

Two-compartment Cell for Visible Light Decomposition of Water by Dye-sensitized Nanoparticle TiO_2 and Platinized WO_3

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Abstract

In order to fabricate a two-compartment cell system with an anion exchange membrane between the two compartments for water splitting by visible light into H_2 and O_2 , each half reaction for H_2 and O_2 evolution was investigated in a single cell. For H_2 production, two kinds of dye-sensitized Pt- TiO_2 photocatalysts under visible light irradiation were investigated using Coumarin 343 (C343) or meso-tetra(4-carboxyphenyl)porphine (TCPP) using KI as an electron donor. The amount of the H_2 gas evolved in the C343-Pt- TiO_2 system was higher than that in the TCPP-Pt- TiO_2 . For O_2 evolution, a photocatalyst Pt- WO_3 was investigated. The amount of O_2 evolution in the Pt- WO_3 system using KBrO_3 as an electron acceptor was much larger than that using NaIO_3 . For the H_2/O_2 gas evolution by using a two-compartment cell, the best system was composed of C343-Pt- $\text{TiO}_2/\text{Na}||\text{Pt-WO}_3/\text{NaIO}_3$. By this system H_2 evolution reached a maximum at 3 h and then decreased slightly until 6 h, however, O_2 evolution showed an induction period compared with the H_2 evolution and then increased with time. The two-compartment cell system exhibited some effect for simultaneous H_2 and O_2 evolution, but it was clarified that the present cell system still needs improvement to prevent recombination between the reduced and the oxidized products.

Keywords: Two-compartment cell; Dye-sensitized TiO_2 catalysts, Tungsten trioxides, Water splitting, Photoelectrochemical water decomposition

1. Introduction

Construction of an artificial photosynthetic system is receiving much attention to create renewable energy for solving global energy resource and pollution problems. Among the artificial photosynthetic systems, water splitting into H_2 and O_2 is one of the most important and fundamental processes. Photoelectrochemical reactions using semiconductor photocatalysts have been investigated since Gerischer started before 1960 [1]. The photoelectrochemical reaction at a single-crystal n- TiO_2 photoanode decomposed water into H_2 and O_2 by UV light under potential-controlled conditions [2, 3]. Since then, various types of photocatalysts for water photodecomposition into H_2 and O_2 have been investigated by many researchers. The stoichiometric photodecomposition of water under UV irradiation on various semiconductors such as Ta_2O_5 [4], ZrO_2 [5], BaTa_2O_6 [6], $\text{K}_4\text{Nb}_6\text{O}_{17}$ [7-9], etc. was reported. Especially, metal oxides such as TiO_2 are attracting a deal of attention because of their stability against photocorrosion

and availability. However, most of the metal oxides are photochemically active only under UV light that occupies only a small fraction (about 4 %) of the solar spectrum due to their wide band gaps. Some oxides such as Fe_2O_3 and WO_3 can absorb visible light, but they cannot evolve H_2 evolution [10, 11]. The development of a useful system for water splitting into H_2 and O_2 have been focused on narrow band gap semiconductors excited by visible light that occupies 50 % of the solar spectrum. Another attempt to fabricate a photosynthetic Z-scheme system (two-step photoexcitation system) for water splitting by visible light was reported by Arakawa and his coworkers [12, 13]. This system conducted under reduced pressure contained a Pt/SrTiO₃ (Cr-Ta doped) photocatalyst as photosystem I (PS I) for H_2 production and a WO_3 photocatalyst as PS II for O_2 production with $\text{I}_3^-/\text{IO}_3^-$ shuttle redox pair. Kudo and his coworkers also reported similar Z-scheme system, which consisted of a Pt/SrTiO₃ (Rh doped) photocatalyst for H_2 production and either BiVO_4 , Bi_2MoO_6 or WO_3 photocatalyst for O_2 production with $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pair [14, 15]. More recently, Domen and his coworkers reported a new photocatalyst producing H_2 from water by using $(\text{Ga}_{1-x}\text{Zn}_x)(\text{N}_{1-x}\text{O}_x)$ with nanoparticles of Rh-Cr mixed oxide [16, 17]. The photocatalytic water decomposition was reported using

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two Pt electrodes (cathode and anode) and a cation-exchange membrane in a two-compartment reactor, in which H_2 was evolved on Pt-TiO₂ photocatalyst under UV irradiation in one compartment containing Br₂/Br⁻ redox pair, and O₂ was evolved in the other compartment containing Fe³⁺/Fe²⁺ redox pair [18]. Such the utilization of a two-compartment system must be an important approach to suppress charge recombination between the oxidized and the reduced products. However, to the best of our knowledge, photodecomposition of water into H₂ and O₂ by using a two-compartment cell has not been investigated for a visible light irradiation system.

