



Relay of positive holes from photoirradiated Pt-loaded TiO₂ particles in an aqueous phase to *t*-butylhydroquinone in an oil phase

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Abstract

Evolution of hydrogen and oxidation of iodide ions proceeded concurrently on photoirradiated Pt-loaded TiO₂ particles which were suspended in an aqueous solution containing potassium iodide. By this reaction part of light energy was converted into chemical energy. This reaction, however, stopped at an early stage when the concentration of tri-iodide (I₃⁻) ions reached a certain level because of preferential reduction of I₃⁻ ions over hydrogen evolution on the surface of the photocatalyst. In order to prevent this back process, we placed an oil phase containing *t*-butylhydroquinone on the aqueous phase containing Pt-loaded TiO₂ and iodide ions. In this system, *t*-butylhydroquinone in the oil phase was oxidized by the I₃⁻ ions produced photocatalytically across the water/oil boundary. Such a relay of electron transfer is effective to lessen the back process of the energy storing photochemical reactions. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Conversion of light energy into chemical energy by means of photochemical reactions has evoked great interests in these years [1–4]. The most promising photochemical energy conversion systems have been based on semiconductor photocatalysts [5–13]. Using some oxide semiconductor particles which absorb UV light, it has been reported that even water can be photo-decomposed [11–13]. Despite these efforts, however, efficient decomposition of water by visible light by means of photochemical or photocatalytic reactions has not been realized. This is probably because decomposition of water is largely endothermic. A possible solution of this problem is a combination of two photoreaction systems. This is the key mechanism of the photosynthesis of green plants for forwarding the largely uphill reaction by sunshine. The scheme of the photosynthetic system also suggests that introduction of an oil (or lipid membrane)/water interface is useful to prevent the back reactions.

By taking the mechanisms of photosynthesis as the model, we have constructed a photochemical system for splitting water, in which oxygen-evolving and hydrogen-evolving systems are combined electrochemically [14]. Another possible approach to the combination of the two systems is utilization of an oil phase containing redox species, which is analogous to the lipid membrane of photosynthesis in the functions. As a prototype of such a system, we constructed a system [9], in which photocatalytic reaction on Pt-loaded TiO₂ photocatalyst produces hydrogen and I₃⁻ ions in the aqueous phase. The I₃⁻ ions then oxidize durohydroquinone in the oil phase. In the system, however, there was a serious problem that part of durohydroquinone was dissolved in the aqueous phase and oxidized on the photoirradiated TiO₂ particles.

In this paper we report an improved system using a redox reaction of *t*-butylhydroquinone/*t*-butylquinone dissolved in a mixed organic solvent. This system is effective in relaying a photocatalytic reaction in an aqueous phase to a redox species in an oil phase, opening a way to chemically combine two photocatalytic systems for decomposition of water.

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2. Experimental

2.1. Materials

TiO₂ powder obtained from Kanto Chemicals was used the photocatalyst, unless otherwise noted. Platinum black powder was purchased from N. E. Chemcat. Decane and decanoic acid were commercially obtained from Tokyo Chemical Industry. *t*-Butylhydroquinone, durohydroquinone, and potassium iodide were purchased from Wako Pure Chemicals as guaranteed-grade reagents and used without further purification. *t*-butylquinone was prepared by oxidation of *t*-butylhydroquinone using vanadium pentoxide as the oxidant according to the reported method [15]. The production of *t*-butylquinone was confirmed from the melting point; 331–332 K [16].

2.2. Preparation of Pt-loaded TiO₂ powder

Pt-loaded TiO₂ photocatalyst was prepared by mixing TiO₂ powder (2.0 g) with platinum black powder (0.043 g) in an agate mortar. The Pt-loaded TiO₂ powder was then heated at 923 K for 1 h under aerated conditions to improve the contact between Pt and TiO₂ and to remove organic contaminants [10].

2.3. Photocatalytic reactions

The Pt-loaded TiO₂ powder (100 mg) was added to aqueous solutions (50 ml) containing 2.0 M potassium iodide and 1.1 M sodium sulfate, whose pH was adjusted to pH 2.4 by adding sulfuric acid. *t*-Butylhydroquinone (6.1×10^{-4} M) was dissolved in the oil phase (50 ml) consisting of decane and decanoic acid (5:4 by weight). These solution were degassed separately by the freeze-pump-and-thaw method. Both of the solutions were poured into a Pyrex glass cell to form the water/oil double phases. Photochemical reactions were carried out under an argon atmosphere. The aqueous phase of the cell was stirred with a rotating magnetic bar and externally photoirradiated using a 500 W high-pressure Hg lamp (Wacom R & D Co.). The rotation rate of the magnetic bar was controlled at such a level that the aqueous and oil phases were separated by an interface. During photoirradiation, the oil phase was shielded with an aluminum foil to prevent photoirradiation. The temperature of the solution was kept at 323 K. In some cases, the photocatalytic reactions were carried out in the cell containing only the aqueous phase.

