Preparation of BaZrO₃–BaTaO₂N solid solutions and the photocatalytic activities for water reduction and oxidation under visible light

Kazuhiko Maeda,^{1,2,*} and Kazunari Domen^{3,*}

¹ Department of Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan. ² Precursory Research for Embryonic Science and Technology (PRESTO), Japan Science and Technology Agency (JST), 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan. ³ Department of Chemical System Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan.

*To whom corresponding author should be addressed.

TEL: +81-3-5734-2239, FAX: +81-3-5734-2284

Email: maeda.k.ah@m.titech.ac.jp, domen@chemsys.t.u-tokyo.ac.jp

To be submitted for publication in *Journal of Catalysis* (special issue)

Keywords

Hydrogen production, Photocatalysis, Solid solution, Solar energy conversion, Visible light

Abstract

Particulate solid solutions between BaTaO₂N and BaZrO₃, having a single-phase perovskite structure, were examined over the Zr/Ta range from 0 to 0.5 as photocatalysts for water splitting under visible light. With increasing BaZrO₃ content (that is, Zr/Ta ratio), the band edge of BaTaO₂N shifted from 660 to 620 nm, due primarily to the contribution from the larger band gap of BaZrO₃ compared to BaTaO₂N. These materials, with modification by the cocatalysts Pt and IrO₂, were capable of reducing and oxidizing water into H₂ and O₂, respectively, under visible light ($\lambda > 420$ nm) in the presence of methanol and silver nitrate as an electron donor and acceptor, respectively. When a small amount of BaZrO₃ was introduced into BaTaO₂N (Zr/Ta $\leq$ 0.05) using a suitably prepared oxide precursor, the highest activity was obtained for both water reduction and oxidation. On the other hand, when added in excess, BaZrO₃ lowered the crystallinity of the solid solution, contributing directly to a decrease in photocatalytic activities, especially for water oxidation. The results of photoelectrochemical measurements indicated that the conduction band minimum and the valence band maximum of BaZrO₃–BaTaO₂N solid solution straddle the water splitting potential.

1. Introduction

Recently, photocatalytic water splitting has attracted considerable attention from the standpoint of solar-to-fuel energy conversion [1, 2]. To efficiently utilize solar energy, it is highly desirable to develop a photocatalytic assembly that works under a wide range of visible light – the main component of solar spectrum. So far, some non-oxide compounds (e.g., Ta₃N₅ [3], LaTiO₂N [4], CaNbO₂N [5], Ga-In-Zn-O-N [6] and Sm₂Ti₂S₂O₅ [7]) have studied as potential candidates for such application, and they show photocatalytic activities for water reduction and oxidation by responding visible photons of up to 600 nm (corresponding to a 2.0 eV band gap) in the presence of suitable electron donors and acceptors. Until very recently, however, no compound with a band gap smaller than 2.0 eV that photocatalytically achieves both water reduction and oxidation had been reported. As the band gap of a

given compound is decreased, the driving forces for water reduction and oxidation should inevitably decrease, making water splitting more difficult.

BaTaO₂N is a perovskite compound with an absorption edge of ca. 660 nm [8–10], and has been reported to exhibit water reduction activity under visible light when a suitable electron donor such as methanol or iodide is employed [11–15]. Although the capacity for light harvesting is very attractive, it had been reported that BaTaO₂N is unable to catalyze water oxidation under visible light even in the presence of an electron acceptor like Ag⁺ [11, 12]. Hence, one might regard BaTaO₂N unsuitable for applications in light-driven water splitting.

Contrary to the previous report, we have very recently demonstrated that carefully prepared perovskite BaZrO₃–BaTaO₂N solid solutions ($0 \leq \text{Zr/Ta} \leq 0.1$) are active for both water reduction and oxidation even under > 660 nm irradiation [16]. This is the first demonstration that a semiconductor having an absorption edge longer than 600 nm achieves the functionality as a photocatalyst to reduce and oxidize water under visible light. In general, photocatalytic activity of a given material is dependent on the preparation method, as it determines physicochemical properties of the material [2]. Thus, investigating the preparation route of a given material is important for enhancing the photocatalytic activity.

In this article, we systematically studied the perovskite BaZrO₃–BaTaO₂N system over the Zr/Ta range of ≤ 0.5 as photocatalysts for water reduction and oxidation under visible light. The photocatalytic behavior is discussed on the basis of the results of physicochemical analyses and photoelectrochemical measurements.

