Effect of ZrO$_2$-Addition on Structure of Sol-Gel Derived TiO$_2$ Nanopowder

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SYNOPSIS
Mesoporous anatase-type ZrO$_2$-doped TiO$_2$ nanocrystals have been prepared via a surfactant-assisted templating method (SATM). The ZrO$_2$-doped TiO$_2$ nanocrystals had high phase stability and maintained anatase structure even calcining at 800°C for 4 h. The ZrO$_2$ dopants present in this system showed inhibitory effect not only to the phase transformation from anatase to rutile phase, but also to the crystallite growth of TiO$_2$.

KEY WORDS
ZrO$_2$-doped TiO$_2$ sol-gel, surfactant-assisted templating method, anatase

1 Introduction
Nanostructured titania (TiO$_2$, titanium dioxide) with controllable structure and narrow particle size has been intensively studied since the development of mesoporous molecular sieves M41S, introduced in the early 1990s$^{1,2}$. Titania nanomaterials have high potential for wide range applications in photoelectronic optical devices, solar cells, gas sensors, photocatalysts and biomaterials$^{3-5}$. Various approaches, including sol-gel process$^6$, hydrolysis$^7$, hydrothermal$^8$, reverse micelle$^9$, surfactant-assisted method$^{10}$, etc., were developed for fabricate titania nanomaterials. To increase the specific surface area and also to improve the mechanical properties of titania nanomaterials other transition and noble metals, such as Zr$^{11}$, Pt$^{12}$, Pd$^{13}$, Au$^{14}$, have been doped by different means. Among various mixed oxides, TiO$_2$-ZrO$_2$ has drawn special attention owing to its versatile catalytic properties$^{15}$. Previous work in our group has shown that the surfactant-assisted templating method (SATM) is a rapid, simple, efficient route for fabricating the mesoporous titania nanocrystals$^{16}$. By using laurylamine hydrochloride (LAHC) and chemical modified tetra (i-propyl) orthotitanate (TiPT) with acetylacetone (ACA) as the template and inorganic precursor, respectively, the anatase-type mesoporous titania nanocrystals with the particle size 7 - 10 nm and surface area in the range of 100 - 140 m$^2$/g were obtained$^{17,18}$.

In this paper, effect of ZrO$_2$ addition on structure of TiO$_2$, prepared via SATM, has been investigated. The major incentive for this work is to improve the titania structural and morphological properties. The present method uses TiPT and zirconyl nitrate as the metal source and dopant, respectively, in the presence of micellar assemblies of LAHC in aqueous system. Structural and morphological characteristics variation in the ZrO$_2$-doped titania nanocrystals with various Ti/Zr ratios were studied.

2 Experimental Procedure
2.1 Sample preparation
Experimental procedures are schematically summarized in Fig. 1. Our studies focused upon the SATM combined with sol-gel process between titanium alkoxides (e.g. TiPT) and zirconium salts (e.g. zirconyl nitrate hydrate) in aqueous solution of micellar surfactant for formation of ZrO$_2$-doped titania nanocrystals. This procedure is based on the controllable sol-gel process in the presence of self assemblies of surfactants in aqueous system. The metal precursor was firstly modified by modifying agent (e.g. ACA) in order to obtain controllable sol-gel process. The micellar assemblies of organic surfactant (e.g. LAHC) play a role as the templating structure for fabricate the well-defined titania nanocrystalline.

Following the formation procedure reported in our previous article$^{16,18}$, acetylacetone (designated ACA, Nacalai Tesque, Inc., Japan) was slowly added to tetra (i-propyl) orthotitanate (designated TiPT, Tokyo Chemical Industry Co., Japan) in a molar ratio of 1:1. The resultant yellow mixture was then combined with 0.1M homogeneous
Fig. 1 Schematic diagram of mesoporous titania nanocrystals preparation.

