Research Article

Chemical Structure of TiO_2 Nanotube Photocatalysts Promoted by Copper and Iron

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TiO_2 nanotubes (TNTs) promoted by copper (5%) (Cu-TNT) and iron (5%) (Fe-TNT) were prepared for visible-light photocatalysis. By X-ray absorption near edge structure (XANES) spectroscopy, it is found that the enhanced photocatalytic degradation of methylene blue (MB) on Cu-TNT and Fe-TNT is associated with the predominant surface photoactive sites A_2 ($(\text{Ti}=\text{O})\text{O}_4$). By extended X-ray absorption fine structure (EXAFS) spectroscopy, the dispersed copper and iron also cause increases in the Ti–O and Ti–(O)–Ti bond distances by 0.01–0.02 and 0.04–0.05 Å, respectively. The decreased Ti–O bonding energy may lead to an increase of photoexcited electron transport. The copper- or-iron promoted TNT can thus enhance photocatalytic degradation of MB under the visible-light radiation.

1. Introduction

Titanium nanotubes (TNTs) having a high surface area, chemical stability (under alkali or acidic conditions), and sunlight sensitization have been employed for potential applications in photoinduced reactions [1], sensitized electrodes [2, 3], and driven water cleavage for hydrogen generation [4]. From environmental perspectives, TNTs are widely used in photocatalytic detoxification of hazardous substances [5, 6], adsorption of organic pollutants [7], and enrichment of heavy metals [8].

Nanotubular and nanowired TiO_2 have a better efficiency for photocatalytic degradation of rhodamine B and methyl orange under solar illumination than the commercialized nano TiO_2 (P25) [9]. However, it was found that the nitrogen-doped TiO_2 nanotube (N-TNT) thin film was not very effective for photocatalytic remediation of oil spill on seawater under the visible-light radiation.

Recently, transition metals such as chromium, iron, nickel, copper, and zinc have been considered as promoters for improving the photoactivity of TNTs. Zhang et al. [10] demonstrated that the $\text{Cr}_2\text{O}_3/\text{TNT}$ nanocomposite could

enhance photocatalytic yield of H_2 under visible-light. By X-ray absorption near edge structure (XANES) and X-ray photoelectron spectroscopy (XPS), Jang and coworkers [11] found that the surface iron species were composed of iron hydrate on TNT (Fe-TNT). Nevertheless, the Fe-TNT had a greater photocurrent generation but poor photocatalytic performances for water splitting and dye degradation. Nickel-intercalated TNT had a greater photocatalytic yield of H_2 than the TNT under ultraviolet (UV) illumination [12]. Interestingly, the hydrated nickel complex was the active sites for reduction of proton in water to H_2 . The CuO dispersed tubular TiO_2 could enhance H_2 yield [13]. A nanosize ZnO decorated TNT was preferable for rhodamine B degradation under UV light [14].

By component-fitted XANES, the catalytic active species such as copper oxide clusters in the channels of ZSM-5 were found playing an important role in catalytic decomposition of heptane and toluene. Speciation of catalytic active sites and reaction paths involved in catalytic degradation of chlorophenols and reduction of NO was also revealed by XANES. Hsiung and coworkers [15] found by XANES that the photoactive species (A_2) ($(\text{Ti}=\text{O})\text{O}_4$) in TiO_2 were

FIGURE 1: Transmission electron microscopic images, selected area electron diffraction patterns, and energy dispersive X-ray spectra of the (a) TNT, (b) Cu-TNT, and (c) Fe-TNT.

responsible for the photocatalytic decomposition of methylene blue (MB). In the present work, copper and iron which are less toxic and easy to obtain were used for preparation of the visible-light photocatalysts (i.e., Cu-TNT and Fe-TNT). To design the effective visible-light Cu-TNT and Fe-TNT photocatalysts, the molecule-scale data such as local bonding environment and oxidation state of the photoactive species especially the A_2 sites are essential. Thus the main objective of the present work was to study nature of the photoactive species in the copper-and-iron promoted TNTs by synchrotron XANES and extended X-ray absorption fine structure (EXAFS).

