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Active BaTaO₂N photocatalysts prepared from an amorphous Ta₂O₅ precursor for overall water splitting under visible light†

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Barium tantalum oxynitride (BaTaO₂N), a photocatalyst active during one-step-excitation overall water splitting under visible light, was synthesized by NH₃-based nitridation of a mixture of BaCO₃ and amorphous Ta₂O₅·3H₂O. H₂ and O₂ were generated from water in stoichiometric amounts and in a stable manner using this material modified with Rh (or Ru), Cr₂O₃ and IrO₂ cocatalysts. This photocatalyst was responsive to visible light up to a wavelength of 540 nm for the water splitting reaction. Trials using nitridation temperatures from 1023 to 1273 K and durations from 0.5 to 20 h indicated that mild nitridation conditions such as 1123 K and 5 h provided high-performance specimens, whereas prolonged nitridation (15–20 h) dramatically decreased the photocatalytic activity. Transient absorption spectroscopy showed that BaTaO₂N generated abundant photoexcited free electrons with long lifetimes due to a low concentration of defects such as oxygen vacancies, but was deactivated after prolonged nitridation. X-ray photoelectron spectra indicated that overly long nitridation generated recombination sites such as Ta³⁺. The mechanism by which active BaTaO₂N was formed was examined, and the high reactivity of the amorphous Ta₂O₅·3H₂O nanoparticles was determined to be important. The use of highly reactive nanoparticles under mild nitridation conditions could allow the future development of high-performance oxynitride photocatalysts for overall water splitting.

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Introduction

Overall water splitting *via* single-step photoexcitation using particulate photocatalysts is recognized as one of the most useful means of achieving sustainable solar hydrogen production, partly because this process can be readily scaled up.^{1,2} As an example, solar hydrogen production from water using Al-doped SrTiO₃ as an ultraviolet (UV) photoresponsive powder photocatalyst has recently been demonstrated in a 100 m² system.³ Even so, the development of cost-effective systems will

require particulate photocatalysts capable of driving one-step-excitation water splitting in response to visible light wavelengths of 400 to 700 nm. To date, studies regarding visible-light-driven photocatalysts have been primarily performed using (oxy)nitrides^{4–7} and oxysulfides. Unfortunately, only a limited number of such compounds, including TaON, Zr-doped TaON,⁸ Ta₃N₅ grown on KTaO₃ (ref. 9) and Y₂Ti₂O₅S₂,¹⁰ have been reported to be photocatalytically active for overall water splitting.

Barium tantalum oxynitride, BaTaO₂N, has a narrow bandgap energy of 1.9 eV along with a robust perovskite structure, and is highly stable in water. Thus, this material is considered a promising catalyst capable of utilizing long-wavelength visible light. Significant work has been devoted over the past two decades to tuning the morphology of BaTaO₂N to obtain a material that is active for water splitting. Complete nitridation based on reaction durations longer than 10 h under a flow of gaseous NH₃ at temperatures higher than 1123 K, both in the absence and presence of a flux, has been employed. BaTaO₂N obtained from these processes has been found to promote half-reactions evolving either H₂ or O₂ when using sacrificial reagents.^{6,7,11–13} This material has also been applied to Z-scheme water splitting as a particulate photocatalyst for hydrogen evolution^{14,15} in combination with WO₃. Very recently, Mg-doped BaTaO₂N was reported to be active for water splitting

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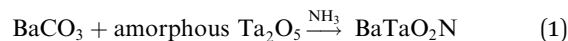


after having Cr_2O_3 and Rh deposited on its surface as cocatalysts.¹⁶ However, only minimal activity was observed without Mg addition. Overall water splitting has not yet been realized on pristine BaTaO_2N particulate photocatalysts, and the successful achievement of this process without the incorporation of dopants remains an important challenge.

The methods used to synthesize BaTaO_2N are now commonly based on direct nitridation of mixtures of various materials, such as barium and tantalum oxides, rather than using a barium tantalate precursor such as $\text{Ba}_5\text{Ta}_4\text{O}_{15}$. During the nitridation of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ by gaseous NH_3 , lattice O atoms are replaced by N atoms in conjunction with reduction by hydrogen obtained from the NH_3 . However, this reaction proceeds from the surface to the interior of the catalyst particles, resulting in inhomogeneous phase formation with variations in the extent of nitridation. In contrast, the nitridation of a mixture involves a solid-phase reaction between barium and tantalum oxides that accompanies the nitridation process and generates a more homogeneous product. Consequently, BaTaO_2N exhibiting improved photocatalytic performance can be obtained. As an example, in prior work a mixture of BaCO_3 , MgO and Ta_2O_5 was directly nitrided in a RbCl flux to produce active Mg-BaTaO₂N.¹⁶

Our own group previously demonstrated that amorphous $\text{Ta}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ nanoparticles can be used as a starting material for the synthesis of TaON and Zr-doped TaON exhibiting very high activity for overall water splitting compared with materials obtained from large crystalline Ta_2O_5 particles.⁸ There are two advantages to the use of amorphous Ta complexes. Firstly, the high reactivity of these materials allows rapid nitridation at relatively low temperatures and so may prevent or at least minimize the formation of reduced $\text{Ta}^{3+}/\text{Ta}^{4+}$ species. Secondly, smaller catalyst particles can be obtained. Thus, the use of amorphous Ta_2O_5 is also an interesting approach to the synthesis of BaTaO_2N photocatalysts for overall water splitting. On this basis, in the present study, BaTaO_2N was prepared by

direct nitridation of amorphous Ta_2O_5 with BaCO_3 via the reaction



while varying the synthesis conditions. The process of producing active BaTaO_2N according to reaction (1) was assessed based on elucidating the various fundamental reaction paths that could take place during nitridation. The present approach is also expected to be applicable to the synthesis of other oxynitrides.

Results and discussion

Characterization of BaTaO_2N

Details regarding the preparation of BaTaO_2N are provided in the Methods section. Briefly, a white precipitate comprising amorphous $\text{Ta}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ($n = 3$; referred to herein as a- Ta_2O_5) was obtained by H_2SO_4 neutralization of an alkaline solution of Na_3TaO_4 in H_2O . This compound was subsequently combined with BaCO_3 and then nitrided in an NH_3 flow at various temperatures between 1073 and 1273 K, employing nitridation durations between 0.5 and 20 h. Fig. 1 shows X-ray diffraction (XRD) patterns for BaTaO_2N specimens prepared at 1123 K with durations from 3 to 20 h. After 3 h of nitridation, intense peaks appeared at $2\theta = 30.7^\circ$ and 43.9° that were attributed to the (110) and (200) planes of BaTaO_2N having a characteristic perovskite structure. The XRD pattern for this sample also contained less intense peaks assigned to Ta_3N_5 and $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ phases. After a 5 h nitridation, the peaks due to the oxide disappeared whereas those related to Ta_3N_5 remained. With increasing nitridation time from 15 to 20 h, the BaTaO_2N peaks became more intense and sharp, indicating a higher degree of crystallinity, while Ta_3N_5 peaks were still observed. Fig. 2 presents UV-visible diffuse reflectance spectra acquired from BaTaO_2N samples prepared at 1123 K with different nitridation

