Facile Synthesis of Thermally Stable Mesoporous Titania Spheres with Excellent Photocatalytic Activity

Su Bin Park, Kumarsrinivasan Sivaranjani, Hyun Jung Na, Zhenghua Li, Yeong-Jin Choi, Young-Jun Yang, and Ji Man Kim*

Advance Publication on the web October 18, 2014 by J-STAGE
doi:10.1246/cl.140877
Facile Synthesis of Thermally Stable Mesoporous Titania Spheres with Excellent Photocatalytic Activity

Su Bin Park, 1 Kumarsrinivasan Sivaranjani, 1 Hyun Jung Na, 1 Zhenghua Li, 1 Yeong-Jin Choi, 1, 2 Young-Jun Yang, 2 and Ji Man Kim* 1, 3

1Department of Chemistry, Sungkyunkwan University, Suwon, 440-746, Republic of Korea
2Amorepacific R&D Center, Yongin, 446-729, Republic of Korea
E-mail: jimankim@skku.edu

Thermally stable mesoporous TiO2 spheres were successfully prepared via in-situ hydrolysis of titanium glycolate precursor. Mesoporous nature was retained even up to 500 °C calcination under static air conditions. Mesoporous TiO2 calcined at 500 °C showed a maximum photocatalytic activity. This is mainly attributed to the better utilization of charge carriers due to the low diffusional length along with high surface area and well-defined nanocrystallinity.

Synthetic dyes are commonly used in many commercial industries. The effluents from these industries are usually highly colored, toxic and carcinogenic in nature. 1–3 As most of the synthetic dyes are resistant to the light or other degradative environmental conditions, it is necessary to remediate these effluents before they are released to the environment. However, common plants treating wastewater are ineffective in removal of dyes. Recently semiconductor photocatalysis is widely used to degrade these pollutants. 4–7 Highly reactive hydroxyl radicals, generated during photocatalysis, can be used to reduce these dye effluents. 8–9 Among the various kinds of photocatalysts, titanium dioxide (TiO2) remains the best active photocatalyst owing to its chemical stability towards photocorrosion, high oxidation potential, low cost and non-toxicity. 10–13

Many natural materials, like seashell and lotus leaf, are composed only with ordinary composition but reveal interesting property owing to their unique morphology. Such complicated natural designs have inspired extensive research in synthesizing materials with controlled structure and morphology, with expectations of achieving novel or enhanced properties. Generally, adsorption and diffusion of reactant molecules to the catalytically active sites are two important steps in heterogeneous photocatalysis. Conventional TiO2 catalysts exhibits low surface areas, in turn, result in minimum adsorption of dye molecules. However, in contrast, porous materials lead to the maximum adsorption of reactant molecules due to their high surface area. Recently mesoporous titania can be widely used for many applications such as photocatalysis, solar cells, lithium-ion batteries, sensors, drug delivery and catalyst supports. 14–17 An ordered mesoporous TiO2 can be prepared through a nano-replication method from ordered mesoporous silica. 18–20 After infiltrating the precursors into the mesopores of silica template, the composite is heated under air conditions, and finally the silica template is removed by chemical etching technique using a base, giving ordered mesoporous TiO2. However, this nano-replication method has some difficulties such as inconvenient infiltration process of precursor, crystal growth outside the mesoporous silica particles during the heat treatment, and proper choice of chemical etching agent. There is also limitation when the metal precursors are not stable in a solution enough to infiltrate them within the mesopores of silica template, due to their fast hydrolysis and precipitation. Moreover along with the high surface area these ordered mesoporous TiO2 will also have longer diffusional lengths which will reduce the life time of charge carriers. Hence, mesoporous TiO2 with disordered pore system is expected to show good photocatalytic activity due to fast diffusion of charge carriers to the surface.

