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Photocatalytic reduction and deposition of metallic ions in aqueous phase[☆]

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Abstract

Experiment of photochemical reduction and deposition of cupric ion by titanium dioxide photocatalyst was carried out. The TiO_2 particles were suspended in the aqueous solution of copper sulphate where sodium formate was added as a hole scavenger. It was shown that cupric ion can be reduced and deposited on TiO_2 surface very rapidly when the TiO_2 particles are embedded at adequately higher densities and formic acid is added at moderate concentrations comparative to or higher than that of cupric ion. The deposition rate depends strongly on the concentration of sodium formate: it increases as the concentration increases. The mechanism of reduction reaction was estimated by the elementary reactions and the adsorption of formic anion. The practical deposition rates can be successfully explained by assuming that the oxidation reaction step of adsorbed formic anion is rate controlling, with the remaining steps being all instantaneously fast. Possibility of photochemical reduction of chromium ion(VI) to nontoxic chromium ion(III) or to metal chromium was also investigated.

Keywords: Photocatalytic reduction; Photocatalysis; Titanium dioxide; Metal deposition; Water purification

1. Introduction

The semiconductors like SnO_2, WO_3, Fe_2O_3, ZnO, TiO_2, CdSe, etc. are known to have photocatalytic function. Among them, titanium dioxide, TiO_2, has been noted for the photochemical reactions such as decomposition of water into hydrogen and oxygen [1], conversion from carbon dioxide to organic carbon [2,3], oxidation and decomposition of organic compounds [4], super-hydrophilic surface [5], photochemical disinfection [6], energy conversion [7], and so on. In particular, the action of oxidizing and decomposing hazardous organic compounds has been applied to purifying air and water pollutions. We previously proposed the method of fabricating TiO_2 film on glass or ceramic plate and developed the tube reactor for water purification [8–10].

This paper aims at elucidating the kinetics of photochemical reduction and deposition of metallic ions in aqueous phase by TiO_2 photocatalyst and showing the possibility of removing valuable or hazardous metallic ions from the contaminated or natural water. The photochemical reduction experiment for cupric ion contained in water was carried out using a laboratory-scale catalyst suspension reactor. It was found that cupric ion can be photochemically reduced and deposited rapidly on the surface of TiO_2 powder when sodium formate is added for hole scavenger at moderate concentrations in the water. The dependency of concentration of sodium formate on the deposition rate was clarified and then the new kinetic equation was proposed, which can explain the practical deposition rate as a function of reaction time and concentrations of relevant chemical species. In order to show the possibility of application to environmental water purification, TiO_2 photocatalytic reduction of hexavalent chromium to trivalent chromium or to metal chromium was also investigated.

2. Concept of photocatalytic reduction

When the semiconductor is illuminated with the ultra violet light beam, the electron at the valence band is excited up to the conduction band, with the positive hole being left at the site where the electron is originally captured. The band gap energy of TiO_2 is 3.2 eV, with the lower level being -0.4 eV and the upper level being 2.8 eV relative to the reduction potential of hydrogen. The reduction potential of

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water lies between the lower and upper levels. The water, thus, can be photochemically decomposed by TiO_2 catalyst [1]. Suppose the water which does contains metallic ions but does not contain dissolved oxygen, it is expected that the excited electron should reduce the metallic ion whereas the positive hole should oxidize the hydroxide ion to produce the radical OH. And if some organic carbon exists in the water, the radical OH should oxide it into carbon dioxide and water, thus be consumed by the oxidation process, which results in suppressing the recombination of excited electron with the positive hole. The reduction reaction of metallic ion would then continuously proceed. We here refer such organic carbon to as “hole scavenger”.

In this experiment, we selected copper for target metal, whose reduction potential is 0.34 eV and lies between the lower and higher levels of the band gap. The points to be clarified are: (1) whether the photochemical reduction reaction of metallic ion does occur truly in the aqueous solution, (2) whether the hole scavenger species is necessary or not for the reduction reaction to proceed, (3) if necessary, how the reaction rate depends on the concentration of hole scavenger species, and (4) what kinetic model is valid for explaining the practical rates of reduction reaction as a function of concentrations of related chemical species.