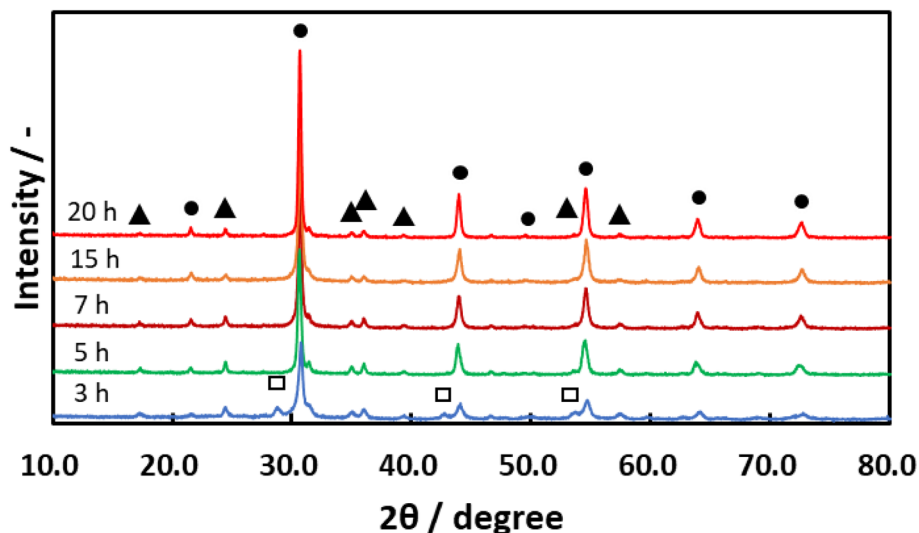


Fig. 1 X-ray diffraction patterns for BaTaO_2N prepared in a flow of NH_3 at 1123 K using durations of 3–20 h. ●: BaTaO_2N , ▲: Ta_3N_5 , and □: $\text{Ba}_5\text{Ta}_4\text{O}_{15}$.



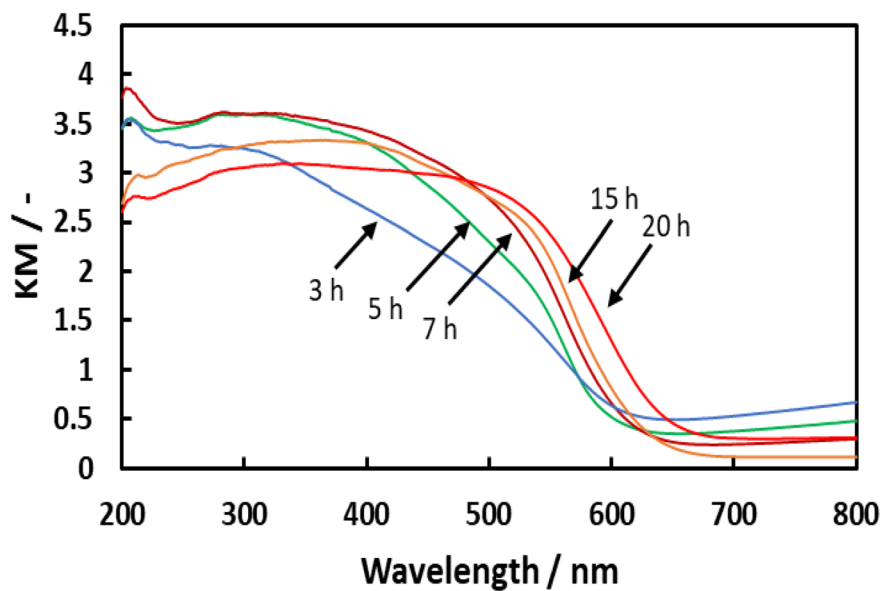


Fig. 2 UV-visible diffuse reflectance spectra obtained from BaTaO₂N prepared in a flow of NH₃ at 1123 K using durations of 3–20 h.

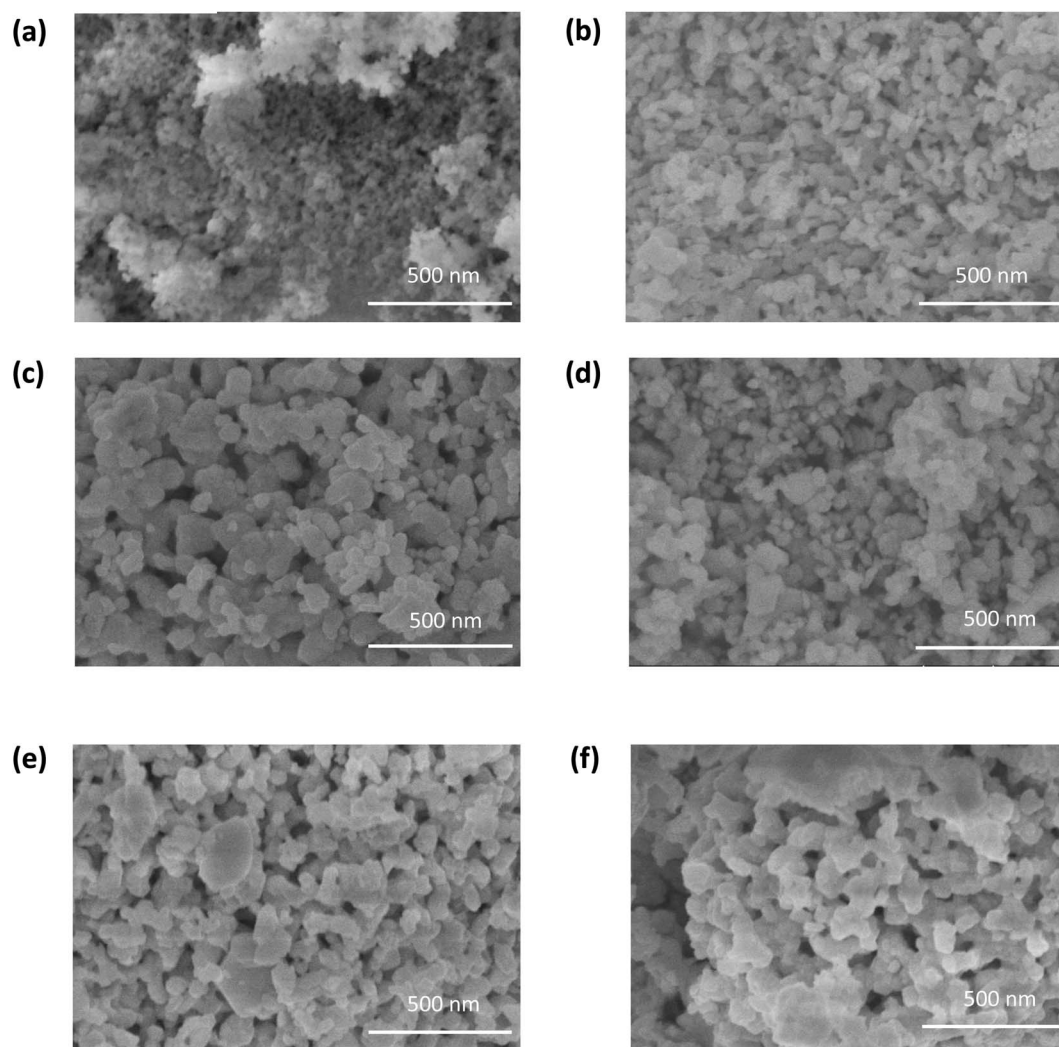


Fig. 3 SEM images of (a) a-Ta₂O₅ and BaTaO₂N prepared in a flow of NH₃ at 1123 K with nitridation durations of (b) 3, (c) 5, (d) 7, (e) 15 and (f) 20 h.



times. The sample treated for 3 h showed absorption that began at approximately 620 nm and increased with decreasing wavelength. Upon increasing the nitridation time to 7 h or longer, the absorption underwent a red shift. The samples nitrided for 3 and 5 h exhibited strong absorption beyond 650 nm but this absorption was reduced with increasing nitridation time. This was also associated with enhanced crystallinity of BaTaO₂N.

