The hydrothermal synthesis of mesoporous TiO$_2$ with high crystallinity, thermal stability, large surface area, and enhanced photocatalytic activity

Dong Suk Kim, Seung-Yeop Kwak*

School of Materials Science and Engineering, Seoul National University, San 56-1, Shillim-dong, Gwanak-ku, Seoul 151-744, Republic of Korea

Received 13 November 2006; received in revised form 1 February 2007; accepted 5 February 2007

Available online 16 February 2007

Abstract

Well-defined spherical mesoporous TiO$_2$ was prepared from a poly(ethylene glycol)-poly(propylene glycol)-based triblock copolymer and titanium isopropoxide mixed with 2,4-pentanedione by using a simple sol–gel approach in aqueous solution. Hydrothermal treatment was performed to increase the crystallinity, thermal stability, surface area, and photocatalytic activity of the mesoporous TiO$_2$. The hydrothermally treated mesoporous TiO$_2$ materials were found to have a high crystallinity with a nanocrystalline anatase structure even in the as-synthesized state, whereas untreated materials were found to have an amorphous or semicrystalline phase prior to calcination at 300 °C. The surface area of hydrothermally treated mesoporous TiO$_2$ was found to exceed 395 m$^2$ g$^{-1}$, whereas the areas of the untreated materials were less than 123 m$^2$ g$^{-1}$.

The pore size distributions of the hydrothermally treated mesoporous TiO$_2$ materials were found to be narrower than those of untreated materials; the average pore size increased from 5.7 to 10.1 nm with increases in the calcination temperature. The photocatalytic activity of hydrothermally treated mesoporous TiO$_2$ is significantly higher than the activities of untreated materials, with a maximum decomposition rate that is three times faster than that of a commercial TiO$_2$, P25. The high photocatalytic activity of mesoporous TiO$_2$ is due to the large surface area and high crystallinity with a nanocrystalline anatase that is induced by the hydrothermal treatment.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Mesoporous TiO$_2$; Hydrothermal treatment; High crystallinity; Surface area; Photocatalytic activity

1. Introduction

Titanium dioxide (TiO$_2$) exhibits useful electrical, optical, and photocatalytic behavior due to the powerful oxidation and reduction properties that arise in it on absorption of photon energy. These properties mean that titanium dioxide is useful in environmental remediation processes such as water and air purification, prevention of stains, and sterilization [1–3]. Many approaches to improve the photocatalytic activity of TiO$_2$ have been tested, and many researchers have pointed out that the photocatalytic activity of TiO$_2$ generally depends on its morphology, crystal composition, crystallinity, and surface area [4–7]. Of these synthetic approaches, hydrothermal treatment is one of the most widely used methods for increasing the crystallinity of TiO$_2$ [8–10]. The application of elevated temperatures and pressures in an aqueous solution facilitates the conversion of amorphous TiO$_2$ into crystalline TiO$_2$ and causes an increase in its crystallinity. Hydrothermal treatment can also be used to change the morphology, microstructure, and phase composition of materials by varying the reaction parameters [11]. However, it has been difficult to achieve a large surface area and high crystallinity simultaneously in nonporous TiO$_2$ by carrying out hydrothermal treatment.

Mesoporous TiO$_2$ has a large surface area because of its confined porous structure and high surface to volume ratio, and so should in principle have high photocatalytic activity, because of the improved access to the active sites of TiO$_2$ [12]. However, much less research has been devoted to improving the photocatalytic activity of mesoporous TiO$_2$ compared to that invested in nonporous or commercial TiO$_2$ [13–17]. The low crystallinity of mesoporous TiO$_2$ with an amorphous or semicrystalline framework is thought to be the main reason for its negligible photocatalytic activity. Increasing the crystallinity through calcination at high temperatures is not expected to be helpful because of the resulting collapse of the mesoporous framework and the consequent loss of surface area. Furthermore, the mesoporous inorganic walls that are active
sites for photocatalytic activity are poisoned by surfactant residues, resulting in a low photocatalytic activity [18–20]. Hydrothermal treatment may be applied to convert the amorphous or semicrystalline mesoporous TiO$_2$ framework into an anatase phase with high crystallinity and a large surface area. However, few precise studies of the application of hydrothermal treatment to the synthesis of mesoporous TiO$_2$ with high crystallinity, thermal stability, large surface area, and high photocatalytic activity have been carried out [21,22].