The products in the solutions were quantitatively analyzed by measuring the UV–VIS spectra of the aliquots of the aqueous and oil phases with a Shimadzu UV-2500 PC spectrophotometer. The spectra of the aqueous phase were measured after the photocatalyst was separated by sedimentation. Amounts of hydrogen produced were determined by gas-chromatography (Shimadzu GC14B and JEOL JGL-20K).

3. Results and discussion

Although there have been some reports on the dynamics of oxidation of iodide ions on TiO₂ particles irradiated by pulsed lasers using oxygen as electron acceptor [17,18], there have been few papers on the above reaction studied under continuous irradiation [19]. This is probably because the net reaction stops owing to the back reactions of the products. Importantly, however, when photocatalyst particles were photoirradiated in the cell containing only the aqueous phase (pH 2.4), generation of tri-iodide (I₃⁻) ions and hydrogen gas was confirmed by UV–VIS spectra and gas-chromatography. The reaction rate was decelerated as the concentration of I₃⁻ ions increase, as shown in Fig. 1. Despite this drawback, for the initial period of irradiation, both I₃⁻ ions and hydrogen were generated photocatalytically at a rate of about 5.7×10^{-6} mol h⁻¹ in a solution at pH 2.4. These rates were about three times higher than those observed in neutral and weakly alkaline solutions using the same photocatalyst [10]. Recently, we found that the reaction rate is largely improved with the quantum efficiency of 1.8% using the TiO₂ powder obtained from Catalysis Society of Japan (JRC-TIO-5) and by optimizing the conditions of Pt-loading. The insert in Fig. 1 illustrates the production of I₃⁻ ions and hydrogen on this photocatalyst. These results suggest that this reaction system has a potential to be utilized for energy conversion, if the back reactions are successfully prevented. The following work of this paper was carried out, before we found efficient photocatalyst, using the TiO₂ powder obtained from Kanto Chemicals.

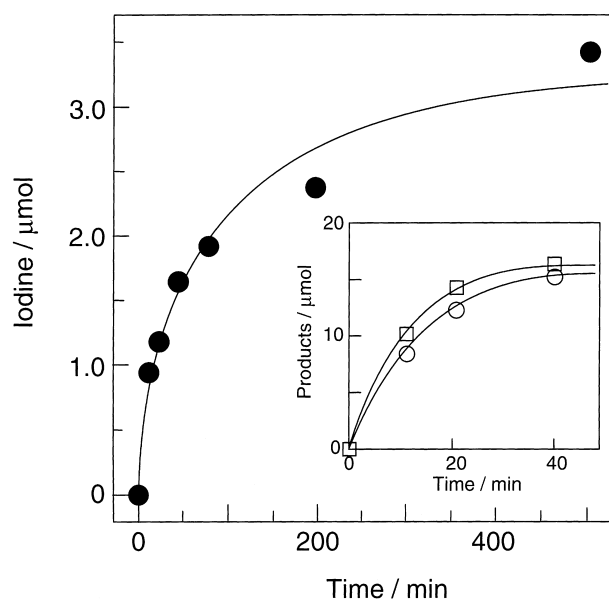


Fig. 1. Generation of I₃⁻ ions by photocatalytic reaction on Pt-loaded TiO₂ particles (Kanto Chemicals, 100 mg) in an aqueous solution (50 ml) of 2.0 M potassium iodide at pH 2.4. Insert shows the improved reaction obtained using different TiO₂ particle (JRC-TIO-5), where generation of hydrogen (□) and I₃⁻ (○) is traced.

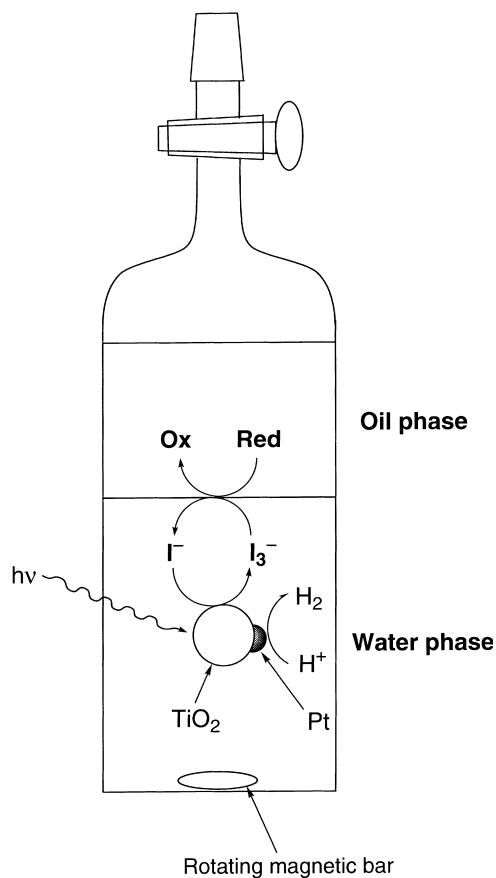


Fig. 2. A schematic of a semiconductor-photocatalyzed reactor having a water/oil boundary.

