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Two step water splitting into H_2 and O_2 under visible light by $ATaO_2N$ (A=Ca, Sr, Ba) and WO_3 with IO_3^-/I^- shuttle redox mediator

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Abstract

Two-step water splitting into H_2 and O_2 under visible light irradiation is examined combining Pt-$ATaO_2N$ (A=Ca, Sr, Ba) as a H_2 evolution photocatalyst and Pt-WO_3 as an O_2 evolution photocatalyst by IO_3^-/I^- shuttle redox-mediator. Overall water splitting proceeds when Pt-$CaTaO_2N$ or Pt-$BaTaO_2N$ is used for H_2 evolution photocatalyst, whereas photo-induced self-oxidative decomposition is predominant for Pt-$SrTaO_2N$. The onset wavelengths of H_2 evolution almost accord with the absorption edges of $CaTaO_2N$ and $BaTaO_2N$. The available wavelength of light for H_2 evolution in the present two-step water splitting system has been extended to 660 nm by using $BaTaO_2N$.

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1. Introduction

Photocatalytic water splitting into H_2 and O_2 over a semiconductor catalyst has recently received much attention due to the potential of this method for the clean production of H_2 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 splittting 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 ($\lambda < 500$ nm) has been successfully utilized to date. Extension of the wavelength region available for water splitting, i.e., the development of new photocatalyst materials

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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, $ATaO_2N$ (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_2 evolution photocatalyst. H_2

evolution and IO_3^- production are shown to proceed stably over $Pt-BaTaO_2N$ in the

presence of an I^- electron donor under visible light up to 660 nm, corresponding to the

photoabsorption of $BaTaO_2N$. Stoichiometric water splitting into H_2 and O_2 under

visible irradiation is demonstrated using a combination of $Pt–BaTaO_2N$ and $Pt–WO_3$

photocatalysts, in which the visible light with wavelengths longer than 600 nm was

utilized for the first time as an H_2 evolution system in two-step water splitting.

2. Experimental

Oxide precursors ($A_2Ta_2O_7$: A=Ca, Sr, Ba) for $ATaO_2N$ were prepared by a

polymerized complex method [10], and then $ATaO_2N$ were obtained by heating $A_2Ta_2O_7$

under NH_3 flow (100 mL min^{-1}) at 1223 K for 20 h. WO_3 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$_2$N was loaded with 0.3 wt% Pt by impregnation from an aqueous H$_2$PtCl$_6$ solution followed by H$_2$ reduction at 473 K for 1 h. In the case of WO$_3$, 0.5 wt% Pt was loaded by impregnation from an aqueous H$_2$PtCl$_6$ 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.
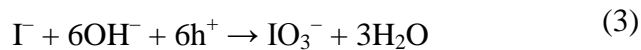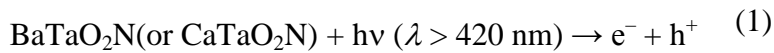
3. Results and discussion

*3.1. H$_2$ evolution on Pt-ATaO$_2$N from aqueous NaI solution*

The X-ray diffraction (XRD) pattern of the prepared ATaO$_2$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$_3$N$_5$ (absorption edge at 600 nm) in the BaTaO$_2$N sample. As shown in Fig. 1, the absorption edge of the prepared ATaO$_2$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_2 evolution on $ATaO_2N$ loaded with Pt was examined in the presence of I^- anions as an electron donor. Figs. 2(a) and (b) show the time courses of H_2 evolution over Pt-$BaTaO_2N$ and Pt-$CaTaO_2N$, respectively, in an aqueous solution of NaI (5 mM) under visible irradiation ($\lambda > 420$ nm). The rate of H_2 evolution gradually decreased during prolonged irradiation and eventually ceased in both cases. The production of IO_3^- anions in the solution was also confirmed, although accurate quantitative determination of IO_3^- was difficult due to the low concentration and adsorption of IO_3^- onto the photocatalyst powder. No H_2 evolution was observed in the absence of I^- anions in the solution. The following reactions are thus considered to occur for both cases of Pt-$BaTaO_2N$ and Pt-$CaTaO_2N$ photocatalysts under visible light:

