Cu-Supported TiO$_2$ with High Visible-Light Photocatalytic Activity Prepared Using Cupric Acetate$^*$

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Abstract: TiO$_2$ photocatalysts can remove harmful substances such as volatile organic compounds (VOCs) under light irradiation. However, they are only activated by ultraviolet light at wavelengths shorter than about 380 nm, so they cannot be used under visible light irradiation. Thus, visible-light-responsive photocatalysts have been extensively studied to enable their indoor use. TiO$_2$ powder supported with Cu(II) ions (Cu(II)/TiO$_2$) has recently been reported to possess visible-light photocatalytic activity. In the present study, we used cupric acetate as a Cu(II) source. We prepared various Cu(II)/TiO$_2$ photocatalysts by changing the amount of cupric acetate and assessed their photocatalytic performance. The performance of Cu(II)/TiO$_2$ photocatalysts was estimated from the rate of decrease in the formaldehyde (HCHO) concentration in the flowing stimulant air under irradiation by a fluorescent lamp or a white LED. The surface properties of Cu(II)/TiO$_2$ photocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS) measurements. The optical reflectance of Cu(II)/TiO$_2$ photocatalysts was measured by using a UV-Vis spectrophotometer. The maximum visible-light photocatalytic activity was observed at a Cu/TiO$_2$ weight ratio of 5.69 [wt%]. The maximum rate of decrease in the HCHO concentration of the Cu(II)/TiO$_2$ photocatalyst was higher than that of a typical commercial TiO$_2$-based visible-light-responsive photocatalyst (Ishihara-Sangyo MPT-623) under the same test conditions. [DOI: 10.1380/ejssnt.2015.143]

Keywords: Titanium oxide; Copper oxides; Environmental engineering; X-ray photoelectron spectroscopy

I. INTRODUCTION

TiO$_2$ photocatalysts have been studied extensively since Fujishima and Honda pioneered the photocatalytic splitting of water on TiO$_2$ electrodes [1, 2]. Photocatalysts can remove harmful substances, such as volatile organic compounds (VOCs), from aqueous solutions under light irradiation, but they are only activated by wavelengths below approximately 380 nm and thus will not function under visible light irradiation.

As a result, visible-light-responsive photocatalysts have been studied extensively and fabricated by various approaches. Several groups have succeeded in doping transition metals into TiO$_2$ photocatalysts and thus obtained visible-light photocatalytic activity [3–6]. Nitrogen-doped TiO$_2$ [7–10] and sulfur-doped TiO$_2$ [11–13] were also found to be photocatalytically active in the visible region, and many researchers have reported their superior performance. However, when the valence band of TiO$_2$ was raised by doping, its oxidation ability dropped below that of undoped TiO$_2$.

Irie et al. succeeded in fabricating Cu(II)/TiO$_2$ photocatalysts [14–19]. They suggested that in these photocatalysts, visible light induced an interfacial charge transfer (IFCT) [14–19] in which electrons in the valence band (VB) of TiO$_2$ were directly transferred to Cu(II), forming Cu(I), while at the same time holes were created in the VB of TiO$_2$. These holes decompose organic substances. In contrast, the Cu(I) produced by the electron transfer is likely to reduce adsorbed O$_2$ through multi-electron reduction, and thus electrons are consumed. It has been reported that the visible-light photocatalytic activity of Cu(II)/TiO$_2$ is higher than that of nitrogen-doped TiO$_2$ [8–20]. The quantum efficiency (QE) of Cu(II)/TiO$_2$ for 2-propanol decomposition under visible light (> 450 nm) was ca. 9% [8, 20]. However, the optimal ratio of Cu to TiO$_2$ remains unknown.

In this study, we used cupric acetate as a Cu(II) source to fabricate Cu(II)/TiO$_2$ photocatalysts. We prepared Cu(II)/TiO$_2$ photocatalysts with various Cu-to-TiO$_2$ ratios by changing the amount of cupric acetate and estimated the performance of these photocatalysts from the rate of decrease in the formaldehyde (HCHO) concentration in the flowing stimulant air under irradiation by a white LED.

