Preparation of nitrogen-doped mesoporous TiO$_2$ with a room-temperature ionic liquid

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ABSTRACT

The nitrogen-doped mesoporous TiO$_2$ (meso N-TiO$_2$) have been prepared by the sol-gel method with room temperature ionic liquids (RTIL) (C$_4$mimBF$_4$) as the template. By $^1$H NMR, interactions between titanium and ionic liquid are observed. The meso N-TiO$_2$ (10-50 nm) possesses the anatase phase with a pore opening of 5-8 nm observed by TEM. The band gap of the meso N-TiO$_2$ is 2.47 eV as determined by DR-UV/VIS. The meso N-TiO$_2$ has a remarkable activity in photocatalytic degradation of methylene blue under visible light ($\lambda$ >400 nm). The extended X-ray absorption fine structure (EXAFS) data show that the Ti-O and Ti-Ti bond distances in the meso N-TiO$_2$ are 1.96 and 3.02 Å, respectively, suggesting that the meso N-TiO$_2$ may be distorted with insertion of nitrogen into the TiO$_2$ matrix.

Keywords: ionic liquid, visible light, photocatalysis, mesoporous TiO$_2$, EXAFS

1 INTRODUCTION

TiO$_2$ has played an important roles in many environmental applications such as photocatalytic degradation of toxic organics, reduction of NO to N$_2$, and splitting of H$_2$O [1-4]. Room temperature ionic liquids (RTILs), so called “green solvents”, can be used in separation, electrochemistry, and catalysis because of its nonvolatile, nonflammable, and thermally stable properties [5-7]. Recently, it is found the RTILs can act as a template for synthesizing novel mesoporous materials by the sol-gel methods [8-10]. The high surface area mesoporous TiO$_2$ (meso TiO$_2$) possesses better photocatalytic activities for degradation of chlorinated organic compounds such as 4-chlorophenol [11,12]. However, TiO$_2$ can only absorb UV light in range of <387 nm, corresponding 5-8% of the solar spectrum. Anion (such as N$_3$) doped TiO$_2$ has been found very active in visible light photocatalysis [13-16].

By extended X-ray absorption fine structure (EXAFS) spectroscopy, it was found that copper oxide clusters in the micropores involved in catalytic reduction of NO and oxidation of 2-chlorophenol [17,18]. These molecule-scale data turn out to be very useful in revealing nature of catalytic active species and reaction mechanisms involved. Thus, the main objective of this work was to study chemical structure of nitrogen-doped mesoporous TiO$_2$ (meso N-TiO$_2$) (synthesized using RTIL as the template) by EXAFS spectroscopy.

2 EXPERIMENTAL

The cation (1-butyl-3-methyl-imidazolium ion, [C$_4$mim]$^+$) of the RTIL ([C$_4$mim][BF$_4$]) was synthesized by refluxing of 0.6 mol of 1-chlorobutane (99.4%, TEDIA) and 0.6 mol of 1-methylimidazole (99%, Acros) at 353 K for 72 h and washed three times with 10 mL of ethyl acetate (HPLC/Spectro, Tedia). The anion solution was prepared by mixing of 0.6 mol of NaBF$_4$ (98%, Acros) and 400 mL of acetone (UST/NP grade, Pharmca) for 24 h. The nitrogen doped mesoporous TiO$_2$ (meso N-TiO$_2$) was synthesized using RTIL as the template. Generally, 15 g of NH$_4$OH (28-30%, J.T. Baker) were adding slowly into a mixture solution which contains 6 g of titanium tetrabutoxide (Ti(OBu)$_4$), 90 mL of isopropenol (90 mL) and 30 g of the RTIL with stirring for 5 h. The mixture was then heated in a teflon lined autoclave at 375 K for 24 h. The as-synthesized meso N-TiO$_2$ was filtered, washed with acetone and calcined at 773 K for 0.5 h. The nitrogen doped TiO$_2$ (N-TiO$_2$) photocatalyst was also synthesized with a similar procedure without the RTIL.

The $^1$H NMR (nuclear magnetic resonance) chemical shifts of the RTIL were determined on a Bruker Avance 300 spectrometer with dimethylsulfoxide (DMSO-d$_6$) as the solvent and internal standard (acquisition time = 1.373 s, actual pulse repetition time = 2 s, number of scans = 32, and excitation pulse-angle = 30$^\circ$). Topologies of the photocatalysts were determined by high resolution transmission electron microscopy (JEM-2100F, JEOL). Diffuse reflectance UV/VIS spectra (DR UV-VIS) of the photocatalysts were also determined on a UV-VIS spectrophotometer (HITACHI U-3010) with a scan speed of 120 nm/min (200-700 nm).

