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Photocatalysis

# Water Oxidation Using a Particulate $BaZrO_3$-$BaTaO_2N$ Solid-Solution Photocatalyst That Operates under a Wide Range of Visible Light**

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Light-driven water splitting into $H_2$ and $O_2$ using a semiconductor photocatalyst is the simplest form of artificial photosynthesis, and the development of which could be considered a noble pursuit in chemistry.[1,2] In nature, photosystems I and II in green plants harvest 700 and 680 nm photons, respectively, oxidizing $H_2O$ into $O_2$ under sunlight, with a quantum yield close to unity. An artificial photosynthetic system should have both solar energy conversion efficiency and light-harvesting capability equivalent to or greater than those of the natural system. Numerous attempts have been made by many researchers to develop such an artificial photosynthetic assembly.[2,3] However, none have yielded satisfactory results in terms of either efficiency or light-harvesting capability. The major obstacle to progress is the lack of a semiconductor material satisfying the stringent requirements of 1) valence (conduction) band potentials sufficiently more positive (negative) to drive water oxidation (reduction); 2) the ability to harvest visible photons of up to 700 nm, which is the absorption maximum for photosystem I in green plants; 3) sufficient stability under irradiation; and 4) low defect density, which can prolong the lifetime of photogenerated carriers to achieve high conversion efficiency.

From the viewpoint of both chemistry and practical applications, it is undoubtedly important to develop a photocatalytic material that harvests a wide range of visible photons. At present, $Ta_3N_5$,[4] $LaTiO_2N$,[5] $CaNbO_2N$,[6] Ga-In-Zn-O-N,[7] and $Sm_2Ti_2S_2O_5$[8] are photocatalysts that have a 600 nm absorption edge, reducing and oxidizing water under visible light ($\lambda > 400$ nm) in the presence of suitable electron donors and acceptors. However, the upper limit to achieve both water reduction and oxidation has remained 600 nm. This is most likely due to the difficulty in developing a material that satisfies the aforementioned requirements. Furthermore, narrowing the band gap of a photocatalyst would increase its absorption of visible light, but decrease the driving force for redox reactions. This would become a more serious concern in water oxidation than in water reduction in terms of kinetics, because water oxidation involves a complicated four-electron process.[9] Nevertheless, the water oxidation reaction is a particularly important step in artificial photosynthesis for solar fuel production, not only water splitting into $H_2$ and $O_2$, but also the reduction of $CO_2$ to methanol or hydrocarbons. Hence the development of a photocatalytic material that is able to oxidize water by responding up to 700 nm light is highly desirable.

Herein, we demonstrate that $BaTaO_2N$ and its solid solutions with $BaZrO_3$ ($Zr/Ta \leq 0.1$), which have single-phase perovskite structure and > 650 nm absorption edge, are active for both photocatalytic water reduction and oxidation under visible light, even though they have relatively small band gaps of 1.7–1.8 eV. Photoelectrochemical water splitting, which is another important application of semiconductor materials for solar-to-fuel conversion,[3] is also demonstrated using a $BaZrO_3$-$BaTaO_2N$ solid solution as an anode material under sunlight. So far, a number of photoanode materials have been developed, and some have achieved high incident photon-to-electron conversion efficiencies (IPCEs) of several tens of percent with an applied bias smaller than the thermodynamically required potential for water electrolysis (1.23 V).[2e,3] However, it should be mentioned that solar energy conversion by water splitting using a single photoanode material with a band gap smaller than 2.0 eV (corresponding to a 600 nm absorption band) had not been demonstrated.

