Enhanced Photocatalytic Activity of TiO₂ Powders (P25) via Calcination Treatment

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1. Introduction

A number of investigations have focused on the semiconductor photocatalyst for its applications in solar energy conversion and environmental purification since Fujishima and Honda discovered the photocatalytic splitting of water on the TiO₂ electrodes in 1972 [1, 2]. Among various oxide semiconductor photocatalysts, titania has been proven to be the most suitable for widespread environmental applications for its biological and chemical inertness, strong oxidizing power, cost effectiveness, and long-term stability against photo- and chemical corrosion [3–6]. However, the practical applications of TiO₂ are greatly limited due to the wide band-gap (anatase ca. 3.2 eV, rutile ca. 3.0 eV) and the resultant low utilization of solar energy and fast recombination of photogenerated electrons and holes [7–9]. Therefore, the photocatalytic activity of titania must be further enhanced from the point of view of practical use and commerce. Many methods have been developed for enhancing the efficiency of the TiO₂ powders. These include doping with metal and nonmetal elements [10–13], dye sensitization [14, 15], and semiconductor coupling [16, 17], and so forth.

It is wellknown that the photocatalytic activity of TiO₂ system mainly depends on its intrinsic properties, such as phase structures, specific surface area, crystallinity, and preparing methods [18]. For example, many studies have confirmed that the anatase phase of titania is a good photocatalytic material due to its low recombination rate of photogenerated electrons and holes [19, 20]. In our previous observations, it was found that the composite of two phases of titania was more beneficial for suppressing the recombination of photogenerated electrons and holes and thus enhanced the photocatalytic activity [21]. In addition, a posttreatment condition is also another important factor that influences the photocatalytic activity of TiO₂ powders. Usually, two principle posttreatment methods have been used to control the physicochemical properties of the TiO₂ powders. One is hydrothermal treatment. Yu et al. [22] demonstrated an obvious increase of photocatalytic activity after hydrothermal treatment of TiO₂ (P25) and thought that the increase in photoactivity can be attributed to the formation of more hydroxyl groups in the surface of TiO₂. Another method is calcination after treatment. By changing the calcination conditions, such as calcination temperatures,
calcination time, and heating rate crystalline products with different compositions, structures, and morphologies have been obtained. Yu et al. suggested that thermal treatment could allow more oxygen molecules to be adsorbed on the surface of TiO₂ [23]. Sato et al. and Zhang et al. thought that an enhancement in photocatalytic activity was ascribed to the fact that the calcination released lattice oxygen from TiO₂ [24, 25]. However, to the best of our knowledge, few studies have been carried out on the synergistic effect of the phase structure, BET surface area, and crystallinity on the photocatalytic activity of TiO₂ powders (P25) after calcination. In the present work, we prepared highly active TiO₂ powder photocatalyst via calcination after treatment of Degussa P25. The photocatalytic activity of the as-prepared TiO₂ powders was evaluated by the photocatalytic oxidation of methyl orange aqueous solution under UV light irradiation in air. The reasons for the enhanced photocatalytic activity of the calcinations-treated TiO₂ samples were discussed.

2. Experimental Section

2.1. Sample Preparation. Commercial Degussa P25 TiO₂ was used as supplied. In a typical calcination process, 1.0 g of P25 powder was transferred into a 30 mL crucible, followed by calcination at 400–800°C in a muffle furnace for 4 h. After the thermal treatment, the crucible containing catalysts was cooled to room temperature to obtain the as-synthesized TiO₂ powders. The calcined P25 and untreated Degussa P25 samples were characterized for evaluating the changes in properties.

2.2. Characterization. The X-ray diffraction (XRD) patterns obtained on an X-ray diffractometer (type D8 ADVANCE) using Cu-Kα irradiation at a scan rate (2θ) of 0.02° s⁻¹ were used to determine the identity of any phase present and their crystallite size. The accelerating voltage and the applied current were 15 kV and 20 mA, respectively. If the sample contains anatase and rutile phases, the phase content of titania can be calculated from the integrated intensities of anatase (101) and rutile (110) peaks, according to the following equation [22]:

\[ f_R = \frac{1.26 I_R}{I_A + 1.26 I_R} \]

