

Photocatalytic Activity of Cu/TiO₂ with Oxidation State of Surface-loaded Copper

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Loading of some metals on TiO₂ surface has been known as one of the successful methods for the improvement of photocatalytic oxidation reaction.¹⁻⁴ The role of loaded metal is trapping and subsequent transfer of photoexcited electrons on TiO₂ surface. However, all conductive metals are not effective for the improvement of photocatalytic activity of TiO₂. It has been so far reported that Au, Ag and Pd are effective,²⁻⁴ but Pt or Ru is detrimental for the photocatalytic oxidation reaction of TiO₂.⁵⁻⁷ One of the important properties required to the loaded metal would be a suitable workfunction value. It is proposed that photocatalytic oxidation reaction is an electrochemical reaction among the TiO₂ conduction band, loaded metal, and electrolytes adsorbed on TiO₂ surface. Energy level of the loaded metal may be defined as its workfunction. Then, the position of workfunction will be critical for the effective transfer of electrons on the conduction band of TiO₂ toward adsorbed electrolytes. Secondly, the loaded metals on TiO₂ should be chemically stable during the photocatalytic oxidation reaction or storage in atmospheric condition. If the loaded metals are oxidized, conductivity of metal will be decreased down and their energy level may be altered from its metallic state. Then, the photocatalytic activity will be degenerated, since they cannot trap or transfer the photoexcited electron efficiently.

In this work, we investigate the effect of oxidation state of loaded Cu on the photocatalytic oxidation reaction. Cu is one of extraordinary metals, which exist stably as metallic form as well as metal oxides in atmospheric condition. In addition, it is expected that the loaded Cu may improve photocatalytic activity of TiO₂, since the workfunction of Cu is quite similar to TiO₂ conduction band and the standard reduction potential of oxygen molecule, which is considered to be a probable electron acceptor in TiO₂ aqueous suspension.⁸ In addition, little study has so far been carried out on the photocatalytic activity of Cu-loaded TiO₂.^{9,10}

Experimental Section

The TiO₂ used in this study was Degussa p25 (47 m²/g, 70% of anatase). Cu was deposited onto TiO₂ by photochemical decomposition of CuSO₄ · 5H₂O. A reagent grade of CuSO₄ · 5H₂O was obtained from Aldrich Chemical Co. and used as received. 1.0 g of TiO₂ was dispersed in aqueous solutions containing various amounts of the CuSO₄ · 5H₂O. Distilled water was added to achieve a total volume of 140 mL. In order to expedite the photodecomposition, 10 mL of ethanol was added in this suspension as a hole scavenger. Then the mixture was transferred to the silica reaction vessel

and 300W Xe lamp (LX300 UV) without UV cut-off filter was used to irradiate the suspensions. After the irradiation for 30 min, the aqueous suspension was then centrifuged and the recovered precipitates were vacuum-desiccated for several hours. The concentration of CuSO₄ · 5H₂O, which was not decomposed during the photochemical decomposition reaction, was evaluated from the characteristic Cu²⁺(aq) absorption peak at around 800 nm and this result was used for the calibration of the loaded Cu concentration on TiO₂. It was found that most of CuSO₄ · 5H₂O was decomposed to metallic Cu. The deposition of Ag on TiO₂ powders was achieved by photodecomposition of AgF (Aldrich Chemical Co.). Detailed preparation procedure is given in previous work.³

For the evaluation of photocatalytic efficiencies of suspended powder samples in the aqueous solution, 1,4-dichlorobenzene (DCB) was utilized as a model compound. 1.5 mg of TiO₂ or metal-loaded TiO₂ powders were added in 100 mL of distilled water and suspended by ultrasonic homogenizer (Cole-Palmer) operated at 20 kHz. 14 mL of dispersed sample was transferred to a Pyrex reactor and 2 mL of 200 μM DCB aqueous solution was added. Total volume of the solution was adjusted to 16 mL and the concentration of DCB to 25 μM. Samples were then irradiated with a 300 W Xe lamp (LX300 UV) with UV cut-off filter. After the irradiation of every 2.5 min, the concentration of remnant DCB in the solution was measured with a Perkin-Elmer 552A UV-visible spectrophotometer.