In the present paper visible light water photodecomposition into H₂ and O₂ is investigated with a two-compartment cell by using a dye-sensitized photocatalyst. We utilized the system reported by Arakawa and his coworkers [10, 19, 20], except carrying out under atmospheric pressure instead of under reduced pressure in order to investigate the effectiveness of a two-compartment cell to separate two half reactions.

2. Experimental

2.1. Materials

Titanium oxide (TiO₂; ST-01, anatase 100 %, average size 7 nm) was purchased from Ishihara Sangyo Co. Ltd. Chloroplatinic acid (H₂PtCl₆ · 6H₂O), sodium iodide, sodium iodate, and acetonitrile (AN) were purchased from Kishida Chemical Co., Ltd., and tungsten trioxide (WO₃), disodium dihydrogen ethylenediamine tetraacetate dihydrate (EDTA · 2H₂O), triethanolamine (TEOA), potassium bromide, and potassium bromate from Kanto Kagaku Co. Ltd. Coumarin 343 was purchased from Aldrich Co. Ltd., and meso-tetra(4-carboxyphenyl)porphine (TCPP) from Porphyrin Products Inc. Ar gas (purity >99 %) was obtained from Nippon Sanso Corp. These chemicals were of the purest grade available and used as received. Anion-exchange membrane (Selemion AMV, thickness 130 μm, styrene-chloromethylstyrene crosslinked copolymer with pendant ammonium cations) was purchased from Asahi Glass Co. Ltd.

2.2. Preparation of platinized TiO₂ and WO₃

Platinization of TiO₂ (0.5 wt% Pt-TiO₂) was carried out using a photodeposition method by irradiating a methanol/H₂O (1 ml/50 ml) suspension of TiO₂ (ST-01, 1.0 g) with a 200 W high-pressure mercury lamp for 8 h in the presence of 0.013 g H₂PtCl₆ · 6H₂O. After irradiation, the filtered Pt/TiO₂ sample was collected and washed with distilled water, and then dried in vacuo overnight (at room temperature) followed by drying at 200 °C. Platinization of WO₃ (0.5 wt% Pt-WO₃) was carried out the same as the

preparation of Pt-TiO₂.

2.3. Adsorption of dye

The Pt-TiO₂ sample adsorbing Coumarin 343, Coumarin 343-Pt-TiO₂ (C343-Pt-TiO₂), was prepared as follows: 1mM Coumarin 343 in AN (40 ml) and 0.2 g Pt-TiO₂ were mixed well and the mixture was stirred for 8 h at room temperature, followed by centrifugation (3000 rpm). The residue collected was dispersed in acetone and then the mixture was again centrifuged. After this procedure was repeated a few times, the material collected was dried in vacuo overnight. TCPP-Pt-TiO₂ was prepared the same as the C343-Pt-TiO₂ sample.

2.4. Photoreaction cells

A cylindrical reactor (Pyrex glass cell, 10 ml) and a two-compartment cell were used. The two-compartment cell was composed of two plastic cells (4.5 cm x 1.0 cm x 1.0 cm) with a small circle window (diameter of 5 mm) between the two cells. The two compartments were separated by an anion-exchange membrane (Selemion) through the window as shown in Fig. 1.

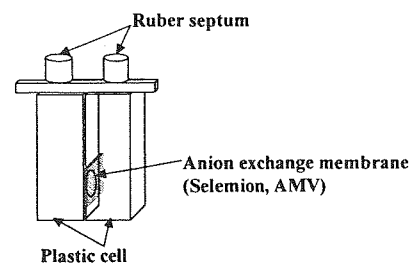


Fig. 1 Two-compartment cell separated by an anion exchange membrane

2.5. Photocatalytic reaction and analysis

The photocatalytic reactions were carried out with the two different types of reactors. One was a cylindrical reactor sealed with a rubber septum, through which the gas phase can be sampled out by a syringe. The other was a two-compartment cell, each of the compartment being sealed with a rubber septum mentioned above. The photocatalytic reaction under visible light irradiation was carried out under magnetic stirring by using a 60W halogen lamp (Hayashi Watch-Woks Co. Ltd., LA-60Me) with a UV cutoff filter (L-42) at the light intensity of 168 mW cm⁻². A sample aliquot of 100 μl gas was taken for the analysis. The H₂ and O₂ gases evolved were analyzed by a gas chromatograph (Shimadzu, GC2014) with a 5A molecular sieve column at 40 °C under Ar carrier gas. All the photoelectrochemical reactions were performed at 25 °C.

