

Experimental Section

Synthesis of oxide precursors.

Precursor oxides were prepared from Na_2CO_3 (99.8%, FUJIFILM Wako Pure Chemical Co.), BaCO_3 (99.9%, Kanto Chemical Co. Inc.), ZnO (99.0%, Kanto Chemicals Co., Inc.) and Ta_2O_5 (99.99% Rare Metallic Co., Ltd.) using NaCl (99.5%, FUJIFILM Wako Pure Chemical Co.) as a flux. The Na:Ba:Zn:Ta:NaCl molar ratio was adjusted to 1:3:1:3:80 and the starting materials were mixed with an alumina mortar for 30 min before being transferred to an alumina crucible. The mixture was subsequently heated in air to 1423 K with a temperature ramp of 10 K min^{-1} , held for 5 h, and then cooled at 10 K min^{-1} . The resulting sample was washed using distilled water to remove the flux, and then dried in a vacuum oven at 313 K overnight. This precursor oxide is denoted using the nominal composition $(\text{Na}_{1/4}\text{Ba}_{3/4})(\text{Zn}_{1/4}\text{Ta}_{3/4})\text{O}_3$ because of its highly complex structure and composition associated with the volatilization of constituent elements and the involvement of several solid solution systems incorporating multinary oxides. A precursor oxide having an excess of Ba was also prepared to compensate for the loss of Ba through volatilization, in which the Na:Ba:Zn:Ta:NaCl molar ratio in the starting mixture was 1:3.3:1:3:80. To examine the effect of incorporating Na and Zn species, precursor oxides to which less Na_2CO_3 and ZnO were added were also prepared, with Na:Ba:Zn:Ta:NaCl molar ratios of 1/3:3:1/3:3:80 and 2/3:3:2/3:3:80. Moreover, precursor oxides without the addition of Na_2CO_3 or ZnO and with the addition of either Na_2CO_3 or ZnO were also prepared. The Na:Ba:Zn:Ta:NaCl molar ratios in the starting mixtures for these materials were adjusted to 0:3:0:3:80, 1:3:0:3:80 and 0:3:1:3:80. The resulting precursor oxides were denoted as BaTaO_x , $\text{Na}_{1/4}\text{Ba}_{3/4}\text{Ta}_{3/4}\text{O}_x$ and $\text{Ba}_{3/4}\text{Zn}_{1/4}\text{Ta}_{3/4}\text{O}_x$, respectively, based on the nominal compositions of the starting materials.

Nitridation of precursor oxides.

Additional BaCO₃ equal to 10% of the initial BaCO₃ amount was added to the precursor oxides to compensate for the volatilization loss of Ba. The mixture was then combined with NaCl (using the same mass as that of the precursor oxide) as a flux and loaded into an alumina boat. The sample was subsequently heated in a tubular furnace to a temperature in the range of 1123–1273 K, applying a temperature ramp of 10 K min⁻¹, and held at the target temperature for 30 h under an NH₃ flow (250 mL min⁻¹) to yield BaTaO₂N. After the tubular furnace was cooled, residual NH₃ was purged with a flow of N₂. (Na_{1/4}Ba_{3/4})(Zn_{1/4}Ta_{3/4})O₃ blended with BaCO₃ and NaCl and nitrided at 1223 K produced BaTaO₂N photocatalyst samples having the highest oxygen evolution activity. For comparison purposes, physical mixtures of Na₂CO₃, BaCO₃, ZnO, Ta₂O₅ and NaCl combined to give Na:Ba:Zn:Ta:NaCl molar ratios of 1:3.3:1:3:80 and 1:3.45:1:3:80 were also nitrided.

Characterization of the materials.

The samples were characterized by powder X-ray diffraction (XRD; MiniFlex300 and RINT-Ultima-III, Rigaku) using Cu-K α radiation and UV-visible diffuse-reflectance spectroscopy (DRS; V-670, JASCO). The morphology of particles was investigated by scanning electron microscopy (SEM; JSM7600F, JEOL). The proportions of Na, Ba, Zn and Ta in the precursor oxides and the nitrided samples were analysed by inductively-coupled plasma optical emission spectroscopy (ICP-OES; ICPS-8100, Shimadzu). In each analysis, a powdered sample (10 mg) was combined with 0.75 g K₂CO₃ and 0.25 g H₃BO₃ and heated to the melting point in a platinum crucible. The resulting salt was then dissolved by adding 10 mL of a 5 wt% aqueous

citrate solution, 4 mL of a hydrochloric acid solution (diluted 1:1) and 1 mL of a 30 wt% aqueous hydrogen peroxide solution. Ultrapure water was subsequently added to give a total volume of 100 mL.