2. Experimental

2.1. Preparation of oxide precursors and BaZrO₃–BaTaO₂N solid solutions

As a precursor for BaTaO₂N, a mixed oxide of Ba and Ta was prepared by the polymerized complex (PC) method, which has usually been applied in the preparation of an oxide precursor containing desired

metal components toward (oxy)nitride synthesis [4, 5, 8, 9]. Approximately 12 mmol of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ (99.9%; Wako Pure Chemicals), and an equimolar amount of BaCO_3 (98%; Kanto Chemicals), 0.48 mol of ethylene glycol (EG) (99.5%; Kanto Chemicals) and 0.12 mol of anhydrous citric acid (CA) (98.0%; Wako Pure Chemicals) were added into a methanol solution (100 mL, 99.8%; Kanto Chemicals). An appropriate amount of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (99%; Kanto Chemicals) was also added and dissolved into the solution, as needed. The as-prepared solution was heated at ca. 400 K to achieve complete dissolution and promote esterification between EG and CA, yielding a glassy resin. The resin was then calcined at ca. 673 K in a mantle heater to complete decomposition. The resulting black powder was subsequently calcined on an Al_2O_3 plate at 1073 K for 2 h in air. The as-prepared Ba–Ta and Ba–Zr–Ta mixed oxide will hereafter be denoted as BaTaO_x and BaZrTaO_x , respectively, for simplicity. A similar experiment was performed using TaCl_5 (99.99%; High Purity Chemicals) as the Ta source instead of $\text{Ta}(\text{OC}_2\text{H}_5)_5$ according to a method reported previously [13–15]. The as-obtained oxide precursor will be referred to as BaTaO_x (ref).

We also prepared another Ba–Zr–Ta–O precursor by impregnating the as-prepared (Zr-free) BaTaO_x samples with BaCl_2 (97%; Kanto Chemicals) and $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, followed by calcination in air at 1073 K for 2 h. The oxide precursor thus obtained will be denoted as $\text{BaZrO}_x/\text{BaTaO}_x$.

The as-prepared oxide precursors were heated to 1223 K at a ramp rate of $10 \text{ K} \cdot \text{min}^{-1}$, and kept at 1223 K for 20 h under flowing NH_3 ($100 \text{ mL} \cdot \text{min}^{-1}$). As a reference, BaTaO_2N was prepared according to a previously reported procedure [13–15], and will hereafter be referred to as BaTaO_2N (ref).

2.2. Preparation of electrodes

The electrodes were prepared by electrophoretic deposition in an acetone solution (50 mL) containing the as-prepared BaZrO_3 – BaTaO_2N solid solution (50 mg) and iodine (10 mg). Two parallel FTO electrodes were immersed in the solution with a 10–15 mm separation, and a 25 V bias was applied between them for 1 min under potentiostat control. The coated area was fixed at $1.5 \times 3.5 \text{ cm}$. To improve

the electron transfer between the BaZrO₃–BaTaO₂N particles and FTO substrate, a TiO₂ layer was deposited by a method we developed previously [16]. The as-prepared electrode was soaked in 0.1 M TiCl₄ in methanol solution, and then dried at 523 K. After repeating this procedure for 5 times, the electrode sample was heated in flowing N₂ (100 mL·min⁻¹) at 673 K for 1 h. The deposited TiO₂ layer helps to improve interparticle electron transfer by reducing the resistance between BaZrO₃–BaTaO₂N particles.

2.3. Modification with cocatalysts

Modification of BaTaO₂N-based particulate materials with nanoparticulate Pt (0.3 wt%) was accomplished by impregnation to improve the water reduction activity. The powder sample was immersed in an aqueous solution containing the appropriate amount of H₂PtCl₆·2H₂O (Kanto Chemicals, 97% Pt) in a water bath. After drying the solution, the resulting powder was collected and heated with H₂ gas (20 kPa) at 473 K for 1 h in a gas circulation system similar to the photocatalytic reaction system described below.

