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Sensitization of TiO_2 particles by dyes to achieve H_2 evolution by visible light

Kazuhiro Hirano, Eiji Suzuki, Akio Ishikawa, Takashi Moroi,
Hidenobu Shiroishi, Masao Kaneko*

Faculty of Science, Ibaraki University, 2-1-1 Bunkyo, Mito, Ibaraki, 310-8512 Japan

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Abstract

Sensitization of titanium dioxide particles platinized and suspended in water was carried out by $Ru(bpy)_3{}^{2+}$, tris(bipirimidine)Ru(II) ($Ru(bpym)_3$) and porphines to induce dihydrogen evolution by visible light in the presence of sacrificial electron donor, EDTA. It was found that $Ru(bpym)_3{}^{2+}$ is an efficient sensitizer for H_2 formation. High concentration of the $Ru(bpy)_3{}^{2+}$ was required to achieve the photosensitization suggesting adsorption of the sensitizer on the TiO_2. Photochemical deposition of platinum from $K_2[PtCl_4]$ was important to prepare active Pt-loaded TiO_2 photocatalyst. Simple mixing of the TiO_2 and Pt powders in a mortar as usually done for preparing conventional photocatalyst was not effective for the present system showing that electronic channeling between the TiO_2 bulk and the Pt is more important than for usual photocatalysts. The H_2 evolution showed an optimum point at pH 7, which was interpreted by the adsorption of the dye on TiO_2. For the tetrakis(4-carboxyphenyl)porphine and tetrakis(4-sulfonicphenyl)porphine sensitizers, only the absorption of light at Q band was effective. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Sensitization; TiO_2; $Ru(bpy)_3{}^{2+}$; EDTA; Photoreaction

1. Introduction

Photocatalysis by titanium dioxide (TiO_2) has been investigated intensively since the first report by Fujishima and Honda [1] on UV light induced water cleavage using TiO_2 photoanode. Many works on TiO_2 photocatalysis concern its particle suspension system. Although UV light cleavage of water by suspended TiO_2 particles was claimed by some groups [2,3], the reproducibility of the system to evolve quantitative H_2 and O_2 is still a problem. The TiO_2 particles photocatalyst is applied for removal of environmentally hazardous substances by Fujishima and coworkers [4] achieving commercialization. Sensitization of the TiO_2 particles for utilizing visible light has been an important subject both in photochemical energy conversion and decomposition of hazardous substances. Adsorption of tris(2,2′-bipyridine-4,4′-dicarboxylic acid)ruthenium(II) ($Ru(dcbpy)_3$) sensitizer on platinized TiO_2 particles (Pt/TiO_2) led to H_2 evolution by visible light with sacrificial donor [5], but the $Ru(bpy)_3{}^{2+}$ complex with no substituent on the bpy ring was not effective. Later, $Ru(bpy)_3{}^{2+}$ has been reported to be effective for H_2 evolution in the presence of a donor molecule [6,7]. Sensitization of Pt/TiO_2 has been achieved also by coating the semiconductor particles with polymer-pendant $Ru(bpy)_3{}^{2+}$ complex to evolve H_2 by visible light in the presence of sacrificial donor (EDTA) [8]. Deposition of zinc porphyrin on Pt/TiO_2 was also used for H_2 formation in the presence of donor [9]. In these sensitization reactions, it was important that the sensitizing dye molecule is adsorbed on the TiO_2 particles.

Sensitization of TiO_2 has also been achieved for its photoanode. Polycrystalline TiO_2 photoanode (anatase) was successfully sensitized by $Ru(dcbpy)_3{}^{2+}$ to give sensitized high photocurrent [10,11], but $Ru(bpy)_3{}^{2+}$ was not effective [10]. Single crystalline and polycrystalline TiO_2 were sensitized by modifying with Nafion coating incorporating $Ru(bpy)_3{}^{2+}$ [12]. Sensitization of a nanoparticle film of TiO_2 by adsorbing polypyridine Ru complex reported by O'Regan and Grätzel [13], which led to a solar cell with nearly 10% light-to-electricity conversion efficiency, evoked great interest in the sensitization of large band-gap semiconductors [13]. Also in the sensitization of TiO_2 photoanode, adsorption of a dye to the semiconductor is an important condition to achieve the sensitization. Although some achievements have been reported about sensitization

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* Corresponding author. Tel.: +81-29-2516967; fax: +81-29-2288374.
E-mail address: kanekom@mito.ipc.ibaraki.ac.jp (M. Kaneko).