Loading of a cobalt oxide co-catalyst.

The BaTaO₂N samples were modified with cobalt oxide (CoO_x) as an oxygen evolution cocatalyst via impregnation and heating under an N₂ flow. In this process, a portion of the BaTaO₂N powder was suspended in an aqueous solution of Co(NO)₃·6H₂O (99.95%, Kanto Chemicals Co., Inc.). The concentration of the solution was designed to give a CoO_x loading of 2 wt% as Co with respect to the photocatalyst. The photocatalyst suspension was then placed on a water bath with constant stirring until it reached complete dryness, after which the powder was transferred to an alumina boat and heated at 1223 K for 1 h under a N₂ flow of 250 mL min⁻¹. This process produced tiny amounts of impurities, possibly attributable to BaTa₂O₆, Ta₂O₅, and Ba₂TaO₃N,^{7,12} but preserved the BaTaO₂N structure as shown in the XRD patterns (Figure S6) and allowed to form intimate contact between BaTaO₂N and CoO_x.

Photocatalytic oxygen evolution reaction.

Photocatalytic oxygen evolution reactions were carried out in a top-irradiation reaction vessel connected to a closed gas circulation system made of Pyrex glass. In each trial, a photocatalyst sample loaded with the CoO_x cocatalyst (0.20 g) was suspended in 120 mL of distilled water containing 10 mmol AgNO₃ (99.9%, FUJIFILM Wako Pure Chemical Co.) as a sacrificial electron acceptor and 0.10 g La₂O₃ (99.9%, High Purity Chemicals) as a pH buffer. The suspension in the reactor was degassed by evacuation to completely remove dissolved air, after

which Ar gas (7 kPa) was introduced to the reaction system as a circulation gas. A 300 W Xe lamp equipped with a dichroic mirror and cut-off filter (Hoya, L42) was used to provide visible light ($420 \text{ nm} < \lambda < 800 \text{ nm}$) from the top of the reactor. The reaction solution was maintained at 288 K with a constant flow of cooling water throughout the reaction. The gas evolved during the illumination was analysed with a gas chromatograph equipped with 5 Å molecular sieve columns and a thermal conductivity detector (Shimadzu, GC-8A), using Ar as the carrier gas. In this reaction, the oxygen evolution rate decreases with time because of deposition of Ag on the surface of the photocatalyst sample. Therefore, the activity was evaluated based on the oxygen evolution rate in the initial one hour.

Measurements of apparent quantum yields.

Apparent quantum yields (AQYs) were determined by performing the photocatalytic oxygen evolution reaction under the same conditions as described above, except that band-pass filters ($\lambda = 420, 500, 600$ and 640 nm) were attached in place of a cut-off filter to provide monochromatic irradiation. AQYs for the oxygen evolution reaction were calculated based on the formula:

$$\text{AQY} = [4 \times n(\text{O}_2)] / n(\text{photons}),$$

where $n(\text{O}_2)$ and $n(\text{photons})$ are the number of oxygen molecules generated and the number of photons received by the reactor over a given time span. The photon flux was measured with a spectroradiometer (LS-100, EKO Instruments).