To study water oxidation, colloidal IrO₂ was adsorbed on these materials. The colloidal IrO₂ solution was prepared by hydrolysis of Na₂IrCl₆ according to a previous method with some modification [17]. Briefly, 0.016 g of Na₂IrCl₆ was dissolved in 50 mL H₂O, and the pH of the solution was adjusted to 11–12 using aqueous NaOH solution. The solution was heated at 353 K for 0.5 h, and then cooled to room temperature by immersion in an ice-water bath. The pH of the cooled solution was slowly adjusted to 9 using aqueous HNO₃ solution. Subsequent heating at 353 K for 0.5 h resulted in a deep blue solution containing colloidal IrO₂, which was diluted to 50 mL in total volume. A 0.12–0.13 g sample was dispersed in ca. 30 mL of the as-prepared colloidal IrO₂ solution (1.5 wt% with respect to catalyst mass), with some dilution. The suspension was subjected to agitation for 1 h at room temperature, followed by centrifugation to collect residual solids. UV-visible spectroscopy showed that in all cases, there was no absorption signal derived from IrO₂ colloids in the supernatant solution, indicating

quantitative adsorption of IrO₂. The IrO₂-loaded samples were dried in a furnace at 343 K overnight. As reported in our previous paper [16], transmission electron microscopy observations revealed that the particle size of the loaded IrO₂ was typically 1–2 nm. For the photoelectrochemical application, adsorption of the as-prepared colloidal IrO₂ was also conducted by soaking the electrode sample in a diluted colloidal solution (ca. 4 vol%) overnight, followed by rinsing with water prior to photoelectrochemical measurements.

2.4. Characterization of catalysts

The samples prepared were studied by powder X-ray diffraction (XRD; RINT-UltimaIII, Rigaku; Cu K α), UV-visible diffuse reflectance spectroscopy (DRS; V-560, JASCO) and scanning electron microscopy (SEM; S-4700, Hitachi). The Brunauer-Emmett-Teller (BET) surface area was measured using a BELSORP-mini (BET Japan) at liquid nitrogen temperature (77 K).

2.5. Photocatalytic reactions

Reactions were carried out in a Pyrex top-irradiation vessel connected to a glass closed gas circulation system. Photoreduction of water was performed by dispersing 100 mg of the Pt-loaded catalyst powder in an aqueous methanol solution (10 vol%, 100 mL) as an electron donor, while water photo-oxidation was conducted by dispersing 100 mg of the as-prepared powder in an aqueous silver nitrate solution (AgNO₃, 10 mM, 100 mL) containing 100 mg of La₂O₃, which buffered the pH of the reactant solution at 8–8.5 during the reaction [3–5, 7]. The reactant solution was evacuated several times to remove air completely, and a small amount of Ar gas (ca. 5 kPa) was introduced into the reaction system prior to irradiation under a 300 W xenon lamp (Cermax, PE300BF) with an output current of 20 A unless otherwise stated. The irradiation wavelength was controlled by the combination of a cold mirror (CM-1), cutoff filter (L-42) and water filter ($\lambda > 420$ nm). The reactant solution was maintained at room temperature by a water bath during the reaction. The evolved gases were analyzed by gas

chromatography (Shimadzu, GC-8A with TCD detector and MS-5A column, argon carrier gas).

Apparent quantum yields (AQYs) for water reduction and oxidation were measured using the same experimental setup, except for the addition of a band pass filter ($\lambda = 420.5$ nm), and were estimated by the equation

$$\text{AQY (\%)} = A \cdot R/I \times 100 \quad (1)$$

where A , R , and I represent coefficients based on the reactions (H_2 evolution, 2; O_2 evolution, 4), the H_2 or O_2 evolution rate, and the rate of incident photons, respectively. The total number of incident photons (ca. 125.5 mW) was measured using a calibrated silicon photodiode. The reproducibility of the gas evolution rate was typically within 10–15% under a given set of reaction conditions.

2.7. Photoelectrochemical measurements

Photoelectrochemical measurements were carried out with a potentiostat (HSV-110, Hokuto Denko) and an electrochemical cell at room temperature. The cell was made of Pyrex glass, and was a three-electrode-type system using a Pt wire and Ag/AgCl electrode as the counter and reference electrodes, respectively, unless otherwise stated. An aqueous Na_2SO_4 solution was used as the electrolyte, which was saturated with N_2 gas prior to the electrochemical measurements. For pH-dependent flat-band potential measurements, the pH of the electrolyte solution was controlled by NaOH and H_2SO_4 . Visible light irradiation ($\lambda = 500$ nm) was conducted from the backside of the working electrode, with a xenon lamp (300 W) as light source, fitted with a cutoff filter and a band pass filter.

