

In Situ XANES Study of CuO/TiO₂ Thin Films During Photodegradation of Methylene Blue

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Abstract. Speciation of copper in the CuO/TiO₂ thin film (synthesized by the doctor-blade deposition method) during photocatalytic decomposition of methylene blue has been studied by in situ X-ray absorption near-edge structural (XANES) spectroscopy. During the UV/VIS radiation (90 min), in the presence of methylene blue, a decrease of Cu(II) and an increase of Cu(0) and Cu(I) fractions in the CuO/TiO₂ thin film are observed by in situ XANES. The r-space Fourier transformation EXAFS (extended X-ray absorption fine structural) spectra also show that the bond distance of Cu–O in the thin film is decreased by 0.03 Å during photocatalytic degradation of methylene blue.

Keywords: CuO/TiO₂, thin film, XANES, photocatalysis.

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INTRODUCTION

TiO₂ has been widely used in photocatalytic degradation of toxic organics. To enhance photocatalytic activities, transition metals such as Fe, Cu, Ni or Au have been doped onto TiO₂ surfaces. Lam and coworker [1] found that copper-modified TiO₂ possesses highly photocatalytic activities for oxidation of resorcinol. Chiang and coworker [2] used CuO-modified TiO₂ to decompose cyanide. The copper-deposited TiO₂ thin film also showed a bactericidal activity under UV light illumination [3]. It seems that copper-doped TiO₂ is playing an important role in photocatalysis.

X-ray absorption spectroscopy can be used in the characterization of valence and local structure (<10 Å) of toxic elements in environmental solids. Molecular-scale data such as coordination number, bond distance, and oxidation state of elements can be determined by X-ray absorption near-edge structural (XANES) and extended X-ray absorption fine structural (EXAFS) spectroscopies. By in situ XANES and EXAFS, we found that copper oxide clusters are involved in catalytic reduction of NO [4]. These molecular-scale data turn out to be very useful in revealing the nature of catalytic active species and the reaction mechanisms involved. The main objective of present work was to study speciation of copper in a CuO/TiO₂ thin film

during photocatalytic degradation of methylene blue (MB) by in situ XANES.

EXPERIMENTAL

The CuO/TiO₂ (atomic ratio Cu/Ti = 0.05) thin films were synthesized by the doctor blade technique [5,6]. Typically, 1.0 grams of titanium oxide powder (P25, degussa) and 0.15 grams of copper(II) nitrate trihydrate (99%, Hanawa) were well mixed in 2 mL of distilled water. In addition, 0.2 mL of acetylacetone (99.5%, Fluka) and 0.5 mL triton X-100 (Sigma) were added in the mixture paste. The mixture paste was immobilized on the glass substrates and calcined at 723 K for 0.5 h. Chemical structure of the photocatalyst was characterized by X-ray powder diffraction spectroscopy (D8 advance, Bruker) with Cu K α (1.542 Å) radiation. Samples were scanned from 10–50° (2 θ) with a scan rate of 5°/min.

In situ copper K-edge XANES spectra of CuO/TiO₂ thin films were measured during photocatalytic degradation of MB in a home-made photoreaction cell [7] on the Wiggler beamline (17C) at the Taiwan National Synchrotron Radiation Research Center (NSRRC). 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 ($\Delta E/E$) of about 1.9×10^{-4} (eV/eV). The absorption

spectra were collected in ion chambers that were filled with helium and nitrogen mixed gases. Beam energy was calibrated by the adsorption edge of Cu foils at an energy of 8979 eV. The absorption edge was determined at the half-high (precisely determined by the derivative) of the XANES spectrum after pre-edge baseline subtraction and normalization to the maximum post edge intensity. Semi-quantitative analyses of the edge spectra were conducted by the least-square fitting of linear combination of standard spectra (such as CuO (Merck Ltd.), Cu₂O (Merck Ltd.), Cu (Merck Ltd.) and MB/CuO (MB adsorbed on CuO)) to the spectrum of the sample. It was found that the XANES fitting percentages almost directly correspond to weight percentages. On average, an uncertainty limit of 5% corresponds to an error of ca. 2.0% in the fitting results. The isolated EXAFS data were normalized to the edge jump and converted to the wave number scale. The Fourier transform was performed on k^3 -weighted EXAFS oscillations in the range of 3.3-11.8 Å⁻¹.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction pattern of the CuO/TiO₂ thin film. The anatase (101) and rutile (110) diffraction peaks were observed in the CuO/TiO₂ thin film (calcined at 723 K). The weight fractions of anatase (70%) and rutile (30%) were determined by the diffraction intensities [8]. Note that the CuO (111) diffraction peak was not found at $2\theta = 35.54^\circ$.

Figure 2 shows the in situ XANES spectra of the CuO/TiO₂ thin film during photocatalytic degradation of MB. The white line absorption at 8994-9002 eV can be attributed to the 1s-to-4p transition that indicates the existence of the Cu(II) species. The zero- and mono-valence copper species are also found in the pre-edge spectrum at 8982 and 8982-8984 eV which can be attributed to the dipole-allowed 1s-to-4p transition, respectively.