In this paper, we report the effects of hydrothermal treatment on the physical properties of mesoporous TiO$_2$, in particular on its crystal composition, thermal stability, pore size distribution, surface area, and photocatalytic activity. The sol–gel approach in aqueous solution with a triblock copolymer and titanium isopropoxide mixed with 2,4-pentanedione was used to synthesize mesoporous TiO$_2$. Hydrothermally treated and untreated materials were calcined at various temperatures and their crystal compositions, thermal stabilities, pore size distributions, surface areas, and photocatalytic activities were compared.

2. Experimental

2.1. Synthesis of mesoporous TiO$_2$ with spherical shape

The triblock copolymer, poly(ethylene glycol)-block-poly(-propylene glycol)-block-poly(ethylene glycol) (EO$_{20}$PO$_{70}$EO$_{20}$, $M = 5800$), titanium(IV) isopropoxide, and 2,4-pentanedione were purchased from Aldrich. All chemicals were used as received without further purification.

The synthesis of mesoporous TiO$_2$ was carried out with the following procedure. Four grams (0.69 mmol) of the triblock copolymer was dissolved in 100 mL of distilled water at 40 °C. After the surfactant had been dissolved sufficiently, 1.5 g (15.3 mmol) of sulfuric acid was added. Titanium (IV) isopropoxide (11.76 g, 41.4 mmol) was mixed with 2,4-pentanedione (4.14 g, 41.4 mmol) in a separate beaker and dropped slowly into the surfactant solution with vigorous stirring. After addition, the reaction was carried out at 55 °C for 2 h without stirring. At first, there was no precipitation, but after several minutes, a light yellow powder was obtained.

2.2. Hydrothermal treatment of mesoporous TiO$_2$

To carry out the hydrothermal treatment, we aged the obtained material at 90 °C for 10 h without stirring. The resulting powder was collected by filtration and thoroughly washed with water and ethanol. In this paper, mesoporous TiO$_2$ material synthesized without hydrothermal treatment is denoted nHTMT, and hydrothermally treated mesoporous TiO$_2$ material is denoted HTMT.

2.3. Calcination of mesoporous TiO$_2$

To eliminate the surfactant, we calcined the materials at 300, 500, and 700 °C (the rate of increase was 1 °C min$^{-1}$) in air. Hydrothermally treated, as-synthesized mesoporous TiO$_2$ is denoted HTMT-As, and the mesoporous TiO$_2$ samples that were hydrothermally treated and calcined at 300, 500, and 700 °C are denoted HTMT-300, HTMT-500, and HTMT-700, respectively. In addition, untreated and as-synthesized mesoporous TiO$_2$ is denoted nHTMT-As, and the mesoporous TiO$_2$ samples that were untreated and calcined at 300, 500, and 700 °C are denoted nHTMT-300, nHTMT-500, and nHTMT-700, respectively.