3. Results and discussion

3.1. Preparation of single-phase BaTaO_2N particles

First of all, we needed to establish a synthetic method enabling the production of single-phase BaTaO_2N (and $\text{BaZrO}_3\text{--BaTaO}_2\text{N}$) particles with high reproducibility, because existing methods have

the disadvantage of generating Ta_3N_5 as a byproduct [13–15]. In the present study, we prepared an oxide precursor by the PC method using BaCO_3 and $\text{Ta}(\text{OC}_2\text{H}_5)_5$ as starting materials, followed by heat treatment with NH_3 at 1223 K for 20 h. The XRD pattern of a sample thus obtained is shown in Figure 1A, which exhibits a single-phase perovskite structure, as distinct from that of the previous sample, BaTaO_2N (ref). Our SEM observations reveal that the morphology of the present BaTaO_2N clearly differs from that of BaTaO_2N (ref), the latter consisting of large agglomerates of primary particles of 100–200 nm in size (Figure 1B), even though there was only a minor change in the precursor used. The specific surface area of the present BaTaO_2N was determined to be $9.4 \text{ m}^2\cdot\text{g}^{-1}$, i.e., larger than that of BaTaO_2N (ref) (ca. $2.5 \text{ m}^2\cdot\text{g}^{-1}$), which is consistent with the results of XRD and SEM analyses. As shown in Figure 1C, light absorption by the BaTaO_2N prepared in this study begins at 700 nm, with a steep absorption edge at 660 nm. The band gap is estimated to be 1.75 eV (Figure S1), in agreement with the reported value [10]. The present BaTaO_2N sample also exhibits a less pronounced background level than the previous BaTaO_2N (ref) sample, indicating that it had a lower defect density than BaTaO_2N (ref). Thus, a single-phase BaTaO_2N perovskite with relatively low defect density was successfully obtained by modifying the preparation method.

To confirm the effectiveness of the single-phase production of BaTaO_2N , visible-light photocatalytic activity of the present BaTaO_2N for water reduction was investigated using methanol as an electron donor. Pt was loaded as a cocatalyst to promote water reduction catalysis. As listed in Table 1, the present BaTaO_2N (entry 1) gave an activity 6 times higher than that of BaTaO_2N (ref) (entry 2). This is presumably attributable to the production of single-phase BaTaO_2N with a lower defect density.

3.2. Formation of solid solution between BaZrO_3 and BaTaO_2N

We employed the abovementioned method using $\text{Ta}(\text{OC}_2\text{H}_5)_5$ for the synthesis of BaZrO_3 – BaTaO_2N solid solutions, as it helps to avoid any complications due to the production of a Ta_3N_5 impurity. Figure 2A shows XRD patterns of samples obtained by nitriding BaZrTaO_x precursors, which were prepared by

the PC method. All samples exhibit single-phase diffraction patterns assignable to perovskite BaTaO₂N. With increasing Zr/Ta ratio, the main peak of the (100) reflection shifted progressively to lower 2θ angles, lying at a position between BaZrO₃ and BaTaO₂N (Figure 2B). This indicates that the samples obtained were solid solutions of BaZrO₃ and BaTaO₂N. According to a report by Grins and Svensson, who prepared BaZrO₃–BaTaO₂N solid solutions by nitriding sol-gel derived Ba-Zr-Ta oxides, the lattice mismatch between BaZrO₃ and BaTaO₂N is approximately 2%, and hence they can form solid solutions over the entire range of substitution [18]. It is also noted that with increasing Zr/Ta ratio, the peak intensity gradually decreased and the peak intensity broadened, indicating that crystallinity decreases with increasing BaZrO₃ content. The reduction of the particle size of BaZrO₃–BaTaO₂N solid solutions was also confirmed by SEM (Figure 3), which is consistent with the results of XRD analysis. In accordance with these changes, the specific surface areas of BaZrO₃–BaTaO₂N solid solutions tended to increase with increasing Zr/Ta ratio.

Figure 2C shows UV-visible DRS for BaZrO₃–BaTaO₂N solid solutions with different Zr/Ta ratios. The absorption band edge of the materials shifts to lower wavelengths with increasing Zr/Ta ratio. In other words, the formation of the BaZrO₃–BaTaO₂N solid solution widens the band gap of BaTaO₂N, which can be reasonably understood, considering the larger band gap of BaZrO₃. As discussed in our previous paper [15], the widened band gap of the BaZrO₃–BaTaO₂N solid solution is thought to result from the hybridization of Zr4d orbitals with Ta5d orbitals. The second plausible explanation is that the concentration of nitrogen in BaZrO₃–BaTaO₂N solid solutions inevitably drops below that in BaTaO₂N. This would lower the valence band potential, leading to a widening of the band gap.

