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Dye-sensitized photocatalysts for efficient hydrogen production from aqueous I^- solution under visible light irradiation

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Abstract

H_2 production from a water–acetonitrile (AN) mixed solution containing iodide electron donor was investigated over dye-sensitized Pt/TiO_2 photocatalysts under visible light irradiation. It was found that H_2 production with good quantum efficiency (~2.5%) took place using merocyanine and coumarin dye-sensitized Pt/TiO_2 photocatalysts, respectively, and an I^- electron donor in a water–acetonitrile mixture (water, 5% by volume). The rates of H_2 evolution were decreased with the increase of the water amount in the mixed solution because of the decrease in energy gap between the redox potential of I_3^-/I^- and the HOMO level of the dye. H_2 evolution was also decreased with the accumulation of produced I_3^- from I^-. However, we have also found that it is possible to prevent the backward reaction, reduction of I_3^- to I^- on Pt metal by using the internally platinized semiconductor $K_4Nb_6O_{17}$ instead of Pt/TiO_2 in water–AN mixed solution.

Keywords: Dye-sensitized photocatalysts; Hydrogen production; Visible light irradiation

1. Introduction

Construction of an efficient system for light energy conversion into chemical energy is one of the most important subjects from the viewpoint of solar light energy utilization. Photocatalytic water splitting into H_2 and O_2 is a promising process for solar energy conversion and storage [1–3], but the satisfactory system workable under visible light irradiation has not yet established. As a strategy for effective visible light harvest, spectra sensitization of wide bandgap semiconductors by dye molecules has been so far studied for photocatalytic H_2 production from water [4–9]. Fig. 1 illustrates the conceptual mechanism of H_2 production over dye-sensitization of TiO_2 semiconductor photocatalyst. Light excitation of the dye sensitizer molecule (S) is followed by charge injection into the TiO_2, producing the oxidized form of the dye (S^+) and conduction band electrons. Then, the electrons reduce water to H_2 on the reduction site (Pt) over TiO_2. The original form of the sensitizer is reformed by accepting an electron from the electron donor such as ethylenediaminetetraacetic acid (EDTA) in the solution, which irreversibly donates electrons and then decomposes. For example, adsorption of dye sensitizers such as $Ru(bpy)_3^{2+}$ or Eosin Y on platinized TiO_2 particles (Pt/TiO_2) led to efficient H_2 evolution from water under visible light in the presence of a sacrificial electron donor such as triethanolamine (TEOA) and EDTA [6–9]. However, most of dye molecules cannot oxidize water into O_2 and consequently decompose in the absence of sacrificial electron donor under irradiation, with a few exceptions of Ru-complex systems combined with heterogeneous catalysts such as IrO_2 [10]. Because the evolution of O_2 from water that requires four electrons abstraction is much harder than kinetically simpler processes of H_2 evolution. The inability of O_2 evolution over sensitizer molecules has prevented the construction of overall water splitting into H_2 and O_2 by dye-sensitized photocatalysts.

We have recently demonstrated a new type of photocatalytic water splitting system in which H_2 and O_2 production processes are combined with an IO_3^-/I^- (or I_3^-/I^-) shuttle redox mediator [11,12]. In this system, the hardest process of water oxidation to O_2 takes place over WO_3 photocatalyst by the combination with reduction of IO_3^- (or I_3^-) to I^- under visible light irradiation. Therefore, a dye-sensitized photocatalyst is applicable to the H_2 production process if it can oxidize I^- to I_3^- accompanied with H_2 production as shown in Fig. 1. It might be easier for dye molecule to oxidize I^- to I_3^-, which requires two electrons abstraction than to oxidize water to O_2. For example, Saupe et al.

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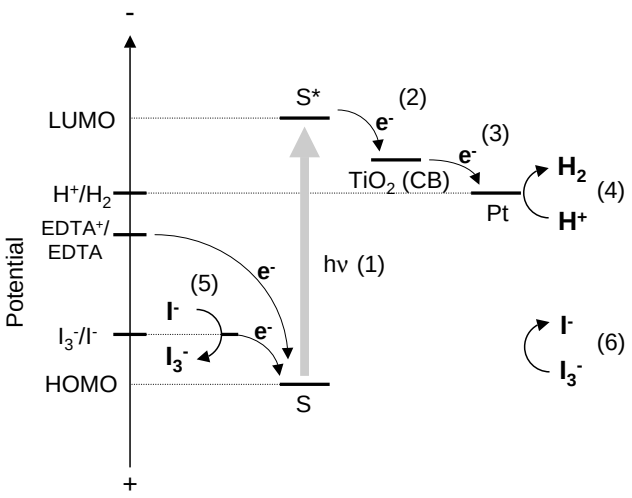

Fig. 1. Energy diagram of H_2 production from water over dye-sensitized Pt/TiO_2 photocatalysts using I^- or EDTA as an electron donor.

have constructed dye-sensitized photocatalysts consisting of a Ru-complex sensitizer and some interlayer platinized layered metal oxides such as $K_4Nb_6O_{17}$, and have demonstrated H_2 and I_3^- production from acidic aqueous solution containing I^- as an electron donor [13]. The present paper describes the H_2 production from aqueous I_3^-/I^- redox solution using dye-sensitized Pt/TiO_2 photocatalyst under visible light irradiation, where organic solvents such as acetonitrile (AN) are found to enhance the H_2 evolution rate significantly.

