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Dye-sensitized H_2 Evolution over TiO_2 and SnO_2 Nanoparticles Depending on Electron Donors

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Combination of porphyrin dyes as a sensitizer with a SnO_2 semiconductor electrode enables alcohols to be used as an electron donor, producing H_2.

Dye-sensitization is a promising strategy for giving visible-light response to wide-band-gap semiconductors with absorption only in ultraviolet region.[1] One of the most remarkable achievements by using dye-sensitization can be found as a dye-sensitized solar cell (DSSC) developed by Grätzel et al.[2] Dye-sensitized semiconductors can also be applied to photocatalysts for hydrogen evolution under visible light, as can be found on H_2-evolution photocatalysts consisting of a dye-sensitized semiconductor as a main light antenna.[3]

Ru complexes have been selected as a sensitizing dye of TiO_2 due to their broad absorption and stability. For example, Ru(II) bipyridyl dyes (e.g., $(n\text{-}Bu_4N)_2[cis\text{-}Ru(dcbpy)_2(SCN)_2]$ (N719 dye), $[Ru(bpy)_2(him)_2]NO_3$, and $[Ru(bpy)_4(L)_1]PF_6$) have been demonstrated to sensitize TiO_2.[4] But, this series of dye should be replaced with organic dyes due to the limited amount of Ru present on the earth.

Organic dyes are artificially designed to possess absorption spectra suitable to the sunlight and high molar extinction coefficients. In fact, xanthene dyes (e.g., eosin Y, merbromine, rhodamine B, and rhodamine 6G),[5] and merocyanine dye[6] have been used as sensitizers of TiO_2 for the H_2 evolution. Also, TCPP (tetrakis(4-carboxyphenyl)porphyrin) and TPPS (tetrakis(4-sulfonatophenyl)porphyrin)) are typical porphyrins which were attempted as the sensitizers,[7] since these have very intense absorption bands in the visible region.

Selection of an electron donor is also critical in H_2 evolution. Many kinds of the donor compounds were employed such as triethanolamine (TEOA),[3,5,7] ethylenediaminetetraacetic acid (EDTA),[7,8] iodide (I^-),[6,9] and acetonitrile[10] in the production of H_2 on dye-sensitized TiO_2. But they are often non-practical due to high cost, high-energy-consuming production, and environmental issues.

Now ethanol is a good candidate as an electron donor among alcohols, methanol (MeOH)[4] and ethanol (EtOH),[11] because it can be produced through bioprocesses. This paper reports on a dye-sensitized SnO_2 photocatalyst for H_2 evolution which enables ones to use ethanol as an electron donor.

Photocatalysis reaction experiments for H_2 evolution were carried out in a sealed quartz cell under a Xe lamp irradiation with a cutoff filter ($\lambda < 390$ nm cut, UV-39, TOSHIBA) as a visible light source. Typically, semiconductor nanoparticles (TiO_2 or SnO_2) photoloaded with Pt (0.3 wt %) were soaked into a methanol solution of dyes, TCPP or TPPS, giving the dye-sensitized Pt-loaded semiconductor nanoparticles (Supporting Information (SI); Figure S1[13]). The nanoparticles were dispersed in an aqueous electron donor solution under Ar atmosphere and irradiated. The photocatalytic activity was determined by measuring the concentrations of produced H_2 in the reaction vessel by a gas chromatography.

Table 1. H_2 productions after 3 h irradiation in the presence of various semiconductor–dye–donor systems[a]

Donor	H_2/µmol			
	TiO_2		SnO_2	
	TCPP	TPPS	TCPP	TPPS
TEOA	9.23	8.43	0	0
MeOH	0	0	6.86	5.98
EtOH	0	0	6.21	4.76
2-PrOH	0	0	4.14	2.89

[a]Reaction conditions: 2.5 mL donor aqueous solution; 0.0025 g dye-sensitized Pt-loaded semiconductor particles; light source: 150 W Xe lamp; irradiation wavelength: $\lambda > 390$ nm; irradiation time: 3 h; Ar saturated.

Table 1 shows the results of H_2 production over the dye-sensitized Pt/semiconductor nanoparticles. As can be seen, not all systems used here showed obvious photosensitization on H_2 evolution. Interestingly, when TCPP or TPPS was used as a dye in the case of TiO_2, only TEOA was the efficient donor, showing obvious photosensitization on H_2 evolution. TCPP–TiO_2–Pt in TEOA showed the highest H_2 evolution rate. When MeOH, EtOH, or 2-propanol (*i*-PrOH) was used as an electron donor, H_2 was not produced at all therein. On the contrary, in the case of SnO_2 used as a semiconductor, the opposite results were obtained for TEOA and alcohol as an electron donor for the photocatalytic H_2 evolution. TEOA was not the efficient donor, showing no photosensitization on H_2 evolution. But when MeOH, EtOH, or *i*-PrOH was used as an electron donor, H_2 was obtained in these systems. It should be noticed that SnO_2 is the efficient semiconductor for the photocatalyst, while TiO_2 does not act as a good semiconductor for the system, especially when alcohols and porphyrin dyes are employed as an electron donor and a sensitizing dye, respectively. And dye-sensitized Pt–SnO_2 acted as a stable photocatalyst in alcohol in photocatalytic reactions (Figures S2 and S3[13]). No H_2 evolution was observed for the present systems without the dye or light irradiation.