II. EXPERIMENTAL

TiO$_2$ photocatalyst thin films were prepared by depositing an ethanol solution containing TiO$_2$ nanoparticles (Ishihara Sangyo ST-01) on a glass plate (25 $\times$ 25 $\times$ 1.1 mm, Tempax) and sintering at 723 K for 2 h.

In order to deposit Cu oxide on a TiO$_2$ film, we used a photodeposition method. We dropped a 1000 µl of cupric acetate solution onto a TiO$_2$ photocatalyst. The photocatalyst was then irradiated by ultraviolet light for 24

TABLE I. Experimental parameters for HCHO removal trials

| Light source | White LED (OHM LT-N40-50K) |
|--------------|---------------------------|
| Irradiance of light source [W/m$^2$] | 30 |
| Gas species | Air containing 1 ppm HCHO |
| Gas flow rate [L/min] | 0.5 |
| Temperature [K] | 298 |
| Humidit [%] | 50 |
| Photocatalyst [mg/cm$^2$] | 1.6 |
| TiO$_2$ cross section [mm$^2$] | 50 $\times$ 100 |

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The concentration of the cupric acetate solution was varied.

For comparison, we prepared a commercially available visible-light-responsive TiO$_2$ photocatalyst film on a glass plate (25 × 25 × 1.1 mm, Tempax) using the same method as in the case of the TiO$_2$ thin films (Ishihara-Sangyo MPT-623). MPT-623 is photocatalytic TiO$_2$ with a platinum compound.

The surface morphology of the photocatalyst films was observed with a scanning electron microscope (JSM-6599M JEOL). The photocatalytic performance of the films was estimated from the rate of decrease in the HCHO concentration in the flowing air. The setup used to determine the extent of HCHO removal is illustrated in Fig. 1. The equipment used consisted of a gaseous HCHO generating system, a reactor for HCHO decomposition, and associated instruments to measure the rate of decrease in HCHO concentration [21, 22]. The relative humidity of the airflow was adjusted by controlling the flow rates of dry air and humid air. The HCHO concentration in the airflow was adjusted by varying the amount of dry air passing through a vessel containing HCHO solution consisting of paraformaldehyde without methanol. The major oxidative and reductive reactions involved in the photodegradation of HCHO are given below. Reactions (2) and (3) represent the oxidation, while reaction (4) represents the reduction [23–25].

$$\text{TiO}_2 \xrightarrow{h_v} e^- + h^+ \quad (1)$$

$$\text{HCHO} + \text{H}_2\text{O} + 2h^+ \rightarrow \text{HCOOH} + 2\text{H}^+ \quad (2)$$

$$\text{HCOOH} + 2h^+ \rightarrow \text{CO}_2 + 2\text{H}^+ \quad (3)$$

$$\text{O}_2 + 4e^- + 4\text{H}^+ \rightarrow 2\text{H}_2\text{O} \quad (4)$$

Glass substrates coated with Cu(II)/TiO$_2$ were placed inside the reactor and irradiated with a white LED (OHM LT-N40-50K) under flowing air containing 1.0 ppm HCHO. The spectral distribution of the white LED is shown in Fig. 2. The HCHO concentration at the outlet of the reactor was measured using an HCHO detector (Shin Kosumosu Denki Form-tector C-XP-308B).

The optical reflectance of the Cu(II)/TiO$_2$ films was obtained using an ultraviolet-visible (UV-vis) spectrophotometer (Shimadzu UV-2450), and XPS measurements were performed to analyze the surface compositions of the films, using a JPS-9010C (JEOL) equipped with a standard Al Kα X-ray source and operating at 10 mA and an acceleration voltage of 12 kV. Charge effects were corrected for the C 1s peak.

III. RESULTS AND DISCUSSION

The surface morphology of a Cu(II)/TiO$_2$ film is shown in Fig. 3. The differences observed between the initial and final HCHO concentrations (see Fig. 4) were due to fluctuations in the flow rate. These fluctuations led to uncertainties in the rate of decrease in HCHO concentration. The highest rate of decrease was estimated from the minimum HCHO concentration with the LED on and from the maximum HCHO concentration among the initial and final HCHO concentrations.
final HCHO concentrations, while the lowest rate of decrease was estimated from the maximum HCHO concentration with the LED on, and from the minimum HCHO concentration among the initial and final HCHO concentrations.

