In Situ XANES Study of CuO/TiO_2 Thin Films during Photodegradation of Methylene Blue

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TiO_2 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 TiO_2 surfaces. Lam and coworker [1] found that copper-modify TiO_2 possesses highly photocatalytic activities for oxidation of resorcinol.

The main objective of present work was to study speciation of copper in a CuO/TiO_2 thin film during photocatalytic degradation of methylene blue (MB) by in situ XANES.

Figure 1 shows the in situ XANES spectra of the CuO/TiO_2 thin film during photocatalytic degradation of MB. The whiteline 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.

The main copper species that were doped on the TiO_2 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/TiO_2 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 increases of Cu(0) (9%) and Cu_2O (39%) fractions in the CuO/TiO_2 thin film were found.

Figure 2 shows the r-space fourier transformation spectra of the CuO/TiO_2 thin film during photocatalytic degradation of MB. Bond distances of CuO and Cu_2O were 1.95 and 1.84 Å, respectively. During photocatalytic degradation of MB, CuO in the CuO/TiO_2 thin film was, to some extent, reduced and the bond distance of Cu-O was decreased by 0.03 Å.

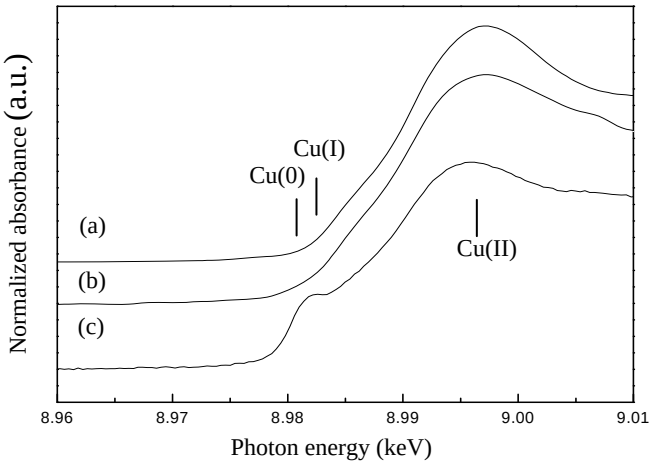

FIGURE 1. The XANES spectra of copper in the (a) CuO/TiO_2 thin film and in the presence of methylene blue under UV radiation for (b) 0 and (c) 90 min.

TABLE 1. The semi-quantitative analyses of the in situ XANES spectra of copper in the CuO/TiO_2 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_2O	-	5%	33%	39%
Cu	-	-	10%	9%
MB/CuO	29%	29%	22%	23%

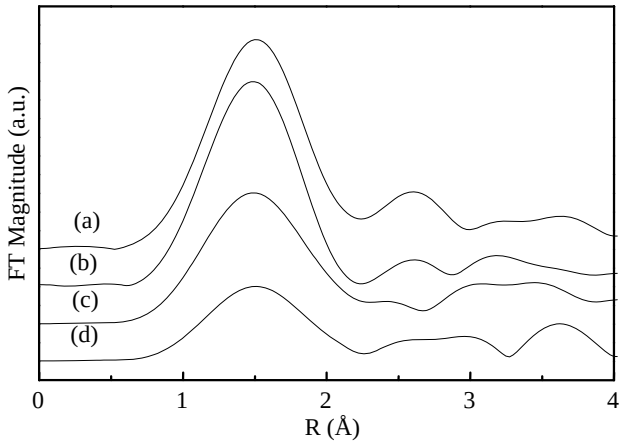

FIGURE 2. The r-space fourier transformation of copper in the CuO/TiO_2 thin film during photocatalytic degradation of methylene blue for (a) 0, (b) 30, (c) 60 and (d) 90 min.

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