2.4. Characterization of mesoporous TiO$_2$

The surface features and morphologies of the materials synthesized were investigated by using Field Emission-Scanning Electron Microscopy (FE-SEM, JEOL JSM-6330F) and High Resolution-Transmission Electron Microscopy (HR-TEM, JEOL JEM-2000 FX II). The crystallite structures of materials synthesized at the various calcination temperatures were investigated by analyzing the X-ray powder diffraction (XRD) patterns obtained with a SIEMENS D5005 D diffractometer equipped with Cu K$_\alpha$ irradiation and a fixed powder source (40 kV, 40 mA). The crystallite sizes were calculated by using the Scherrer equation ($\phi = K \lambda / \beta \cos \theta$), where $\phi$ is the crystallite size, $\lambda = 0.154$ nm, which is the wavelength of the X-ray irradiation, $K$ usually taken as 0.89, $\beta$ is the peak width at half-maximum height, and $\theta$ is the diffraction angle of the (1 0 1) peak. The specific surface area and pore size distribution were characterized by analyzing the $N_2$ adsorption and desorption isotherms obtained at 77 K using Micrometrics ASAP 2000 equipment. All the materials were degassed at 200 °C and 10$^{-6}$ Torr for 10 h prior to these measurements. The surface areas of the materials were calculated with the Brunauer–Emmett–Teller (BET) equation, and their pore-size distributions were determined by using the Barrett–Joyner–Halenda (BJH) formula from the desorption branch. Thermogravimetric analysis (TGA) was carried out by using a TGA Q500. The atmosphere was air and the heating rate was 10 °C min$^{-1}$. The UV–Vis reflectance spectra were measured by using a Varian Cary-5000 spectrometer over a range of 200–700 nm.

2.5. Measurement of photocatalytic activity

The photocatalytic activity of each mesoporous TiO$_2$ sample was evaluated by measuring the degradation of methylene blue (MB) in an aqueous solution at room temperature. A quartz cell of 13 mm o.d. (11 mm i.d.) with the length of 250 mm was used with four UV lamps producing 15 W UV-A as light sources. Twenty-five milliliters of methylene blue (50 ppm) and 25 mg of sample was placed in the quartz cell surrounded by the four UV lamps. In each experiment, prior to UV irradiation, the reaction solution was magnetically stirred in the dark for 30 min until adsorption/desorption equilibrium was reached. The solution was then irradiated under UV light with continuous magnetic stirring. A fixed quantity of the solution was removed at regular intervals and filtered through a syringe filter. The degradation of methylene blue was analyzed by using a Shimadzu 2101PC.
UV-Vis scanning spectrophotometer in the range 500–700 nm. A test with a commercial TiO₂, P25, was also conducted under the same experimental conditions.

3. Results and discussion

3.1. FE-SEM and HR-TEM analysis

FE-SEM images of the as-synthesized TiO₂ and hydrothermally treated material (HTMT-As) are shown in Fig. 1a and b. The particles have well-defined spherical morphology, with a diameter range of 2–3 μm. Fig. 1b shows a magnified image for one particle, in which pores with irregular size can be seen. The pore structure consists of a wormhole-like pore array, and the wall of the mesoporous framework consists of interconnected TiO₂ nanoparticles. In order to investigate the properties of the pores, HR-TEM images of HTMT-300 were obtained, as shown in Fig. 1c and d. A wormhole-like pore structure is also evident in the TEM image shown in Fig. 1c. Disordered channels are packed randomly and form a three-dimensional mesoporous framework; this result is consistent with the FE-SEM images (Fig. 1b). Further HR-TEM observation was carried out, and it was found that the pore walls consist of aggregated nanocrystalline anatase with an average crystallite size of about 7 nm (Fig. 1d).

3.2. XRD analyses of hydrothermally treated and untreated materials

The wide angle X-ray diffraction (XRD) patterns of the nHTMT and HTMT materials were investigated to analyze the effects of the hydrothermal treatment on their crystallite phases and crystallinities (Fig. 2). For nHTMT-As and nHTMT-300, there were no diffraction peaks, which indicates the presence of an amorphous phase with low crystallinity or semicrystalline with very small crystallites (Fig. 2a). In the case of nHTMT-500, a diffraction peak due to an anatase phase is present, and a small peak due to a rutile phase is present for nHTMT-700. The average crystallite sizes were calculated from the anatase peak (1 0 1) with the Scherrer equation, and were found to be 6.7 nm (nHTMT-500) and 64.4 nm (nHTMT-700). In contrast to the results for the nHTMT materials, anatase phase diffraction peaks were observed for the as-synthesized HTMT materials, with a crystallite size of about 6.0 nm (Fig. 2b). This result implies that the amorphous phase of mesoporous TiO₂ can be successfully converted to an anatase phase by carrying out hydrothermal treatment. The intensity of the diffraction peak becomes stronger and better resolved with increases in the calcination temperature, indicating increases in the anatase crystallite size: 7.3 nm (HTMT-300), 11.8 nm (HTMT-500), and 22.3 nm (HTMT-700). The phase transformation from
anatase to rutile does not occur in TiO₂ materials during calcination at 700 °C, and the crystallite growth rates of the HTMT materials were found to be lower than those of the nHTMT materials. The stability of the anatase phase up to 700 °C can be attributed to the small crystallite sizes in the inorganic domain. Thermodynamic phase stability is generally dependent on particle size, and the anatase structure is more stable thermodynamically than the rutile structure at particle sizes below approx. 14 nm [23]. Furthermore, Wu and coworkers reported that the SO₄²⁻ anion which was used with acidic condition in our system can also stabilize and retard the growth of crystalline anatase [24]. Table 1 lists the crystallite sizes and phases of nHTMT and HTMT materials calcined at various temperatures.

