

Photocatalytic oxygen evolution using BaNbO₂N modified with cobalt oxide under photoexcitation up to 740 nm†

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BaNbO₂N was activated for photocatalytic sacrificial water oxidation and reduction by modifying the starting material for nitridation and loading appropriate cocatalysts. Addition of BaCO₃ to the Ba₅Nb₄O₁₅ precursor improved the crystallinity and uniformity of BaNbO₂N as a nitridation product, leading to higher oxygen evolution activity. BaNbO₂N generated oxygen from an aqueous AgNO₃ solution under illumination up to 740 nm.

Water splitting on semiconductor photocatalysts has received much attention for large-scale production of renewable hydrogen from solar energy and water.^{1–8} The hydrogen thus produced is storable and can be efficiently converted into electricity or heat at any desired time using fuel cells. Moreover, hydrogen can be employed to produce feedstock in the chemical industry.² Since visible and infrared rays account for the greater portion of solar energy, it is necessary to extend the wavelength region available for photocatalytic water splitting by developing narrow band gap semiconductors. In fact, photocatalytic materials active for water splitting under irradiation up to wavelengths of 600 nm or even longer are needed to achieve a high solar energy conversion efficiency at a reasonable quantum efficiency.² However, photocatalysis is triggered by photoexcited electrons and holes, which relax to the bottom of the conduction band and the top of the valence band, respectively. Thus, it

Broader context

Water splitting on semiconductor photocatalysts has received much attention for the large-scale production of renewable hydrogen from solar energy and water. Photocatalysts should be active for water splitting under irradiation up to 600 nm or even longer wavelengths in order to achieve a high solar energy conversion efficiency at a reasonable quantum efficiency. In this regard, BaNbO₂N is a promising candidate because of its small band gap energy of 1.7 eV, allowing light absorption up to 740 nm. The present study demonstrates that BaNbO₂N can be activated for photocatalytic water oxidation and reduction in the presence of sacrificial reagents by modifying the starting material for nitridation and loading appropriate cocatalysts. BaNbO₂N generates oxygen from an aqueous AgNO₃ solution under illumination up to 740 nm, the longest wavelength ever reported for (oxy)nitride photocatalysts. In addition, BaNbO₂N has a conduction band edge that is more negative than the hydrogen evolution potential. This means that BaNbO₂N electrodes could drive photoelectrochemical water splitting with a smaller applied voltage than other visible-light-driven oxide photoanodes. The promising semiconducting properties of BaNbO₂N in solar water splitting and the critical roles of the cocatalysts in boosting the photocatalytic activity will be key to achieving practical solar fuel production.

is more challenging to drive photocatalytic water splitting as the band gap energy decreases.

Perovskite-type and relevant semiconductors modified with appropriate cocatalysts have produced a variety of benchmarks in the field of photocatalytic water splitting. La-doped NaTaO₃ shows excellent quantum efficiencies for overall water splitting under UV light (56% at 270 nm)⁹ and Rh-doped SrTiO₃ is used as a hydrogen evolution photocatalyst in Z-scheme water splitting under visible light.¹⁰ Non-oxide perovskite-type materials also exhibit promising activity in water splitting. Porous single-crystalline LaTiO₂N modified with CoO_x as an oxygen evolution cocatalyst exhibited a quantum efficiency of 27% at 440 nm for an oxygen evolution reaction in the presence of Ag⁺ cations as sacrificial electron acceptors.¹¹ BaTaO₂N and its solid solutions with BaZrO₃ have attracted growing interest owing to its response to long-wavelength photons up to 660 nm and the ability to generate both hydrogen and oxygen in the presence of

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† Electronic supplementary information (ESI) available: Detailed experimental, SEM images, XRD patterns, DRS, hydrogen evolution reaction, and *J*-*E* curves of the samples. See DOI: 10.1039/c3ee42951b



sacrificial reagents.¹² In photoelectrochemical applications, in which necessary electrodes can be readily fabricated *via* electrophoretic deposition¹³ and particle transfer¹⁴ using photocatalyst powder, photoanodes of SrNbO₂N decorated with IrO₂ can utilize photons up to 700 nm for water oxidation.¹³ The various physical and semiconducting properties of perovskite-type materials, a consequence of their adjustable compositions and structural stability, allow flexible synthetic routes and establish the potential of perovskite-type photocatalysts for use in versatile approaches to solar energy conversion. Spectroscopic and computational studies are also active to understand band structures of perovskite-type photocatalysts.^{15–17}

