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Oxidation of Water under Visible-Light Irradiation over Modified $BaTaO_2N$ Photocatalysts Promoted by Tungsten Species**

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In recent years, photocatalytic water splitting on illuminated semiconductor powder has attracted considerable attention as a potential way to produce the solar fuel H_2 from renewable resources.[1] Water oxidation is a particularly important step in artificial photosynthesis for solar fuel production not only for water splitting but also for CO_2 reduction.[2] Because the main spectral component of sunlight is visible light ($400 < \lambda < 800$ nm), the development of heterogeneous water oxidation systems that operate under a wide range of visible light is currently a hot topic in chemistry.

To effectively use solar energy, a narrow-gap semiconductor like (oxy)nitrides and oxysulfides is highly desirable.[1b,3] However, narrowing the band gap of a photocatalyst decreases 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.[2] It will also become difficult for a semiconductor to meet the thermodynamic requirement for water splitting; that is, the valence band maximum and the conduction band minimum should straddle the water-splitting potential, when the band gap energy decreases. While a photocatalyst having a band gap smaller than 2 eV and the ability to reduce and oxidize water is highly desirable for efficient solar energy conversion,[3] however, such a photocatalyst had not been developed until very recently.

We have experimentally demonstrated that the reduction and oxidation of water are both possible using perovskite $BaTaO_2N$ and the solid-solution materials with $BaZrO_3$ ($0 \leq Zr/Ta \leq 0.1$) that have band gaps of 1.7–1.8 eV.[4] This is the first example of producing H_2 and O_2 from water under visible-light irradiation using a semiconductor having a band gap lower than 2 eV. However, the $BaZrO_3$-$BaTaO_2N$ solid solutions have a drawback in that the water oxidation activity is very low (about 0.03% apparent quantum yield, AQY, at 420 nm). The cause of the low activity for water oxidation is most likely due to the valence band potential being close to the water oxidation potential, as suggested by photoelectrochemical measurements.[4b]

In such a situation, one may think that it is possible to tune the band-edge positions of a semiconductor by replacing the original constituent element with another.[1d] Taking $BaTaO_2N$ for example, it would be easy to expect that the valence band maximum shifts to more positive potential if the concentration of nitrogen, which forms the upper part of the valence band,[1b] is reduced. This is actually achievable by making a solid solution with a wide-gap oxide semiconductor, which is in general known as "band-gap enerineering".[1d] From the viewpoint of efficient solar energy use, however, this may not be preferable because the reduction of the nitrogen concentration in $BaTaO_2N$ results in a blue shift of the absorption edge, downgrading the good light absorption capability.[4] Thus, the ordinary strategy has a limitation, and a new way to enhance photocatalytic activity needs to be developed.

Here we report that the activity of water oxidation of $BaTaO_2N$ photocatalyst can be enhanced by the introduction of pentavalent tungsten species, while maintaining the small band gap. In general, doping transition-metal cations having partly filled d orbitals into semiconductor photocatalysts contributes to a significant drop in photocatalytic activity.[1d] Such doped elements form a donor or accepter level in the forbidden band of the material, which may case by case act as a center for absorption at visible wavelengths. However, doping also obstructs prompt migration of photogenerated electrons or holes at the surface and in the material bulk, since the dopant frequently provides a discreet energy level rather than an energy band.[1d] Nevertheless, introducing pentavalent W species having a $[Xe]4f^{14}5d^1$ electron configuration into $BaTaO_2N$ is exceptionally effective to enhancing the oxidation activity of water.

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W-modified $BaTaO_2N$ powder samples were prepared by heating the oxide precursors of $BaWO_x/BaTaO_x$ under a flow of NH_3 at 1223 K for 20 h. The detail of the catalyst preparation is included in the Experimental Section. XRD analysis showed that the as-prepared materials exhibited single-phase diffraction patterns similar to perovskite $BaTaO_2N$ (see Figure S1 in the Supporting Information). The diffraction peak positions remained largely unchanged even upon introduction of W species. This appears reasonable considering the very small difference in ionic radius between Ta^{5+} and W^{6+} (or W^{5+}): Ta^{5+}, 0.78 nm; W^{6+}, 0.74 nm; and W^{5+}, 0.76 nm,[5] and the fact that the amount of W species introduced was very small. It was confirmed by transmission electron microscopy (TEM) observations and energy dispersive X-ray analysis that particles containing only Ba and W as metallic components could not be identified on the surface of the nitrided sample (Figure S2), precluding possible segregation of W-containing particles on the surface of nitrided samples. TEM observations also indicated that the nitrided particles are aggregated to form larger secondary particles. The specific surface areas of the prepared samples decreased with increasing the W/Ta ratio from 9.5 $m^2 g^{-1}$ (for W/Ta = 0) to 3.7 $m^2 g^{-1}$ (for W/Ta = 0.05).

