I. INTRODUCTION

TiO$_2$ is a semiconducting oxide that has been widely used in photocatalysis because of its photocatalytic activity under ultraviolet irradiation [1,2]. Its application in the purification of water or air has been particularly useful [3]. It is well known that the photocatalytic activity of TiO$_2$ is strongly dependent on its surface area, crystalline structure and synthesis method. A series of methods have been reported to improve the photocatalytic efficiency such as increasing the surface area, crystalline structure and synthesis method. These methods have been used in mesoporous TiO$_2$ to synthesize transitional metal oxides including TiO$_2$. In 1995 mesoporous TiO$_2$ was first synthesized by using this template-directing approach [12]. Since then, many methods have been used in mesoporous TiO$_2$ synthesis using the supramolecular assembly theory. Among these methods, in 1998, Yang created a simple routine for synthesizing mesostructure of TiO$_2$ by using block copolymers as structure-directing agents and TiCl$_4$ as the precursor. This method costs less. In addition, this synthesis method is easy for mesoporous TiO$_2$ films fabrication. However, the report about photocatalytic activity of mesoporous TiO$_2$ prepared by Yang’s method is still rather lacking, and few studies about the roles of surface area and crystallinity of mesoporous photocatalyst have been reported.

In this work, mesoporous TiO$_2$ powders and films with worm-like channels were synthesized by an evaporation-induced self-assembly approach. The as-prepared samples were calcined at different temperature to investigate the effect of calcined temperature on the mesostructure and the photocatalytic activity. Acetaldehyde photodegradation in gas phase was employed to evaluate the photocatalytic activity of mesoporous TiO$_2$. Results showed that all the calcined powder samples exhibited higher photocatalytic activities than that of Degussa P25. The sample calcined at 400°C, which showed higher activity than other samples, possessed a homogeneous pore diameter of about 6.0 nm and an 11.0 nm crystalline anatase pore wall, as well as large surface area of 117 m$^2$/g. It was speculated that two factors of surface area and crystallinity affected the photocatalytic activity of mesoporous TiO$_2$ photocatalyst. The mesoporous TiO$_2$ films fabricated by spin-coating also had high photocatalytic activities.

Key words: Mesoporous TiO$_2$, Photocatalysis, Acetaldehyde, Photodegradation

ARTICLE

Photocatalytic Degradation of Acetaldehyde on Mesoporous TiO$_2$: Effects of Surface Area and Crystallinity on the Photocatalytic Activity

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Mesoporous TiO$_2$ powder and films with worm-like channels were synthesized by an evaporation-induced self-assembly approach. The as-prepared samples were calcined at different temperature to investigate the effect of calcined temperature on the mesostructure and the photocatalytic activity. Acetaldehyde photodegradation in gas phase was employed to evaluate the photocatalytic activity of mesoporous TiO$_2$. Results showed that all the calcined powder samples exhibited higher photocatalytic activities than that of Degussa P25. The sample calcined at 400°C, which showed higher activity than other samples, possessed a homogeneous pore diameter of about 6.0 nm and an 11.0 nm crystalline anatase pore wall, as well as large surface area of 117 m$^2$/g. It was speculated that two factors of surface area and crystallinity affected the photocatalytic activity of mesoporous TiO$_2$ photocatalyst. The mesoporous TiO$_2$ films fabricated by spin-coating also had high photocatalytic activities.

Key words: Mesoporous TiO$_2$, Photocatalysis, Acetaldehyde, Photodegradation

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spin-coating and calcined at different temperatures, and their photocatalytic activity was investigated.

II. EXPERIMENTS

A. Preparation of catalyst

The synthesis of mesoporous TiO$_2$ was similar to the route reported by Yang which is a general synthesis routine for trans-metal oxide mesostructure [15]. In a typical synthesis, 1 g of pluronic P123 (EO$_{70}$PO$_{70}$EO$_{70}$, M$_{av}$ = 5800, Aldrich) was dissolved in 10 g of absolute ethanol, then 0.01 mol of TiCl$_4$ was added with vigorous stirring for 0.5 h. The resulting sol solution was gelled in an open Petri dish at 40 °C oven for 4 days (static state). The as-made bulk samples were then calcined at 400, 500, and 600 °C for 5 h in air with the heating ramp of 3 °C/min to remove the surfactant. The calcined samples were labeled as MT400, MT500, and MT600 according to the calcination temperatures, respectively. The films were fabricated by spin-coating and MT600 according to the calcination temperatures, respectively. The films were fabricated by spin-coating at 800 r/min for 3 s and then 3000 r/min for 10 s. The films were calcined at 400, 500, and 600 °C for 1 h in air with the heating ramp of 3 °C/min.

