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EFFICIENT HYDROGEN PRODUCTION FROM WATER BY VISIBLE LIGHT EXCITATION OF FLUORESCEIN-TYPE DYES IN THE PRESENCE OF A REDOX CATALYST AND A REDUCING AGENT

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A hydrogen production system for visible light without an electron relay, efficient in the high pH region, is constructed with some fluorescein derivatives in the presence of a redox catalyst and a sacrificial reducing agent.

For H_2 production from water with visible light, only a limited number of dyes such as $Ru(bipy)_3^{2+}$ and water soluble zinc porphyrins have been used as efficient photocatalysts.[1)] It is well studied that fluorescein and its halogenated derivatives are photo-reduced in the presence of a reducing agent, forming very stable semi-reduced radicals in high pH region.[2-8)] Here, we report that these dyes also serve as efficient photocatalysts in the presence of triethanolamine(TEOA) as a reducing agent by making use of a high reducing power of the semi-reduced radicals, i.e., these radicals can reduce water to produce H_2 with the aid of platinum catalyst. The absorption peaks of these dyes in the visible region are situated at around 500 nm.

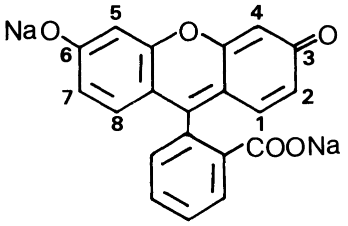
As the redox catalyst, platinized TiO_2 powder or colloidal Pt was used. Pt was deposited photochemically on the surface of TiO_2 powder (4 wt%, Aerosil P-25, average grain size 300 Å),[9)] and the colloidal Pt catalyst was stabilized with polyvinylpyrrolidone(PVP).[10)] H_2 was detected by a mass spectrometer and a manometer, as described previously.[11)] When an aqueous solution of each dye (5×10^{-3}M, 10 ml, pH= 12.5 adjusted with NaOH) in the presence of Pt/TiO_2 (0.3 g) and TEOA (5×10^{-1}-10^{-2}M) was irradiated with visible light from a 500 W Xe lamp filtered with a 460 nm cutoff glass filter, the H_2 gas produced was observed as streams of bubbles in a 280 ml Pyrex glass bulb. In Table 1 are shown the initial rates of H_2 production in these systems. When D_2O was used instead of H_2O, D_2 was 79% of the produced H_2 gas, DH 19% and H_2 2%. This result suggests that H_2 is produced from water.

These systems are so-called two-component systems, i.e., electron relay free systems.[12,13,14)] The most efficient system was obtained with dibromofluorescein and the H_2 production rate was 7.1 ml/h with the visible light. In a recent study,[15] we determined the quantum efficiency of H_2 production in $Ru(bipy)_3^{2+}$-Pt/TiO_2 system to be $1.7x10^{-3}$. This corresponded to a rate of H_2 production of 0.10 ml/h under the visible light illumination. The spectral profile of the present system is similar to that of $Ru(bipy)_3^{2+}$ system, so that from the rate of the production of 7.1 ml/h, we can infer a quantum efficiency of about 0.1. This value is almost equal to that of one of the most efficient three-component systems, $Ru(bipy)_3^{2+}$-methylviologen(MV^{2+})-collodial Pt in the presence of ethylene-diamine-tetra-acetic acid (EDTA), 0.13.[16]

Table 1. Initial Rates of H_2 Production

Dye	Initial rate of H_2 production (ml/h)
(a) fluorescein	0.5
(b) gallein	0.0
(c) dichlorofluorescein	1.2
(d) dichlorofluorescein diacetate	1.4
(e) dibromofluorescein	7.1
(f) mercurochrome	2.3

dye ($5x10^{-3}$M), Pt/TiO_2 (0.3g), TEOA (10^{-1}M), pH=12.5, visible light (λ>460nm) from a 500 W Xe lamp.



