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Author(s)	Higashi, Masanobu; Abe, Ryu; Teramura, Kentaro; Takata, Tsuyoshi; Ohtani, Bunsho; Domen, Kazunari
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# Two step water splitting into H<sub>2</sub> and O<sub>2</sub> under visible light by ATaO<sub>2</sub>N (A=Ca, Sr, Ba) and WO<sub>3</sub> with IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox mediator

Masanobu Higashi<sup>a</sup>, Ryu Abe<sup>b</sup>, Kentaro Teramura<sup>a</sup>, Tsuyoshi Takata<sup>a</sup>, Bunsho Ohtani<sup>b</sup>, Kazunari Domen<sup>a,\*</sup>

 <sup>a</sup> Faculty of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
 <sup>b</sup> Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan

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#### Abstract

Two-step water splitting into  $H_2$  and  $O_2$  under visible light irradiation is examined combining Pt-ATaO<sub>2</sub>N (A=Ca, Sr, Ba) as a H<sub>2</sub> evolution photocatalyst and Pt-WO<sub>3</sub> as an O<sub>2</sub> evolution photocatalyst by IO<sub>3</sub><sup>-</sup>/I<sup>-</sup> shuttle redox-mediator. Overall water splitting proceeds when Pt-CaTaO<sub>2</sub>N or Pt-BaTaO<sub>2</sub>N is used for H<sub>2</sub> evolution photocatalyst, whereas photo-induced self-oxidative decomposition is predominant for Pt-SrTaO<sub>2</sub>N. The onset wavelengths of H<sub>2</sub> evolution almost accord with the absorption edges of CaTaO<sub>2</sub>N and BaTaO<sub>2</sub>N. The available wavelength of light for H<sub>2</sub> evolution in the present two-step water splitting system has been extended to 660 nm by using BaTaO<sub>2</sub>N.

\* Corresponding author. FAX: +81-3-5841-8838. *E-mail:* domen@chemsys.t.u-tokyo.ac.jp (K. Domen).

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# 1. Introduction

Photocatalytic water splitting into H<sub>2</sub> and O<sub>2</sub> over a semiconductor catalyst has recently received much attention due to the potential of this method for the clean production of H<sub>2</sub> from water utilizing solar energy. Although various photocatalysts that work under ultraviolet (UV) irradiation have been developed [1, 2], the utilization of visible light, comprising almost half of all incident solar energy on the surface of the Earth, is indispensable from the viewpoint of practical solar energy conversion. Photocatalytic overall water splitting under visible light irradiation has recently been accomplished by two different approaches [3-9]. The development of a practically effcient system has then become an active research field, with most research focused on the extension of the wavelength region available for water splitting as well as on the improvement in the quantum yeild. A two-step water splitting system utilizing a reversible redox couple such as iodate/iodide  $(IO_3^{-}/I^{-})$  [5-9] is possibly the most promising way of extending the available light region, because the photon energy required to drive each photocatalyst is smaller than in the one-step process. However, only a limited part of the visible spectrum  $(\lambda < 500 \text{ nm})$  has been successfully utilized to date. Extension of the wavelength region available for water splitting, i.e., the development of new photocatalyst materials absorbing a broader region of visible light, is therefore indispensable for practical  $H_2$  production using solar radiation.

In this work, a series of mixed oxynitrides, ATaO<sub>2</sub>N (A=Ca, Sr, Ba), with an absorption edge longer than that of simple oxynitride, TaON, was prepared and applied in the two-step photo-excitation water splitting system as an H<sub>2</sub> evolution photocatalyst. H<sub>2</sub> evolution and  $IO_3^-$  production are shown to proceed stably over Pt-BaTaO<sub>2</sub>N in the presence of an  $\Gamma$  electron donor under visible light up to 660 nm, corresponding to the photoabsorption of BaTaO<sub>2</sub>N. Stoichiometric water splitting into H<sub>2</sub> and O<sub>2</sub> under visible irradiation is demonstrated using a combination of Pt-BaTaO<sub>2</sub>N and Pt-WO<sub>3</sub> photocatalysts, in which the visible light with wavelengths longer than 600 nm was utilized for the first time as an H<sub>2</sub> evolution system in two-step water splitting.