B. Structure characterization

Both small-angle X-ray powder diffraction (SAXRD) and wide-angle X-ray powder diffraction measurements were performed on a Rigaku Ultima III X-ray diffractometer using Cu K$_\alpha$ radiation(λ=1.5406 Å). Nitrogen adsorption-desorption isotherms were collected on a Micromeritics Tristar-3000 surface area and porosity analyzer at 77 K after the sample had been degassed in a flow of N$_2$ at 180 °C for 5 h. The BET surface area was calculated from the linear part of the BET plot ($P/P_0$=0.1-0.25). Total pore volume was taken from the volume of N$_2$ adsorbed at $P/P_0$=0.995. Average pore diameter was estimated using the desorption branch of the isotherm and the Barrett-Joyner-Halenda (BJH) formula. The pore size distribution plots are obtained by using the BJH model. The UV-Vis diffuse reflectance spectrum was measured on a UV-Vis spectrometer (UV-2550, Shimadzu). High-resolution transmission electron micrographs (HRTEM) were obtained by employing a TECNAI G$^2$ F20 high-resolution transmission electron microscope with a 200 kV accelerating voltage. The samples for TEM were prepared by dispersing the final powders in ethanol and the dispersion was dropped on carbon-copper grids.

C. Photocatalytic properties

The photocatalytic activity experiments on the mesoporous TiO$_2$ for the oxidation of acetaldehyde in air were performed at room temperature using a gas-closed system with a quartz window. In a typical process, 0.1 g of mesoporous TiO$_2$ powders was placed on a 4-cm$^2$ glass groove. The glass with powder photocatalyst (or films) was then put into a 224 mL reactor, which was filled with air to one atmospheric pressure. For comparing the effect of different treatment temperatures on mesoporous TiO$_2$ photocatalytic activity, acetaldehyde (10 µL of 40% CH$_3$CHO aqueous solution) was injected into the reactor to generate a high-concentration acetaldehyde gas. The optical system for the catalytic reaction utilized a 300 W Xe arc lamp (focused through a shutter window). The light irradiated the photocatalyst through a quartz window. In addition, a gas pump was used for accelerating gas diffusion. CO$_2$ and acetaldehyde were detected by GC (CO$_2$, GC-8A with TCD detector, shimadzu; acetaldehyde, GC-14B with FID detector, shimadzu).

III. RESULTS AND DISCUSSION

A. Structural and compositional analysis

The SAXRD pattern of the as-prepared sample shows an obvious peak at high d-spacing which indicates an ordered supramolecular templated inorganic structure. But, no obvious peaks are observed for all calcined samples, indicating that the formation of less ordered mesoporous structures (see supplementary materials). The wide-angle XRD of mesoporous TiO$_2$ calcined at different temperatures were performed (shown in Fig.1). The diffraction peaks in the 2θ range of 20°-75° can be indexed to a pure anatase phase (JCPDS, No.21-1272) for TiO$_2$ with a body centered tetragonal crystalline structure for all samples. Average crystal sizes calculated by Scherrer equation from the broadening of the (101) XRD peak of anatase phase are 11.0 and 14.2 nm for mesoporous TiO$_2$ calcined at 400 and 500 °C, respectively. Because of the growth of the grains, the crystal size of TiO$_2$ increased to 18.3 nm after calci-
TABLE I Physicochemical properties of mesoporous TiO$_2$ powders calcined at different temperatures

<table>
<thead>
<tr>
<th>Calcined temperature/°C</th>
<th>Crystal size/nm</th>
<th>Surface area/(m$^2$/g)</th>
<th>D-BJH/nm</th>
<th>$V_{\text{total}}$/cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>11.0(0.3)</td>
<td>117</td>
<td>6.0</td>
<td>0.2413</td>
</tr>
<tr>
<td>500</td>
<td>14.2(0.2)</td>
<td>78</td>
<td>7.8</td>
<td>0.2080</td>
</tr>
<tr>
<td>600</td>
<td>18.3(0.2)</td>
<td>43</td>
<td>8.0</td>
<td>0.1236</td>
</tr>
</tbody>
</table>