Fig. 3 provides the SEM images of various specimens. The original amorphous Ta₂O₅ used as a raw material evidently was made of particles having a fluffy, cloud-like shape with sizes of 20–30 nm. The nitridation of this compound with BaCO₃ at 1123 K produced aggregates of irregularly shaped particles roughly 50–150 nm in size. With increasing nitridation duration to 15–20 h, these irregularly shaped particles partly grew into large aggregates and connected with one another. Raising the nitridation temperature to 1173–1273 K caused the particle shape to vary and produced sintered structures (Fig. S1†). Fig. S2(a) and (b)† show the HR-TEM images of a-Ta₂O₅ and BaTaO₂N, respectively. In contrast to a-Ta₂O₅ with amorphous structural characteristics, BaTaO₂N exhibits crystalline lattice fringes.

Water splitting reaction

Fig. 4 summarizes the extent of H₂O decomposition in response to Xe lamp illumination of a BaTaO₂N specimen nitrided at 1123 K for 5 h and loaded with Rh, Cr₂O₃ and IrO₂ as cocatalysts. Both H₂ and O₂ were generated in stoichiometric amounts during the initial stage of the reaction and the quantities of these gases increased linearly during the reaction. During the second and third runs following the evacuation of gaseous products, the gas amounts produced were nearly the same as those in the first run. The stoichiometric and constant production of H₂ and O₂ in these trials clearly indicates that one-step-excitation overall water splitting took place. Fig. 5 plots

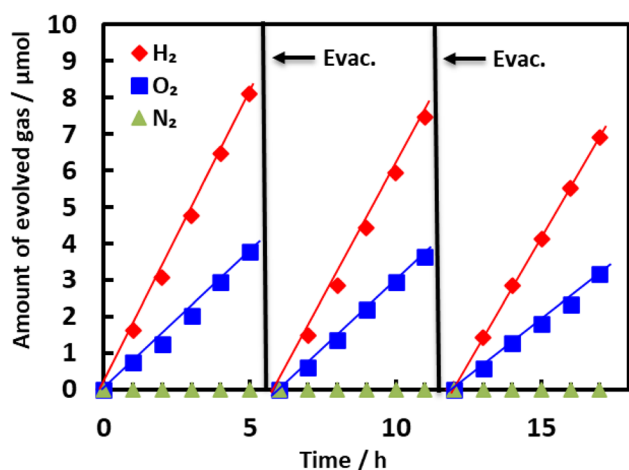


Fig. 4 Evolution of various gases over time during the water splitting reaction over Rh/Cr₂O₃/IrO₂-loaded BaTaO₂N under visible light ($\lambda > 420$ nm). BaTaO₂N was prepared by nitridation at 1123 K for 5 h and was loaded with 2 wt% Rh, 1 wt% Cr₂O₃ and 0.3 wt% IrO₂ as cocatalysts. Reaction conditions: lamp source: 300 W Xe lamp, reaction temperature: 288 K, and background pressure: Ar at 5 kPa.

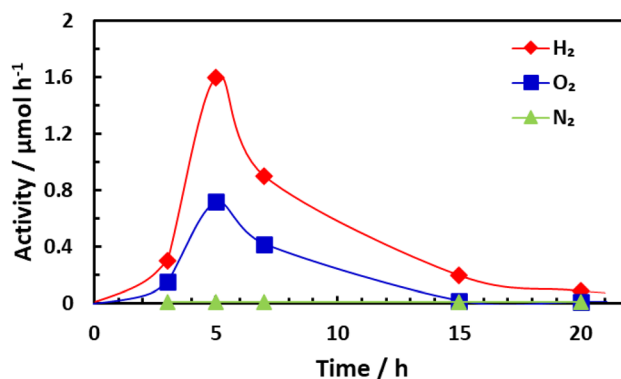


Fig. 5 Effects of nitridation time on the photocatalytic activity of BaTaO₂N during the water splitting reaction. BaTaO₂N was prepared by nitridation at 1123 K for varying durations and was loaded with 2 wt% Rh, 1 wt% Cr₂O₃ and 0.3 wt% IrO₂ as cocatalysts. Reaction conditions: lamp source: 300 W Xe lamp ($\lambda > 420$ nm), reaction temperature: 288 K, and background pressure: Ar at 5 kPa.

H₂ and O₂ production as functions of nitridation time as a means of assessing photocatalytic activity. The activity is seen to have increased sharply over the range of 3–5 h, passed through a maximum at 5 h, and then decreased over the range of 7–15 h. The H₂ evolution for BaTaO₂N heated for 20 h was lower than 6% of that for 5 h and little O₂ evolution was observed with this sample. The effect of the nitridation duration on the activity of BaTaO₂N after processing at 1173 or 1073 K is presented in Fig. S3 and S4,† respectively. The maximum activity appeared after 2 and 15 h at 1173 and 1073 K, respectively. Fig. S5† summarizes the changes in activity over a wide variety of nitridation times and temperatures in the form of a three-dimensional map. It is evident that lower nitridation temperatures required longer durations to achieve suitable water splitting activity. Out of this wide range of times and temperatures, the combination of 1123 K and 5 h provided the highest photocatalytic activity during overall water splitting.

As shown in Fig. 1, BaTaO₂N contained a small amount of Ta₃N₅. To avoid or at least suppress the formation of the Ta₃N₅ phase, the Ba/Ta ratio for the initial mixture of BaCO₃ and a-Ta₂O₅ was varied between 0.9 and 1.2. Fig. 6(a) shows XRD patterns for samples prepared by nitridation at 1123 K for 5 h. Peaks related to the Ta₃N₅ phase remained present at a Ba/Ta ratio of 1.1 but nearly disappeared at Ba/Ta = 1.2, while peaks due to Ba₅Ta₄O₁₅ appeared. The ratio of the intensity of the Ta₃N₅ peaks to the BaTaO₂N peaks is plotted against the Ba/Ta ratio in Fig. 6(b), and this ratio is seen to decrease with increasing ratio. The photocatalytic activity of the catalyst (as assessed based on H₂ and O₂ evolution) increased beginning at Ba/Ta = 0.9 and peaked at Ba/Ta = 1, with dramatic decreases as the ratio was further increased to a value of 2 (Fig. 6(c)). A Ba/Ta ratio of 1 was determined to provide the highest activity regardless of the presence of Ta₃N₅. Although it is possible that the Ta₃N₅ phase contributed to photocatalysis, the poor correlation between the amount of Ta₃N₅ phase and the activity of the material suggests that this phase had only a minimal effect on the photocatalytic activity of BaTaO₂N. Water splitting trials