(a) fluorescein Na salt
(b) 4,5 : OH
(c) 2,7 : Cl
(d) 2,7 : Cl, 3,6 : $OCOCH_3$
(e) 4,5 : Br
(f) 2,7 : Br, 5 : HgOH

Although the system with Pt/TiO_2 was efficient and the results reproducible, collodial Pt also served as the reducing catalyst. Consequently, these two-component systems are quite different from those based on the dye sensitization of a semiconductor. For instance, in the system $Ru(bipy)_3^{2+}$-Pt/TiO_2 and EDTA, the existence of TiO_2 is indispensable for H_2 production.[15] Moreover, the H_2 production rates increase with heavier halogen substitution, indicating a heavy atom effect on the intersystem crossing. It is known that these fluorescein-type dyes in alkaline aqueous solution are photo-reduced in the presence of a reducing agent via the lowest triplet states and form very stable semi-reduced dyes.[2-8] By taking these facts into account, we assume the following reaction scheme for this H_2 production reaction

$$\text{Dye} \xrightarrow{h\nu} {}^1\text{Dye*} \qquad \text{(excitation)} \qquad (1)$$

$$ {}^1\text{Dye*} \longrightarrow {}^3\text{Dye*} \qquad \text{(intersystem crossing)} \qquad (2)$$

$$^{3}\mathrm{Dye}^{*} + \mathrm{Red} \longrightarrow \mathrm{Dye}^{\overset{-}{\cdot}} + \mathrm{Red}^{\overset{+}{\cdot}} \quad \text{(formation of semi-reduced dye)} \qquad (3)$$

$$\mathrm{Red}^{\overset{+}{\cdot}} \longrightarrow \text{decomposition} \qquad (4)$$

$$\mathrm{Dye}^{\overset{-}{\cdot}} + H_2O \xrightarrow[\mathrm{Pt}]{} \mathrm{Dye} + 1/2\ H_2 + OH^- \quad (H_2 \text{ production}) \qquad (5)$$

This reaction is analogous to that of other two-component systems without an electron relay such as $\mathrm{Ru(bipy)}_3^{2+}$-PtO_2,12) proflavine-Pt/PVA13) and chromium(III) complexes-Pt/PVA14) in the presence of triethylamine, EDTA or TEOA, and EDTA, respectively. However, H_2 production for dibromofluorescein is more efficient than it is in other relatively stable two-component systems. For instance, the rate for dibromofluorescein is several times larger than that for proflavine. The quantum efficiency for the chromium complexes is almost the same as for dibromofluorescein, but the turn-over number of chromium complexes is very small, about 4.14) Another characteristics of this system is the fact that the reaction is efficient in the high pH region, since the semi-reduced dyes are stable in alkaline solution. A comparison of this system with others is summarized in Table 2. However, the reaction rate decreases gradually over long time irradiation. The turn-over number of dibromofluorescein obtained at present is about 100, but this value might be improved with a choice of better conditions.17)

Table 2. Comparison of the Characteristics of H_2 Production Systems.

Dye	Absorption peak (nm)	Electron relay	Redox catalyst	H_2 production(a) rate (ml/h)	pH	Reducing agent
dibromo-fluorescein	508	——	Pt-PVP	7.1	12.5	TEOA
proflavine (b)	445	——	Pt-PVP	2.4	7.0	TEOA
$\mathrm{Ru(bipy)}_3^{2+}$ (c)	452	MV^{2+}	Pt-PVP	2.9 18)	5.0	EDTA
$\mathrm{Ru(bipy)}_3^{2+}$ (d)	452	——	Pt-TiO_2	0.1	5.0	EDTA

(a) Visible light from a 500 W Xe lamp filtered with a 460 nm cutoff filter for the dibromofluorescein system, a 390 nm filter for the proflavine system and a 440 nm filter for the $\mathrm{Ru(bipy)}_3^{2+}$ systems, respectively. (b), (c) The experimental conditions were chosen as same as those of reference 13) and 16), respectively. (d) Dye sensitized Pt/TiO_2 system.15)

By making use of a high reducing power of the semi-reduced dye, we constructed a relatively efficient photogalvanic cell <semiconductor or Pt (light)|dibromofluorescein, TEOA|Pt (dark)> in which the open voltage was about 800 mV and the short circuit current was about 40 $\mu A/cm^2$.[17)]

Because of the long-lived nature of the semi-reduced intermediate species, these dyes play the role of both photocatalysts and electron relays in three-component systems. It is well known that stable semi-reduced dyes can also be formed in the presence of ethanol, 2-propanol or phenol,[4,6)] so that these organic compounds might be albe to serve as reducing agents for H_2 production. In fact, we have produced H_2 in the presence of ethanol instead of TEOA, although the production rate was small (0.11 ml/h).[17)]

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18) The hydrogen production efficiency is rather small compared to that of the literature,[16)] probably because of the particle size effect of Pt colloid on the H_2 production efficeincy as was reported by J. Kiwi and M. Grätzel, Nature, 281, 657 (1979).

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