where \( I_A \) and \( I_R \) represent the integrated intensity of the anatase (101) and rutile (110) peaks, respectively. With (1), the phase contents of anatase and rutile in TiO₂ samples can be calculated. The average crystallite sizes of anatase and rutile were determined according to the Scherrer equation. Crystallite sizes and shapes were observed using transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) (JEOL-2010F at 200 kV). The samples for TEM observation were prepared by dispersing the TiO₂ powders in an absolute ethanol solution under ultrasonic irradiation; the dispersion was then dropped on carbon-copper grids. The Brunauer-Emmet-Teller surface area (\( S_{BET} \)) of the powders was analyzed by nitrogen adsorption in a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). All the samples were degassed at 180°C prior to nitrogen adsorption measurements. The BET surface area was determined by multipoint BET method using the adsorption data in the relative pressure (\( P/P_0 \)) range of 0.05–0.3. Desorption isotherm was used to determine the pore-size distribution via the Barret-Joyner-Halender (BJH) method, assuming a cylindrical pore modal [26–28]. The nitrogen adsorption volume at the relative pressure (\( P/P_0 \)) of 0.994 was used to determine the pore volume and average pore size. The morphologies of TiO₂ powders were observed using scanning electron microscopy (SEM) (type JSM-7001F, Japan) with an acceleration voltage of 20 kV. Infrared (IR) spectra on pellets of the samples mixed with KBr were recorded on a Nicolet 5700 FTIR spectrometer at a resolution of 0.09 cm⁻¹. The concentration of the samples was kept at about 0.25–0.3%.

2.3. Measurement of Photocatalytic Activity. The photocatalytic activity evaluation of TiO₂ powders for the photocatalytic decolorization of methyl orange aqueous solution was performed at ambient temperature. The detailed experimental process can be found in our previous studies [5]. The photocatalytic decolorization of methyl orange aqueous solution is a pseudo-first-order reaction and its kinetics may be expressed as \( \ln(c_0/c) = kt \), where \( k \) is the apparent rate constant, and \( c_0 \) and \( c \) are the adsorption-desorption equilibrium and reaction concentrations of aqueous methyl orange, respectively.

3. Results and Discussion

3.1. Phase Structure. The effect of calcination temperature on phase structures was studied using XRD. Figure 1 shows the XRD patterns of P25 powders before and after calcination at different temperatures for 4 h. It can be seen that all the samples were composed of both rutile and anatase phases. Further observation shows that with increasing calcination temperature form 400 to 500°C, the intensity of both anatase and rutile peaks gradually increases, indicating an enhancement of crystallization. With further increasing temperature from 600 to 800°C, the intensities of anatase diffraction peaks decreased gradually and ultimately disappeared, and meanwhile the intensities of rutile diffraction peaks steadily became stronger. Therefore, the calcination temperature obviously influences the crystallization and phase composition of the P25 powders. The effects of calcination temperatures on physical properties of P25 TiO₂ powders are shown in Table 1. It can be seen that the mass fraction of rutile phase slightly increases with increasing calcination temperature. Before calcination, the mass fraction of rutile was ca. 27.3%. At 700°C, the content of rutile reached ca. 90.8%. No anatase phase was detected at 800°C, which is in good agreement with results in the literature [29]. Therefore, it is reasonable to suggest that high calcination temperature results in the phase transformation from anatase to rutile. Usually, phase transformation is accompanied with crystal growth.
Table 1: Effect of temperature on physicochemical properties of TiO₂ samples.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phase content</th>
<th>Crystalline size (nm)</th>
<th>S_{BET} (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>A: 72.7; R: 27.3</td>
<td>29.5</td>
<td>45.7</td>
<td>0.177</td>
<td>7.57</td>
<td>41.5</td>
</tr>
<tr>
<td>400</td>
<td>A: 72.7; R: 27.3</td>
<td>31.7</td>
<td>25.9</td>
<td>0.0929</td>
<td>8.24</td>
<td>27.1</td>
</tr>
<tr>
<td>500</td>
<td>A: 66.4; R: 33.6</td>
<td>33.8</td>
<td>22.7</td>
<td>0.0597</td>
<td>10.7</td>
<td>19.4</td>
</tr>
<tr>
<td>600</td>
<td>A: 55.2; R: 44.8</td>
<td>48.6</td>
<td>18.7</td>
<td>0.0503</td>
<td>10.5</td>
<td>17.0</td>
</tr>
<tr>
<td>700</td>
<td>A: 9.8; R: 90.2</td>
<td>63.2</td>
<td>8.59</td>
<td>0.0177</td>
<td>14.4</td>
<td>7.00</td>
</tr>
<tr>
<td>800</td>
<td>R: 100</td>
<td>99.0</td>
<td>4.39</td>
<td>0.00831</td>
<td>15.5</td>
<td>3.45</td>
</tr>
</tbody>
</table>