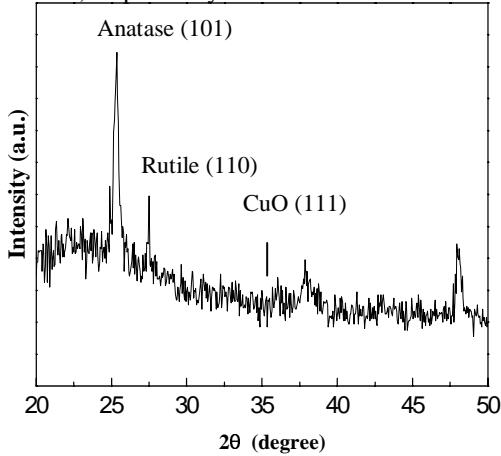


FIGURE 1. The XRD pattern of the CuO/TiO₂ thin film.

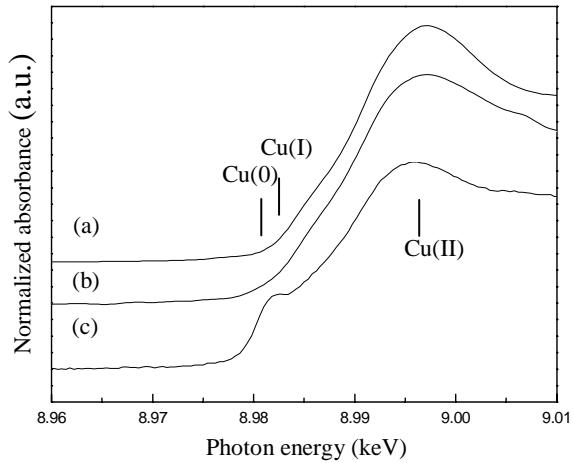


FIGURE 2. The XANES spectra of copper in the (a) CuO/TiO₂ thin film and in the presence of methylene blue under UV radiation for (b) 0 and (c) 90 min.

The main copper species that were doped on the TiO₂ thin film is Cu(II). During photocatalytic degradation of MB, little perturbation of copper was found in the XANES spectra. Prolonging the UV/VIS radiation to 90 min, fractions of Cu(0) and Cu(I) species in the CuO/TiO₂ thin film were increased. It seems that CuO is the electron acceptor during photocatalysis.

The least-square component fitting of in situ XANES spectra during photocatalytic degradation of MB is shown in Table 1. Prior to UV/VIS radiation, the main copper species in the thin film were CuO (71 %) and MB/CuO (29%). Under UV/VIS radiation for 90 min, a decrease of Cu(II) (CuO (29%) and MB/CuO (23%)) and an increase of Cu(0) (9%) and Cu₂O (39%) fractions in the CuO/TiO₂ thin film were found.

Figure 3 shows the r-space Fourier transformation spectra of the CuO/TiO₂ thin film during photocatalytic degradation of MB. Bond distances of CuO and Cu₂O were 1.95 and 1.84 Å, respectively. During photocatalytic degradation of MB, CuO in the CuO/TiO₂ thin film was, to some extent, reduced and the bond distance of Cu-O was decreased by 0.03 Å.

TABLE 1. The semi-quantitative analyses of the in situ XANES spectra of copper in the CuO/TiO₂ thin film during photocatalytic degradation of methylene blue

Copper species	UV/VIS radiation time (min)			
	0	30	60	90
CuO	71%	66%	35%	29%
Cu ₂ O	-	5%	33%	39%
Cu	-	-	10%	9%
MB/CuO	29%	29%	22%	23%

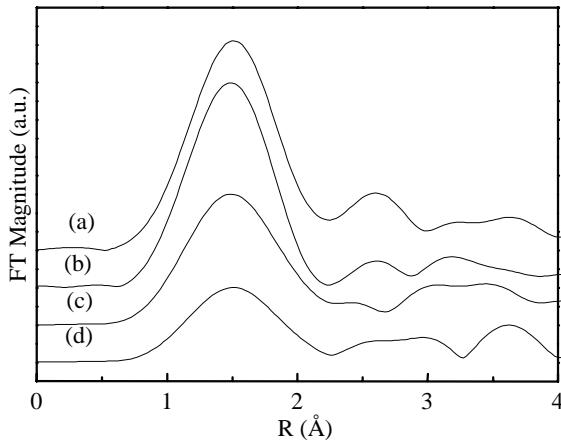


FIGURE 2. The r-space fourier transformation of copper in the CuO/TiO₂ thin film during photocatalytic degradation of methylene blue for (a) 0, (b) 30, (c) 60 and (d) 90 min.

CONCLUSION

The XANES spectra show that the main copper species doped on the TiO₂ thin film is Cu(II). During the UV/VIS radiation (90 min), in the presence of MB of Cu(II) and an increases of Cu(0) and Cu(I) fractions in the CuO/TiO₂ thin film are observed by in situ XANES. The r-space Fourier transformation EXAFS (extended X-ray absorption fine structural) spectra also show that the bond distance of Cu-O in the thin film is decreased by 0.03 Å during photocatalytic degradation of MB.

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