Nb-based perovskite-type oxynitrides have smaller band gap energies than the corresponding Ta-based oxynitrides because of the higher electronegativity of Nb.¹⁸ BaNbO₂N is of particular interest for solar energy conversion because of its narrow band gap of 1.7 eV although it was found to be inactive for both photocatalytic oxygen and hydrogen evolution reactions.¹⁹ In the present study, however, we successfully activated BaNbO₂N for both of these reactions by modifying the preparation conditions of the starting material for nitridation and loading suitable cocatalysts such as CoO_x (ref. 11 and 20) and Pt. Here, we report the effect of the preparation conditions for BaNbO₂N on its physical properties and photocatalytic activity for O₂ evolution.

BaNbO₂N was prepared by nitriding Ba₅Nb₄O₁₅ under an NH₃ flow. Ba₅Nb₄O₁₅ was prepared by calcining a mixture of BaCO₃ and Nb₂O₅, with NaCl added as a flux at 1173 K unless otherwise noted. After a slow cool-down to room temperature, the oxide sample was rinsed with copious amounts of distilled water to eliminate the NaCl flux. BaCO₃ was added to Ba₅Nb₄O₁₅ before nitridation to suppress the possible generation of niobium oxynitride.¹⁹ The precursor was nitrided at 1202 K for 15 h under an NH₃ flow of 200 mL min⁻¹. Excessive Ba species generated during the nitridation were dissolved by aqua regia. Photocatalytic reactions were carried out using a closed-circulation system. BaNbO₂N was modified with nanoparticles of CoO_x and Pt, which served as cocatalysts for oxygen and hydrogen evolution, respectively. Aqueous solutions of AgNO₃ and CH₃OH were used for sacrificial oxygen and hydrogen evolution reactions, respectively. The reaction vessel was evacuated to remove air before irradiation. The light source used was a 300 W Xe lamp equipped with cutoff filters. Evolved gases were analysed by gas chromatography. Other experimental details are described in the ESI.†

Fig. 1A shows X-ray diffraction (XRD) patterns of samples at different preparation stages. Ba₅Nb₄O₁₅ was obtained by calcining the starting materials at 1173 K with a NaCl flux while unreacted BaCO₃ remained as a by-product in the absence of the flux. A mixture of Ba₅Nb₄O₁₅ and BaCO₃ at a Ba/Nb ratio of 2.00 was converted into BaNbO₂N and by-products originating from excessive Ba-species. XRD-pure BaNbO₂N was obtained by dissolving the by-products by treatment with aqua regia. On the other hand, Ba₅Nb₄O₁₅ calcined at 1423 K remained partly unreacted when nitrided under the same conditions (data not shown), presumably because of the larger particle size of the oxide. Scanning electron microscopy (SEM) observation revealed