XRD patterns of particulate $BaZrO_3$-$BaTaO_2N$ solid solutions ($Zr/Ta \leq 0.1$) are shown in the Supporting Information, Figure S1a. All samples exhibit a single-phase diffraction pattern identical to that of $BaTaO_2N$. The XRD peak position tended to shift to lower 2$\theta$ angles with increasing Zr/Ta ratio, although this shift was very small. According to a report by Grins and Svensson, who prepared $BaZrO_3$-$BaTaO_2N$ solid solutions (with some byproduction of $Ta_3N_5$) by nitriding sol-gel derived Ba-Zr-Ta oxides, the lattice mismatch between $BaZrO_3$ and $BaTaO_2N$ is approximately 2%, and hence they

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can form solid solutions over the entire range of substitution.[10] In the present case, however, it appeared that the $BaZrO_3$ component in these 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 ($Zr/Ta \leq 0.1$).

The diffuse reflectance spectra (DRS) for the same set of samples are shown in the Supporting Information, Figure S1b. Light absorption by the $BaTaO_2N$ prepared in this study begins at 700 nm, with a steep absorption edge at 660 nm. With increasing Zr/Ta ratio, the absorption edge shifted slightly to shorter wavelengths, and was accompanied by a reduction of the background level in the wavelength range of 700–800 nm. The absorption edge shift can be explained in terms of the difference in band gap between $BaTaO_2N$ (ca. 1.7–1.8 eV[11]) and $BaZrO_3$ (ca. 4.8–4.9 eV[12]). The less-pronounced background level observed in the solid solution materials compared to $BaTaO_2N$ ($Zr/Ta = 0$) indicates that they have a lower defect density than $BaTaO_2N$.[5,6]

Transmission electron microscope (TEM) images of the $BaZrO_3$-$BaTaO_2N$ solid solution ($Zr/Ta = 0.05$) are shown in the Supporting Information, Figure S1c. These images revealed that the as-prepared solid solution consisted primarily of well-crystallized particles of 50–200 nm in size, with some aggregation, as indicated by the clear lattice fringes of the particles. No $BaZrO_3$ particles could be distinguished on the surface. Thus, we successfully prepared $BaZrO_3$-$BaTaO_2N$ solid solutions with relatively low defect densities and absorption edges of 650–660 nm. Specific surface areas of these samples, as determined by nitrogen adsorption at 77 K, tended to decrease with increasing Zr/Ta ratio from 9.5 $m^2 g^{-1}$ ($Zr/Ta = 0$) to 4.5 $m^2 g^{-1}$ ($Zr/Ta = 0.1$).

The successful preparation of single-phase $BaTaO_2N$ and the solid solutions with $BaZrO_3$ allowed a fair evaluation of the photocatalytic activity for water oxidation, which had not been possible to date because of the difficulty in synthesizing $BaTaO_2N$ without any impurities.[13] When $BaTaO_2N$ modified with a colloidal $IrO_2$ cocatalyst was examined as a water oxidation photocatalyst under visible light ($\lambda > 420$ nm) in the presence of $AgNO_3$ as an electron acceptor, $O_2$ evolution was clearly observed (Table 1, entry 1). No gas evolution was detected in the dark or without photocatalyst sample. The as-prepared $BaTaO_2N$ also exhibited activity for water reduction using methanol as an electron donor and a Pt cocatalyst (Table 1, entry 5).[14] Photocatalytic activities of the as-prepared $BaZrO_3$-$BaTaO_2N$ solid solutions for water reduction and oxidation were also measured in a similar manner, and the results are listed in Table 1. All samples exhibited activities for both water reduction and oxidation; the rates of $H_2$ and $O_2$ evolution both increased with increasing Zr/Ta ratio up to 0.05 and then decreased. On the basis of the results of $H_2$ and $O_2$ evolution, it is concluded that $BaZrO_3$-$BaTaO_2N$ solid solutions ($0 \leq Zr/Ta \leq 0.1$) satisfy the thermodynamic requirements for water splitting, that is, the tops of the valence band of the materials are located at a more positive potential than the water oxidation potential, while the bottoms of the conduction band are located at a more negative potential than the water reduction potential.

