ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 110 (1997) 307-311

Metal powder addition effect on the photocatalytic reactions and the photo-generated electric charge collected at an inert electrode in aqueous TiO_2 suspensions

Katsuhiko Hirano *, Hideo Asayama, Akio Hoshino, Hiroshi Wakatsuki

Shibaura Institute of Technology 9-14, Shibaura 3 chome, Minatoku, Tokyo 108, Japan

Accepted 16 June 1997

Abstract

The photocatalytic reaction in an aqueous TiO_2 suspension has been found to be enhanced by the addition of some metal powders such as copper, silver, nickel and cobalt into the suspension. Just mixing a metal powder into the suspension gave nearly the same efficiency as metal-loading on the semiconductor particles. The effect is attributed to the rapid transfer of the photogenerated electrons from the TiO_2 to the metal particles, resulting in the effective separation of the electrons and holes.

The photo-current measurements were performed using inert collecting electrodes in the suspensions of TiO_2, where formate was added as a hole scavenger, with and without a metal powder. Higher anodic photocurrent was obtained in the presence of a metal than in its absence, indicating that the metal-mediated electron transfer reaction occurs more effectively from the electron-rich TiO_2 particles to the collecting electrode than the direct discharge of the electron-rich TiO_2 on the collecting electrode.

Keywords: TiO_2; Metal powder; Photocurrent; Collecting electrode

1. Introduction

Photocatalytic reactions using a semiconductor electrode (SC) are initiated by the holes and excited electrons generated on the SC by light illumination, the oxidation by the former and the reduction by the latter occurring simultaneously on the same particles. Metal-loaded SC particles are generally used for avoiding the rapid recombinations of the holes and electrons, because the excited electrons immediately transfer to metal site; consequently the separation of holes and electrons is enhanced.

Our previous work for the photo-oxidation of acetic acid in aqueous TiO_2 suspension proved that mixing copper powder into the suspension promotes the catalytic yields almost as efficiently as metal loading on SC particles [1]. The effect was explained to be due to the rapid transfer of the excited electrons to copper particles at the collision between SC and metal particles, resulting in the separation of the electrons from the holes [2]. It offers a practical advantage in the utilisation of photocatalytic reactions widely that the troublesome treatment of metal-loading on SC particles is not necessary, instead only mixing metal powder into the SC suspension is needed.

The purpose of the present work is to give more insight into the effect of metal powder addition on the photocatalytic reactions by adding various kinds of metals, not only copper but also other metals such as silver, nickel and cobalt. For further corroboration of the metal-assisted charge separation on the photo-generated SC particles, the photocurrent measurements in TiO_2 suspensions are also performed by means of the collecting electrode according to the method reported by Bard and coworkers [3–5] and Peterson et al. [6], in which the photo-generated electric charge on the SC particles are collected at an inert electrode like platinum immersed in the suspension. We measured the photocurrents in the TiO_2 suspensions with and without metal powder and examined the effect of the metal on the photocurrent.

2. Experimental

All chemicals including TiO_2 (anatase) and metal powders, which were prepared electrochemically, were reagent grade as supplied from Wako Pure Chemical Co., except silver powder which was purchased from Kojima Chemical Co. The purity of these metals were more than 99% and the mean diameters of the metal particles were between 2 and 3 μm.

---

* Corresponding author.

PII S1010-6030(97)00201-3

Photocatalytic reactions in TiO_2 suspension mixed with a metal powder were carried out as follows. Titanium dioxide powder (0.5 g) and a metal powder (0.5 g) were sonically suspended into 4.0 mol dm^{-3} methanol solution (80 ml) prepared with Millipore water in cylindrical pyrex cell (110 ml) equipped with a flat window through which the light entered. The cell was purged with helium gas for 1 h to eliminate the oxygen dissolved in solution before illumination. The light source was a 100 W mercury lamp. The cell was placed at the position of the distance 10 cm from the lamp, and the suspension was illuminated at room temperature with vigorously stirring. The temperature of the sample solution rose up to 40°C during illumination.

Gaseous products were analysed on a GC 380 gas chromatogragh (GLS), equipped with a thermal conducting detector, a molecular sieve, 5 Å column and helium carrier gas. Before the analysis of the gaseous products, 2 ml of sulfuric acid solution (volume ratio of water and conc. $H_2SO_4 = 9:4$) was added into the sample suspension using a syringe through the silicone gum septum in order to expel CO_2 dissolved in the solution. After filtering out the suspension formate (as formic acid), the liquid phase was analysed by HPLC equipped with an ion-exchange column (Shodex KC-811) and a UV 430 nm detector. Formaldehyde was determined by the colorimetric analysis using chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid). Copper(II) ion presence was analysed by an atomic absorption analysis; in this case, sulfuric acid was not added into the sample solution after illumination.