2. Experimental

The preparation methods for the TNT have been described [16, 17]. Typically, a mixture of 0.625 g of TiO_2 (P25, Degussa) and 12.5 mL of a NaOH (5 M) solution was heated at 473 K for 24 h in a Teflon-lined autoclave. The product slurry was

filtered and washed with 300 mL of 0.01 M HNO_3 solution. The filtered solid was dried at 333 K for 6 h. To prepare copper-and-iron dispersed TNTs (Cu- and Fe-TNTs), $\text{Cu}(\text{NO}_3)_2$ (JT Baker), or $\text{Fe}(\text{NO}_3)_3$ (JT Baker) at a molar ratio of Cu- or Fe-to-Ti of 0.1 was mixed with the TNT powder in 100 mL of H_2O . A Na_2CO_3 (JT Baker) solution was used to adjust the pH values of the Cu-TNT and Fe-TNT mixtures to 7 and 5, respectively. The Cu-TNT or Fe-TNT slurry was dried at 373 K for 24 h.

The surface morphologies of the TNT, Cu-TNT, and Fe-TNT were also analyzed by field-emission scanning electron microscopic (FE-SEM) analyzer (XL-40FEG, Philips) coupled with energy dispersive X-ray spectrometry (EDS). Cross-sectional topologies of the TNT, Cu-TNT, and Fe-TNT were also determined by transmission electron microscopy (TEM) (CM-200 TWIN, Philips) functioning with the selected area electron diffractometry (SAED). The sunlight absorption characteristics of the nanosize TiO_2 (Kanto Chemical), TNT, Cu-TNT, and Fe-TNT were measured on

a diffuse reflectance ultraviolet-visible (DR UV-Vis) spectrophotometer (Cary 100 Conc, Varian). Nitrogen adsorption/desorption isotherms of the nanosize TiO_2 , TNT, Cu-TNT, and Fe-TNT were studied on a surface area analyzer (COULTER SA3100, Beckman), and their pore size distributions were also obtained by the Barrett-Joyner-Halenda (BJH) calculation.

Photocatalytic degradation of methylene blue (KATAYAMA Chemical) effected by the nanosize TiO_2 , TNT, Cu-TNT, or Fe-TNT was performed on a home-made photoreactor [18]. 0.01 g of the nanosize TiO_2 , TNT, Cu-TNT, or Fe-TNT photocatalyst was suspended in the MB ($20 \text{ mg}\cdot\text{L}^{-1}$) aqueous solution (50 mL) with magnetic stirring and cooling water circulation (Medel-B401D, Firstek Scientific) to maintain the reaction system at 298 K. The photocatalysts suspended MB solution was well stirred in the dark for 1 h prior to the photocatalytic experiments. A 300 W Xenon lamp solar simulator (no. 91160A, Newport) combined with an AM 1.5 G filter (no. 59044, Oriel) was served as the light source. The power density of the irradiation was fixed at $100 \text{ mW}\cdot\text{cm}^{-2}$ by the use of a reference solar cell and meter (no. 91150, Oriel). The concentration of the MB was measured by a UV-Vis spectrophotometer (Cary 100 Conc, Varian) at the maximum absorbance of 662 nm.

The EXAFS and XANES spectra of the TNT, Cu-TNT, and Fe-TNT photocatalysts and model compounds such as $\text{Cu}(\text{OH})_2$ (Showa), $\text{Fe}(\text{OH})_3$ (Alfa Aesar), and Cu^{2+} or $\text{Fe}^{3+}/\text{MCM-41}$ (prepared by impregnation of $\text{Cu}(\text{NO}_3)_3$ (JT Baker) or $\text{Fe}(\text{NO}_3)_3$ (JT Baker) on MCM-41 and dried at 383 K for 8 h) were collected on the Wiggler beam line at the Taiwan National Synchrotron Radiation Research Center. The storage ring was operated at the energy of 1.5 GeV. A Si (111) double-crystal monochromator was used for beam energy selection at the energy resolution ($\Delta E/E$) of 1.9×10^{-4} (eV/eV). The beam energy was calibrated by the use of the maximum absorption edge of Ti, Cu, and Fe foils at 4966, 8979, and 7112 eV, respectively. The k^3 -weighted $\chi(k)$ oscillations were Fourier-transformed from k to R spaces using the UWXAFS 3.0 program coupled with the FEFF 8.0 code [19]. A Bessel window function was activated in the k ranges of 2.5–12, 3.1–13.7, and 3.1–12.1 $\text{\AA}^{-1}$ for Ti, Cu, and Fe K-edges, respectively. The S_0^2 (many-body factor) was fixed at 0.9 to reduce the parameter variables during the fitting. For the XANES spectra analysis, the Gaussian-Lorentzian calculation was employed for the curve deconvolution. Fittings of the model compounds to the experimental data have errors of $\pm 0.01 \text{ \AA}$ and $\pm 0.02 \text{ \AA}$ in bond distances and $\pm 10\%$ and $\pm 25\%$ in coordination numbers (CNs) for the first and second fitting shells, respectively.