2. Experimental

2.1. Preparation of dye-sensitized Pt/TiO_2 photocatalyst

A Pt (0.5 wt.%) loaded TiO_2 catalyst (Pt/TiO_2) was prepared as follows: TiO_2 powder (anatase, 320 m^2/g, Ishihara Co. Ltd. ST-01) was stirred in an aqueous methanol solution (H_2O:MeOH = 99:1 by volume) containing a required amount of H_2PtCl_6 and irradiated by a high-pressure Hg lamp for 12 h. Photoreduction of H_2PtCl_6 to Pt particles took place, and highly dispersed Pt particles were deposited on the TiO_2 surface. After filtrating and washing by distilled water, the powder was heated at 200 °C for 2 h in vacuum to remove methanol residue from the catalyst. A merocyanine dye (NK-2045, Hayashibara Biochemical Laboratories) and a coumarin dye (C-343, Aldrich) shown in Fig. 2, were used as photosensitizers of the catalyst. The dye was adsorbed onto Pt/TiO_2 by stirring the Pt/TiO_2 powder (0.5 g) in a mixture of dye and acetonitrile solvent (1 mM in 100 ml) at room temperature for 12 h in the dark. After filtrating and washing by acetone, the sample was dried and kept in the dark. As shown in Fig. 2, the Pt/TiO_2 samples adsorbed with the merocyanine and the coumarin (denoted, hereafter, as M-Pt/TiO_2 and C-Pt/TiO_2) showed broad absorption from 400 to 650 nm and from 400 to 550 nm, respectively.

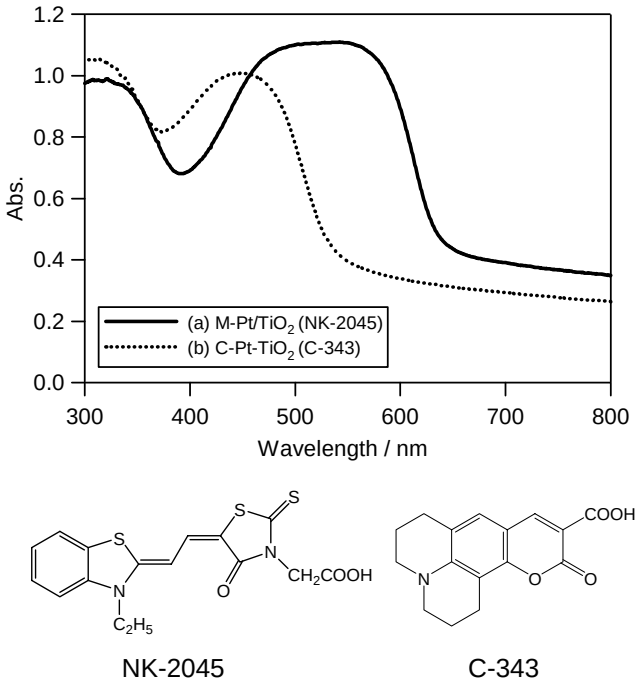

Fig. 2. UV–vis spectra of Pt/TiO_2 particles adsorbed with merocyanine (M-Pt/TiO_2 (a)) and coumarin (C-Pt/TiO_2 (b)), and structures of the dyes.

2.2. Preparation of dye-sensitized $Pt/H_4Nb_6O_{17}$ photocatalysts

$K_4Nb_6O_{17}$ was prepared by calcination of a stoichiometric mixture of K_2CO_3 and Nb_2O_5 in a platinum crucible at 1200 °C for 15 min. The preparation of platinized $K_4Nb_6O_{17}$ (0.5 wt.% of Pt loaded) was carried out following two methods [17]. For introducing Pt particles as co-catalysts into interlayer spaces of catalyst, $K_4Nb_6O_{17}$ powder was stirred in aqueous solution containing $\{Pt(NH_3)_4\}Cl_2$ at room temperature for 3 days, and then methanol was added into the solution and irradiated by high-pressure Hg lamp for 12 h for photocatalytic reduction of $Pt(NH_3)_4^{2+}$ to metallic Pt. After washing, the sample was stirred in 0.5 N HCl aqueous solution for 12 h to exchange K^+ ions at interlayer space into H^+. As prepared sample is referred to as Pt(in–ex)/$H_4Nb_6O_{17}$, in which Pt metal particles are exist both in external and interlayer space of $H_4Nb_6O_{17}$. The Pt(in–ex)/$H_4Nb_6O_{17}$ sample treated with 3:1 concentrated HCl/HNO_3 at about 90 °C for 1 h in order to remove Pt particles deposited on external sites of catalyst. It is referred to as Pt(in)/$H_4Nb_6O_{17}$. For the deposition of Pt particle on the external surface, $K_4Nb_6O_{17}$ was converted into $H_4Nb_6O_{17}$ by stirring in 0.5 N HCl aqeous first; and after that, the sample was stirred in aqueous solution containing H_2PtCl_6 with UV irradiation for 12 h. In this case, $PtCl_6^{2-}$ anion cannot intercalate into the interlayer space of $H_4Nb_6O_{17}$ because of electronic restitution between the $PtCl_6^{2-}$ anion and the anionic framework of $H_4Nb_6O_{17}$. As prepared sample is referred to as Pt(ex)/$H_4Nb_6O_{17}$. The adsorption

of merocyanine NK-2045 onto $Pt/H_4Nb_6O_{17}$ samples was carried out as same procedure as the Pt/TiO_2 case.

