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Citation	Chemical Communications, 24, 3577-3579 <a href="https://doi.org/10.1039/b905935k">https://doi.org/10.1039/b905935k</a>
Issue Date	2009-06-28
Doc URL	<a href="http://hdl.handle.net/2115/43142">http://hdl.handle.net/2115/43142</a>
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Type	article (author version)
File Information	CC24_3577-3579.pdf



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# Robust Dye-sensitized Overall Water Splitting System with Two-step Photoexcitation of Coumarin Dyes and Metal Oxide Semiconductors

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Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

First published on the web Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

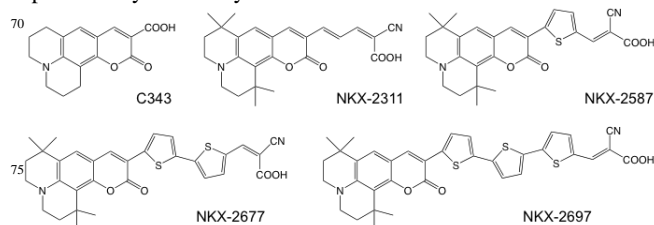
**Photocatalytic splitting of water into H<sub>2</sub> and O<sub>2</sub> under visible light irradiation is achieved using a coumarin dye-adsorbed lamellar niobium oxide for hydrogen evolution.**

Water splitting using semiconductor photocatalysts has been extensively studied as a candidate for hydrogen (H<sub>2</sub>) production using solar energy. Although many photocatalysts that work efficiently under ultraviolet (UV) irradiation have been developed, only a few visible light responsive photocatalysts have been reported for overall water splitting, *i.e.*, the simultaneous production of H<sub>2</sub> and O<sub>2</sub>.<sup>1-3</sup> The difficulty in achieving overall water splitting using visible light is primarily due to the difficulty in tuning the band levels of inorganic, especially oxide, semiconductor photocatalysts. Scaife pointed out in 1980 that it is intrinsically difficult to develop an oxide semiconductor photocatalyst having both a sufficiently negative conduction band level for H<sub>2</sub> production and a narrow band gap allowing visible light absorption, because of the deeply positive level of the valence band formed by the O-2p orbital.<sup>4</sup> Recent studies have therefore focused on the hybridization of the O-2p with other orbital such as N-2p (*e.g.* oxynitrides),<sup>1</sup> as well as the construction of two-step photoexcitation systems<sup>2,3</sup> using shuttle redox mediators such as IO<sub>3</sub><sup>-</sup>/I<sup>-</sup>. On the other hand, various organic dyes, including Ru-complexes, have shown to possess both a sufficiently negative energy level (LUMO) for H<sub>2</sub> production as well as visible light absorption.<sup>5</sup> Furthermore, fine-tuning of energy levels (HOMO and LUMO) of organic dyes is much easier compared to oxides, as has been shown for dye-sensitized solar cells.<sup>6</sup> However, such a simple dye molecule by itself cannot oxidize water into O<sub>2</sub>. The evolution of O<sub>2</sub> from water, which requires the abstraction of four electrons, is hard for the simple dye molecules. Although non-sacrificial H<sub>2</sub> production using a combination of a dye-sensitized photocatalyst with a reversible iodine redox mediator (I<sub>3</sub><sup>-</sup>/I<sup>-</sup>) has been demonstrated,<sup>7</sup> overall water splitting using a dye-sensitized photocatalyst has not yet been achieved in an aqueous solution, possibly due to the lack of stability of the dye molecule, especially in its oxidized state.