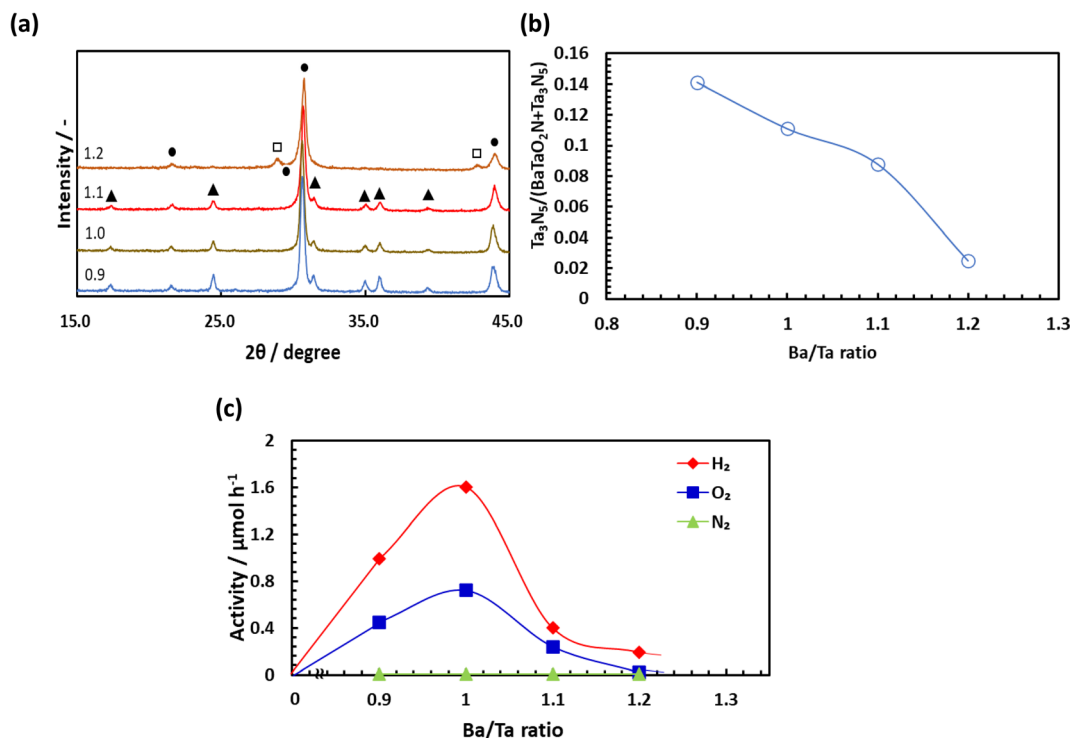


Fig. 6 (a) X-ray diffraction patterns for BaTaO₂N prepared using various Ba/Ta ratios in the starting mixture, (b) the ratio of the intensity of the Ta₃N₅ XRD peak to the sum of the intensities of the BaTaO₂N and Ta₃N₅ peaks as a function of the Ba/Ta ratio, and (c) the photocatalytic activity of Rh/Cr₂O₃/IrO₂-loaded BaTaO₂N (as reflected in the evolution of gaseous products) during the water splitting reaction as a function of the Ba/Ta ratio. BaTaO₂N was prepared by nitridation at 1123 K for 5 h and was loaded with 2 wt% Rh, 1 wt% Cr₂O₃ and 0.3 wt% IrO₂ as cocatalysts. Reaction conditions: lamp source: 300 W Xe lamp ($\lambda > 420$ nm), reaction temperature: 288 K, and background pressure: Ar at 5 kPa.

were also carried out under argon at pressures of 5, 20 or 50 kPa. As shown in Fig. S6,[†] at least 80% of the original activity was maintained even at 50 kPa, indicating that the effect of background pressure on the photocatalytic activity was not especially strong. Fig. S7[†] shows changes in the amounts of H₂ and O₂ in the gas phase after turning the light irradiation off (in the dark). Their decreases were 4% for 3 h, indicating that the extent of the backward reaction from H₂/O₂ to H₂O is low.

Effects of cocatalysts

The photocatalytic activity of the catalyst during water splitting was found to vary with changes in the amounts of Rh, Cr₂O₃ and IrO₂ that were deposited. Specifically, the activity increased with increasing Rh loading up to 4 wt% (Fig. S8[†]). Small amounts of Cr₂O₃ (meaning concentrations in the range of 0.5 to 1.0 wt%) were also found to lead to high photocatalytic activity (Fig. S9[†]). The concentration of IrO₂ did not have a large effect, such that even a low concentration of 0.3 wt% was sufficient to promote oxygen evolution during water splitting. Annular dark-field STEM images and STEM-EDS elemental maps were obtained to assess the states of Rh, Cr₂O₃ and IrO₂ deposited on BaTaO₂N. As shown in Fig. 7, the BaTaO₂N particles were found to have uniform distributions of Ba, Ta, O and N. However, Rh particles on Rh/Cr₂O₃/IrO₂-BaTaO₂N were determined to form aggregates on the BaTaO₂N particles while Cr₂O₃ loaded by photodeposition were concentrated on the Rh particles. This

last result was indicative of a core-shell structure that has been previously proposed for this type of cocatalyst.^{17–19} IrO₂ was likely to have been uniformly distributed over the BaTaO₂N surface, but the evidence for this was not as clear because of the poor color pattern of the associated images, possibly owing to the low concentration of this cocatalyst.

To see the role of the cocatalysts, the water splitting reaction was tested for Rh/Cr₂O₃- and IrO₂-loaded BaTaO₂N, separately. As shown in Fig. S10(a),[†] Rh/Cr₂O₃-loaded BaTaO₂N was able to produce H₂ and O₂, indicating the effectiveness of Rh/Cr₂O₃ cocatalysts for water splitting. However, the evolution of O₂ was slightly low, compared to the case of Rh/Cr₂O₃/IrO₂-loading. Fig. S10(b)[†] shows no activity of IrO₂-loaded BaTaO₂N for the water splitting reaction. From these results, it is concluded that IrO₂ has the ability of promoting O₂ evolution.

To better understand the effect of the cocatalysts on the activity, Ru was used in place of Rh, together with Cr₂O₃ and IrO₂. Fig. 8(a) shows the results for the water splitting reaction on Ru/Cr₂O₃/IrO₂-BaTaO₂N. These data demonstrate that both H₂ and O₂ were evolved and that the amounts of these gases increased in an essentially linear fashion as the irradiation time was increased. As shown in Fig. 8(b), Ru metal provided almost the same level of activity as Rh although the highest activities were obtained at 1 to 2 wt% Ru whereas 4 wt% Rh was required for optimal performance (Fig. S11[†]). Fig. S12[†] provides an annular dark-field STEM image and STEM-EDS elemental maps



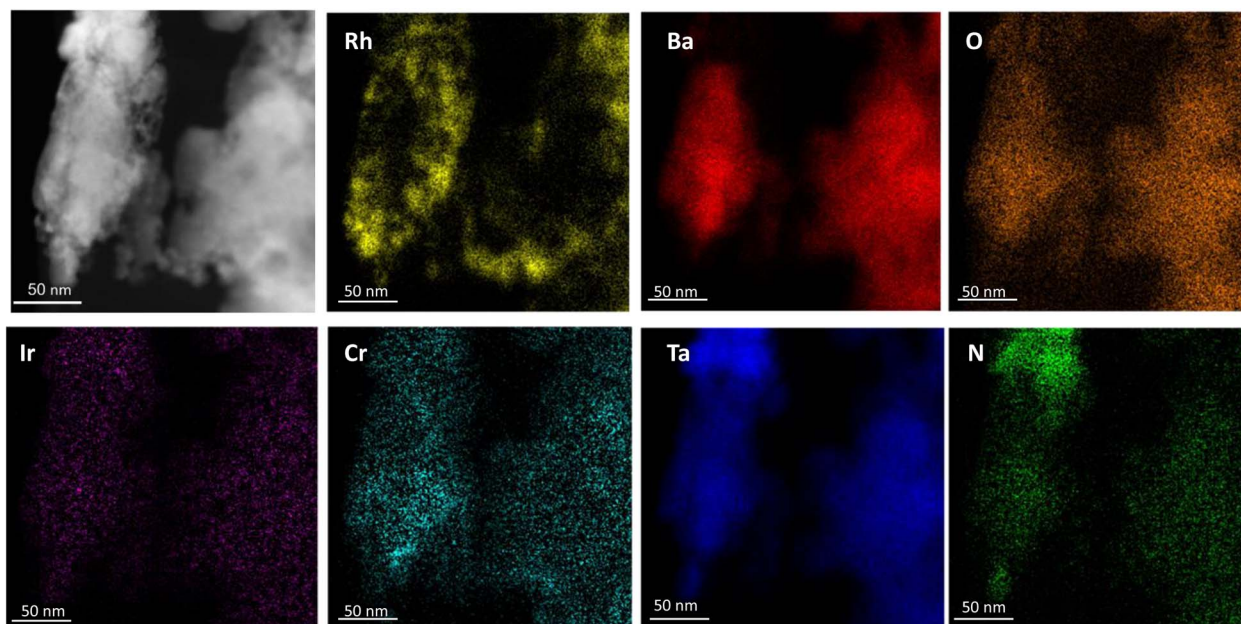


Fig. 7 Annular dark-field STEM images and STEM-EDS elemental maps for Rh/Cr₂O₃/IrO₂-loaded BaTaO₂N. BaTaO₂N was prepared by nitridation at 1123 K for varying durations and was loaded with 4 wt% Rh, 1 wt% Cr₂O₃ and 0.3 wt% IrO₂ as cocatalysts.