2.3. Photocatalytic reaction

Photocatalytic reactions were performed using a Pyrex glass reactor connected to a closed gas-circulation system. The catalyst powder (50 mg) was introduced to an acetonitrile–water mixed solution (100 ml) containing 10 mmol of NaI in the reactor, then the suspension was stirred using a magnetic stirrer bar. The system was thoroughly degassed by several cycles of evacuation and Ar gas introduction, and then the suspension was irradiated from the top of the reactor by a 300 W Xe lamp with a cut-off filter (Hoya L-42, $\lambda > 410$ nm). Under the reduced pressure, bumping of suspension took place and some of catalyst powder adhered to the inside wall of grass reactor. Furthermore, the water and acetonitrile vapor condensed on the inside wall of the closed gas-circulation system. To prevent these problems, argon gas (200 Torr) was introduced into the system before irradiation, and the reactor temperature was maintained constant at 15 °C during the reaction using cooling water. The evolution of H_2 gas was analyzed by an on-line gas chromatograph (TCD, molecular sieve 5A). The amount of I_3^- ion produced was determined by the absorption spectra of the solution obtained from UV–vis spectroscopy.

2.4. Electrochemical measurement

The redox potentials of dyes and I_3^-/I^- were estimated by both cyclic voltammetry (CV) and differential pulse voltammetry (DPV) using a conventional three-compartment cell composed of a Pt or carbon working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode in a saturated aqueous KCl solution. The reference electrode was equipped with salt bridge to decrease liquid junction potential. Mixture of acetonitrile and water was used as a solvent, and the supporting electrolyte was 0.1 M $LiClO_4$. Because of irreversible CV profiles by anodic oxidation for these dyes in water-containing solutions, the oxidation potentials (HOMO level) of the merocyanine and coumarin dyes were determined by the DPV.

3. Results and discussions

3.1. H_2 evolution over dye-sensitized TiO_2 photocatalysts in water–AN mixed solution

Both merocyanine NK2045 and coumarin C343 were studied so far as a sensitizer for Graetzel cell consisting of a dye-sensitized TiO_2 photoelectrode and an I_3^-/I^- redox in the organic solvent such as acetonitrile [14–16]. This indicates that these dyes have the suitable ground (HOMO) and excited (LUMO) states for the efficient electron transfer. That is, two key electron transfer steps, electron injection from an excited dye to the TiO_2 conduction band and an oxidation of I^- to I_3^- (shown in Fig. 1 as (2) and (5), respectively), occur efficiently in AN solvent. For the photocatalytic H_2 production from water, however, the solution must contain water as a reactant. Therefore, H_2 evolution was tested both in a water–AN mixture (water, 5% by volume) and in water. Both solutions contain 0.1 M of NaI as an electron donor. Fig. 3 shows the time course of H_2 evolution over M-Pt/TiO_2 (a) and C-Pt/TiO_2 (b) under irradiation of visible light ($\lambda > 410$ nm). In both cases, the rate of H_2 evolution from the water–AN mixture was higher than that from the water. Especially, the rate of H_2 evolution over M-Pt/TiO_2 from water–AN mixture was about 20 times higher than that from water. When the reaction was carried out in a water–AN mixture, no H_2 evolved in the absence of I^-, and the amount of I_3^- produced by the oxidation of I^- was confirmed to be the stoichiometric amount to the evolved H_2 gas. The turnover number of the merocyanine dye molecule for H_2 produced was calculated

