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Journal of Photochemistry and Photobiology A: Chemistry 118 (1998) 41–44

Journal of
Photochemistry
and
Photobiology
A: Chemistry

Photocatalytic oxidation of water on TiO₂-coated WO₃ particles by visible light using Iron(III) ions as electron acceptor

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Received 22 June 1998; accepted 12 August 1998

Abstract

Photocatalytic oxidation of water on TiO₂-coated WO₃ particles was studied using iron(III) ions as the electron acceptor with the aim of constructing a photochemical energy conversion system. Although WO₃ photocatalysts can utilize part of visible light, the reaction was decelerated as the concentration of iron(II) ions in solution increased. This was a marked contrast with the reaction using TiO₂ photocatalysts, whose photocatalytic activity is scarcely affected by iron(II) ions in solution. In order to modify the surface of WO₃ particles, they were coated with a thin TiO₂ layer. Using such photocatalysts, the harmful effect by iron(II) ions on the WO₃ photocatalyst was restrained to some extent, and the efficiency of photooxidation of water by visible light was improved. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tungsten trioxide; Titanium dioxide; Oxygen; Water splitting; Photochemical energy conversion

1. Introduction

Splitting of water by solar light is a goal of chemical conversion and storage of solar energy [1–4]. Some oxides have been reported to be effective to split water into hydrogen and oxygen under UV irradiation [5–7]. However, there are still hurdles to split water by visible light. To overcome the difficulties, we have been studying to combine two photocatalytic reaction systems [8]. One is for oxidation of water [9] and the other is for reduction of water [10].

For the oxidation of water, iron(III) ion was found to be especially efficient as the electron acceptor for TiO₂ photocatalysts, because of its specific adsorption on the surface of TiO₂ [9]. When normal electron acceptors such as halogens are utilized, the reduced forms such as halide ions generated by the photocatalytic reaction are good hole acceptors, leading to the inhibition of oxidation of water. In the case of iron(III) ions, however, their strong affinity to TiO₂ prevents the adsorption of iron(II) ions. This results in the continuation of oxidation of water even in the presence of iron(II) ions in solution [9].

In order to achieve water splitting by visible light, the reactions should be operated by semiconductor photocatalysts with band gaps smaller than that of TiO₂. Among the

photocatalysts, WO₃ powder has been reported to be capable of oxidizing water by visible light in the wavelength region up to 500 nm using iron(III) ions as the electron acceptor [11,12]. However, we found that the reaction decelerates as the concentration of iron(II) increases. In this study, in order to prevent this drawback, we tried to modify the surface properties of WO₃ particles by coating with a thin TiO₂ layer.

2. Experimental

2.1. Materials

WO₃ particles with the purity of 99.99% was obtained from Furu-uchi Chemical. Iron(III) chloride and iron(II) chloride were obtained from Wako Pure Chemical as a guaranteed-grade reagent. Titanium tetraisopropoxide was obtained from Kanto Chemical as guaranteed-grade reagents. All other chemicals used in the experiments were purchased from commercial sources as guaranteed-grade reagents and used without further purification.

2.2. Preparation of TiO₂-coated WO₃ powder

Colloidal solution of TiO₂ was prepared as follows [13]. Methanol solution of titanium tetraisopropoxide (5% by

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volume) prechilled to 0°C was slowly added drop by drop to vigorously stirred hydrochloric aqueous solution (pH 1.5), which was also cooled at 0°C. The solution was continuously stirred for 30 min at this temperature to make TiO₂ colloid. Then, WO₃ powder was added to the solution, and stirred vigorously for 30 min at room temperature. The TiO₂-coated WO₃ powder was obtained by vacuum-evaporating the solvent at 80°C, and heat treated at 600°C in air for 2 h.

2.3. Photocatalytic reaction

In the experiments of photocatalytic reactions, WO₃ powder (100 mg) or TiO₂-coated WO₃ powder (100 mg) was added to aqueous solutions (50 ml) containing iron(III) chloride. Some experiments were carried out in aqueous solutions containing both iron(III) and iron(II) ions. The pH of the solutions was adjusted to 2.4 by adding aqueous solution of sulfuric acid. Photocatalytic reactions were carried out in a Pyrex flask. Oxygen dissolved in the solution was removed by repeating freeze-pump-and-thaw cycles. A 500 W xenon lamp (Wacom, KXL-500F) was used as the light source. The light beam was passed through a L-42 filter (Hoya) to cut-off wavelengths shorter than 420 nm. During the photo-irradiation, the photocatalyst powder was suspended in the solutions with a magnetic stirrer. Oxygen evolved was determined by gas-chromatography and the amount was determined using an oil-manometer. Changes in concentrations of iron(II) ions and iron(III) ions in solution were determined from UV-VIS absorption spectra, which were measured with a Shimadzu UV-2500PC spectrophotometer. Before the spectroscopic measurements, iron(II) ions were colored by complexing with 2,4,6-tris(2-pyridyl)-s-triazine (TPTZ), which was obtained from Dojind Laboratories, in solutions at pH 4.6, and iron(III) ions were colored by complexing with chloride ions in solutions of 6 mM hydrochloric acid.