***Table 1:*** Photocatalytic activities of $BaZrO_3$-$BaTaO_2N$ catalysts for water reduction and oxidation under visible light ($\lambda > 420$ nm).[a]

| Entry | Zr/Ta ratio in $BaZrO_3$-$BaTaO_2N$ | Cocatalyst | Activity [$\mu mol\,h^{-1}$] | |
|---|---|---|---|---|
| | | | $H_2$[b] | $O_2$[c] |
| 1 | 0 | 1.5 wt% $IrO_2$ | – | 3.1 |
| 2 | 0.025 | | – | 6.7 |
| 3 | 0.05 | | – | 7.7 |
| 4 | 0.1 | | – | 3.6 |
| 5 | 0 | 0.3 wt% Pt | 8.1 | – |
| 6 | 0.025 | | 13.8 | – |
| 7 | 0.05 | | 14.1 | – |
| 8 | 0.1 | | 8.4 | – |

[a] Reaction conditions: catalyst (100 mg), aqueous solution (100 mL), xenon lamp (300 W) light source fitted with a cold mirror (CM-1), Pyrex top-irradiation-type reaction vessel. [b] From aqueous methanol solution (10 vol%). [c] From aqueous silver nitrate solution (10 mM) containing $La_2O_3$ (100 mg) as a buffer.

It was also found that $IrO_2$-loading is indispensable to achieving stable water oxidation over $BaTaO_2N$-based photocatalysts. These photocatalysts can produce $O_2$ from aqueous silver nitrate solution even in the absence of $IrO_2$, but with extensive $N_2$ evolution owing to decomposition of the material (Figure 1 a. The decomposition consumes photogenerated holes that would otherwise be consumed in the oxidation of water, and can be represented as in Equation (1):[2b]

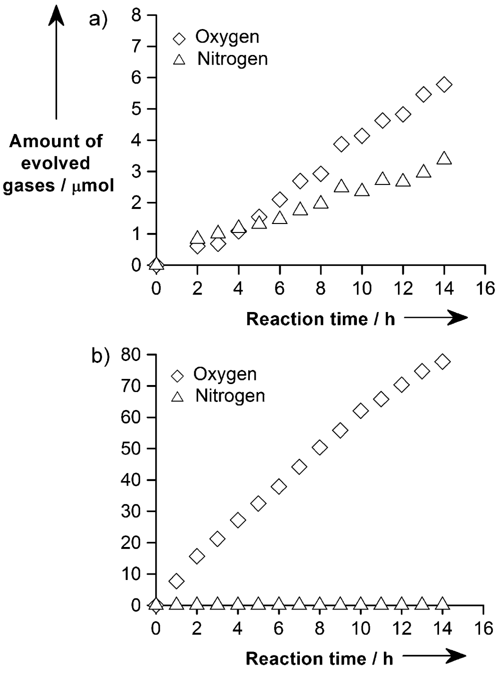

***Figure 1.*** Time courses of $O_2$ evolution on a) unmodified $BaZrO_3$-$BaTaO_2N$ ($Zr/Ta = 0.05$) and b) 1.5 wt% $IrO_2$-loaded analogue under visible light ($\lambda > 420$ nm) from silver nitrate solution containing 100 mg of $La_2O_3$. Reaction conditions: catalyst (100 mg), aqueous silver nitrate (10 mM, 100 mL) as reactant solution, xenon lamp (300 W) light source with cutoff filter, top-irradiation-type reaction vessel.

$$2\,N^{3-} + 6\,h^{+} \rightarrow N_2 \qquad (1)$$

This undesirable decomposition reaction could be minimized by modifying the $BaTaO_2N$-based photocatalysts with $IrO_2$, which are known to be one of the most active water oxidation promoters.[15] As seen in Figure 1b, $IrO_2$ modification promoted $O_2$ evolution while suppressing $N_2$ evolution. The slight decrease in reaction rate with time is due mainly to the deposition of metallic silver on the catalyst surface, which blocks light absorption and obstructs active sites.[4–8] It should be noted that $N_2$ evolution owing to the decomposition of $BaZrO_3$-$BaTaO_2N$ became negligibly slow (below detection limit) upon $IrO_2$ modification. These results strongly suggest that the loaded $IrO_2$ capture photogenerated holes migrating from $BaZrO_3$-$BaTaO_2N$, serving as efficient $O_2$ evolution sites. Furthermore, XRD analyses showed that the diffraction peaks of the $BaZrO_3$-$BaTaO_2N$ solid solution remained unchanged during the reaction (except for the emergence of diffraction peaks from Ag species; Supporting Information, Figure S2), indicating the stability of this material.