Calcination time: 4 h

A and R denote anatase and rutile, respectively. Average crystalline size of TiO₂ was determined by XRD using Scherrer equation. The BET surface area was determined by multipoint BET method using the adsorption data in P/P₀ range from 0.05 to 0.3. Pore volume and average pore size were determined by nitrogen adsorption volume at P/P₀ = 0.994. The porosity is estimated from the pore volume determined using the desorption data at P/P₀ = 0.994.

As the calcination temperature is raised, XRD reflections corresponding to both the anatase and rutile phase become narrower, which indicates the increase of crystallite size. The average crystallite size was shown in Table 1. The average crystallite size of samples treated at lower temperature (below 500 °C) increased slightly from about 29.5 to 33.8 nm (see Table 1). However, higher temperature caused rapid increase of crystallite size up to about 63.2 and 99 nm for samples calcined at 700 and 800 °C, respectively. The similar results were observed by Görsk et al. [30] for five different samples of TiO₂ calcinated at 400–750 °C.

3.2 FT-IR. The preparation methods and conditions could affect the hydroxylation state of titania powders. The FT-IR spectroscopy of the P25 before and after calcination treatment of 4 h is shown in Figure 2. It is believed that the broad peak at 3400 and the peak at 1650 cm⁻¹ correspond to the surface-adsorbed water and hydroxyl groups, respectively. The main peak at 400–700 cm⁻¹ was attributed to Ti-O stretching and Ti-O-Ti bridging stretching modes [31]. Notably, with increasing temperature, the surface-adsorbed water and hydroxyl groups decreased slightly. This was due to the decrease of specific surface areas and pore volume (as shown in Table 1), which caused the reduction of the adsorbed water [32]. According to our previous study, the hydroxyl groups on the surface of samples contribute to enhancement of the photocatalytic activity [33], because they can interact with photogenerated holes, which gives better charge transfer and inhibits the recombination of electron-hole pairs [34, 35].
3.3. UV-Vis Spectra. Usually, calcination temperature obviously affects light absorption characteristics of TiO₂ [36–38]. The influences of temperature on the light absorption characteristics of TiO₂ powders are shown in Figure 3. A significant increase at wavelengths shorter than 420 nm could be attributed to absorption of light caused by the excitation of electrons from the valence band to the conduction band of TiO₂. A red shift of the absorbance spectra of TiO₂ powders calcined at 500 and 700°C in the band gap transition was observed as compared with the uncalcined P25 powders. The differences in adsorption were attributed to the change of crystallite size and phase structure (see Table 1).

The adsorption edges shifted toward longer wavelengths for the powders after calcination at 500 and 700°C. This clearly indicated a decrease in the band gap energy of TiO₂. To further explore the effect of calcination temperature on the absorption edge, the band gap energy can be estimated from a plot of \((h\nu\alpha)^1/2\) versus photon energy \((h\nu)\). The intercept of the tangent to the plot will give a good approximation of the indirect band gap energy for TiO₂. The relation between the absorption coefficient \(\alpha\) and incident photon energy \((h\nu)\) can be written as \(\alpha = B_i(h\nu - E_g)^{1/2}/h\nu\), where \(B_i\) is absorption constants for indirect transitions [39–41]. Since absorbance \((A)\) is proportional to absorption coefficient \(\alpha\), we use absorbance \((A)\) to substitute absorption coefficient \(\alpha\) [40].

Plots of \((h\nu\alpha)^2\) versus photon energy \((h\nu)\) for TiO₂ powders are shown in Figure 4. The band gap energies estimated from the intercept of the tangents of the plots are 3.37, 3.25, and 3.10 eV for the P25 powders before and after calcination at 500 and 700°C for 4 h, respectively. This showed that the band gap of TiO₂ samples monotonically became narrower with increasing calcinations temperatures. This may be due to the following factors: (1) an increase in the crystallite size resulted in the decrease of band gap energy, which was in accordance with previous results reported by Xiao et al. [42]; (2) lower value of band gap for samples after calcination at 500 and 700°C may be a result of phase transformation from anatase to rutile [30].