In order to prevent the back reactions, we have studied the systems having a water/oil boundary [9], as shown in Fig. 2. Our aim is to maintain the concentration of I_3^- ions as low as possible by the redox reactions between the I_3^- ions and redox species added to the oil phase. Although the system looks simple, the requirements of the redox species and solvents are severe. For example, their redox potentials must match with that of I^-/I_3^- , and both components of a redox couple must be soluble in the oil phase and must not be soluble in the aqueous phase. In our previous work, we constructed a system using durohydroquinone as the electron donor and *p*-xylene as the organic solvent [9]. In this system, the scheme illustrated by Fig. 2 was not fully achieved because a small amount of durohydroquinone dissolved in the aqueous phase.

After testing many kinds of hydroquinone derivatives, such as 2-methylhydroquinone, 2,5-di-phenylhydroquinone, and 2-methyl-1,4-dihydroxynaphthalene, and organic solvents, such as tetrahydronaphthalene, 2-octanone, and octanoic acid, we found that the combination of redox couple of *t*-butylhydroquinone/*t*-butylquinone and a mixed solvent of decane and decanoic acid (5:4 by weight) can be a good candidate. Addition of decanoic acid to the solvent was necessary to improve the solubility of *t*-butylhydroqui-

none in the oil phase. It was confirmed from UV absorption spectra that both *t*-butylhydroquinone and *t*-butylquinone are not soluble in the water phase.

The redox potential of *t*-butylquinone/*t*-butylhydroquinone measured in a mixed solvent of acetonitrile and water (9:4 by volume) was determined to be about 0.31 V (vs. Ag/AgCl) from the average of oxidation and reduction peak potentials of cyclic voltammogram. The redox potential suggests that *t*-butylhydroquinone is oxidizable by I^-/I_3^- in the aqueous phase. However, the redox potentials are usually affected by the environments. Hence, the oxidation of *t*-butylhydroquinone in the mixed solvent of decane and decanoic acid by I^-/I_3^- in aqueous phase across the interface was tested by measuring the change in the absorption spectra. As shown in Fig. 3, with the elapse of time, the absorption band due to *t*-butylhydroquinone (290 nm) decreased and a new absorption band peaking at 309 nm appeared, which completely agreed with that of authentic *t*-butylquinone. This results indicates that *t*-butylhydroquinone can be oxidized by I_3^- ions which are generated in the aqueous phase as the result of the photocatalytic reaction on Pt-loaded TiO_2 particles. The reaction rate through the interface of about 7 cm^2 was $2.0 \times 10^{-6}\text{ mol h}^{-1}$, which was lowered as the concentration of I_3^- ions in the aqueous phase decreased.

By photoirradiation of the photocatalyst in the aqueous phase, on which the mixed organic solvent containing *t*-butylhydroquinone ($6.1 \times 10^{-4}\text{ M}$) was placed, hydrogen and I_3^- ions were generated. In the oil phase, as the photoirradiation continued, the absorption due to *t*-butylhydroquinone decreased, and a shoulder at around 320 nm due to the absorption of *t*-butylquinone increased. The solid line in Fig. 4 shows the decrease of *t*-butylhydroquinone in the oil phase during the photoirradiation, which was determined from the spectral changes. Contrary to this case, no decrease of *t*-butylhydroquinone was observed when no iodide ions were added to the aqueous phase, as shown by the broken line, or when no TiO_2 particles were added. These results indicate that the reaction scheme shown in Fig. 2 is realized by the present system, in which the I^-/I_3^- couple mediates the redox reaction between TiO_2 and *t*-butylhydroquinone across the two phases.

The rate of the decrease of *t*-butylhydroquinone in the oil phase under the photoirradiation in the double-phase system was about $8.6 \times 10^{-7}\text{ mol h}^{-1}$. This rate is lower than the initial rate of the generation of I_3^- ions in the aqueous phase, which was $5.7 \times 10^{-6}\text{ mol h}^{-1}$, when measured without the oil phase. The lowered rate for the oxidation of *t*-butylhydroquinone in the double-phase system suggests that the rate was limited by the redox reaction between *t*-butylhydroquinone and I_3^- ions across the water/oil boundary. More precisely, the low concentration of I_3^- ions in the aqueous phase is considered to limit the reaction rate. Although the reaction rate of the present double-phase system is still low, it is important that a possible means to sustain energy storing process is demonstrated.