The presence of W-species in the prepared samples was confirmed by means of X-ray photoelectron spectroscopy (XPS), as shown in Figure S3. The $W4f_{7/2}$ XPS peak position of the nitrided sample was almost the same as that of the corresponding oxide precursor, indicating that the valence state of W in the surface of the nitrided sample is almost entirely hexavalent.

UV/Vis diffuse reflectance spectra (DRS) of the same set of the samples are shown in Figure 1. $BaTaO_2N$ without W species showed a steep absorption edge at around 660 nm, based on electron transition from the valence band formed by hybridized N2p and O2p orbitals to the conduction band consisting of empty Ta5d orbitals.[1b] In addition to the absorption edge at 660 nm, the nitrided samples had an additional absorption feature at longer wavelength region, which was more pronounced with increasing the W/Ta molar ratio in the sample. This absorption band can be assigned to pentavalent W species.[6,7] The observed trend therefore means that with increasing the W/Ta ratio in the precursor, the density of pentavalent W species increased in the as-prepared materials. In contrast, the corresponding oxide precursor having a W/Ta ratio of 0.05 did not give such absorption band at longer wavelengths, meaning that the W species in the oxide precursor is hexavalent. Because the W^{6+} cation easily undergoes reduction by accepting electrons[6,7] especially in reductive atmosphere like high-temperature ammonia, the change in the valence state of W from hexavalent to pentavalent before and after nitridation is reasonably understood. However, as mentioned earlier, X-ray photoelectron spectroscopy (XPS) revealed that the valence state of the W species was essentially identical before and after nitridation (see Figure S3 in the Supporting Information). Presumably, surface W species in the nitride sample might be oxidized to hexavalent species when the sample was exposed to air.

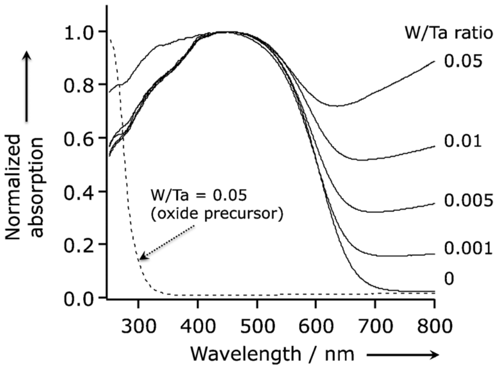

Figure 1. UV/Vis diffuse reflectance spectra of the nitrided samples with different W/Ta molar ratio.

Thus, it can be concluded that pentavalent W species are incorporated into the lattice of $BaTaO_2N$. Fawcett et al. synthesized a perovskite oxynitride consisting of Sr^{2+} and W^{5+} cations, with the composition of $SrWO_2N$.[8] Although a Ba-W oxynitride ($Ba_3W_2(O,N)_8$) having a layered hexagonal structure has been reported,[9] a perovskite-type oxynitride containing Ba and W has yet to be synthesized to date. Similar to the $ATaO_2N$ (A = Ca, Sr, Ba) perovskite series,[10] nevertheless, it may be possible to synthesize $BaWO_2N$ by modifying the preparation condition. If it is the case, the valence state of W in $BaWO_2N$ is pentavalent, consistent with the results of UV/Vis diffuse reflectance spectroscopy. Considering the contribution of hexavalent W species as revealed by XPS (Figure S3), the as-prepared samples will be represented hereafter as $BaWO_xN_y$-$BaTaO_2N$ for simplicity.

Using the as-prepared $BaWO_xN_y$-$BaTaO_2N$ samples, water oxidation was conducted under visible-light irradiation. Figure 2 shows the initial rate of O_2 evolution as a function of the W/Ta molar ratio. Prior to reaction, the tested samples were modified with 1–2 nm IrO_2 colloidal nanoparticles as O_2 evolution sites.[4a] The O_2 evolution rate increased abruptly

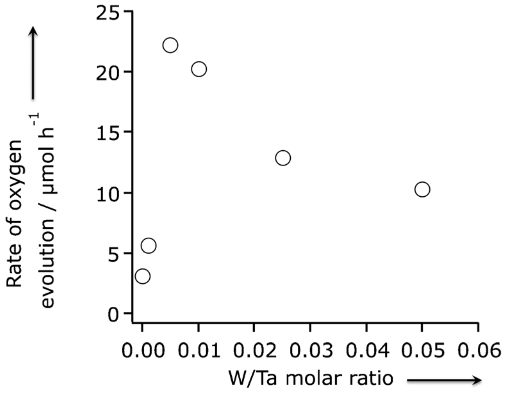

Figure 2. Photocatalytic activity of $BaWO_xN_y$-$BaTaO_2N$ samples with different W/Ta ratios for the oxidation of water under visible-light ($\lambda > 420$ nm) irradiation. Reaction conditions: catalyst, 100 mg (1.5 wt% IrO_2-loaded); aqueous silver nitrate solution (10 mM, 100 mL) with 100 mg La_2O_3 for O_2 evolution; light source, xenon lamp (300 W) with cutoff filter; Pyrex top-irradiation-type reaction vessel.

with an increase in the W/Ta ratio to reach a maximum at W/Ta = 0.005, beyond which it began to decrease. It should be noted that the rate of O_2 evolution achieved by the optimal sample (W/Ta = 0.005) was seven times faster than that of $BaTaO_2N$.