Metal colloidal solutions of copper and silver, which were used instead of metal powder suspensions for comparison, were prepared by reducing the salts of copper sulfate and silver nitrate with hydrazine, respectively. The original concentration of the colloidal solutions thus obtained were 2.0×10^{-3} mol dm^{-3} copper and 2.1×10^{-3} mol dm^{-3} silver, respectively. These solutions were prepared just before use and diluted for the sample solutions.

Metal(Cu) loaded TiO_2 catalysts, which were also used for comparison with metal powder suspension, were prepared by the method of photochemical deposition [7].

The photocurrent measurements using a Pt collecting electrode in TiO_2 slurry were performed as almost the same way as reported by Bard et al. [3]. A pyrex H cell (sample volume 60 ml) equipped with a flat optical window to allow illumination was used. Both collector and counter electrodes were platinum plates (10×10 mm^2). The counter electrode was placed in a compartment separated from the slurry-containing electrode by fine-porosity glass frit. Silver/silver chloride was used as a reference electrode. The collecting (working) electrode was kept, by a potentiostat (TOHO GIKEN PS-02), at the same potential as that of the suspension before illumination. The cell was purged with pure nitrogen for 1 h prior to the illumination to eliminate the oxygen dissolved in the solution, then illuminated in the same way as described above. The suspensions containing nickel and cobalt were stirred by the stirring bar (non-magnetic) which was connected to the motor positioned above the reaction cell since these metal powders attached to the magnetic stirring bar if it were used. The transient photocurrents were recorded on a recorder (YOKOGAWA MODEL 305711).

3. Results and discussion

3.1. Photocatalytic reactions in TiO_2 suspended aqueous solutions mixed with metal powder

Photo-oxidations of 4.0 mol dm^{-3} methanol solutions were carried out in various TiO_2 suspensions. The products, both of hydrogen (Fig. 1) and formaldehyde (Fig. 2), increased with illumination time in all suspensions (80 ml) of TiO_2 (0.5 g) only, TiO_2 (0.5 g) and copper powder (0.5 g), TiO_2 (0.5 g) and 1.0×10^{-3} mol dm^{-3} colloid, and copper-loaded (6%) TiO_2 (0.5 g). Other products such as formic acid and carbon dioxide were formed but in minor amounts during the illumination time. It is obvious that the

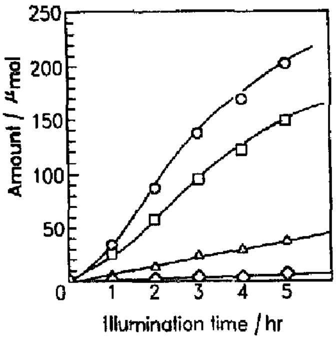

Fig. 1. Dependence of hydrogen formation on the illumination time in the photocatalytic reaction of methanol (4.0 mol dm^{-3}) in various kinds of aqueous suspensions of TiO_2 (80 ml). ○, Cu (6 wt.%)/TiO_2 (0.5 g); □, Cu powder (0.5 g)+TiO_2 (0.5 g); Δ, Cu colloid (1.0×10^{-3} mol dm^{-3}+TiO_2 (0.5 g); ◇, TiO_2 (0.5 g).

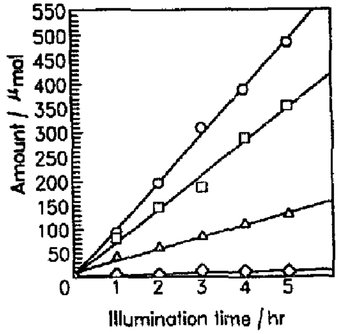

Fig. 2. Dependence of formaldehyde formation on the illumination time in the photocatalytic reaction of methanol (4.0 mol dm^{-3}) in various kinds of aqueous suspensions of TiO_2 (80 ml). ○, Cu (6 wt.%)/TiO_2 (0.5 g); □, Cu powder (0.5 g)+TiO_2 (0.5 g); Δ, Cu colloid (1.0×10^{-3} mol dm^{-3}+TiO_2 (0.5 g); ◇, TiO_2 (0.5 g).

metal powder addition significantly promoted the photocatalytic reaction as metal-loading on the SC particles. Similar results were obtained when silver powder was used instead of copper as shown in Figs. 3 and 4.