obtained from a cross-sectional sample of Ru/Cr₂O₃/IrO₂-BaTaO₂N. These results confirm that Ru metal was uniformly dispersed over BaTaO₂N in the form of small particles. Thus, the difference in the amount of metal required to obtain high activity between Ru and Rh was likely related to the higher degree of dispersion of the former. Fig. S13[†] shows a HR-TEM image and its EDS mappings. The oval shaped Ru metal particles are attached on BaTaO₂N and surrounded by a thin Cr₂O₃ layer, which indicates the formation of a core-shell structure.

Prior to the water splitting trials, a Cr₂O₃ layer was applied to Rh by photo-reduction of Cr⁶⁺ to Cr³⁺ using a K₂CrO₄ solution containing 10% CH₃OH as a sacrificial reagent. After Rh-loaded BaTaO₂N was illuminated in an aqueous K₂CrO₄ solution

without CH₃OH, water splitting was found to proceed with the generation of stoichiometric amounts of H₂ and O₂ (Fig. S14(a)[†]). It should also be noted that Cr₂O₃ could be loaded on Rh without the aid of a sacrificial reagent to produce a Cr₂O₃/Rh core-shell structure, after which the water splitting reaction would take place. As shown in Fig. 9, the activity increased with increasing K₂CrO₄ concentration, and the highest activity was obtained at approximately 0.22 mM.

The effect of pH on the photocatalytic activity of Rh-loaded BaTaO₂N in aqueous K₂CrO₄ solutions was also assessed. The data in Fig. S14(b)[†] establish that the photocatalytic activity increased with increasing pH from 7 to 9. However, a sharp drop in activity occurred at pH 10 because Cr₂O₃ was highly soluble

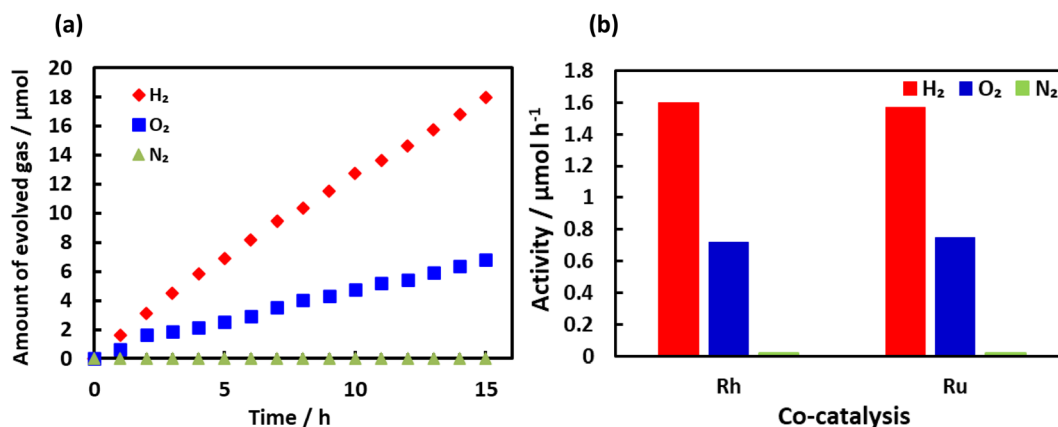


Fig. 8 (a) Evolution of gaseous products during the water splitting reaction over Ru-loaded BaTaO₂N under visible light. Cocatalysts: Ru at 4 wt%, Cr₂O₃ at 1 wt% and IrO₂ at 0.3 wt%. (b) Comparison of the photocatalytic activities during the water splitting reaction using Ru and Rh cocatalysts. Cocatalysts: Rh at 2 wt% or Ru at 1 wt%, Cr₂O₃ at 0.3 wt% and IrO₂ at 0.3 wt%. BaTaO₂N was prepared by nitridation at 1123 K for 5 h. Reaction conditions: lamp source: 300 W Xe lamp ($\lambda > 420$ nm), reaction temperature: 288 K, and background pressure: Ar at 5 kPa.



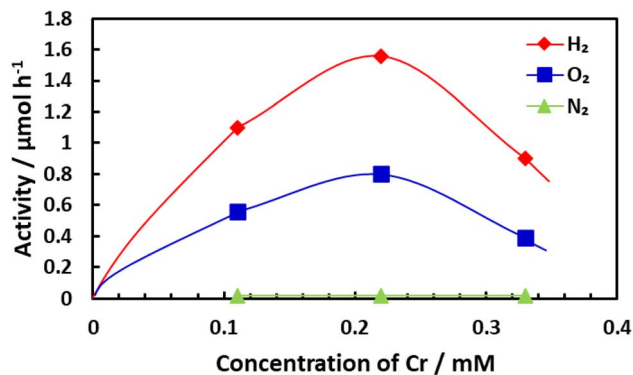


Fig. 9 Effects of the Cr concentration in aqueous solution on the photocatalytic activity of Rh-loaded BaTaO₂N during the water splitting reaction. In these trials, 2 wt% Rh-loaded BaTaO₂N was dispersed in an aqueous solution of K₂CrO₄. A concentration of 0.22 mM K₂CrO₄ corresponded to a loading of 1 wt% Cr on BaTaO₂N. BaTaO₂N was prepared by nitridation at 1123 K for 5 h. Reaction conditions: lamp source: 300 W Xe lamp ($\lambda > 420$ nm), reaction temperature: 288 K, and background pressure: Ar at 5 kPa.

in the alkaline medium. The activity enhancements observed at pH 8 and 9 were possibly related to reductions in the energy barrier to oxygen evolution with increasing OH⁻ concentration. This outcome is in agreement with the results obtained from previous photoelectrochemical analyses of BaTaO₂N electrodes, in which oxygen evolution was enhanced at higher pH values.²⁰

Fig. 10 plots the apparent quantum yield (AQY) obtained from Rh/Cr₂O₃/IrO₂-loaded BaTaO₂N, together with the optical absorption of the material. The AQY at 400 nm was 0.1% but this value gradually decreased beginning at 420 nm and then dropped sharply at around 500 nm and exhibited a slower decline above 540 nm. These changes in the AQY were roughly analogous to those in optical absorption. Even though the AQY for this material was relatively low, it is noteworthy that the overall water splitting reaction proceeded at a long wavelength of 540 nm. Fig. 11 summarizes the results of the water splitting

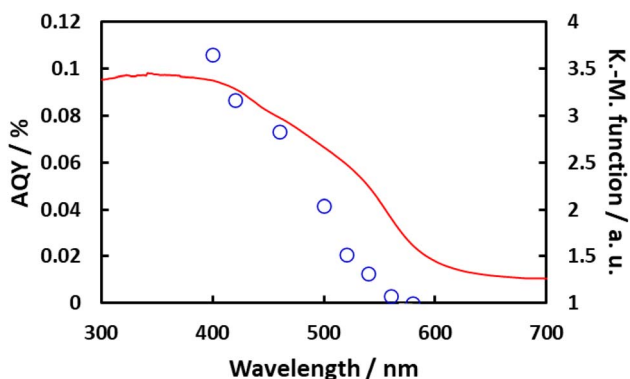


Fig. 10 AQY (O) and absorption (solid line) data for Rh/Cr₂O₃/IrO₂-loaded BaTaO₂N as a function of wavelength. BaTaO₂N was prepared by nitridation at 1123 K for 5 h and was loaded with 2 wt% Rh, 1 wt% Cr₂O₃ and 0.3 wt% IrO₂ as cocatalysts. Reaction conditions: lamp source: 300 W Xe lamp, reaction temperature: 288 K, and background pressure: Ar at 5 kPa.