The present paper reports the first example of overall water splitting under visible light using a simple organic dye as a photosensitizer for the H<sub>2</sub> production part. We found that coumarin dyes with an oligo-thiophene moiety between the donor and acceptor parts show reversible oxidation-reduction cycles stably even in an aqueous solution. These dyes can be used as stable photocatalysts for stoichiometric production of H<sub>2</sub> and triiodide (I<sub>3</sub><sup>-</sup>) from an aqueous solution containing an

iodide (I<sup>-</sup>) electron donor when combined with an internally platinumized layered niobium oxide (Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>) semiconductor.<sup>7</sup> Overall water splitting was then achieved by combining the coumarin dye-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> with tungsten oxide (WO<sub>3</sub>) photocatalyst, which can reduce I<sub>3</sub><sup>-</sup> back to I<sup>-</sup> accompanied by the oxidation of water into O<sub>2</sub> under visible light irradiation.

A coumarin dye (C343) was purchased from Aldrich. Other coumarin dyes (NKX series)<sup>6-a</sup> were provided by Hayashibara Biochemical Laboratories, Inc. Japan. The molecular structures are shown in Fig. 1. These dye were adsorbed on the surface of internally platinumized potassium niobate (Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>), which was prepared by the previously reported method.<sup>7-c</sup> The Detailed preparation procedures of coumarin dye-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalyst and IrO<sub>2</sub>-Pt/WO<sub>3</sub> photocatalyst, are provided in the supporting information, with other experimental conditions for photocatalytic activity test and electrochemical measurements.

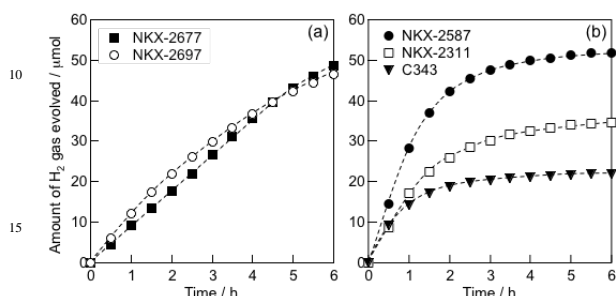


**Fig. 1** Molecular structures of coumarin dyes

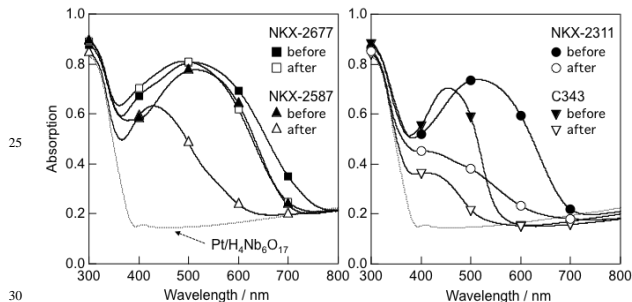
Fig. 2 shows the time course of H<sub>2</sub> evolution over coumarin dye-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalysts suspended in aqueous potassium iodide (KI) solution under visible light irradiation. Steady H<sub>2</sub> evolution proceeded over the NKX-2677 and NKX-2697 dye-adsorbed photocatalysts (Fig. 2-a), and nearly the same amount of I<sub>3</sub><sup>-</sup> anion as H<sub>2</sub> gas was detected in the solutions after the reaction in both cases (*e.g.*, H<sub>2</sub>: 48 μmol; I<sub>3</sub><sup>-</sup>: 47 μmol for NKX-2677). The molar amount of evolved H<sub>2</sub> exceeded the amount of the dye molecules contained in 50 mg of photocatalyst powder (NKX-2677: ca. 0.55 μmol; NKX-2697: ca. 0.52 μmol). The diffuse reflectance spectra for these photocatalysts after the reaction was found to be almost the same as before the reaction, except for a slight shift of the absorption edge to a shorter wavelength, as shown in Fig. 3-a (spectra of NKX-2697 are shown in Fig. S1). This shift is attributable to the change in alignment of the dye molecules on the surface of the Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> semiconductor during the stirring in the aqueous solution rather than to the decomposition of dye molecules, because a similar shift was also observed when the photocatalysts were stirred in an aqueous KI solution in the

dark. The findings indicate that the following reactions took place over the NKX-2677 and NKX-2697 dye-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalysts under visible light irradiation:

