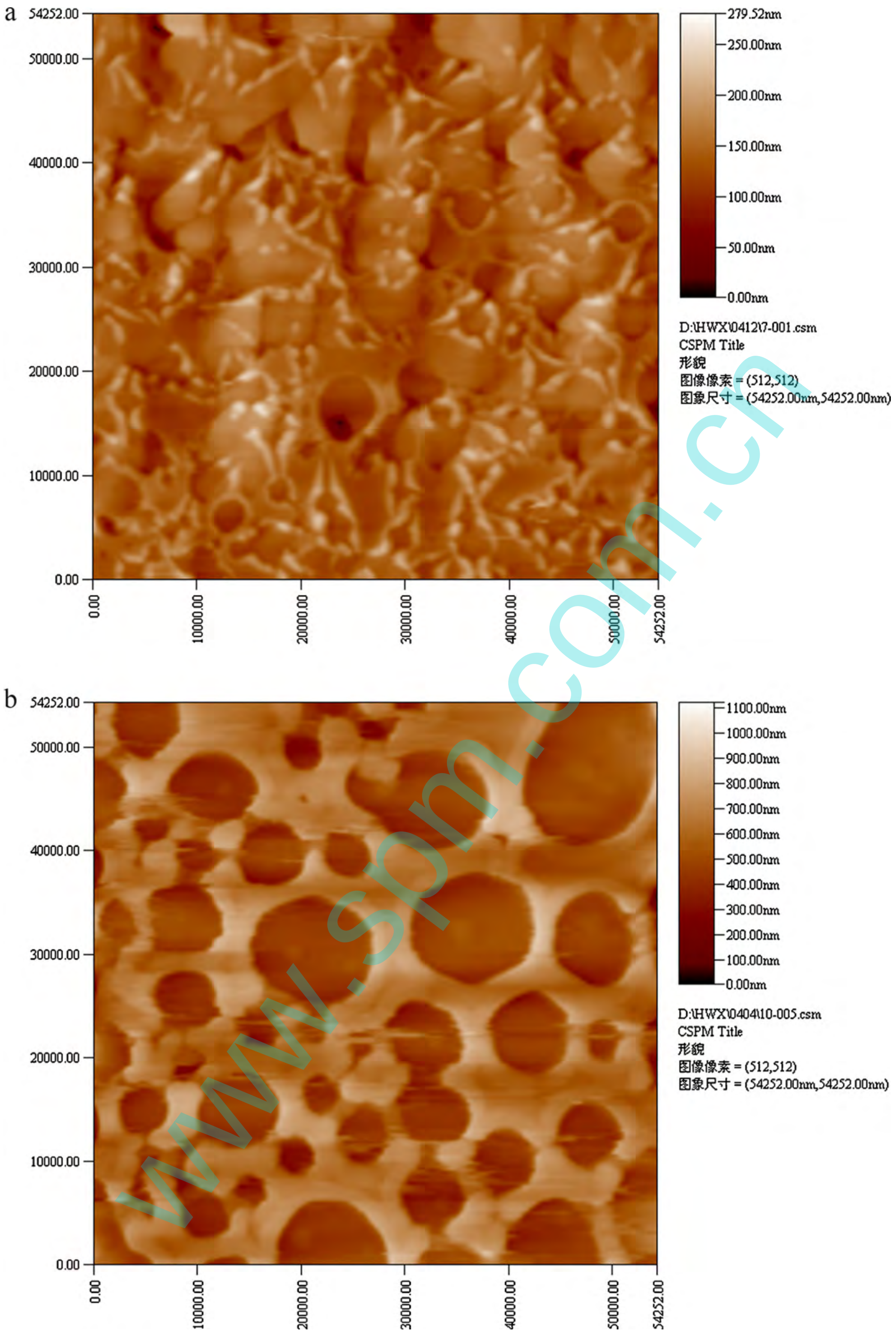


Fig. 6. AFM images of TiO_2 films (a) A2—AcAc:DEA = 1:1; (b) A3—AcAc:DEA = 2:3.

as the total surface area to the projected area in the horizontal plane.

On the other hand, the drop lies on a mixture of liquid (which constitutes the film) and solid (the “islands” which emerge above the sea of liquid). The contact angle of such a drop can be deduced from an argument due to Cassie and Baxter [31]

$$\cos\theta_c \varnothing_s + \varnothing_s \cos\theta_0 \qquad (2)$$

where θ_c and θ_0 are the Cassie contact angle and the Young contact angle, respectively, and $\varnothing_s$ is the area fraction