3.3. BET and BJH analysis

To investigate the surface areas and thermal stabilities of the mesoporous TiO₂ samples, we analyzed the variations of the N₂ adsorption and desorption isotherms of the nHTMT and HTMT materials with calcination temperature (Fig. 3a and b). For nHTMT-As and nHTMT-300, no hysteresis loops were found (Fig. 3a), and the surface areas were found to be 10 and 108 m² g⁻¹, respectively. For nHTMT-500, stepwise adsorption and desorption branches and a surface area of 123 m² g⁻¹ were found. However, the surface area of nHTMT-700 is lower, 47 m² g⁻¹. It seems that the surfactant is not sufficiently eliminated from nHTMT-As and nHTMT-300 until temperatures above 300 °C is reached. For nHTMT-500 and nHTMT-700, the surfactant is slowly eliminated by calcination, but the resulting surface area is low because of the crystallite growth that occurs at high calcination temperatures (Fig. 3a and Table 1). However, the hydrothermally treated materials (HTMT) have a large surface area, even HTMT-As, which was not calcined (Fig. 3b and Table 2); for these materials a hysteresis loop with a stepwise adsorption and desorption branch was observed for a wide range of pressures (P/P₀), and which has a surface area of 395 m² g⁻¹. The HTMT surface areas were found to be 295 m² g⁻¹ (HTMT-300), 209 m² g⁻¹ (HTMT-500), and 87 m² g⁻¹ (HTMT-700); these materials decrease with increasing calcination temperature due to the growth of the crystallite size (see Fig. 3b and Table 1). However, the decrease in the surface areas of the HTMT materials with calcination temperature is not as marked as that for the nHTMT materials, which indicates that the hydrothermal treatment increases the thermal stability of the mesoporous framework. The low thermal stability of the nHTMT materials is produced by the collapse of the pore

Table 1
Crystallite sizes and phases of nHTMT and HTMT materials calcined at various temperatures

<table>
<thead>
<tr>
<th>Untreated materials</th>
<th>Hydrothermally treated materials</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Samples</strong></td>
<td><strong>Crystallite size (nm)ᵃ</strong></td>
</tr>
<tr>
<td>nHTMT-As</td>
<td>–</td>
</tr>
<tr>
<td>nHTMT-300</td>
<td>–</td>
</tr>
<tr>
<td>nHTMT-500</td>
<td>6.7</td>
</tr>
<tr>
<td>nHTMT-700</td>
<td>64.4</td>
</tr>
</tbody>
</table>

ᵃ Crystallite sizes were calculated by Scherrer equation from XRD data.
structure during calcination due to the phase transformation from amorphous to anatase or rutile phases. Therefore, when an amorphous phase is present in an as-synthesized material before calcination, the mesoporous framework is easily destroyed during the calcination process. However, because the hydrothermal treatment converts the amorphous phase into anatase, there is no phase transformation during calcination, indicating that the mesoporous framework has high thermal stability [22].