XRD patterns of TiO₂ powders in glancing angle mode were obtained using a Philips diffractometer (PW3020) with a monochromated high intensity CuK_{α1} radiation (λ=1.5405 Å). The oxidation state of Cu for the Cu/TiO₂ samples, was examined by X-ray photoelectron spectroscopy (XPS, SSI-2803S). X-ray absorption near edge spectra (XANES) for Cu K-edge were obtained using the 3C1 EXAFS beamline in Pohang Light Source (PLS). Each spectrum was obtained at the fluorescence mode with a solid detector.

Results and Discussion

Photocatalytic activity of Cu/TiO₂ samples with the concentration of loaded Cu is described in Figure 1. Catalytic activity was defined as overall degradation rate constant, since the photocatalytic oxidation reaction of aqueous organic molecules with TiO₂ suspensions approximated to first-order kinetics. The optimum concentration of Cu providing the maximized photocatalytic efficiency is 0.5-1.0 mole percent relative to TiO₂. Photocatalytic activity of

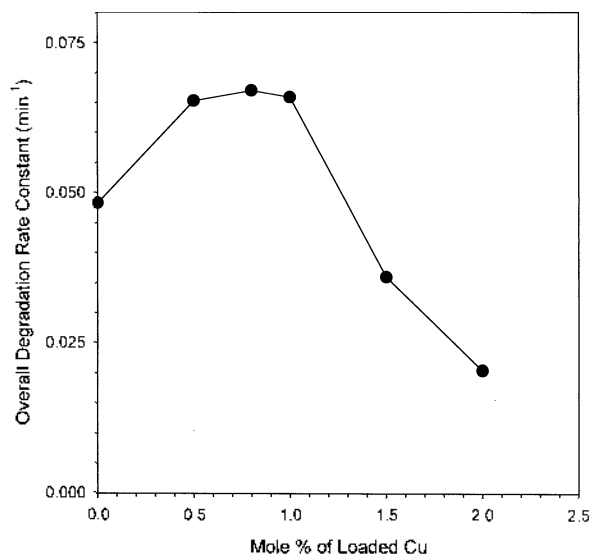


Figure 1. Photocatalytic activity of Cu/TiO₂ samples with the concentration of surface-loaded Cu (Model compound: DCB, 25 μM).

0.8% Cu/TiO₂ is approximately 1.4 times of that of pure TiO₂.

Previously, we reported that Ag is greatly effective in improving photocatalytic activity of TiO₂.³ Photocatalytic activity of 1.5 mole % Ag/TiO₂ is about 2.0 times of that of pure TiO₂. It is considered that the high efficiency of Ag/TiO₂ originates from the effective electron-transfer capability of Ag clusters. The workfunction of Ag is 4.26 eV. Hence, the energy level of Ag is denoted to -0.24V in NHE, which is located at slightly higher level than the conduction band of TiO₂ (-0.1V in NHE), and in addition it is close to the electrochemical potential of oxygen reduction in aqueous solution [O₂ (aq) + e⁻ → O₂⁻ (aq), E⁰ = -0.56V in NHE].^{11,12} as is described in Figure 2. Thus, it is considered that the loaded Ag on TiO₂ can promote the transfer of electrons in TiO₂ conduction band to outer oxygen, which is dissolved in water. The same argument can also be applied to Cu/TiO₂ system. The workfunction of Cu is 4.65 eV, which is relatively close to that of Ag, much differently from other noble metals such as Pt, Ru, or Rh. Therefore, the role of Cu on TiO₂ surface is considered to be expedition of electron transfer as Ag does. Relatively lower photocatalytic activity of Cu/TiO₂ than that of Ag/TiO₂ is ascribed to the location of Cu energy level, which is not so much appropriate in transferring the electrons to outer oxygen as that of Ag (see Figure 2).

