Photocatalytic activity of Cu-doped titania prepared by controlling the Cu distribution

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Cu-doped titania powders were prepared from the sol–gel reaction systems containing titanium tetraisopropoxide (TTIP) and copper(II) nitrate with different compositions. The copper(II) nitrate was added to the sol containing TTIP after a specific reaction period of the TTIP polymerization in order to control the Cu distribution in the titania. The Cu localization on the titania nanoparticle surface was indirectly estimated by the Cu chelation of 8-hydroxyquinoline on the surface. The photocatalytic activities of the samples concerning the decomposition of organic substances were quantified by the amount of the hydroxyl radical formed during ultraviolet (UV) and visible irradiations. The titania with dispersed Cu on the surface demonstrated a higher activity than that with dispersed Cu inside the bulk titania. The electrons in the titania conduction band caused by the UV photoexcitation were effectively transferred to the impurity states of Cu2+ on the titania surface. Some electrons in the titania valence band were directly transferred to the impurity states of Cu2+ upon the visible photoexcitation. Consequently, these processes suppressed the electron–hole charge recombination in the titania. It was confirmed again that a slight amount of the Cu highly dispersed only on the titania surface rather than inside the titania bulk was favorable for its high photocatalytic performance.

Key-words : Sol–gel method, Titania, Copper distribution, Photocatalysis

1. Introduction

Photocatalysts, mainly titania-based compounds, have been frequently used for the decomposition of hazardous organic substances and the self-cleaning of some material surfaces.1,2) Therefore, the preparation technology for such photocatalysts should be established in order to definitely obtain the guaranteed functions sufficient to mineralize the substrates or make them harmless for the general users. Metal-doping into titania is an effective method to prepare visible-light-driven photocatalysts whereas titania requires ultraviolet (UV) light to induce the photocatalytic reaction. Some metal ion-doped titania consisting of uniform nano-sized crystalline particles as active photocatalysts can be synthesized by the sol–gel method.3–8)

It has been reported that Cu-doping is a valid precedent for visible light activation because it results in impurity states at a potential level between the titania valence band (V.B.) and conduction band (C.B.), which can directly accept the electrons in the V.B. during the visible light irradiation.4,6,10) In addition, the impurity states trap the charge separated electrons in the C.B. These processes suppress the electron–hole charge recombination, i.e., the titania–Cu states electron transfer enhances the photo-reduction and photooxidation reactions. This interaction is influenced by the Cu distribution in the titania nanoparticle due to structural factors such as accessibility and interactivity of the reactants.12) However, the Cu distribution at an atomic level is difficult to be visually observed by general analyses because the amount of the effective Cu is very low, i.e., much less than 1 mol% versus the Ti amount.11,12)

In our previous study, Cu-doped titania (Cu-TiO2) was prepared by the refluxing of a homogeneous mixture of copper and titanium alkoxides.11,12) The refluxing improved the Cu2+ dispersion in the titania and formed effective Ti-O-Cu bonds, which induced the electronic interaction between the Ti and Cu. The main factors in such high Cu2+ dispersion should be the use of the copper alkoxide and refluxing of the systems. The Cu-TiO2 containing a slight amount of Cu (0.1 mol%) demonstrated the highest photocatalytic performance for methylene blue degradation. A higher amount of Cu deactivated the photocatalysts due to significant decreases in the specific surface area, hydrophilicity, and light permeation.11,12) The photocatalytic activity also depended on the Cu2+ distribution in the titania, which certainly promotes the electron transfer

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[Received July 28, 2020; Accepted October 28, 2020]
2. Experimental procedures

2.1 Preparation of photocatalysts

Copper(II) nitrate trihydrate (S grade) obtained from Wako Pure Chemicals was used without further purification. The other materials were obtained and used as reported in our previous study.11,12)

