Microstructure and photocatalytic activity of mesoporous TiO$_2$ film coated on an aluminum foam

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ABSTRACT

A TiO$_2$ film was synthesized via a surfactant assisted sol–gel process and dip-coated on the surface of an open-celled aluminum foam. The film shows a typical mesoporous structure composed of anatase crystalline grains with the average size of 10 nm, and has the thickness of about 3.5 μm as well as the BET surface area of 78.1 m^2/g. It exhibits high photocatalytic efficiency toward the decomposition of formaldehyde at continuous flow mode. The relatively small grain size of TiO$_2$ and relatively thick mesoporous structure, which is favorable for high photochemical activity and the mass transfer of the reactants, should be responsible for the properties.

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1. Introduction

It has long been the main method for the practical applications in the environmental protection fields by immobilizing photocatalyst TiO$_2$ onto solid substrates [1–15]. The substrate not only provides the support for the TiO$_2$ film but also guarantees the utilization efficiency of film as high as possible, thus it is critical in the photocatalytic applications. Many materials have been used as the substrates such as activated carbon fiber [1], coal fly ash [2], porous carbon [3] and anodic alumite [4] etc. These materials usually show disappointing mechanical properties and poor permeability, which restrict their applications in most environments. Recently, reticulated macroporous metal foams received much attention as the film supporters and the results demonstrated that the combination of TiO$_2$ and the substrate with high porosity was effective for improvement of photodecomposition rate [5–8].

It is well known that the film-type photocatalyst often suffers from decreased surface area compared with the powdery one. Therefore, it is of most importance to process TiO$_2$ as film with porous structure. Many researchers [9–14] reported that the mesoporous TiO$_2$ films synthesized via a surfactant assisted sol–gel process display outstanding photocatalytic activity because of favorable transmission between the polluted matter and the catalysts. Besides, the high concentration of surfactant makes the formation of fine nanocrystallites, which is favorable for high photochemical reaction rates. Hence, the TiO$_2$ film with high surface area originating from mesoporous structure deserves further study.

In the present study, an open-celled aluminum foam with high porosity (93%) was used as the substrate. The mesoporous TiO$_2$ film was synthesized via a surfactant assisted sol–gel process and dip-coated on the cell wall of the substrate. The photocatalytic property was evaluated by examining the efficiency in decomposing formaldehyde (HCHO) at room temperature.

2. Experimental

2.1. Sol synthesis

TiO$_2$ sol was prepared by the following steps: dissolving 8.5 mL Ti (OC$_4$H$_9$)$_4$ (C.P.) in 15 mL ethanol with 30 min stirring to form a first solution; adding another solution containing 15 mL ethanol, 3.6 mL deionized water and 8.5 mL acetic acid into the first solution to form a sol; subsequently, adding 30 mL polyoxyethylenesorbitan monooleate (Tween 80, Aldrich) into the sol with vigorous stirring for 6 h to keep homogeneous mixing.

2.2. Preparation of samples

The aluminum foam ingots were fabricated according to the reference [16]. The tubular samples were cut from the ingots into the size of internal diameter 21 mm, external diameter 41 mm and height 35 mm. Then they were cleaned with acetone and deionized water followed by drying in air. The TiO$_2$ coating on aluminum foam (defined as Cat 1) was prepared by a simple dip-coating process and then calcined at 500 °C for 2 h. For comparison, aluminum foam supported Degussa P25 film (Cat 2) was prepared via a wash-coating method, which was conducted by dipping the substrate samples into

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titania slurry with 3 wt.% P25 to obtain the same amount of catalyst to that of Cat 1 after calcinations.

2.3. Characterization of the TiO₂ film

The phase composition, structure and morphology of TiO₂ film were characterized by high resolution-transmission electron microscope (HR-TEM, JEM-2010F) and field-emission scanning electron microscope (FEI Sirion 200). The specific surface area was calculated from the nitrogen adsorption isotherm obtained by the BET method using a micromeritics ASAP 2020 M^{+C}. The size and distribution of pores were evaluated by the density function theory [17].

