ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 137 (2000) 63–69

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Steady hydrogen evolution from water on Eosin Y-fixed TiO_2 photocatalyst using a silane-coupling reagent under visible light irradiation

Ryu Abe [b], Koujirou Hara [a], Kazuhiro Sayama [a], Kazunari Domen [b], Hironori Arakawa [a,*]

[a] National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
[b] Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received 23 March 2000; received in revised form 6 July 2000; accepted 3 August 2000

Abstract

A chemical fixation of xanthene dyes on platinized TiO_2 particles via silane-coupling reagent was attempted in order to construct a stable dye-sensitized photocatalyst system in water. The Eosin Y fixed Pt-TiO_2 (E.Y-TiO_2) exhibited steady H_2 production from aqueous triethanolamine solution (TEOA aq.) under visible light irradiation for long time, and the H_2 evolution reproduced even after the exchange of TEOA aq., while the H_2 evolution from the mixture of Eosin Y (E.Y) and Pt-TiO_2 ceased in 10 h. The turnover number of the dye molecule fixed on TiO_2 surface reached more than 10,000, and the quantum yield of the E.Y-TiO_2 at 520 nm was determined to be about 10%. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Eosin Y; Photocatalyst; Silane-coupling reagent; Pt-TiO_2; Water-splitting; Dye-sensitization

---

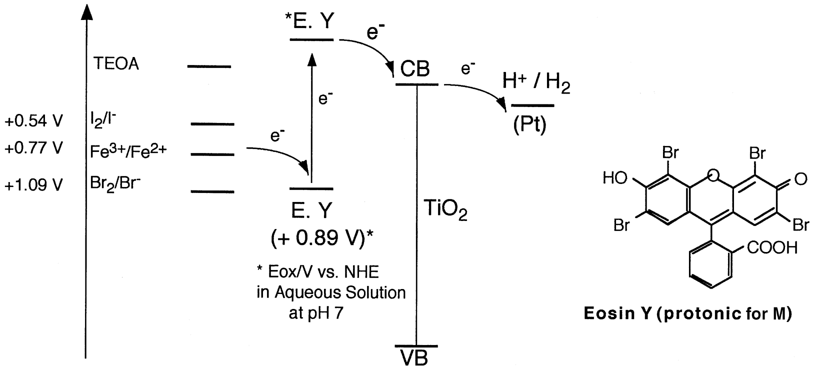
1. Introduction

A great number of attempts on H_2 production from water using semiconductor photocatalyst have been made with a view to constructing solar energy conversion systems to chemical energy. There are many reports about the stoichiometric decomposition of water into H_2 and O_2 under UV irradiation on various semiconductors such as TiO_2 [1–3], Ta_2O_5 [4], $BaTa_2O_6$ [5], $K_4Nb_6O_{17}$ [6] and so on. However, there is no reproducible report about the water splitting by visible light, which occupies the most part of solar light. Some oxide semiconductors that absorb visible light, such as Fe_2O_3 and WO_3, have no potential for H_2 evolution, and sulfide and carbide semiconductors are not stable. In order to achieve efficient water splitting by solar light, it is necessary to develop new photocatalytic systems that effectively work under visible light region. One of the strategies using visible light is dye-sensitization of semiconductor. However, it is difficult to apply the dye-sensitized semiconductors for direct water splitting because of the difficulty in O_2 formation through four-electron process on simple sensitizer. Recently, we suggested new water splitting approach combining two photocatalytic reactions, i.e. water reduction and water oxidation via some redox mediators, in order to divide the large energy required for the water splitting into two steps. For example, we had reported the efficient O_2 evolution on RuO_2-WO_3 photocatalyst under visible light irradiation [7] and the H_2 evolution under UV irradiation in the presence of Fe^{3+}/Fe^{2+} redox couple [8]. In this approach, it is theoretically possible to apply the dye-sensitized photocatalysts to the H_2 production system, as far as the dye has a potential to oxidize the redox mediator as shown in Scheme 1. In this study, we report H_2 production from water on a dye-sensitized photocatalyst consists of a xanthene dye and TiO_2 particles under visible light irradiation. Some workers had reported that the mixture of some xanthene dyes and Pt-TiO_2 in aqueous triethanolamine solution (TEOA aq.) exhibited H_2 production abilities under visible light irradiation, however, the H_2 evolution rate was not stable over long time irradiation [9–11]. In these systems, only the dye molecules directly adsorbed on the TiO_2 surface cause the sensitization, not those in the bulk of the solution [12,13]. Thought the dye having carboxyl groups could be fixed by ester-like linkage on TiO_2 in organic solvent [14], the linkage was not stable in water because of hydrolysis. In order to overcome the unstableness of the dye-sensitized photocatalyst in water, we attempted a strong chemical