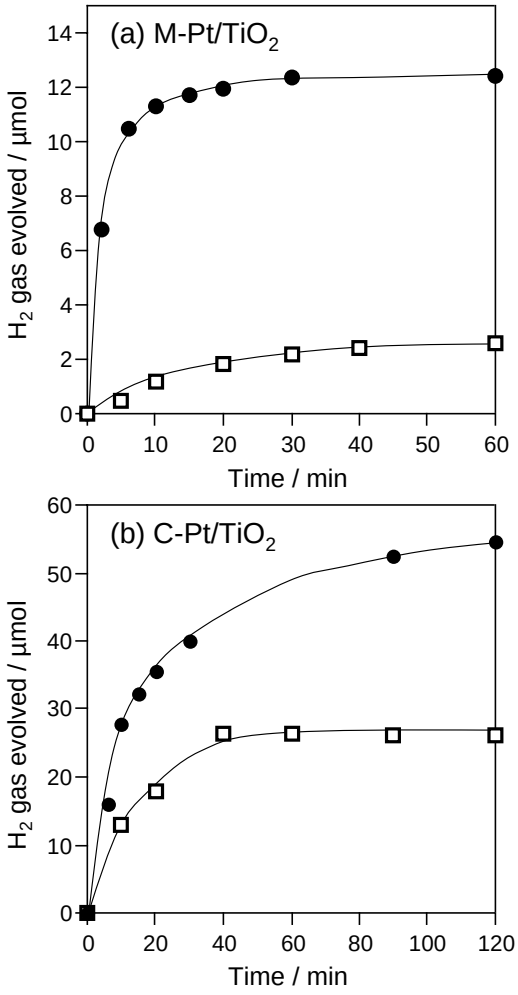

Fig. 3. H_2 evolution over (a) M-Pt/TiO_2 and (b) C-Pt/TiO_2 photocatalysts from a water–acetonitrile mixture (water, 5% by volume) including NaI (0.1 M) (●) and an aqueous NaI (0.1 M) solution (□) under visible light irradiation ($\lambda > 410$ nm).

to be about nine in the case of the reaction in water–AN mixture shown in Fig. 3(a). No change was observed in the absorption spectra of the photocatalysts before and after the reaction in the case of water–AN solution, whereas a little decrease in absorption was observed in the case of the water. No H_2 evolution was observed over Pt/TiO_2 without dye-adsorption under visible light ($\lambda > 410$ nm); this indicates that no direct photo-excitation of TiO_2 semiconductor had taken place. These results indicate that the following reactions took place in water–AN mixed solution under visible light irradiation; the numbers in parentheses corresponding to those in Fig. 1:

$$S + h\nu \rightarrow S^* \quad \text{(excitation of dye)} \tag{1}$$

$$S^* \rightarrow S^+ + e^-(CB)$$
(electron injection to conduction band of TiO_2) (2)

$$e^-(CB) \rightarrow e^-(Pt) \quad \text{(electron transfer to Pt)} \tag{3}$$

$$e^-(Pt) + H^+ \rightarrow \tfrac{1}{2}H_2 \quad (H_2 \text{ production on Pt}) \tag{4}$$

$$S^+ + I^- \rightarrow S + \tfrac{1}{2}I_2(\tfrac{1}{2}I_3^-)$$
(regeneration of dye ground state) (5)

As shown in Fig. 3, the rate of H_2 evolution decreased with the irradiation time, and the H_2 evolution was finally terminated in all cases. However, H_2 evolution was observed again by replacement of the solution to new one that containing no I_3^- but I^-. Furthermore, no H_2 evolution was observed when the photocatalytic reaction was initiated in the presence of I_3^- (I_3^-, 10 mM; I^-, 100 mM). It is thus presumed that the termination of H_2 evolution was not caused by the deactivation of the photocatalyst itself but by the competitive reduction of I_3^- instead of water on the reduction site (Pt) of the photocatalyst:

$$e^-(Pt) + \tfrac{1}{2}I_2(\tfrac{1}{2}I_3^-) \rightarrow I^-$$
(backward reaction of I_3^- to I^- on Pt) (6)

Because this backward reaction (scheme (6)) competitively proceeds with the reduction of water, H_2 evolution (scheme (4)) terminates when the concentration of I_3^- in the solution reaches a certain value, in other words, a quasi-equilibrium level under irradiation. After this, only the undesirable backward reaction ($I_3^- \rightarrow I^-$) proceeds over the photocatalyst.

In the both cases of M-Pt/TiO_2 and C-Pt/tiO_2, the amount of I_3^- produced by the oxidation of I^- was confirmed to be smaller than the stoichiometric amount to the evolved H_2 gas, when reaction was carried out in water containing 0.1 M of NaI. And the decrease in absorption spectra of the photocatalysts was observed after the reaction. These indicate that some side reactions were competitively taken place with the oxidation of I^- to I_3^- (scheme (5)). A part of the oxidized dye molecules possibly reacted with water and decomposed in aqueous solution:

$$S^+ + H_2O \rightarrow \text{decomposition product} \tag{7}$$

Actually, in the both case of M-Pt/TiO_2 and C-Pt/tiO_2, it was observed that the original color of the dyes gradually decreased after a long time irradiation in water, while they were stable in water–AN mixture.