3.4. BET Surface Areas and Pore Distribution. Figure 5 shows nitrogen adsorption-desorption isotherms of the P25 powders before and after calcination at 500 and 700°C. It can be seen that all the samples show a type H3 hysteresis according to BDDT classification [26], indicating the presence of mesopores (2–50 nm). Moreover, the observed hysteresis loops of the obtained samples are difficult to be observed, suggesting the presence of large pores (>50 nm) [43, 44]. Further observation indicates that with increasing calcination temperature, the hysteresis loops shift to higher relative pressure range and the areas of the hysteresis loops decrease. This indicated that the average pore size increased and the volume of pore decreased with increasing calcination temperatures [45]. When the calcination temperature is higher than 700°C, the hysteresis loops of the obtained samples are difficult to be observed, indicating that some pores collapse during the calcination. The pore size distribution calculated from the desorption branch of the isotherm is presented.
in Figure 6. It can be seen that calcination temperature significantly influences the pore size distribution of the TiO$_2$ powders. Before calcination, the P25 TiO$_2$ has a wide pore size distribution from mesopore to macropore. With increasing calcination temperatures, the curves of the pore size distribution shift to the macropore region and the pore volumes decrease slowly. At 700°C, the pore size distribution becomes even, indicating the disappearance of pores [6]. Usually, the average pore size is connected with the TiO$_2$ crystallite size and the average pore size increased with an increase in the crystallite size of TiO$_2$ powders [21, 22, 46, 47]. Accordingly, the decrease of pore volume located at 2–10 nm for the calcined P25 powders indicated the decrease of smaller TiO$_2$ crystallites (<10 nm). This is in good agreement with the XRD analysis in which smaller anatase crystallites were transformed into rutile phase. Table 1 shows the physical properties of the P25 powders before and after calcination treatment at different temperatures for 4 h. Before calcination treatment, P25 TiO$_2$ shows a large BET-specific surface area, and its value reaches 45.7 m$^2$/g. After calcination treatment above 400°C, the BET-specific surface areas of the P25 samples clearly decrease. Further observation shows that with increasing calcination temperatures, the BET-specific surface areas, pore volumes, and porosity steadily decrease; meantime, the average pore size increases.

3.5. **SEM and TEM.** The calcination process also affects the morphologies of the resulting P25 TiO$_2$ powders. Figure 7 shows SEM images of the P25 TiO$_2$ powders before and after calcination treatment at 400, 500, and 700°C for 4 h. It can be seen from Figure 7(a) that before calcination treatment, the powders are smaller aggregated particles, resulting in a high porous volume due to aggregation among tiny TiO$_2$ particles (see Figure 6). Conversely, after calcination treatment, the powders are composed of larger agglomerated particles. This may be caused by the phase transformation from anatase to rutile, resulting in the decrease in the pore volume (as shown in Table 1). It is interesting to observe from Figure 7 that with increasing calcination temperature from 400 to 700°C, the particle sizes of the aggregates gradually increase. This may be ascribed to the fact that the interaction of smaller particles results in their aggregation into many spherical particles with bigger sizes. The morphology and microstructures of P25 TiO$_2$ powders are further investigated by TEM and HRTEM analysis. Figure 8(a) shows a typical TEM image of the TiO$_2$ powders after calcination at 500°C for 4 h. It can be seen that the particles exhibit a relatively uniform particle size distribution. The average size of the primary particles estimated from the TEM image is about 35 nm, which is in good agreement with that calculated from the XRD pattern using Scherrer equation (33.8 nm). Further observation indicates that a large number of mesopores come from the aggregation of primary particles or crystallites. Figure 8(b) presents a typical HRTEM lattice image of the TiO$_2$ nanoparticles after calcination at 500°C for 4 h. The selected area electron diffraction (SAED) patterns (inset in Figure 8(b)) reveal the polycrystalline nature of the anatase and rutile phases for the P25 TiO$_2$ powders. By measuring the lattice fringes, the resolved interplanar distances are ca. 0.35 and 0.33 nm, corresponding to the (101) planes of anatase and the (110) planes of rutile, respectively. This further confirms the mixed biphase structures of the sample after calcination at 500°C for 4 h.