---

[*] Corresponding author. Tel.: +81-298-61-4410; fax: +81-298-61-4524
E-mail address: h.arakawa@home.nimc.go.jp (H. Arakawa).

PII: S1010-6030(00)00351-8



Scheme 1. Dye-sensitized photocatalyst for H_2 evolution system in two-steps water splitting.

fixation of dye on TiO_2 particles, by utilizing dehydration of carboxyl group of xanthene dyes with amino group of silane-coupling reagent fixed on TiO_2 surface.

2. Experimental

2.1. Materials

The xanthene dyes (E.Y free acid, Merbromine, 2′,7′-dichlorofluorecein, Rhodamine B and Rhodamine 6G) were purchased from Aldrich, and used without further modification. Four TiO_2 samples were used for the chemical fixation of E.Y: TiO_2-P-25 (55 $m^2\,g^{-1}$, Aerosil); TiO_2-ST-01 (Anatase, 320 $m^2\,g^{-1}$, Ishihara Co. Ltd.); TiO_2-TTO-55N (Rutile, 40 $m^2\,g^{-1}$, Ishihara Co. Ltd.) and TiO_2-IT-PA (Amorphous, 220 $m^2\,g^{-1}$, Idemitsu Co. Ltd.). The silane-coupling of TiO_2 was carried out as follows. Silane-coupling reagent (γ-aminopropyltriethoxysilane, Shin-Etsu Co. Ltd.) was stirred in EtOH aqueous solution (EtOH 95 ml + H_2O 5 ml) for 1 h at room temperature. The quantity of silane-coupling reagent was theoretically calculated to form monolayer on the TiO_2 surface for the respective surface area of TiO_2 particles. After the stirring, TiO_2 particle (3 g) was added into the solution and stirred for 1 h. Then, the TiO_2 powder was filtered and dehydrated by heating at 383 K for 15 min. Synthesis of amide-linked E.Y by the dehydrate coupling of a carboxyl group of E.Y with propylamine modified TiO_2 particle was carried out using dicyclohexylcarbodiimide (DCC) as a dehydrating reagent. The propylamine modified TiO_2 (2 g), E.Y (0.05 g) and DCC (0.1 g) were added into 100 ml of THF, and refluxed at 353 K for 6 h. After filtration and air-drying, the sample was stirred twice in EtOH aq. (pH = 12, adjusted by NaOH aq.) for 24 h and twice in distilled water for 12 h to remove excess dyes which physically adsorbed or attached with ester bond on the TiO_2 surface. The TiO_2 particles treated with silane-coupling reagent and E.Y is referred to as Eosin Y-TiO_2 hereafter. The desorption of E.Y from TiO_2 surface occurred in highly basic solution, and this was used to determine the amount of dye molecules fixed on the TiO_2 surface. Stirring Eosin Y-TiO_2 (0.1 g) in a NaOH aq. (1.0 mol dm^{-3}) for 24 h resulted in complete desorption of the dye.