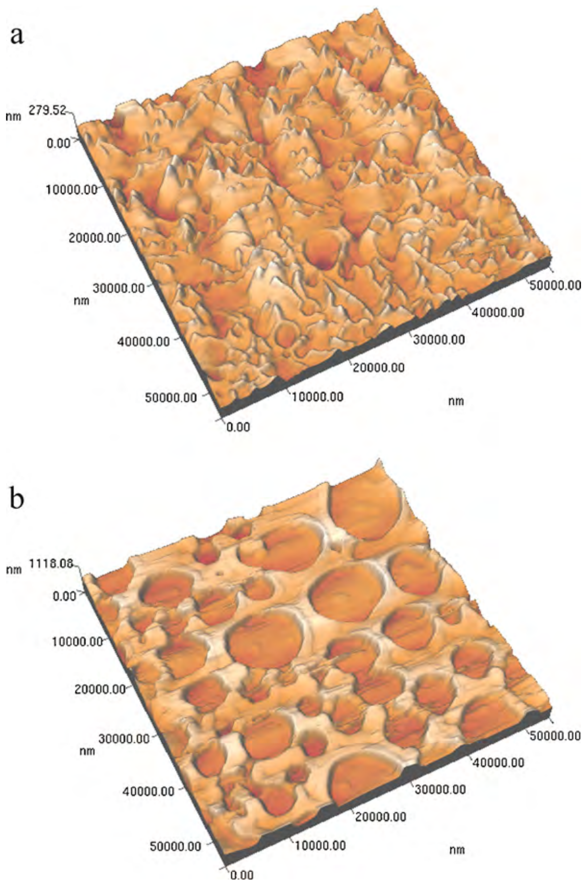


Fig. 7. AFM of TiO_2 films (a) A2—AcAc:DEA = 1:1; (b) A3—AcAc:DEA = 2:3.

of dry solid "islands" in the mixed surface beyond the drop.

In this series of experiments, the wetting behavior of the experiments observed stem from porosity-driven superhydrophilicity. The wetting regime of TiO_2 porous films, therefore, can be deduced from the Wenzel–Cassie regimes' transition criterion ($\theta_c = \arccos(d/(4h+d))$) [25]. The hydrophilic state switches from Wenzel regime to Cassie regime will occur if the CA of the flat surface is smaller than the critical contact angle, θ_c.

As shown in Figs. 6 and 7, the pore depths of A2, A3 are 84.8 ± 10 nm, 553.8 ± 10 nm respectively. The corresponding diameters for the samples A2–A3 are about 1 and 8 μm, respectively. According to the measured water CAs of the prepared porous TiO_2 films shown in Fig. 4, the CA decreased slightly to 23. 3° when small cracks appeared in sample A1. For this porous substrate with a diameter of 0.1 μm and a hole depth of 84.8 ± 10 nm, the impregnating condition can be satisfied which indicates that the sample A2 was in the complete Cassie state. Besides, further increase in holes depth to 553.8 ± 10 nm raised the trend and resulted in the decrease in CA to 6.5°. Therefore, if we apply the Cassie impregnating model developed for porous and heterogeneous surface, we can explain the observed experimental observation well.

According to Cassie impregnating wetting model, in which the test liquid can remain trapped below the drop, also leads to a superhydrophilic behavior. In superhydrophilic case where a film invades the solid texture, we should not consider these rough surfaces as homogeneous surface any more when it is rough and porous. As shown in Fig. 8, the reason is the gaps between the peaks were filled with another material (the test liquid) so that the "real" surface, on which a liquid drop was placed, consisted of two different materials. The drop lies on a mixture of liquid (which constitutes the film) and solid (the "islands" which emerge above the sea of liquid).

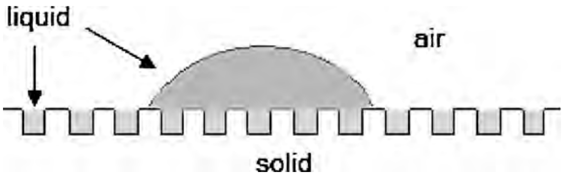


Fig. 8. In the case where a film invades the solid texture, a drop lies on a solid/liquid composite surface.

4. Conclusions

Synthesis of sol–gel process derived nanoporous TiO_2 films from tetrabutyl titanate in the presence of stabilizing agents (diethanolamine (DEA) and acetylacetone (AcAc)) was performed. It has been found that the development of phase separation, which results from the admixture of DEA and AcAc, significantly affects the microstructure of the obtained TiO_2 interconnected or isolated porous film. The development of cracks and pores structure was based on DEA amount and time scale of the sol–gel transition. This process makes it possible to produce porous surfaces without resorting to template agents. The final pores of thin films could be obtained by the volatilization, decomposition and combustion of the solvent phase through heat treatment. Deducing from the Wenzel–Cassie regimes' transition criterion, the wettability of porous TiO_2 thin films prepared from phase separation can be characterized by the Cassie–Baxter model. The topography consisted of two different materials (the test liquid and solid) generates an efficient decreasing of the contact angle.

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