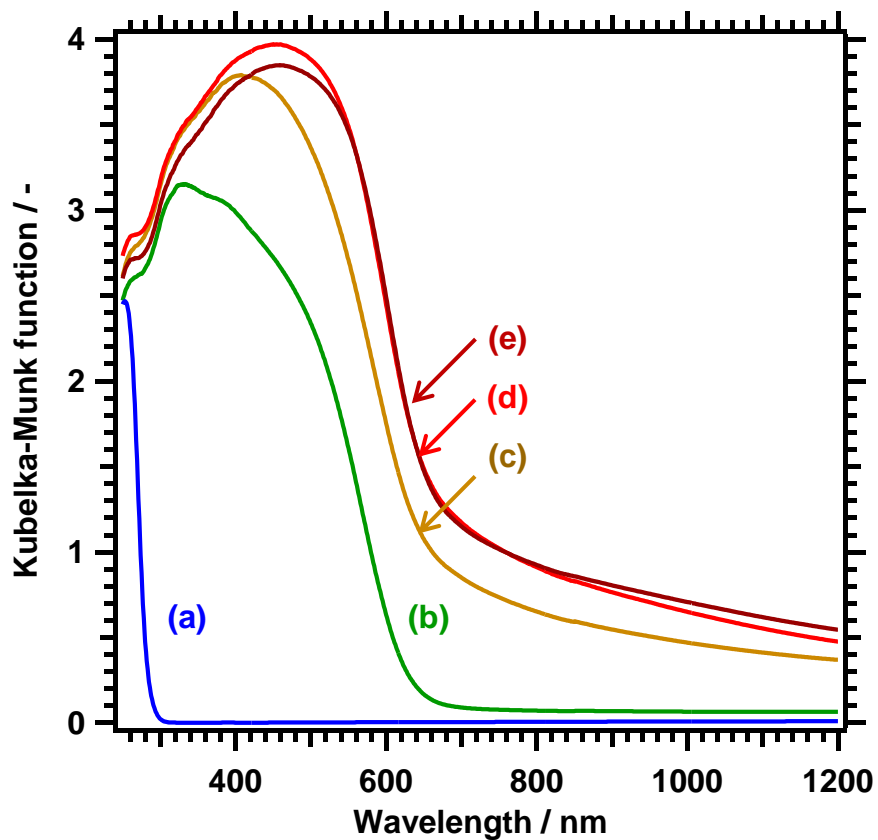


Figure S1. DRS data for (a) $(\text{Na}_{1/4}\text{Ba}_{3/4})(\text{Zn}_{1/4}\text{Ta}_{3/4})\text{O}_3$ and (b-e) BaTaO_2N samples obtained from nitriding $(\text{Na}_{1/4}\text{Ba}_{3/4})(\text{Zn}_{1/4}\text{Ta}_{3/4})\text{O}_3$ blended with BaCO_3 and NaCl at (b) 1123, (c) 1173, (d) 1223, and (e) 1273 K.