3. Results and Discussion

The TEM images, SAED patterns, and EDS spectra of the TNT, Cu-TNT, and Fe-TNT photocatalysts are shown in Figure 1. The TNTs having a nanotube structure are 100–200 nm in length, 10–20 nm in the opening at both ends, and 3–5 nm in the wall thickness. It seems that the nanosize copper and iron aggregates are formed on the internal

FIGURE 2: Diffuse reflectance ultraviolet-visible spectra of the (a) nanosize TiO_2 , (b) TNT, (c) Cu-TNT, and (d) Fe-TNT.

surfaces of the TNT. The EDS spectra indicate that about 5.3% of Cu and 4.2% of Fe are dispersed on the Cu-TNT and Fe-TNT, respectively.

The DR UV-Vis spectra of the nanosize TiO_2 , TNT, Cu-TNT, and Fe-TNT are shown in Figure 2. The TNTs have intensive absorption edges at 200–400 nm with a very small absorption at 500 nm. Note that the Cu- and Fe-TNT have extended to visible-light absorption range of 400–800 nm.

The TNT possessing a surface area of $213\text{--}235 \text{ m}^2\cdot\text{g}^{-1}$ which was determined and calculated using the data obtained from the N_2 adsorption/desorption isotherms is much greater than the nanosize TiO_2 ($42 \text{ m}^2\cdot\text{g}^{-1}$). In Figure 3, it is clear that the hysteresis loops at $P/P_0 > 0.8$ for the TNTs in the N_2 adsorption and desorption isotherms may be associated with the nanotubular conformation. Figure 3 also shows that the pore size distribution of the TNT, Cu-TNT, and Fe-TNT is between 50 and 100 nm while the nanosize TiO_2 has a relatively less pore structure (10–40 nm). The adsorbed N_2 volume of the TNTs is in the range of $550\text{--}700 \text{ cm}^3\cdot\text{g}^{-1}$ which is greater than that of the nanosize TiO_2 by 5–7 times.

As the Cu-TNT and Fe-TNT have a visible-light absorption capacity, photocatalytic degradation of MB was determined on a solar simulator. Figure 4 shows photocatalytic degradation of MB effected by the TNT, Cu-TNT, and Fe-TNT. For comparison, the photocatalytic activity of the nanosize TiO_2 was also determined. It seems that the nanosize TiO_2 and TNT are not very active ($<25\%$) in photocatalytic degradation of MB under sunlight illumination for 240 min, while notably the Cu-TNT and Fe-TNT possess greater MB degradation efficiencies, that is, 86% and 92%, respectively. Note that the enhanced photocatalytic activity of the Cu-TNT and Fe-TNT may be associated with the extended visible-light absorption range.

To better understand the photocatalytic sites of the TNT, Cu-TNT, and Fe-TNT, their XANES and EXAFS spectra of the Ti, Cu, and Fe K-edges were measured. Figure 5 shows the Ti K-edge XANES spectra of the Cu-TNT and Fe-TNT. It is clear that the dispersed Cu and Fe have little perturbation on distribution of the A_1 , A_2 , and A_3 species for the TNTs,

FIGURE 3: N_2 adsorption/desorption isotherms and the corresponding Barrett-Joyner-Halenda pore size distribution of the (a) nanosize TiO_2 , (b) TNT, (c) Cu-TNT, and (d) Fe-TNT.

which may be associated with the tetrahedral (TiO_4), square pyramid ($(\text{Ti}=\text{O})\text{O}_4$), and octahedral (TiO_6) titanium oxide structures, respectively, within the preedge of 4963–4973 eV [15, 20]. Note that the A_2 species which may account for the photoactive sites are predominant (51–54%) on the Cu-TNT and Fe-TNT.