The pore size distributions of the nHTMT and HTMT materials were analyzed by using the BJH method for the desorption branch (Fig. 3c and d). For nHTMT-As and nHTMT-300, pore size distributions were not observed. nHTMT-500 was found to have a low pore size distribution intensity, with an average pore size of 4.7 nm. For nHTMT-700, a broad pore size distribution was obtained, with an average pore size of 13.7 nm. However, for all the HTMT materials, narrow and strong pore size distribution peaks were observed. For HTMT-As, the average pore size was found to be 5.7 nm, with a pore volume of 0.51 cm$^3$ g$^{-1}$. The pore sizes slowly increase with increases in the calcination temperature: 6.9 nm (HTMT-300), 7.9 nm (HTMT-500), and 10.1 nm (HTMT-700). The HTMT materials have larger average pore sizes than the nHTMT materials at low calcination temperatures because of the temperature dependence of the physical properties of the PEO block of the triblock copolymer surfactant. In the case of the nHTMT materials, the PEO block is strongly attached to the inorganic wall because TiO$_2$ nanoparticles form at the site of the PEO block, which has hydrophilic properties at the reaction temperature of 55 °C. Therefore, the surfactant is not easily eliminated for calcination near 300 °C. However, in the case of the HTMT

Table 2

Surface areas, pore sizes, and pore volumes of hydrothermally treated and untreated mesoporous TiO$_2$ materials calcined at various temperatures.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Pore size (nm)$^a$</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
<th>Samples</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Pore size (nm)$^a$</th>
<th>Pore volume (cm$^3$ g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nHTMT-As</td>
<td>10</td>
<td>~</td>
<td>0.014</td>
<td>HTMT-As</td>
<td>395</td>
<td>5.7</td>
<td>0.51</td>
</tr>
<tr>
<td>nHTMT-300</td>
<td>108</td>
<td>2.8</td>
<td>0.078</td>
<td>HTMT-300</td>
<td>295</td>
<td>6.9</td>
<td>0.45</td>
</tr>
<tr>
<td>nHTMT-500</td>
<td>123</td>
<td>4.7</td>
<td>0.147</td>
<td>HTMT-500</td>
<td>209</td>
<td>7.9</td>
<td>0.41</td>
</tr>
<tr>
<td>nHTMT-700</td>
<td>47</td>
<td>13.7</td>
<td>0.160</td>
<td>HTMT-700</td>
<td>87</td>
<td>10.1</td>
<td>0.28</td>
</tr>
</tbody>
</table>

$^a$ Average pore sizes were calculated by using the BJH formula for the desorption branch.

$^b$ As-synthesized samples were degassed at 200 °C and 10$^{-6}$ Torr for 10 h prior to the measurements.
materials, the hydrothermal treatment is performed at 90 °C, so the PEO block has more hydrophobic properties. Therefore, the size of the hydrophobic domain increases during the hydrothermal treatment, which results in a weaker interaction between the surfactant and the inorganic wall. This means that the average pore size of the HTMT materials is increased, and the surfactant is easily eliminated with ethanol washing or a low calcination temperature. To further investigate the effect of the hydrothermal treatment on the elimination of surfactant, we performed TGA analyses of the nHTMT-As and HTMT-As materials (Fig. 4). In the TGA results for nHTMT-As, the first weight loss region is between RT and 120 °C, due to the removal of absorbed H2O. In the second weight loss region between 350 and 500 °C, the surfactant decomposes. The amount of surfactant in nHTMT-As is about 15 wt.% (Fig. 4a), but the TGA analysis for HTMT-As shows that nearly 2 wt.% surfactant decomposes (Fig. 4b). This result indicates that the hydrothermal treatment affects the elimination of the surfactant and also aids the formation of the mesoporous structure. Table 2 summarizes the surface areas, pore sizes, and pore volumes of the nHTMT and HTMT materials calcined at various temperatures.