The solutions of the sol–gel reaction for preparation of the Cu-TiO₂ consisted of 6.8 cm³ of TTIP, copper(II) nitrate (0.05–0.15 mol% of the Ti amount), 40.0 cm³ of ethanol, and 0.21 cm² of hydrochloric acid as a catalyst for the sol–gel transition. The solution without Cu was also prepared for comparison. The preparation procedures of the titania and three types of the Cu-TiO₂ with different Cu distributions are explained in detail as follows:

First, ethanol and hydrochloric acid were mixed, TTIP was dropped into the mixture, then the resulting solution was agitated in a glove box at ambient temperature, and labeled S-0. Furthermore, copper(II) nitrate was dissolved in the solution by agitation. The resulting solution was heated at 373 K for 3–4 days until the gelation occurred, and labeled G-Cu-2. Third, S-0 was heated at 373 K for 3–4 days until gelation occurred, then copper(II) nitrate was mixed with the gel, and labeled G-Cu-3.

All the resulting gels were dried at 373 K for 2 h, treated with 50 cm³ of water at 353 K, heated at 373 K for 1 h, then heated at 773 K for 3 h. The photocatalyst powder samples prepared from G-0, G-Cu-1, G-Cu-2, and G-Cu-3 were labeled P-0, P-Cu-1, P-Cu-2, and P-Cu-3, respectively.

2.2 Characterization of photocatalysts

Scanning electron microscope (SEM) observation and X-ray diffraction (XRD), ultraviolet–visible (UV–Vis) spectroscopic and X-ray photoelectron spectroscopic (XPS) analyses of the samples were conducted by the previously reported methods.11,12) The specific surface areas, average pore sizes, and total pore volumes of the samples were measured as previously reported using a volumetric gas adsorption instrument (BEL Japan, BELSORP-Max N-VP-CM).13,14)

Each 0.10 g photocatalyst sample was added to 25 cm³ of an 8-hydroxyquinoline (HQ) ethanol solution (3.8 × 10⁻⁴ mol dm⁻³) and agitated in the dark for 12 h, for which the adsorption of HQ had equilibrated. The relative amount of the HQ adsorbed on each sample was quantified by UV–Vis spectroscopy.

2.3 Evaluation of photocatalysts

Each 5.0 mg photocatalyst sample was added to 50 cm³ of a solution containing terephthalic acid (3.0 × 10⁻³ mol dm⁻³) and sodium hydroxide (1.0 × 10⁻² mol dm⁻³). The resulting suspensions were agitated in a glass beaker during near-UV light irradiation (300–400 nm, 7.90 × 10⁻⁵ W cm⁻²) from a 10-W black light bulb (Yazawa BL-10) and visible light irradiation (6.59 × 10⁻⁵ W cm⁻²) from a 150-W xenon lamp (Hamamatsu Photonics C2577) using a 430-nm-short cutoff filter. The terephthalic acid was used for quantitative analysis of the hydroxyl radical caused by the photocatalytic water oxidation, resulting in the production of fluorescent 2-hydroxy terephthalic acid.15,16) The fluorescence spectra of the solutions filtered using a membrane filter (Advantec DISMIC-25AS) were obtained as a function of the light irradiation time as previously reported.11,12)

3. Results and discussion

3.1 Characterization of the photocatalysts

Figure 1 shows SEM images of the titania and the 0.11 mol-% Cu-TiO₂ powder samples prepared in the present study. They apparently consisted of about 15–35 nm-sized primary particles as shown in Table 1. The XRD patterns and crystallite sizes of the samples are shown in Fig. 2 and Table 1, respectively. The patterns of the typical anatase type titania were observed in all the samples and the crystallite sizes were estimated to be 25–50 nm, which were somewhat larger than the apparent particle sizes because...
The apparent primary particles were actually sintered to form the necking particles. Figure S2 shows the adsorption isotherms of the nitrogen gas for the powder samples. The specific surface area and pore properties of the powder samples are also shown in Table 1. There was no significant difference in the particle properties of the present titania and Cu-TiO$_2$ samples, indicating that the preparation procedure did not significantly influence the particle properties of the samples due to the low amount of the Cu, i.e., 0.11 mol %. Strictly speaking, the crystal growth tended to be somewhat suppressed in P-Cu-1 because the Cu ions were dispersed in the system from the initial stage of the sol–gel reaction.