Fig. 5 shows the effect of copper content in the TiO_2 suspension on the yields of hydrogen and formaldehyde. The product yields in the presence of various metal powders such as cobalt, nickel, silver and copper are summarised in Table 1 for hydrogen and for formaldehyde. All of these metals except cobalt promotes the photocatalytic oxidation of methanol in the TiO_2 suspension. Copper is the most effective of these metals.

We reported previously that the photocatalytic oxidation of acetic acid on TiO_2 powders suspended in water (Photo-Kolbe Reaction) is significantly enhanced by addition of copper powder [1]. The effects of other metals than copper, such as cobalt, nickel and silver, on the Photo-Kolbe Reaction were examined in this work. The results as well as those of copper are shown in Table 2, indicating that these metals also promote photocatalysis.

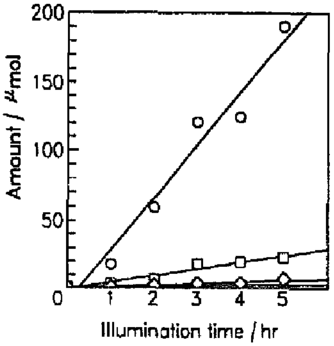

Fig. 3. Dependence of hydrogen formation on the illumination time in the photocatalytic reaction of methanol (4.0 mol dm^{-3}) in various kinds of aqueous suspensions of TiO_2 (80 ml). ○, Ag (6 wt.%)/TiO_2 (0.5 g); □, Ag powder (0.5 g) + TiO_2 (0.5 g); △, Ag colloid (1.0 × 10^{-3} mol dm^{-3} + TiO_2 (0.5 g); ◇, TiO_2 (0.5 g).

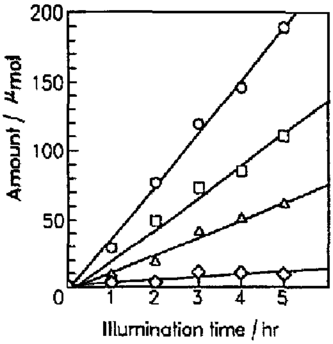

Fig. 4. Dependence of formaldehyde formation on the illumination time in the photocatalytic reaction of methanol (4.0 mol dm^{-3}) in various kinds of aqueous suspensions of TiO_2 (80 ml). ○, Ag (6 wt.%)/TiO_2 (0.5 g); □, Ag powder (0.5 g) + TiO_2 (0.5 g); △, Ag colloid (1.0 × 10^{-3} mol dm^{-3} + TiO_2 (0.5 g); ◇, TiO_2 (0.5 g).

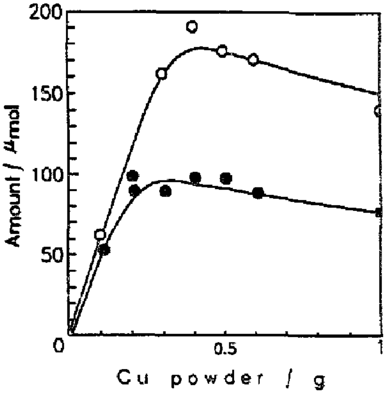

Fig. 5. Effect of copper powder addition on the photocatalytic formations of hydrogen (●) and formaldehyde (○) from an aqueous suspension of TiO_2 (0.5 g/80 ml) containing 4.0 mol dm^{-3} methanol. Illumination time, 3 h.

Table 1
Effect of metal powder addition on the photocatalytic reaction of methanol (4.0 mol dm^{-3}) in an aqueous suspension of TiO_2 (0.5 g/80 ml). Metal powder: 0.5 g/80 ml

Metal	Product yield (μmol h^{-1})	
	H_2	HCHO
None	1	3
Cu	30	60
Ag	5	20
Ni	9	24
Co	tr	3

Table 2
Effect of metal powder addition on the photocatalytic reaction of acetic acid (4.6 mol dm^{-3}) in an aqueous suspension of TiO_2 (0.5 g/80 ml). Metal powder: 0.5 g/80 ml

Metal	Product yields (μmol h^{-1})			
	H_2	CH_4	C_2H_6	CO_2
None	tr	23	20	12
Cu	tr	230	140	128
Ag	tr	23	20	13
Ni	40	23	20	10
Co	80	20	15	8

When iron powder was used as a metal, chemically-catalysed reactions occurred and a lot of hydrogen was generated both from methanol and acetic acid solutions even in the dark. Therefore the results for the iron powder addition were not shown here.

The enhancement of the photocatalytic reactions in TiO_2 suspension by metal powder addition was explained as follows; the oxidation of organic molecules by holes is a rapid process, hence the electrons are left on the SC particles, which transfer to metal particles when the TiO_2 and metal particles collide each other, and consequently the hole–electron separations are enhanced.