2.2. Photocatalytic reaction

Photocatalytic reactions were performed using a closed gas-circulation system. In the case of physically mixed system of dye and Pt-TiO_2, 50 μmol of each xanthene dyes and 0.3 g of Pt-TiO_2 (P25, Pt 0.1 wt.%) were stirred in 250 ml of TEOA aq. (pH = 7 adjusted by HCl aq.) in Pyrex grass cell, and deaerated completely by pumping away of gas phase time after time, and argon gas (35 Torr) was introduced into the system. Then, the solution was irradiated from outside of the cell by a 300 W Xe lamp with 460 nm cut off filter. In the case of the preparation of Pt-loaded Eosin Y-TiO_2, 0.3 g of catalyst was stirred in 250 ml of TEOA aq. (pH = 7) in which 0.1–0.5 wt.% of H_2PtCl_6 was added for photo deposition, and irradiated by the Xe lamp with 460 nm cut off filter. The evolution of H_2 was analyzed by on-line gas chromatography (TCD, molecular sieve 5 Å). Quantum yields of Pt-loaded Eosin Y-TiO_2 were determined with 520 nm light obtained through a band-pass filter from 300 W Xe lamp. The light intensity was measured with a thermopile power meter (SCIENTECH, 382UV5).

3. Results and discussion

3.1. Hydrogen evolution on physically mixed system of several xanthene dyes and Pt-TiO_2

Fig. 1 shows photo productions of H_2 on several xanthene dyes mixed with Pt-TiO_2 (TiO_2 P25, Pt 0.1 wt.%) in TEOA aq. All these dyes exhibited higher activities for H_2 evolution than the well-known sensitizer $Ru(bpy)_3^{2+}$ in this experimental condition. As seen in Fig. 1, the H_2 yields strongly depended on the structure of the dye used. The Rhodamine group dyes (Rhodamine B and Rhodamine 6G) exhibited steady H_2 evolution rates, however, they

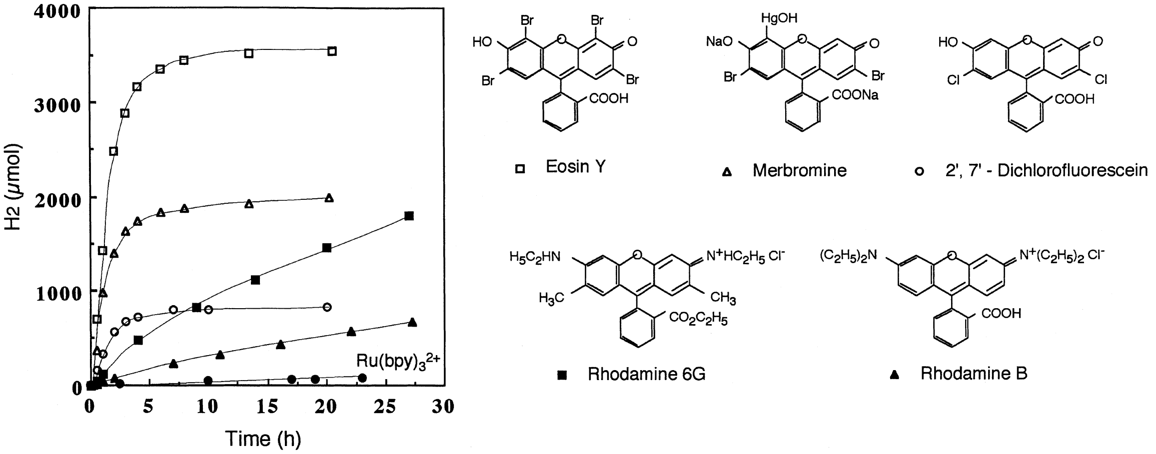


Fig. 1. H_2 evolution from TEOA aq. on physically mixed system of several xanthene dyes (50 μmol) and Pt-TiO_2 (TiO_2-P25, Pt 0.1 wt.%) under visible light irradiation (≥460 nm).