The $O_2$ evolution activity was also found to depend on the amount of $IrO_2$ loading (Supporting Information, Figure S3). The activity improved with increasing $IrO_2$ loading, reaching a maximum at around 1.5 wt %, and then decreased gradually. At the optimal loading condition, the activity was an order of magnitude higher than that achievable using the unmodified catalyst. TEM observations revealed that the 1.5 wt % sample, which showed the highest activity, exhibited a good dispersion of $IrO_2$ nanoparticles with a typical size of 1–2 nm. By contrast, densely loaded $IrO_2$ nanoparticles are observed in the 2.5 wt % sample (Supporting Information, Figure S4). The enhancement of activity with amount of $IrO_2$ loading is thought to be attributable to an increase in the density of active sites for $O_2$ evolution, while the decrease in activity above 1.5 wt % is associated with excess loading, which reduces the density of photocatalytic active sites and/or hinders light absorption by the photocatalyst. Thus, it was concluded that with appropriate kinetic control of the photooxidation reaction, the stability of the present catalytic system can be improved with respect to the degradation of the oxynitride material.

It is important to examine, for any given photoreaction system, the wavelength response for the reaction. Figure 2 shows the dependence of the rate of $O_2$ evolution on the wavelength of incident light using the $IrO_2$-loaded $BaZrO_3$-$BaTaO_2N$ solid solution, along with the DRS for the $BaZrO_3$-$BaTaO_2N$ material. The rate of $O_2$ evolution decreases with increasing cutoff wavelength. The longest wavelength suitable for the reaction is 660 nm (for the corresponding time course data, see the Supporting Information, Figure S5), which corresponds to the absorption edge of $BaZrO_3$-$BaTaO_2N$. This clearly indicates that the reaction proceeds by light absorption of the material. The photoresponse of this material for $H_2$ evolution was also confirmed, as plotted in Figure 2. The apparent quantum yields of $H_2$ and $O_2$ evolution under the present reaction conditions were about 0.06 % and 0.03 %, respectively, at 420 nm.

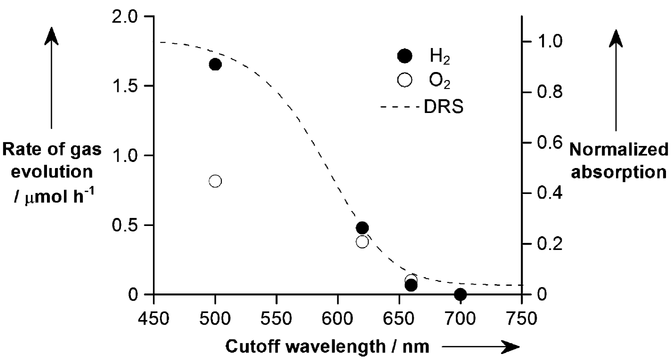

*Figure 2.* Dependence of rates of $H_2$ and $O_2$ evolution by $BaZrO_3$-$BaTaO_2N$ (Zr/Ta = 0.025) on the cutoff wavelength of incident light. Reaction conditions: catalyst (50 mg), cocatalyst: 0.3 wt % Pt for $H_2$ evolution and 0.5 wt % $IrO_2$ for $O_2$ evolution, aqueous methanol (10 vol %, 100 mL) for $H_2$ evolution and silver nitrate solution (10 mM, 100 mL) with 100 mg $La_2O_3$ for $O_2$ evolution, xenon lamp (300 W) light source with cutoff filter, Pyrex top-irradiation-type reaction vessel.