3. Experimental

The experimental set up is shown in Fig. 1. The reactor was a glass made cylindrical cell with 6.5 cm in diameter and 18 cm in height, along the center of which the 7 W UV lamp (Harclon Co. Ltd.) with the peak wave length of 253.7 nm is placed. TiO_2 powder of anatase structure (ST-01; Ishihara Co. Ltd.) was used as photocatalyst. The averaged diameter of the powder was 17 nm and the specific area is 300 m^2/g. The water to be treated was prepared by diluting copper sulphate, $CuSO_4 \cdot 5H_2O$ (99.5%; Kishida Co. Ltd.) in distilled water so that the concentration cupric ion might be 50 mg/l. Sodium formate, HCOONa [abbreviated as RNa], was used as the hole scavenger [11] and was added in the water at concentrations ranging from 0 to 0.1 mol/l.

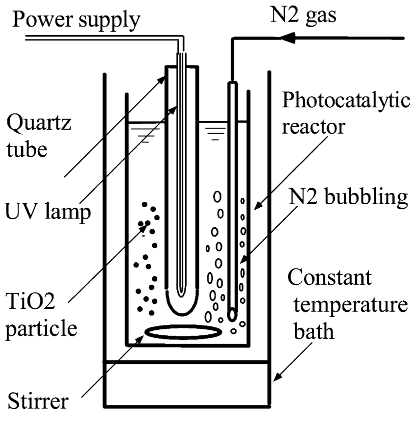

Fig. 1. Experimental set up.

In experiment, 400 ml aqueous solution was filled in the reactor. The TiO_2 powder was suspended uniformly by a stirrer at densities at ranging from 500 to 2000 mg/l. Nitrogen gas was sparged at the rate of 140 ml/min to keep the water free from dissolved oxygen. The reactor was placed inside the water bath (SWC-900, Nissin Co. Ltd.) controlled at constant temperature, 18 °C. The UV light was illuminated after the water was bubbled by nitrogen gas for 30 min and when TiO_2 powder was uniformly suspended. About 13 ml of treated water was sampled every 2 min at the beginning stage and at adequate time intervals at later stage and the TiO_2 powder in the sample was separated from the water phase by a centrifuge. The concentration of metallic ion in the sample water was measured by sodium diethyldithiocarbamate colorimetry using a double beam photo-spectrometer (UV-1600, Shimazu Co. Ltd.). The amount of metal deposited on the surface of TiO_2 powder was determined separately by inductively coupled plasma spectrometry, ICP (SPS4000, Seiko Instruments Co. Ltd.). The pH of treated water was measured at the same time intervals.

In order to show the possible application to water purification, we selected chromium(VI) as one of the representative toxic metals. We prepared the aqueous solution of chromium trioxide, CrO_3, with the concentration of 10 mg Cr(VI)/l and conducted the experiment of photochemical reduction of hexavalent chromium to nontoxic trivalent chromium.

4. Results and discussion

Fig. 2 shows the change in concentration of cupric ion in the aqueous phase with time passage after the UV lamp is illuminated. The initial concentration of cupric ion is adjusted at 50 mg/l and the density of suspended TiO_2

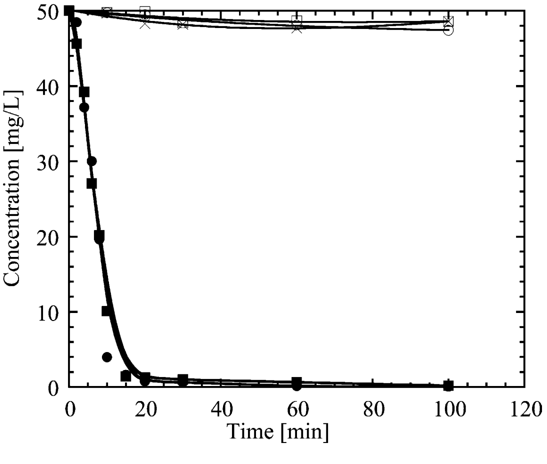

Fig. 2. Change in Cu^{2+} concentration with time at (●) 500 mg TiO_2/l with RNa; (■) 2000 mg TiO_2/l with RNa; (×) 2000 mg TiO_2/l without RNa; (○) 2000 mg TiO_2/l without UV; (□) UV only, with initial concentrations $[Cu^{2+}] = 50$ mg/l, $[HCOONa] = 0.1$ mol/l.