3.4. Diffuse reflectance spectra analysis

To investigate the band gap energy of HTMT-300, HTMT-500, and HTMT-700, we analyzed the diffuse reflectance spectra (Fig. 5). Direct band gap energy of these materials can be calculated by plotting \((ahv)^2\) versus excitation energy and extrapolating the linear part of the curve to \((ahv)^2 = 0\) [25,26]. The band gap energies were estimated to be 3.16, 3.14, and 3.08 eV for HTMT-300, HTMT-500, and HTMT-700, respectively. As found in the XRD results, the crystallite sizes increase as the calcinations temperature increases. The absorption band shifts toward the longer wavelength region with the increase in the crystallite sizes of samples, which indicates a decrease in the band gap energy. This phenomenon could be caused by the quantum size effects of semiconductors. In the quantum size effect, the band gap energy decreases as the crystallite size increases [22,27].

3.5. Photocatalytic activity

The photocatalytic activities of the nHTMT and HTMT materials were determined by carrying out the degradation of methylene blue in aqueous solution under UV irradiation. Figure 6 shows the changes in the relative concentration of methylene blue as a function of the time of UV irradiation for nHTMT (a) and HTMT materials (b).
methylene blue solution under UV-irradiation (Fig. 6). For nHTMT-As and nHTMT-300, no degradation of methylene blue was observed over a long period. Such behavior is probably due to the low crystallinity present in these materials, and to surfactant residue impurities in their pore walls (see Tables 1 and 2). For nHTMT-500 and nHTMT-700, there was some degradation of methylene blue, but the efficiencies of degradation were inferior to that of the commercial TiO2, P25 (Fig. 6a). However, the photocatalytic activities of the HTMT materials are superior to that of P25 (Fig. 6b). For HTMT-300 and HTMT-500, the methylene blue solutions were almost fully degraded and became transparent within 45 min under UV light, whereas the solution containing P25 was still somewhat bluish at that time. In plots of ln(Cf/C0) versus UV irradiation time, straight lines were found for all the materials, indicating that the degradation of methylene blue is a first order process (Fig. 7). The fastest degradation rate was 0.127 min\(^{-1}\) (HTMT-500), which is three times faster than that of P25 (0.042 min\(^{-1}\)), and nine times faster than that of nHTMT-500 (0.014 min\(^{-1}\)).

Table 3 lists the rates of degradation of methylene blue of nHTMT, HTMT, and the commercial TiO2, P25.

This higher-than-expected photocatalytic activity can be explained in terms of the large surface area, small crystallite size, and high crystallinity results from hydrothermal treatment. All HTMT materials have better photocatalytic activities than those of all nHTMT materials because of large surface area and high crystallinity. Generally, large surface area is likely to exhibit better photocatalytic activity, because a large surface area provides more active sites for adsorbing methylene blue solution. However, large surface area does not always give better photocatalytic activity. Although HTMT-300 (395 m\(^2\) g\(^{-1}\)) has a larger surface area than HTMT-500 (295 m\(^2\) g\(^{-1}\)), its photocatalytic activity is lower (see Fig. 7 and Table 3). This result indicates that the degree of crystallinity is also a significant factor in the photocatalytic activity, because the degree of crystallinity of HTMT-500 is higher than that of HTMT-300 (see Fig. 2 and Table 1). It has been proven that the photocatalytic activity increases with increases in the crystallinity for a constant crystallite size by Peng et al. [22] and Ohtani et al. [28]. In the effect of crystallite size, mesoporous TiO2 with larger crystallite size showed lower photocatalytic activity. Although HTMT-700 has higher crystallinity than HTMT-500, it has a lower photocatalytic activity than HTMT-500, which is due to the increase in the crystallite size and to the decrease in the surface area that results from increasing the calcination temperature (see Tables 1 and 2). It has been commonly accepted that smaller crystallite size corresponds to more powerful redox ability because smaller crystallite size induces a larger band gap which causes the rate of electron–hole recombination to be slower [22,27]. Since the HTMT-500 has a larger band gap than the HTMT-700, its photocatalytic activity is higher (see Figs. 5 and 7). Therefore, we conclude that the photocatalytic activity of mesoporous TiO2 is strongly dependent on the surface area, the crystallinity, and the crystallite size, but the effects of these factors on the photocatalytic activity are interdependent. Further investigation of how the pore size and the mesoporous structure affect the photocatalytic activity is necessary.

