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Photocatalytic activities enhanced for decompositions of organic compounds over metal-photodepositing titanium dioxide

Sha Jin, Fumihide Shiraishi*

Department of Biochemical Engineering and Science, Faculty of Computer Science and Systems Engineering,
Kyushu Institute of Technology, 680-4 Kawazu, Iizuka 820-8502, Japan

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Abstract

Three kinds of metals (Pd, Cu, and Pt) have been photodeposited either individually or simultaneously on a transparent thin film of titanium dioxide (TiO_2) that covers the inside surface of a Pyrex glass tube and the photocatalytic activities of these preparations have been investigated based on the oxidative decompositions of 2,4-dinitrophenol (DNP), formaldehyde (HCHO), and trichloroethylene (TCE) dissolved in aqueous solutions. The initial rate of DNP decomposition by Pd/TiO_2 is 2.5 times higher than that by TiO_2. Similarly, the initial rate of HCHO decomposition by Pd/TiO_2 is increased by 5.1 times. Such remarkable enhancements in the photocatalytic decompositions are also obtained with $Pd–Cu/TiO_2$ and $Pd–Cu–Pt/TiO_2$. Furthermore, Pd/TiO_2 is effective to promote the photocatalytic decomposition of TCE. This is different from the experimental result that was recently reported by other researchers, who used Pd/TiO_2 particles in the form of aqueous slurries. Microscopic observations of the metals deposited on the TiO_2 films reveal that the morphologies of the metal-photodepositing TiO_2 preparations are remarkably different from that of the TiO_2 film; each metal possesses its own coating pattern. A series of the photocatalytic reaction experiments indicate that the photocatalytic activities of the metal-depositing TiO_2 preparations are superior to that of the TiO_2 film and are highly stable.

Keywords: Photocatalyst; Titanium dioxide; Metal-photodeposition; Photocatalytic decomposition; Germicidal lamp

1. Introduction

Semiconductor photocatalysis has become increasingly promising technology in environmental remediation. Of various types of photocatalysts, titanium dioxide (TiO_2) is now under intensive investigation for practical application in antimicrobial, deodorization, air and water purifications, and wastewater treatment.

The photocatalytic reaction may drastically be promoted or retarded by doping TiO_2 with a certain kind of metal. In the past two decades, numerous reports have been published on the photocatalytic activities that were enhanced in the production of hydrogen and oxygen from a mixture of water and alcohol by platinum- and/or ruthenium-doped TiO_2 photocatalysts [1–5]. The photocatalytic oxidation of acetic acid over TiO_2 was also markedly enhanced by dissolved copper ions [6]. Similarly, the photocatalytic decomposition of toluene in aqueous TiO_2 suspension was significantly promoted in the presence of copper, ferrous, and manganese ions [7]. However, there was no promoting effect on the photocatalytic decomposition of phenol in the presence of silver ion [8]. Moreover, many other reports are available on metal-doped TiO_2 preparations to efficiently decompose toxic compounds. Several of the preparations showed positive effects [9–11], while others presented negative ones [9,10,12–14]. A combination of photocatalysis and ozonolysis gave a much better result for the decomposition of 2,4-dichlorophenoxyacetic acid in water [15]. The efficiencies in the decompositions of ethanes or ethenes in aqueous TiO_2 suspensions were increased by addition of hydrogen peroxide [16]. Furthermore, the use of RuO_2-doped TiO_2 powder [17] or RuO_2 and Pt-doped TiO_2 particles induced water cleavage by visible light in water photolysis systems [18–20]. These experimental results clearly indicate that it is worthwhile to further make an effort for finding out metallized TiO_2 photocatalysts that may give higher photocatalytic activities in the decomposition of environmental pollutants.

Many of the experimental studies on the photocatalyses have been carried out in a slurry-type reaction system with fine TiO_2 particles suspended in an aqueous solution [2,3,5,6,9,17,18,21–26]. From the standpoint of practical

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* Corresponding author. Tel.: +81-948-29-7827; fax: +81-948-29-7801.
E-mail address: fumi@bse.kyutech.ac.jp (F. Shiraishi).

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application, however, it is obvious that such a reaction manner has an intrinsic drawback to the separation of fine particles from the solution in order to re-use TiO_2 particles. Since the sizes of the TiO_2 particles synthesized range usually from 10 to 300 nm, it is apparent that high running cost is inevitably required for such a downstream processing. To overcome this drawback, immobilizations of TiO_2 on many kinds of solid materials have been performed. For example, a glass tube was coated with a transparent thin film of TiO_2 to decompose acetaldehyde in the air [27–32]. Also, TiO_2 was immobilized on a Pyrex glass, quartz glass, and stainless steel to decompose malic acid [33]. It is apparent that the immobilization of TiO_2 contributes greatly to the practical application of semiconductor photocatalysis.

Several kinds of metals have been immobilized on TiO_2 particles by sol–gel method [4,34], mechanical mixing [24,35], chemical deposition [23], precipitation–reduction [24], and photodeposition [23,36]. Although the difference in the metallizing method may cause, more or less, some difference in the activity or reaction mechanism of the photocatalyst preparation, this matter is not clear.

In the present work, three kinds of metals (Pd, Cu, and Pt) are photodeposited on a thin film of TiO_2 to increase the photocatalytic activity of TiO_2 and the characteristics of these metal-photodepositing TiO_2 (M/TiO_2) preparations are investigated in the photocatalytic decompositions of several organic compounds. The inside surface of a Pyrex glass tube is coated with a thin film of TiO_2 by the hydrogen peroxide method [37], followed by photodeposition of the metals either individually or simultaneously. This prepared glass tube is set in an annular-flow photocatalytic reactor [27] to measure the photocatalytic activities for the oxidative decompositions of 2,4-dinitrophenol (DNP), formaldehyde (HCHO), and trichloroethylene (TCE). Moreover, the surfaces of the M/TiO_2 preparations are observed microscopically.