### 2. Experimental

Oxide precursors ( $A_2Ta_2O_7$ : A=Ca, Sr, Ba) for ATaO<sub>2</sub>N were prepared by a polymerized complex method [10], and then ATaO<sub>2</sub>N were obtained by heating  $A_2Ta_2O_7$  under NH<sub>3</sub> flow (100 mL min<sup>-1</sup>) at 1223 K for 20 h. WO<sub>3</sub> powder was provided by Kojundo Chemical, and other chemicals used in the experiments were purchased from commercial sources as guaranteed reagents and used without further purification. The

ATaO<sub>2</sub>N was loaded with 0.3 wt% Pt by impregnation from an aqueous H<sub>2</sub>PtCl<sub>6</sub> solution followed by H<sub>2</sub> reduction at 473 K for 1 h. In the case of WO<sub>3</sub>, 0.5 wt% Pt was loaded by impregnation from an aqueous H<sub>2</sub>PtCl<sub>6</sub> solution followed by calcination at 623 K in air for 30 min. Photocatalytic reactions were carried out in a Pyrex reaction vessel connected to a closed gas circulation system. The two photocatalyst powders (0.1 g of each) were suspended in distilled water using a magnetic stirrer, and the required amount of solute (e.g., NaI) was added to the suspension. The suspension was then thoroughly degassed and 5 kPa of Ar was introduced. The suspension was irradiated using a Xe lamp (300 W) fitted with a cut-off filter and water filters to eliminate light in the UV and infrared regions, respectively. The evolved gases were analyzed by on-line gas chromatography, and the amounts of  $I_3^-$  and  $IO_3^-$  anions produced by the reactions were determined by UV-visible absorption spectroscopy and ion chromatography, respectively.

### 3. Results and discussion

# 3.1. H<sub>2</sub> evolution on Pt-ATaO<sub>2</sub>N from aqueous NaI solution

The X-ray diffraction (XRD) pattern of the prepared ATaO<sub>2</sub>N (A=Ca, Sr, Ba) samples accords with the perovskite structures (Fig. S1) in Refs. [11, 12], with impurity peaks at trace levels assignable to  $Ta_3N_5$  (absorption edge at 600 nm) in the BaTaO<sub>2</sub>N sample. As shown in Fig. 1, the absorption edge of the prepared ATaO<sub>2</sub>N samples were confirmed to be 520, 600, and 660 nm, respectively, shifting to longer wavelengths with the increase in the ionic radius ( $Ca^{2+} < Sr^{2+} < Ba^{2+}$ ).

The H<sub>2</sub> evolution on ATaO<sub>2</sub>N loaded with Pt was examined in the presence of  $\Gamma$  anions as an electron donor. Figs. 2(a) and (b) show the time courses of H<sub>2</sub> evolution over Pt-BaTaO<sub>2</sub>N and Pt-CaTaO<sub>2</sub>N, respectively, in an aqueous solution of NaI (5 mM) under visible irradiation ( $\lambda > 420$  nm). The rate of H<sub>2</sub> evolution gradually decreased during prolonged irradiation and eventually ceased in both cases. The production of IO<sub>3</sub><sup>-</sup> anions in the solution was also confirmed, although accurate quantitative determination of IO<sub>3</sub><sup>-</sup> was difficult due to the low concentration and adsorption of IO<sub>3</sub><sup>-</sup> onto the photocatalyst powder. No H<sub>2</sub> evolution was observed in the absence of  $\Gamma$  anions in the solution. The following reactions are thus considered to occur for both cases of Pt-BaTaO<sub>2</sub>N and Pt-CaTaO<sub>2</sub>N photocatalysts under visible light:

$$BaTaO_2N(or CaTaO_2N) + h\nu (\lambda > 420 \text{ nm}) \rightarrow e^- + h^+ \quad (1)$$

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \to \mathrm{H}_{2} \tag{2}$$

$$\Gamma + 6OH^- + 6h^+ \rightarrow IO_3^- + 3H_2O$$
<sup>(3)</sup>

The cessation of H<sub>2</sub> production observed during prolonged irradiation can be explained by the backward reaction taking place over the reduction site (Pt) of the photocatalyst. That is, the preferential reduction of  $IO_3^-$  anion to  $\Gamma$  occurs instead of water reduction [4, 6-8]:

$$IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^-$$
 (4)

As shown in Fig. 2, the amount of  $H_2$  produced on Pt-CaTaO<sub>2</sub>N was larger than that on Pt-BaTaO<sub>2</sub>N, suggesting that the backward reaction (Eq. (4)) depends on photocatalyst materials.

