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Transmittance change of the TiO_2 thin film by photoreductive deposition of Cu(II)

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Abstract

Photoreductive deposition of Cu^{2+} on TiO_2 thin film prepared by sol–gel method has been investigated by measuring a change of transmittance of the film. The transmittance decreased with irradiation time, corresponding to a decrease of the Cu^{2+} concentration in the solution. Removal percent of Cu^{2+} ions from the solution was obtained to be 80–98%. On the other hand, the transmittance change (ΔT) was greatly affected by experimental conditions: the ΔT value increased when the thicker films or films fired at higher temperature were used or when the same film was employed repeatedly. With the initial concentrations of Cu^{2+} more than 100 ppm, induction periods (I.P.) of 45–240 min were observed before the transmittance decreased. When $Na_2C_2O_4$ was used as a sacrificial donor instead of HCOONa, the decrease rate for Cu^{2+} concentration in the solution became slightly lower. However, with $Na_2C_2O_4$, no induction period was observed and the ΔT values were two times as high as those with HCOONa.

Keywords: Titanium dioxide; Photodeposition; Sol–gel method

1. Introduction

Metal ions with standard redox potentials more positive to the conduction band of TiO_2, e.g. Ag^+, Cr^{6+}, Hg^{2+} and Pt^{4+}, have been reported to be easily photodeposited under nitrogen atmosphere [1,2]. The solution must be purged with nitrogen because oxygen is reduced preferentially by conduction band electrons. Foster et al. studied reversible photoreductive deposition and oxidative dissolution of Cu^{2+} in TiO_2 suspension [3]. We performed kinetic studies for the photoreduction of Cu^{2+} ions and clarified the rate law [4]. The metal ions such as Ni^{2+} and Mn^{2+} whose standard redox potentials are rather negative were also reduced photocatalytically in the presence of oxalate or formate ions [5,6]. Rajh and co-workers investigated effect of surface modification of TiO_2 nanoparticles with bidentate ligands on reduction of Pb^{2+} and Cd^{2+} [7,8]. For a practical purpose, TiO_2 immobilized on supporting materials is preferable to the suspension system because of the elimination of filtration process to recover the catalyst. Tennakone and Wijayantha employed an immobilized TiO_2 to extract Pb and Hg from an aqueous solution [9]. We have paid attention to Cu deposition on a TiO_2 film not from a viewpoint of elimination of separation step but from the observation of the drastic change in color of the film. In an aqueous TiO_2 suspension containing Cu^{2+} and sodium formate, the color of TiO_2 turned to purple due to the reductive deposition of Cu^{2+}during irradiation. On the other hand, when TiO_2 thin films were used for the experiments, the color of the films changed from transparent to metallic. Such a remarkable change in color might be applied for detection or even determination of Cu^{2+} concentration in the solution. In this paper, we describe a change of transmittance of the film together with that of Cu^{2+} concentration under various conditions.

2. Experimental

A mixture of 3.9 ml HNO_3, 540 ml H_2O and 45 ml $Ti(OC_3H_7)_4$ was peptized at room temperature for 3 days to form a highly dispersed colloidal solution. This sol was then dialyzed in a cleaned, molecularly porous dialysis tube (Spectra/Por, molecular weight cut-off 3500) until a value of approximately pH 4 was obtained. An indium–tin oxide glass (ITO: 0.8 cm × 4 cm) was dipped into the obtained transparent sol for 30 min, then withdrawn at the rate of 0.5 cm min^{-1} and dried in the air for 30 min. The back side of the glass was covered with cellophane tapes to avoid the film formation. The dipping–drying procedure was repeated

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five times and then the film on the ITO was fired at 200 °C for 4 h. Slide glasses were also used as substrates but the TiO_2 films peeled off during the Cu deposition.

The ITO covered with TiO_2 film (TiO_2/ITO) was stood against the wall of a quarts standard cell (1.25 cm × 1.25 cm × 4.5 cm, optical length: 1 cm) which contained 50 ppm Cu^{2+} (as $Cu(NO_3)_2$) and 0.1 mol dm^{-3} HCOONa at pH 3.6. The cell was capped with a silicone rubber and two needles were used as inlet and outlet for nitrogen which was purged through the solution for 30 min before irradiation and in the upper gas phase during the irradiation. A 15 W black light bulb (Toshiba EFD15BLB, 14.5 cm long) was used as the light source and the photon flux entering the cell was determined to be $(5.26 \pm 0.06) \times 10^{-8}$ einstein s^{-1} using tris(oxalato)ferrate(III) actinometer. The reaction temperature was maintained at 26.8 ± 0.2 °C. The transmittance of the cell was measured at the wavelength of 420 nm (Shimadzu UV-1600) although it did not depend on the wavelength in the region of 400–550 nm. The Cu^{2+} concentration in the solution was analyzed by inductively coupled plasma spectroscopy (Varian, ICP-AES Liberty Series II).