Figure 3 shows the UV–vis diffuse reflectance spectra of the titania and the 0.11 mol % Cu-doped titania powder samples. All the samples displayed UV absorption at a wavelength shorter than ca. 400 nm assigned to the titania band gap. In addition to this, the Cu-TiO$_2$ samples displayed a visible absorption, which was higher in the order of P-Cu-1, P-Cu-2, and P-Cu-3. Especially P-Cu-1 more strongly absorbed than the others. The visible absorption should mainly originate from the oxygen defects as reported in a previous paper after consideration of the low amount of the Cu.$^{11),12)}$ The Cu bulk doping also caused substitution of the Cu species for Ti$^{4+}$ in the networks and a shift in the band gap to the lower energy.$^9\) On the other hand, the surface doping (grafting) of Cu(II) ions caused impurity states just below the edge level of the C.B. of the titania due to the potential of the Cu(II)/Cu(I) redox couple, inducing the red shift in the absorption edge.$^9,10)$

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Table 1. Average particle sizes, crystallite sizes, and pore characteristics of the titania and the 0.11 mol % Cu-doped titania powder samples

| Sample | P-0 | P-Cu-1 | P-Cu-2 | P-Cu-3 |
|--------|-----|--------|--------|--------|
| Average particle size/nm | 29.9 | 15.3 | 34.4 | 25.4 |
| Crystallite size/nm | 40.1 | 25.1 | 50.4 | 44.7 |
| Specific surface area/m$^2$ g$^{-1}$ | 51.8 | 42.4 | 38.9 | 40.1 |
| Average pore size/nm | 5.93 | 5.98 | 10.7 | 12.5 |
| Total pore volume/cm$^3$ g$^{-1}$ | 0.0767 | 0.0635 | 0.104 | 0.126 |

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Fig. 1. SEM images of the titania and the 0.11 mol % Cu-doped titania powder samples, (a) P-0, (b) P-Cu-1, (c) P-Cu-2, and (d) P-Cu-3.

Fig. 2. XRD patterns of the titania and the 0.11 mol % Cu-doped titania powder samples, (1) P-0, (2) P-Cu-1, (3) P-Cu-2, and (4) P-Cu-3.

Fig. 3. UV–vis diffuse reflectance spectra of the titania and the 0.11 mol % Cu-doped titania powder samples, (1) P-0, (2) P-Cu-1, (3) P-Cu-2, and (4) P-Cu-3.
The visible absorption can also originate from the electron transition from the V.B. to the Cu impurity states in the present Cu-TiO₂ samples. However, the visible absorption was changed by the preparation procedure of the sample, i.e., the difference in the reaction period of TTIP in the sol–gel system at which the fixed amount of Cu was added.

Figure 4 shows the XPS spectra of the Ti 2p, O 1s, and Cu 2p electrons for the titania and the 0.11 mol %–Cu-doped titania powder samples, (1) P-0, (2) P-Cu-1, (3) P-Cu-2, and (4) P-Cu-3.

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Figure 4 shows the XPS spectra of the Ti 2p, O 1s, and Cu 2p electrons for the titania and the 0.11 mol %–Cu-doped titania powder samples, (1) P-0, (2) P-Cu-1, (3) P-Cu-2, and (4) P-Cu-3.