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

$$2H^+ + 2e^- \rightarrow H_2 \quad (2)$$

$$I^- + 6OH^- + 6h^+ \rightarrow IO_3^- + 3H_2O \quad (3)$$

The cessation of H_2 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 I^- occurs instead of water reduction [4, 6-8]:

$$IO_3^- + 3H_2O + 6e^- \rightarrow I^- + 6OH^- \qquad (4)$$
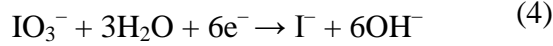
As shown in Fig. 2, the amount of H_2 produced on Pt-CaTaO$_2$N was larger than that on Pt-BaTaO$_2$N, suggesting that the backward reaction (Eq. (4)) depends on photocatalyst materials.

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:

$$2N^{3-} + 6h^+ \rightarrow N_2 \qquad (5)$$

A considerable amount of N_2 evolved on a Pt-SrTaO$_2$N sample accompanied by H_2 evolution under visible light irradation in the solution containing NaI (Fig. S2). This can be explained by the self-oxidative decomposition of SrTaO$_2$N material as described above. At present, the reason of the instability of SrTaO$_2$N among ATaO$_2$N samples is not clear.

3.2. Overall water splitting on Pt-ATaO$_2$N + Pt-WO$_3$ with IO_3^-/I^- shuttle redox mediator

Overall water splitting under visible light was attempted using a combination of Pt-ATaO$_2$N and Pt-WO$_3$ as a photocatalyst of O_2 evolution. As reported previously, the Pt-WO$_3$ photocatalyst possesses a unique reactivity for the oxidation of water, realizing selective O_2 evolution in the presence of IO_3^- electron acceptor even at low IO_3^- concentration [6, 7]. The combination of Pt–BaTaO$_2$N and Pt–WO$_3$ photocatalysts

resulted in simultaneous H_2 and O_2 evolution from NaI aqueous solution under visible light ($\lambda > 420$ nm) at a stoichiometric ratio ($H_2:O_2 = 2:1$), as shown in Fig. 3(a). No gas evolution was observed in the absence of I^- 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 I^-. The first step involves water reduction to H_2 and I^- oxidation to IO_3^- over Pt-BaTaO$_2$N, and the second step involves IO_3^- reduction to I^- and water oxidation to O_2 over Pt-WO$_3$. 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$_2$N and Pt-WO$_3$ 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$_2$N and Pt-WO$_3$ failed to split water (Fig. S3), probably due to the self-oxidative decomposition of SrTaO$_2$N material mentioned above.

Based on the absorption spectrum of BaTaO$_2$N, it is expected that H_2 evolution over Pt-BaTaO$_2$N proceeds by the absorption of visible light at wavelengths up to 660 nm. The wavelength dependence of H_2 evolution on Pt-BaTaO$_2$N was examined during the overall water splitting reaction with two Xe illuminators (A and B). Illuminator A emits light at

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wavelengths longer than 420 nm (4.32×10^{22} photons $\cdot$ h^{-1} 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 (2.54×10^{22} photons $\cdot$ h^{-1} at 500 nm $< \lambda <$ 660

nm), which excites BaTaO$_2$N but not WO$_3$ (absorption edge at 450 nm). As the

concentration of IO$_3^-$ in the solution did not increase during the overall splitting reaction

(Fig. 3(a)), the H$_2$ evolution rate on Pt-BaTaO$_2$N should be much slower than the O$_2$

evolution rate on Pt-WO$_3$. Therefore, if BaTaO$_2$N can absorb more photons, simultaneous

light irradiation from illuminators A and B would lead to the enhancement of H$_2$ and O$_2$

evolution rates because of the increase of total incident photons. The measured H$_2$

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$_2$N (absorption edge at 520 nm) and Pt-WO$_3$ is also

presented for camparison in Fig. 4. In the case of BaTaO$_2$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$_2$N enhanced by increasing total incident photons; overall reaction rates

consequently increased (data not shown). The degree of enhancement in H$_2$ 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$_2$N at wavelengths up to 660 nm contributes to H$_2$ evolution in the overall water splitting reaction. As for the CaTaO$_2$N, the enhancement of H$_2$ evolution was observed at wavelength below 520 nm, which agrees with the absorption edge of CaTaO$_2$N.

