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Two step water splitting into H₂ and O₂ under visible light by ATaO₂N (A=Ca, Sr, Ba) and WO₃ with IO₃⁻/I⁻ shuttle redox mediator

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Abstract

Two-step water splitting into H₂ and O₂ under visible light irradiation is examined combining Pt-ATaO₂N (A=Ca, Sr, Ba) as a H₂ evolution photocatalyst and Pt-WO₃ as an O₂ evolution photocatalyst by IO₃⁻/I⁻ shuttle redox-mediator. Overall water splitting proceeds when Pt-CaTaO₂N or Pt-BaTaO₂N is used for H₂ evolution photocatalyst, whereas photo-induced self-oxidative decomposition is predominant for Pt-SrTaO₂N. The onset wavelengths of H₂ evolution almost accord with the absorption edges of CaTaO₂N and BaTaO₂N. The available wavelength of light for H₂ evolution in the present two-step water splitting system has been extended to 660 nm by using BaTaO₂N.

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Keywords: Photocatalyst; Z-scheme; two step water splitting; oxynitride; ATaO₂N

1. Introduction

Photocatalytic water splitting into H₂ and O₂ over a semiconductor catalyst has recently received much attention due to the potential of this method for the clean production of H₂ 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 efficient 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 yield. A two-step water splitting system utilizing a reversible redox couple such as iodate/iodide (IO₃⁻/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

absorbing a broader region of visible light, is therefore indispensable for practical H₂ production using solar radiation.

In this work, a series of mixed oxynitrides, ATaO₂N (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 H₂ evolution photocatalyst. H₂ evolution and IO₃⁻ production are shown to proceed stably over Pt-BaTaO₂N in the presence of an I⁻ electron donor under visible light up to 660 nm, corresponding to the photoabsorption of BaTaO₂N. Stoichiometric water splitting into H₂ and O₂ under visible irradiation is demonstrated using a combination of Pt-BaTaO₂N and Pt-WO₃ photocatalysts, in which the visible light with wavelengths longer than 600 nm was utilized for the first time as an H₂ evolution system in two-step water splitting.

2. Experimental

Oxide precursors (A₂Ta₂O₇; A=Ca, Sr, Ba) for ATaO₂N were prepared by a polymerized complex method [10], and then ATaO₂N were obtained by heating A₂Ta₂O₇ under NH₃ flow (100 mL min⁻¹) at 1223 K for 20 h. WO₃ 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

ATaO₂N was loaded with 0.3 wt% Pt by impregnation from an aqueous H₂PtCl₆ solution followed by H₂ reduction at 473 K for 1 h. In the case of WO₃, 0.5 wt% Pt was loaded by impregnation from an aqueous H₂PtCl₆ 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 I₃⁻ and IO₃⁻ anions produced by the reactions were determined by UV-visible absorption spectroscopy and ion chromatography, respectively.

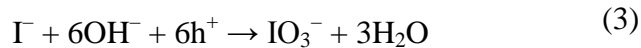
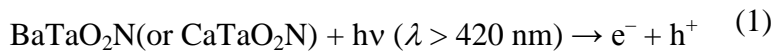
3. Results and discussion

3.1. H₂ evolution on Pt-ATaO₂N from aqueous NaI solution

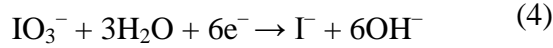
The X-ray diffraction (XRD) pattern of the prepared ATaO₂N (A=Ca, Sr, Ba) samples accords with the perovskite structures (Fig. S1) in Refs. [11, 12], with impurity peaks at trace levels assignable to Ta₃N₅ (absorption edge at 600 nm) in the BaTaO₂N sample. As shown in Fig. 1, the absorption edge of the prepared ATaO₂N samples were confirmed to

be 520, 600, and 660 nm, respectively, shifting to longer wavelengths with the increase in the ionic radius ($\text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$).

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:



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]:



As shown in Fig. 2, the amount of H₂ produced on Pt-CaTaO₂N was larger than that on Pt-BaTaO₂N, suggesting that the backward reaction (Eq. (4)) depends on photocatalyst materials.

We note that no N₂ 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 (N³⁻) are oxidized to N₂ by photo-generated holes:



A considerable amount of N₂ evolved on a Pt-SrTaO₂N sample accompanied by H₂ evolution under visible light irradiation in the solution containing NaI (Fig. S2). This can be explained by the self-oxidative decomposition of SrTaO₂N material as described above. At present, the reason of the instability of SrTaO₂N among ATaO₂N samples is not clear.