Visible-light photocatalytic activities of the as-prepared BaZrO₃–BaTaO₂N solid solutions for water reduction and oxidation were examined. As shown in Figure 4 (triangles), all tested samples were active for both water reduction and oxidation. However, the activities were strongly dependent on the Zr/Ta ratio. The water reduction activity increased with increasing Zr/Ta ratio, reaching a maximum at Zr/Ta = 0.05, beyond which it gradually began to drop. This trend in water reduction is identical to that observed

in our previous study on BaZrO₃–BaTaO₂N solid solutions containing Ta₃N₅ impurities [15]. A similar trend was observed in water oxidation, but the maximum photocatalytic activity was found over a narrow Zr/Ta ratio range.

For both water reduction and oxidation, the decrease in activity at higher Zr/Ta ratios is most likely caused by the monotonic decrease in crystallinity, as observed by XRD (Figure 2A) and SEM (Figure 3). While the improved activity for water reduction from Zr/Ta = 0 to 0.05 appears to be due to the enhanced driving force for redox reactions stemming from the blue shift of the absorption edge (Figure 2C) as was discussed in our previous paper [15], the enhanced activity for water oxidation from Zr/Ta = 0 to 0.01 cannot be explained in terms of the absorption edge position. The absorption edge positions of the Zr/Ta = 0 and 0.01 samples are almost identical. Furthermore, the Zr/Ta = 0.01 sample, which exhibited a higher activity for water oxidation but comparable activity for water reduction, has a more pronounced background level due to anionic vacancies at longer wavelengths. This is inconsistent with the results for the water oxidation reaction. The reason for the activity increase remains unclear. The small amount of Zr species incorporated in BaTaO₂N might have a positive effect only in the case of water oxidation photocatalysis.

3.3. Improved photocatalytic performance of BaZrO₃–BaTaO₂N solid solutions

Forming solid solutions between BaZrO₃ and BaTaO₂N with suitable compositions by applying a previous method [13–15] with some modification improved the photocatalytic activities for both water reduction and oxidation, compared to a similarly prepared BaTaO₂N sample (Figure 4). However, the optimal Zr/Ta conditions for water reduction and oxidation were different, and at least three problems emerged in BaTaO₂N as a result of the solid solution formation with BaZrO₃. The first one was the monotonic decrease in crystallinity with increasing Zr/Ta ratio in the solid solution, as observed in Figure 2A. In general, lowering the crystallinity of a given photocatalyst decreases activity, because of the shorter lifetime of electron-hole pairs [19, 20]. This is also evident from the results of photocatalytic

reactions shown in Figure 4. The second problem was the blue shift in the absorption edge of BaTaO₂N. The blue shift may not necessarily have a negative impact on photocatalytic activity because it enhances the driving force for surface redox reactions. Nevertheless, from the viewpoint of the efficiency of utilization of the solar spectrum, it would be better to harvest more visible photons. The last problem was the generation of reduced Ta species, as can be seen from the more pronounced background level in DRS (Figure 2C), especially in solid solutions having a lower Zr/Ta ratio (although this had a positive effect on water oxidation but not on water reduction). During the nitridation of Ta⁵⁺-containing oxide precursors into the corresponding nitrided products, Ta⁵⁺ ions were reduced by H₂ derived from the disassociation of NH₃ at high temperature, generating reduced Ta species [21–23]. As a result, anionic vacancies are formed to restore the charge balance of the crystal. Thus, the presence of reduced tantalum species strongly suggests that these crystals contain a significant number of anionic vacancies that can function as traps of photogenerated electrons and holes.

A new preparation route was examined to address the abovementioned problems in the synthesis of BaZrO₃–BaTaO₂N solid solutions, especially those with lower Zr/Ta ratios (≤ 0.1). In order to minimize the incorporation of excess BaZrO₃ into BaTaO₂N, which leads to an undesirable widening of the band gap and lowering of the crystallinity of BaTaO₂N, first, a BaTaO_x free of any Zr species was prepared, followed by modification with Ba-Zr oxide species. The resulting composite of BaZrO_x/BaTaO_x was nitride as before.

Figure 5A shows XRD patterns of the as-prepared samples, along with the data for the BaZrTaO_x precursor (Zr/Ta = 0.05) nitrided at the same condition. All samples exhibit a single-phase diffraction pattern identical to that of BaTaO₂N. The XRD peak position tended to shift to lower 2θ angles with increasing Zr/Ta ratio (Figure 5B), although this shift was very small compared to the sample prepared by nitriding the BaZrTaO_x precursor having the same Zr/Ta ratio (0.05). It is most likely that the BaZrO₃ component in these new samples was distributed mainly near the surface, but the degree of segregation was too small to be detected by XRD, owing to the relatively low concentration of the component

(Zr/Ta $\leq$ 0.1). It should also be noted that no change could be observed in the diffraction peak intensity despite the Zr/Ta ratio range examined ($\leq$ 0.1) [24], indicative of similar degree of crystallinity. As shown in Figure S2, no noticeable change could be identified in the primary particle size.