were relatively low compared with the initial rates of E.Y group dyes (E.Y, Merbromine, 2′,7′-dichlorofluorecein). In the case of the E.Y group dyes, high H_2 evolution rates were observed in initial period, but leveled off after 4–5 h of irradiation and finally stopped. In the E.Y group dyes, it was observed that the original color of the dye in the solution gradually decreased after 4–5 h of irradiation. As shown in Fig. 2, the UV–VIS spectra of the E.Y in TEOA aq. remarkably changed after the 20 h of photo irradiation with Pt-TiO_2, in which the main adsorption band of original E.Y around 500 nm decreased. This phenomenon was also observed for Merbromine and 2′,7′-dichlorofluorecein, but not for the Rhodamine group. In the case of the Rhodamine group, the UV–VIS spectra did not change even after the 27 h of reaction as shown in Fig. 3, while the absorption bands slightly decreased because of the adsorption of dye to the TiO_2 surface. These results indicate that the disappearance of the absorption bands around 500 nm, so-called photo bleaching, is mainly responsible for the inactivation of E.Y group dyes under visible light irradiation. The photo bleaching of E.Y proceeded rapidly when E.Y was irradiated in TEOA aq. without Pt-TiO_2. As shown in Fig. 4, the absorption bands around 500 nm decreased by the 25 min of irradiation. It was observed that the disappeared absorption of E.Y around 500 nm gradually recovered by exposed to air after the short time irradiation (5 min, same condition as in Fig. 4), indicating the presence of reduced species in the solution. However, the absorption did not recover when E.Y was irradiated in TEOA aq. for long time. Therefore, it is considered that some stable species of E.Y formed by long time irradiation, which have no adsorption in visible region. In the case of physically mixed system

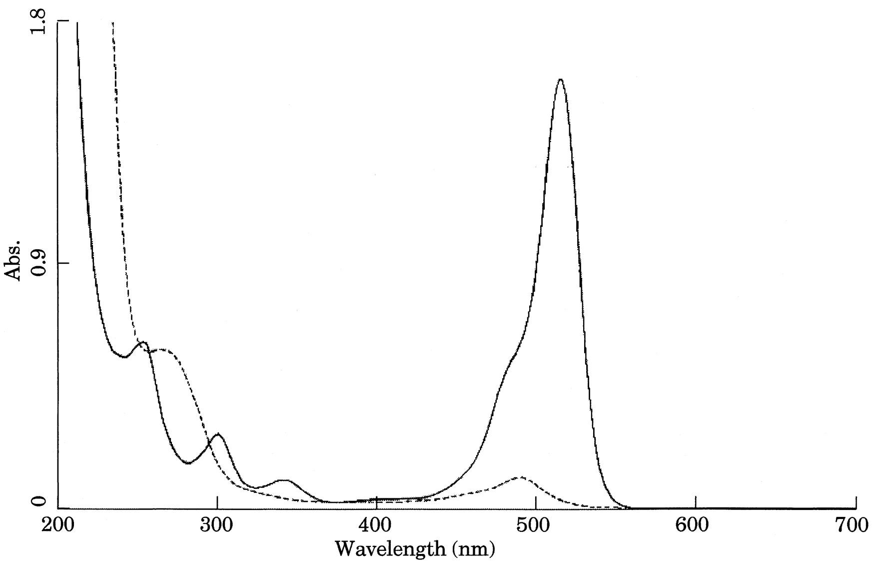


Fig. 2. UV–VIS spectra of E.Y in TEOA aq. before (—) and after (- - -) the photo reaction of Fig. 1.

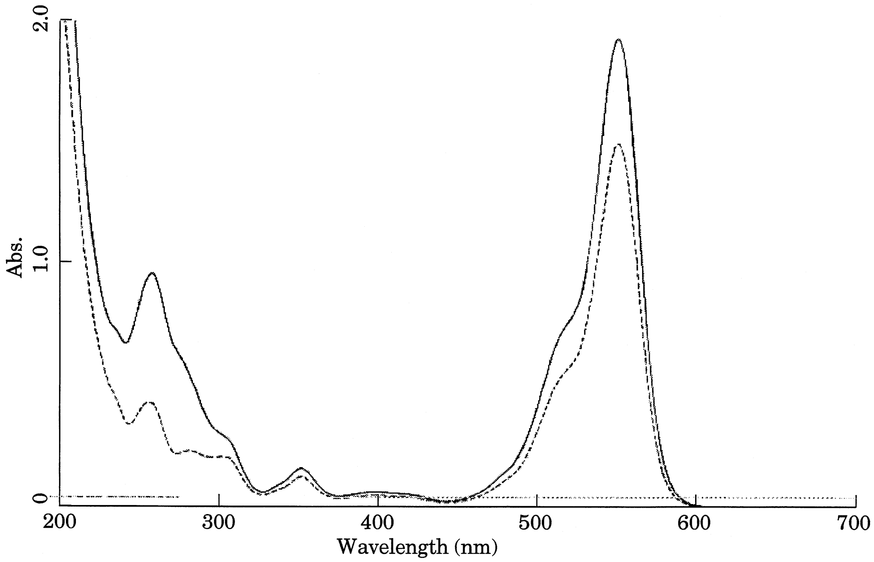


Fig. 3. UV–VIS spectra of Rhodamine B in TEOA aq. before (—) and after (- - -) the photo reaction of Fig. 1.