2. Experimental

2.1. Materials

Titanium tetraisopropoxide (TIP) was purchased from Katayama Chemicals Co. Ltd. (Tokyo). Isopropyl alcohol (IPA), $Pd(NO_3)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, and $H_2PtCl_6{\cdot}6H_2O$ were obtained from Wako Pure Chemical Industries Ltd. (Osaka). A 31% (v/v) aqueous H_2O_2 solution was a product of Mitsubishi Chemical Co. Ltd. (Tokyo). A 6 W germicidal lamp (GL6; Sankyo Denki, Tokyo), which emits a UV light with a wavelength of 254 nm, was used as a light source of the photocatalytic decomposition. Two 6-W blacklight blue fluorescent lamps (National, FL6BL-B, Matsushita Denki, Tokyo), emitting a UV light with wavelengths of 300–400 nm, were used as a light source for photodeposition.

2.2. Preparation for a coating solution of titanium dioxide

A mixture of 29.69 g of TIP and 31.39 g of isopropyl alcohol with a molar ratio of 1:5 was well-mixed for 2 h at 5 °C. To this solution under vigorous mixing, a mixture of 7.53 g of water and 31.39 g of IPA was slowly added by dripping the wall surface of the vessel. After completion of this addition, the solution was further mixed for 4 h at 5 °C. The aqueous solution of TIP, IPA, and H_2O (a molar ratio of 1:10:4) thus obtained was filtered under aspiration to collect a white cake of titanium oxide on the filter. This cake was dried for 5 h in an oven at 100 °C, sometimes being taken out and roughly broken to pieces in order to shorten the drying time. Thereafter, the cake was further finely broken and dried for 15 h in an oven at 100 °C. Fine particles of amorphous titanium dioxide thus prepared were stored in a desiccator kept at a room temperature.

The amorphous titanium oxide (0.5 g) was dissolved in 10 ml of aqueous H_2O_2 solution and kept under vigorous mixing for 2 h at 25 °C. After keeping it statically for 1 h to gel, 60 ml of aqueous H_2O_2 solution was added and then mixed vigorously for about 2 days at 25 °C until generation of bubbles came to a stop. Consequently, a transparent yellow-colored solution was obtained.

2.3. Coating a glass tube with titanium dioxide

Prior to coating with TiO_2, a Pyrex glass tube (140 mm long and 28 mm in inside diameter) was immersed in an IPA solution and ultrasonically cleaned. The yellow-colored TiO_2 solution was poured into the glass tube rotating slowly, so that the inner surface was thoroughly covered with the viscous liquid solution. The glass tube was stood on end to remove an excessive liquid by gravitational dropping and then calcined for 1 h in a furnace at 400 °C. This procedure was repeated five times under the same condition, where the final calcination was carried out at 500 °C. Consequently, a transparent thin film of titanium oxide in anatase form was formed on the inside surface of the glass tube.

2.4. Photodepositing metals on a thin film of TiO_2

The reagents, $Pd(NO_3)_2$, $Cu(NO_3)_2{\cdot}3H_2O$, and $H_2PtCl_6{\cdot}6H_2O$, were used to deposit metals on the TiO_2 film under UV-illumination. To obtain a depositing solution, one to three of these chemical compounds (0.02–0.1 M) were dissolved in an aqueous solution of 0.2 M methanol. The one end of the glass tube coated with the TiO_2 film was plugged with a rubber stopper and 15 ml of the depositing solution was poured from the other end. After plugging the pouring end as well with a rubber stopper, the glass tube was fixed to the metal-photodepositing apparatus (Fig. 1) that was made by utilizing the body of a peristaltic pump (GILSON, Model M312, France). The glass tube was rotated at a speed of seven turns per minute under illumination with two 6 W

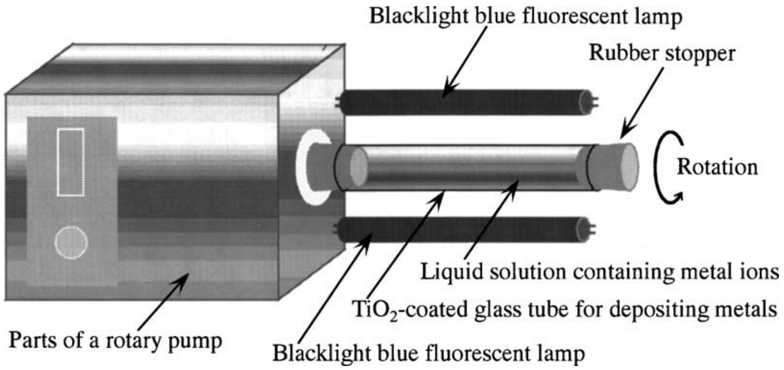

Fig. 1. Schematic of the apparatus for photodeposition of metals on a thin film of TiO_2 coated on the inside surface of a glass tube.

blacklight blue fluorescent lamps. During UV-illumination, the whole body of the apparatus was covered with an aluminum wheel to prevent from the leakage of UV-light. For the optimization of the preparation condition, the photodeposition time was changed between 1 and 20 h according to the magnitude of the metal ion concentration. As a result of the photodeposition, the surface of the transparent TiO_2 film was slightly black-colored. After washing the surface of the glass tube with distilled water, the activities of the metal-photodepositing TiO_2 (M/TiO_2) preparations were measured in an annular-flow photocatalytic reactor system, described below.