3.2. Overall water splitting on Pt-ATaO₂N + Pt-WO₃ with IO₃⁻/I⁻ shuttle redox mediator

Overall water splitting under visible light was attempted using a combination of Pt-ATaO₂N and Pt-WO₃ as a photocatalyst of O₂ evolution. As reported previously, the Pt-WO₃ photocatalyst possesses a unique reactivity for the oxidation of water, realizing selective O₂ evolution in the presence of IO₃⁻ electron acceptor even at low IO₃⁻ concentration [6, 7]. The combination of Pt-BaTaO₂N and Pt-WO₃ photocatalysts

resulted in simultaneous H₂ and O₂ evolution from NaI aqueous solution under visible light ($\lambda > 420$ nm) at a stoichiometric ratio (H₂:O₂ = 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 IO₃⁻ and I⁻. The first step involves water reduction to H₂ and I⁻ oxidation to IO₃⁻ over Pt-BaTaO₂N, and the second step involves IO₃⁻ reduction to I⁻ and water oxidation to O₂ over Pt-WO₃. 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-CaTaO₂N and Pt-WO₃ also resulted in a stoichiometric water splitting although a small amount of N₂ evolution took place in the beginning of the reaction, as shown in Fig. 3(b). On the other hand, the combination of Pt-SrTaO₂N and Pt-WO₃ failed to split water (Fig. S3), probably due to the self-oxidative decomposition of SrTaO₂N material mentioned above.

Based on the absorption spectrum of BaTaO₂N, it is expected that H₂ evolution over Pt-BaTaO₂N proceeds by the absorption of visible light at wavelengths up to 660 nm. The wavelength dependence of H₂ evolution on Pt-BaTaO₂N 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 (4.32×10^{22} photons \cdot h⁻¹ at 420 nm < λ < 660 nm); the rate of H₂ 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 < λ < 660 nm), which excites BaTaO₂N but not WO₃ (absorption edge at 450 nm). As the concentration of IO₃⁻ in the solution did not increase during the overall splitting reaction (Fig. 3(a)), the H₂ evolution rate on Pt-BaTaO₂N should be much slower than the O₂ evolution rate on Pt-WO₃. Therefore, if BaTaO₂N can absorb more photons, simultaneous light irradiation from illuminators A and B would lead to the enhancement of H₂ and O₂ evolution rates because of the increase of total incident photons. The measured H₂ evolution rate under simultaneous light irradiation (illuminators 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-CaTaO₂N (absorption edge at 520 nm) and Pt-WO₃ is also presented for comparison in Fig. 4. In the case of BaTaO₂N, the ratio of 1.36 was obtained with the cut-off wavelength of illuminator B at 500 nm, indicating that the H₂ evolution rate on Pt-BaTaO₂N enhanced by increasing total incident photons; overall reaction rates consequently increased (data not shown). The degree of enhancement in H₂ 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 BaTaO₂N at wavelengths up to 660 nm contributes to H₂ evolution in the overall water splitting reaction. As for the CaTaO₂N, the enhancement of H₂ evolution was observed at wavelength below 520 nm, which agrees with the absorption edge of CaTaO₂N.

4. Summary

The combination of Pt-BaTaO₂N (or Pt-CaTaO₂N) and Pt-WO₃ in the presence of IO₃⁻/I⁻ as a shuttle redox mediator was demonstrated to achieve overall water splitting into H₂ and O₂ under visible light. It was confirmed that the absorption of BaTaO₂N at wavelengths up to 660 nm contributes to the H₂ 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 H₂ evolution system. These results indicate the potential of a two-step water splitting system utilizing a broader region of the visible spectrum.

Acknowledgement

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Figure Captions

Fig. 1. UV-vis diffuse reflectance (DR) spectra of (a) CaTaO₂N, (b) SrTaO₂N and (c) BaTaO₂N.

Fig. 2. Time course of photocatalytic evolution of H₂ using (a) Pt-BaTaO₂N and (b) Pt-CaTaO₂N 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 H₂ and O₂ using a mixture of 0.3 wt% Pt-ATaO₂N (A = Ba (a), Ca (b)) and 0.5 wt% Pt-WO₃ suspended in a 5 mM NaI aqueous solution under visible light ($\lambda > 420$ nm). Pt-ATaO₂N: 0.1 g, Pt-WO₃: 0.1 g.

* Accumulated gases in the reaction system were removed by evacuation 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) WO₃, (b) CaTaO₂N and (c) BaTaO₂N, illuminator A: ($\lambda > 420$ nm), illuminator B: ($\lambda > X$ nm, X: cut-off wavelength), r_A : H₂ evolution rate (illuminator A), r_{A+B} : H₂ evolution rate (illuminator A and B).