3. Results and discussion

The films fabricated from the sols aged for 7–30 days indicated induction periods (I.P.) before the transmittance decreased. Thus, the dipping process was conducted with the freshly prepared sol. Fig. 1 depicted that the concentrations of Cu^{2+} ions in the solution decreased with the irradiation time, which corresponded well to a decrease in the transmittance of the film. The transmittance decreased so much in the first 100 min and then decreased gradually to a limiting value, during which 93% Cu^{2+} ions were removed from the solution. The Cu deposited on the film was recovered as Cu^{2+} ions when the film was immersed in a HNO_3 aqueous solution (pH 3) which was exposed to air.

Table 1 listed the change of transmittance (ΔT) during the irradiation for 6 h and removal percent (defined as the percentage of the Cu^{2+} concentration decreased divided by the initial Cu^{2+} concentration) on the film which was used repeatedly for the photoreductive deposition. The film was treated with the HNO_3 solution to dissolve Cu^{2+} ions after each run. It is noted that the removal percent of Cu^{2+} ions was not changed, 89.8 ± 2.6%, but the value of ΔT increased by repeating the photodeposition: the ΔT value at the fifth run was 2.3 times higher than that at the first run. This finding is explainable by considering that the Cu^{2+} ions were removed by photodeposition as Cu(I), some of which were subsequently reduced to Cu(0) which decreased lights transmitted through the film more effectively than Cu(I). Foster et al. reported by using Degussa P-25 powders that photoreduction yielded purple Cu-TiO_2 species which was assignable to Cu(I) by EPR spectroscopy [3]. By repeating the experiments on the same film, the recombination between photogenerated holes and electrons was suppressed and more electrons were available for photoreduction to Cu(0), leading to an increase in the ΔT value. This suppression may be due to a trace Cu (Cu(I) or Cu(0)) remained in the film, which were irremovable by the dissolution process in the HNO_3 solution.

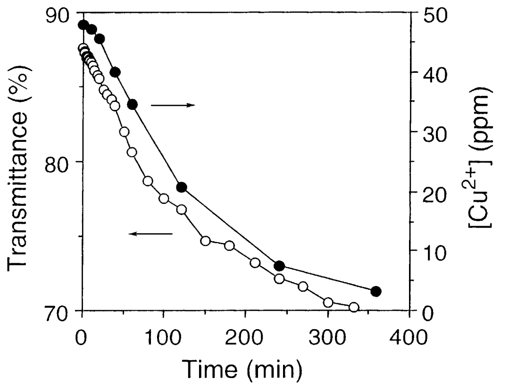

Fig. 1. Time course of transmittance (○) of the film and the Cu^{2+} concentration in the aqueous solutions (●).

Table 1
Change of the transmittance and removal percent in the repeated experiments

Run	ΔT (%)	Removal (%)
1	25.4	89.2
2	39.0	90.8
3	44.8	84.7
4	56.7	88.9
5	57.7	95.3

The film preparation was repeated on the TiO_2/ITO which had been fired at 200 °C in order to change thickness of the film. The ΔT value increased with an increase in the thickness as Table 2 listed. This finding is also explainable in terms of photogenerated electrons. Thicker films contained more amounts of TiO_2 which produced more photogenerated electrons available to produce Cu(0).

Table 2
Effect of film thickness on ΔT and removal percent

Times[a]	ΔT (%)	Removal (%)
1	26.0	89.5
2	35.0	89.7
3	32.2	85.7
5	45.0	80.5
7	45.6	79.9

[a] Dipping–drying and firing processes were repeated one to seven times.

The effect of the initial Cu^{2+} concentrations on the photodeposition was examined. The removal more than 90% was always achieved in the range of 50–200 ppm as shown in Table 3. The induction periods were observed with Cu^{2+} more than 100 ppm and increased with an increase in the initial concentrations: the transmittance of the film with 200 ppm Cu^{2+} began to decrease after irradiation for

Table 3
Effect of concentration of Cu(II) on ΔT, removal percent and induction periods[a]

$[Cu^{2+}]$ (ppm)[b]	ΔT (%)	Removal (%)	I.P. (min)
50	31.3	90.2	
100	26.3	94.5	45–50
150	24.5	97.6	120
200	23.3	94.4	240

[a] The ΔT value and the removal percent were estimated for 6 h after the induction periods.

[b] The unit ppm means mg/l in this article.

240 min. The ICP measurements indicated that the Cu^{2+} concentration in the solution decreased during the induction periods, suggesting that the Cu^{2+} ion was removed as Cu(I). The photogenerated electrons are consumed by reducing Cu^{2+} ions in the solution or Cu(I) deposited on the film. When the initial Cu^{2+} concentration is high, the photogenerated electrons reduce Cu^{2+} ions to Cu(I) exclusively. Thus, the induction periods increased with the initial Cu^{2+} concentration. As the Cu(I) adsorbed on the film increases, the reduction of Cu(I) to Cu(0) proceeds and then, the transmittance began to decrease.

When sodium oxalate was used as a sacrificial donor instead of HCOONa, the time course in the Cu^{2+} concentration was not very different from that with HCOONa whereas the ΔT value increased twice as shown in Fig. 2.