Metals can be also reducing agents which are oxidised by holes on the SC particles as suggested previously [2]. The copper(II) ion was detected as a product of the photocatalytic reaction of 4.0 mol dm^{-3} methanol in the TiO_2 suspension (0.5 g/80 ml) with copper (0.5 g/80 ml); however, the yield of Cu(II) ion was found to be 8.0 μmol h^{-1}, which was extremely less than other oxidation products. This fact indicates that the metal particles can react less effectively with the holes on the TiO_2 particles than the organic molecules such as methanol and acetic acid.

The mixed powders of TiO_2 and copper, after being used as catalysts, were examined by X-ray diffraction analysis. No diffraction pattern due to substances other than TiO_2 and copper was observed. Therefore the copper metal oxidation by the holes does not play a significant role in the photocatalytic reactions discussed here. However, when the mixed catalyst was re-used more than three times repeatedly, the X-ray diffraction pattern due to cuprous oxide was detected slightly.

3.2. Photocurrent measurement

Bard and coworkers [3–5] measured the photo-generated electronic charges on the SC particles as a photocurrent by collecting on the inert electrodes (platinum) immersed in the suspension. We attempted here to measure the photocurrent in the illuminated suspensions of TiO_2 with and without metal powders by using a platinum plate as a collecting electrode.

Fig. 6 shows the photocurrent responses measured in various suspensions containing TiO_2 only, TiO_2 and copper, and copper-loaded TiO_2. All of these suspensions contain 0.2 mol dm^{-3} Na_2SO_4 and 0.1 mol dm^{-3} sodium formate. We used sodium formate as a hole scavenger here instead of methanol or acetic acid, because formate ion reacts fast with holes forming carbon dioxide and no other product which might react further. The anodic photocurrents were observed in all of these suspensions.

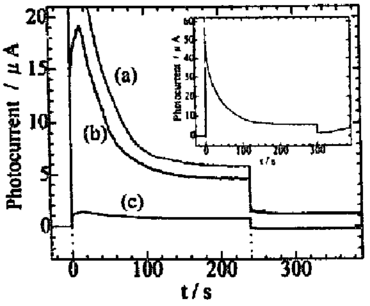

Fig. 6. Photocurrent responses at Pt electrode in 0.2 mol dm^{-3} Na_2SO_4 with 0.1 mol dm^{-3} HCOONa. (a) Cu (6 wt.%)/TiO_2 (0.05 g/60 ml) slurry; (b) Cu (0.05 g) and TiO_2 (0.05 g) in 60 ml slurry; (c) TiO_2 (0.05 g/60 ml) slurry. Inset: total figure of (a).

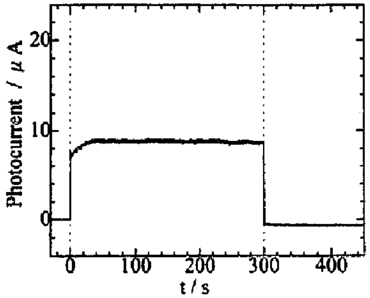

Fig. 7. Photocurrent response at Pt electrode for the slurry (60 ml) of TiO_2 (0.05 g) and silver (0.05 g) containing 0.2 mol dm^{-3} Na_2SO_4 and 0.1 mol dm^{-3} HCOONa.

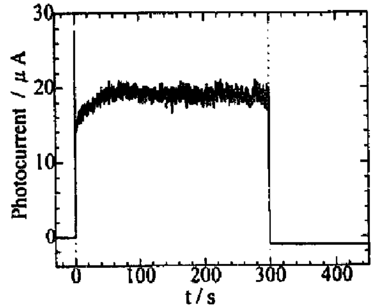

Fig. 8. Photocurrent response at Pt electrode for the slurry (60 ml) of TiO_2 (0.05 g) and nickel (0.05 g) containing 0.2 mol dm^{-3} Na_2SO_4 and 0.1 mol dm^{-3} HCOONa.

These anodic currents are owing to the discharge of the electron-rich SC particles on the collecting electrode since the photo-generated holes on the SC particles are consumed rapidly by reacting with formate ions and the electrons remain on the SC particles. The fact that a higher photocurrent was obtained in the suspension containing both TiO_2 and copper than in the suspension containing only TiO_2 proves that the copper mediated electron transfer from the electron-rich SC particles to the collecting electrode occurs more effectively than the direct electron discharge of the SC particles on the collecting electrode.