Table 1
Amount of copper deposited on TiO_2 by an ICP analysis

Time (min)	Cu to Ti (wt.%)	Deposited copper (mg)	
10	0.68/17.0	11.9	16.0[a]
20	1.54/35.4	13.1	19.5[a]

[a] Evaluated from concentration change.

particles is at 500 or 2000 mg/l. The solid symbols show the data obtained for the aqueous solution when the sodium formate is added at 0.1 mol/l, whereas the open symbols show the data for the aqueous solution with sodium formate free. In this figure, the data from blank tests are also included: the cross symbols show the data when the UV light is not illuminated and the open squares show the data when the UV light is illuminated alone (without TiO_2 pariticles). As shown in this figure, the cupric ion concentration decreases less than 2 mg/l within around 20 min: it decreases in proportion to reaction time at the beginning stage. The reduction reaction kinetics is thus found to follow the zero order with respect to cupric ion concentration and the rate is independent of the density of TiO_2 particles at this experimental condition. In contrast, the cupric ion concentration changes very scarcely when sodium formate is not added in the water or in the blank tests. This shows that the decrease of cupric ion concentration can be attributed not to adsorption or to any other physicochemical effects due to UV irradiation but to photochemical reduction reaction.

Table 1 shows the weight ratios of copper to titanium and the amounts of deposited copper determined by ICP for the samples of TiO_2 particles that were used in the reduction experiment carried out separately at 1250 mgTiO_2/l. Although the amount of deposited copper determined by ICP is 13–25% lower than that evaluated from the decrease of the cupric ion concentration, this provides clear evidence that copper is photochemically deposited on the surface of TiO_2 particles. The lower value determined by ICP might be attributed to some amount of deposited copper being removed from the surface of TiO_2 particles into water.

Fig. 3 shows the changes in copper ion concentration with reaction time at the catalyst density of 500 mg TiO_2/l when sodium formate is added at 0.1 mol/l, 1.47×10^{-3} mol/l (100 mg/l) and at 7.35×10^{-4} mol/l (50 mg/l). This figure shows that the rate of deposition strongly depends on the concentration of sodium formate: the rate of reduction reaction increases with the increase of the concentration of sodium formate and the reaction scarcely proceeds without sodium formate. This implies that sodium formate should act as hole scavenger and suppresses the recombination of the excited electron with the positive hole. It is considered that the OH radicals produced from OH^- oxidized by the positive holes should attack to decompose the formic anion $HCOO^-$ when sodium formate exists in the aqueous phase. When sodium formate does not exist in the aqueous phase, the excited electron would be recombined with the positive holes, which results in losing the photocatalytic reduction function.

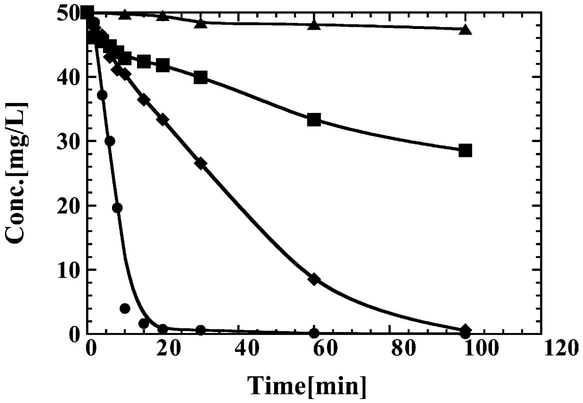

Fig. 3. Change in Cu^{2+} concentration with time at 500 mg TiO_2/l, $[Cu^{2+}] = 50$ mg/l: [HCOONa] = (●) 0.1 mol/l; (◆) 1.47×10^{-3} mol/l (100 mg/l); (■) 7.35×10^{-4} mol/l (50 mg/l); and (▲) 0 mol/l.

The reduction reaction of copper (copper sulphate) is expressed by the following overall reaction,

$$\tfrac{1}{2}CuSO_4 + HCOONa \rightarrow \tfrac{1}{2}Cu + \tfrac{1}{2}Na_2SO_4 + CO_2 + \tfrac{1}{2}H_2 \qquad (1)$$

The elementary reactions presumed as this reaction are shown in Table 2. Considering that the rate of reduction reaction depends strongly on the concentration of sodium formate and the reaction does not proceed when sodium formate is not added in the aqueous phase, the overall reaction is thought to be controlled by Eq. (9), the elemental step of oxidation reaction of formic ion. We here assume that the formic anions should be adsorbed on the surface of TiO_2 particle according to Langmuir's type of mono-molecular layer adsorption. Let C_M and C_R be the concentrations of metallic ion and formic anion, respectively, the rate of reduction reaction of cupric ion can then be expressed by the following equations:

$$\frac{dC_M}{dt} = \frac{dC_R}{dt} = -\frac{1}{2}k\frac{K_{ad}C_R}{1 + K_{ad}C_R}[OH] \qquad (12)$$

where k is the rate constant for the oxidation reaction of formic acid and K_{ad} the adsorption equilibrium constant.