3.2. Influence of the water ratio to acetonitrile (H_2O/AN) on H_2 evolution

Fig. 4 shows the rates of H_2 evolution over M-Pt/TiO_2 (merocyanine NK2045) and C-Pt/TiO_2 (coumarine C343) photocatalysts in the water–acetonitrile mixed solutions with different ratios of water to AN (5–100% by volume) under visible light irradiation ($\lambda > 410$ nm). The mixed solution contains 0.1 M of NaI as an electron donor. The rates of H_2 evolution over the M-Pt/TiO_2 (Fig. 4(a)) were significantly decreased with the increase of water ratio, and the rates were quite low in the range of water ratio over 50%. On the other hand, the influence of the water ratio to AN on H_2 evolution rate was not so marked over the C-Pt/TiO_2 and a relatively high rate of H_2 evolution was observed even in the 100% of water as shown in Fig. 4(b). The excited state (LUMO) levels of the dyes (merocyanine (NK2045): ca. −1.7 V, coumarin (C343): ca −1.6 V versus NHE at pH 7 in water) are almost the same and negative enough for the efficient electron injection to the conduction band level of TiO_2 (ca. −0.5 V versus NHE at pH 7). Actually, H_2 evolution proceeded over M−Pt/TiO_2 even in aqueous solution when EDTA, a sacrificial electron donor, was used instead of I^- as shown in Fig. 4(c). It was, therefore, speculated that the increase of the water ratio hindered the electron transfer process from I^- to oxidized dye (HOMO level), which is typically shown in Fig. 1 as the step 5. To investigate the influence of water to the electron transfer process, we car-

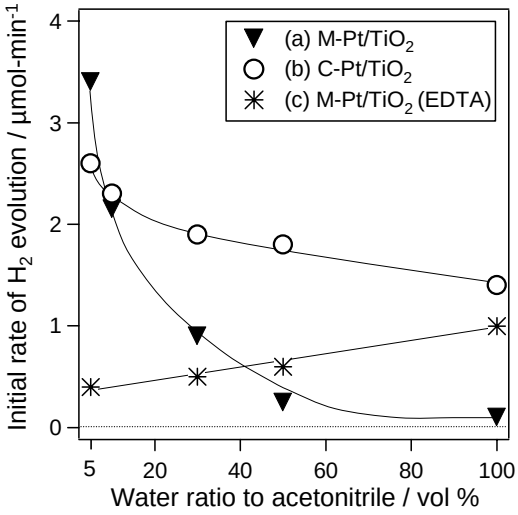

Fig. 4. Rates of H_2 evolution from mixtures with different ratios of water to acetonitrile (5–100% by volume) including 0.1 M of NaI over M-Pt/TiO_2 (a) and over C-Pt/TiO_2 (b), and that from water–acetonitrile mixture including 0.1 M of EDTA over M-Pt/TiO_2 (c).

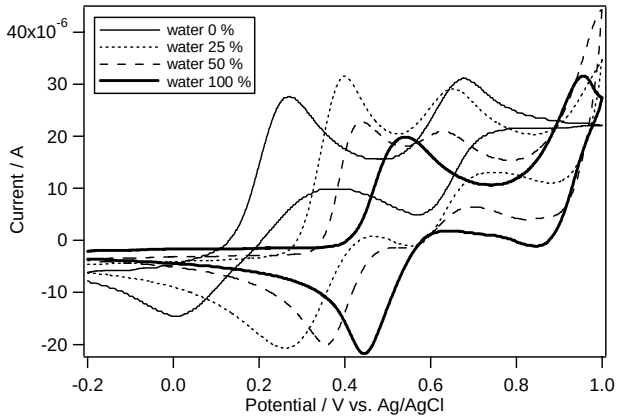

Fig. 5. Cyclic voltammograms of I_2 (1 mM)/NaI (10 mM) redox couple in water–acetonitrile mixtures (water ratio, 0–100% by volume) containing 0.1 M $LiClO_4$ as supporting electrolyte.

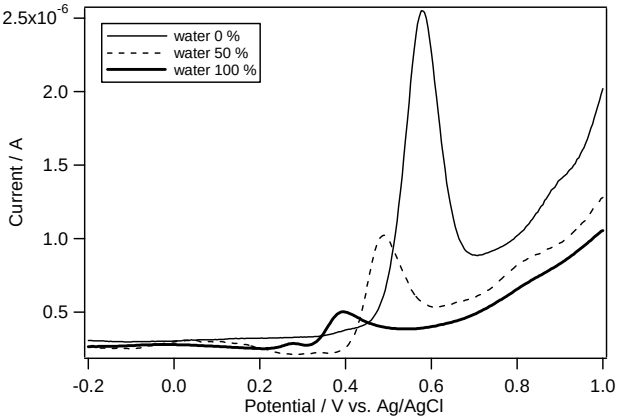

Fig. 6. Differential pulse voltammograms of merocyanine dye (NK2045, 1 mM) in water–acetonitrile mixture (water ratio, 0–100% by volume) containing 0.1 M $LiClO_4$ as supporting electrolyte.

ried out electrochemical measurement to determine redox potentials of I_3^-/I^- and dyes in water–AN mixed solution.

3.3. Changes in redox potentials of I_3^-/I^- and dyes in water–acetonitrile mixed solution

The cyclic voltammetry (CV) curves for an I_3^-/I^- redox couple (I_2−1 mM, NaI-10 mM) are shown in Fig. 5. The CV curve in an acetonitrile (water, 0%) displays two reversible oxidation peaks at 0.25 and 0.66 V (versus Ag/AgCl); corresponding to the oxidation of I^- to I_3^- ($3I^- \rightarrow I_3^- + 2e^-$) and that of I_3^- to I_2 ($2I_3^- \rightarrow 3I_2 + 2e^-$), respectively [18,19]. Two reversible oxidation peaks at 0.53 and 0.94 V are observed in water (water, 100%); the former one is corresponding to the oxidation of I^- to I_3^- ($3I^- \rightarrow I_3^- + 2e^-$) [19]. Judging from the much lower solubility of I_2 in water than in acetonitrile, the other one at 0.95 is probably due to not the oxidation of I_3^- to I_2 perhaps but the oxidation of I_3^- to IO_3^-. Concerning the oxidation peak of I^- to I_3^-, the peak position positively shifted with the increase of water ratio.