Figure 3 shows the corresponding time course data of IrO_2-loaded $BaWO_xN_y$-$BaTaO_2N$ (W/Ta = 0.005), which exhibited the highest activity, and $BaTaO_2N$. The amount of evolved O_2 increased with increasing reaction time in both cases. The slight decrease in reaction rate with time is mainly due to the deposition of metallic silver on the catalyst surface, which blocks light absorption and obstructs active sites.[4a] N_2 evolution owing to the decomposition of the $BaTaO_2N$ component[4a] was negligible (above the detection limit). The water oxidation activity of $BaWO_xN_y$-$BaTaO_2N$ (W/Ta = 0.005) was higher than that of the previously reported $BaZrO_3$-$BaTaO_2N$ solid solution, one of the best water oxidation photocatalysts in terms of the available wavelength of light.[4]

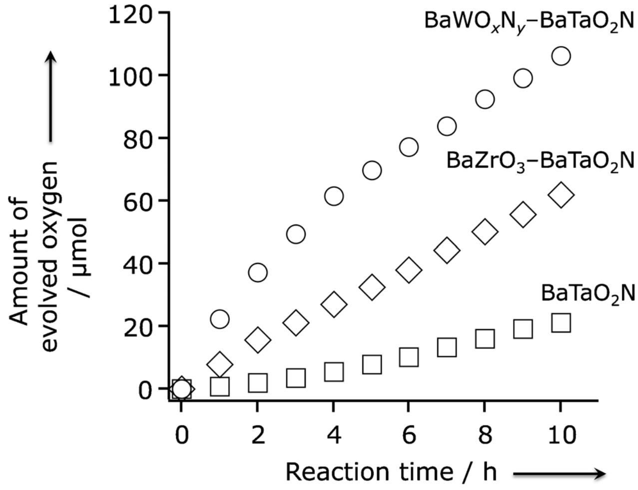

Figure 3. Time courses of the evolution of O_2 on $BaTaO_2N$ and $BaWO_xN_y$-$BaTaO_2N$ (W/Ta = 0.005) under visible-light ($\lambda > 420$ nm) irradiation from silver nitrate solution containing 100 mg of La_2O_3. Reaction conditions: catalyst, 100 mg (1.5 wt% IrO_2-loaded); aqueous silver nitrate (10 mM, 100 mL); light source, xenon lamp (300 W) with cutoff filter; top-irradiation-type reaction vessel. The data for the $BaZrO_3$-$BaTaO_2N$ solid solution (Zr/Ta = 0.05) is also shown for comparison (Ref. [4a]).

Recently, Yi et al. reported that Ag_3PO_4 gave a very high AQY for photochemical O_2 evolution (about 90% at 420–440 nm).[11] However, this material only works under irradiation by light of wavelengths shorter than 530 nm because of the relatively wide band gap. More importantly, the material undergoes self-reductive decomposition under band gap irradiation in the absence of Ag^+ ions as external electron acceptors, producing O_2 from water along with the deposition of Ag on the surface. In contrast to these inherent drawbacks of Ag_3PO_4, the present $BaWO_xN_y$-$BaTaO_2N$ acts as a stable photocatalyst for water oxidation even under irradiation by light of wavelengths > 600 nm (Figure S4) without any noticeable change in its structure, as confirmed by XRD analysis (Figure S5).

Thus, a distinct promotional effect of modification by W species on water oxidation by $BaTaO_2N$ was demonstrated. As shown in Figure 1, introducing W species into $BaTaO_2N$ led to an increase in the density of pentavalent W species. As mentioned earlier, it is known that the introduction of transition-metal cations with d electrons into semiconductor photocatalysts generally results in a loss of photoresponse likely due to the localized character of the d orbitals and strong interaction between the d electrons and photo-excited electrons and/or holes.[1d,g] However, the results presented above are clearly different from the "general" behavior and are thus unusual, as $BaWO_xN_y$-$BaTaO_2N$ samples exhibited an enhanced activity for water oxidation compared to $BaTaO_2N$ despite the increased population of pentavalent W species (Figure 2), which have an electron configuration of $[Xe]4f^{14}5d^1$. As shown in Figure S4, it is also clear that the broad absorption appearing at 700–800 nm (see Figure 1) assignable to W^{5+} species is not available for the reaction.