Table 2
Elementary reactions in photocatalytic reduction

$\frac{1}{2}CuSO_4 \rightarrow \frac{1}{2}Cu^{2+} + \frac{1}{2}SO_4{}^{2-}$	(1)
$HCOONa \rightarrow HCOO^- + Na^+$	(2)
$HCOOH = HCOO^- + H^+$	(3)
$H_2O = H^+ + OH^-$	(4)
$h\nu \rightarrow h^+ + e^-$	(5)
$\frac{1}{2}Cu^{2+} + e^- \rightarrow \frac{1}{2}Cu$	(6)
$H^+ + e^- \rightarrow \frac{1}{2}H_2$	(7)
$OH^- + h^+ \rightarrow OH$	(8)
$HCOO^-(ad) + OH \xrightarrow{k} CO_2{}^- + H_2O$	(9)
$CO_2{}^- + h^+ \rightarrow CO_2$	(10)

The initial conditions are,

$$C_M = C_{M0} \quad t = 0 \tag{13}$$

$$C_R = C_{R0}, \quad t = 0 \tag{14}$$

Integrating of Eq. (12) gives

$$C_M = \tfrac{1}{2}C_R + C_{M0} - \tfrac{1}{2}C_{R0} \tag{15}$$

$$\frac{1}{K_{ad}}\ln\left[1+\frac{2(C_M - C_{M0})}{C_{R0}}\right] + 2(C_M - C_{M0}) = -k[\mathrm{OH}]t \tag{16}$$

when $C_R \gg C_M$ or $K_{ad} \gg 1$, Eq. (16) becomes

$$C_M = -\tfrac{1}{2}k[\mathrm{OH}]t + C_{M0} \tag{17}$$

when $C_R \ll C_M$, or $K_{ad} \ll 1$, on the contrary, Eq. (16) becomes

$$C_M = C_{M0} - \tfrac{1}{2}C_{R0}(1 - \mathrm{e}^{-kK_{ad}[\mathrm{OH}]t}) \tag{18}$$

The concentration C_R in these equations can be equated with the concentration of sodium formate, C_{RNa}, because the sodium formate would perfectly dissociate in the aqueous phase. Note that HCOOH can exist predominantly as ionic form rather than molecular form at pH's at our experimental conditions (pH = 6–8): the dissociation constant takes a relatively larger value, $K_a = 1.77 \times 10^{-4}$ mol/l. Eq. (17) indicates that the cupric ion concentration should decrease linearly when the concentration of sodium formate is more than that of metallic ion, and Eq. (18) indicates that the cupric ion concentration should decrease in the exponential behavior approaching a constant value, $C_{M0} - C_{R0}/2$ ($C_{M0} - C_{RNa0}/2$) when the concentration of sodium formate is less than that of metallic ion. These results deduced from our kinetic model are consistent with the experimental data as shown in Fig. 3. The rate constant can be determined from the linear relation, namely by comparing Eq. (17) with the experimental data at [RNa] = 0.1 mol/l, being determined as $k\,[\mathrm{OH}] = 9.96 \times 10^{-7}$ mol/l. The adsorption constant K_{ad}, on the other hand, can be determined as $K_{ad} = 1.36 \times 10^2$ l/mol comparing Eq. (18) with the experimental data at [RNa] = 7.35×10^{-4} mol/l.

In Fig. 4, the cupric ion concentrations calculated from Eq. (16) are compared with the experimental data. The calculated results are found to be closely related to the experimental data. The proposed kinetic model is valid to explain the time-dependency of cupric ion concentration and the dependency of the concentration of sodium formate on the rate of photochemical reduction reaction.