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of large band-gap semiconductors, the details are still open for investigation. Moreover, this is an important subject for future solar energy conversion, and hence warrants further investigation.

The present authors have carried out sensitization of Pt-loaded TiO_2 powder suspension simply by dissolving in an aqueous phase high concentration of a conventional $Ru(bpy)_3^{2+}$, $Ru(bpym)_3$, or water-soluble porphyrines to achieve visible light H_2 evolution in the presence of a sacrificial electron donor, and found that some water-soluble sensitizers are more efficient for H_2 production than the known $Ru(bpy)_3$ derivatives; the sensitization behavior is reported here.

2. Experimental

2.1. Materials

TiO_2 particles used are P-25 donated by the Nippon Aerosil, and TiO-5 standard sample from the Catalysis Society of Japan. $Ru(bpy)_3^{2+}$ was prepared and purified according to the procedure reported elsewhere [14]. Tetrakis-(4-carboxyphenyl)porphine (TPPC) was purchased from Porphyrin Products, tetrakis(4-sulfonicphenyl)porphine (TPPS) acid from Tokyo Kasei Kogyo, and tetrakis(4-pyridylphenyl)porphine (TPPPy) from Aldrich. H_2PtCl_6, ethylenediaminetetraacetic acid disodium salt (EDTA), PtO_2, RuO_2, Pt-black and other chemicals are of commercially available purest grade.

Pt-loaded TiO_2 particles were prepared by photodeposition of Pt from a H_2PtCl_6 aqueous solution in the presence of methanol as electron donor. TiO_2 particles (1 g) were suspended in 200 ml water containing H_2PtCl_6 (8 mg) and 2 vol.% methanol followed by irradiation with a 100 W high pressure mercury lamp (Sen Light, HLR100T-1) under air for 8 h to obtain TiO_2 with 0.3 wt.% loaded Pt (abbreviated to P-25/Pt and TiO-5/Pt). The Pt-loaded TiO_2 was washed with a large excess of water. Pt-loaded TiO_2 was also prepared by simply mixing TiO_2 and Pt-black (or RuO_2) in a mortar.

2.2. Photoreaction

Photocatalytic reaction was carried out in water containing Pt-loaded TiO_2 suspension, dissolved sensitizer and EDTA under argon with magnetic stirring. TiO_2/Pt for which Pt was deposited photochemically was suspended in water and treated under ultrasonication before use. A 500 W xenon lamp was used as a light source with UV cutoff filter (L-42, Toshiba Glass). Two sets of the filter were used to assure cutoff of the UV light. After the reaction, the gaseous products were analyzed by a gas chromatograph (Shimadzu, GCPT-4P) with a molecular sieve 5A column and argon carrier gas.

Table 1
Results of hydrogen production from water by visible light using platinized TiO_2 suspension system[a]

$Ru(bpy)_3^{2+}$ concentration (mM)	TiO_2 (P-25)/Pt (g)[b]	Filter	H_2 evolution (μl)
0.1	0.05	L-42	687.7
–	0.05	L-42	32.8
0.1	–	L-42	2.7
–	0.05	–	2696.4
0.1	–[c]	L-42	0.0

[a] Light source: 500 W Xe lamp (2 h); pure water: 3 ml; electron donor: EDTA 0.01 M.

[b] Platinum was loaded at 0.3 wt.% per TiO_2.

[c] Platinum black 0.77 μmol (the amount of the Pt equals that of Pt on TiO_2) TiO_2/Pt: platinum was loaded on the TiO_2 powder using the photochemical deposition method.