It was observed that Cu/TiO₂ samples left in atmospheric condition were gradually changed in their color from purple to pale-gray, and the photocatalytic efficiencies were accordingly decreased down with the elapse of storing time in air. It is speculated that the decrease of photocatalytic activity is closely related to the oxidation of surface-loaded Cu on TiO₂. In this work, we prepared several Cu/TiO₂ oxidized at different conditions and characterized the oxidation states of Cu for these samples, to investigate the correlation between the oxidation state of loaded Cu and the photocatalytic activ-

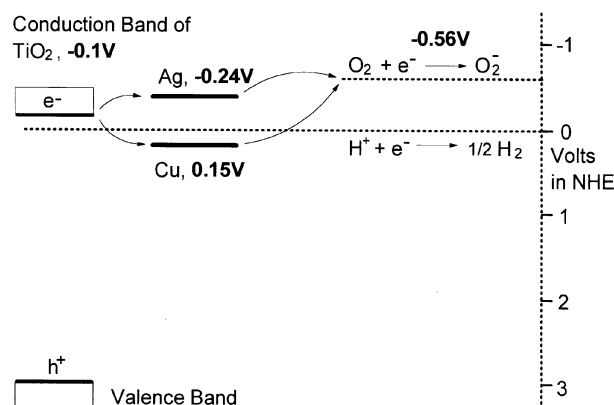


Figure 2. Schematic energy diagram of TiO₂ loaded metals, and several electrolytes.

ity. 0.8 mole % Cu/TiO₂, presenting optimized photocatalytic activity, was annealed at 200 and 300 °C for 30 min in oxygen atmosphere, respectively. Photocatalytic activity of annealed Cu/TiO₂ samples was greatly decreased, compared with that of as-prepared Cu/TiO₂, as is described in Figure 3. The colors of the samples annealed at 200-300 °C in oxygen were changed to gray. Cu clusters on TiO₂ may not be metallic Cu. For the X-ray diffraction measurement, Cu has been loaded on a low-crystallized anatase TiO₂ film, since the crystallographic phase of Cu in 0.8 mole % Cu/TiO₂ can not be identified by XRD and in addition CuO (111) peak is overlapped with anatase (112) peak of TiO₂ powders. As is shown in Figure 4, the loaded Cu in as-prepared Cu/TiO₂ sample is identified to metallic copper. In the XRD patterns for the sample annealed at 200 °C in oxygen, 35.6° peak is indexed to Cu₂O (100) phase and a small peak at around 38.7° is denoted to CuO (111) and anatase (112). For the samples annealed at 300 °C, Cu species on TiO₂ is mainly CuO phase. This indicates that most of metallic Cu clusters

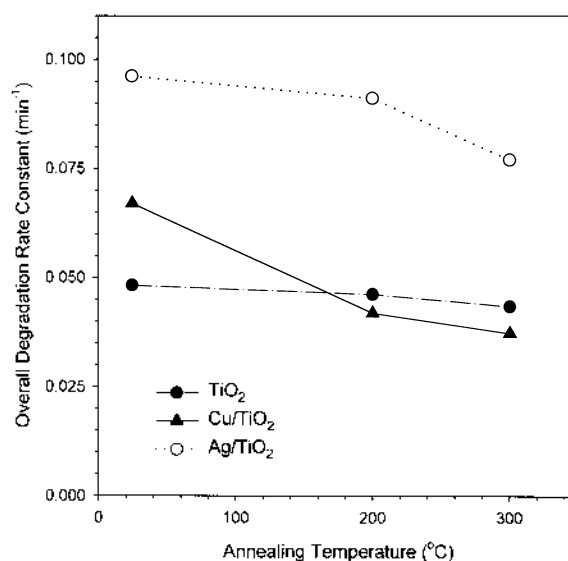


Figure 3. Photocatalytic activity of TiO₂, Cu/TiO₂, Ag/TiO₂ samples with the oxidation temperature (For Cu/TiO₂ the concentration of Cu is 0.8 mole %, and for Ag/TiO₂ that of Ag is 1.5 mole % relative to TiO₂).