2.4. Evaluation of activity of photocatalysts

A stable HCHO flow with the concentration of 20 ppm was pumped into a $\phi 45 \times 300$ mm cylindrical reactor at the rate of 1 L/min. There were five uniformly arrayed tubular aluminum foam samples coated with TiO₂ films in the reactor, a 15 W UV light lamp ($\lambda = 365$ nm) was put in the axis center that emitted a light irradiation of approximate 800 μm/cm². The concentration of HCHO in real time was detected by a gas chromatograph equipped with a flame ionization detector and a 2 m stainless steel column (GDX-403). The conversion of HCHO was calculated according to the consumption of HCHO.

3. Results and discussion

3.1. Crystal structure of TiO₂ film

As shown in Fig. 1a, the size of crystalline grain in the TiO₂ film is about 8–10 nm, which is beneficial to the activity of catalyst due to the particle size effect [9,13]. The inserted SAED shows that there is no amorphous diffusion ring, indicating that the TiO₂ film has completely crystallized. From the lattice stripe in Fig. 1b (d = 0.35 nm), it is found that the crystal structure of TiO₂ film presents an anatase type, which has been demonstrated to have better photocatalytic activity compared with other crystal phases [13,15].

3.2. Morphology and textural structure of TiO₂ film

As seen from Fig. 2, the TiO₂ film shows the type IV isotherm with type H3 hysteresis loop, which is the main characteristic of well-defined mesoporous materials [9–12]. It presents large BET surface area (78.1 m²/g), and the average pore diameter is about 12 nm as shown in the inserted figure, which is due to the formation of a mesoporous structure by using Tween 80 as the pore-directing agent. It is consistent with the report that high concentration of surfactant
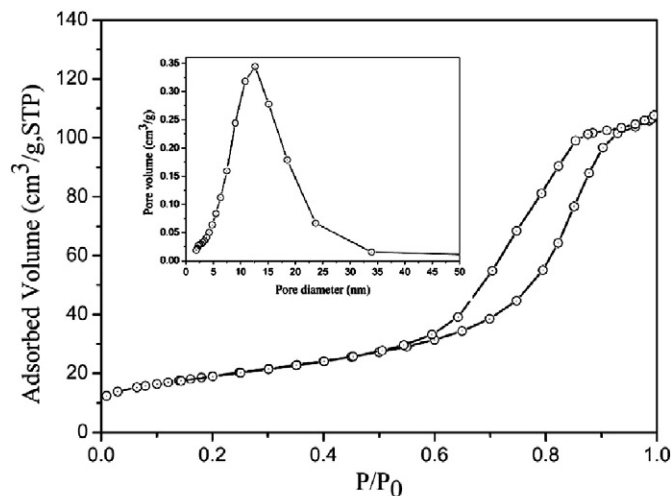

Fig. 2. Nitrogen adsorption–desorption isotherm and pore size distribution of TiO₂ film.

combined with suitable heat treatment can enhance the pore coalescence and multimicellar interactions in the sol–gel and thus lead to high porosity and large pores [12].

Fig. 3a shows the morphology of aluminum foam coated with TiO₂ film, which exhibits a homogeneous feature. From the higher magnification images in Fig. 2b and c, it can be observed that the TiO₂ film is quite smooth and has a thickness of about 3.5 μm. This can be interpreted by the formation of a mesoporous TiO₂ film which generally obeys a S°I° assembling route if a self-assembling sol–gel process and a nonionic surfactant are employed, and thus leads to the formation of a thick frame work, being favorable for improving the structural stability and photocatalytic capacity of TiO₂ film [9,18].