2.5. Photocatalytic reactor system

The photocatalytic reactor [27] used for this study was a cylindrical plastic vessel in which a 6 W germicidal lamp, surrounded by a quartz glass tube to protect the germicidal lamp from direct contact with an aqueous solution, flowing through an annulus between the inner surface of the vessel and the outer surface of the quartz glass tube, was located at the axis of the vessel. The Pyrex glass tube, whose inside surface was coated with TiO_2 or M/TiO_2, was inserted into the annulus so as to stick to the inner wall of the vessel. The liquid volume in the reactor was 57 ml and the width of the annulus was 2 mm.

The total liquid volume for the photocatalytic decomposition was 250 ml for DNP and 500 ml for HCHO and TCE. The initial reactant concentration was set at about $8\,\mathrm{mg\,l^{-1}}$ for DNP, about $10\,\mathrm{mg\,l^{-1}}$ for HCHO, and about $30\,\mathrm{mg\,l^{-1}}$ for TCE. The reactant solution was magnetically well-mixed in a flask of 500 ml in inlet volume and recirculated at a flow rate of $1000\,\mathrm{ml\,min^{-1}}$ with a peristaltic pump (EYELA, RP-1000, Tokyo Rikakikai Co. Ltd., Tokyo) through the annular-flow photocatalytic reactor described above. After 10 min, the germicidal lamp in the photocatalytic reactor was turned-on to illuminate the photocatalyst surface. A small amount of the reaction mixture was withdrawn from the flask at appropriate time intervals to determine the reactant or product concentration.

Since the present experimental system was based on the volume of the reactant solution that was sufficiently large compared with the surface area of the TiO_2 film, there was little effect of the dark adsorption on the reactant concentration.

2.6. Measurement of photocatalytic activities and microscopic observation of TiO_2 and M/TiO_2 preparations

The DNP concentration was determined by measurement of an absorbance at 357 nm using a spectrophotometer (UV-240, Shimadzu Co., Kyoto). The HCHO concentration was spectrophotometrically measured with an analytical reagent kit (Wako Pure Chemical Industries Ltd., Tokyo). In the photocatalytic decomposition of TCE, the concentration of chloride ion produced was spectrophotometrically determined by Schales–Schales method with an analytical reagent kit (Wako Pure Chemical Industries Ltd., Tokyo). The surfaces of the TiO_2 and M/TiO_2 preparations were observed by SEM (S900; HITACHI, Tokyo) and optical microscopy (KENIS Model TK; Kagaku Kyoeisha Co. Ltd., Tokyo).

3. Results and discussion

3.1. Photocatalytic activities of M/TiO_2 for DNP decomposition

The metals Pd, Cu, and Pt on the TiO_2 film were photodeposited over 20 h using an aqueous solution containing each metal at 0.02 M and these M/TiO_2 preparations were used to photocatalytically decompose DNP at an initial concentration of $8\,\mathrm{mg\,l^{-1}}$. These results are compared with the result by TiO_2 alone in Fig. 2. It is clear that all the M/TiO_2 preparations decompose DNP more rapidly than does TiO_2 alone. For example, when compared at 180 min, the DNP concentration is still at $1.5\,\mathrm{mg\,l^{-1}}$ for the case of TiO_2 alone, but is almost zero for the cases of M/TiO_2.

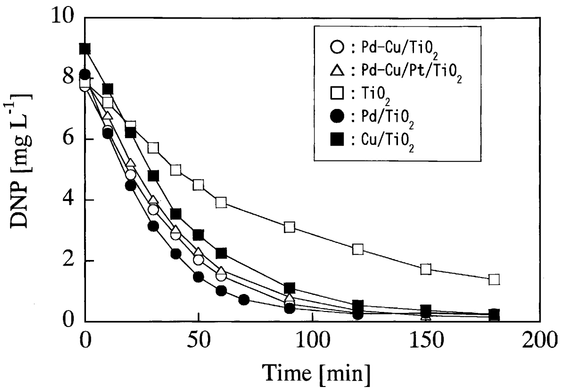

Fig. 2. Photocatalytic decompositions of DNP by M/TiO_2 preparations.

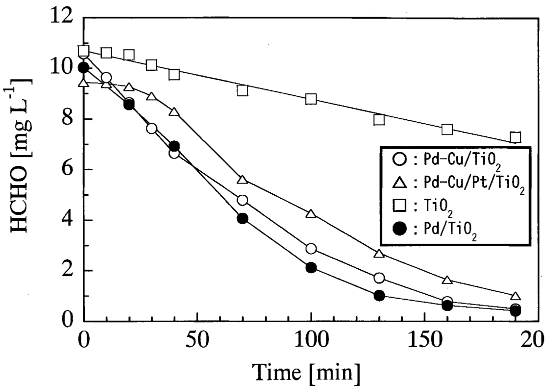

Fig. 3. Photocatalytic decompositions of HCHO by M/TiO_2 preparations.

The initial rates of DNP decomposition between the TiO_2 and M/TiO_2 photocatalysts were calculated from the slopes of the data points in Fig. 2 and the result is given in Table 1. The Pd–Cu/TiO_2, Pd–Cu–Pt/TiO_2, and Cu/TiO_2 preparations have nearly equal initial decomposition rates, which are about 1.9 times as large as that of TiO_2 alone. The Pd/TiO_2 preparation possesses the largest initial decomposition rate, which is 2.5 times larger than that of TiO_2 alone.