The DRS for the same set of samples are shown in Figure 5C. With increasing Zr/Ta ratio, the absorption edge shifted slightly to shorter wavelengths, accompanied by a continuous reduction of the background level in the wavelength range of 700–800 nm. It should be noted that the background level in the new sample is much less pronounced than that in the old sample (prepared from the BaZrTaO_x precursor). Thus, the new preparation method allows for the preparation of BaZrO₃–BaTaO₂N solid solutions with relatively low anionic vacancies and an absorption edge of 650–660 nm, while preserving the crystallinity of the pristine BaTaO₂N.

Photocatalytic activities of the new BaZrO₃–BaTaO₂N solid solutions for water reduction and oxidation were measured as before. The rates of H₂ and O₂ evolution both increased with increasing Zr/Ta ratio up to 0.05, and then decreased. The highest activities recorded here were also higher than those obtained using the solid solution samples shown in Figure 4 (circles), with the same optimal Zr/Ta ratio for H₂ and O₂ evolution. As shown in Figure 5A, the new BaZrO₃–BaTaO₂N solid solution did not show any serious decrease in crystallinity or generation of reduced tantalum species, which were major issues in the previous solid solution samples. These features would enhance their photocatalytic performance. The AQY of H₂ and O₂ evolution under the present reaction conditions were about 0.06 and 0.03% at 420 nm, respectively.

3.4. Estimation of band-edge potentials

It was thus shown that carefully prepared BaZrO₃–BaTaO₂N solid solutions are active for both water reduction and oxidation, despite the relatively long absorption edges, meaning that the conduction and valence band potentials straddle the water splitting potential. The actual band-edge positions of BaZrO₃–BaTaO₂N were then evaluated by measuring the onset potentials of photocurrent generated

from the IrO₂/TiO₂/BaZrO₃–BaTaO₂N/FTO electrode in electrolyte solutions with various pH values [25–27]. Current-voltage curves were measured under intermittent visible light ($\lambda = 500$ nm) and from negative to positive potential with a scan rate of 5 mV·s⁻¹ in aqueous Na₂SO₄ solution adjusted to pH 4.4, 8.4, and 11.2 by H₂SO₄ or NaOH. As shown in Figure 6, an anodic photocurrent was observed at all pH conditions tested. It has been demonstrated in our previous study that the anodic photocurrent generated from IrO₂/TiO₂/BaZrO₃–BaTaO₂N/FTO electrode originates mainly from water oxidation [16]. The onset potential, corresponding to the flat-band potential (E_{FB}), shifted in the negative direction with increasing pH. The energy difference between the conduction band edge potential (E_{CB}) and E_{FB} is assumed to be ca. 0.1~0.3 eV considering the n-type semiconducting character of BaZrO₃–BaTaO₂N [28–29]. On the basis of the band gap of BaZrO₃–BaTaO₂N (1.8 eV), the valence band edge potential (E_{VB}) is estimated to be 1.8 V more positive than E_{CB} .

Figure 7 shows the conduction and valence band-edge potentials of the IrO₂/TiO₂/BaZrO₃–BaTaO₂N/FTO electrode as a function of pH. The positions of the conduction band minimum and the valence band maximum of BaZrO₃–BaTaO₂N are dependent on pH, with a variation of approximately –50 mV/pH. The estimated band edge positions of BaZrO₃–BaTaO₂N are satisfactory for water oxidation at all pH against H₂ evolution at the counter electrode, in agreement with the results of photocatalytic reactions (Figure 4) [30]. However, it should be noted that the energy difference between the water oxidation potential and the valence band maximum is at most ~0.3 eV, smaller than those of other (oxy)nitride materials (e.g., Ta₃N₅ and LaTiO₂N) [25, 27]. This might be one plausible explanation why BaZrO₃–BaTaO₂N exhibits a relatively low AQY for water oxidation (< 0.1%), different from Ta₃N₅ and LaTiO₂N that are able to oxidize water into O₂ with AQYs at least an order of magnitude greater than BaZrO₃–BaTaO₂N [3, 4].