We note that no  $N_2$  evolution was observed during the reaction in both cases. It has been reported that some (oxy)nitrides suffer from self-oxidative decomposition [13], whereby nitrogen anions ( $N^{3-}$ ) are oxidized to  $N_2$  by photo-generated holes:

$$2N^{3-} + 6h^+ \rightarrow N_2 \tag{5}$$

A considerable amount of  $N_2$  evolved on a Pt-SrTaO<sub>2</sub>N sample accompanied by H<sub>2</sub> evolution under visible light irradation in the solution containing NaI (Fig. S2). This can be explained by the self-oxidative decomposition of SrTaO<sub>2</sub>N material as described above. At present, the reason of the instability of SrTaO<sub>2</sub>N among ATaO<sub>2</sub>N samples is not clear.

# 3.2. Overall water splitting on Pt-ATaO<sub>2</sub>N + Pt-WO<sub>3</sub> with $IO_3^{-}/\Gamma$ shuttle redox mediator

Overall water splitting under visible light was attempted using a combination of Pt-ATaO<sub>2</sub>N and Pt-WO<sub>3</sub> as a photocatalyst of O<sub>2</sub> evolution. As reported previously, the Pt-WO<sub>3</sub> photocatalyst possesses a unique reactivity for the oxidation of water, realizing selective O<sub>2</sub> evolution in the presence of  $IO_3^-$  electron acceptor even at low  $IO_3^-$  concentration [6, 7]. The combination of Pt–BaTaO<sub>2</sub>N and Pt–WO<sub>3</sub> photocatalysts

resulted in simultaneous H<sub>2</sub> and O<sub>2</sub> evolution from NaI aqueous solution under visible light ( $\lambda > 420$  nm) at a stoichiometric ratio (H<sub>2</sub>:O<sub>2</sub> = 2:1), as shown in Fig. 3(a). No gas evolution was observed in the absence of  $\Gamma$  anions in the solution under visible light irradiation, and no reaction took place in the dark. These results indicate that overall water splitting proceeds by a two-step photo-excitation process combined with redox cycling between  $IO_3^-$  and  $\Gamma$ . The first step involves water reduction to  $H_2$  and  $\Gamma$  oxidation to  $IO_3^$ over Pt-BaTaO<sub>2</sub>N, and the second step involves  $IO_3^-$  reduction to  $\Gamma$  and water oxidation to O<sub>2</sub> over Pt-WO<sub>3</sub>. The apparent quantum efficiency for overall water splitting of this combination was determined to be ~ 0.1 % at 420–440 nm. The use of combination of Pt-CaTaO<sub>2</sub>N and Pt-WO<sub>3</sub> also resulted in a stoichiometric water splitting although a small amount of  $N_2$  evolution took place in the beginning of the reaction, as shown in Fig. 3(b). On the other hand, the combination of Pt-SrTaO<sub>2</sub>N and Pt-WO<sub>3</sub> failed to split water (Fig. S3), probably due to the self-oxidative decomposition of SrTaO<sub>2</sub>N material mentioned above.

Based on the absorption spectrum of  $BaTaO_2N$ , it is expected that  $H_2$  evolution over  $Pt-BaTaO_2N$  proceeds by the absorption of visible light at wavelengths up to 660 nm. The wavelength dependence of  $H_2$  evolution on  $Pt-BaTaO_2N$  was examined during the overall water splitting reaction with two Xe illuminators (A and B). Illuminator A emits light at