TIPT + ACA
LAHC (aq)

Sol
Stirred at RT, 1 h
Stirred at 40°C, 24 h

Kept at 80°C, 72 h

Gel
Dried at 80°C, overnight

Dried gel
Calcined at 500°C

Titania powder

Fig. 2 TG-DTA thermograms of as-prepared 0.05 mol% ZrO₂-doped titania powder derived under the molar ratio [Ti+Zr]/[ACA] = 1, [Ti+Zr]/[LAHC] = 4, and dried at 80°C in air atmosphere.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using a TGA apparatus (DTG-50, Shimadzu) under air atmosphere. The programmed heating rate was 10°C/min. Transmission electron microscopic (TEM) and selected area electron diffraction (SAED) observations were performed on a transmission electron microscope (JEOL JEM-200CX) at 200 kV. The X-ray diffraction (XRD) analysis was performed on a micro X-ray diffractometer (Model RINT-2100, Rigaku) with Cu–Kα radiation (λ = 1.54 Å) at 40 kV and 40 mA, and a scan rate of 2° (2θ)/min. The average crystalline size (Dav) of titania nanocrystals was estimated from the X-ray line broadening of the [101] diffraction peak of anatase, according to the Debye-Scherrer equation. The nitrogen adsorption isotherms were obtained with a nitrogen adsorption apparatus (BELSORP18 PLUS). The powders were further degassed under vacuum at 200°C for 2 h before measurements to evacuate the physisorbed moisture. Adsorption data in the range of relative pressure p/p₀ = 0.05–0.50 were used to calculate the Brunauer-Emmett-Teller specific surface area (S_BET) of the synthesized titania materials. The pore volume was evaluated from the adsorbed amount at a relative pressure 0.99.

3 Results and Discussion

Characteristics of titania-based nanocrystals

Fig. 2 shows TG-DTA result of the as-prepared ZrO₂-doped titania powder derived under the molar ratio [Ti+Zr]/[ACA] = 1, [Ti+Zr]/[LAHC] = 4, and dried at 80°C in air atmosphere. The as-synthesized powder underwent a total weight loss of 24.4% with decomposition steps in 200–500°C. Endothermic peaks and weight loss in the range of 100–200°C can be attributed to desorption of water. Exothermic peaks at 359°C and 452°C can be attributed to the decomposition of organics substances, including some amount of surfactants, modifying agent and TIPT-ACA adducts. The result indicates that organic substances and adducts are almost eliminated at 500°C.

The effect of molar ratios of Ti/Zr on the phase composition of fabricated ZrO₂-doped titania nanocrystals prepared by this present method was investigated by XRD.
The XRD patterns of bulk titania-based powders derived under various molar ratios of Ti/Zr and calcined at 500 °C in air are shown in Fig. 3. The calcined pure titania and titania powders doped with less than 10 mol% Zr exhibited only the diffraction peaks indexed the anatase-type structure. The precipitation of zirconia occurred for ZrO₂-doped titania nanocrystals (Ti/Zr = 90/10 mol%) because of the rate of hydrolysis of titania precursor and dopant did not coincide well. All samples in Fig. 3 showed similar XRD patterns attributed to [101], [103], [004], [112], [200], [105], [211], and [204] reflections, respectively, indicating the formation of anatase phase structure of titania nanocrystals.

Effect of the addition of small amount of ZrO₂ dopants on the thermal stability of synthesized titania-based nanocrystals was investigated. The XRD patterns of pure and ZrO₂-doped titania nanocrystals (Ti/Zr = 99.5/0.5 mol%) calcined at various calcination temperatures (500 – 900 °C) for 4 h are compared in Fig. 4. As shown in Fig. 4(a), calcined up to 600 °C, only the anatase phase of titania was identified. The rutile phase was observed at the calcination temperature higher than 600 °C. For the ZrO₂-doped titania nanocrystals (Ti/Zr = 99.5/0.5 mol%) system, as shown in Fig. 4(b), the rutile peaks were observed at temperature higher than 800 °C. These results are in agreement with the previous article reported by Kim et al. It is clear that the addition of ZrO₂ dopants to the reaction system has a great effect to retard the phase transformation from anatase to rutile phase of titania nanocrystals. Yang and Ferreira have reported that the effect of doped Zr species on the phase transformation due to the increasing of strain energy as a result of the substitution of Zr⁴⁺ ions for Ti⁴⁺. It can be also noticed that the XRD patterns of ZrO₂-doped titania nanocrystals calcined at 700 °C and higher show the XRD peaks attributed to tetragonal zirconia together with anatase and rutile peaks of titania.