4. Summary

The combination of Pt-BaTaO$_2$N (or Pt-CaTaO$_2$N) and Pt-WO$_3$ in the presence of IO$_3^-$/I$^-$ as a shuttle redox mediator was demonstrated to achieve overall water splitting into H$_2$ and O$_2$ under visible light. It was confirmed that the absorption of BaTaO$_2$N at wavelengths up to 660 nm contributes to the H$_2$ 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$_2$ 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) $CaTaO_2N$, (b) $SrTaO_2N$ and (c) $BaTaO_2N$.

Fig. 2. Time course of photocatalytic evolution of H_2 using (a) Pt-$BaTaO_2N$ and (b) Pt-$CaTaO_2N$ photocatalysts (0.1 g) suspended in a 5 mM NaI aqueous solution under visible light ($\lambda > 420$ nm).
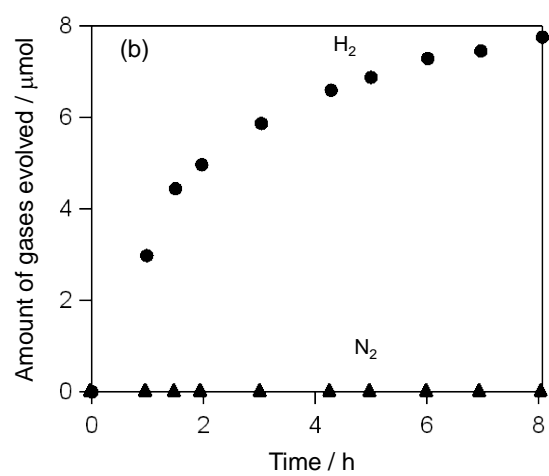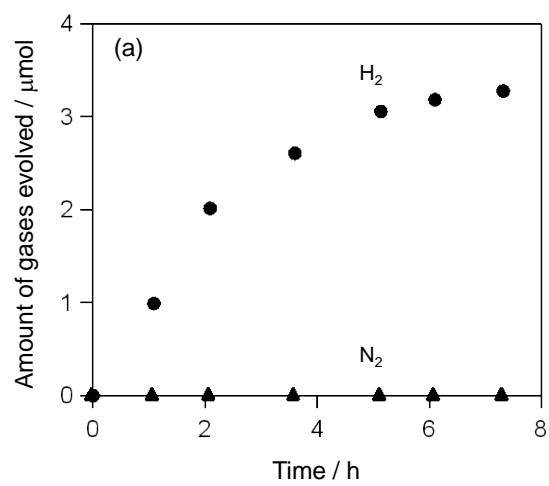
Fig. 3. Time course of photocatalytic evolution of H_2 and O_2 using a mixture of 0.3 wt% Pt-$ATaO_2N$ (A = Ba (a), Ca (b)) and 0.5 wt% Pt-WO_3 suspended in a 5 mM NaI aqueous solution under visible light ($\lambda > 420$ nm). Pt-$ATaO_2N$: 0.1 g, Pt-WO_3: 0.1 g.