It was thus demonstrated that the prepared $BaTaO_2N$-based materials having a single-phase perovskite structure and an absorption edge of ca. 660 nm were photocatalytically active for both water reduction and oxidation under visible light. It is surprising that a narrow-band-gap compound such as $BaZrO_3$-$BaTaO_2N$ solid solution can reduce and oxidize water, giving $H_2$ and $O_2$, respectively, under visible light irradiation, because the thermodynamic requirements for achieving water splitting using a semiconductor become more stringent as the band gap of the material decreases. To our knowledge, this is the first report of a photocatalytic material that is capable of both reducing and oxidizing water even under irradiation above 660 nm.

The fact that $BaZrO_3$-$BaTaO_2N$ solid solution ($0 \leq Zr/Ta \leq 0.1$) has suitable band gap positions for water splitting, wide visible light absorption band, and the ability to reduce and oxidize water also led us to apply this material as an electrode in a water-splitting photoelectrochemical cell. For electrode preparation, the as-prepared $BaZrO_3$-$BaTaO_2N$ powder was deposited on a fluorine-doped tin oxide (FTO) substrate by electrophoretic deposition. A post-necking treatment to promote interparticle electron transfer[2e,16] was performed on the as-deposited $BaZrO_3$-$BaTaO_2N$ electrode using $TiCl_4$, and this was followed by heating under $N_2$ at 673 K for 1 h to deposit $TiO_2$ layer on the $BaZrO_3$-$BaTaO_2N$ particles. The thickness of the deposited $TiO_2$/$BaZrO_3$-$BaTaO_2N$ layer was 4–5 μm (Supporting Information, Figure S6). As a water oxidation promoter, colloidal $IrO_2$ was adsorbed on the post-necked $BaZrO_3$-$BaTaO_2N$ electrode, if needed.

Current–voltage experiments (Supporting Information, Figure S7) showed that a $TiO_2$-modified $BaZrO_3$-$BaTaO_2N$/FTO electrode generated an anodic photocurrent upon intermittent visible light irradiation ($\lambda = 500$ nm), with an onset potential of around $-0.1$ V vs. RHE. It should be noted that in this case, only the $BaZrO_3$-$BaTaO_2N$ component is activated by visible light during the measurement, because the band gaps of FTO (F-doped $SnO_2$) and any polymorph of $TiO_2$ are too large to harvest 500 nm photons.[17] Thus, $BaZrO_3$-$BaTaO_2N$ behaves as an n-type semiconductor. Furthermore, the more negative photocurrent onset potential than 0 V (vs. RHE) suggests that $BaZrO_3$-$BaTaO_2N$ has a potential to split water without applying external bias, which is consistent with the results of photocatalytic reactions (Table 1). Without $TiO_2$ deposition, the $BaZrO_3$-$BaTaO_2N$/FTO electrode generated little photocurrent, which is due primarily to the large resistance in the electrode structure, as discussed in our previous study.[16] When colloidal $IrO_2$ was adsorbed on the post-necked electrode, the anodic photoresponse improved across the entire potential range studied. In particular, the photocurrent onset potential shifted in the negative direction to ca. $-0.3$ V vs. RHE. This clearly indicates that loading colloidal $IrO_2$ onto $BaTaO_2N$ promotes water oxidation, in good agreement with the results of photocatalytic reactions (Figure 1). The IPCE of the present $IrO_2$/$TiO_2$/$BaZrO_3$-$BaTaO_2N$/FTO electrode for water oxidation was calculated to be approximately 1.0 % at 1.2 V vs. RHE under 500 nm monochromatic light.