As shown in Fig. 6, the oxidation peak of merocyanine NK2045 was observed at 0.58 V (versus Ag/AgCl) in acetonitrile. Contrary to the case of the I_3^-/I^- redox couple, the peak position shifted negatively with the increase of water ratio. Similar trend, the negative shift of potential with the increase of water, was observed in the coumarin dye (C343).

Because we used a Ag/AgCl reference electrode containing KCl aqueous solution in water–AN mixed solutions, some liquid junction potentials might be introduced into the electrochemical measurements. To estimate the liquid junction potential produced between the reference electrode and the water–AN mixed solution, we carried out CV measurement of the ferricenium ion–ferrocene (Fc^+/Fc) redox couple that is generally used as a standard voltammetric reference. Fig. 7 shows the CV curves for an Fc^+/Fc redox couple. The peak position also negatively shifted with the increase of water ratio in analogy with those of the dyes.

3.4. Relationship between the change in redox potential and the H_2 evolution rates

The oxidation potentials of the I_3^-/I^- and the Fc^+/Fc determined by half-wave potential ($E_{1/2} = (E_{oxid} + E_{red})/2$) of CV profiles and those of the dyes determined by peak potentials (E_p) of DPV are plotted as a function of the water ratio in Fig. 8. It is clear that the oxidation potential of the I_3^-/I^- redox shifted positively, and HOMO level of the dyes shifted negatively with the increase of water ratio to AN. The shifts of both potentials of I_3^-/I^- redox and dyes in the other way causes a decrease in the energy gap (ΔG) between the I_3^-/I^- redox and the HOMO level of dyes with the increase of water ratio. The decrease of ΔG certainly causes the decrease of efficiency of electron transfer from I^- to oxidized dye, and results in a lower rate of H_2 evolution in a water-rich solution. It is considered that at least 0.2–0.4 V of ΔG is required for the efficient electron transfer from I^- to oxidized dye sensitizers [20]. Because the merocyanine dye (NK2045) possesses relatively negative HOMO level, the ΔG (≈0.4 V in acetonitrile) became quite small with the

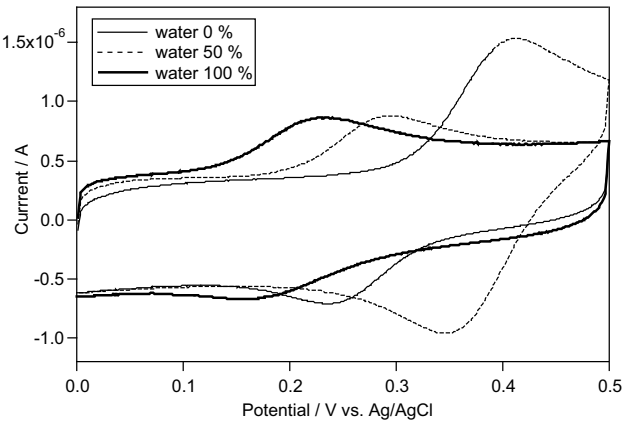

Fig. 7. Cyclic voltammograms of ferricenium ion–ferrocene (Fc^+/Fc) redox couple in water–acetonitrile mixtures containing 0.1 M $LiClO_4$ as supporting electrolyte.

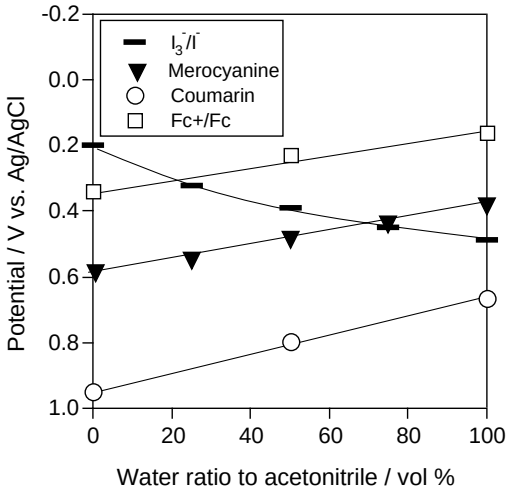

Fig. 8. Oxidation potentials (vs. Ag/AgCl) of merocyanine dye (NK2045), coumarin dye (C343), I_3^-/I^- redox couple and ferricenium ion–ferrocene (Fc^+/Fc) redox couple in water–acetonitrile mixtures.

increase of water ratio, and finally became 0 V at the water ratio around 70%. The small ΔG is certainly responsible for the low H_2 evolution rate over the M-Pt/TiO_2 photocatalyst in a water-rich solution. On the other hand, the ΔG between the I_3^-/I^- and the HOMO level of the coumarin (C343) is larger enough (≈0.8 V in acetonitrile) than the value generally required for the electron transfer from I^- to oxidized dye because the HOMO level is more positive than that of the merocyanine. Therefore, about 0.2 V of ΔG still exists between the I_3^-/I^- redox potential and the HOMO level of coumarin dye (C343) even in water. Consequently, the decrease in H_2 evolution rate with the increase of water ratio was not remarkable over C−Pt/TiO_2 and a relatively high rate of H_2 evolution was observed even in water (water, 100%) as shown in Fig. 4.