It may also seem that the introduction of W species into $BaTaO_2N$ lowers the conduction band minimum because the potential of W4d orbitals is more positive than that of Ta5d orbitals.[12] To investigate this possibility, photoelectrochemical measurements were performed using porous electrodes of $BaWO_xN_y$-$BaTaO_2N$ and $BaTaO_2N$. As shown in Figure S6, both electrodes generated anodic current derived from the oxidation of water upon irradiation of visible light ($\lambda >$ 500 nm), and the photocurrent increased with anodic polarization, indicating a typical behavior of n-type semiconductor.[1f] However, the onset potential of the photocurrent for the oxidation of water, which corresponds to the flat-band potential typically located at a potential of 0.1–0.3 V more positive than the conduction band minimum in an n-type semiconductor,[13] in the $BaWO_xN_y$-$BaTaO_2N$ electrode was almost the same as that recorded using $BaTaO_2N$. A similar level of photocurrent was observed both in $BaWO_xN_y$-$BaTaO_2N$ and $BaTaO_2N$. In addition, the band gap energy of $BaTaO_2N$ remained almost unchanged even upon modification by W species (Figure 1). These results indicate that modification by W species did not largely alter the band gap structure of $BaTaO_2N$ except for donor levels formed by pentavalent W species, and that the introduced W species did not behave as a cocatalyst as well.

A $BaTaO_2N$ powder was prepared by heating Ba-Ta mixed oxides at 1223 K for 20 h under a flow of NH_3.[4] During this process, the production of many nitrogen vacancies is expected, because the conversion of metal oxide into oxynitride and the concomitant decomposition of the oxynitride occur simultaneously at such high temperatures.[1b] The nitrogen vacancies become the origin of n-type semiconducting character of $BaTaO_2N$. In the case of $BaWO_xN_y$-$BaTaO_2N$, the introduced W^{5+} species should form a donor level just below the conduction band, which would strengthen the n-type semiconducting character of $BaTaO_2N$. As a result, it is expected that the upward band-bending character of n-type $BaTaO_2N$ is more pronounced, leading to a situation where the oxidation of water is preferable because holes in the valence band are able to migrate easily to the surface according to the upward band-bending. Thus, one plausible explanation for the enhanced oxidation of water is a pronounced upward band-bending character of $BaWO_xN_y$-$BaTaO_2N$.

In this situation, however, the migration of electrons in the conduction band to the surface should become difficult due to a Schottky barrier at the solid–liquid interface.[14] Nevertheless, due to the large driving force for the reduction of Ag^+, the negative impact by introduction of W^{5+} ions on the reduction reaction, if any, might not be significant. Conversely, the driving force for the reduction of water is much smaller than that for the reduction of Ag^+ ions; the difference in the potential between the reduction of water and Ag^+ ions is approximately 1.3 V at pH 8–8.5.[15] Thus, the negative impact caused by W^{5+} species would be more pronounced in the reduction reaction of water. These ideas could explain the results of the photocatalytic oxidation of water (Figure 3) and reduction; as shown in Table S1, the rate of H_2 evolution from an aqueous methanol solution on $BaWO_xN_y$-$BaTaO_2N$ (W/Ta = 0.005) was approximately 70 % of that recorded using $BaTaO_2N$. However, too much introduction of W^{5+} species had a negative effect on the oxidation activity of water (Figure 2). Presumably, the introduced W^{5+} species would also work as recombination centers between photogenerated electrons and holes.

The idea of the strengthened n-type character in $BaWO_xN_y$-$BaTaO_2N$ may seem to contradict the result of photoelectrochemical analysis (Figure S6), which indicated that the difference in photoresponse between $BaWO_xN_y$-$BaTaO_2N$ and $BaTaO_2N$ was very small. Nevertheless, it should be noted that the photocurrent density of these electrodes is limited primarily by interparticle electron transfer; in fact, post-necking treatment with TiO_2 is necessary to obtain a measurable photocurrent.[4a]

In summary, $BaWO_xN_y$-$BaTaO_2N$ ($0 < W/Ta \leq 0.05$) exhibited a water oxidation activity higher than the pristine $BaTaO_2N$, even though $BaWO_xN_y$-$BaTaO_2N$ contained an increased density of d electrons that originates from pentavalent W species. Although further research is required and the electron–hole dynamics in this material needs to be investigated, the finding that an intentional introduction of transition-metal cations with partly filled d orbitals into a narrow-gap oxynitride improves the activity of water oxidation while maintaining the original band-edge positions presents important new possibilities for the photocatalysis of water oxidation under visible-light irradiation, because there are many visible-light-responsive (oxy)nitrides that can harvest visible photons to oxidize water.[1] The present result is therefore very encouraging and is expected to be a new strategy to enhance the activity of water oxidation of a semiconductor photocatalyst.

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