4. Conclusion

The BaZrO₃–BaTaO₂N systems ($\text{Zr/Ta} \leq 0.5$) were studied as photocatalysts for H₂ and O₂ evolution from water under visible light. Despite the long absorption edges, solid solutions of BaZrO₃ and BaTaO₂N are capable of reducing and oxidizing water under visible light, consistent with the results of photoelectrochemical measurements. By refining the preparation method, it was found that reducing the density of defects and improving the crystallinity while preventing Zr(IV) ions from being diffused into the BaTaO₂N lattice are essential to improving photocatalytic activities of BaZrO₃–BaTaO₂N for water reduction and oxidation.

Acknowledgments

This work was supported by the PRESTO/JST program “Chemical Conversion of Light Energy”. The authors would also like to acknowledge the Grant-in-Aid for Specially Promoted Research (No. 23000009) of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan, and Advanced Low Carbon Technology Research and Development Program (ALCA) of the Japan Science and Technology Agency (JST). One of the authors (K.M.) thanks the Nippon Sheet Glass Foundation for Materials Science and Engineering for funding support.

References and Notes

1. A. Kudo, Y. Miseki, Chem. Soc. Rev. 38 (2009) 253.
2. K. Maeda, J. Photochem. Photobiol. C: Photochem. Reviews 12 (2011) 237.
3. G. Hitoki, A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, K. Domen, Chem. Lett. 31 (2002) 736.
4. A. Kasahara, K. Nukumizu, G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, J. Phys. Chem. A 106 (2002) 6750.
5. B. Siritanaratkul, K. Maeda, T. Hisatomi, K. Domen, ChemSusChem 4 (2011) 74.

6. K. Kamata, K. Maeda, D. Lu, Y. Kako, K. Domen, *Chem. Phys. Lett.* 470 (2009) 90.
7. A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *J. Am. Chem. Soc.* 124 (2002) 13547.
8. F. Pors, R. Marchand, Y. Laurent, P. Bacher, G. Roult, *Mater. Res. Bull.* 23 (1988) 1447.
9. X. Gouin, R. Marchand, Y. Laurent, F. Gervais, *Solid State Commun.* 93 (1995) 857.
10. Y.-I. Kim, P. M. Woodward, K. Z. Baba-Kishi, C. W. Tai, *Chem. Mater.* 16 (2004) 1267.
11. G. Hitoki, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi, K. Domen, *Electrochem.* 70 (2002) 463.
12. D. Yamasita, T. Takata, M. Hara, J. N. Kondo, K. Domen, *Solid State Ionics* 172 (2004) 591.
13. M. Higashi, R. Abe, K. Teramura, T. Takata, B. Ohtani, K. Domen, *Chem. Phys. Lett.* 452 (2008) 120.
14. M. Higashi, R. Abe, T. Takata, K. Domen, *Chem. Mater.* 21 (2009) 1543.
15. T. Matoba, K. Maeda, K. Domen, *Chem. Eur. J.* 17 (2011) 14731.
16. K. Maeda, K. Domen, *Angew. Chem., Int. Ed.* 51 (2012) 9865.
17. A. Harriman, I. J. Pickering, J. M. Thomas, P. A. Christensen, *J. Chem. Soc., Faraday Trans. 1* 84 (1988) 2795.
18. J. Grins, G. Svensson, *Mater. Res. Bull.* 29 (1994) 801.
19. A. Yamakata, T. Ishibashi, H. Kato, A. Kudo, H. Onishi, *J. Phys. Chem. B* 107 (2003) 14383.
20. F. Amano, A. Yamakata, K. Nogami, M. Osawa, B. Ohtani, *J. Am. Chem. Soc.* 130 (2008) 17650.
21. K. Maeda, H. Terashima, K. Kase, M. Higashi, M. Tabata, K. Domen, *Bull. Chem. Soc. Jpn.* 81 (2008) 927.
22. K. Maeda, M. Higashi, D. Lu, R. Abe, K. Domen, *J. Am. Chem. Soc.* 132 (2010) 5858.
23. S. S. K. Ma, K. Maeda, K. Domen, *Catal. Sci. Technol.* 2 (2012) 818.
24. The reproducibility in the XRD peak intensity was within ~10% from batch to batch.
25. A. Ishikawa, T. Takata, J. N. Kondo, M. Hara, K. Domen, *J. Phys. Chem. B* 108 (2004) 11049.
26. K. Ogisu, A. Ishikawa, Y. Shimodaira, T. Takata, H. Kobayashi, K. Domen, *J. Phys. Chem. C* 112

(2008) 11978.