These results indicate clearly that the photocatalytic activity of TiO_2 is certainly increased when the metals, especially, Pd, are photodeposited on the TiO_2 film.

3.2. Photocatalytic activities of M/TiO_2 for HCHO decomposition

The decompositions of HCHO dissolved in aqueous solutions by TiO_2 alone and M/TiO_2 preparations were further investigated and the results are compared in Fig. 3. As in the case of DNP, the M/TiO_2 preparations can quickly lower the HCHO concentration. By contrast, the TiO_2 preparation without metal-deposition decomposes HCHO very slowly.

The initial rates of HCHO decomposition for the TiO_2 and M/TiO_2 preparations were calculated from the experimental data in Fig. 3 and the result is given in Table 1. Surprisingly, the initial decomposition rates of Pd–Cu/TiO_2, Pd–Cu–Pt/TiO_2, and Pd/TiO_2 are 5.1, 4.3, and 5.0 times, respectively, larger than that of TiO_2 alone.

It is obvious that the M/TiO_2 photocatalysts prepared by the photodeposition method can certainly promote the photocatalytic decompositions of organic compounds, compared to the case of TiO_2 alone. Enhancements in the photocatalytic activities of the M/TiO_2 preparations may result from the inhibition of a spontaneous recombination between the hole and electron occurring on the surface of excited TiO_2 [38] by the metals deposited by photodeposition on the TiO_2 film.

Obviously, the photocatalytic decomposition of HCHO is remarkably accelerated by the M/TiO_2 photocatalysts prepared in the present work. In a previous paper, Shiraishi et al. [27] studied a method to simultaneously carry out the photolytic sterilization of *Escherichia coli* and the photocatalytic decomposition of HCHO in the annular-flow photocatalytic reactor having a germicidal lamp (254 nm) as a sole light source. In this reactor system, *E. coli* was instantaneously killed, whereas the HCHO concentration was slowly decreased because of a limitation on the photocatalytic activity of TiO_2. Introduction of the M/TiO_2 photocatalyst to this reactor system is clearly useful to accelerate the oxidative decomposition of HCHO.

3.3. Photocatalytic activities of M/TiO_2 preparations for TCE decomposition

To reconfirm the usefulness of the M/TiO_2 preparations, the decompositions of TCE by Pd/TiO_2 and Cu/TiO_2 were further examined. The result is given in Table 1. As in the cases of DNP and HCHO decompositions, the photocatalytic activity for the decomposition of TCE is also certainly

Table 1
Comparison of initial rates for photocatalytic decompositions of several reactants by M/TiO_2 preparations (metal ion concentration, 20 mM; deposition time, 20 h)

Reactant	Initial rate of decomposition ($mg\,l^{-1}\,min^{-1}$)				
	TiO_2	Pd–Cu/TiO_2	Pd–Cu–Pt/TiO_2	Pd/TiO_2	Cu/TiO_2
DNP	0.0181	0.0340	0.0332	0.0406	0.0342
HCHO	0.00482	0.0246	0.0209	0.0239	–
TCE	0.0195	–	–	0.0438[a]	0.0349[b]

[a] Pd^{2+} concentration, 100 mM; deposition time, 5 h.

[b] Cu^{2+} concentration, 100 mM; deposition time, 5 h.

increased by photodeposition. The activity of the Pd/TiO_2 preparation is higher than that of the Cu/TiO_2 preparation, indicating that Pd is an effective metal to increase the photocatalytic activity when preparation is made by the photodeposition method as employed in the present work. The initial formation rates of Cl^- by Pd/TiO_2 and Cu/TiO_2 are about 2.2 and 1.8 times, respectively, greater than that of TiO_2 alone.

The increases in the rates of TCE decomposition by the Pd/TiO_2 preparation are quite different from the experimental result recently reported by Chen et al. [23], who obtained a result that the photocatalytic activity of Pd/TiO_2 for TCE is lower than that of TiO_2. This may be explained by the differences in the type of the Pd/TiO_2 preparation and in the amount of the deposited Pd. In the present work, the metals were photodeposited on the surface of the TiO_2 film that was firmly fixed on the glass tube, while Chen et al. photodeposited Pd on TiO_2 particles and used them in the form of aqueous slurries. To prevent from overdeposition on the TiO_2 surface, moreover, we deliberately adjusted the metal ion concentrations to a low level and photodeposited metals rotating the glass tube that contained a coating solution.

3.4. Optimization of metal-depositing condition

As described above, Pd contributes greatly to increases in the decomposition rates of DNP, HCHO, and TCE. In the following, therefore, investigation on the metal-depositing condition will be limited to Pd/TiO_2.

Table 2 compares the initial rates of DNP decomposition by the Pd/TiO_2 prepared under various conditions. A high photocatalytic activity was obtained at a Pd concentration of 20 mM and a photodeposition time of 20 h. The magnitude of this photocatalytic activity is more than two times of that of TiO_2 alone. In the practical application, however, the photodeposition time of 20 h is obviously too long. Therefore, Pd was photodeposited over 5 h at the same Pd concentration, but the photocatalytic activity of the Pd/TiO_2 preparation was somewhat low. The Pd concentration was increased up to 100 mM, so that the Pd/TiO_2 thus prepared showed the highest photocatalytic activity. When the deposition time was shorter and longer than 5 h, the Pd/TiO_2 preparations gave lower photocatalytic activities. Likewise, when the photodeposition was made at a higher Pd concentration, the photocatalytic activity was reduced. In these cases, the whole surface of the thin film of photocatalyst certainly turned brownish. As a result, we consider that the decrease in the photocatalytic activity is due to the fact that many titanium dioxide particles were covered with Pd and hardly excited by UV-irradiation. On the other hand, the decrease in the photocatalytic activity for the photodeposition at a lower Pd concentration is considered due to an insufficient deposition amount of Pd, which resulted in an unsatisfactory separation of the electron from the positive hole. As described later, we attempted to characterize the Pd particles on the TiO_2 film by means of SEM observation, but could not identify the particles. From the result in Table 2, we thus conclude that the photodeposition time of 5 h at the Pd concentration of 100 mM is the best condition to prepare Pd/TiO_2.