- (1)  $S + h\nu (\lambda > 400 \text{ nm}) \rightarrow S^*$  (excitation of dye)
- (2)  $S^* \rightarrow S^+ + e^-$  (electron injection to H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub>)
- (3)  $e^- + H^+ \rightarrow 1/2 H_2$  (H<sub>2</sub> production on Pt)
- (4)  $S^+ + \Gamma^- \rightarrow S + 1/2 I_2$  (1/2 I<sub>3</sub><sup>-</sup>) (regeneration of dye)



**Fig. 2** Time course of photocatalytic H<sub>2</sub> evolution by coumarin dye-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalysts (50 mg) suspended in a 0.1 M aqueous KI solution (100 mL) under visible light ( $\lambda > 400 \text{ nm}$ ).

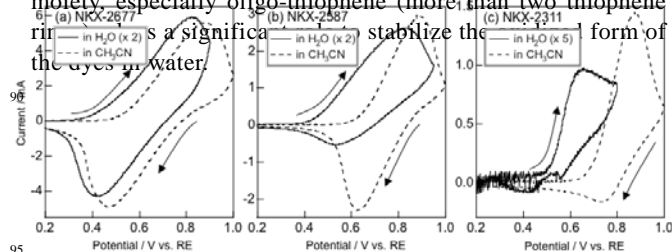


**Fig. 3** Diffuse reflectance spectra of coumarin dye-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalysts before and after the reaction in Fig. 2.

On the other hand, the rate of H<sub>2</sub> production gradually decreased with irradiation time in the case of other coumarin dyes (C-343, NKX-2311, and NKX-2587), as shown in Fig. 2-b, while the rates of H<sub>2</sub> production were relatively high in initial period. The molar amount of liberated I<sub>3</sub><sup>-</sup> was smaller than the amount of H<sub>2</sub> evolved in each case (*e.g.*, H<sub>2</sub>: 32 μmol; I<sub>3</sub><sup>-</sup>: 25 μmol for NKX-2311). The diffuse reflectance spectra of these dyes changed significantly by the reaction, as shown in Fig. 3. Such a significant change was not observed when the photocatalysts were stirred in the dark, indicating that the change in the spectra was caused by photochemical processes and not by physical processes such as desorption of dye molecules from the Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> surface. It is likely that the oxidized state (S<sup>+</sup>) of these dyes reacted with water before accepting an electron from the  $\Gamma^-$  anions and then became photo-inactive species. It is to be noted that the rate of H<sub>2</sub> evolution was negligibly low when the collected photocatalyst powder was irradiated again in a fresh KI solution, while in the case of NKX-2677 and NKX-2697, the dyes exhibited almost the same rate of H<sub>2</sub> production again.

To examine the stability of the dye molecules in the aqueous solution, the oxidation and reduction behaviors of these dyes were analyzed by cyclic voltammetry (CV) in both