wavelengths longer than 420 nm ( $4.32 \times 10^{22}$  photons  $\cdot$  h<sup>-1</sup> at 420 nm <  $\lambda$  < 660 nm); the rate of  $H_2$  evolution was denoted as  $r_A$ . In contrast, illuminator B produces light longer than 500 nm with various cut-off filters ( $2.54 \times 10^{22}$  photons  $\cdot$  h<sup>-1</sup> at 500 nm <  $\lambda$  < 660 nm), which excites BaTaO<sub>2</sub>N but not WO<sub>3</sub> (absorption edge at 450 nm). As the concentration of IO<sub>3</sub><sup>-</sup> in the solution did not increase during the overall splitting reaction (Fig. 3(a)), the  $H_2$  evolution rate on Pt-BaTaO<sub>2</sub>N should be much slower than the O<sub>2</sub> evolution rate on Pt-WO<sub>3</sub>. Therefore, if BaTaO<sub>2</sub>N can absorb more photons, simultaneous light irradiation from illuminators A and B would lead to the enhancement of H<sub>2</sub> and O<sub>2</sub> evolution rates because of the increase of total incident photons. The measured H<sub>2</sub> evolution rate under simultaneous light irradiation (iluminators A and B) is denoted as  $r_{A+B}$ . Fig. 4 plots the ratio  $(r_{A+B}/r_A)$  as a function of the cut-off wavelength of illuminator B. A similar result with Pt-CaTaO<sub>2</sub>N (absorption edge at 520 nm) and Pt-WO<sub>3</sub> is also presented for camparison in Fig. 4. In the case of BaTaO<sub>2</sub>N, the ratio of 1.36 was obtained with the cut-off wavelength of illuminator B at 500 nm, indicating that the  $H_2$  evolution rate on Pt-BaTaO<sub>2</sub>N enhanced by increasing total incident photons; overall reaction rates consequently increased (data not shown). The degree of enhancement in H<sub>2</sub> evolution  $(r_{A+B}/r_A)$  decreased with the increasing cut-off wavelength, eventually reaching unity, indicating no enhancement under irradiation at wavelengths longer than 660 nm. These

results clearly demonstrate that the absorption of  $BaTaO_2N$  at wavelengths up to 660 nm contributes to  $H_2$  evolution in the overall water splitting reaction. As for the  $CaTaO_2N$ , the enhancement of  $H_2$  evolution was observed at wavelength below 520 nm, which agrees with the absorption edge of  $CaTaO_2N$ .

### 4. Summary

The combination of Pt-BaTaO<sub>2</sub>N (or Pt-CaTaO<sub>2</sub>N) and Pt-WO<sub>3</sub> in the presence of  $IO_3^{-}/\Gamma$  as a shuttle redox mediator was demonstrated to achieve overall water splitting into H<sub>2</sub> and O<sub>2</sub> under visible light. It was confirmed that the absorption of BaTaO<sub>2</sub>N at wavelengths up to 660 nm contributes to the H<sub>2</sub> evolution process. This is the first example of the overall water splitting system in which visible light longer than 600 nm is effectively utilized for the H<sub>2</sub> evolution system. These results indicate the potential of a two-step water splitting system utilizing a broader region of the visible spectrum.

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# **Figure Captions**

Fig. 1. UV-vis diffuse reflectace (DR) spectra of (a) CaTaO<sub>2</sub>N, (b) SrTaO<sub>2</sub>N and (c) BaTaO<sub>2</sub>N.

Fig. 2. Time course of photocatalytic evolution of H<sub>2</sub> using (a) Pt-BaTaO<sub>2</sub>N and (b) Pt-CaTaO<sub>2</sub>N photocatalysts (0.1 g) suspended in a 5 mM NaI aqueous solution under visible light ( $\lambda > 420$  nm).

Fig. 3. Time course of photocatalytic evolution of H<sub>2</sub> and O<sub>2</sub> using a mixture of 0.3 wt% Pt-ATaO<sub>2</sub>N (A = Ba (a), Ca (b)) and 0.5 wt% Pt-WO<sub>3</sub> suspended in a 5 mM NaI aqueous solution under visible light ( $\lambda > 420$  nm). Pt-ATaO<sub>2</sub>N: 0.1 g, Pt-WO<sub>3</sub>: 0.1 g.

\* Accumulated gases in the reaction system were removed by evaculation at 8 and 14 h.

Fig. 4. Dependence of ratios  $(r_{A+B}/r_A)$  on the cut-off wavelength of incident light (illuminator B), and UV-vis DR spectra of (a) WO<sub>3</sub>, (b) CaTaO<sub>2</sub>N and (c) BaTaO<sub>2</sub>N, illuminator A:  $(\lambda > 420 \text{ nm})$ , illuminator B:  $(\lambda > X \text{ nm}, X: \text{ cut-off wavelength})$ ,  $r_A: H_2$  evolution rate (illuminator A),  $r_{A+B}$ : H<sub>2</sub> evolution rate (illuminator A and B).



Figure 1



Figure 2



Figure 3



Figure 4