Next, direct splitting of water into $H_2$ and $O_2$ by sunlight was attempted using a photoelectrochemical cell consisting of $IrO_2$-modified $TiO_2$/$BaZrO_3$-$BaTaO_2N$/FTO as a working electrode and a Pt wire cathode. As shown in Figure 3, stoichiometric $H_2$ and $O_2$ evolution was observed under simulated sunlight, and the amounts increased with time.[18] Neither current nor gas was generated in the dark. Half the number of electrons that flowed during photoelectrolysis corresponded to slightly less than the amount of gas evolution, presumably because of the consumption of the evolved $H_2$ and $O_2$ on the Pt wire cathode.[19] The average rates of $H_2$ and $O_2$ evolution recorded were 0.5 and 0.25 $\mu mol\,h^{-1}$, respectively, corresponding to a solar energy conversion efficiency of 0.0011 %. Thus, $BaZrO_3$-$BaTaO_2N$ was shown to be applicable as a solar energy transducer by water splitting, despite the relatively small band gap energy.

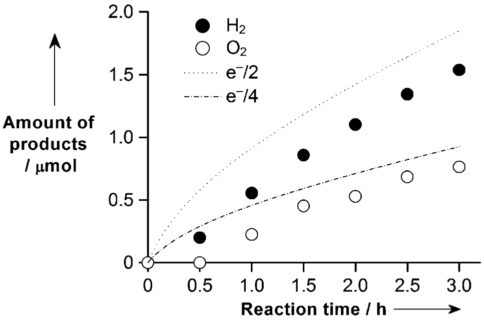

***Figure 3.*** Time course of $H_2$ and $O_2$ evolution in photoelectrochemical water splitting at $+1.0$ V vs. a Pt wire cathode under simulated sunlight. The experiment was conducted in 0.1 M aqueous $Na_2SO_4$ solution (pH 5.9) using $IrO_2$-loaded $TiO_2$/$BaZrO_3$-$BaTaO_2N$ electrode (5.25 $cm^2$).

In conclusion, although no semiconductor material has been reported to date as being capable of both photocatalytically reducing and oxidizing water under irradiation above 660 nm, the present study has demonstrated that $BaZrO_3$-$BaTaO_2N$ solid solutions having band gaps of 1.7–1.8 eV can potentially fit the bill. Loading $IrO_2$ nanoparticles as cocatalysts for water oxidation was found to be indispensable for achieving stable, efficient water oxidation using these $BaZrO_3$-$BaTaO_2N$ solid solutions in the case of both photocatalysis and photoelectrolysis. Solar energy conversion was shown to be achievable with stoichiometric production of $H_2$ and $O_2$ from water if one employs $BaZrO_3$-$BaTaO_2N$ as an anode material in a photoelectrochemical cell with an external bias of 1.0 V versus Pt cathode (with no reference electrode). $BaZrO_3$-$BaTaO_2N$ solid solution can thus be regarded as the closest artificial photosynthetic material to the natural system regarding the available wavelength.

Another encouraging result is that $BaZrO_3$-$BaTaO_2N$ with some modification is capable of producing $O_2$ from aqueous solution containing $IO_3^-$ as an electron acceptor (Supporting Information, Figure S8). Different from water oxidation using a $Ag^+$ electron acceptor, this reaction is energetically up-hill ($\Delta E^0 = -0.143$ V), converting light energy into chemical energy in the form of $O_2$ and $I^-$. Although the water oxidation rate in this non-sacrificial process was very slow compared to the sacrificial system, it is suggested that non-sacrificial overall water splitting into $H_2$ and $O_2$ using $BaZrO_3$-$BaTaO_2N$ is in principle possible according to the Z-scheme principle in the presence of an $IO_3^-/I^-$ redox mediator, as $BaZrO_3$-$BaTaO_2N$ also works as a photocatalyst to reduce $H^+$ into $H_2$ using $I^-$ as an electron donor.[20] To achieve 650 nm water splitting, the quality of $BaZrO_3$-$BaTaO_2N$ photocatalyst must be further improved, and our research is ongoing along this line.

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[14] It has been reported that $BaTaO_2N$ could photocatalyze water reduction to give $H_2$ from aqueous solution containing a suitable electron donor. However, the reported "$BaTaO_2N$" contained $Ta_3N_5$ as an impurity (Ref. [13]). It was also found that no $H_2$ was produced from aqueous methanol solution under visible light in the absence of Pt/$BaZrO_3$-$BaTaO_2N$.

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