As shown in Fig. 7, the potential of Fc^+/Fc redox couple negatively shifted with the increase of water ratio in analogy with those of the merocyanine and coumarin dyes. This indicates that the negative shift of the dyes was observed because of the liquid junction produced between the reference electrode and water–AN mixed solutions. Therefore, we can conclude that the water–AN mixed solution significantly affected to the potential of I_3^-/I^- redox couple rather than to those of the dye molecules.

3.5. *Efficiency of dye-sensitized Pt/TiO_2 photocatalysts for H_2 evolution*

We examined the quantum efficiency for the H_2 evolution over M-Pt/TiO_2 and C-Pt/TiO_2 photocatalyst under the irradiation of monochromatic light at around the maximum adsorption wavelength of each dyes, 517 and 440 nm, respectively. The apparent quantum efficiencies in the water–AN mixed solution (water, 5% by volume) were 1.8% (at 517 nm) and 2.5% (at 440 nm) for M-Pt/TiO_2 and C-Pt/TiO_2, respectively. In spite of the lower quantum efficiency, M-Pt/TiO_2 exhibited higher rate of H_2 evolution than C-Pt/TiO_2 in the AN-rich solution (water, 5%) under the continuous irradiation ($\lambda > 410$ nm) as shown in Fig. 4, because M-Pt/TiO_2 can absorb wider range of visible light than C-Pt/TiO_2 as seen in Fig. 2. However, the efficiency over M-Pt/TiO_2 significantly decreased with the increase of water ratio. Consequently, C-Pt/TiO_2 exhibited higher rates of H_2 evolution than M-Pt/TiO_2 in the solution with water ratio from 10 to 100%. These results indicate that the consideration of the appropriate HOMO level of dye, not only the adsorption range in visible light of dye, is very important to design H_2 evolution over dye-sensitized photocatalyst using I^- electron donor in solutions containing water. As described in previous section, gradual degradation of dye molecule was observed over both M-Pt/TiO_2 and C-Pt/TiO_2 photocatalysts when reaction was carried out in aqueous solution. It is certainly due to the reaction between the oxidized dye and water molecule. From this point of view, the development of stable dye sensitizer molecules in water is also desirable.

3.6. *Suppressing the backward reaction from I_3^- to I^- using internally platinized $K_4Nb_6O_{17}$ with anionic framework*

As mentioned in a previous section, the H_2 evolution in this photocatalytic system is readily suppressed by competitive reduction of I_3^- to I^- in the solution as shown in Fig. 3. To solve this problem, we applied the strategy suggested by Saupe et al. [13], in which internally platinized layered materials such as $K_4Nb_6O_{17}$ were used to suppress the backward reaction (I_3^- to I^-) proceeding on the Pt metal. As shown in Fig. 9(a), $K_4Nb_6O_{17}$ consists of octahedral units of NbO_6 that form a two-dimensional layered structure via bridging oxygen atoms. The layers are negatively charged and K^+ cations exist between the layers to compensate for the negative charge of the layers. The layered materials $K_4Nb_6O_{17}$ and $H_4Nb_6O_{17}$ (protonic form) possess ion-exchange property that allows the intercalation of cationic species and small molecules such as H_2O, but not allows that of anionic species such as I_3^- because of electronic restitution between the anionic species and negative charge of the layers [13]. By using $K_4Nb_6O_{17}$ (or $H_4Nb_6O_{17}$) with Pt metal particles in the interlayer space, the reduction of water preferentially proceeds to the reduction of I_3^- because the reduction site, Pt metal, is spatially separated from the anionic species I_3^-. Conceptual scheme is shown in Fig. 9(b). We prepared some kinds of the platinized $H_4Nb_6O_{17}$ samples; introduction of Pt co-catalyst to only interlayer space Pt(in)/$H_4Nb_6O_{17}$, to both interlayer and external space Pt(in–ex)/$H_4Nb_6O_{17}$ and to only external space Pt(ex)/$H_4Nb_6O_{17}$. Then merocyanine dye (NK2045) samples were examined for H_2 production from water–AN solution (water, 5%) containing NaI under visible light irradiation. As shown in Fig. 10, the rate of H_2 evolution and the total amount of H_2 strongly depended on