3. Results and discussion

Various combinations between dye-sensitized photocatalyst and redox carrier for H₂ evolution was investigated in order to use the half reaction for photodecomposing water into H₂ and O₂ under visible light irradiation using a cylindrical cell made of Pyrex glass that does not transmit the light below the wavelength of 300 nm. A L-42 cutoff filter was used in order to utilize only visible light over 420 nm. The results are shown in Table 1. In this

Table 1 Effects of C343 and TCPP sensitizers on H₂ evolution for 2 h in aqueous solutions containing various donors using a cylindrical cell, irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻²

Photocatalyst	Donor (mM)	H ₂ evolution/ μ l
C343-Pt-TiO ₂	NaI (100)	12.7
C343-Pt-TiO ₂	KBr (100)	35.1
C343-Pt-TiO ₂	EDTA (100)	1498.6
C343-Pt-TiO ₂	TEOA (10 wt %)	740.4
TCPP- Pt-TiO ₂	NaI (AN 95 %)	2.7
TCPP- Pt-TiO ₂	EDTA (100)	54.8

C343, Courmarin 343; TCPP, meso-tetra(4-carboxyphenyl)porphine; C343-Pt-TiO₂ (5 mg); AN, acetonitrile; TEOA, triethanolamine; EDTA, disodium dihydrogen ethylenediaminetetraacetate dehydrate

table, two kinds of dye-sensitized Pt-TiO₂ photocatalysts were investigated using Coumarin 343 (C343) and meso-tetra(4-carboxyphenyl)porphine (TCPP). The latter (TCPP) was selected in order to improve the exciton diffusion length [21-23], enhance the interfacial electron injection yield [24], and

Table 2 Effects of various photocatalysts and acceptors on O₂ evolution for 2 h in aqueous solutions containing various donors using a cylindrical cell, irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻²

Photocatalyst	Acceptor (mM)	O ₂ evolution/ μ l
WO ₃	NaIO ₃ (10)	tr.
Pt-WO ₃	NaIO ₃ (10)	38.8
Pt-WO ₃	KBrO ₃ (100)	168.9

WO₃ (20 mg), Pt(0.5 wt %)-WO₃ (20 mg)
tr. ; trace

also improve the charge transport properties [25-27]. Especially, it was reported that TCPP showed a good photon-to-current

dyes in a dye-sensitized solar cell [28]. In the case of the C343-Pt-TiO₂ system, H₂ evolution was observed when using electron donors such as NaI and KBr as shown in Table 1. When using the donors such as EDTA or TEOA, the amount of H₂ gas evolved was clearly much larger than that when using the donors mentioned above. The amount of the H₂ gas evolved in the C343-Pt-TiO₂ was higher than that in the TCPP-Pt-TiO₂ both for the NaI and EDTA systems. Based on these results the C343-Pt-TiO₂ was adopted for H₂ evolution half reaction to investigate water photodecomposition into H₂ and O₂ as mentioned later.

In order to investigate photocatalysts for O₂ evolution by utilizing visible light, WO₃ semiconductor was used because of its narrow bandgap (2.7 eV, < 460 nm) [29]. The O₂ evolution by light irradiation (400-450 nm) has already been reported using WO₃ in an aqueous H₂SO₄ solution containing FeCl₃ by Darwent et al [30]. Table 2 shows that the O₂ evolution under visible light irradiation (> 420 nm) was dependent on the kind of electron acceptors and photocatalysts. As reported previously [31], when using NaIO₃ as an electron acceptor and WO₃ as a photocatalyst, O₂ evolution was not observed. However, when using Pt-WO₃ with a NaIO₃ aqueous solution, O₂ gas was clearly evolved. The amount of O₂ evolution in the Pt-WO₃ system using KBrO₃ was much larger than that using NaIO₃. In the following two-compartment cell the Pt-WO₃/NaIO₃ system for O₂ evolution was mainly investigated.