3.5. Microscopic observations of TiO_2 and M/TiO_2 preparations

An attempt was undertaken to characterize the metals deposited on the surface of the TiO_2 film by means of SEM observation. We found the presence of several fine particles, but it was unable to identify if these particles were the metals deposited.

On the other hand, it was easily visible to the naked eye that compared with the TiO_2 film, the condition of the surface of each M/TiO_2 preparation had been certainly changed after the photodeposition treatment. Therefore, the same samples were observed by an optical microscope with a magnification of 400. The result is presented in Fig. 4. It is clear that the TiO_2 film has a smooth and colorful surface. On the other hand, the surface of the Pd/TiO_2 preparation is slightly black-colored, suggesting that Pd is widely distributed on the TiO_2 film. In the case of the Cu/TiO_2 preparation, Cu covers the TiO_2 surface in a netlike pattern. Obviously, the Pd–Cu/TiO_2 and Pd–Cu–Pt/TiO_2 preparations possess the coating patterns that are typical of Pd and Cu. From the principle of the photodeposition, it is clear that each metal is present on the surface of the TiO_2 film.

3.6. Photocatalytic activities of M/TiO_2 preparations

Fig. 5(a) compares the time courses of the DNP concentration in two runs for the DNP decomposition using the same Pd/TiO_2 preparation. In this case, the first run was performed just after the preparation was made, while the second run was after 6 months; during the period of 6 months, more than 20 runs were performed using the same Pd/TiO_2 preparation. There is little difference between the time courses of the DNP concentration in the two runs. Similarly, Fig. 5(b) compares the time courses of the HCHO concentration in two runs for the decomposition of HCHO using two different

Table 2

Comparison of initial rates for photocatalytic decomposition of DNP by Pd/TiO_2 photocatalysts prepared by photodeposition under different conditions of palladium ion concentrations and deposition times

Pd^{2+} concentration (mM)	0	20	20	100	100	100
Deposition time (h)	0	20	5	5	1	8
Initial decomposition rate (mg l^{-1} min^{-1})	0.0181	0.0406	0.0344	0.0414	0.0299	0.0359

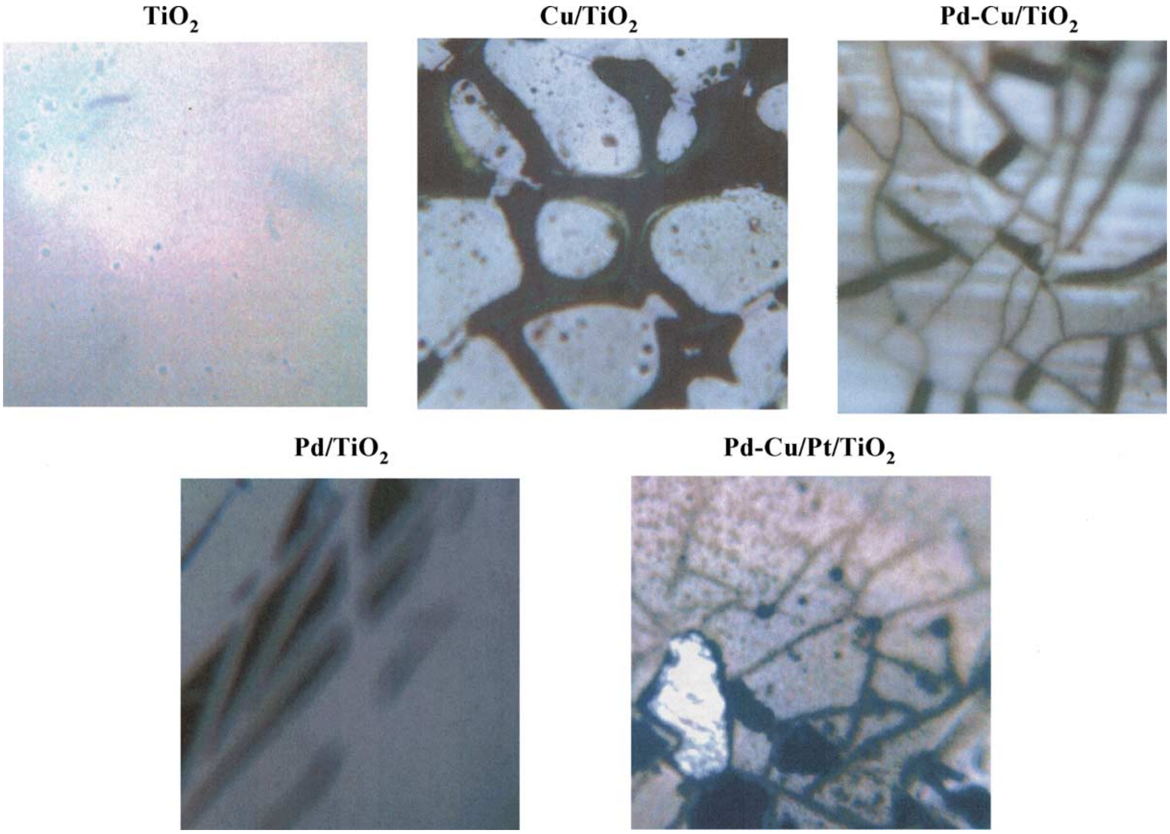

Fig. 4. Optical microscope photographs of the surfaces of TiO_2 and M/TiO_2 preparations.