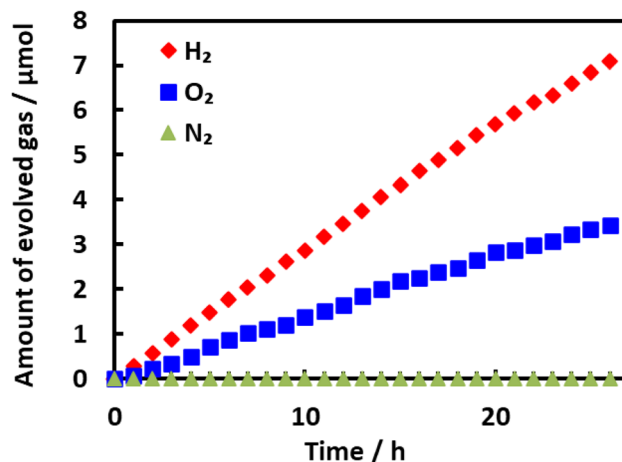


Fig. 11 Steady evolution of gaseous products during the water splitting reaction on Rh/Cr₂O₃/IrO₂-loaded BaTaO₂N under simulated light. BaTaO₂N was prepared by nitridation at 1123 K for 5 h and was loaded with 2 wt% Rh, 1 wt% Cr₂O₃ and 0.3 wt% IrO₂ as cocatalysts. Reaction conditions: lamp source: AM 1.5G solar radiation, reaction temperature: 288 K, and background pressure: Ar at 5 kPa.

reaction on Rh/Cr₂O₃/IrO₂-BaTaO₂N when irradiated using a solar simulator. Constant generation of both H₂ and O₂ from H₂O was observed during prolonged irradiation and the solar-to-hydrogen (STH) yield was estimated to be $5 \times 10^{-4}\%$. This value is slightly higher than $4 \times 10^{-4}\%$ reported for Mg-doped BaTaO₂N.¹⁶

Mechanism of active BaTaO₂N formation

It is important to have an understanding of the mechanism responsible for the formation of photocatalytically active BaTaO₂N. The generation of BaTaO₂N from a mixture of BaCO₃ and α -Ta₂O₅ in a flow of NH₃ involves several parallel reaction paths, but these can be simplified by dividing them into several separate processes, as summarized in Fig. S15(a).[†] Here, reaction path (1) involves the rapid formation of an oxide precursor having the general formula BaTaO_{*x*} (but most likely Ba₅Ta₄O₁₅) at increasing temperatures, followed by nitridation of this oxide. In contrast, path (2) proceeds *via* the selective formation of an oxynitride precursor such as amorphous BaTaO_{*x*}N_{*y*} at low temperatures followed by complete nitridation. In path (3), the nitridation of α -Ta₂O₅ to TaON proceeds preferentially after which reaction with BaCO₃ occurs to produce BaTaO₂N in a flow of NH₃. The nitridation of TaON to Ta₃N₅ readily proceeds, as demonstrated in prior work, and the reaction between Ta₃N₅ and BaCO₃ is a well-known oxynitride reaction in N₂.²⁰ In this process, some unreacted Ta₃N₅ also remains in the product. There have been several reports that BaCN₂ is formed by the nitridation of BaCO₃, but XRD peaks related to BaCN₂ were not observed and so the contribution of this reaction to BaTaO₂N formation was likely negligible.^{21–23} Reaction paths (1) to (5) were examined by synthesizing BaTaO₂N *via* each path, with the results presented in Fig. S15(b).[†] Both reaction paths (1) and (2) were found to generate BaTaO₂N that was active for overall water splitting. However, the latter showed higher activity than



the former, indicating that path (2) is superior. In contrast, the processes from path (3) to (5) resulted in the formation of inactive BaTaO₂N. The generation of highly active BaTaO₂N *via* reaction path (2) clearly demonstrates the importance of the reactivity of a-Ta₂O₅, which allows rapid nitridation even at low temperatures. To confirm the validity of this concept, large crystalline Ta₂O₅ particles were used instead of a-Ta₂O₅ for BaTaO₂N preparation using the same nitridation conditions as were applied in trials with a-Ta₂O₅. The photocatalytic activity of the resulting BaTaO₂N after Rh/Cr₂O₃/IrO₂ loading was negligibly small, confirming the importance of amorphous Ta₂O₅. One of the functions of amorphous a-Ta₂O₅ particles is that it has higher reactivity than crystalline Ta₂O₅, which enables BaTaO₂N synthesis at low temperatures and thus small particle formation. In addition, it is likely that the reaction with BaCO₃ will proceed uniformly, compared to crystalline Ta₂O₅ that consists of crystalline planes with different reactivity. These

functions of amorphous a-Ta₂O₅ are thought to result in the formation of high-quality BaTaO₂N.

The plot of photocatalytic activity against nitridation time in Fig. 5 indicates that the high activity of BaTaO₂N nitrided for 5 h was greatly decreased after 15 to 20 h of nitridation. Transient absorption spectroscopy (TAS) was employed to analyze the photoexcited states of active and inactive BaTaO₂N prepared by nitridation at 5 and 20 h, respectively. The TAS data in Fig. 12(a) and (b) contain two absorption features in the range 17 000–5000 cm⁻¹ and below 4000 cm⁻¹. These can be assigned to deeply trapped electrons and free electrons, respectively.^{24,25} Increasing the nitridation time from 5 to 20 h drastically altered the shape of the spectrum. Specifically, the intensity of the peak related to deeply trapped electrons was significantly increased whereas that of the free electron peak decreased. These results suggest that the concentration of mid-gap states capable of deeply trapping photogenerated electrons was increased by