3.3. Photocatalytic activity of TiO₂ film

In order to identify the photocatalytic activity of mesoporous TiO₂ film, aluminum foam supported Degussa P25 film and the bare one without catalyst loading (defined as Cat 3) were also measured in the same condition. Fig. 4 gives the conversion of HCHO in the presence of three samples. It is seen that the Cat 1 has the highest photo-efficiency, where the conversion has reached and saturated 99% after 30 min. The Cat 2 shows about 85% conversion, while the Cat 3 presents less 5% conversion during the whole process, which suggests that the bare aluminum foam or single UV light has little effect on the decomposition of HCHO.
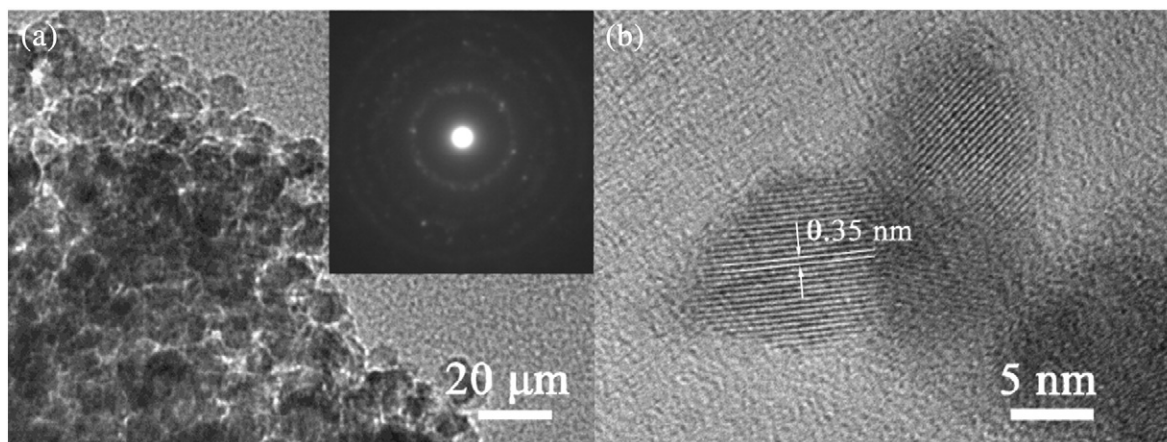

Fig. 1. (a) TEM image of TiO₂ film (inset is SAED); (b) the crystal lattice stripe image of TiO₂ film.
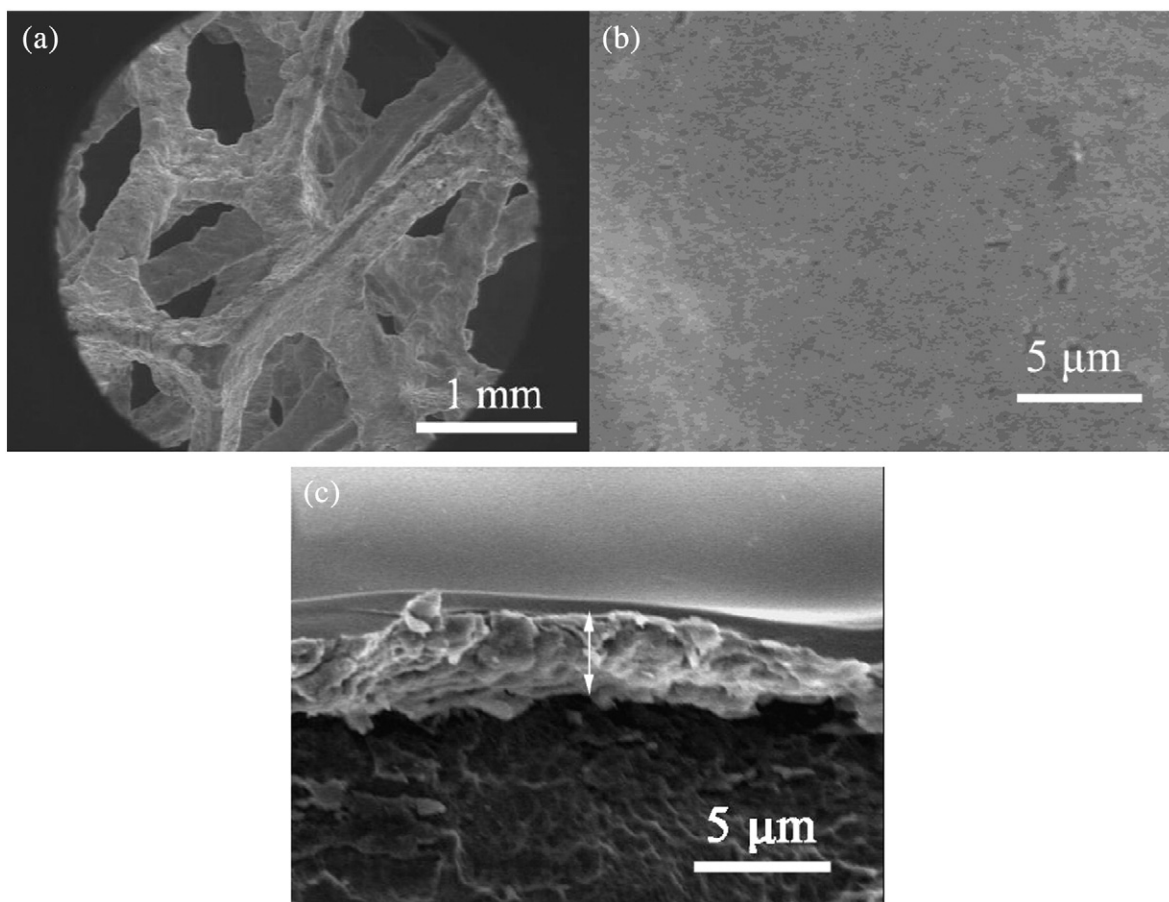
Fig. 3. Surface morphologies of (a) aluminum foam coated with TiO$_2$ film; (b) TiO$_2$ film and (c) the cross-section of the film.

