

# Photocatalytic overall water splitting under visible light by TaON and WO<sub>3</sub> with an IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox mediator

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Received (in Cambridge, UK) 22nd April 2005, Accepted 31st May 2005

First published as an Advance Article on the web 24th June 2005

DOI: 10.1039/b505646b

Photocatalytic water splitting into H<sub>2</sub> and O<sub>2</sub> under visible-light irradiation ( $\lambda > 420$  nm) is demonstrated using the oxynitride Pt-TaON for H<sub>2</sub> evolution and a Pt-WO<sub>3</sub> catalyst for O<sub>2</sub> evolution in an IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox-mediated system.

Photocatalytic water splitting into H<sub>2</sub> and O<sub>2</sub> by semiconducting catalysts has received much attention due to the potential of technology for the production of clean fuel H<sub>2</sub> from water using solar energy. The development of a photocatalytic system that functions efficiently under visible light, representing almost half of the available solar spectrum, is therefore indispensable for the practical utilization of solar energy. The present authors have recently reported several stable non-oxide photocatalysts, (oxy)-nitrides and oxysulfides, as potential candidates for visible light-induced water splitting.<sup>1-5</sup> The valence bands of these materials are populated by N 2p and S 3p orbitals, respectively, mixed with O 2p, resulting in more negative valence band levels and smaller band gaps compared to oxide semiconductors. For example, oxynitride TaON with a band gap of 2.5 eV (absorption edge at 500 nm) has conduction and valence band edges of *ca.* -0.3 and +2.2 V vs. NHE (pH 0), respectively, sufficient for overall water splitting into H<sub>2</sub> and O<sub>2</sub>.<sup>5</sup> Our group has also recently developed a two-step water splitting system in which two different photocatalysts are combined using an IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox mediator.<sup>6-8</sup> In this system, visible light can be utilized more efficiently than in conventional water splitting systems because the energy required to drive each photocatalytic system is reduced. However, the number of visible light-driven photocatalysts available for this system remains limited, and all of the existing materials are oxide semiconductors (*e.g.*, WO<sub>3</sub>) or oxide-based semiconductors (*e.g.*, metal cation-doped SrTiO<sub>3</sub>).<sup>7-9</sup>

The present paper reports the first application of an oxynitride photocatalyst to this two-step water splitting system with an IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox mediator. H<sub>2</sub> evolution and IO<sub>3</sub><sup>-</sup> production are shown to proceed over Pt-TaON in the presence of an I<sup>-</sup> electron donor under visible light, and stoichiometric water splitting into H<sub>2</sub> and O<sub>2</sub> under visible-light irradiation is demonstrated using a combination of Pt-TaON and Pt-WO<sub>3</sub> photocatalysts.

TaON powder was prepared by heating Ta<sub>2</sub>O<sub>5</sub> powder under an NH<sub>3</sub> flow (20 ml min<sup>-1</sup>) at 1123 K for 15 h. WO<sub>3</sub> powder (99.99%) was provided by Koujundo Chemical, and other chemicals used in the experiments were purchased from

commercial sources as guaranteed reagents and used without further purification. The TaON was loaded with Pt (0.3 wt%) by impregnation from aqueous {Pt(NH<sub>3</sub>)<sub>4</sub>}Cl<sub>2</sub> solution followed by H<sub>2</sub> reduction for 2 h at 573 K. In the case of WO<sub>3</sub>, Pt (0.5 wt%) was loaded by impregnation from aqueous H<sub>2</sub>PtCl<sub>6</sub> solution followed by calcination in air for 1 h at 773 K. Photocatalytic reactions were carried out in a Pyrex reaction vessel connected to a closed-gas circulation system. The two photocatalytic powders (0.2 g of each) were suspended in distilled water under agitation using a magnetic stirrer, and the required amount of solute (*e.g.*, NaI) was added to the suspension. The suspension was then thoroughly degassed. Argon gas (40 Torr) was introduced into the system, and the suspension was irradiated by a Xe lamp (300 W) fitted with a cut-off and water filters to eliminate light in the ultraviolet (UV) and infrared regions, respectively. The evolved gases were analyzed by on-line gas chromatography, and the abundance of I<sub>3</sub><sup>-</sup> and IO<sub>3</sub><sup>-</sup> anions produced by the reactions was determined by UV-visible absorption spectroscopy and ion chromatography, respectively.