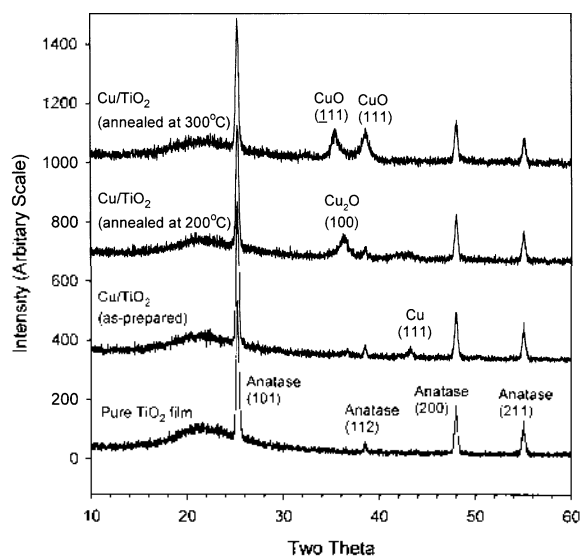


Figure 4. XRD patterns of Cu-loaded TiO_2 films annealed at several temperatures (TiO_2 film in anatase phase was deposited on a silica substrate at 450°C with MOCVD method. Cu was deposited on TiO_2 film by photodecomposition method with $0.001\text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$ aqueous solution.).

in Cu/TiO_2 samples are oxidized to Cu_2O by annealing at 200°C and they are converted to CuO phase by annealing at 300°C . However, the XRD results here do not provide the direct proof for the oxidation state of Cu, because the XRD patterns are not obtained from the Cu/TiO_2 powder samples presenting optimized photocatalytic activity. Hence, XPS spectra were obtained for the 0.8 mole % Cu/TiO_2 samples. As is shown in Figure 5 (a), the binding energy of $\text{Cu } 2p_{3/2}$ for fresh Cu/TiO_2 is 932.7 eV and that of the samples annealed at 200°C and 300°C is 933.2 and 933.4 eV , respectively. This indicates that Cu in as-prepared Cu/TiO_2 is metallic and the samples oxidized at 200°C and 300°C involve CuO phase. However, the presence of Cu_2O phase is unclear. Oxidation state of Cu was also analyzed by X-ray absorption spectroscopy. XANES spectra of Cu K-edge region were observed for the two Cu/TiO_2 samples (see Figure 6). Compared to fresh Cu/TiO_2 , samples annealed at 300°C show extra absorption peak at around 8978 eV , even though it is not clear with poor intensity of signal, which is caused by the low concentration of Cu in the samples. The peak at around 8978 eV is identified to the transition from $1s$ to $3d$.^{13,14} This is another proof that the oxidation state of Cu is +2 for the sample annealed at 300°C .

As a reference experiment, pure TiO_2 and Ag/TiO_2 samples were annealed at the same condition. Photocatalytic activity of pure TiO_2 was slightly decreased with the annealing process as is shown in Figure 3. Ag/TiO_2 was also decreased in photocatalytic efficiency, but their percentage of decrease is considerably smaller than that of Cu/TiO_2 . XPS spectra in Figure 5 (b) present that the binding energies of $\text{Ag } 3d_{5/2}$ line were not appreciably changed with the annealing treatment at 200°C or 300°C . This indicates that the loaded Ag on TiO_2 still exists as metallic state and this explains why photocatalytic activity of Ag/TiO_2 sample is