Pd/TiO_2 preparations that were made by different person. Again, there is little difference between the time courses of the HCHO concentration in the two runs. These two results clearly indicate that the photocatalytic activity of the Pd/TiO_2 preparation is very stable and reproducible. We also obtained the same results for other M/TiO_2 preparations. Thus, it is clear that the photodeposition technique used in the present work is useful.

Table 3 compares the photocatalytic activities of metallized TiO_2 photocatalysts prepared by various researchers. The experimental data indicates that the metallization of TiO_2 does not always yield a positive effect on the photocatalytic decomposition and, conversely, the metallization of TiO_2 with a certain metal may cause a negative effect [9,12,23]. In the present work, however, the UV-illuminated M/TiO_2 certainly decomposed DNP, HCHO, and TCE at higher speeds than those of UV-illuminated TiO_2, as shown in Figs. 2 and 3 and Table 1, respectively. These distinct enhancements in the decomposition rates may be partly explained based on the rate-limiting step in a series of

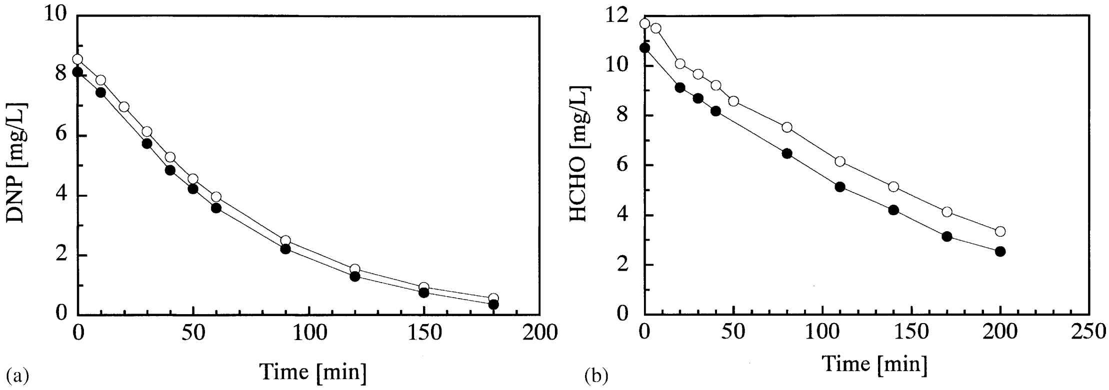

Fig. 5. Stability and reproducibility of photocatalytic activities of Pd/TiO_2. (a) Photocatalytic decompositions of DNP by the same Pd/TiO_2 just after preparation and after 6 months. (b) Photocatalytic decompositions of HCHO by two Pd/TiO_2 preparations made by different person.

Table 3
Comparison of photocatalytic activities of metallized TiO_2 preparations

Researchers	Method	Catalyst	Performance of photocatalyst
Lindner et al. (1997)	Photodeposition	UV100TiO_2	15[a]
		UV100TiO_2/1 wt.% Pt	30[a]
		UV100TiO_2/1 mM $Cu(NO_3)_2$	24[a]
		UV100TiO_2/10 mM $Cu(NO_3)_2$	26[a]
		UV100TiO_2/100 mM $Cu(NO_3)_2$	4.5[a]
		P25 TiO_2/10 mM $Cu(NO_3)_2$	5.0[a]
		P25 TiO_2/1 wt.% Pt	12[a]
		UV100TiO_2/10 mM $AgNO_3$	8.0[a]
Herrmann et al. (1997)	Chemical mixing	TiO_2	0.30[b]
		TiO_2/Ag^+	0.14[b]
		TiO_2/Ag^+ ($h\nu$)	0.20[b]
		TiO_2 Degussa P-25 (5 mg)	1.93[b]
Chen et al. (1999)	Physical mixing	TiO_2	0.88[c]
		Pd/TiO_2	0.36[c]
Chen et al. (1999)	Photodeposition	TiO_2	0.64[d]
		Pd/TiO_2	0.66[d]
This work	Photodeposition	TiO_2	50.1[e]
		Pd–Cu–Pt/TiO_2	78.7[e]
		Pd–Cu/TiO_2	80.6[e]
		Pd/TiO_2	87.5[e]
		Cu/TiO_2	76.7[e]
This work	Photodeposition	TiO_2	11.8[f]
		Pd–Cu–Pt/TiO_2	30.0[f]
		Pd–Cu/TiO_2	48.9[f]
		Pd/TiO_2	50.1[f]

[a] Conversion of dichloroacetic acid (%).
[b] Rate constant of malic acid decomposition ($min^{-1}\ TiO_2\ m^{-2}$).
[c] Cl^- produced in oxidation of chloroform (mM).
[d] Cl^- produced in oxidation of TCE (mM).
[e] Conversion of DNP after 1 h (%).
[f] Conversion of HCHO after 1 h (%).

the elementary reactions relating to the photocatalytic decomposition (Table 4). The photocatalytic decomposition taking place in an aqueous solution is controlled by the hole-trapping by hydroxyl groups attached to the surface Ti(IV) atoms to form hydroxyl radicals [26]. Since the metal deposited on the TiO_2 film easily gains positively-charged holes, as expressed by Eq. (6) in Table 4, the recombination of holes with electrons, as expressed by Eq. (3) in Table 4, is inhibited and the formation of hydroxyl radical on the TiO_2 surface, as expressed by Eqs. (4) and (5) in Table 4, is significantly enhanced compared to the case of TiO_2 alone. Consequently, the photocatalytic decomposition rate can be markedly improved owing to the increase in the hydroxyl radical concentration. This reasoning may be supported by a conclusion of Brown and Darwent [38] that a rapid removal of holes from the TiO_2 particles is very important to prevent the recombination of holes with electrons.