Fig. 5 shows the changes in pH in the reduction of cupric ions. The experimental conditions are listed in the figure caption. For the every case, the pH increases with time. If the kinetic model as shown in Table 1 is true, the hydrogen and hydroxide ions would be consumed at the same amount and the pH would not change in the process of reaction, which is contrary with the experimental results. In order to make clear this problem, we measured pH in the aqueous phase which does not contain copper sulphate. As shown in Fig. 6, the results show that the pH increases with reaction time even when the water does not contain cupric ions. The recombination of excited electron with positive hole is again suppressed by sodium formate, which results in noticeable change in pH at [RNa] = 0.1 mol/l. The increase of pH in this case can be attributed to hydrogen generation, namely to photochemical reduction of hydrogen ions to hydrogen molecules, with the elementary reaction: $\mathrm{H}^+ + \mathrm{e} \rightarrow (1/2)\mathrm{H}_2$. Thus, the hydrogen ions would be converted into hydrogen and be removed away as the gases from the water phase to the surrounding air. Such reaction may possibly occur competitively with the reduction reaction of cupric ion even in our reaction system, which is the reason why the pH increases with reaction time in the process of reduction of cupric ions. Interestingly, in Fig. 5, noticeable change in pH

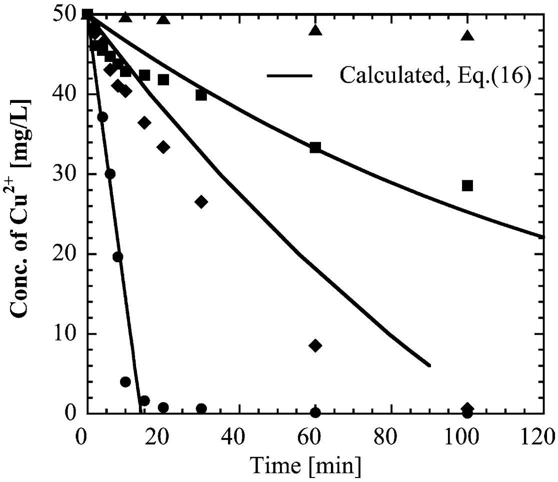

Fig. 4. Time-course of Cu^{2+} concentration at 500 mg $\mathrm{TiO_2}$/l: [HCOONa] = (●) 0.1 mol/l; (◆) 1.47×10^{-3} mol/l (100 mg/l); (■) 7.35×10^{-4} mol/l (50 mg/l); (▲) 0 mol/l.

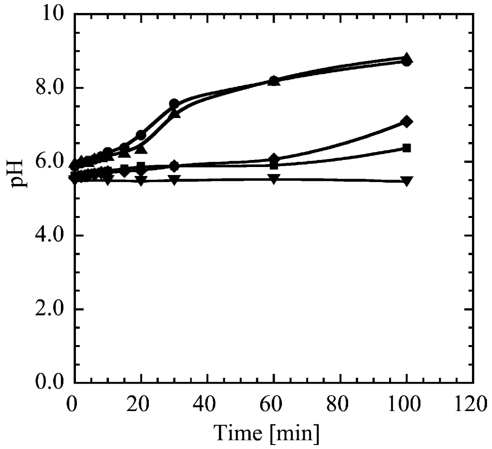

Fig. 5. Change in pH with time at 500 mg $\mathrm{TiO_2}$/l, $[\mathrm{Cu}^{2+}]$ = 50 mg/l: [HCOONa] = (●) 0.1 mol/l; (▲) 0.1 mol/l (2000 mg $\mathrm{TiO_2}$/l); (◆) 1.47×10^{-3} mol/l (100 mg/l); (■) 7.35×10^{-4} mol/l (50 mg/l); (▼) 0 mol/l.

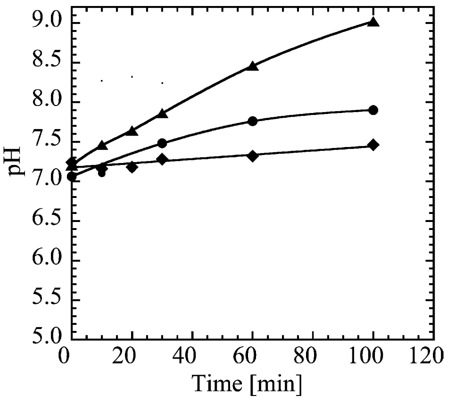

Fig. 6. Change in pH with time in the case of metallic ion free at 200 mg TiO_2/l: (●) TiO_2 + UV; (◆) TiO_2 not illuminated; (▲) TiO_2 + UV with 0.1 mol/l HCOONa.