Figure 5 shows the results of the HCHO removal test for various Cu(II)/TiO$_2$-films. Figures 3 and 5 indicate that the photocatalysts were able to remove HCHO under white LED irradiation and thus exhibited visible-light photocatalytic activity. It can also be seen that the concentration of the cupric acetate solution has an optimal value for visible-light photocatalytic activity. For comparison, the rate of decrease in HCHO concentration for the MPT-623 film is plotted in Fig. 5. The maximum rate of decrease in HCHO concentration obtained for the Cu(II)/TiO$_2$ film was twice as high as that obtained for the MPT-623 film under the same test conditions. The above results suggest the effectiveness of Cu(II)/TiO$_2$ for indoor use. The amount of Cu on TiO$_2$ was 91 μg/cm$^2$ under the optimum condition. This value was calculated by using the concentration and dropping quantity of cupric acetate solution, the molar masses of Cu and cupric acetate. The results indicate that the Cu-to-TiO$_2$ weight ratio was 5.69% under the optimum condition. The process whereby Cu(II)/TiO$_2$ films were prepared in this study was simple and inexpensive, because no platinum was used.

The Cu $2p_{3/2}$ spectra of Cu(II)/TiO$_2$ obtained from the XPS analyses are shown in Fig. 6. The XPS spectrum shows a typical Cu $2p_{3/2}$ peak with a measured binding energy of 955.3 eV. A satellite peak was obtained in the Cu $2p_{3/2}$ spectra with a measured binding energy of 945.2 eV. In general, the satellite peaks in Cu $2p$ spectra are used as evidence for compounds containing divalent copper [26, 27]. Figure 7 shows the atomic ratio of Cu and TiO$_2$ on the surface of a Cu(II)/TiO$_2$ film, which is calculated from the Cu $2p_{3/2}$ and Ti $2p_{3/2}$ peak heights. We can see the atomic ratio of Cu and TiO$_2$ on the surface increasing with the concentration of cupric acetate solution. According to the results of our XPS analysis, the Cu/Ti (Cu/TiO$_2$) atomic ratio in the vicinity of the optimum
FIG. 8. Optical reflectance of Cu(II)/TiO$_2$ and Cu(OH)$_2$.

condition is about 20%. This is higher than the Cu/TiO$_2$ weight ratio estimated from the concentration. This is presumably because XPS is a surface chemical analysis technique (typically the top 10 nm) and Cu occurs only on the TiO$_2$ surface.

Figure 6 plots the reflectance of Cu(II)/TiO$_2$ vs. the concentration of the cupric acetate solution. As a result of supporting Cu, the TiO$_2$ photocatalyst exhibited visible light absorption, primarily in the blue and red regions of the spectrum. For comparison, the reflectance of Cu(OH)$_2$ powder is shown in Fig. 8, where it can be seen that Cu(II)/TiO$_2$ and Cu(OH)$_2$ absorb light in the similar visible region. The UV-visible measurement results presented above are similar to those obtained by other researchers [14, 26]. The above results suggest that some of the Cu on the TiO$_2$ surface exists as Cu(OH)$_2$. This is supported by the XPS results in Fig. 6, because the copper in Cu(OH)$_2$ is divalent.

In a high-concentration cupric acetate solution (1.625 wt%), the photocatalyst performs less efficiently. This is probably due to a combination of two effects. First, the number of TiO$_2$ surface active sites decreases owing to excess Cu(OH)$_2$. CuO, or recrystallized cupric acetate on the TiO$_2$ surface. Second, the visible light falling on the TiO$_2$ films decreases because Cu(OH)$_2$ absorbs visible light.

The photocatalytic activity might improve if recrystallized cupric acetate can be removed.

