

Preparation of nitrogen-doped mesoporous TiO₂ with a room-temperature ionic liquid

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ABSTRACT

The nitrogen-doped mesoporous TiO₂ (meso N-TiO₂) have been prepared by the sol-gel method with room temperature ionic liquids (RTIL) (C₄mimBF₄) as the template. By ¹H NMR, interactions between titanium and ionic liquid are observed. The meso N-TiO₂ (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-TiO₂ is 2.47 eV as determined by DR-UV/VIS. The meso N-TiO₂ 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-TiO₂ are 1.96 and 3.02 Å, respectively, suggesting that the meso N-TiO₂ may be distorted with insertion of nitrogen into the TiO₂ matrix.

Keywords: ionic liquid, visible light, photocatalysis, mesoporous TiO₂, EXAFS

1 INTRODUCTION

TiO₂ has played an important roles in many environmental applications such as photocatalytic degradation of toxic organics, reduction of NO to N₂, and splitting of H₂O [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 TiO₂ (meso TiO₂) possesses better photocatalytic activities for degradation of chlorinated organic compounds such as 4-chlorophenol [11,12]. However, TiO₂ can only absorb UV light in range of <387 nm, corresponding 5-8% of the solar spectrum. Anion (such as N, S, and P) doped TiO₂ 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 TiO₂ (meso N-TiO₂) (synthesized using RTIL as the template) by EXAFS spectroscopy.

2 EXPERIMENTAL

The cation (1-butyl-3-methyl-imidazolium ion, [C₄mim]⁺) of the RTIL ([C₄mim][BF₄]) 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 NaBF₄ (98%, Acros) and 400 mL of acetone (UST/NP grade, Pharmca) for 24 h. The nitrogen doped mesoporous TiO₂ (meso N-TiO₂) was synthesized using RTIL as the template. Generally, 15 g of NH₄OH (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 isopropanol (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-TiO₂ was filtered, washed with aceton and calcined at 773 K for 0.5 h. The nitrogen doped TiO₂ (N-TiO₂) photocatalyst was also synthesized with a similar procedure without the RTIL.

The ¹H NMR (nuclear magnetic resonance) chemical shifts of the RTIL were determined on a Bruker Avance 300 spectrometer with dimethylsulfoxide (DMSO-d₆) 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°). 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 ($<0.01 \text{ \AA}^{-1}$) of the Debye-Waller factors. The Fourier transform was performed on k^3 -weighted EXAFS oscillations in the range of $3.7\text{-}14.2 \text{ \AA}^{-1}$.

Photocatalytic degradation of methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$) 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 ($7.8\times10^{-6} \text{ moleL}^{-1}$) 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 TiO_2 structure, the RTIL ($[\text{C}_4\text{mim}]^+[\text{BF}_4]^-$) acts as a template. The ^1H NMR chemical shifts of the $[\text{C}_4\text{mim}][\text{BF}_4]$ and $\text{Ti(OBu)}_4/[\text{C}_4\text{mim}][\text{BF}_4]$ are shown in Figure 1. As the titanium oxide precursor (Ti(OBu)_4) is mixed with the RTIL, little perturbation is found at δ 0.88, 1.24, 1.75, 3.83, and 4.14 for ^1H in the long chain of the $[\text{C}_4\text{mim}]^+$. The ^1H on the cationic five-ring (H_A and H_B) possesses upfield shifts (H_A $89.03 \rightarrow 8.97$; H_B $87.72, 7.65 \rightarrow 7.50, 7.47$) in the mixture of Ti(OBu)_4 and $[\text{C}_4\text{mim}][\text{BF}_4]$, suggesting chemical interactions between titanium and cationic five-ring of the ionic liquid.

The TEM images and electron diffraction patterns of N- TiO_2 and meso N- TiO_2 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- TiO_2 and meso N- TiO_2 are 2.54 and 2.47 eV, respectively as observed by DR-UV/VIS spectroscopy. The select area electron diffraction (SAED) patterns indicate that the N- TiO_2 and meso N- TiO_2 have mainly the anatase phase. It is also clear that the meso N- TiO_2 has pore openings of 5-8 nm in the TEM bright field images.

EXAFS spectra of the photocatalysts were recorded and analyzed in the range of $3.7\text{-}14.2 \text{ \AA}^{-1}$. Table 1 shows the structural parameters determined by the best fitting of the EXAFS spectra. In all EXAFS data analyzed, the Debye-Waller factors ($\Delta\sigma^2$) are less than 0.01 \AA^{-1} . The 1st (Ti-O) and 2nd (Ti-Ti) bond distances of the nanosize N- TiO_2 and meso N- TiO_2 are 1.96 and $3.02\text{-}3.04 \text{ \AA}$, respectively, which are very different from those of the bulky TiO_2 (1.95 and 3.07 \AA). Insertion of nitrogen in the TiO_2 matrix as well as more surface Ti atoms may be the factors that cause the distortion of chemical structure of TiO_2 . Note that

coordination numbers of nanosize particle are generally decreased [21, 22]. As expected, a less coordination numbers of the 1st and 2nd shells for the N- TiO_2 (5.2 and 2.4) and meso N- TiO_2 (2.2 and 1.4) photocatalysts are also found if compared with those of the bulky TiO_2 (5.5 and 3.3).