of dyes and Pt-TiO$_2$ in TEOA aq., only the exited dye molecules adsorbed at the semiconductor–solution interface will contribute to the H$_2$ evolution and will revert to ground state by injecting an electron into the semiconductor and accepting an electron from TEOA as indicated in Scheme 2(I). On the other hands, the exited dye molecules free in the solution will change to its reduced species by accepting electron from TEOA as shown in Scheme 2(II), because following electron injection into Pt-TiO$_2$ could not take place. As indicated by Tokumaru et al., xanthene dyes such as E.Y give one-electron reduced trianion radical species on cathodic reduction as shown in Scheme 2(b) [15]. It is likely that the hydrogenated species of E.Y, as shown in Scheme 2(c), for example, were formed by disproportionation between the two reduced species, similarly to the thionine and leuco-thionine case in photo galvanic cell [16]. In the hydrogenated species of the dye, the π-electron-conjugated system disappears at its central six-membered ring. The disappearance of the conjugated system will cause the fade of absorption spectra in visible region, and consequently cause the inactivation of dye under visible light irradiation. We concluded that the cessation of H$_2$ evolution on E.Y group dyes was mainly caused by the formation of highly reduced and hydrogenated species of dyes in TEOA aq. The absorption peak shift from 520 to 490 nm was observed by irradiation without Pt-TiO$_2$,

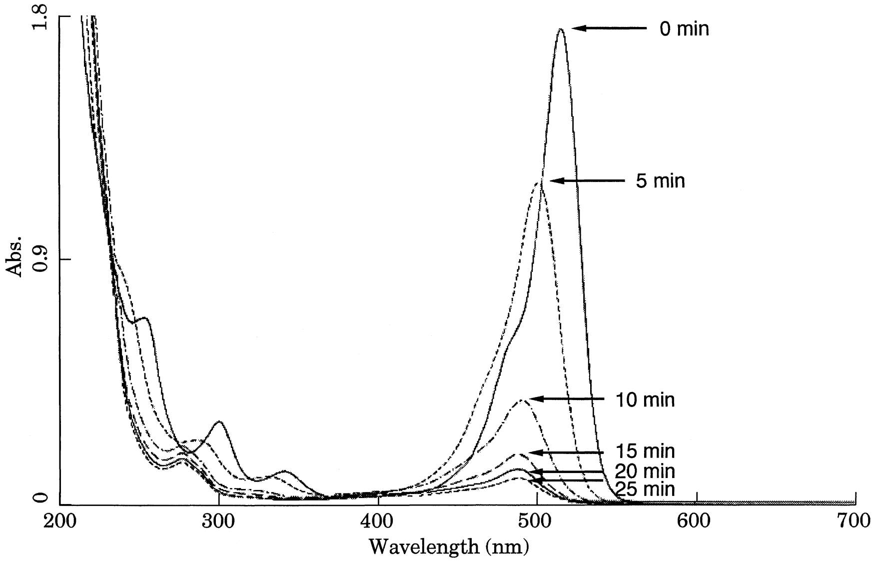
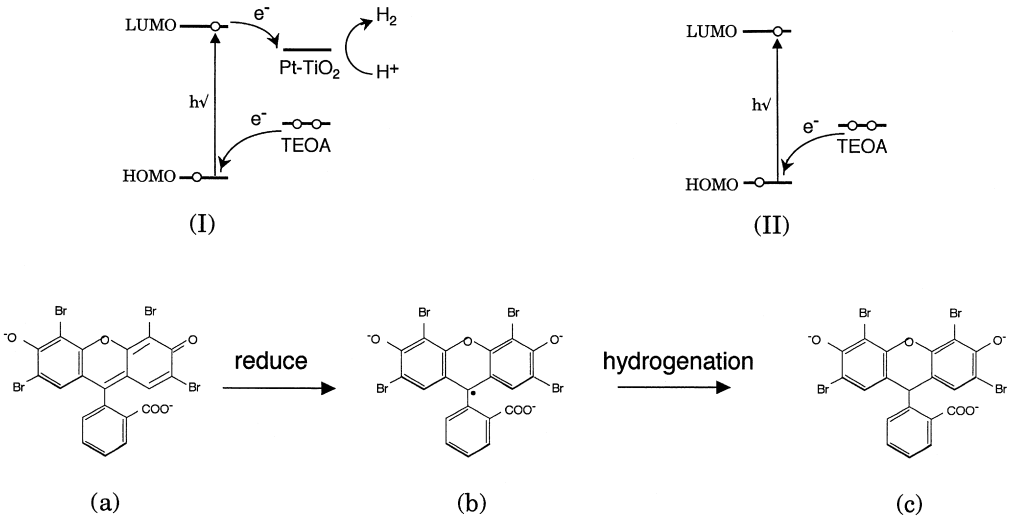