In order to investigate the characteristics of the two-compartment cell, the following experiments were carried out. One compartment contained photocatalyst (either C343-Pt-TiO₂ or Pt-WO₃) for either H₂ or O₂ evolution with NaI or NaIO₃, respectively, and the other only H₂O. The time-course of the gas evolution (H₂ or O₂) is shown in Fig. 2. It was elucidated that in the two-compartment cell system, either H₂ or O₂ can be

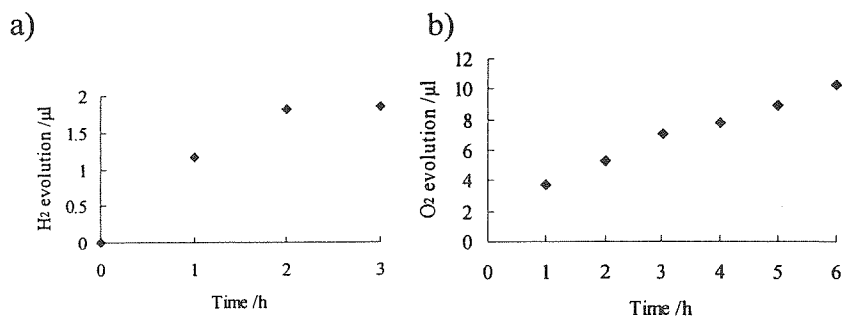


Fig.2 Time-course of gas evolution by using two-compartment cell separated by an anion exchange membrane; a) C343-Pt(0.05 wt%)-TiO₂(5 mg)/NaI(80 mM)|H₂O, b) Pt-WO₃(10 mg)/NaIO₃(5 mM)|H₂O, irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻².

conversion efficiency (IPCE) value among the porphyrin-based photochemically produced, and analyzed.

Fig. 3 shows that the permeability characteristics of anion exchange membrane (Selemion) for redox mediators (I_3^- or IO_3^-)

compartment contained Pt-WO₃ suspension in water and the other a 0.1 M NaIO₃ aqueous solution. O₂ evolution increased with time

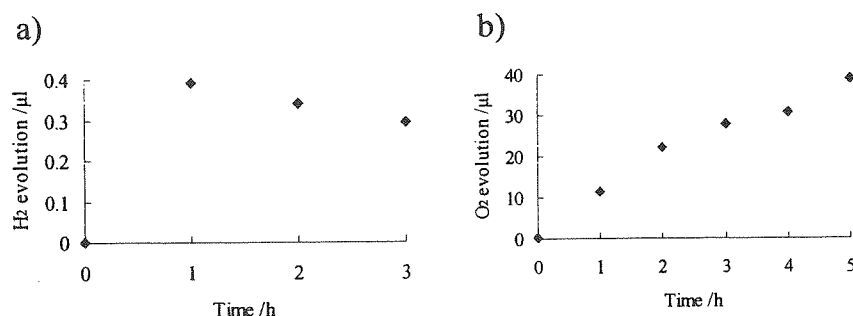


Fig.3 Time-course of gas evolution by using two-compartment cell separated by an anion exchange membrane, each compartment containing either 2.0 ml catalyst aqueous suspension or 2.0 ml redox mediator aqueous solution; a) C343-Pt(0.05 wt%)-TiO₂(5 mg) | NaI(100 mM), b) Pt-WO₃(10mg) | NaIO₃(100 mM), irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻².

using the two-compartment cell is suited for our purpose. For the H₂ evolution system (Fig. 3a), one compartment contained

until 3h showing that IO₃⁻ ion works as the electron acceptor for O₂ production after permeating through the ion exchange

Table 3 Results of photochemical H₂ and O₂ evolution by using two-compartment cell, irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻² (pH 5.5-5.9)

System	H ₂ evolution/μl	O ₂ evolution/μl
C343-Pt-TiO ₂ (5mg)/NaI(800mM) Pt-WO ₃ (10mg)/NaIO ₃ (80mM)	0	12.3 (3h)
C343-Pt-TiO ₂ (5mg)/NaI(400mM) Pt-WO ₃ (10mg)/NaIO ₃ (80mM)	0	12.4 (3h)
C343-Pt-TiO ₂ (5mg)/NaI(160mM) Pt-WO ₃ (10mg)/NaIO ₃ (80mM)	0	16.8 (3h)
C343-Pt-TiO ₂ (5mg)/NaI(80mM) Pt-WO ₃ (10mg)/NaIO ₃ (80mM)	0.1(1h)	27.6 (3h)