Figure 3 shows the photocatalytic degradation of MB ($7.8\times10^{-6} \text{ moleL}^{-1}$) on the N- TiO_2 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- TiO_2 photocatalyst, about 73% of MB is degraded within 14 hours. Interestingly, on the meso N- TiO_2 photocatalyst, in the early stage, the conversion of MB is as high as 50%. After radiation of seven hours, the meso N- TiO_2 has a conversion of 87%.

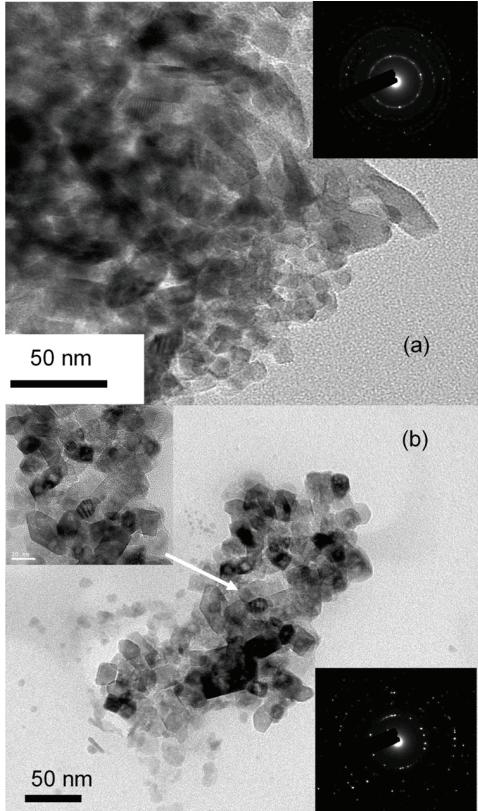
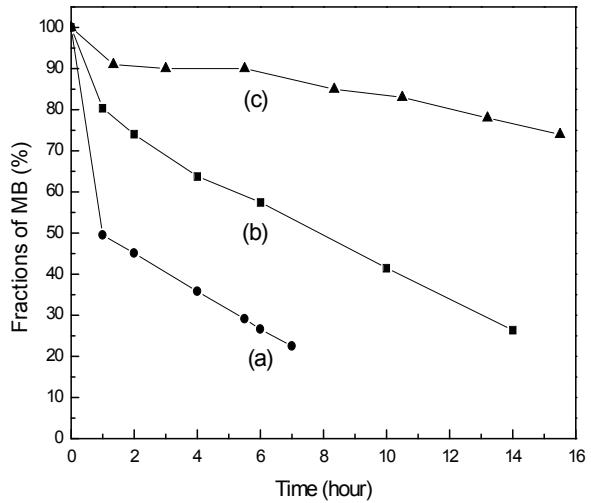
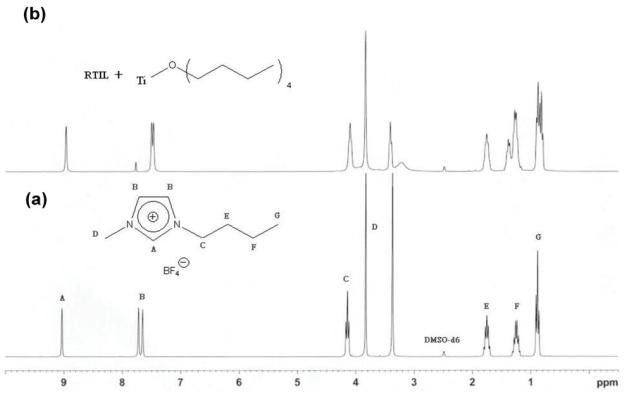
4 CONCLUSIONS

The meso N- TiO_2 visible-light photocatalyst can be synthesized with the sol-gel method using the ionic liquid (C_4mimBF_4) as the template. By ^1H NMR, interactions between Ti and the cationic five-ring of the ionic liquid are observed. The meso N- TiO_2 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- TiO_2 are 1.96 and 3.02 \AA , respectively, suggesting distortion of the TiO_2 framework caused by facts of the increasing surface Ti atoms and insertion of nitrogen in the TiO_2 matrix. The meso N- TiO_2 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.

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	Shell	R (\AA)	CN	$\sigma^2(\text{\AA}^2)$
Meso N-TiO ₂	Ti-O	1.96	2.2	0.0043
	Ti-Ti	3.02	1.4	0.0050
N-TiO ₂	Ti-O	1.96	5.2	0.0067
	Ti-Ti	3.04	2.4	0.0039
TiO ₂	Ti-O	1.95	5.5	0.0074
	Ti-Ti	3.07	3.3	0.0057

R: bond distance

CN: coordination number

σ^2 : Debye-Waller factor

Table 1: Speciation data (by EXAFS) of meso N-TiO₂ and N-TiO₂