Fig. 4. UV–VIS spectra change of E.Y in TEOA aq. irradiated in the absence of Pt-TiO$_2$.



Scheme 2. Expected photoelectron transfer on dye molecules at the solution–semiconductor interface (I) and on dye molecules free in solution. Structure of Eosin Y (a) and one-electron reduced species (b). An expected structure of Eosin Y formed by further reduction or disproportionation (c).

as shown in Fig. 4. The shifted absorption spectrum was very similar to that of fluorecein, moreover, the solution after 5 min irradiation had a strong luminescence. Therefore, it is speculated that some bromides of E.Y were removed and fluorecein-like species might be formed as indicated by Imamura et al. [17]. For the achievement of steady H_2 evolution, a fixation of dye would be necessary to make the dyes always contacted with TiO_2 surface.

3.2. Chemical fixation of E.Y on TiO_2 surface with silane-coupling reagent and H_2 evolution on E.Y-TiO_2

Fujihira and co-workers had reported a photo electrochemical cell consisted of Rhodamine B and TiO_2 electrode, in which the dye was chemically fixed via amide bonding on semiconductor surfaces using silane-coupling reagent [18]. This fixation method via amide bonding would be suited for dye-sensitized photocatalyst used in aqueous solutions, because it is more resistant to hydrolysis in water than ester. Therefore, we attempted the fixation of E.Y on several TiO_2 particles using silane-coupling reagent. Fig. 5 shows the absorption spectra of the each E.Y fixed TiO_2 particles with silane-coupling reagent (E.Y-TiO_2) after the wash treatment with NaOH mixture solution of water and ethanol. The absorbancies of the respective E.Y-TiO_2 around 500 nm were approximately proportional to the respective surface areas of TiO_2 particles. When E.Y was fixed on TiO_2 particles without silane-coupling reagent by refluxing in THF, the

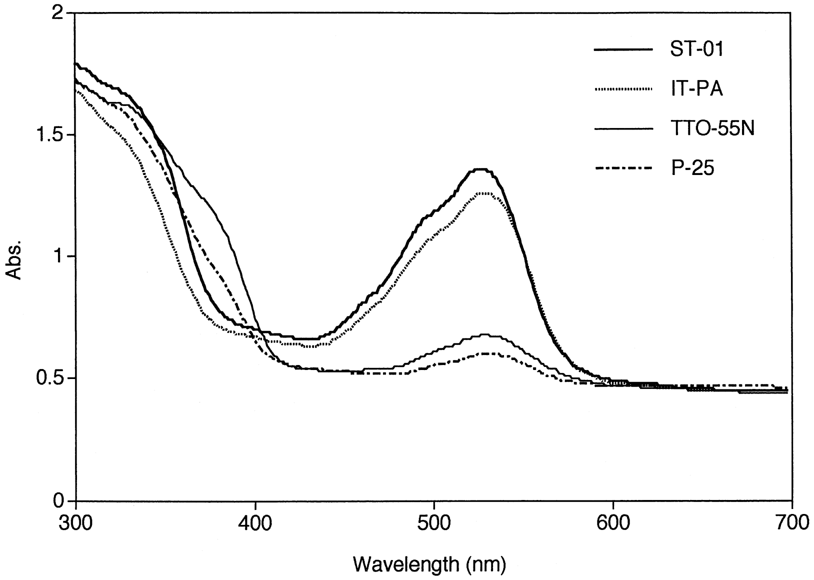


Fig. 5. UV–VIS spectra of the Eosin Y fixed TiO_2 particles.