Ti K-edge (4.966 keV) XANES spectra of the photocatalysts were collected at 298 K on the Wiggler beamline (17C) at the Taiwan National Synchrotron Radiation Research Center. The electron storage ring was operated at energy of 1.5 GeV (ring current = 120-200 A). A Si(111) double-crystal monochromator was used for selection of energy with an energy resolution ($\Delta E/E$) about 1.9 × 10$^{-4}$ (eV/eV). Beam energy was calibrated by the adsorption edge of a Ti foil at an energy of 4966 eV. The
isolated EXAFS data were normalized to the edge jump and converted to the wavenumber scale. The structural parameters that were varied during the refinements include the bond distance and variance. Coordination numbers of Ti were systematically varied in the course of the analysis within a given fitting range. Fitting of data to model compounds was performed using FEFFIT from UWXAFS 3.0 in combination with multiple scattering code FEFF 8.0 programs [19]. The FEFFIT was used to determine the best fitting results with a minimum (< 0.01 Å⁻¹) of the Debye-Waller factors. The Fourier transform was performed on k²-weighted EXAFS oscillations in the range of 3.7-14.2 Å⁻¹.

Photocatalytic degradation of methylene blue (MB, C₁₆H₁₀N₃S) was determined on a home-made photoreactor with a total reflection system [20]. Typically, 0.03 g of the photocatalysts were suspended in the MB (7.8×10⁻⁶ moleL⁻¹) aqueous solution (50 mL) with magnetic stirring. A 20 W tungsten lamp (Newport, model 63205) with water filter (Spectra-physics, model 61945) and 400 nm cut-off window were used as the visible light source. The concentration of MB was determined by UV-VIS spectroscopy (at 665 nm).

3 RESULTS AND DISCUSSION

To form the mesopore TiO₂ structure, the RTIL ([C₅mim][BF₄]) acts as a template. The ¹H NMR chemical shifts of the [C₅mim][BF₄] and Ti(OBu)₄/[C₅mim][BF₄] are shown in Figure 1. As the titanium oxide precursor (Ti(OBu)₄) is mixed with the RTIL, little perturbation is found at δ0.88, 1.24, 1.75, 3.83, and 4.14 for ¹H in the long chain of the [C₅mim]⁺. The ¹H on the cationic five-ring (H₃ and H₄) possesses upfield shifts (H₃ δ9.03 → 8.97; H₄ δ7.72, 7.65 → 7.50, 7.47) in the mixture of Ti(OBu)₄ and [C₅mim][BF₄], suggesting chemical interactions between titanium and cationic five-ring of the ionic liquid.

The TEM images and electron diffraction patterns of N-TiO₂ and meso N-TiO₂ are shown in Figure 2. The particle sizes of the photocatalysts are in range of 10-50 nm. Note that the band gap absorptions of the N-TiO₂ and meso N-TiO₂ are 2.54 and 2.47 eV, respectively as observed by DRUV/VIS spectroscopy (at 665 nm).

EXAFS spectra of the photocatalysts were recorded and analyzed in the range of 3.7-14.2 Å⁻¹. Table 1 shows the structural parameters determined by the best fitting of the EXAFS spectra. In all EXAFS data analyzed, the Debye-Waller factors (Δσ²) are less than 0.01 Å⁻¹. The 1st (Ti-O) and 2nd (Ti-Ti) bond distances of the nanosize N-TiO₂ and meso N-TiO₂ are 1.96 and 3.02-3.04 Å, respectively, which are very different from those of the bulky TiO₂ (1.95 and 3.07 Å). Insertion of nitrogen in the TiO₂ matrix as well as more surface Ti atoms may be the factors that cause the distortion of chemical structure of TiO₂. Note that coordination numbers of nanosizesize particle are generally decreased [21, 22]. As expected, a less coordination numbers of the 1st and 2nd shells for the N-TiO₂ (5.2 and 2.4) and meso N-TiO₂ (2.2 and 1.4) photocatalysts are also found if compared with those of the bulky TiO₂ (5.5 and 3.3).

Figure 3 shows the photocatalytic degradation of MB (7.8×10⁻⁶ moleL⁻¹) on the N-TiO₂ photocatalysts under the visible light radiation. Without a photocatalyst, about 26% of MB can be degraded under radiation for 15.5 hours. On the N-TiO₂ photocatalyst, about 73% of MB is degraded within 14 hours. Interestingly, on the meso N-TiO₂ photocatalyst, in the early stage, the conversion of MB is as high as 50%. After radiation of seven hours, the meso N-TiO₂ has a conversion of 87%.

4 CONCLUSIONS

The meso N-TiO₂ visible-light photocatalyst can be synthesized with the sol-gel method using the ionic liquid ([C₄mim]BF₄) as the template. By ¹H NMR, interactions between Ti and the cationic five-ring of the ionic liquid are observed. The meso N-TiO₂ possesses an anatase phase with pore openings of 5-8 nm. The refined EXAFS data show that the Ti-O and Ti-Ti bond distances in the meso N-TiO₂ are 1.96 and 3.02 Å, respectively, suggesting distortion of the TiO₂ framework caused by facts of the increasing surface Ti atoms and insertion of nitrogen in the TiO₂ matrix. The meso N-TiO₂ has a very high photocatalytic reactivity, for instance, under the radiation of visible light for seven hrs, a conversion of 87% in degradation of MB can be obtained.

REFERENCES

Table 1: Speciation data (by EXAFS) of meso N-TiO$_2$ and N-TiO$_2$

<table>
<thead>
<tr>
<th>Shell</th>
<th>R (Å)</th>
<th>CN</th>
<th>$\sigma^2$(Å$^2$)</th>
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<td>Ti-O</td>
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<td></td>
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</table>

R: bond distance
CN: coordination number
$\sigma^2$: Debye-Waller factor