Cu-Supported TiO₂ with High Visible-Light Photocatalytic Activity Prepared Using Cupric Acetate*

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TiO₂ 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 studied extensively to enable their indoor use. TiO₂ powder supported with Cu(II) ions (Cu(II)/TiO₂) 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)/TiO₂ photocatalysts by changing the amount of cupric acetate and assessed their photocatalytic performance. The performance of Cu(II)/TiO₂ 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)/TiO₂ photocatalysts were analyzed by X-ray photoelectron spectroscopy (XPS) measurements. The optical reflectance of Cu(II)/TiO₂ photocatalysts was measured by using a UV-Vis spectrophotometer. The maximum visible-light photocatalytic activity was observed at a Cu/TiO₂ weight ratio of 5.69 [wt%]. The maximum rate of decrease in the HCHO concentration of the Cu(II)/TiO₂ photocatalyst was higher than twice that of a typical commercial TiO₂-based visible-light-responsive photocatalyst (Ishihara-Sangyo MPT-623) under the same test conditions. [DOI: 10.1380/ejsnt.2015.143]

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I. INTRODUCTION

TiO₂ photocatalysts have been studied extensively since Fujishima and Honda pioneered the photocatalytic splitting of water on TiO₂ 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 TiO₂ photocatalysts and thus obtained visible-light photocatalytic activity [3–6]. Nitrogen-doped TiO₂ [7–10] and sulfur-doped TiO₂ [11–13] were also found to be photocatalytically active in the visible region, and many researchers have reported their superiority. However, when the valence band of TiO₂ was raised by doping, its oxidation ability dropped below that of undoped TiO₂.

Irie *et al.* succeeded in fabricating Cu(II)/TiO₂ 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 TiO₂ were directly transferred to Cu(II), forming Cu(I), while at the same time holes were created in the VB of TiO₂. These holes decompose organic substances. In contrast, the Cu(I) produced by the electron transfer is likely to reduce adsorbed O₂ through multi-electron reduction, and thus electrons are consumed. It has been reported that the visible-light photocatalytic ac-

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
Humidity [%]	50
Photocatalyst [mg/cm ²]	1.6
TiO ₂ cross section [mm ²]	50 × 100

tivity of Cu(II)/TiO₂ is higher than that of nitrogen-doped TiO₂ [8–20]. The quantum efficiency (QE) of Cu(II)/TiO₂ for 2-propanol decomposition under visible light (> 450 nm) was ca. 9% [8, 20]. However, the optimal ratio of Cu to TiO₂ remains unknown.

In this study, we used cupric acetate as a Cu(II) source to fabricate Cu(II)/TiO₂ photocatalysts. We prepared Cu(II)/TiO₂ photocatalysts with various Cu-to-TiO₂ 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

TiO₂ photocatalyst thin films were prepared by depositing an ethanol solution containing TiO₂ nanoparticles (Ishihara Sangyo ST-01) on a glass plate (25 × 25 × 1.1^t mm, Tempax) and sintering at 723 K for 2 h.

In order to deposit Cu oxide on a TiO₂ film, we used a photodeposition method. We dropped a 1000 μ l of cupric acetate solution onto a TiO₂ photocatalyst. The photocatalyst was then irradiated by ultraviolet light for 24

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FIG. 1. Schematic of the apparatus used to determine HCHO removal.

FIG. 2. Spectral distribution of the white LED (OHM LT-N40-50K) employed in this study.

h. 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 ($25 \times 25 \times 1.1^t$ 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 experimental conditions are listed in Table I. 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 air-flow was adjusted by controlling the flow rates of dry air and humid air. The HCHO concentration in the airflow

FIG. 3. Surface morphology of the Cu(II)/ TiO_2 film.

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].

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 Kosumusu Denki Form-tector C-XP-308B).

The optical reflectance of the Cu(II)/ TiO_2 films was obtained using a 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 $K\alpha$ 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

FIG. 4. Time variation of HCHO concentration (Cu(II)/TiO₂, 1.625 wt%)

FIG. 6. XPS spectra of Cu(II)/TiO₂.

FIG. 5. Dependence of the rate of decrease in HCHO concentration over Cu(II)/TiO₂ under white LED irradiation on the concentration of cupric acetate solution.

FIG. 7. Atomic ratio of Cu to Ti calculated by XPS peak height.

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)/TiO₂-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)/TiO₂ 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)/TiO₂ for indoor use. The amount of Cu on TiO₂ was 91 $\mu\text{g}/\text{cm}^2$ 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-TiO₂ weight ratio was 5.69% under the optimum condition. The process whereby Cu(II)/TiO₂ films were prepared in this study was simple and inexpensive, because no platinum was used.

The Cu 2p_{3/2} spectra of Cu(II)/TiO₂ 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 TiO₂ on the surface of a Cu(II)/TiO₂ 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 TiO₂ on the surface increasing with the concentration of cupric acetate solution. According to the results of our XPS analysis, the Cu/Ti (Cu/TiO₂) atomic ratio in the vicinity of the optimum

FIG. 8. Optical reflectance of Cu(II)/TiO₂ and Cu(OH)₂.

condition is about 20%. This is higher than the Cu/TiO₂ 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 TiO₂ surface.

Figure 6 plots the reflectance of Cu(II)/TiO₂ vs. the concentration of the cupric acetate solution. As a result of supporting Cu, the TiO₂ 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)/TiO₂ 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 TiO₂ 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 TiO₂ surface active sites decreases owing to excess Cu(OH)₂, CuO, or recrystallized cupric acetate on the TiO₂ surface. Second, the visible light falling on the TiO₂ 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)/TiO₂. The maximum rate of decrease in HCHO concentration obtained for the Cu(II)/TiO₂ film was twice as high as that for a MPT-623 film under the same test conditions. This demonstrates the effectiveness of Cu(II)/TiO₂ for indoor use. Efforts are underway to further optimize the fabrication process and develop a new performance assessment test.

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