3. Results and discussion

Typical data of the photocatalytic reaction using TiO_2 with photodeposited Pt are summarized in Table 1. The H_2 produced in the presence of $Ru(bpy)_3^{2+}$ far exceeds the H_2 without the sensitizer showing that the Ru complex works as a sensitizer. In the reference experiments, H_2 was not formed in the absence of TiO_2 or in the presence of only Pt without TiO_2. Irradiation of the whole system (Pt-loaded $TiO_2/Ru(bpy)_3^{2+}$/EDTA) without cutoff filter produced a lot of H_2 because of direct excitation of the TiO_2.

Action spectrum for the H_2 production was measured and shown in Fig. 1. The photoconversion efficiency was estimated from the amount of evolved H_2. Although it was difficult to distinguish H_2 formation between sensitized process and direct TiO_2 excited one at the wavelength region near 400 nm, it is evident by the H_2 formation in the region

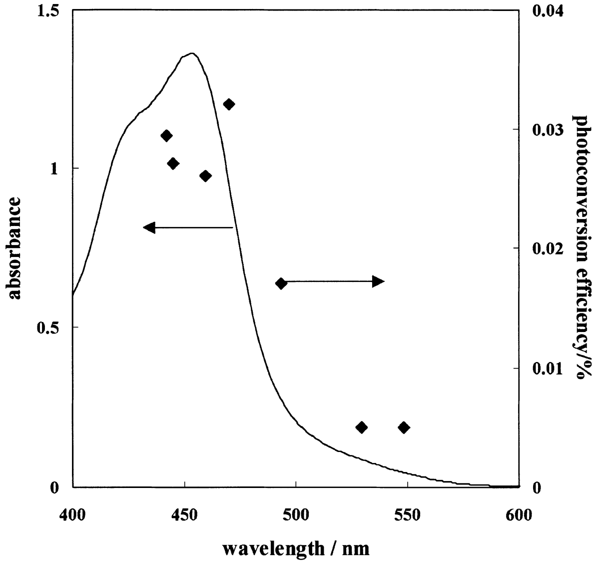

Fig. 1. Absorption spectrum of $Ru(bpy)_3^{2+}$ solution and photoaction spectrum of EDTA/$Ru(bpy)_3^{2+}$/TiO_2/Pt system for H_2 evolution. EDTA (0.1 M), $Ru(bpy)_3^{2+}$ (0.1 mM), TiO_2 (TiO-5)/Pt (0.3 wt.%) (0.05 g), Xe lamp (500 W).

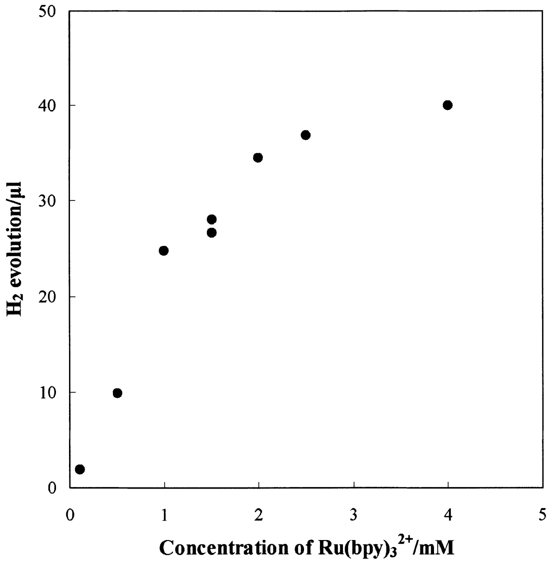

Fig. 2. The relationship between the amount of evolved H_2 against $Ru(bpy)_3{}^{2+}$ concentration. EDTA (0.1 M), TiO_2 (TiO-5)/Pt (0.3 wt.%) (0.05 g), Xe lamp (500 W), cutoff filter Y-44 (two sets).