C343-Pt-TiO₂ suspension in water and the other a 0.1 M NaI aqueous solution. The H₂ evolution increased in the first stage due to the I⁻ ion permeated from the other compartment, and reached a maximum after 1h and then decreased gradually with time probably due to the recombination between the formed H₂ and IO₃⁻. It is exhibited any way that the I⁻ ion works as an electron donor to produce H₂ after permeating through the anion exchange membrane. In another experiment for O₂ evolution, one

membrane from the other compartment. These results show that the redox pair can permeate with each other through the membrane.

In order to investigate the optimum conditions concerning water splitting into H₂ and O₂ by using the C343-Pt-TiO₂/NaI|Pt-WO₃/NaIO₃ system in the two-compartment cell, the experiments in various concentrations of NaI with constant concentration of NaIO₃ (80 mM) were carried out and the

Table 4 Results of photochemical H₂ and O₂ evolution by using two-compartment cell, irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻² (pH 4.9-5.6)

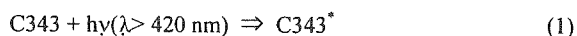
System	H ₂ evolution/μl	O ₂ evolution/μl
C343-Pt-TiO ₂ (5mg)/NaI(80mM) Pt-WO ₃ (10mg)/NaIO ₃ (40mM)	2.0(2h)	20.2 (3h)
C343-Pt-TiO ₂ (5mg)/NaI(80mM) Pt-WO ₃ (10mg)/NaIO ₃ (10mM)	1.4 (2h)	12.2 (3h)
C343-Pt-TiO ₂ (5mg)/NaI(80mM) Pt-WO ₃ (10mg)/NaIO ₃ (5mM)	3.2 (3h)	1.7 (3h)
C343-Pt-TiO ₂ (5mg)/NaI(80mM) Pt-WO ₃ (10mg)/NaIO ₃ (1mM)	2.9 (1h)	0 (3h)

results are shown in Table 3. The H₂ evolution was not observed in almost all the cases. On the other hand, the amount of the O₂ evolution increased with decreasing the concentration of NaI and the best condition for O₂ evolution was at 80 mM NaI. It means that I⁻ anions dissociated from NaI affect on the O₂ evolution in the other compartment through the anion-exchange membrane. In another experiment, the ratios of NaI/NaIO₃ redox pair with constant concentration of NaI (80 mM) were changed and the results are shown in Table 4. The O₂ evolution decreased with decreasing the concentration of NaIO₃, and O₂ evolution in a 1 mM NaIO₃ aqueous solution was not observed showing that the concentration of a NaIO₃ aqueous solution was needed to be at least more than 5 mM for O₂ production in this system. Among the ratio of NaI/NaIO₃ redox pair from 2 to 80, the best condition was under the ratio of 16.

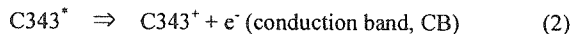
As shown in the Scheme 1, the reaction mechanism of water splitting by using the two-compartment cell is represented as follows:

1. Mechanism of H₂ evolution and I₃⁻ or IO₃⁻ production in the C343-Pt-TiO₂/NaI system.

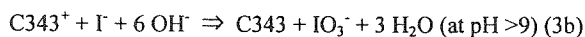
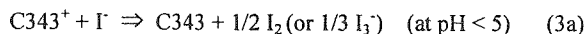
(excitation of dye by visible light)



(electron injection to CB of TiO₂)



(regeneration of dye under ground state)



(both the reactions take place at 5 < pH < 9)

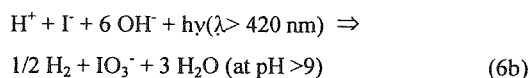
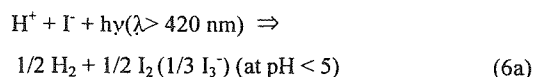
(electron transportation to Pt)



(H₂ production on Pt)

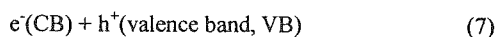
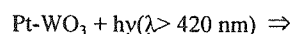