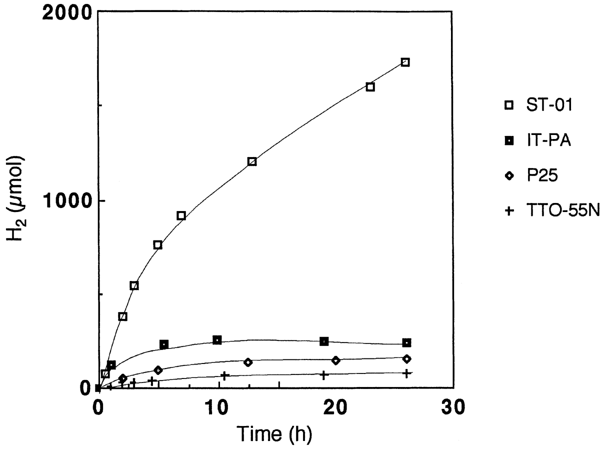


Fig. 6. H_2 evolution from TEOA aq. on the Eosin Y fixed TiO_2 particles under visible light irradiation (≥460 nm). H_2PtCl_6 aq. (0.1 wt.%) was added into TEOA aq. before reaction.

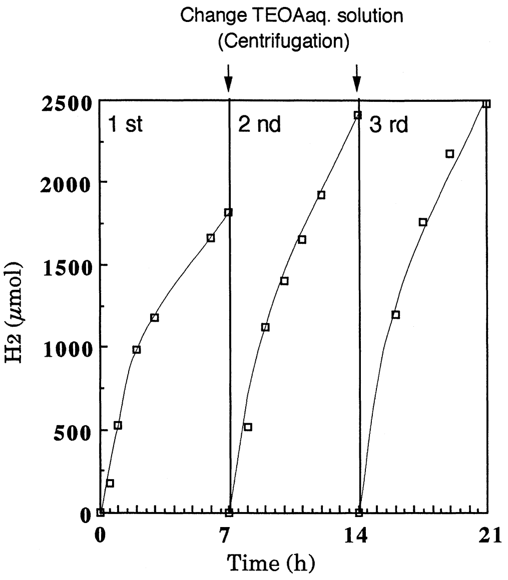


Fig. 7. H_2 evolution from TEOA aq. on the Eosin Y fixed TiO_2-ST-01 under visible light irradiation (≥460 nm). H_2PtCl_6 aq. (0.5 wt.%) was added into TEOA aq. before first run. The catalyst was collected by centrifugation after 7 h of irradiation, added into new TEOA aq. and irradiated.