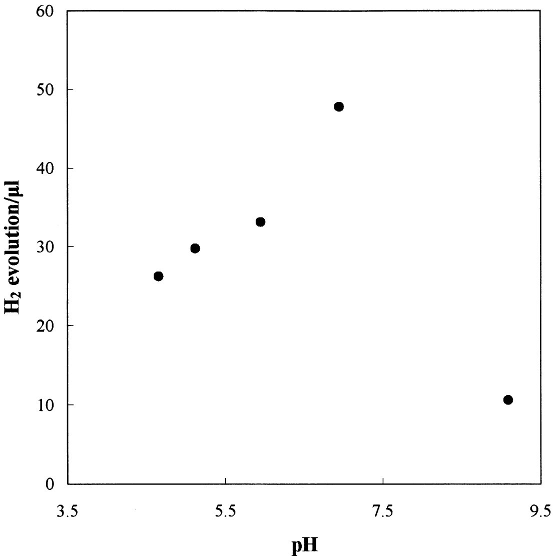

Fig. 3. Relationship of the amount of H_2 produced and pH. The pH of the solutions was adjusted with either NaOH or HCl. EDTA (0.1 M), $Ru(bpy)_3{}^{2+}$ (1 mM), TiO_2 (TiO-5)/Pt (0.3 wt.%) (0.05 g), Xe lamp (500 W), cutoff filter Y-44 (two sets).

from 400 to 500 nm that the complex having its absorption maximum at 450 nm induces the photochemical event.

An interesting aspect of the present sensitized reaction is the concentration conditions of the sensitizer required to achieve the photocatalysis. Sensitizer concentrations usually used in a solution photoreaction in a micromolar to sub-millimolar orders are not sufficient for the present sensitization. The dependence of H_2 evolution on the complex concentration is shown in Fig. 2. Only under high concentrations, the H_2 formation took place efficiently with visible light. In these conditions, most of the incident photons are absorbed by the sensitizer. There could be two reasons why such high concentration of the sensitizer is needed for H_2 evolution. One is the competition between H_2 evolution (second-order reaction) and the recombination of the separated charges (first-order reaction). The other is the difference of the photoinjection efficiency between the adsorbed dye and the free dye in the solution. Grätzel et al. reported an efficient solar cell composed of TiO_2 nanoparticle films and adsorbed sensitizer molecule. Adsorption equilibrium constant of $Ru(bpy)_3{}^{2+}$ on the TiO_2 would be very small because the color of TiO_2 particles did not change when the particle was immersed in 1 mmol dm^{-3} $Ru(bpy)_3{}^{2+}$ aqueous solution for a day, so that high concentration condition would be needed to increase the adsorption of the dye molecule. The result of Fig. 2 is most probably interpreted by sensitization with adsorbed sensitizer molecules.

The effect of pH on the H_2 evolution is shown in Fig. 3. The H_2 evolution showed an optimum point at pH 7. The surface of TiO_2 has amphoteric character due to hydroxyl groups [16].

$$\text{Ti–OH}_2{}^+ \rightleftarrows \text{Ti–OH} + \text{H}^+, \quad pK_1 = 5.76$$

$$\text{Ti–OH} \rightleftarrows \text{Ti–O}^- + \text{H}^+, \quad pK_2 = 8.38$$

The increase of H_2 evolved with the pH might reflect the dissociation of the surface OH groups on the TiO_2, which can facilitate the adsorption of the cationic dye on the TiO_2 surface [5,17]. However, in high pH regions electron injection from the excited sensitizer would be difficult because the conduction band of TiO_2 shifts to higher level with the increase of the pH. In addition, donating ability of EDTA would be lower because of protonation at low pH [8]. These factors would bring about the pH dependence of Fig. 3.

The effect of the loaded amount of Pt on TiO_2 at pH 4.5 is shown in Fig. 4. The decrease after the optimum point is interpreted by the over-coverage of the surface by the Pt resulting in the decrease of the effective TiO_2 surface to be utilized by the sensitizer.