(overall reaction at the cathode compartment)

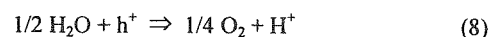


2. Mechanism of O₂ evolution in the Pt-WO₃ / NaIO₃ system.

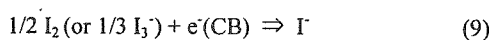
(charge separation on WO₃ by visible light)



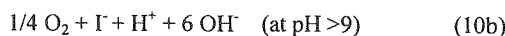
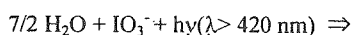
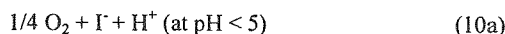
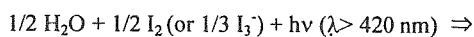
(O₂ production on Pt-WO₃)



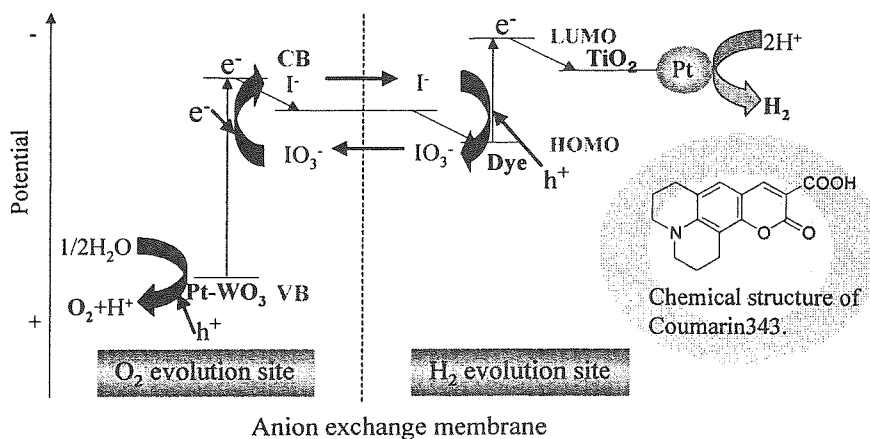
(reduction of IO₃⁻ to I⁻ by electrons)



(overall reaction at the anode compartment)



The first step involves the excitation of C343 dye on the Pt-TiO₂ (Eq.1) by visible light irradiation followed by injection of electrons from the excited dye into CB of TiO₂ (Eq.2). The dye (C343⁺) formed after injecting electron into CB of TiO₂ is re-reduced by I⁻ to produce C343 with producing I₂ (or I₃⁻) or IO₃⁻ (Eq.3a and 3b) depending on the pH. The produced I₂ (or I₃⁻) or IO₃⁻ anions are permeated through the anion exchange membrane into the other compartment containing Pt-WO₃ suspension in a NaIO₃ aqueous solution. On the other hand, the electrons injected into CB are transported to Pt on TiO₂ (Eq.4) resulting in H⁺ reduction to produce H₂ there (Eq.5). The second mechanism involves the photoinduced charge separation in the WO₃ to



Scheme 1 H₂ and O₂ evolution reaction by using a C343-Pt-TiO₂/NaI | Pt-WO₃/NaIO₃ system in a two-compartment cell, under visible light irradiation.

produce electron (e^-) in the CB and hole (h^+) in the VB (Eq.7), and then H_2O reacts with h^+ on the WO_3 to produce O_2 (Eq.8). On the other hand, the I_2 (or I_3^-) or IO_3^- anions are reduced to I^- by electrons from CB of WO_3 (Eq.9a and 9b). The produced I^- anions are permeated through the anion exchange membrane into the other compartment containing C343-Pt-TiO₂ in a NaI aqueous

in O_2 evolution is ascribable to the needed time for the accumulation of IO_3^- anion (or I_2/I_3^-) (Fig. 4). Based on the mechanism, when the concentration of IO_3^- (or I_2/I_3^-) reached at some level, the rate of H_2 evolution might decrease because of undesirable backward reaction due to the reduction of IO_3^- or I_2/I_3^- . On the other hand, O_2 gas evolution increased with time until 6 h,