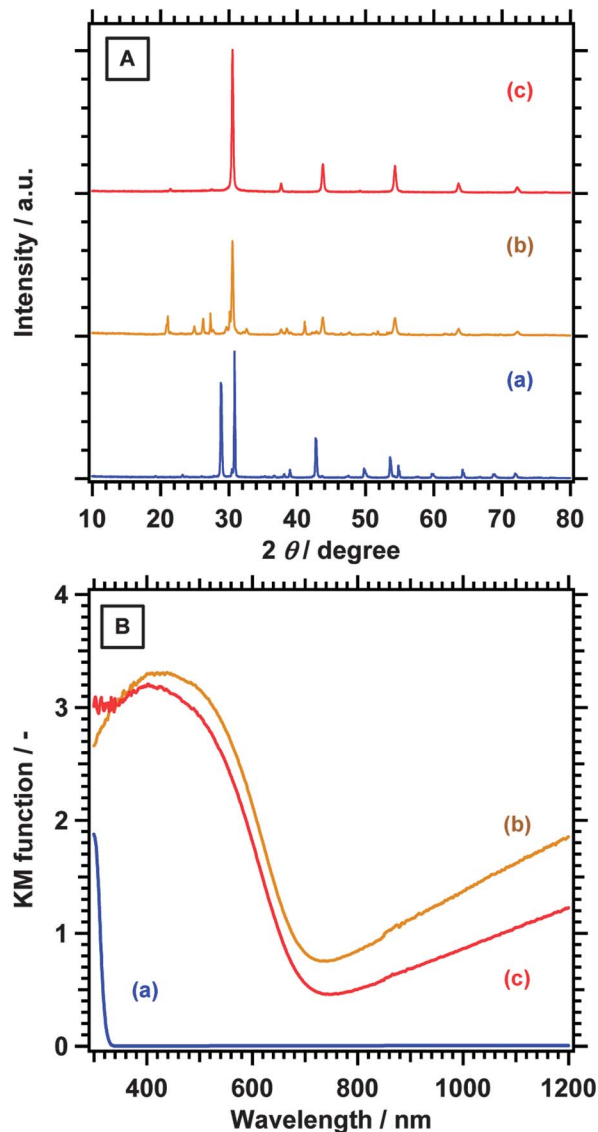


Fig. 1 (A) XRD patterns and (B) UV-Vis DRS for (a) Ba₅Nb₄O₁₅ prepared by the flux method, (b) BaNbO₂N nitrided from a mixture of Ba₅Nb₄O₁₅ and BaCO₃ with a Ba/Nb ratio of 2, and (c) BaNbO₂N after treatment with aqua regia.

that particles of the nitridation product were huge aggregates, several micrometres in size, and consisted of partly fused grains (Fig. S1†). After the aqua regia treatment, most of the particles became porous. This is presumably because the excessive Ba species between BaNbO₂N domains, which were compressed during the crystallographic conversion from Ba₅Nb₄O₁₅ to BaNbO₂N, were dissolved. XRD-pure BaNbO₂N was also obtained at different Ba/Nb ratios between 1.25 and 2.00 after treatment with aqua regia (Fig. S2†). Note that NbO_xN_y was easily produced as a by-product in our previous work particularly when the Ba/Nb ratio was lower than 2.00.¹⁹ The full width at half maximum of the (110) peak at 30.5–30.6° decreased from 0.246 to 0.213, 0.210, and 0.207 as the Ba/Nb ratio increased from 1.25 to 1.50, 1.75, and 2.00, respectively. This suggests that higher Ba/Nb ratios in the precursor oxide could improve the crystallinity and uniformity of the nitridation products.



In the diffuse reflectance spectra (DRS) of the nitridation products, the onset of light absorption characteristics of the band gap excitation of BaNbO_2N was observed at around 740 nm (Fig. 1B). Additional light absorption was observed in the longer wavelength region, which could be attributed to defects such as reduced B-site cations (Nb) and anion vacancies.^{18,19,21} The background absorption was weakened by the aqua regia treatment, suggesting that defect species on the surface were eliminated to some extent. However, considerable background absorption remained even after the acid treatment. This indicated that the bulk of BaNbO_2N also held reduced Nb species and anion vacancies. Since no diffraction peaks other than those for the perovskite-type material were observed, such defect phases could be expressed nominally as solid solutions of BaNbO_2N with BaNbO_3 containing Nb^{4+} states and/or $\text{BaNbO}_{2-\delta_1}\text{N}_{1-\delta_2}$ with anion deficiencies if crystalline. In addition, amorphous defect by-products could contribute to the background absorption although their impact could not be determined unambiguously. The addition of BaCO_3 to $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ was expected to weaken the light absorption due to defect species, similar to the case of LaTiO_2N nitrided from $\text{La}_2\text{Ti}_2\text{O}_7$ with La deficiency.²² In reality, however, the intensity of the background absorption increased by the addition of BaCO_3 to $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ (Fig. S3†). Moreover, the nitridation of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ obtained at higher temperatures than 1173 K tended to result in stronger background light absorption. The generation of defect species was not controllable solely by the Ba/Nb ratio during nitridation, presumably because it was too sensitive to the degree of nitridation from $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ to BaNbO_2N , which was in turn governed by both the nitridation conditions and the nature of the precursor oxides.

Fig. 2 shows reaction time courses for photocatalytic oxygen evolution using BaNbO_2N loaded with the CoO_x cocatalyst.