The effect of the deposition method is compared between photochemical deposition and simple mixing deposition (Table 2). Photochemical deposition of platinum from

Table 2
Results of hydrogen production from water by visible light using TiO_2 suspension system[a]

Sensitizer concentration (mM)	TiO_2 (TiO-5)/ catalyst (g)[b]	H_2 evolution (μl h^{-1})
$Ru(bpy)_3{}^{2+}$ (1.00)	TiO_2/Pt (0.05)[c]	23.3
$Ru(bpy)_3{}^{2+}$ (1.00)	TiO_2/Pt (0.05)[d]	4.7
$Ru(bpy)_3{}^{2+}$ (1.00)	TiO_2/RuO_2 (0.05)[d]	0.6

[a] Light source: 500 W Xe lamp (1 h); pure water: 3 ml; electron donor: EDTA 0.1 M.

[b] Catalyst was loaded at 0.3 wt.% per TiO_2.

[c] Photodeposition of Pt on TiO_2.

[d] Mixing of Pt or RuO_2 and TiO_2.

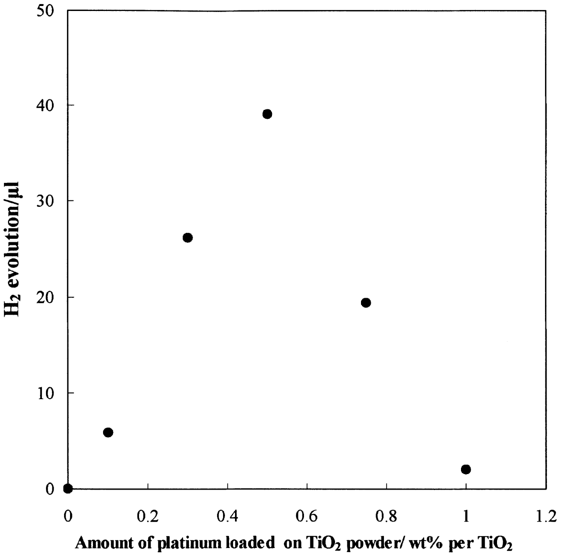

Fig. 4. Relationship between H_2 evolution and amount of Pt. EDTA (0.1 M), $Ru(bpy)_3^{2+}$ (1 mM), TiO_2 (TiO-5) (0.05 g), Xe lamp (500 W), cutoff filter Y-44 (two sets), pH 4.5.

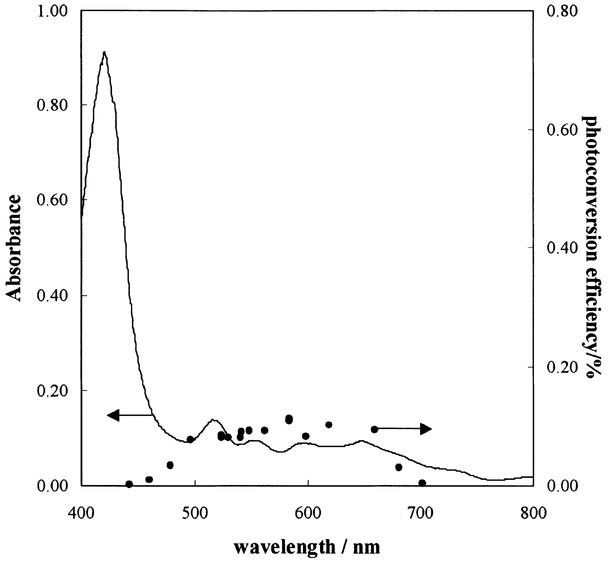

Fig. 5. Absorption spectrum of TiO_2-TPPC and photoaction spectrum of EDTA/TPPC/TiO_2/Pt system for H_2 evolution. EDTA (0.1 M), TPPC (0.25 mM) TiO_2 (TiO-5)/Pt (0.3 wt.%) (0.05 g), Xe lamp (500 W).

$K_2[PtCl_4]$ was important to prepare active Pt-loaded TiO_2 photocatalyst. Simple mixing of the TiO_2 and Pt powders in a mortar as usually done for preparing conventional photocatalyst was not effective for the present system. The Pt would be deposited on the TiO_2 surface by the photodeposition method where electron channeling exists, while Pt is loaded on the TiO_2 surface randomly by the mixing method. Due to this reason, the Pt particles by photodeposition method would be able to efficiently evolve H_2.