Photocatalytic H<sub>2</sub> evolution was found to occur over the Pt-loaded TaON catalyst in aqueous solution containing I<sup>-</sup> anions as an electron donor under visible light ( $\lambda > 420$  nm), as shown in Fig. 1. The production of IO<sub>3</sub><sup>-</sup> anions in the solution was also confirmed, while the accurate determination of the amount of IO<sub>3</sub><sup>-</sup> was difficult because of the quite low concentration. Neither O<sub>2</sub> nor N<sub>2</sub> gases were evolved during this photoreaction. Therefore, the reactions taking place over the Pt-TaON photocatalyst under visible light are considered to be as follows:



Fig. 1 Time course of photocatalytic evolution of H<sub>2</sub> using Pt (0.3 wt%) TaON photocatalyst (0.2 g) suspended in a 5 mM NaI aqueous solution (pH 7 without adjustment) under visible light ( $\lambda > 420$  nm).

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(photoexcitation of photocatalyst)



(reduction of water to  $\text{H}_2$  by electrons)



(oxidation of  $\text{I}^-$  to  $\text{IO}_3^-$  by holes)

The results also indicate that the  $\text{I}^-$  anions act as effective electron donors in the presence of the TaON photocatalyst. The rate of  $\text{H}_2$  evolution decreased gradually over time, and ceased when the concentration of  $\text{IO}_3^-$  anions produced in the solution reached a certain level. These results indicate that the backwards reaction described below, that is, the reduction of  $\text{IO}_3^-$  to  $\text{I}^-$ , which is a thermodynamically favorable reaction, proceeds preferentially in place of the reduction of water when the concentration of  $\text{IO}_3^-$  reaches this threshold level.



(backward reduction of  $\text{IO}_3^-$  to  $\text{I}^-$ )

Consequently, the undesirable recycled reaction ( $\text{IO}_3^- \leftrightarrow \text{I}^-$ , combination of eqns. (3) and (4)), which consumes electrons ( $\text{e}^-$ ) and holes ( $\text{h}^+$ ), eventually became dominant. A similar trend has been observed for  $\text{H}_2$  production over Pt– $\text{TiO}_2$ -anatase and Pt– $\text{SrTiO}_3$ : Cr/Ta (SrTiO<sub>3</sub> codoped with Cr and Ta) photocatalysts in the presence of  $\text{I}^-$  electron donors.<sup>6–8</sup>

Overall water splitting under visible light was attempted by combining the Pt–TaON catalyst with the Pt– $\text{WO}_3$  photocatalyst for  $\text{O}_2$  evolution. As reported previously, the Pt– $\text{WO}_3$  photocatalyst possesses a unique reactivity for the oxidation of water, allowing selective  $\text{O}_2$  evolution in the presence of  $\text{IO}_3^-$  electron acceptors even at low  $\text{IO}_3^-$  concentrations.<sup>7,8</sup> As shown in Fig. 2, the combination of Pt (0.3 wt%)–TaON and Pt (0.5 wt%)– $\text{WO}_3$  photocatalysts resulted in simultaneous  $\text{H}_2$  and  $\text{O}_2$  evolution (initial rates:  $\text{H}_2$ ,  $24 \mu\text{mol h}^{-1}$ ;  $\text{O}_2$ ,  $12 \mu\text{mol h}^{-1}$ ) from NaI aqueous solution (5 mM, pH 7 without adjustment) under visible light ( $\lambda > 420 \text{ nm}$ ). The quantum efficiency for overall water splitting was



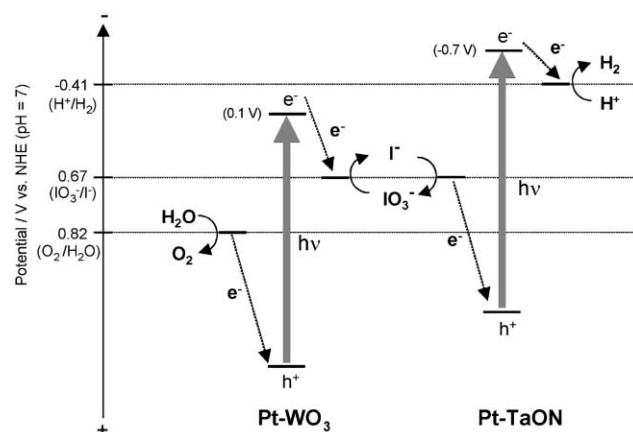
**Fig. 2** Time course of photocatalytic evolution of  $\text{H}_2$  and  $\text{O}_2$  using a mixture of Pt (0.3 wt%)–TaON (0.2 g) and Pt (0.5 wt%)– $\text{WO}_3$  (0.2 g) suspended in a 5 mM NaI aqueous solution (pH 7 without adjustment) under visible light ( $\lambda > 420 \text{ nm}$ ).