27. C. Le Paven-Thivet, A. Ishikawa, A. Ziani, L. Le Gendre, M. Yoshida, J. Kubota, F. Tessier, K. Domen, J. Phys. Chem. C 113 (2009) 6156.
28. D. E. Scaife, Sol. Energy 25 (1980) 41.
29. Y. Matsumoto, J. Solid State Chem. 126 (1996) 227.
30. We have conducted photoelectrochemical measurements in a similar manner for BaZrO₃–BaTaO₂N having larger Zr/Ta ratios in order to evaluate the change in band-edge positions with respect to Zr/Ta ratios. While these electrode samples exhibited anodic photocurrent upon visible light ($\lambda = 500$ nm), however, the photocurrent onset potential overlapped with a water reduction current, making it difficult to determine the onset potential (Figure S3). Nevertheless, the photocurrent onset potential tended to shift to negative potentials with increasing the Zr/Ta ratios. It suggests that the formation of solid solution with BaZrO₃ lifts up the conduction band maximum of BaTaO₂N, consistent with our initial interpretation (ref. 15).

Table 1. Photocatalytic activities of BaTaO₂N-based catalysts for water reduction and oxidation under visible light ($\lambda > 420$ nm)^a

Entry	Oxide precursor	Ta ₃ N ₅ byproduct ^b	Relative background absorption ^c	Specific surface area / m ² g ⁻¹	Initial H ₂ evolution rate / $\mu\text{mol h}^{-1}$
1	BaTaO _x	No	Weaker	9.4	8.1
2	BaTaO _x (ref)	Yes	Stronger	2.5	1.4

^a Reaction conditions: catalyst, 100 mg; 10 vol.% aqueous methanol solution 100 mL; light source, xenon lamp (300 W) fitted with a cold mirror (CM-1); reaction vessel, Pyrex top-irradiation type. ^b Judged from XRD data. ^c Judged from the absorption background level at wavelengths longer than 650 nm.

Figure captions

Figure 1. (A) XRD patterns, (B) SEM images, and (C) UV-visible DRS of the as-prepared BaTaO₂N and BaTaO₂N (ref).

Figure 2. (A) XRD patterns and (B) DRS of samples obtained by nitriding BaZrTaO_x precursors with different Zr/Ta ratios.

Figure 3. SEM images of samples obtained by nitriding BaZrTaO_x precursors with different Zr/Ta ratios.

Figure 4. Photocatalytic activities of BaZrO₃–BaTaO₂N solid solutions prepared from different precursors and Zr/Ta ratios for water reduction and oxidation under visible light ($\lambda > 420$ nm). Reaction conditions: catalyst, 100 mg; cocatalyst, 0.3 wt% Pt for H₂ evolution and 1.5 wt% IrO₂ for O₂ evolution; aqueous methanol solution (10 vol%, 100 mL) for H₂ evolution and silver nitrate solution (10 mM, 100 mL) with 100 mg La₂O₃ for O₂ evolution; light source, xenon lamp (300 W) with cutoff filter; reaction vessel, Pyrex top-irradiation type. Solid triangle, H₂ (from BaZrTaO_x); open triangle, O₂ (from BaZrTaO_x); solid circle, H₂ (from BaZrO_x/BaTaO_x); open circle, O₂ (from BaZrO_x/BaTaO_x). Gas evolution rates plotted here were recorded at the initial stage of reaction (~1 h).

Figure 5. (A) XRD patterns and (B) DRS of samples obtained by nitriding BaZrO_x/BaTaO_x precursors with different Zr/Ta ratios. The data for BaZrO₃–BaTaO₂N (Zr/Ta = 0.05) prepared from BaZrTaO_x are shown in the panel B and C (dotted line) for comparison.

Figure 6. Current-voltage curves in 0.1 M aqueous Na₂SO₄ solution at various pH conditions under intermittent visible light irradiation ($\lambda = 500$ nm) for IrO₂/TiO₂/BaZrO₃–BaTaO₂N/FTO electrodes (5.25 cm²). Scan rate: 5 mV·s⁻¹.

Figure 7. Dependence of conduction and valence band edge potentials for BaZrO₃–BaTaO₂N (Zr/Ta = 0.025) on pH of electrolyte, as determined from photocurrent measurements (see Figure 6).

Figure 1a

Figuer 1b

Figure 1c

Figure 2a

Figure 2b

Figure 2c

Figure 3

Figure 4

Figure 5a

Figure 5b

Figure 5c

Figure 6-1

Figure 6-2

Figure 6-3

Figure 7

Graphical Abstract