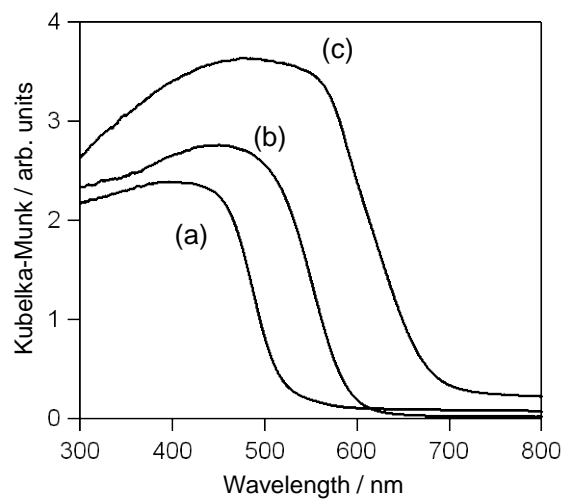


Figure 1

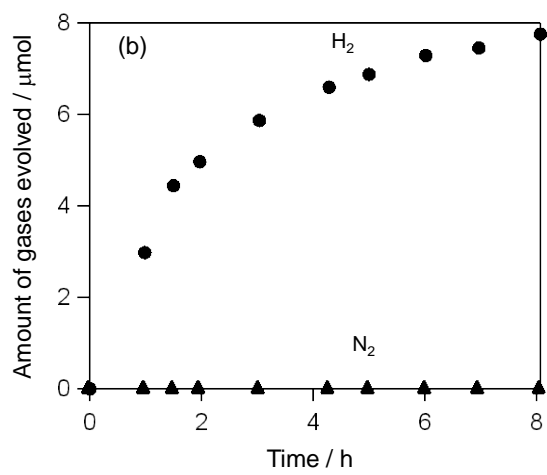
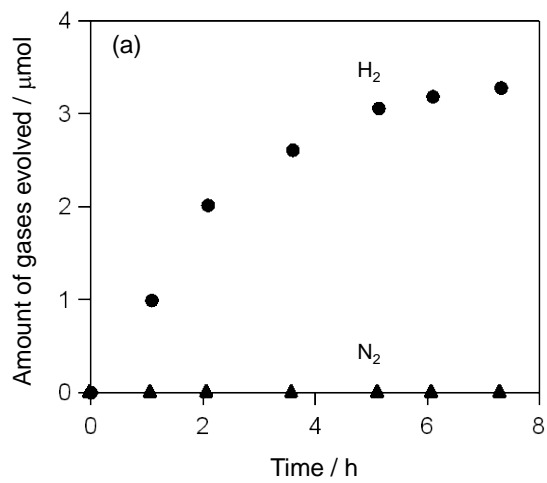


Figure 2

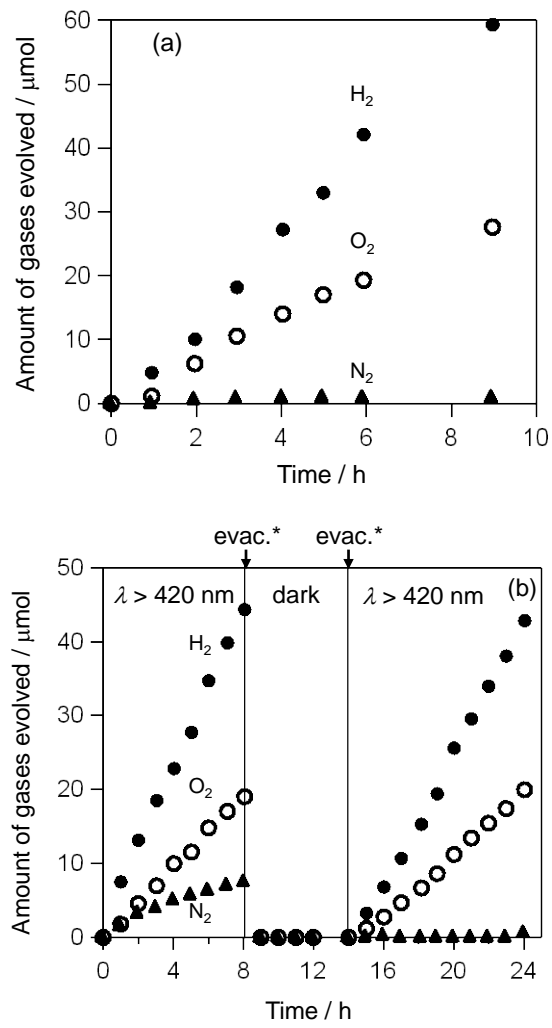


Figure 3

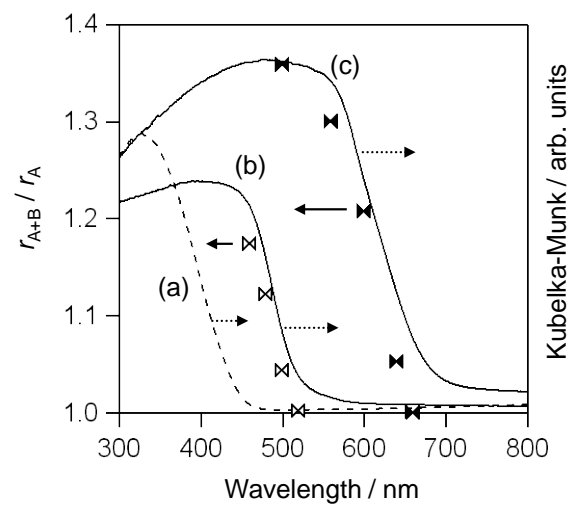


Figure 4