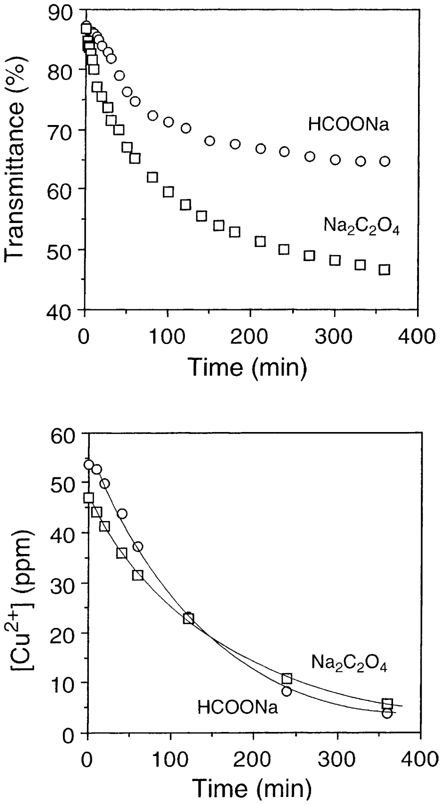

Fig. 2. Time course of transmittance and the Cu^{2+} concentration in the presence of HCOONa or $Na_2C_2O_4$ as a sacrificial donor.

Table 4
Effect of concentration of Cu(II) on ΔT in the presence of $Na_2C_2O_4$ as a sacrificial donor

$[Cu^{2+}]$ (ppm)	ΔT (%)
50	43.6
150	54.0
200	58.6

The ΔT value with $Na_2C_2O_4$ increased with the initial concentration of Cu^{2+} ions: 43.6, 54.0, and 58.6%, respectively, for 50,150, and 200 ppm Cu^{2+} as shown in Table 4. In contrast to the results with HCOONa, no induction period was observed and the films with the Cu^{2+} more than 150 ppm peeled partly during the photodeposition so that removal percent was not estimated. The Cu^{2+} exists as $[Cu(H_2O)_6]^{2+}$ or $[Cu(C_2O_4)_2]^{2-}$, respectively, in the presence of HCOONa or $Na_2C_2O_4$ [4]. The surface charges on the TiO_2 depended on the preparation method of the colloidal sols but it is positive in the aqueous solutions of pH 3.6 [10]. Thus, due to electrostatic interaction, the photoreduction of $[Cu(C_2O_4)_2]^{2-}$ occurs more easily on the TiO_2 film than that of $[Cu(H_2O)_6]^{2+}$. Induction periods were not observed, which may suggest that the $[Cu^{I}(C_2O_4)_2]^{3-}$ formed by reaction with photogenerated electrons is rapidly converted to $[Cu^{0}(C_2O_4)]^{2-}$ via intermolecular electron transfer.

$$[Cu(C_2O_4)_2]^{2-} + e^- \rightarrow [Cu^{I}(C_2O_4)_2]^{3-} \rightarrow [Cu^{0}(C_2O_4)]^{2-} + CO_2 + CO_2{}^{-}. \quad (1)$$

The effect of the firing temperature on the ΔT value was examined. It has been reported that the oxidation rate of organic compounds on TiO_2 photocatalysts decreased with an increase in the firing temperature, which was attributable to a decrease in the specific surface area of the TiO_2 [6,11]. This is the reason that we used a low firing temperature like 200 °C as a normal condition. However, the ΔT value was only 4.5% on the films fired at 100 °C and increased with the firing temperature: the ΔT value at 300 or 400 °C was, respectively, 1.5 or 2.2 times higher than that at 200 °C. Besides the removal percent of the films fired at 100 °C was only 74.6% and that above 200 °C was constant to be 91.0 ± 1.2%. These findings suggest that the surface area of the films is not important. The XRD measurements of the TiO_2 pellets which were prepared by firing the xerogels obtained from drying the colloidal sols indicated that only the peaks due to anatase were observed at 100 °C, the anatase crystals grew at 200 °C and started to convert into rutile at 300 °C although the anatase form was predominant even at 400 °C [12]. It is gathered that the crystal growth is important to increase the ΔT value. This may relate to surface morphologies which inhibit the recombination process.

4. Conclusions

The transmittance of the TiO_2 film decreased due to photoreductive deposition of Cu^{2+}. The time-course of the transmittance corresponds to that of the Cu^{2+} concentration in the solution. This fact suggests that the transmittance change can be applied to determine Cu^{2+} concentration. Higher transmittance change is required to obtain higher sensitivity of the analysis. This study indicates experimental conditions to get high ΔT values: (i) the thicker films or films fired at higher temperature are favorable; (ii) high concentrations of Cu^{2+} are unfavorable due to induction periods; (iii) $Na_2C_2O_4$ as a sacrificial reagent is more suitable than HCOONa. Based on these results, we are now continuing the research using thicker films fired at 400 °C with $Na_2C_2O_4$ for the microanalysis of Cu^{2+} ions.

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