FIG. 2 Barret-Joyner-Halenda (BJH) pore size distribution plots (a) and $N_2$ adsorption-desorption isotherms of mesoporous TiO$_2$ calcined at different temperatures (b).

nation at 600 °C (Table I). It is well known that the growth of nanocrystal usually leads to the collapse of the mesoporous framework, which broadens the diameter distribution of channels. Also, titania has a rather low nucleation-to-growth rate, making the nanoparticles grow to a diameter of 10-20 nm [16]. Compared with the report of Yang [15], the results indicate that the samples were over calcined, which changed the narrow distribution of channels. But, the over calcination is beneficial to remove the surfactant completely.

The pore size distributions and $N_2$ adsorption-desorption isotherms of mesoporous TiO$_2$ calcined at different temperatures are shown in Fig.2. All the isotherms reveal stepwise adsorption and desorption (type IV isotherms), which is characteristic of mesoporous materials. The porosity of these mesoporous materials gradually decreases when the calcination temperature increased (Fig.2(b)). The pore-size distribu-

FIG. 3 Plots of $\alpha^{1/2}$ versus photon energy (a) and UV-Vis absorbance spectra (b) of mesoporous TiO$_2$ calcined at 400, 500, and 600 °C.

tion plot shows that the sample calcined at 400 °C exhibits a mean pore diameter of 6.0 nm with a narrow distribution. This narrow pore size distribution remained after calcination at 500 °C with a slight increase in pore size (7.8 nm). However, further heating at 600 °C increased the average pore size to 8.0 nm with a broadened pore size distribution. Moreover, both surface area and pore volume of the MT600 decreased dramatically.

The BET surface area and pore volume are summarized in Table I. The BET surface area and mesopore volume of the materials were relatively high (117 m$^2$/g, 0.24 cm$^3$/g) when the sample was calcined at 400 °C. At an elevated temperature of 600 °C, they decreased to 43 m$^2$/g and 0.12 cm$^3$/g, respectively. This is an indication of collapse of the pore wall.

Figure 3(a) shows the band gap energies estimated from the $(\alpha h\nu)^{1/2}$ versus photon energy plots and UV-Vis spectrum (Fig.3(b)). The band gap spectrum is transformed from the UV-Vis spectrum based on the

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following equation [17-19]:

$$\alpha(\nu) = A(\hbar\nu - E_g)^n$$  \hspace{1cm} (1)

where $\alpha$, $\nu$, $E_g$, and $n$ are the absorption coefficient, incident light frequency, band gap and constant, respectively, for an allowed indirect optical transition $n=2$. The band gap was determined by extrapolating the linear part of the plot to $\alpha^{1/2}=0$. The results show that the band gap of MT500 ($3.16 \text{ eV}$) is slightly larger that of MT600 ($3.12 \text{ eV}$). This may be due to the pore walls growth of mesoporous TiO$_2$ with increasing thermal treatment temperature because of the quantum size effect. The band gap of MT400 is $3.15$ eV, which is very close to the band gap energy of MT500. This may mainly result from the slight amount of remaining carbon because of low calcination temperature. To sum up, no obvious difference in light absorption can be seen for the different calcination temperature samples.

In order to observe the mesostructure directly, TEM and HRTEM were performed. In the TEM images of MT400, the mesoporous TiO$_2$ shows a wormhole-like mesostructure without long-range order on the edges of the sample (Fig.4(a)), in good agreement with the SAXRD result. In the HRTEM images (Fig.4(b)) of the same sample, anatase nanocrystals (lattice $d_{(101)}=3.5$ Å) are clearly observed to be embedded in the channel walls. These nanocrystals connect with one another to form crystalline framework walls of the mesopore.

B. Photocatalytic performances

Acetaldehyde is known as a key indoor air pollutant and is also largely formed as an intermediate during photocatalytic oxidation of other organic compounds. Figure 5 shows the increasing rate of carbon dioxide produced from the photocatalytic degradation of acetaldehyde on MT400, MT500, MT600 and Degussa P25 under UV light irradiation. The increasing CO$_2$ product coming from the acetaldehyde oxidation in the photocatalytic reactor can be depicted in the following equation.

$$2\text{CH}_3\text{CHO} + 5\text{O}_2 \rightarrow \text{4CO}_2 + 4\text{H}_2\text{O}$$  \hspace{1cm} (2)

For comparison, 0.1 g of SiO$_2$ was placed into photocatalytic reactor and tested under the same conditions as that of mesoporous TiO$_2$, no increase of CO$_2$ concentration was observed. This proves that the produced CO$_2$ comes from the photodecomposition of acetaldehyde on mesoporous TiO$_2$.