The copper mediated electron transfer from the photo-irradiated semiconductor to a metal electrode has been observed also in other ways, as we reported previously [8], in which a n-TiO_2 disk and platinum ring electrodes were used. In this experiment, the RRDE was immersed in the suspension of copper particles containing 0.2 mol dm^{-3} Na_2SO_4, and the n-TiO_2 disk electrode was illuminated under the open-circuit condition with the rotational rate of 2500 rpm, resulting in the anodic current detected on the platinum ring electrode which was kept at the same potential as the rest potential in the dark condition.

Photocurrents measured in TiO_2 suspensions containing metals other than copper are shown in Figs. 7 and 8. Steady anodic photocurrents, instead of the transient time-dependent

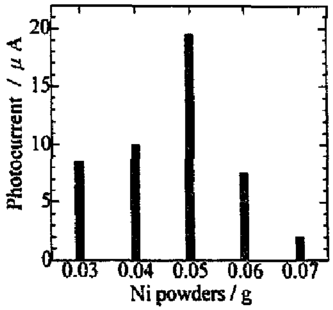

Fig. 9. Effect of the amount of Ni powder added on the photocurrent in the illuminated TiO_2 suspension (60 ml).

current as obtained in the suspension with copper,[1] were observed in suspensions with both silver and nickel. In the case of the suspension with cobalt, however, detecting the photocurrent was prevented by much noisy current, the reason of which is unknown.

The photocurrent increased with increasing amount of the metal in each suspension and attained a maximum, then decreased with further increasing metal, as shown in Fig. 9 for nickel. Similar figures were obtained for the other two metals. The decrease of the photocurrent at higher concentration of the metal might be due to the light shielding by the metal particles. The photocurrents in Figs. 6, 7 and 8 are all those obtained at the concentration of each metal which gave the highest values. These increases of photocurrent by adding a metal into the suspension suggest that these metal particles aided the electron transfer from the photo-irradiated TiO_2 particles to the collecting electrode, consequently assisting the separation of the photo-generated holes and electrons.

Comparing the results of the photocurrent measurement with those of photocatalytic reactivity, there should be some correspondence on the effect of each metal. The results obtained here, however, are not sufficient enough for discussing quantitatively the correlation between the abilities of the photocurrent enhancement and of the photocatalysis promotion for each metal, because the photocurrents measured by the method used here would have been influenced by many factors such as the stirring method of the suspension, which would affect the collision frequencies between particles, and the capacity of keeping electrons of a metal on the surface, which would be related to the hydrogen overvoltage of the metal. Further examinations are needed for clarifying the details about the roles of the added metals in the photo-irradiated TiO_2 suspensions.

4. Summary and conclusion

1. Photocatalytic reactions of methanol and acetic acid in TiO_2 suspensions were promoted by adding some metal powders such as copper, silver, nickel and cobalt into the suspension. Copper was the most effective for the enhancement of these reactions.
2. Photocurrents were measured in the TiO_2 suspensions by using an inert collecting electrode (Pt) and the effects of the metal powder addition on the photocurrents were examined. The anodic photo-current were obtained both in the suspensions with and without the metals. The metals, copper, silver and nickel, enhanced the anodic photocurrent while cobalt did not.

These results are indicative of the rapid electron abstraction by metal from the illuminated SC particles and of the effective separation of photo-generated electrons and holes; consequently resulting in the enhancement of photocatalytic reactions by the addition of metal powders.

Acknowledgements

The authors wish to thank the referees for their helpful suggestions.

References

[1] K. Hirano, T. Nagashima, S. Inoue, U. Asami, R. Takagi, Denki Kagaku 56 (1988) 373.
[2] K. Hirano, K. Inoue, T. Yatsu, J. Photochem. Photobiol. A 64 (1992) 255.
[3] W.W. Dunn, Y. Aikawa, A.J. Bard, J. Am. Chem. Soc. 103 (1981) 3456.
[4] W.W. Dunn, Y. Aikawa, A.J. Bard, J. Electrochem. Soc. 128 (1981) 222.
[5] M.D. Ward, A.J. Bard, J. Phys Chem. 86 (1982) 3599.
[6] M.W. Peterson, J.A. Turner, A.J. Nozik, J. Phys. Chem. 95 (1991) 221.
[7] B. Kraeutler, A.J. Bard, J. Am. Chem. Soc. 100 (1978) 4317.
[8] K. Hirano, K. Funaki, A. Hoshino, Denki Kagaku 61 (1993) 446.

---

[1] The steady photocurrent was also observed in the suspension with copper as well as in those with silver and nickel, when NaCl was used as a supporting electrolyte instead of Na_2SO_4, the reason for which is unknown.