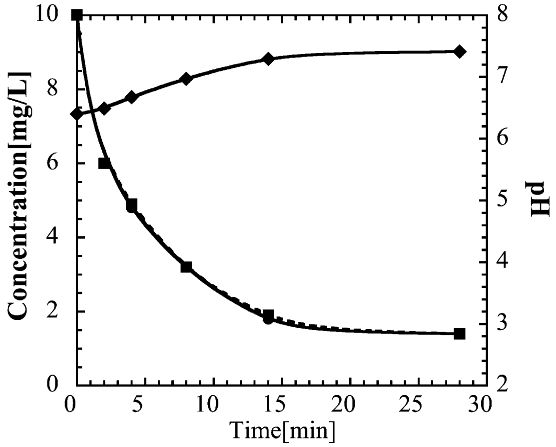

Fig. 7. Change in chromium ion(VI) concentration and pH with time at 1000 mg TiO_2/l, $[Cr^{6+}] = 10$ mg/l, [HCOONa] = 0.1 mol/l: (●) Cr^{6+}; (■) total Cr; (◆) pH.

is found in around 80 min at $[RNa] = 7.35 \times 10^{-4}$ mol/l, in around 60 min at $[RNa] = 1.47 \times 10^{-3}$ mol/l, and in around 10 min at $[RNa] = 0.1$ mol/l. Thus, the change in pH becomes noticeable after cupric ions are deposited away from the water phase to the solid phase, namely after the competitive cupric ion reduction reaction decreases.

Fig. 7 shows the change in concentration of chromium(VI) and total chromium with time when the aqueous solution of chromium trioxide with the initial concentration of 10 mg/l was treated by TiO_2 photocatalyst. As shown in this figure, both concentrations of chromium(VI) and total chromium decrease rapidly to 1.4 mg/l within 15 min just in the similar manner. This indicates that chromium(VI) can be reduced to nontoxic chromium(III) and possibly to metallic chromium deposited on the surface of TiO_2. The untreated amount corresponding to 1.4 mg/l might be attributed to the equilibrium ionic species which can dissolve as hexavalent chromium in water. Chromate ion(VI), for instance, can coexist with chromite ion(III) at the ratio $[CrO_4^{2-}]/[CrO_3^{3-}] = 0.06$ at pH = 8.5 and at the standard potential.

5. Conclusions

Experiments for TiO_2 photocatalytic reduction of metallic ions were carried out and the mechanism of the reduction reaction was discussed. The results are summarized as given follows:

1. Cupric ion can be reduced to metal by TiO_2 photocatalytic reaction. The photochemical reduction proceeds only when the hole scavenger species like sodium formate is added in the aqueous phase. The rate of reduction depends strongly on the concentration of hole scavenger. It increases with the increase of the concentration of hole scavenger.
2. The rate of reduction is independent of the density of suspended TiO_2 particles at densities more than an adequate value, namely than 200 mg/l in this experiment.
3. The rate of photochemical reduction of cupric ions can be explained by assuming that the kinetic step of elementary oxidation reaction of adsorbed formic anion by OH radical is the rate controlling.
4. Chromium(VI), the toxic metallic ion, can be reduced to nontoxic chromium metal by TiO_2 photocatalytic reaction.

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References

[1] A. Fujishima, K. Honda, Nature 238 (1972) 37–38.
[2] K.R. Thampi, J. Kiwi, M. Gratzel, Nature 327 (1987) 506–508.
[3] K. Adachi, K. Ohta, T. Mizuno, Solar Energy 53 (1994) 187–190.
[4] K. Okamoto, Y. Yamamoto, H. Tanaka, A. Itaya, Bull. Chem. Soc. Japan 58 (1985) 2015–2022.
[5] T. Watanabe, Ceramics (in Japanese) 31 (1996) 837–840.
[6] K. Hashimoto, A. Fujishima, Ceramics (in Japanese) 31 (1996) 815–820.
[7] B. O'Regan, M. Grazel, Nature 353 (1991) 737–740.
[8] A. Toyoda, L. Zhang, T. Kanki, N. Sano, J. Chem. Eng. J. 33 (2000) 188–191.
[9] L. Zhang, T. Kanki, N. Sano, A. Toyoda, Solar Energy 70 (2001) 331–337.
[10] L. Zhang, T. Kanki, N. Sano, A. Toyoda, Separation and Purification Tech. 31 (2003) 105–110.
[11] S. Yamasaki, S. Iwai, J. Yano, H. Taniguchi, J. Phys. Chem. A 105 (2001) 11285–11290.