Table 4
Elementary reactions relating to photocatalytic decompositions of organic compounds by M/TiO_2

$$\text{Excitation}: TiO_2 \xrightarrow{h\nu} e^- + h^+ \quad (1)$$
$$\text{Adsorption}: \text{subs} + \text{ads} \leftrightarrow \text{subs}_{ads} \quad (2)$$
$$\text{Recombination}: e^- + h^+ \rightarrow \text{heat} \quad (3)$$
$$h^+ + H_2O_{ads} \rightarrow OH^\bullet + H^+ \quad (4)$$
$$h^+ + 2OH^-_{ads} \rightarrow OH^\bullet + OH^- \quad (5)$$
$$M^{n+} + e^- \rightarrow M^{(n-1)+} \quad (6)$$
$$H_2O \leftrightarrow H_2O_{ads} \quad (7)$$

The term “ads” means that the substance is at an adsorption site.

4. Conclusions

Three kinds of metals were deposited on a thin film of titanium dioxide and their photocatalytic activities were compared in the decompositions of DNP, HCHO, and TCE in aqueous solutions. The experimental results indicated that the rate of the photocatalytic decomposition can be remarkably improved with all the M/TiO_2 preparations (Pd/TiO_2, Pd–Cu/TiO_2, Cu/TiO_2, and Pd–Cu–Pt/TiO_2). This marked improvement was obtained in the decomposition of HCHO. Microscopic observations of the metals deposited on the TiO_2 film revealed that their morphologies are quite different from that of the TiO_2 film and each metal possesses its own coating pattern. In conclusion, the technique to photodeposit metals, such as Pd, Cu, and Pt, on the thin film of TiO_2 is very useful to increase the rate of the photocatalytic decomposition of organic compounds in aqueous solutions.

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References

[1] A. Sobczynski, A.J. Bard, A. Campion, M.A. Fox, T. Mallouk, S.E. Webber, J.M. White, Photoassisted hydrogen generation: Pt and CdS supported on separate particles, J. Phys. Chem. 91 (1987) 3316.

[2] H. Kanno, Y. Yamamoto, H. Harada, TiO_2-based photocatalysts prepared from titanium isopropoxide and aqueous electrolyte solutions, Chem. Phys. Lett. 121 (1985) 245.

[3] T. Kawai, T. Sakata, Photocatalytic hydrogen production from liquid methanol and water, J. Chem. Soc., Chem. Commun. 102 (1980) 694.

[4] S.C. Moon, H. Mametsuka, E. Suzuki, Y. Nakahara, Characterization of titanium-boron binary oxides and their photocatalytic activity for stoichiometric decomposition of water, Catal. Today 45 (1998) 79084.

[5] D. Duonghong, E. Borgarello, M. Gratzel, Dynamics of light-induced water cleavage in colloidal systems, J. Am. Chem. Soc. 103 (1981) 4685.

[6] M. Bideau, B. Claudel, L. Faure, H. Kazouan, The photo-oxidation of acetic acid by oxygen in the presence of titanium dioxide and dissolved copper ions, J. Photochem. Photobiol. A: Chem. 61 (1991) 269.

[7] E.C. Butler, A.P. Davis, Photcatalytic oxidation in aqueous titanium dioxide suspensions: the influence of dissolved transition metals, J. Photochem. Photobiol. A: Chem. 70 (1993) 273–283.

[8] A. Sclafani, L. Palmisano, E. Davi, Photocatalytic degradation of phenol by TiO_2 aqueous dispersions: rutile and anatase activity, New J. Chem. 14 (1990) 265.

[9] M. Lindner, J. Theurich, D.W. Bahnemann, Photocatalytic degradation of organic compounds: accelerating the process efficiency, Water Sci. Technol. 35 (1997) 79.

[10] M. Tajima, M. Niwa, Y. Fujii, Y. Koinuma, R. Aizawa, S. Kushiyama, S. Kobayashi, K. Mizuno, H. Ohuchi, Decomposition of chlorofluorocarbons on W/TiO_2-ZrO_2, Appl. Catal. B: Environ. 14 (1997) 97.

[11] D. Bockelmann, R. Goslich, D. Bahnemann, Solar Thermal Energy Utilization, Springer, Heidelberg, 1992.

[12] J.-M. Herrmann, H. Tahiri, Y. Ait-Ichou, G. Lassaletta, A.R. Gonzalez-Elipe, A. Fernandez, Characterization and photocatalytic activity in aqueous medium of TiO_2 and Ag-TiO_2 coatings on quartz, Appl. Catal. B: Environ. 13 (1997) 219.

[13] A. Sclafani, L. Palmisano, M. Schiavello, Res. Chem. Intermed. 18 (1992) 211.

[14] L. Palmisano, V. Augugliaro, A. Sclafani, M. Schiavello, Activity of chromium-ion-doped titania for the dinitrogen photoreduction to ammonia and for the phenol photodegradation, J. Phys. Chem. 92 (1988) 6710.

[15] T.S. Muller, Z. Sun, G. Kumar, K. Itoh, M. Murabayashi, The combination of photocatalysis and ozonolysis as a new approach for cleaning 2,4-dichlorophenoxyaceticacid polluted water, Chemosphere 36 (1998) 2043.