The crystalline size of the anatase structured materials estimated using Debye-Scherrer equation and S BET of titania-based nanocrystals calcined at 500 °C and 600 °C for 4 h are given in Table 1. Fig. 5 presents TEM images and nitrogen adsorption isotherms of the mesoporous pure and ZrO₂-doped titania nanocrystals calcined at 500 °C for 4 h. The size of anatase titania nanocrystals decreased from ca. 10 – 20 nm for pure titania nanocrystals to ca. 7 – 15 nm for ZrO₂-doped titania (Ti/Zr = 99.5/0.5 mol%) nanocrystals.
Table 1 Effect of ZrO$_2$-doping on the crystallite size and specific surface area of TiO$_2$-based nanocrystals.

<table>
<thead>
<tr>
<th>Zr concentration$^a$</th>
<th>Crystalline size (nm) $^b$</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500$^\circ$C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure TiO$_2$</td>
<td>13</td>
<td>73</td>
<td>0.248</td>
</tr>
<tr>
<td>0.5 mol%</td>
<td>12</td>
<td>77</td>
<td>0.250</td>
</tr>
<tr>
<td>1 mol%</td>
<td>11</td>
<td>71</td>
<td>0.195</td>
</tr>
<tr>
<td>3 mol%</td>
<td>11</td>
<td>50</td>
<td>0.176</td>
</tr>
<tr>
<td>5 mol%</td>
<td>11</td>
<td>41</td>
<td>0.151</td>
</tr>
<tr>
<td>600$^\circ$C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pure TiO$_2$</td>
<td>17</td>
<td>37</td>
<td>0.169</td>
</tr>
<tr>
<td>0.5 mol%</td>
<td>15</td>
<td>44</td>
<td>0.198</td>
</tr>
<tr>
<td>1 mol%</td>
<td>14</td>
<td>43</td>
<td>0.204</td>
</tr>
<tr>
<td>3 mol%</td>
<td>14</td>
<td>26</td>
<td>0.164</td>
</tr>
</tbody>
</table>

$^a$ [Ti+Zr]/[ACA]=1, [Ti+Zr]/[LAHC]=4, calcined at 500$^\circ$C and 600$^\circ$C for 4 h.

$^b$ Estimated from the line broadening of the [101] diffraction peak of anatase, according to the Debye-Scherrer equation.

The ZrO$_2$–doped titania (Ti/Zr = 99.5/0.5 mol %) exhibited highest $S_{\text{BET}}$. The crystalline size decreased with increasing the amount of ZrO$_2$ dopants, indicating that the presence of small amount of ZrO$_2$ dopants is obviously suppress the crystallite growth, which is in good agreement with the results by Hirano et al.22). Because the ionic radius of Zr$^{4+}$ (ca. 0.072 nm) is larger than that of Ti$^{4+}$ (ca. 0.061 nm), Zr$^{4+}$ ions introduced to the titania framework by the combination of SATM and sol-gel process would not enter to the titania framework to form a stable solid solution. These Zr$^{4+}$ ions would gradually migrate to the surface of titania nanocrystals during the calcination process performed. The energy necessary for the movement of anatase grain boundary then increases and the driving force for the anatase grain boundary migration decreases. The crystalline growth is thereby suppressed.

4 Conclusions
Our work demonstrates that by using this present method based on SATM combined with sol-gel using micellar assemblies of LAHC as templating structure, it is possible to fabricate mesoporous ZrO$_2$–doped titania nanocrystals with small crystalline size, high thermal stability and high surface area. The 0.5 mol% ZrO$_2$–doped titania showed highest surface area. The anatase phase mesoporous structure was obtained in limitation of less than 10 mol% of ZrO$_2$ dopant. The ZrO$_2$ dopants play a role in retard the anatase to rutile phase transformation of titania nanocrystals during calcined at various temperatures and also suppress the crystallite growth.

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Fig.5 TEM micrographs and N$_2$ adsorption isotherms of (a)-(b) pure titania and (c)-(d) ZrO$_2$-doped titania (Ti/Zr=99.5/0.5 mol%) nanocrystals (inset; SAED of nanocrystals) calcined at 500°C.