Photofluorescence spectra of each sensitizing dye, TCPP and TPPS, in a solution under the presence and the absence of TiO_2 or SnO_2 colloids were measured to study the luminescence quenching processes. The semiconductor colloidal suspension in water was prepared by sonication for more than 30 min. The fluorescence spectra of all solutions were collected in a 1 cm-quartz-cell under photoexcitation (F7000, Hitachi, Japan). The specific amount of the semiconductor suspension was succes-

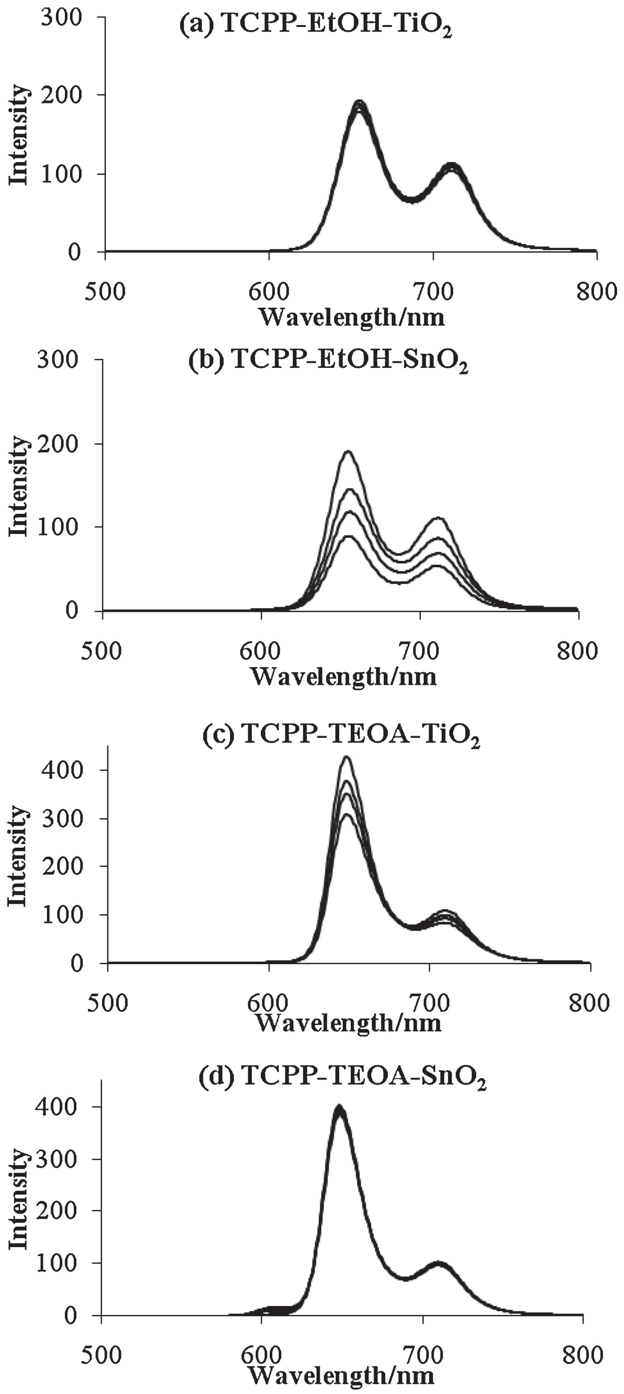

Figure 1. Fluorescence spectra of TCPP in EtOH in the presence of colloidal TiO_2 (a) and SnO_2 (b) and TCPP in TEOA in the presence of colloidal TiO_2 (c) and SnO_2 (d). The concentrations of the colloid were 0, 1×10^{-4}, 2×10^{-4}, and $4 \times 10^{-4}\,M^{-1}$. The excitation wavelengths were 410 (for TCPP) and 415 nm (for TPPS), respectively.

sively added dropwise into the dye solution and then the fluorescence spectra were measured at room temperature after waiting for 5 min with Ar bubbling to reach equilibrium.

Figure 1 shows the effect of the colloid on the fluorescence spectra of the dyes. In TCPP–EtOH solution, the intensity of the fluorescence emission decreased depending on the increased concentrations of colloidal SnO_2, exhibiting a typical quenching behavior. On the other hand, when TiO_2 was dropped into TCPP–EtOH solution, the intensity of the fluorescence changed only slightly, showing no quenching. On the contrary, we observed typical fluorescence quenching when colloid SnO_2 was dropped into TCPP–EtOH solution, but no quenching for TCPP–TEOA solution. Kamat observed the quenching of the fluorescence of organic compounds with carboxy groups and attributed it to the electron transfer from the excited state of the compounds to the semiconductor nanoparticles through the carboxylic groups.[12] Therefore, it is concluded that an electron transfer proceeds between the excited TCPP molecule and the CB of SnO_2 in the presence of ethanol, but no electron transfer between the excited TCPP molecule and the CB of TiO_2 does.

We examined the adsorption of the dye molecules on the semiconductor nanoparticles in the systems used for the photocatalysis reaction and the photofluorescence quenching experiments. When the dye-sensitized TiO_2 or SnO_2 particles were dispersed into the MeOH or TEOA solutions, the dyes on the particles surfaces were desorbed into the solutions immediately, and the adsorption and desorption processes reach to their equilibrium. Even after reaching to the equilibrium, TCPP-sensitized TiO_2 particles still possessed the amount of TCPP adsorbed on TiO_2 surface as $0.94 \times 10^{-6}\,mol\,g^{-1}$ in TEOA and $1.94 \times 10^{-6}\,mol\,g^{-1}$ in MeOH. TCPP-sensitized SnO_2 particles still possessed the amount of TCPP adsorbed on TiO_2 surface as $0.79 \times 10^{-6}\,mol\,g^{-1}$ in TEOA and $1.28 \times 10^{-6}\,mol\,g^{-1}$ in MeOH. Therefore, the electron transfer between the excited dye in the adsorption state and the semiconductor nanoparticles should be controlled by the coexisting molecules added as the electron donors to the systems.

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13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.