### 3.6. Mechanism

Mesoporous TiO2 was obtained for a range of reaction conditions produced by varying the concentration of surfactant, the molar ratio of surfactant to precursor, pH, and the reaction temperature. The use of surfactant concentrations higher than 6 wt.% in aqueous solution produces an amorphous gel, and concentrations of surfactant below 1 wt.% yield no precipitation. Molar ratios of surfactant to titanium precursor between 1:20 and 1:100 were found to be suitable for obtaining the powders, and under other conditions there is no precipitation of powder. Mesoporous TiO2 can only be obtained with H\(_2\)SO\(_4\), whereas under other acidic conditions such as those produced by HCl, HBr, HNO\(_3\), and H\(_3\)PO\(_4\), either there is no precipitation of powder or a nonporous structure forms. H\(_2\)SO\(_4\) concentrations from 0.05 to 0.3 M were found to be suitable for obtaining the powder, but either a gel state or no precipitation result from the use of other concentrations. The reaction temperature was the important factor to control the morphology from non-ordered to well-defined spherical shape. Above 35 °C reaction temperature, spherically shaped particles of mesoporous TiO2 were synthesized, but irregular particle shapes of materials were obtained below 35 °C. The change of morphology with the reaction temperature may be considered to exert influence...
on the degree of the micelle formation of triblock copolymer surfactant. The triblock copolymer surfactant forms micelles in the aqueous solution in the temperature range 35–80 °C, because the PPO block is more hydrophobic than the PEO block (Scheme 1, stage A). Therefore, when the modified precursor Ti(OPr)i3acac [29,30] produced by mixing 2,4-pentanedione (acetylacetone) and titanium isopropoxide in a 1:1 molar ratio was dissolved in micelle solution, TiO2 nanoparticles can only form at PEO block sites because only the PEO block is soluble in the aqueous solution (Scheme 1, stage B). Further hydrolysis and condensation of the titanium precursor leads to the growth of larger TiO2 nanoparticles, which slowly aggregate. As the TiO2 nanoparticles aggregate further, the TiO2 particles become microscopic, and form well-defined mesoporous TiO2 particles with spherical shapes (Scheme 1, stage C). At this stage, it is supposed that micelle surrounds mesoporous TiO2, helping the formation of spherical shape. After hydrothermal treatment and calcination, mesoporous TiO2 particles with well-defined spherical shapes are obtained (Scheme 1, stage D). The SEM image in Fig. 1b shows that the mesoporous TiO2 is composed of TiO2 nanoparticles, which confirms the mechanism. A similar mechanism involving the aggregation of TiO2 nanoparticles resulting in mesoporous TiO2 spheres was proposed by Lou et al. [31] and Zhang et al. [32].

4. Conclusion

This paper has shown that hydrothermal treatment significantly affects the physical properties of mesoporous TiO2, in particular the crystal composition, crystallinity, thermal stability, surface area, pore size distribution, and photocatalytic activity. XRD analysis was used to show that hydrothermal treatment facely converts amorphous mesoporous TiO2 into anatase TiO2 and inhibits increases in the crystallite size. Higher surface areas and larger average pore sizes were obtained in HTMT materials than in nHTMT materials, as confirmed with BET and BJH analyses, because of the easy elimination of surfactant. The thermal stability of the mesoporous framework also increases as a result of the hydrothermal treatment. The high photocatalytic activity of the HTMT materials in degradation of methylene blue can be explained in terms of their high crystallinities, large surface areas and small crystallite sizes. The use of aqueous solution as the reaction medium is environmentally friendly, and large amounts of materials can be synthesized with just one reaction at low cost. This method is expected to be applicable to the syntheses of other mesoporous transition metal oxides, and thus to be useful in many applications, such as photocatalysts, photovoltaics, and electronic sensors.

Acknowledgment

This study was supported by the Ministry of Environment, Republic of Korea, through the Eco-Technopia 21 project.

References