As expected, the calcination temperature affected the photocatalytic activity of TiO$_2$ to oxidize acetaldehyde in a gas-phase medium. The results show that all the mesoporous TiO$_2$ calcined at different temperatures exhibit higher photocatalytic activities than Degussa P25.
(surface area: 50 m²/g), and the activities of mesoporous TiO₂ were gradually decreased with increasing calcination temperature up to 600 °C. The increasing rates of carbon dioxide on the UV-irradiated TiO₂ were 5.67, 5.41, and 4.93 µmol/min for MT400, MT500, and MT600, respectively. Because of the adsorption of acetaldehyde on TiO₂ photocatalyst, the decreasing rate of acetaldehyde was less than half of the increasing rate of carbon dioxide. After 18 min photocatalytic reaction, the photocatalytic conversion rates of acetaldehyde to carbon dioxide were 58%, 55%, 49%, and 32% for MT400, MT500, MT600, and Degussa P25, respectively.

Analyses of the photocatalytic activities of mesoporous TiO₂ films calcined at 400, 500, and 600 °C were performed. After being irradiated by full-arc Xe lamp light for 17 h, the mesoporous TiO₂ films can significantly decompose acetaldehyde to produce CO₂. Similar with mesoporous TiO₂ powder, the photocatalytic activities of mesoporous TiO₂ films were gradually decreased with increasing sintering temperature up to 600 °C. In view of the tiny mass of mesoporous TiO₂, the films also exhibit a high photocatalytic activity. The increased rates of CO₂ concentration in the gas-closed system were 31.20, 27.30, and 19.80 µmol/m²·min for the films calcined at 400, 500, and 600 °C, respectively.

As is well known, photocatalytic reaction is carried out on the surface of photocatalyst. The larger the surface area of the photocatalyst is, the more reaction sites are, which is in favor of the activity. Crystallinity is another important factor to influence the photocatalytic activity because a poorly crystallized crystal with defects always leads to the recombination of photogenerated electrons and holes at defect positions [21,22]. Since there is no obvious difference in photoabsorption for mesoporous TiO₂ calcined at 400, 500, and 600 °C. The high photocatalytic performances of MT400 may be rationalized from their pore-wall structure as well as a large surface area that offers more active sites for carrying out catalytic reactions. Though the surface area of MT500 was decreased remarkably, the photocatalytic activity of MT500 is similar to that of MT400. This could be due to the better crystallinity of MT500 compared to MT400. Therefore, it is speculated that both surface area and crystallinity directly affect the photocatalytic activities of mesoporous TiO₂. For obtaining high photocatalytic activity of mesoporous materials, enhancing surface area and crystallinity is significant. However, this is a trade-off situation for the synthesis of mesoporous photocatalyst because the high crystallinity usually leads to the collapse of channels which decreases the surface area [16]. Therefore, there is an optimum calcination temperature, which results in the optimum balance of surface area and crystallinity of photocatalyst. The photocatalytic activity of mesoporous TiO₂ calcined at 400 °C is the highest in all samples, indicating that 400 °C may be very close to the optimum. Actually, many factors affect the activity and selectivity of photocatalysts, such as surface structure, surface defects, surface disorder, and surface charge [23,24]. It is necessary to investigate the factors related to photocatalytic activity in further experiments.

IV. CONCLUSION

Mesoporous TiO₂ materials with worm-like channels were successfully synthesized using an EISA method. The structures, morphologies, compositions, optical properties and photocatalytic activities of the products were characterized. All the calcined mesoporous anatase TiO₂ exhibited higher photocatalytic activity than Degussa P25 in photodegradation of gas phase acetaldehyde. The photocatalytic activity of mesoporous TiO₂ gradually decreased with the increase of calcination temperature. The mesoporous TiO₂ films fabricated by spin-coating also have high photocatalytic activities. In synthesizing mesoporous TiO₂ photocatalyst, two factors of surface area and crystallinity both affect the photocatalytic activity. 400 °C calcined temperature is the optimum temperature for the balance of...
surface area and crystallinity.

V. ACKNOWLEDGMENTS

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