2.4. Adsorptivity of iron(II) or iron(III) ions on the semiconductor powders

To determine the adsorptivity of iron(II) and iron(III) ions on WO₃ and TiO₂, the WO₃ or TiO₂ powder (500 mg) was added to 6 mM hydrochloric aqueous solutions (10 ml) containing iron(III) chloride or iron(II) chloride at various concentrations. The powder was suspended in the solutions with a magnetic stirrer for 10 min. After the adsorption of iron ions, the changes in the concentrations of iron(II) and iron(III) ions in the solutions were determined from UV-VIS absorption spectra.

3. Results and discussion

When sacrificial electron donors, such as ethanol, were added to the solutions, the photocatalytic reactions on WO₃

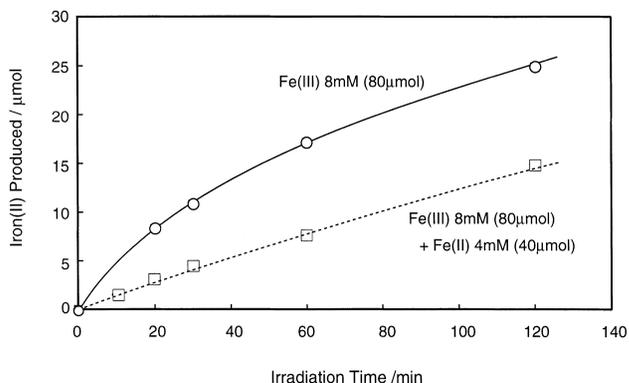


Fig. 1. Photocatalytic reduction of iron(III) ions to iron(II) ions, which takes place with oxidation of water on photoirradiated WO₃ particles. The reactions were carried out under the irradiation of visible light in a solution of 8 mM iron(III) ions (solid line) and in a solution of 8 mM iron(III) ions and 4 mM iron(II) ions (broken line).

powder proceeded at very high rates under illumination of visible light. These reaction rates were high even without addition of electron acceptors to the solution. Under these conditions, however, WO₃ particles changed from pale yellow to green, and gradually lost its photocatalytic activity. Such a change has been well known to be due to the reduction of WO₃ itself by the electrons formed in the particles [14,15]. On the other hand, when iron(III) ions are added to the aqueous solution of ethanol, the change in the WO₃ particles is prevented. In this case, the electrons are efficiently transferred from WO₃ particles to iron(III) ions in solution, and the reaction continues.

Since iron(III) ions are very effective electron acceptors, even water is oxidized in the absence of sacrificial electron donors such as ethanol in solution [11,12]. As the result of the photocatalytic oxidation of water, oxygen and iron(II) ions are obtained as the stoichiometric ratio of 1 : 4 under illumination of visible light. The time course of the production of iron(II) ions in solution is shown in Fig. 1. As is evident in the result, the reaction rate declined as the reaction continued due to the increase of the concentration of iron(II) ions in the solution. The reaction rate was much lowered when the reaction was started in the solution containing iron(II) ions, as shown by a broken line. This is a marked contrast to the case of TiO₂ photocatalyst, whose activity for oxidation of water was scarcely influenced by iron(II) ions in the solution, when an enough amount of iron(III) ions was present [9]. From the measurements of the adsorptivity of iron(II) and iron(III) ions on TiO₂ powder, we found that iron(III) ions are preferentially adsorbed on TiO₂ surface over iron(II) ions [9]. Because of the specific adsorptivity, when both iron(II) and iron(III) ions are present in solution, the surface of TiO₂ is covered solely with iron(III) ions, leading to the inertness of the TiO₂ photocatalyst to iron(II) ions.

The adsorptivity of iron(II) and iron(III) ions on WO₃ is shown in Fig. 2(a) and (b), in which their adsorptivity on TiO₂ is also illustrated. Although the adsorption properties

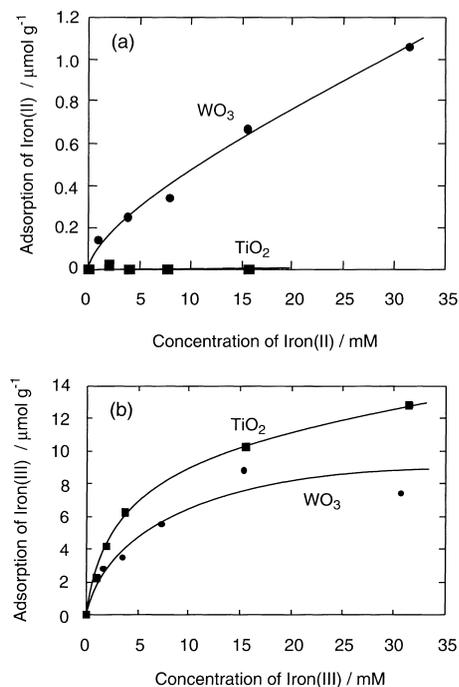


Fig. 2. Adsorptivity of iron(II) and iron(III) ions on WO₃ and TiO₂ particles; (a) for iron(II) ions, (b) for iron(III) ions.

of iron(III) ions on WO₃ are similar to those on TiO₂ (Fig. 2(b)), the adsorption of iron(II) ions on WO₃ is much stronger than that on TiO₂ (Fig. 2(a)). Iron(II) ions generated photocatalytically on WO₃ powder are, therefore, not expected to be completely desorbed from the surface.