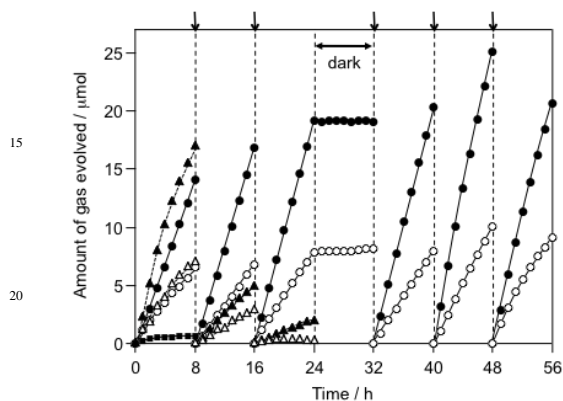
aqueous and acetonitrile (AN) solutions. Since these dyes, except for C-343, are barely soluble in an aqueous solution with a neutral pH, the CV measurements were carried out using nano-porous TiO<sub>2</sub> electrodes with the dyes adsorbed on them.<sup>6-c</sup> Fig. 4 shows the CV profiles of NKX-2311, NKX-2587, and NKX-2677 in water or dehydrated AN solution containing 0.1 M of LiClO<sub>4</sub> as a supporting electrolyte (CV curves of NKX-2697 are shown in Fig. S2). In all cases, a current peak was observed with an applied anodic potential above +0.4 V (vs. reference), which indicates oxidation of the dye molecule into an oxidized state (S<sup>+</sup>). On the other hand, the reduction behavior strongly depended on the structure of the dye molecule. In the case of NKX-2677, a reversible current peak was observed during the reversed cathodic scanning in both solvents, indicating that the oxidized state (S<sup>+</sup>) possesses a relatively long lifetime even in water and can be reduced back to the original state by accepting an electron during cathodic potential sweep (Fig. 4-a). Such a reversible oxidation-reduction behavior of NKX-2677 and NKX-2697 was observed even in repeated CV scanning several times. Although this reversible behavior was observed for NKX-2587 in AN, the reduction current peak was much lower than the oxidation peak in water (Fig. 4-b). In the case of NKX-2311, the reduction current peak was much lower than the oxidation peak even in AN, and no reduction peak was observed in water (Fig. 4-c). These results indicated that the oxidized state of these dyes (NKX-2311, NKX-2587) reacted with the H<sub>2</sub>O molecules irreversibly and formed inactive species, as suggested by the results of the photocatalytic reactions (Fig. 2 and 3). Considering molecular structure of the coumarin dyes used, it is concluded that a thiophene moiety, especially oligo-thiophene (more than two thiophene rings), is a significant factor to stabilize the oxidized form of the dyes in water.



**Fig. 4** CV curves of coumarin dyes adsorbed on a porous TiO<sub>2</sub> electrode in a dehydrated acetonitrile (AN) or aqueous solution containing 0.1 M of LiClO<sub>4</sub> as a supporting electrolyte: the scan rate was 100 mV s<sup>-1</sup>. Ag/AgCl in saturated aqueous NaCl solution and Ag/Ag<sup>+</sup> in 0.01 M AgNO<sub>3</sub> acetonitrile solution were used as a reference electrode in aqueous and AN solutions, respectively.

Overall water splitting under visible light was then attempted by combining the dye-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalyst with the WO<sub>3</sub> photocatalyst for O<sub>2</sub> evolution.<sup>2</sup> In the present study, IrO<sub>2</sub> and Pt co-loaded WO<sub>3</sub> photocatalyst (IrO<sub>2</sub>-Pt/WO<sub>3</sub>) was applied to achieve steady O<sub>2</sub> evolution in the presence of the I<sub>3</sub><sup>-</sup> anion in aqueous KI solution. It was found that the IrO<sub>2</sub>-Pt/WO<sub>3</sub> showed better activity for O<sub>2</sub> evolution than Pt/WO<sub>3</sub> in the presence of I<sub>3</sub><sup>-</sup> in KI solution.

As shown in Fig. 5, the combination of NKX-2677-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> and IrO<sub>2</sub>-Pt/WO<sub>3</sub> yielded simultaneous H<sub>2</sub> and O<sub>2</sub> evolution in an almost stoichiometric ratio. The reaction proceeded without appreciable deactivation even after 48-h photoirradiation. The total amount of evolved H<sub>2</sub>, ca. 116 μmol, exceeded the amount of dye molecules adsorbed on Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (ca. 0.55 μmol). It is to be noted that no gas evolution was observed in darkness (the 4<sup>th</sup> run). Also, no H<sub>2</sub> evolution was observed when only IrO<sub>2</sub>-Pt/WO<sub>3</sub> was irradiated in KI solution.