The weak Cu 2p peaks were observed at around 932–934 eV in the Cu-TiO₂ samples due to the low amount of Cu. The peaks at 932.8 and 933.8 eV were assigned to the Cu⁺ and Cu²⁺ species, respectively. Based on this, P-Cu-1 and P-Cu-2 mainly contained the Cu⁺ species whereas P-Cu-3 mainly contained the Cu²⁺ species related to the amount of the oxygen defects in the samples. The internal Cu doping can induce reduction of the samples resulting in formation of the oxygen defects and Cu⁺ species. The XPS measurements indicated that the Cu-TiO₂ prepared by adding the Cu after a specific reaction period of the TTIP dispersed Cu²⁺ as an impurity on the titania surface. As Cu²⁺ is homogeneously dispersed in the titania particle surface and substituted for Ti⁴⁺ in the networks, a charge transfer from the Ti⁴⁺ to the Cu²⁺ is expected to occur. This is significantly enhanced on the particle surface whereas the charges are delocalized in the bulk.

3.2 Cu distribution in titania

General analyses are difficult to visually reveal the Cu distribution in the titania particle at an atomic level under the present conditions of the Cu content. The Cu localization on the titania particle surface can be indirectly estimated by the metal chelation of HQ. This should be a valid method because the deprotonated ion, quinolate, is a typical ligand and readily forms a metal chelate not only in solutions, but also on surfaces of solids such as particles. Figure S3 shows the UV–vis diffuse reflectance spectra of the titania and Cu-TiO₂ samples adsorbing HQ. A broad absorption band was observed in the visible range assigned to the metal chelates of quinolate, i.e., the Ti and Cu chelates. The intensities at 420 nm for the titania and Cu-TiO₂ samples are shown in Fig. 5. The amount of the metal chelate generally increased with an increase in the Cu content although the standard deviation was high. A higher amount of the metal chelate was clearly adsorbed on the Cu-TiO₂ prepared by adding the Cu after the longer reaction period of TTIP. The amount was higher in the order of P-Cu-3, P-Cu-2, and P-Cu-1. The Cu species on the titania particle surface more easily bonded to the quinolate compared to those in the bulk. The Cu species more strongly interacted than the Ti species due to the higher electron affinity or negativity of Cu. Consequently, the Cu-TiO₂ prepared by adding the Cu after the longer reaction period of TTIP dispersed a higher amount of the
metal quinolate on the surface. These results indicated formation of not only the oxygen defects, but also the Cu impurity states in the Cu-TiO₂ samples.

3.3 Photocatalytic activity

It was observed that the XPS spectra did not significantly change during the photocatalytic experiments. The Cu species had not dissolved into the water phase. Figure S4 shows the fluorescence spectra of 2-hydroxy terephthalic acid formed after 0–60 min of UV irradiation using the titania and 0.09 mol% Cu-TiO₂ samples. The time courses of the changes in the fluorescence intensities at 426 nm with the UV irradiation is shown in Fig. 6 in order to examine the produced hydroxyl radicals. The changes in the intensities for the 60-min light irradiation are also shown in Fig. 7. Additionally, the time courses of the changes in the fluorescence intensities with the visible irradiation and the changes in the intensities for the 180-min light irradiation are also shown in Figs. 8 and 9, respectively.

[Graphs and images are not transcribed as text.]
The formation rate of the hydroxyl radical under the UV and visible light conditions for the Cu-TiO₂ prepared by initially adding TTIP and Cu, i.e., P-Cu-1, was higher than that for the normal titania as shown in our previous study.¹¹,¹² The photocatalytic activity for the hydroxyl radical formation was improved by the efficient titania–Cu species electron transfer due to the high Cu dispersion in the titania and formation of effective Ti-O-Cu bonds. The formation rate of the hydroxyl radical under the visible light condition was much slower than that under the UV light condition. The Cu-TiO₂ prepared by adding the Cu after the longer reaction period of TTIP, i.e., P-Cu-2 and especially P-Cu-3, clearly exhibited a much faster reaction rate, i.e., higher activity.¹² The Cu-TiO₂ prepared by adding the Cu before the TTIP reaction and after the shorter reaction period of TTIP, i.e., P-Cu-1 and P-Cu-2, demonstrated lower performances due to formation of the oxygen defects and Cu⁺ species. With respect to the Cu content, 0.07–0.09 mol % Cu and 0.11 mol % Cu were the most effective amount for P-Cu-1 and P-Cu-3 and for P-Cu-2.