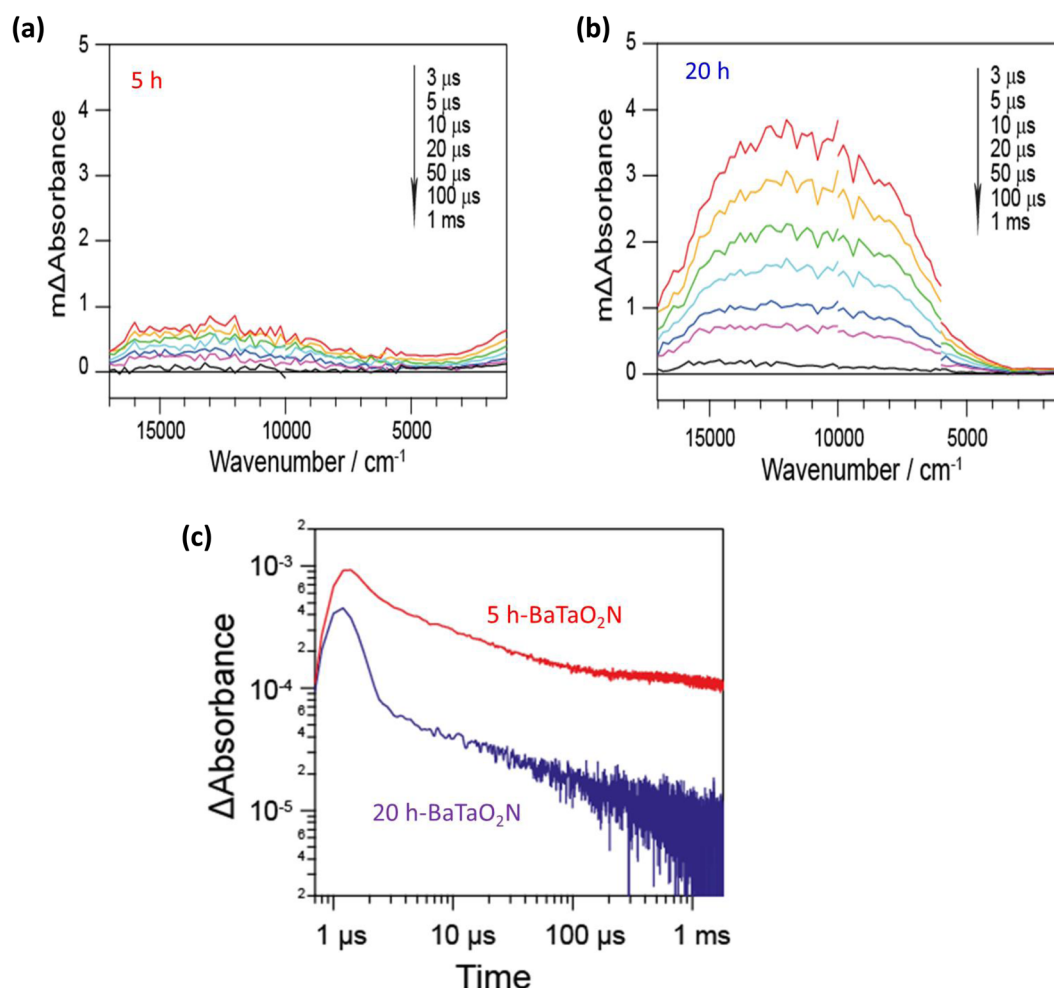


Fig. 12 (a) and (b) Time-resolved spectra and (c) decay kinetics of BaTaO₂N prepared by nitridation at 1123 K for 5 or 20 h. Active and inactive BaTaO₂N specimens were obtained by nitridation at 1123 K for 5 and 20 h, respectively (see Fig. 5). The TA spectra were obtained by scanning the probe energy from 17 000–1200 cm⁻¹ (0.15–2.1 eV). In the mid-IR region (6000–1200 cm⁻¹), an IR beam emitted by a MoSi₂ coil was used, while, in the visible to near-IR region (17 000–6000 cm⁻¹), a probe beam generated by a halogen lamp was focused on the sample. During the acquisition of the transient decay profile of photoexcited free electrons, the absorption signal was monitored at 2000 cm⁻¹ (5000 nm) after irradiation with 470 nm laser pulses (fluence: 1 mJ per pulse) at a frequency of 1 Hz to achieve bandgap excitation of photocarriers in BaTaO₂N. Measurements were carried out in a N₂ atmosphere at room temperature.



extending the nitridation time. Furthermore, the absorption in the region of 5000–16,000 cm^{-1} was very low in the case of the specimen nitrided for 5 h but very high for the 20 h specimen. It is therefore evident that the number of electrons trapped in vacancies was much smaller in the former compared with the latter. Fig. 12(c) shows the TAS data obtained at 5000 nm (2000 cm^{-1}) from samples nitrided for 5 and 20 h. The signal generated by the former material decayed very slowly and maintained a high level of intensity whereas that for the latter decayed more rapidly to a very low level. The intensity of the TA signal is correlated with the population of free electrons and so these results indicate that the 5 h specimen was able to generate long-lived free electrons. It is apparent that the active 5 h sample had a very low density of trap sites induced by defects (such as oxygen vacancies) and a high level of long-lived free electrons, both of which contributed to its excellent photocatalytic performance. Prolonged nitridation (15–20 h) increased the concentration of oxygen vacancies and other defects capable of deeply trapping photogenerated electrons.

The effect of oxygen vacancies was investigated by producing inactive BaTaO₂N *via* a 15 h nitridation and then exposing this material to a N₂ atmosphere containing 100 ppm O₂ at 823 K for 2 h. As shown in Fig. S16,† the initial low photocatalytic activity was increased by a factor of 5 and H₂ and O₂ were generated in a nearly stoichiometric ratio. The incorporation of oxygen in the specimen evidently recovered its original activity. This finding provides evidence that the oxygen vacancies formed by prolonged nitridation deactivated BaTaO₂N. Analyses by X-ray photoelectron spectroscopy (XPS) as presented in Fig. S17(a) and (b)† demonstrated that the intensities of the Ta 4f peaks (associated with Ta³⁺) were much higher in the case of BaTaO₂N nitrided for 20 h compared with the 5 h specimen. Because Ta³⁺ sites can act as recombination centers for photoexcited electrons and holes, increasing the number of these sites decreased the photocatalytic activity. Together, these TAS and XPS results confirm the exceptional performance of the photocatalytically active BaTaO₂N obtained by 5 h nitridation and explain the enhanced performance of this material during the water splitting reaction.

Conclusions

To the best of our knowledge, this work represents the first-ever demonstration of one-step-excitation overall water splitting using pristine BaTaO₂N. The direct nitridation of a mixture of amorphous Ta₂O₅ (Ta₂O₅·3H₂O) nanoparticles and BaCO₃ produced a BaTaO₂N photocatalyst active for overall water splitting under visible light extending to a wavelength of 540 nm following modification with Rh (or Ru), Cr₂O₃ and IrO₂ as cocatalysts. The photocatalytic activity was found to be greatly affected by the concentrations of the cocatalysts, and the optimal amounts were determined to be 4 wt% (2 wt% for Ru), 1 wt% and 0.3 wt%, respectively. A wide range of nitridation conditions was examined with temperatures from 1023 to 1273 K and times from 0.5 to 20 h, and the highest activity was obtained for mild NH₃-based nitridation at 1123 K for 5 h. Even though a low nitridation temperature was employed, extending

the duration to 15–20 h produced BaTaO₂N with negligible activity. Analyses by TAS clearly showed that the active BaTaO₂N contained the largest population of photoexcited free electrons, and that these electrons had long lifetimes owing to a small number of defects. The mechanism by which BaTaO₂N was formed during NH₃ nitridation from the present mixture of starting materials was assessed, and the elevated reactivity of amorphous Ta₂O₅ nanoparticles is thought to be an important aspect of this process. Although the efficiency of the photocatalysis remains very low, the concept of employing highly reactive nanoparticles shows promise and could be used in future to develop high-quality oxynitride photocatalysts.

Methods

Synthesis of BaTaO₂N

Na₃TaO₄ was initially prepared as a starting material for the synthesis of amorphous tantalum oxides. In this process, Ta₂O₅ (99.99%, Rare Metal Co.) and NaOH (98%, Fujifilm Wako Pure Metal Co.) were thoroughly mixed at a Na : Ta molar ratio of 5 : 1. The mixture was then transferred to an alumina crucible and heated in air at 623 K for 12 h. The resulting solid generated an XRD pattern containing peaks attributable to Na₃TaO₄ and to excess NaOH. This product was subsequently dissolved in H₂O by sonication and stirring to produce an aqueous solution of Na₈[Ta₆O₁₉] with a pH close to 13.^{26–28} This alkaline solution was neutralized by adding H₂SO₄ until a white precipitate was observed at pH 7 based on the protonation of [Ta₆O₁₉]⁸⁻ anions followed by decomposition to produce amorphous hydrous tantalum, Ta₂O₅·*n*H₂O. The precipitate was washed five times with pure water to remove residual Na₂SO₄ and then dried overnight under vacuum at 313 K. The XRD pattern of the product confirmed its amorphous structure and the material was then converted to crystalline Ta₂O₅ by heating in air at 1023 K. Thermogravimetric/differential thermal analysis data showed that the amorphous hydrous tantalum oxide had the formula Ta₂O₅·3H₂O. This material is referred to herein as a-Ta₂O₅.