**Fig. 5** Time courses of photocatalytic evolution of H<sub>2</sub> (closed) and O<sub>2</sub> (open) using a mixture of coumarin dye-adsorbed (circles: NKX2677, triangles: NKX 2587, square: NKX2311) Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> (50 mg) and IrO<sub>2</sub>-Pt/WO<sub>3</sub> (100 mg) suspended in a 5 mM of KI aqueous solution under visible light ( $\lambda > 400$  nm). Arrows indicate evacuation of gas phase.

These results demonstrate that overall water splitting proceeded with a two-step photoexcitation combined with a redox cycle between I<sub>3</sub><sup>-</sup> and I<sup>-</sup>. The first step involves water reduction to H<sub>2</sub> and I<sup>-</sup> oxidation to I<sub>3</sub><sup>-</sup> over NKX-2677-adsorbed Pt/H<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalyst, and the second step involves I<sub>3</sub><sup>-</sup> reduction to I<sup>-</sup> and water oxidation to O<sub>2</sub> over IrO<sub>2</sub>-Pt/WO<sub>3</sub>. Steady and simultaneous H<sub>2</sub> and O<sub>2</sub> evolution was also achieved by using NKX-2697, which has three thiophene rings (Fig. S3). On the other hand, the rate of gas evolution using NKX-2587, which has one thiophene ring, drastically decreased with prolonged irradiation time. In the case of the NKX-2311 dye, which has no thiophene ring, only a small amount of H<sub>2</sub> was evolved in the initial period. These results again indicate that the oligo-thiophene moiety in the coumarin dyes plays an essential role to stabilize dye molecules during photocatalytic overall water splitting. One possible explanation for the necessity of the poly-thiophene unit is that the positive charge of the oxidized dye is delocalized over the oligo-thiophene moiety and its reactivity toward H<sub>2</sub>O is lowered, while the positive charge can accept an electron from the I<sup>-</sup> anion regenerating the original ground state of the dye. We have examined the effect of light irradiation on the dyes adsorbed on nanocrystalline TiO<sub>2</sub> films under ambient conditions and found that the dyes, not only coumarin dyes, containing an oligothiophene moiety showed higher stability compared to those without oligothiophene moiety.<sup>8</sup> The transient absorption spectroscopy have strongly suggested that the positive charge in such dye located on the

oligo-thiophene moiety.<sup>8</sup> The results in stability test under ambient condition have also suggested that the dyes with oligo-thiophene moiety have durability to O<sub>2</sub> molecules, not only to H<sub>2</sub>O. Actually, H<sub>2</sub> production stably proceeded over NKX-2677 dye-sensitized photocatalysts even when the reaction was initiated in the presence of considerable amount of O<sub>2</sub> in gas phase (e.g., 200 μmol of O<sub>2</sub>).

In summary, dye-sensitized overall water splitting under visible light irradiation was demonstrated for the first time using a simple organic dye molecule as a photosensitizer for H<sub>2</sub> evolution, WO<sub>3</sub> photocatalyst for O<sub>2</sub> evolution, and I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple as a shuttle redox mediator. The photocatalytic activity test and electrochemical measurements indicated that the oxidized states of the coumarin dyes having oligo-thiophene unit in their structure are stable even in water to achieve sustaining overall water splitting. Although, at present, the quantum efficiency of dye-sensitized H<sub>2</sub> evolution is still low (e.g., < 0.1% at 500 nm for the NKX-2677 system), improvements in efficiency are in progress by structural design of the dye molecules optimized for both H<sub>2</sub> production and I<sup>-</sup> oxidation, as well as optimization of lamellar niobate.

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- <sup>†</sup> Electronic Supplementary Information (ESI) available: The Detailed preparation procedures of photocatalyst, detailed experimental conditions for photocatalytic activity test and electrochemical measurements, results on NKX-2697 adsorbed photocatalyst, potential diagram with reaction scheme. See DOI: 10.1039/b000000x/
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- 5