adsorbed dye was completely removed by the wash treatment. These results indicate that the fixation of dye via silane-coupling reagent was more stable than that via ester linkage. Photo productions of H_2 on the E.Y-TiO_2 are shown in Fig. 6. Except for the E.Y-TiO_2-IT-PA, they all exhibited steady H_2 evolution even after 20 h of irradiation, thought some decreases of H_2 evolution rates were observed in initial 10 h. In the case of E.Y-TiO_2-IT-PA, the H_2 evolution stopped after 10 h, and the red color of E.Y completely disappeared after the reaction in a similar manner as the physically mixed system. The cessation of H_2 evolution may be caused by ineffective electron transfer for H_2 evolution because of the low conductivity of the amorphous TiO_2-IT-PA. Among the E.Y-TiO_2, E.Y-TiO_2-ST-01 showed the highest activity for H_2 production under visible light, and the color of E.Y retained even after 26 h of irradiation. Furthermore, the H_2 evolution on E.Y-TiO_2-ST-01 reproduced even after the exchange of TEOA aq. as shown in Fig. 7. The desorption of E.Y to the solution was not observed. The reproducibility would indicate that the H_2 evolution was not derived from dyes free in solution, but from the dyes fixed on TiO_2 surface. The turn-over number of the E.Y molecules fixed was calculated to be about 10,000 from the amount of dye fixed (ca. 1.5 μmol/0.3 g) and the total amount of H_2 evolved (ca. 7000 μmol). Good reproducibility of H_2 evolution was observed at least within fifth runs. The quantum yield of E.Y-TiO_2-ST-01 at 520 nm was determined to be about 10% in the same condition as Fig. 7. Steady H_2 evolution was achieved by the dye fixation, however, the initial H_2 evolution rate was low compared with that of the physically mixed system of E.Y and Pt-TiO_2 (Fig. 1). There are three reasons for the lower activity in the dye fixed system. First, amount of dye molecules on the Pt-TiO_2 was small, therefore, the light harvest efficiency was low. Second, the inhabitation of electron transfer from the exited dye to TiO_2 by silane-coupling reagent. Third, the difference in H_2 production mechanism between the physically mixed system and the dye-fixed system. In the case of physically mixed system of xanthene dyes and Pt-TiO_2, the H_2 production is caused by the direct electron transfer from the reduced dye to Pt metal as well as the electron transfer through the TiO_2 conduction band. For example, H_2 evolution proceed in the presence of xanthene dye, TEOA and colloidal Pt, because of the high reducing power and long-lived nature of the semi-reduced xanthene dye [9]. On the other hands, in the dye-fixed system, the electron transfer mainly takes place through the TiO_2conduction band. Though the dye-fixed system has the disadvantage that initial hydrogen generation is lower than the physically mixed system by the above-mentioned reasons, it possesses several advantages such as stability and less influence of pH. The further researches are now under investigation.

Acknowledgements

The authors are sincerely grateful to Professor Emeritus K. Tokumaru at University of Tsukuba for his useful suggestions.

References

[1] S. Sato, J.M. White, Chem. Phys. Lett. 72 (1980) 83.
[2] K. Sayama, H. Arakawa, J. Chem. Soc., Faraday Trans. 93 (1997) 1647.
[3] T. Tabata, N. Nishida, Y. Masaki, K. Tabata, Catal. Lett. 34 (1995) 245.
[4] K. Sayama, H. Arakawa, J. Photochem. Photobiol. A 77 (1994) 243.
[5] H. Kato, A. Kudo, Chem. Phys. Lett. 295 (1998) 487.

[6] A. Kudo, A. Tanaka, K. Domen, K. Maruya, K. Aika, T. Onishi, J. Catal. 111 (1988) 67.
[7] K. Sayama, R. Yoshida, H. Kusama, K. Okabe, Y. Abe, H. Arakawa, Chem. Phys. Lett. 277 (1997) p387.
[8] G.R. Bamwenda, K. Sayama, H. Arakawa, J. Photochem. Photobiol. A: Chem. 122 (1999) 175.
[9] K. Hashimoto, T. Kawai, T. Sakata, Chem. Lett. (1983) 709.
[10] H. Misawa, H. Sakuragi, Y. Usui, K. Tokumaru, Chem. Lett. (1983) 1021.
[11] T. Shimidzu, T. Iyoda, Y. Koide, J. Am. Chem. Soc. 107 (1985) 35.
[12] H. Gerischer, J. Photochem. Photobiol. 16 (1972) 243.
[13] R. Memming, J. Photochem. Photobiol. 16 (1972) 325.
[14] K. Murakoshi, G. Kano, Y. Wada, S. Yanagida, H. Miyazaki, M. Matsumoto, S. Murasawa, J. Electroanal. Chem. 396 (1995) 27.
[15] Y. Nishimura, H. Sakuragi, K. Tokumaru, Denki Kagaku 2 (1994) 183.
[16] E. Rabinowitch, J. Chem. Phys. 8 (1940) 551.
[17] K. Kimura, T. Miwa, M. Imamura, Bull. Chem. Soc. Jpn. 43 (1970) 1329.
[18] T. Osa, M. Fujihira, Nature 264 (1976) 349.