BaTaO₂N was prepared by a solid state reaction. In this synthesis, BaCO₃ (99.99%, Rare Metallic Co.) and a-Ta₂O₅ were thoroughly mixed in an agate mortar containing a drop of C₂H₅OH. The resulting mixture was placed in an alumina crucible and directly nitrided under a flow of NH₃ at a rate of 500 mL min⁻¹ and at various temperatures from 1023 to 1273 K with durations ranging from 0.5 to 20 h. The resulting BaTaO₂N was washed with dilute HCl and water in conjunction with sonication, removed by filtration and then vacuum dried at 313 K for 2 h.

Loading of cocatalysts on BaTaO₂N

The cocatalysts were typically loaded onto BaTaO₂N in the order Rh, Cr₂O₃ and IrO₂. The Rh was deposited using an impregnation method. In this process, a solution of RhCl₃·3H₂O (99.9%, Wako Pure Chemical Co. Ltd.) in water was added dropwise to BaTaO₂N powder until incipient wetness was obtained. After drying, the powder was heated under a flow of H₂ (10%)/N₂



(90%) at 573 K for 1 h so as to convert the Rh compound to Rh metal particles on BaTaO₂N. The Rh loadings on these specimens were in the range 1 to 4 wt%. A Cr₂O₃ layer was applied by dispersing a quantity of Rh-loaded BaTaO₂N in an aqueous K₂CrO₄ solution containing 10 vol% CH₃OH as a sacrificial reagent with subsequent illumination (>350 nm) for 4 h. This procedure reduced Cr⁶⁺ to Cr³⁺ on the Rh metal surfaces to produce a core-shell structure in which Rh metal particles were covered with Cr₂O₃. This structure helped to suppress backward reactions involving H₂ and O₂, as has been reported previously.^{17,18} Following this, colloidal IrO₂ nanoparticles obtained from the hydrolysis of Na₂IrCl₆ in an aqueous alkaline solution^{29,30} were loaded onto the catalyst at a concentration of 0.3 wt%. The resulting photocatalysts are referred to herein as IrO₂/Cr₂O₃/Rh-BaTaO₂N. In the case of Ru impregnation, RuCl₃·3H₂O (Kanto Ltd, >95%) was used, and nearly the same procedure as that described above was applied except that the loading was in the range 0.5 to 2 wt% and the reduction temperature was 623 K.

Water splitting reaction

Overall water splitting was performed using a closed gas circulation apparatus equipped with a gas chromatograph (GC 8 A, Shimadzu, with a thermal conductivity detector, molecular sieve 5 A column and Ar as the carrier gas). A Pyrex top-illuminated reaction vessel was connected to the reaction apparatus and used as the reactor. In each trial, a quantity of the Rh/Cr₂O₃/IrO₂-loaded BaTaO₂N photocatalyst (0.2 g) was dispersed in ultrapure water (150 mL) having a pH of approximately 7 unless otherwise specified. After complete removal of dissolved gases in the water, the reactor was filled with Ar to a background pressure of 5 kPa and then illuminated with a 300 W xenon lamp coupled with a cold mirror and a cut-off filter (L42, λ > 420 nm) or a solar simulator (SAN-EI electronic, XRS40S1, AM 1.5G, 100 mW cm⁻²) with continuous agitation using a magnetic stirrer. The temperature of the reactant solution was maintained at 288 K with a flow of cooling water.

Characterization

XRD patterns for the various samples were acquired using a Rigaku RINT-Ultima III diffractometer with a Cu Kα radiation source. The absorption characteristics of the specimens were assessed using UV-visible diffuse reflectance spectroscopy employing a spectrophotometer (JASCO V-670DS), with Kubelka-Munk conversion of the data. Scanning transmission electron microscopy (STEM) images were obtained with a JEOL JEM-2800 instrument. Energy dispersive X-ray spectroscopy (EDS) data together with STEM images were obtained with a JEOL JEM-2800 system equipped with an Oxford Instruments X-MAX 100TLE SDD detector. XPS data were acquired using powder samples fixed on conductive carbon adhesive tape without a conductive Al pillar. Spectra were acquired with a KRATOS ULTRA2 instrument having an Al Kα source and equipped with a charge neutralizer. The binding energy values for these spectra were calibrated based on the C 1s peak at 284.4 eV.

Microsecond-millisecond TAS analyses were performed using a pump-probe Nd:YAG laser system (Continuum, Surelite I; duration: 6 ns) equipped with custom-built spectrometers.^{31,32} The TA spectra were obtained by scanning with probe energy from 17 000 to 1200 cm⁻¹ (0.15–2.1 eV). Photoexcited carriers in the mid-infrared (IR) region (6000–1200 cm⁻¹) were probed using an IR beam emitted by a MoSi₂ coil that was applied to a film sample. The transmitted IR beam was then passed through a monochromatic grating spectrometer and to a mercury-cadmium-telluride detector (Kolmar). Photocarriers in the visible to near-IR region (17 000–6000 cm⁻¹) were analyzed using a probe beam generated from a halogen lamp that was focused on the sample. Reflected light from the sample entered the grating spectrometer and was sent to a Si photodetector. The output electric signal was processed using an alternating current coupled amplifier (Stanford Research Systems, SR560, bandwidth: 1 MHz), and the time resolution of the spectrometer was limited to 1 μs by the bandwidth of the amplifier. The transient decay profile for photoexcited free electrons was captured by monitoring the absorption signal at 2000 cm⁻¹ (5000 nm). The bandgap excitation of photocarriers in BaTaO₂N was assessed using 470 nm laser pulses (fluence: 1 mJ per pulse) at a frequency of 1 Hz. In preparation for these analyses, a portion of the BaTaO₂N powder was dispersed in water, drop-cast onto a CaF₂ substrate, and dried naturally in air overnight to obtain a powder film with a density of approximately 1.1 mg cm⁻². Analyses were carried out in a N₂ atmosphere at room temperature.

Apparent quantum yield

The AQY for one step photoexcitation overall water splitting was obtained from trials under illumination of a 300 W Xe lamp (Asahi Spectra, MAX-303) using a bandpass filter with a full width at half maximum of 15 nm. The center wavelength was varied from 400 to 480 nm in intervals of 20 nm and the number of incident photons was monitored using a diffraction grating spectroradiometer (EKO Instr. Co., LS-100). The AQY value was calculated as

$$\text{AQY (\%)} = [2 \times N(\text{H}_2)]/N(\text{photon}) \times 100,$$

where $N(\text{H}_2)$ and $N(\text{photon})$ are the number of H₂ molecules evolved and incident photons, respectively.

Solar-to-hydrogen (STH) energy conversion efficiency

Water splitting reactions were conducted under simulated sunlight generated using a solar simulator (Sanei Electric Co., XES-40S1). The STH values were calculated as

$$\text{STG (\%)} = (R(\text{H}_2) \times \Delta G)/(I \times A) \times 100$$

where $R(\text{H}_2)$, ΔG , I and A are the rate of hydrogen evolution (the number of H₂ molecules h⁻¹) during the overall water splitting reaction, the Gibbs energy of the reaction producing gaseous hydrogen and oxygen from liquid water (237 kJ mol⁻¹ at 298 K), the energy intensity (80 mW cm⁻²) of the AM 1.5G solar



radiation employed (equivalent to 0.8 sun), and the illuminated sample area (38.5 cm²), respectively.

Conflicts of interest

There are no conflicts to declare.

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