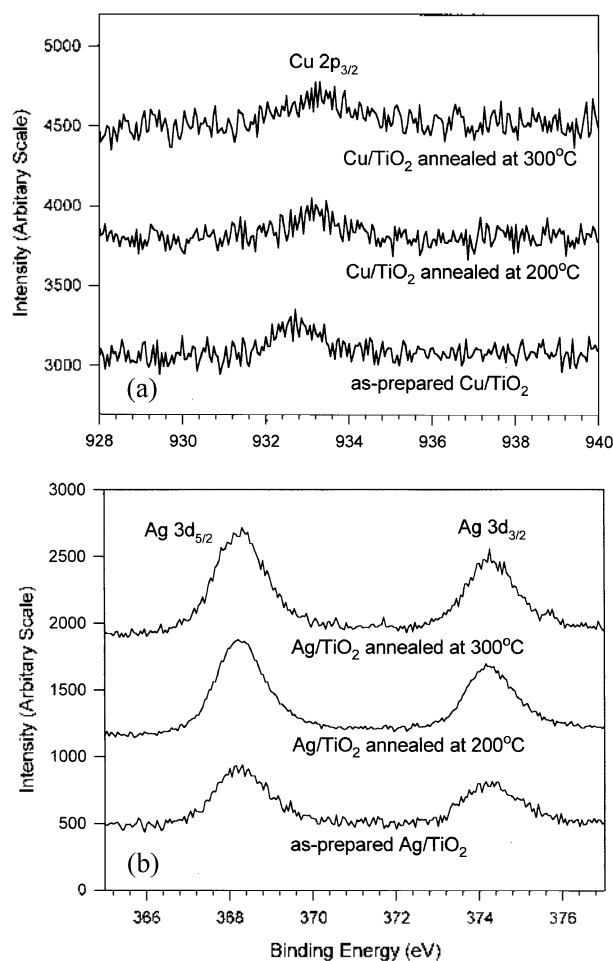


Figure 5. XPS spectra of Cu/TiO_2 and Ag/TiO_2 samples annealed at several temperatures (The concentration of Cu is 0.8 mole % and that of Ag is 1.5 mole %.); (a) Cu/TiO_2 ; (b) Ag/TiO_2 .

less decreased than that of Cu/TiO_2 .

It is derived that the metallic Cu on TiO_2 improves photo-

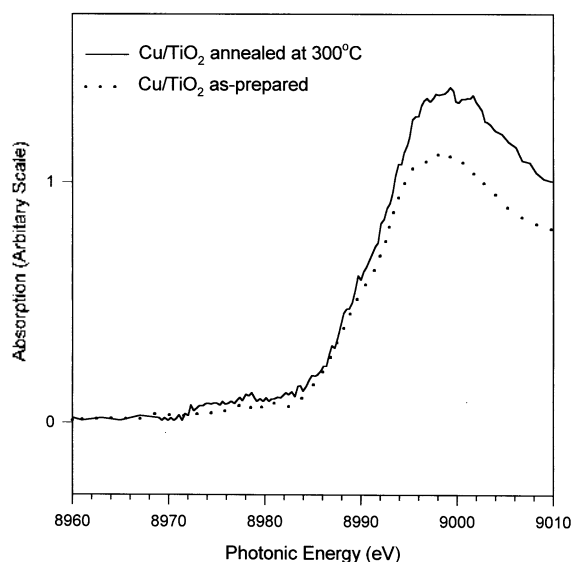


Figure 6. XANES spectra of Cu K-edge region for Cu/TiO_2 samples (The concentration of Cu is 0.8 mole %).

catalytic activity of TiO_2 . When Cu is oxidized to CuO, photocatalytic efficiency is greatly decreased down. The activity is even poorer than that of pure TiO_2 sample. It is expected that CuO clusters on TiO_2 are not effective in the transfer of photoexcited electrons on the TiO_2 conduction band. This supports our hypothesis, that is, the role of loaded metal on TiO_2 surface is the expedition of electron transfer from TiO_2 conduction band to outer system.

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