Obviously, the relatively thick and mesoporous structure as well as the small grain size of the TiO$_2$ film are responsible for the high photocatalytic activity. The mesoporous structure not only promotes the mass transfer during the photochemical reaction, but also increases the BET surface area of the film and thus increases the UV light absorbance [19,20]. Moreover, the grain size of 8–10 nm has been proved to be optimal for the photocatalytic activity because it is helpful for the establishment of a balance between the electron–hole recombination rate and active surface area [13].

4. Conclusion

A mesoporous TiO$_2$ film with the grain size of about 10 nm was prepared by a surfactant assisted sol–gel process and dip-coated on the surface of an open-celled aluminum foam. The film shows excellent photocatalytic activity at room temperature, and 99% of formaldehyde was eliminated at the flow rate of 1 L/min.

Fig. 4. Changes of conversion rate of HCHO with reaction time in the presence of different samples.

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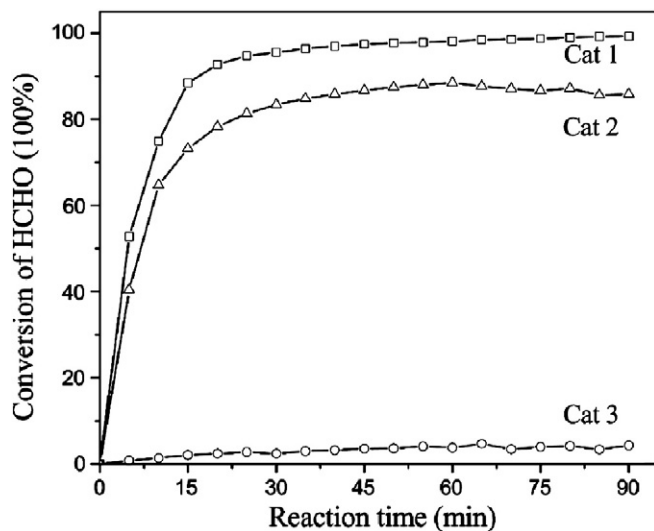[11] Choi H, Sofranko AC, Dionysiou DD. Adv Funct Mater 2006;16:1067–74.

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