In the present work, we report on the synthesis of mesoporous TiO2 with spherical morphology and anatase framework through a simple in-situ hydrolysis of titanium glycolate. 21, 22 The mesoporous TiO2 spheres exhibited excellent thermal stability as well as high photocatalytic activity for dye degradation. 23, 24 It is expected that high surface area of the material associated with well-defined mesopore and nanocrystalline framework enhances the light harvesting properties by increasing the mobility of charge carriers as well as minimizing the defects. 25

To synthesize a titanium glycolate precursor, 2 mL of titanium (IV) butoxide (Aldrich, 97%) was mixed with 50 mL of ethylene glycol (Samchun Chemicals, 99.9%), and then the solution was stirred at room temperature. After 8 h, a solution containing 170 mL of acetone (Samchun Chemicals) and 2.7 mL of deionized water was poured into the mixture, and the final mixture was vigorously stirred for 1 h at room temperature. The white precipitate was centrifuged, washed with ethanol three times, and dried at 80 °C for 24 h. 1.5 g of the titanium glycolate precursor, thus obtained, was mixed with 120 mL of deionized water, and the mixture was heated under reflux conditions for 1 h with vigorous stirring. The white precipitate was collected by centrifugation, washed with deionized water three times, and finally dried at 80 °C for 24 h, producing spherical mesoporous TiO2 (MT) material. For further use, the MT material was calcined under static air conditions at different temperatures from 100 to 700 °C for 1 h. The MT materials, thus obtained, are denoted MT-x, where x stands for calcination temperature.

Figure 1 shows powder X-ray diffraction (XRD) patterns of the MT-x materials that were calcined at different temperatures. All the peaks in the XRD pattern could be indexed to anatase phase of TiO2 (JCPDS File: 21-1272), 26 which are stable up to 500 °C. A small fraction of rutile phase (< 1%) is also observed in MT-500, and the percentage of rutile peaks increases with increasing the calcination temperature. Calcination at high temperatures, above 500 °C leads to the formation of thermodynamically stable rutile phase. As shown in Figure 1, crystallite size was also gradually increases with increasing the calcination
temperature. Crystallite sizes were calculated by using Debye–Scherrer equation and shown in Table 1. MT-x materials (x = 200 – 500) materials show a low angle peak between 0.8 and 1° and demonstrate the presence of a mesoporous framework (Supporting information). Unlike structurally ordered mesoporous materials, no other peaks corresponding to different planes were observed at 2θ < 5°, highlighting the disordered nature of mesoporosity. Further, no low angle peak was observed for MT-600 and MT-700 indicates that the material is not mesoporous in nature.

Table 1. Physical properties of MT-x materials

<table>
<thead>
<tr>
<th>Material</th>
<th>( S_{\text{BET}} )^a (m(^2)/g)</th>
<th>( V_{\text{Total}} )^b (cm(^3)/g)</th>
<th>Pore size ( c ) (nm)</th>
<th>Grain size ( d ) (nm)</th>
<th>Rate constant (x10(^{-5}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>MT</td>
<td>285</td>
<td>0.30</td>
<td>2.3</td>
<td>4.6</td>
<td>-</td>
</tr>
<tr>
<td>MT-100</td>
<td>223</td>
<td>0.29</td>
<td>4.0</td>
<td>4.8</td>
<td>6.14</td>
</tr>
<tr>
<td>MT-200</td>
<td>182</td>
<td>0.28</td>
<td>5.0</td>
<td>5.2</td>
<td>10.8</td>
</tr>
<tr>
<td>MT-300</td>
<td>148</td>
<td>0.27</td>
<td>6.4</td>
<td>6.3</td>
<td>13.6</td>
</tr>
<tr>
<td>MT-400</td>
<td>115</td>
<td>0.24</td>
<td>7.4</td>
<td>8.0</td>
<td>18.8</td>
</tr>
<tr>
<td>MT-500</td>
<td>51</td>
<td>0.10</td>
<td>8.9</td>
<td>14.3</td>
<td>19.6</td>
</tr>
<tr>
<td>MT-600</td>
<td>7</td>
<td>0.03</td>
<td>-</td>
<td>25.0</td>
<td>10.9</td>
</tr>
<tr>
<td>MT-700</td>
<td>3</td>
<td>0.01</td>
<td>-</td>
<td>36.2</td>
<td>1.80</td>
</tr>
</tbody>
</table>

\(^{a}\)BET surface areas calculated from the N\(_2\) adsorption. 
\(^{b}\)Total pore volumes measured at \( p/p_0 = 0.99\). 
\(^{c}\)Calculated BJH method from N\(_2\) adsorption branches. 
\(^{d}\)Calculated by Debye-Scherrer equation from XRD peaks.