Figure 6 shows the component-fitted copper and iron K-edges XANES spectra of the Cu-TNT and Fe-TNT, respectively. In the copper and iron XANES spectra at 8977–8987

and 7111–7125 eV, respectively, the 1s-to-4p and 1s-to-3d transitions are observed [21, 22]. About 83% of adsorbed Cu^{2+} and 17% of $\text{Cu}(\text{OH})_2$ are found in the Cu-TNT photocatalyst, and the Fe-TNT contains adsorbed Fe^{3+} (47%) and $\text{Fe}(\text{OH})_3$ (53%).

Table 1 shows speciation data of the TNT, Cu-TNT, and Fe-TNT studied by EXAFS. The k^3 -weighted EXAFS oscillations are Fourier-transformed from k to R spaces using the Bessel function in the k ranges of 2.5–12 (Ti), 3.1–13.7 (Cu),

FIGURE 4: Photocatalytic degradation of methylene blue on the (a) nanosize TiO_2 , (b) TNT, (c) Cu-TNT, and (d) Fe-TNT under sunlight illumination (AM 1.5 G). The inset shows the spectrum of the sunlight source.

FIGURE 5: The Ti K-edge XANES and the Gaussian-Lorentzian deconvoluted spectra of the (a) Cu-TNT and (b) Fe-TNT. The dotted and solid lines represent fittings and experimental data, respectively.

and 3.1–12.1 (Fe) $\text{\AA}^{-1}$, respectively. It is found that the TNT possesses Ti–O and Ti–(O)–Ti bond distances of 1.87 and 3.10 $\text{\AA}$ and CNs of 4.2 and 4.7, respectively. In the presence of copper and iron, the Ti–O shell of the TNT is slightly perturbed. However, an increased bond distance of 0.04–0.05 $\text{\AA}$ for the Ti–(O)–Ti shell is observed. In the separate

FIGURE 6: The Cu and Fe K-edges XANES spectra of the (a) Cu-TNT and (b) Fe-TNT, respectively. The empty and filled symbols represent the fitting and fractions of standards calculated by the linear combination algorithm. The experimental data are shown in solid lines.

TABLE 1: Speciation data of the TNT, Cu-TNT, and Fe-TNT studied by EXAFS.

	Shells	Coordination number	Bond distance ($\text{\AA}$)	Debye-Waller factor (σ^2 ($\text{\AA}^2$))
TNT	Ti–O	4.2	1.87	0.01
	Ti–(O)–Ti	4.7	3.10	0.01
Cu-TNT	Ti–O	5.0	1.89	0.01
	Ti–(O)–Ti	4.1	3.14	0.01
Fe-TNT	Cu–O	3.2	1.94	0.01
	Ti–O	4.1	1.88	0.01
	Ti–(O)–Ti	6.7	3.15	0.01
	Fe–O	5.4	1.96	0.01

experiment, it was found that the nanosize TiO_2 dispersed with surface CuO having the Cu–O bond distance of 1.93–1.94 $\text{\AA}$ and CN of 1.2 in the first shell can, to some extent, enhance the photocatalytic yield of H_2 and dye decomposing in sea water [23]. It was also observed by *in situ* XANES and XPS that electron donation (from the photoexcited nanosize TiO_2 thin film) to the surface CuO might occur [24]. The component-fitted XANES data suggest that Cu^{2+} and Fe^{3+}

may be attributable to entrapment of photoexcited electrons from TNTs during photocatalytic degradation of MB under the visible-light irradiation.

4. Conclusions

The TNTs promoted by surface copper and iron possess relatively high photocatalytic degradation of MB (86% for Cu-TNT and 92% for Fe-TNT) under visible-light irradiation for 240 min. By component-fitted XANES, it is clear that the enhanced photocatalytic degradation of MB with the Cu-TNT and Fe-TNT is due to the predominant surface photoactive sites (A_2). The dispersed copper and iron on TNT have, to some extent, caused an increase in the Ti–(O)–Ti bond distances (0.04–0.05 Å). With the promotion of the surface copper and iron, the TNT can, therefore, enhance photocatalytic degradation of MB under the visible-light radiation.

Conflict of Interests

The authors declare no competing financial interests.

Acknowledgments

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