The lower selectivity of the adsorption of iron(III) ions on WO₃ particles suggests the difficulty of the construction of a water splitting system using the WO₃ photocatalyst, because iron(II) ions are more easily oxidized than water. Among the electron acceptors applicable to oxidation of water, however, iron(III) ions seem to be one of the best materials, especially when one aims at combining the system with a hydrogen evolution system to attain total water splitting [8]. Hence, we tried to improve the specific adsorptivity of WO₃ particles toward iron(III) ions by coating the surface with a thin TiO₂ layer.

The photocatalytic activity of WO₃ particles loaded with various amounts of TiO₂ was examined for the oxidation of water in the solution of iron(III) ions and in the solution containing both iron(II) and iron(III) ions. In Fig. 3, the amounts of iron(II) ions produced by 30 min photocatalytic reaction on these photocatalysts are summarized. Even in the case of the solution of iron(III) ions, the reaction was affected by the iron(II) ions generated in the course of the photocatalytic reaction. As is evident, the activity of the photocatalyst is improved by loading some amounts of TiO₂ on WO₃. The effect of TiO₂-coating is more drastic for the reactions started with the solutions containing both iron(II) and iron(III) ions than those with the iron(III) solutions. These results suggest that the harmful effect by iron(II) ions

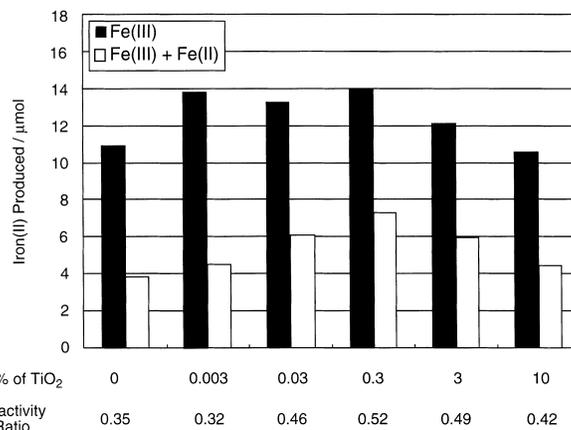


Fig. 3. Amount of iron(II) ions produced concomitantly with oxygen evolution by visible-light irradiation of TiO₂-coated WO₃ particles for 30 min in the solution containing 8 mM iron(III) chloride (black bars), and in the solution containing 8 mM iron(III) chloride and 4 mM iron(II) chloride (white bars). The weight percent of TiO₂ loaded, and the ratio of the reactivity in the solution containing both iron(II) and iron(III) ions to that in the solution containing only iron(III) ions are shown beneath the graph.

on the oxidation of water is lessened by the TiO₂ coating. This effect became most significant by loading about 0.3 wt% TiO₂ on the WO₃ particles.

Judging from the surface area of the WO₃ powder (4.7 m²/g), the average thickness of the TiO₂ layer for the photocatalyst loaded with 0.3 wt% TiO₂ is estimated to be about 0.14 nm. However, it is unlikely that the TiO₂ layer is coated uniformly. The electrons are considered to be transferred from the core WO₃ particle to iron(III) ions on the sites where bare WO₃ surface is exposed and where a thin TiO₂ layer is coated. On the TiO₂ coated surface, the electrons are supposed to be transferred through the TiO₂ layer about or less than 1 nm thick by the tunneling mechanism to the iron(III) ions adsorbed on the TiO₂ layer. The iron(II) ions thus produced are expected to be desorbed from the surface of the TiO₂ layer because of their low affinity to TiO₂. This leads to the prevention of the oxidation of iron(II) ions on the photocatalyst, and to the enhanced reactivity.

When the TiO₂ layer becomes too thick, the tunneling probability of electrons is lowered. Furthermore, the transfer of holes to water molecules is hindered by the thick TiO₂ layer. These negative effect should lead to the lowering of the photocatalytic activity by loading more than 3 wt% TiO₂, as seen in Fig. 3. We expect that higher photocatalytic activity will be attained, if we can regulate the morphology of the TiO₂ layer, namely, coverage and thickness of the TiO₂ layer.

4. Conclusion

We demonstrated that photooxidation of water by visible light on WO₃ particles using iron(III) ions as the electron

acceptor is improved by coating the WO_3 particles with a thin TiO_2 layer. The TiO_2 layer provides the sites which enable preferential adsorption of iron(III) ions over iron(II), leading to oxidation of water even in the presence of iron(II) ions in solution. The results are useful to construct a water splitting system by visible light.

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