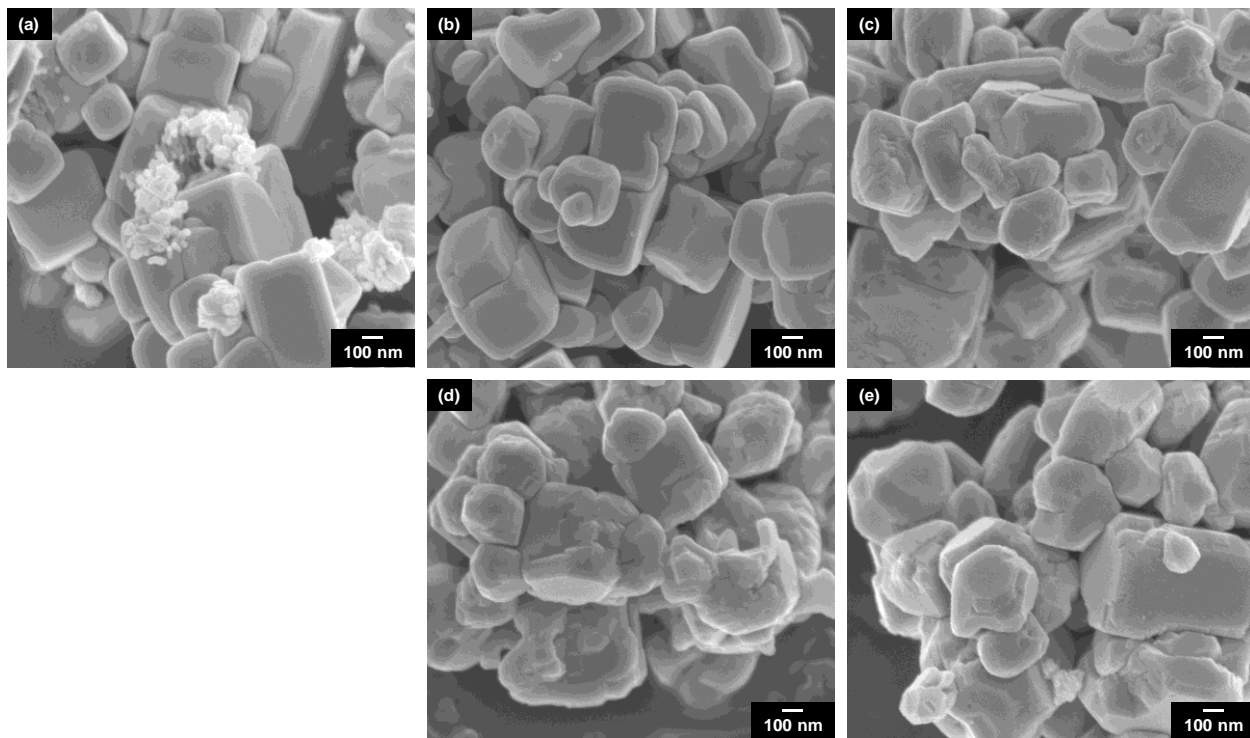


Figure S2. SEM images of (a) $(\text{Na}_{1/4}\text{Ba}_{3/4})(\text{Zn}_{1/4}\text{Ta}_{3/4})\text{O}_3$ and (b-e) BaTaO_2N samples obtained from nitriding $(\text{Na}_{1/4}\text{Ba}_{3/4})(\text{Zn}_{1/4}\text{Ta}_{3/4})\text{O}_3$ blended with BaCO_3 and NaCl at (b) 1123, (c) 1173, (d) 1223, and (e) 1273 K.