[*] 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_3, (b) $CaTaO_2N$ and (c) $BaTaO_2N$, illuminator A: ($\lambda > 420$ nm), illuminator B: ($\lambda > X$ nm, X: cut-off wavelength), r_A: H_2 evolution rate (illuminator A), r_{A+B}: H_2 evolution rate (illuminator A and B).
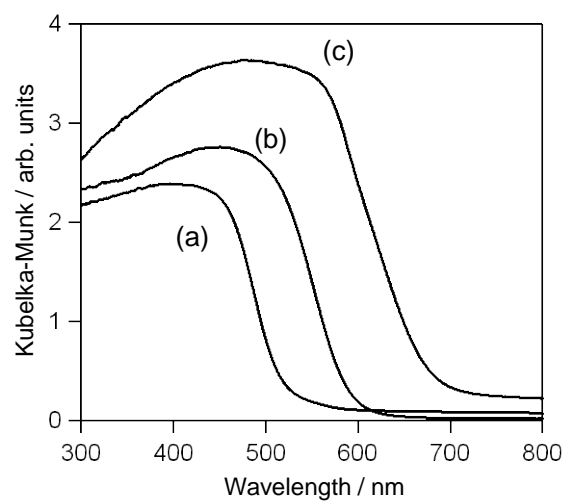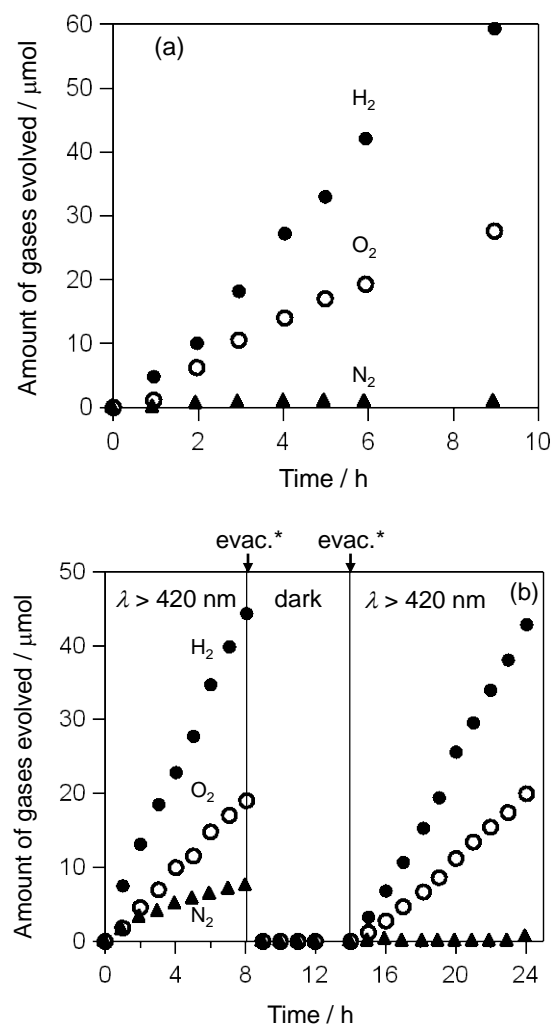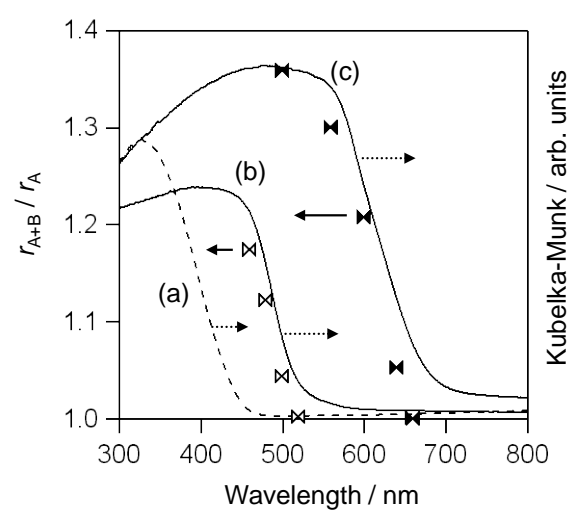
Figure 1

Figure 2

Figure 3

Figure 4