IV. CONCLUSION

In present paper, we optimized the amount of Cu on Cu(II)/TiO$_2$. The maximum rate of decrease in HCHO concentration obtained for the Cu(II)/TiO$_2$ film was twice as high as that for a MPT-623 film under the same test conditions. This demonstrates the effectiveness of Cu(II)/TiO$_2$ for indoor use. Efforts are underway to further optimize the fabrication process and develop a new performance assessment test.

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[1] A. Fujishima and K. Honda, Nature 238, 37 (1972).
[2] A. Fujishima, X. Zhang, and D. A. Tryk, Surf. Sci. Rep. 63, 515 (2008).
[3] Y. Matsumoto, J. Kurimoto, Y. Amagasaki, and E. Sato, J. Electrochem. Soc. 127, 2148 (1980).
[4] K. E. Karakitsou and X. E. Verykios, J. Phys. Chem. 109, 025105 (2005).
[5] W. Choi, A. Termin, and M. R. Hoffmann, J. Phys. Chem. B 109, 10251 (2005).
[6] H. Yamashita, M. Harada, J. Misaka, M. Takeuchi, and M. Anpo, J. Photochem. Photobiol. A 148, 257 (2002).
[7] Y. Yokosuka, K. Nishikori, Y. Tatsumi, K. Oki, N. Tanaka, and T. Fujii, Kankyo Kagaku Nenpo 146, 454 (2002).
[8] R. Asahi, T. Motikawa, T. Ohwaki, K. Aoki, and Y. Taga, Science 293, 269 (2001).
[9] Z. Lin, A. Orlov, R. M. Lambert, and M. C. Payne, J. Phys. Chem. 109, 20948 (2005).
[10] Z. Zhao and Q. J. Liu, J. Phys. D 41, 025105 (2008).
[11] T. Umebayashi, T. Yamaki, H. Ito, and K. Asahi, Appl. Phys. Lett. 81, 454 (2002).
[12] T. Ohno, T. Mitsui, and M. Matsumura, Chem. Lett. 32, 364 (2003).
[13] Y. Murakami, B. Kasahara, and Y. Nosaka, Chem. Lett. 36, 330 (2007).
[14] H. Irie, S. Miura, K. Kamiya, and K. Hashimoto, Chem. Phys. Lett. 457, 202 (2008).
[15] H. Irie, K. Kamiya, T. Shibamuna, S. Miura, D. A. Tryk, T. Yokoyama, and K. Hashimoto, J. Phys. Chem. C 113, 10761 (2009).
[16] R. Nakamura, A. Okamoto, H. Osawa, H. Irie, and K. Hashimoto, J. Am. Chem. Soc. 129, 9596 (2007).
[17] C. Creutz, B. S. Brunschwig, and N. Sutin, J. Phys. Chem. B 109, 10251 (2005).
[18] C. Creutz, B. S. Brunschwig, and N. Sutin, J. Phys. Chem. B 110, 25181 (2006).
[19] X. Qiu, M. Miyachi, K. Sunada, M. Minoshima, M. Liu, Y. Lu, D. Li, Y. Shimodaira, Y. Hosogi, Y. Kuroda, and K. Hashimoto, ACS Nano 6, 1609 (2012).
[20] H. Irie, K. Kamiya, T. Shibamuna, S. Miura, D. A. Tryk, T. Yokoyama, and K. Hashimoto, J. Phys. Chem. C 113, 10761 (2009).
[21] Y. Tanaka, K. Sugimoto, A. Shimizu, and H. Taoda, Aichiken Sangy Gijutu Kenkyujo Kenkyu Hokoku, 3, 10 (2004) [in Japanese].
[22] JIS R 1751-4 (2013).
[23] T. Noguchi, A. Fujishima, P. Sawunyama, and K. Hashimoto, Environ. Sci. Technol. 32, 3831 (1998).
[24] J. Peral and D. F. Ollis, J. Catal. 136, 554 (1992).
[25] M. A. Aguado, M. A. Anderson, and C. G. Hill, Jr., J. Mol. Catal. A 89, 165 (1994).
[26] J. Yu and J. Ran, Energy Environ. Sci. 4, 1364 (2011).
[27] N. S. McIntyre and M. G. Cook, Anal. Chem. 47, 2208 (1975).