The effect of other sensitizers is shown in Table 3. Tris(bipyrimidine)ruthenium(II) showed much higher efficiency than $Ru(bpy)_3^{2+}$. This result could be explained by the higher affinity of $Ru(bpym)_3^{2+}$ on the TiO_2 surface than the $Ru(bpy)_3^{2+}$. In addition to the Ru complexes, porphine derivatives were effective as sensitizer. The degree of adsorption on the TiO_2 could be one of the reasons why TPPS has lower activity than TPPC [15]. Different electron density in excited states or redox potential might be another reason. The action spectrum for the H_2 evolution by the TPPC/TiO_2/Pt system was measured and compared with the absorption spectrum of TPPC/TiO_2 in Fig. 5. Although the plots for this action spectrum are scattered, it is evident that the hydrogen evolution is induced with light absorption by the Q band and not by the Soret band.

Table 4 shows the results by using other donor compounds instead of EDTA. Among the donors tested only EDTA and triethanolamine (TEOA) were effective to produce H_2. The dependence of H_2 evolved in a TEOA solution on pH was different from that in an EDTA solution. This would be because the oxidation of TEOA in an acidic solution is slower than that in an alkaline solution [8]. Reversible donors such as Fe^{2+}, hydroquinone (HQ), ascorbic acid, and phenol were

Table 3
Typical data of H_2 production in photochemical H^+ reduction by using various sensitizers[a]

Sensitizer concentration (mM)	TiO_2 (TiO-5)/ catalyst (g)[b]	H_2 evolution (µl h^{-1})
$Ru(bpy)_3^{2+}$ (1.00)	TiO_2/Pt (0.05)	23.3
$Ru(bpym)_3^{2+}$ (1.00)	TiO_2/Pt (0.05)	80.1
$Ru(dcbpy)_3^{4-}$ (0.25)	TiO_2/Pt (0.05)	17.8
TPPC (0.25)	TiO_2/Pt (0.05)	149.9
TPPS (0.25)	TiO_2/Pt (0.05)	54.5
TPPPy (0.25)	TiO_2/Pt (0.05)	2.1

[a] 500 W Xe lamp (1 h); pure water: 3 ml; electron donor: EDTA 0.1 M.

[b] TiO_2/catalyst: platinum was loaded on the TiO_2 powder using the photochemical deposition method.

Table 4
Results of hydrogen production from water by visible light using TiO_2 suspension system[a]

Donor concentration (mM)	Sensitizer concentration (mM)	H_2 evolution (µl)	pH
TEOA (1.00)	$Ru(bpy)_3^{2+}$ (1.00)	13.2	~11
TEOA (1.00)	$Ru(bpy)_3^{2+}$ (1.00)	6.9	7.3
TEOA (1.00)	$Ru(bpy)_3^{2+}$ (1.00)	0.2	6.0
Ascorbic acid (0.10)	$Ru(bpy)_3^{2+}$ (0.10)	0.4	[b]
Phenol (0.10)	$Ru(bpy)_3^{2+}$ (0.10)	0.0	[b]
Acetone	$Ru(bpy)_3^{2+}$ (0.10)	0.3	[b]
Methanol	$Ru(bpy)_3^{2+}$ (0.10)	0.0	[b]
$FeCl_2$ (1.00)	$Ru(bpy)_3^{2+}$ (1.00)	0.0	[b]
HQ (1.00)	$Ru(bpy)_3^{2+}$ (1.00)	0.0	[b]

[a] Light source: 500 W Xe lamp (1 h); pure water: 3 ml; catalyst: TiO_2/Pt (0.05 g/0.3 wt.%).

[b] pH is not adjusted.

not effective. In a conventional H_2 formation system by UV irradiation using platinized TiO_2 suspension and sacrificial donor in water, methanol is effective as a donor leading to efficient H_2 production in which the methanol scavenges the holes formed in the TiO_2 by direct excitation. In the present system, methanol does not work at all as a donor supporting that the present system is a sensitized one which does not produce holes in the TiO_2 bulk.

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