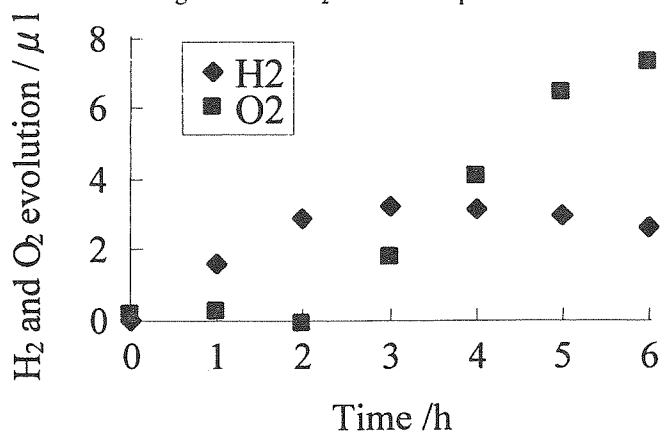


Fig.4 Time-course of gas evolution by using two-compartments cell separated by an anion exchange membrane, each compartment containing 2.5 ml catalyst aqueous suspension; C343-Pt (0.05 wt%)-TiO₂(5 mg) /NaI(80 mM)| Pt-WO₃(10mg)/NaIO₃ (5 mM), irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻².

Table 5 Results of photochemical H_2 and O_2 evolution by using two-compartment cell, irradiated by a 60 W halogen lamp through a UV cutoff filter (L-42) with a light intensity of 168 mW cm⁻²

System	H ₂ evolution/μl	O ₂ evolution/μl
C343-Pt-TiO ₂ (5mg)/NaI(80mM) Pt-WO ₃ (10mg)/NaIO ₃ (10mM)	1.4 (2h)	12.2 (3h)
C343-Pt-TiO ₂ (5mg)/KBr(80mM) Pt-WO ₃ (10mg)/KBrO ₃ (10mM)	0.2 (0.5h)	3.3 (3h)

solution again to be utilized as electron donors for H_2 production. It was reported that both I_2 (or I_3^-) and IO_3^- were produced in solution of pH 5-9 over Pt-TiO₂ (anatase) [32]. In our experiments both the I_2 (or I_3^-) and IO_3^- formation took place (Eq.3a and b) because the NaI aqueous solution containing C343-Pt-TiO₂ (anatase) was at pH from 5.1 to 5.9. All the redox ions produced in the compartments can permeate through the anion exchange membrane with each other.

Fig. 4 shows the time-course of H_2 and O_2 evolution under the best conditions, C343-Pt-TiO₂(5mg)/NaI(80mM)|Pt-WO₃(10mg)/NaIO₃(5mM), in Table 4. H_2 evolution reached a maximum at 3 h and then decreased slightly until 6 h, however, O_2 evolution was delayed compared with H_2 evolution and then increased with time. Taking the above mechanism into account, it is strongly suggested that the initial concentration of NaIO₃ for O_2 evolution has to be needed at least over 5 mM in this system although the IO_3^- anion (or I_2/I_3^-) can be supplied through the anion exchange membrane from the H_2 evolution cell (Table 3). Similarly, the reason of delay

probably because the reduction of O_2 by I^- is difficult due to its 4 e^- process.

As shown in Tables 1 and 2, when using Br^-/BrO_3^- redox pair, the amount of the gas evolution (H_2 or O_2) was much larger than that when using I^-/IO_3^- redox pair. Therefore, the experiment with the two-compartment cell was carried out by using Br^-/BrO_3^- redox pair and the result is shown in Table 5. When using Br^-/BrO_3^- redox pair under these conditions ($Br^-/BrO_3^- = 80$ mM/10 mM), the amount of the gas evolution was much lower than that when using I^-/IO_3^- redox pair, although the quantitative H_2/O_2 evolution by I^-/IO_3^- redox pair was not achieved under the present conditions.

4. Conclusion

The photocatalytic system using both C343-Pt-TiO₂ and Pt-WO₃ as a photocatalyst with a two-compartment cell under 1 atm demonstrated that water was decomposed into H_2 and O_2 under visible light irradiation when using I^-/IO_3^- shuttle redox pair. In a best system H_2 evolution reached a maximum at 3 h and then

decreased slightly until 6 h, however, O_2 evolution was delayed compared with H_2 evolution. The two-compartment cell system exhibited some effect for simultaneous H_2 and O_2 evolution, but it was clarified that the present cell system still needs improvement to prevent recombination between the reduced and the oxidized products.

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