3.6. **Photocatalytic Activity.** The photocatalytic activity of the P25 TiO$_2$ before and after calcination at various temperatures was evaluated by photocatalytic oxidation of methyl orange (MO) aqueous solution under UV light irradiation in air. Figure 9 shows the relationship between the apparent rate constants ($k$) of MO degradation and calcination temperatures. Prior to calcination, the P25 TiO$_2$ showed high photocatalytic activity with a rate constant of $6.02 \times 10^{-3}$, which is a well known and recognized as an excellent photocatalyst. It has been reported that the P25 TiO$_2$ photocatalyst consists of an amorphous state together with a mixture of anatase and rutile [48]. Further observation indicates that the calcined sample at 400°C for 4 h shows a higher photocatalytic activity with a rate constant of $10.2 \times 10^{-3}$. This may be due to the fact calcination treatment enhanced the phase transformation of the P25 TiO$_2$ powders from amorphous to anatase. The rate constants increase with increasing calcination temperatures. The enhancement of photocatalytic activity at elevated calcination temperatures can be ascribed to an obvious improvement in anatase crystallinity (as shown in Figure 1). At 500°C, the $k$ reaches the highest value of $12.1 \times 10^{-3}$. With further increasing the calcination temperature, the $k$ decreases slightly. This is due to the decrease in specific surface areas and the content of anatase (as shown in Table 1). The highest photocatalytic activities of the calcined samples at 500°C might be explained by the optimal mass ratio of rutile to anatase.

Generally, photocatalytic activity of mesoporous TiO$_2$ is strongly dependent on its phase structure, crystallite size, surface areas, and pore structure. Larger specific surface area allows more organic reactants to be absorbed onto the surface of the photocatalyst, while higher pore volume results
in a rapider diffusion of various inorganic products during the photocatalytic reaction. Therefore, it is expected that the uncalcined sample exhibits a relative high photocatalytic activity due to its large specific surface areas and pore volume. However, the powders with a large surface area are usually associated with large amounts of crystalline defects or weak crystallization, which favor the recombination of photogenerated electrons and holes, leading to a poor photoactivity. Therefore, the large surface area is a requirement, but not a decisive factor. It is well known that the mixture of anatase and rutile TiO₂ has higher degradation efficiency than pure anatase for the oxidation of various organic compounds [48–50]. Moreover, the content of rutile has played important role in photocatalytic reaction. For example, Bacsa et al. found that the catalyst with 30% rutile content showed a maximum catalytic activity for the photocatalyzed degradation of p-coumaric acid [51]. It was reported the TiO₂ powders containing 77% anatase and 23% rutile had highest photocatalytic activity in degradation of 4-chlorophenol [52]. Thus, the mass ratio of rutile to anatase is another important factor that influences the photocatalytic efficiency [53, 54]. In our present work, the uncalcined P25 powders possess a large specific surface area of 45.7 m²/g. After calcination at 500°C, the specific surface areas decrease to 22.7 m²/g. Such a large decrease in specific surface area should lead to a decrease in the photocatalytic activity. However, the 500°C sample shows the highest photocatalytic activity. The increase of photocatalytic activity at 500°C might be due to the enhancement of anatase crystallization and increase of rutile content in photocatalysts (as shown in Figure 1 and Table 1). The former is beneficial to reduce the recombination rate of the photogenerated electrons and
holes due to the decrease in number of the defects. The latter can enhance the transfer and separation of photogenerated electrons and holes, implying that the mass ratio of rutile to anatase also obviously influences photocatalytic activity and an optimal rutile-to-anatase mass ratio is probably ca. 1:2 according to our results. According to the aforementioned deduction, it is not difficult to explain that the 700 and 800°C samples show a lower photocatalytic activity than the 500°C sample due to the increase of rutile content in photocatalysts.

4. Conclusion

Calcination treatment exhibits a marked influence on the microstructures and photocatalytic activity of the P25 TiO₂ powders. With increasing calcination temperature, the average crystallite size, average pore size, and rutile content increase. In contrast, the BET-specific surface areas, pore volumes, and porosity steadily decrease. The synergistic effect of the phase structure, BET surface area, and crystallinity on the photocatalytic of TiO₂ powders (P25) after calcination was investigated. An optimal calcination temperature (500°C) was determined. The photocatalytic activity of TiO₂ powders at an optimal calcination temperature was nearly 2 times higher than that of the uncalcined P25 TiO₂. The highest photocatalytic activities of the calcined samples at 500°C for 4 h might be ascribed to the enhancement of anatase crystallization and the optimal mass ratio (ca. 1:2) of rutile to anatase.

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