[16] T. Hisanaga, K. Harada, K. Tanaka, Photocatalytic degradation of organochlorine compounds in suspended TiO_2, J. Photochem. Photobiol. A: Chem. 54 (1990) 113.

[17] T. Ohno, F. Tanigawa, K. Fujihara, S. Izumi, M.M., Photocatalytic oxidation of water by visible light using ruthenium-doped titanium dioxide powder, J. Photochem. Photobiol. A: Chem. 127 (1999) 107.

[18] J. Lobedank, E. Bellmann, J. Bendig, Sensitized photocatalytic oxidation of herbicides using natural sunlight, J. Photochem. Photobiol. A: Chem. 108 (1997) 89.

[19] E. Borgarello, J. Kiwi, M. Gratzel, E. Pelizzetti, M. Visca, Visible light induced water cleavage in colloidal solutions of chromium-doped titanium dioxide particles, J. Am. Chem. Soc. 104 (1982) 2996.

[20] E. Borgarello, M. Kiwi, E. Pelizzetti, M. Visca, J. Gratzel, Sustained water cleavage by visible light, J. Am. Chem. Soc. 103 (1981) 6324.

[21] A. Sclafani, M. Mozzanega, P. Pichat, Effect of silver deposits on the photocatalytic activity of titanium dioxide samples for the dehydrogenation or oxidation of 2-propanol, J. Photochem. Photobiol. A: Chem. 59 (1991) 181.

[22] M. Anpo, T. Shima, S. Kodama, Y. Kubokawa, Photocatalytic hydrogenation of CH_3CCH with H_2O on small-particle TiO_2: size quantization effects and reaction intermediates, J. Phys. Chem. 91 (1987) 4305.

[23] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Photocatalyzed oxidation of alcohols and organochlorides in the presence of native TiO_2 and metallized TiO_2 suspensions. Part I. Photocatalytic activity and pH influence, Water Res. 33 (1999) 661.

[24] B. Ohtani, M. Kakimoto, S. Nishimoto, T. Kagiya, Photocatalytic reaction of neat alcohols by metal-loaded titanium(IV) oxide particles, J. Photochem. Photobiol. A: Chem. 70 (1993) 265.

[25] J. Chen, D.F. Ollis, W.H. Rulkens, H. Bruning, Kinetic processes of photocatalytic mineralization of alcohols on metallized titanium dioxide, Water Res. 33 (1999) 1173.

[26] C.A. Martin, M.A. Baltanas, A.E. Cassano, Photocatalytic decomposition of chloroform in a fully irradiated heterogeneous photoreactor using titanium oxide particulate suspensions, Catal. Today 27 (1996) 221.

[27] F. Shiraishi, K. Toyoda, S. Fukinbara, E. Obuchi, K. Nakano, Photolytic and photocatalytic treatment of an aqueous solution containing microbial cells and organic compounds in an annular-flow reactor, Chem. Eng. Sci. 54 (1999) 1547.

[28] S. Fukinbara, F. Shiraishi, K. Nakano, Characteristics of the photocatalytic reactor with an annular array of glass tubes surrounding a light source. 1. Selection of a light source and photocatalyst support, CELSS J. 13 (2001) 1.

[29] S. Fukinbara, F. Shiraishi, Characteristics of the photocatalytic reactor with an annular array of glass tubes surrounding a light source: 2. Kinetic analysis, CELSS J. 13 (2001) 11.

[30] S. Wang, F. Shiraishi, K. Nakano, Decomposition of formic acid in a photocatalytic reactor with a parallel array of four light sources, J. Chem. Tech. Biotechnol. 77 (2002) 805.

[31] S. Wang, F. Shiraishi, K. Nakano, A synergistic effect of photocatalysis and ozonation on decomposition of formic acid in an aqueous solution, Chem. Eng. J. 87 (2002) 261.

[32] J.-H. Xu, F. Shiraishi, Photocatalytic decomposition of acetaldehyde in air over titanium dioxide, J. Chem. Tech. Biotechnol. 74 (1999) 1096.

[33] A. Fernandez, G. Lassaletta, V.M. Jimenez, A. Justo, A.R. Gonzalez-Elipe, J.-M. Herrmann, T.H.Y. Ait-Ichou, Preparation and characterization of TiO_2 photocatalysts supported on various rigid supports (glass, quartz and stainless steel). Comparative studies of photocatalytic activity in water purification, Appl. Catal. B: Environ. 7 (1995) 49.

[34] R.T. Ranjit Viswannathan, Photocatalytic reduction of nitrite and nitrate ions over doped TiO_2 catalysts, J. Photochem. Photobiol. A: Chem. 107 (1997) 215.

[35] A.V. Vorontsov, E.N. Savinov, Z. Jin, Influence of the form of photodeposited platinum on titania upon its photocatalytic activity

in CO and acetone oxidation, J. Photochem. Photobiol. A: Chem. 125 (1999) 113.

[36] B. Kraeutler, A.J. Bard, Heterogeneous photocatalytic preparation of supported catalysts. Photodeposition of platinum on TiO_2 powder and other substrates, J. Am. Chem. Soc. 100 (1978) 4317.

[37] K. Matsuo, T. Takeshita, K. Nakano, Formation of thin films by the treatment of amorphous titania with H_2O_2, J. Cryst. Growth 99 (1990) 621.

[38] G.T. Brown, J.R. Darwent, Methyl orange as a probe for photooxidation reactions of colloidal TiO_2, J. Phys. Chem. 88 (1984) 4955.