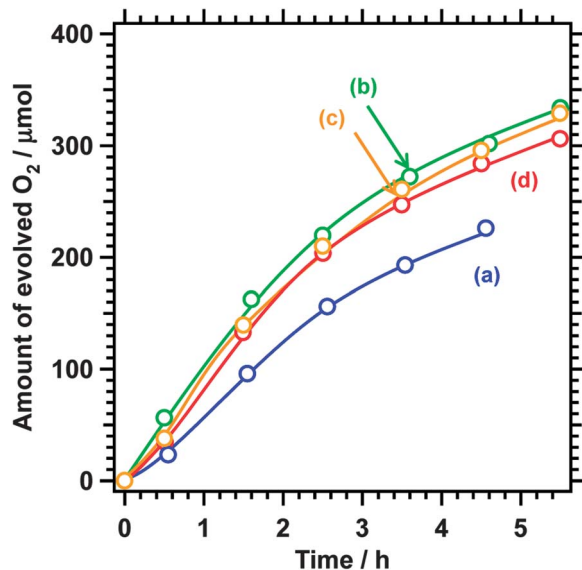


Fig. 2 Reaction time courses for oxygen evolution under visible light ($\lambda > 410$ nm) using 2 wt% CoO_x -loaded BaNbO_2N nitrided at a Ba/Nb ratio of (a) 1.25, (b) 1.50, (c) 1.75, and (d) 2.00. Photocatalyst, 0.20 g; solution, 200 mL of 50 mM AgNO_3 aqueous solution containing 0.20 g of La_2O_3 ; and light source, 300 W Xe lamp.

Oxygen evolution was observed under visible light illumination ($\lambda > 410$ nm) regardless of the Ba/Nb ratio during nitridation. The gradual decrease in the oxygen evolution rates was due to photodeposition of Ag, which blocked the surface of the photocatalyst and shielded the incident light. A small amount of nitrogen (5 μmol at most) was also generated at the initial stage of the reaction because of oxidation of the outmost surface of BaNbO_2N . Seemingly, the loading of CoO_x as an oxygen evolution cocatalyst suppressed self-oxidation of nitride ions in the oxynitride. Similar behaviours are commonly observed for the oxygen evolution reaction on (oxy)nitride photocatalysts.^{12,19,20} By contrast, unmodified BaNbO_2N did not generate any oxygen under illumination. BaNbO_2N loaded with Pt also showed activity for hydrogen evolution although the activity was very low (0.04 $\mu\text{mol h}^{-1}$, Fig. 3). In our previous work, Pt-loaded BaNbO_2N did not show activity for hydrogen evolution.¹⁹ The hydrogen evolution observed in the present study may be due to the modifications to the preparation and nitridation conditions for the oxide precursor, which yielded BaNbO_2N free from NbO_xN_y by-products. The above results indicate that BaNbO_2N has a band gap straddling the oxygen and hydrogen evolution potentials and that modification with an oxygen evolution cocatalyst is essential for activating BaNbO_2N for the reaction. In addition, BaNbO_2N was applicable to photoelectrochemical water oxidation under simulated solar irradiation when processed into a photoanode by the particle transfer method¹⁴ (Fig. S4†) while having a more negative conduction band edge than the hydrogen evolution potential. It is thus expected that the external bias voltage to drive hydrogen evolution on a counter electrode could be minimized.

The oxygen evolution rates were increased by adding BaCO_3 to $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ as a starting material for nitridation. The XRD patterns of the samples indicated that the crystallinity and

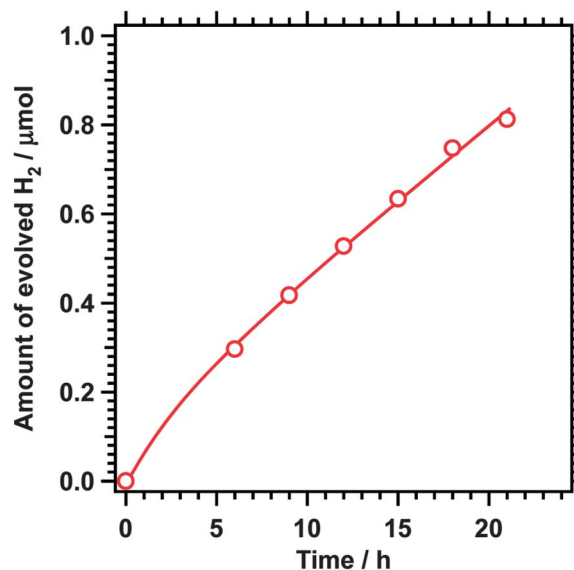


Fig. 3 Reaction time course for hydrogen evolution under visible light ($\lambda > 410$ nm) using 1 wt% Pt-loaded BaNbO_2N nitrided at a Ba/Nb ratio of 1.75. Photocatalyst, 0.20 g; solution, 200 mL of 80 vol% aqueous CH_3OH solution; and light source, 300 W Xe lamp.