Fig. 7. Changes in the fluorescence intensities of 2-hydroxy terephthalic acid for the 60-min-UV irradiation using the titania and Cu-doped titania samples, (a) P-Cu-1, (b) P-Cu-2, and (c) P-Cu-3.

Fig. 8. Time courses of the changes in the fluorescence intensities of 2-hydroxy terephthalic acid in order to estimate the hydroxyl radicals produced during the visible light irradiation using (1) the titania and the (2) 0.05, (3) 0.07, (4) 0.09, (5) 0.11, (6) 0.13, and (7) 0.15 mol % Cu-doped titania samples, (a) P-Cu-1, (b) P-Cu-2, and (c) P-Cu-3.
respectively, generally corresponding to ca. 0.1 mol% Cu as previously reported \(^8,^{11,12}\).

The impurity states of Cu\(^{2+}\) formed on the titania particle surface effectively accepted the electrons transferred to the titania C.B. by the UV light absorption. Some electrons in the V.B. were directly transferred to the Cu impurity states by the visible light absorption, which was very weak. These processes consequently suppressed the electron–hole recombination in the titania. The high Cu localization only on the titania surface rather than the dispersion inside the titania bulk effectively promoted the reduction of the oxygen species adsorbed on the surface active sites. Such a reduction reaction readily collected the electrons, prevented the charge recombination, and efficiently produced the active hydroxyl radicals.

4. Conclusions

The Cu distribution in the Cu-doped titania was controlled by varying the reaction conditions of the sols containing TTIP and copper(II) nitrate, i.e., adding Cu\(^{2+}\) before initiating the reaction of TTIP or after a specific reaction period of the TTIP. Influences of the Cu distribution in the titania particle and the titania–Cu species electron transfer on the photocatalytic activity were summarized in detail again for references to the practical and applicable uses of such photocatalysts. Based on the XPS measurements, the Cu-TiO\(_2\) prepared by adding the Cu\(^{2+}\) after a certain reaction period of TTIP dispersed Cu\(^{2+}\) as an impurity on the titania surface. On the other hand, the Cu-TiO\(_2\) prepared by adding the Cu after the shorter reaction period of TTIP contained higher amounts of oxygen defects and Cu\(^{+}\) species. The Cu localization on the titania nanoparticle surface was indirectly estimated by the Cu chelation of HQ on the surface, resulting in successfully observing only a slight amount of the Cu. The Cu-TiO\(_2\) prepared by adding the Cu after the longer reaction period of TTIP dispersed a higher amount of the metal quinolate on the surface. The photocatalytic activities of the powder samples were quantified by the amount of the hydroxyl radical produced for organic molecule decomposition under UV and visible light conditions. The titania dispersing the Cu on the surface demonstrated a higher activity than that dispersing the Cu inside the bulk titania. The electrons in the titania C.B. caused by the UV photoexcitation were effectively transferred to the impurity states of Cu\(^{2+}\) on the titania surface. Some electrons in the titania V.B. were directly transferred to the impurity states of Cu\(^{2+}\) upon the visible photoexcitation. Consequently, these processes suppressed the electron–hole charge recombination in the titania. It was confirmed again that a slight amount of the Cu highly dispersed only on the titania surface rather than inside the titania bulk resulted in its higher photocatalytic performance.

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![Fig. 9. Changes in the fluorescence intensities of 2-hydroxy terephthalic acid for the 180-min-visible irradiation using the titania and Cu-doped titania samples, (a) P-Cu-1, (b) P-Cu-2, and (c) P-Cu-3.](a) (b) (c)
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