\(N_2\) adsorption-desorption isotherms were measured to investigate the textural properties of the MT-x materials. Figure 2 shows \(N_2\) adsorption-desorption results and the corresponding Barret–Joyner–Halenda (BJH) pore size distribution curves of the MT-x materials. Type-IV isotherms with H\(_2\) hysteresis loop are observed until the calcination temperature of 500 °C, which are typical characteristics of mesoporous materials.\(^{27}\) MT-600 and MT-700 materials lose their mesoporosities mainly due to the formation of rutile phases with large crystallite sizes. Surface area of all MT-x materials are shown in Table 1, which decrease with increasing the calcination temperature. Interestingly, pore size is getting increased with the calcination temperature which will be discussed later. The MT-500 has the largest pore size of around 8.9 nm.

Particle morphologies of the MT-x materials were investigated by scanning electron microscopy (SEM). As shown in Figure 3, all the MT-x materials exhibited well-defined spherical morphologies with diameters of about 300 nm, and the surface of these spheres became smoother after calcination at 600 °C. Unlike other synthesis routes, in the present work, the spherical morphology is maintained even after the calcination at 700 °C. It is clearly visible that the surface of the spherical MT-x particles (x = 100 – 500) consists of the agglomeration of small nanoparticles, which generate the mesopores.

Figure 2. \(N_2\) adsorption-desorption isotherm studies, and pore size distribution (in-set) measured from the above isotherms of mesoporous MTx materials.

Figure 3. SEM images of MT-x materials: A. MT, and B–H. MT-100 to MT-700.
particles and the same leads to aggregates with significant extra framework void space. The void spaces between nanocrystalline TiO$_2$ framework acts as mesopores.\textsuperscript{28} By increasing the calcination temperature, the TiO$_2$ nanoparticles are growing in bigger size and arranging in such a way, which increases the pore size, as illustrated in Figure 4d. The particle size of MT-300 and MT-500 is calculated from TEM images and it is around 7.1 and 15.4 nm, respectively.

**Figure 3.** TEM images: A. MT-300, B. MT-500 and C. MT-700, and D. Schematic diagram to explain the increase of pore size with increasing the calcination temperature.

**Figure 5.** Photocatalytic degradation of methylene blue with MT-x materials under UV irradiation using a 16 W UV lamp.

In order to evaluate the photocatalytic ability of the MT-x materials, the degradation experiments of methylene blue were carried out under UV irradiation using a 16 W UV lamp. Figure 5 shows the photocatalytic activity of MT-x materials. Among all, MT-500 catalyst shows the highest activity, which is probably due to the high surface area, large mesopore size and high crystallinity. Moreover, the presence of small amount of rutile phase in the MT-500 material helps in charge separation in turn reduces the recombination probability. Hence, MT-500 acts as the best photocatalyst for dye degradation reactions. The activity of all the catalysts follows the order given below: MT-500 > MT-400 > MT-300 > MT-600 > MT-200 > MT-100 > MT-700. Even though the MT-100 and MT-200 material have high surface area, the photocatalytic activities are low, probably due to the lack of surface crystallinity and the remaining organic species come from the glycolate precursor. The MT-700 shows very low activity due to the presence of rutile phase and very low surface area.

In summary, the mesoporous TiO$_2$ spheres was successfully synthesized through a simple in-situ hydrolysis process. The mesoporous TiO$_2$ spheres are thermally stable up to 500 °C, which possess unique properties such as spherical morphology, well-defined mesoporosity, high surface area and good nanocrystallinity. The MT-500 material exhibits the highest photocatalytic activity towards the degradation of methylene blue.

This work was supported by the Korean Health Technology R&D Project, Ministry of Health & Welfare, Republic of Korea (No. HN10C005).

**References and Notes**