uniformity of the nitridation products were improved by the addition of BaCO₃ to the precursor. This would improve oxygen evolution rates, because higher crystallinity and uniformity are thought to be favourable for higher photocatalytic activity owing to the lower probability of carrier trapping. Similar results were reported for LaTiO₂N (ref. 23) and Ta₃N₅,²⁴ where the photocatalyst samples with sharper XRD peaks exhibited higher oxygen evolution activity. On the other hand, the background absorption due to defect species was progressively enhanced. The influence of defect species on photocatalytic oxygen evolution in the presence of sacrificial reagents is still controversial. In the present study, they likely did not contribute to charge trapping and recombination significantly. The present results demonstrate that adding an appropriate amount of BaCO₃ to the precursor oxide could modify the structural properties and improve the photocatalytic activity of BaNbO₂N. More comprehensive synthesis and analysis of BaNbO₂N samples are currently underway.

Fig. 4 shows the dependence of the initial oxygen evolution rate on the cutoff wavelength of the incident light, where BaNbO₂N nitrided at a Ba/Nb ratio of 1.5 and modified with 2 wt% cobalt oxide was employed. The DRS trace of the sample is also shown for comparison. Photocatalytic oxygen evolution from the AgNO₃ solution was observed up to a cutoff wavelength of 740 nm (0.2 μmol h⁻¹) although the oxygen evolution rate decreased as the cutoff wavelength increased. The apparent quantum efficiency of the oxygen evolution reaction was measured to be 0.04% at 640 ± 30 nm. The onset of light absorption reasonably matched the longest wavelength available for photocatalytic oxygen evolution. On the other hand, continuous light absorption by defect species did not contribute to photocatalysis. Thus, it was concluded that water oxidation

proceeded *via* band gap transitions for the BaNbO₂N photocatalyst.

Conclusion

We demonstrated activation of BaNbO₂N by loading a CoO_x cocatalyst for photocatalytic O₂ evolution under visible light. The apparent quantum efficiency of the reaction using CoO_x-loaded BaNbO₂N was lower than the value for the porous single-crystalline LaTiO₂N,¹¹ likely because of the smaller band gap energy of BaNbO₂N (smaller by 0.4 eV) in addition to insufficient optimization of the preparation conditions for the material. Nevertheless, BaNbO₂N can utilize photons up to 740 nm for photocatalytic O₂ evolution. This wavelength is the longest ever reported for an (oxy)nitride photocatalyst. Managing longer wavelength photons could help overcome the barrier against effective production of solar fuel *via* water splitting.² Moreover, BaNbO₂N had a band gap straddling the hydrogen and oxygen evolution potentials. This means that overall water splitting and unassisted photoelectrochemical water splitting could be achieved under illumination of red light by improving the semi-conducting quality of the BaNbO₂N photocatalyst. These findings motivate further studies on refinement of the nitridation and cocatalyst loading conditions,^{11,20} modifications of oxide precursors,^{23,24} and doping²⁵ to improve the photocatalytic and photoelectrochemical activity of BaNbO₂N.

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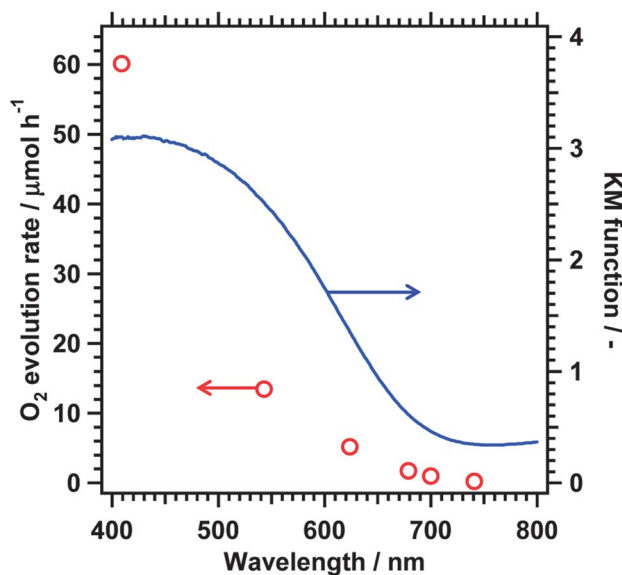


Fig. 4 Dependence of the initial oxygen evolution rate of 2 wt% CoO_x-loaded BaNbO₂N on the cutoff wavelength of the incident light. The DRS trace of the BaNbO₂N used is also shown. Photocatalyst, 0.10 g; solution, 200 mL of 50 mM aqueous AgNO₃ solution containing 0.20 g of La₂O₃; and light source, 300 W Xe lamp.



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