determined to be *ca.* 0.4% at 420 nm under the same conditions as for Fig. 2.<sup>10</sup> The efficiency of the present system is comparable to other systems using the  $\text{SrTiO}_3$  based photocatalysts.<sup>7–9</sup> No  $\text{N}_2$  evolution was detected during the photoreaction, and no gas evolution was observed in darkness. The reaction proceeded without notable deactivation even after 100 h, and the total amount of  $\text{H}_2$  gas evolved reached *ca.* 1.5 mmol, exceeding the stoichiometric amount of the photocatalysts (TaON, 0.95 mmol;  $\text{WO}_3$ , 0.86 mmol) and  $\text{I}^-$  (1.25 mmol) in the solution. No structural change of the photocatalysts could be detected by X-ray diffraction analysis after the photoreaction.

These results therefore demonstrate that overall water splitting proceeds by a two-step photo-excitation combined with a redox cycle between  $\text{IO}_3^-$  and  $\text{I}^-$ , as shown in Fig. 3. The first step involves water reduction to  $\text{H}_2$  and  $\text{I}^-$  oxidation to  $\text{IO}_3^-$  over Pt–TaON, and the second step involves  $\text{IO}_3^-$  reduction to  $\text{I}^-$  and water oxidation to  $\text{O}_2$  over Pt– $\text{WO}_3$ . It should be noted that the rate of  $\text{H}_2$  evolution over the combined Pt–TaON/Pt– $\text{WO}_3$  system was higher than over Pt–TaON alone (Fig. 1; *ca.*  $1 \mu\text{mol h}^{-1}$ ). The prompt reduction of  $\text{IO}_3^-$  to  $\text{I}^-$  over Pt– $\text{WO}_3$  is considered to maintain a very low concentration of  $\text{IO}_3^-$  in the solution during the photoreaction, effectively suppressing the undesirable backwards reaction of  $\text{IO}_3^-$  reduction to  $\text{I}^-$  over Pt–TaON, which cumulatively reduces the rate of  $\text{H}_2$  evolution when Pt–TaON is used alone.

Although TaON exhibits high efficiency (QE = 34% at  $\lambda = 420\text{--}500 \text{ nm}$ ) for water oxidation to  $\text{O}_2$  in the presence of  $\text{Ag}^+$  as an electron acceptor,<sup>2</sup> efficient  $\text{O}_2$  evolution over TaON in the presence of  $\text{IO}_3^-$  could not be achieved. This is considered to be attributable to the efficiency of  $\text{I}^-$  as an electron donor over TaON, as indicated by the  $\text{H}_2$  evolution in the presence of  $\text{I}^-$ . That is, photo-excited electrons over TaON reduce  $\text{IO}_3^-$  to  $\text{I}^-$ , and the  $\text{I}^-$  produced readily reacts with photo-generated holes over TaON, preventing  $\text{O}_2$  evolution.

In summary, the oxynitride TaON was applied for the first time to the two-step overall splitting of water through combination with  $\text{WO}_3$  using  $\text{IO}_3^-/\text{I}^-$  as a shuttle redox mediator. The Pt-loaded TaON photocatalyst exhibited activity for water reduction to  $\text{H}_2$  and  $\text{I}^-$  oxidation to  $\text{IO}_3^-$ , leading to stoichiometric overall water splitting under visible light irradiation by combination with Pt– $\text{WO}_3$ .



**Fig. 3** Speculated reaction mechanism for water splitting over Pt–TaON and Pt– $\text{WO}_3$  with an  $\text{IO}_3^-/\text{I}^-$  shuttle redox mediator.

This work was supported by the Fund for Young Researchers from the Ministry of Education, Culture, Sports, Science, and Technology of Japan, and also was supported by the Solution-Oriented Research for Science and Technology (SORST) program of the Japan Science and Technology Corporation (JST).

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- 10 Apparent quantum efficiencies ( $\Phi$ ) for overall water splitting were calculated by the equation  $\Phi(\%) = (4R/I) \times 100$ , where  $R$  is the  $H_2$  evolution rate (molecules  $h^{-1}$ ) and  $I$  is the rate of incident photon absorption at 420 nm (photons  $h^{-1}$ ).  $I$  was determined using a bandpass filter (MZ0420, Asahi Spectra) and a thermopile power meter (S310, Scientech) to measure the number of photons reaching the solution. It should be noted that 4 photons are required for the production of one molecule of  $H_2$  in the case of two-step water splitting using a redox mediator, while 2 photons are required for the same process in conventional one-step water splitting.