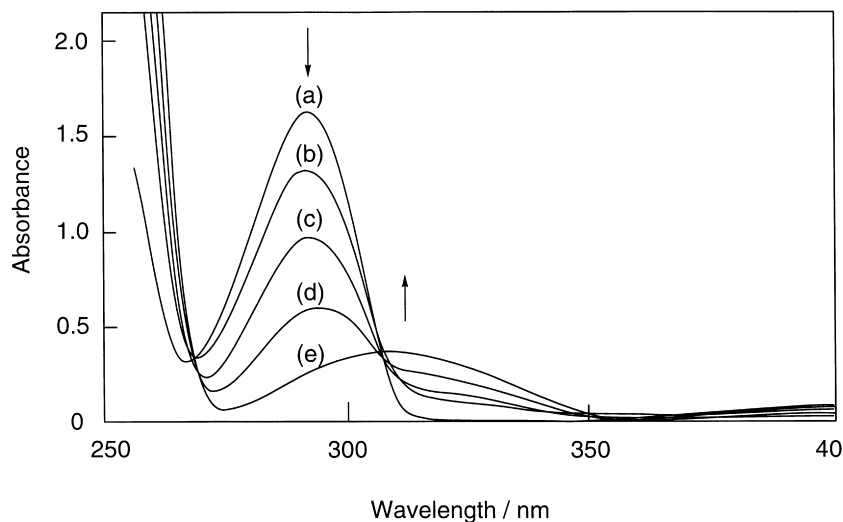


Fig. 3. Changes in the absorption spectra of the oil phase containing *t*-butylhydroquinone by addition of I_3^- ions to the aqueous phase. The oil phase is a mixed solution (50 ml) of decane and decanoic acid (5:4 by weight) containing *t*-butylhydroquinone (6.0×10^{-4} M). The aqueous phase contained iodine (6.0×10^{-4} M), potassium iodide (5.2×10^{-1} M), and sodium sulfate (2.0 M). The absorption spectra were obtained with the passage of time: (a) 0, (b) 140, (c) 190, (d) 335, and (e) 1075 min. The spectra were obtained using the mixed solvent as the reference.

If we take the experimentally determined redox potential of 0.31 V vs. Ag/AgCl is applicable to the double phase system, free energy change of about 128 kJ mol^{-1} is expected by the relay of the reaction demonstrated in this work. For reference, the standard enthalpy change for dehydrogenation of hydroquinone is about $143.5 \text{ kJ mol}^{-1}$ [20]. These values indicate that the present system has some meaning as the energy storing system by itself. Recently, we found that bromide ions are oxidized on photoirradiated

Pt-loaded TiO_2 particles concomitantly with hydrogen evolution from water [14], and that iron(III) ions are reduced to iron(II) ions concomitantly with oxygen evolution from water on photoirradiated TiO_2 [8]. The present system is expected to be applied to the combination of such kinds of hydrogen and oxygen evolution reactions. The combined systems are advantageous to the decomposition of water by visible light because the needed large energy can be divided into two steps.

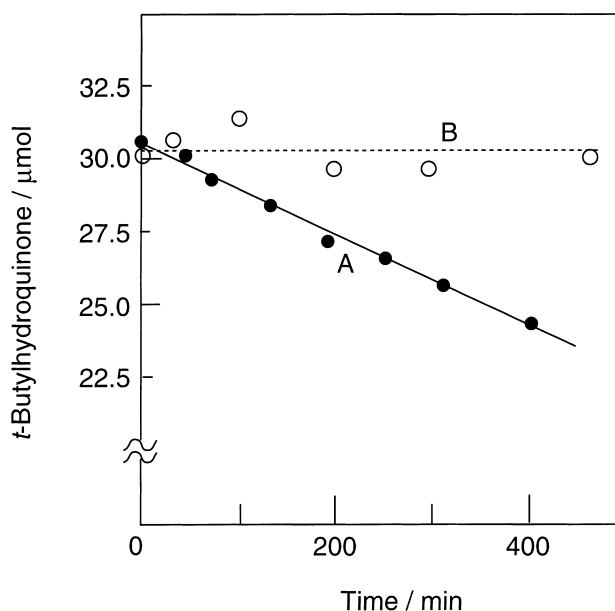


Fig. 4. Change in the concentration of *t*-butylhydroquinone in the oil phase as the result of the semiconductor photocatalyzed reactions in the cell having a water/oil interface. (A) In the presence of iodide ions (2.0 M) in the aqueous phase, (B) in the absence of iodide ions.

4. Conclusion

We have demonstrated a new photocatalytic reaction system in which the concentration of the product in the aqueous phase can be maintained low through a redox reaction with a hydroquinone compound dissolved in the oil phase. This system is beneficial to the prevention of back reactions, which are always the problem of the photochemical systems for storing chemical energy.

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