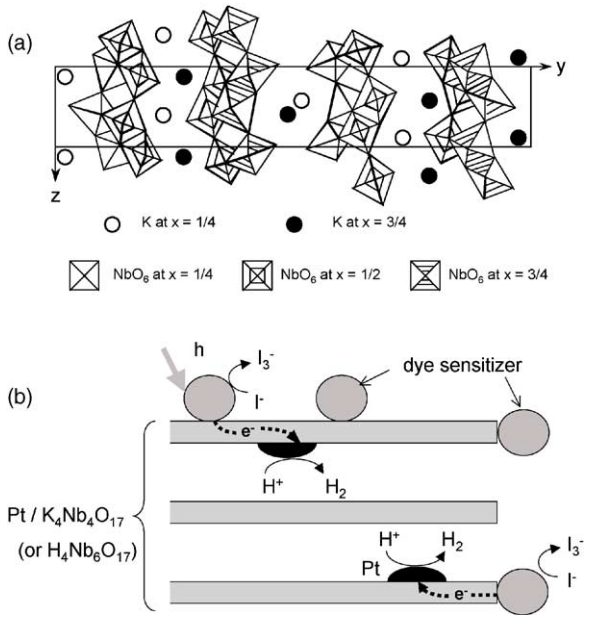

Fig. 9. Crystal structure of $K_4Nb_6O_{17}$ (a) and conceptual scheme of H_2 production from water over intertnally platinized $K_4Nb_6O_{17}$ semiconductor using I^- as an electron donor (b).

the Pt loaded site. The M-Pt(ex)/$H_4Nb_6O_{17}$ with Pt particles only at external space showed very low activity and the total amount of H_2 evolved was quite small. On the other hand, the M-Pt(in)/$H_4Nb_6O_{17}$ with internally sited Pt particles, exhibited high H_2 evolution rate. The H_2 evolution proceeded over M-Pt(in)/$H_4Nb_6O_{17}$ photocatalyst even after 70 μmol of H_2 was evolved, while the H_2 evolution terminated over M-Pt/TiO_2 when ca. 17 μmol of H_2 was evolved. These results clearly indicate that the internally platinized

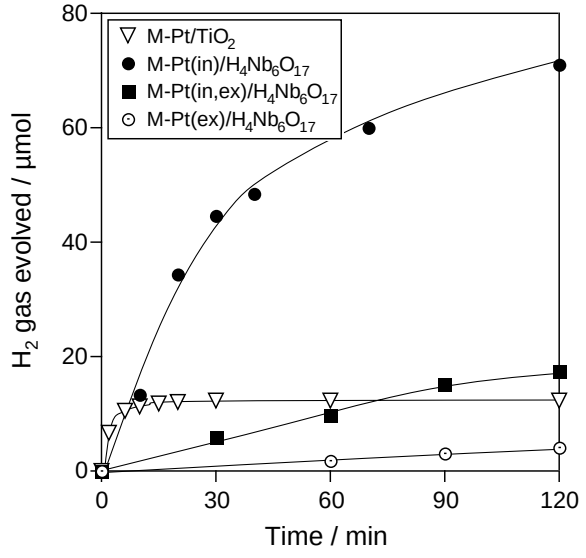

Fig. 10. H_2 evolution over merocyanine-sensitized Pt(in)/$H_4Nb_6O_{17}$, Pt(in–ex)/$H_4Nb_6O_{17}$, Pt(ex)/$H_4Nb_6O_{17}$ and Pt/TiO_2 photocatalysts from a water–acetonitrile mixture (water, 5% by volume) including NaI (0.1 M) under visible light irradiation (λ > 410 nm).

$H_4Nb_6O_{17}$ has ability to prevent the backward reaction, the reduction of I_3^- to a considerable extent. It should be noted that the M-Pt(in)/$H_4Nb_6O_{17}$ showed high initial H_2 evolution rate comparable to M-Pt/TiO_2 photocatalyst in spite of the much smaller amount of the dye molecules adsorbed on Pt(in)/$H_4Nb_6O_{17}$ (ca. 0.04 μmol/50 mg) than that on Pt/TiO_2 (ca. 4 μmol/50 mg).

4. Conclusion

We have demonstrated that an efficient H_2 production from water proceeds under visible light irradiation over merocyanine or coumarin dye-sensitized Pt/TiO_2 photocatalysts using a water–acetonitrile mixed solution including I^- as an electron donor. We have also found that the rate of H_2 evolution decreased with the increase of water ratio in the solution. From the results of electrochemical measurements, it was suggested that the decrease in H_2 production with the increase of water ratio is due to the decrease of energy gap (ΔG) between the I_3^-/I^- redox potential and the HOMO level of the dyes. Relatively a high rate of H_2 evolution was observed even in aqueous solution over the coumarin-sensitized Pt/TiO_2 photocatalyst because the coumarin dye possesses sufficiently positive HOMO level compared with the oxidation potential of I^-. However, some degradation of the dye molecules was observed in aqueous solution. It is necessary to take the influence of solvent on the energy potentials and the stability of dye molecules into account in constructing an efficient dye-sensitized photocatalysis system in aqueous solutions. Furthermore, we found that it is possible to prevent the backward reaction, reduction of I_3^- to I^- on Pt metal, by using the internally platinized semiconductor $H_4Nb_6O_{17}$ instead of Pt/TiO_2 in water–AN mixed solution.

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