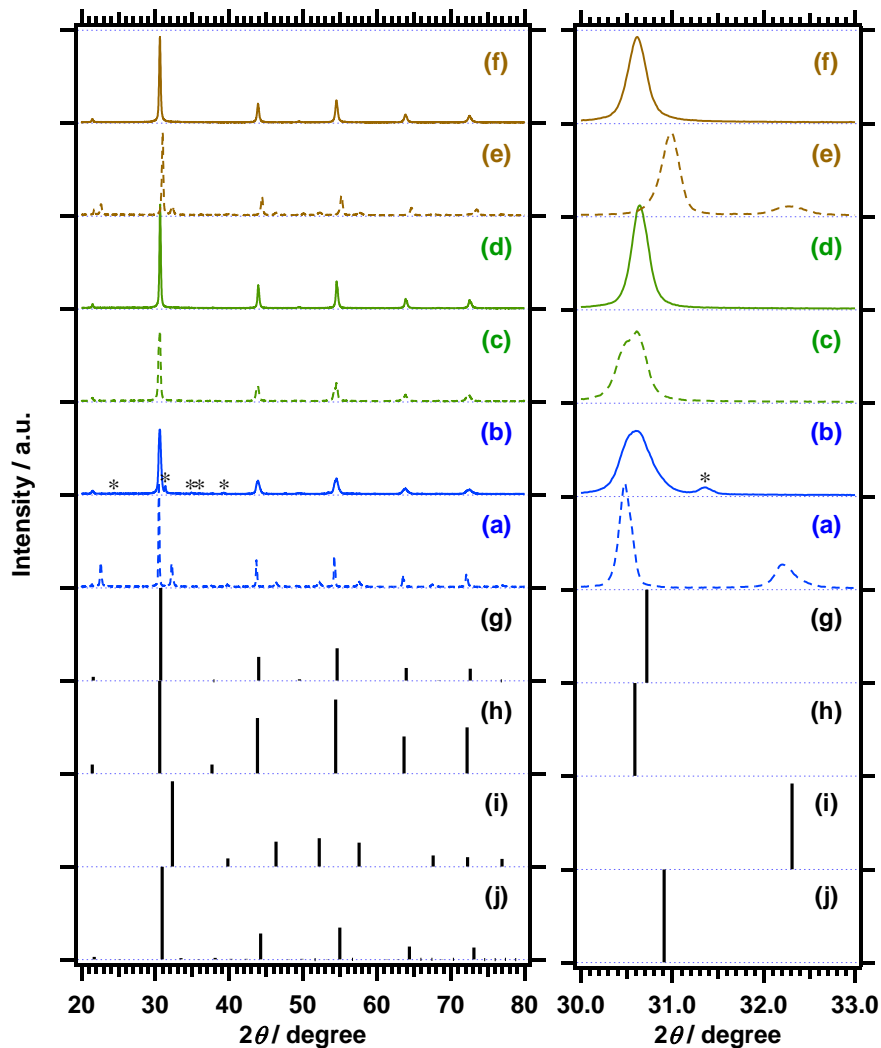


Figure S3. XRD patterns for (a) BaTaO_x , (b) BaTaO_2N obtained from nitriding BaTaO_x , (c) NaBaTaO_x , (d) BaTaO_2N obtained from nitriding NaBaTaO_x , (e) BaZnTaO_x , and (f) BaTaO_2N obtained from nitriding BaZnTaO_x , along with reference XRD patterns for (g) BaTaO_2N , (h) $\text{Ba}(\text{Na}_{1/4}\text{Ta}_{3/4})\text{O}_3$, (i) NaTaO_3 , and (j) $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$. The precursor oxides were blended with BaCO_3 and NaCl and nitrided at 1223 K. The peaks indicated by an asterisk (*) are attributed to a Ta_3N_5 phase.

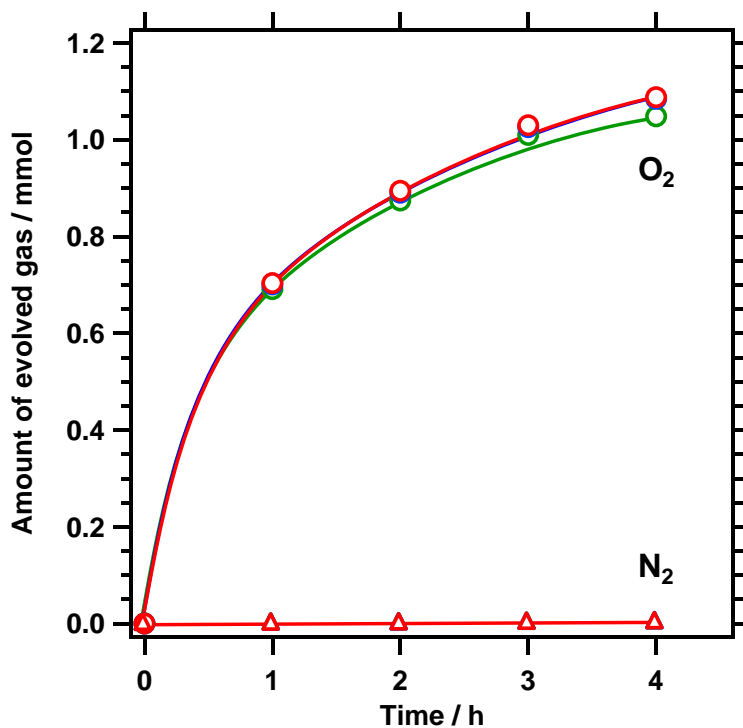


Figure S4. Time courses of gas evolution during the oxygen evolution reaction using BaTaO₂N nitrated from (Na_{1/4}Ba_{3/4})(Zn_{1/4}Ta_{3/4})O₃ blended with BaCO₃ and NaCl at 1223 K. Circles and triangles represent oxygen and nitrogen, respectively. The reactions were carried out three times, and Sample 1, 2, and 3 are depicted in red, blue, and green markers, respectively. The oxygen and nitrogen evolution rates were $699 \pm 13 \mu\text{mol h}^{-1}$ and below $1 \mu\text{mol h}^{-1}$. Reaction conditions: photocatalyst, 0.2 g CoO_x-loaded BaTaO₂N; reaction solution, 120 mL distilled water containing 10 mmol AgNO₃ and 0.10 g La₂O₃; reaction temperature, 288 K; light source, 300 W Xe lamp ($420 \text{ nm} < \lambda < 800 \text{ nm}$).

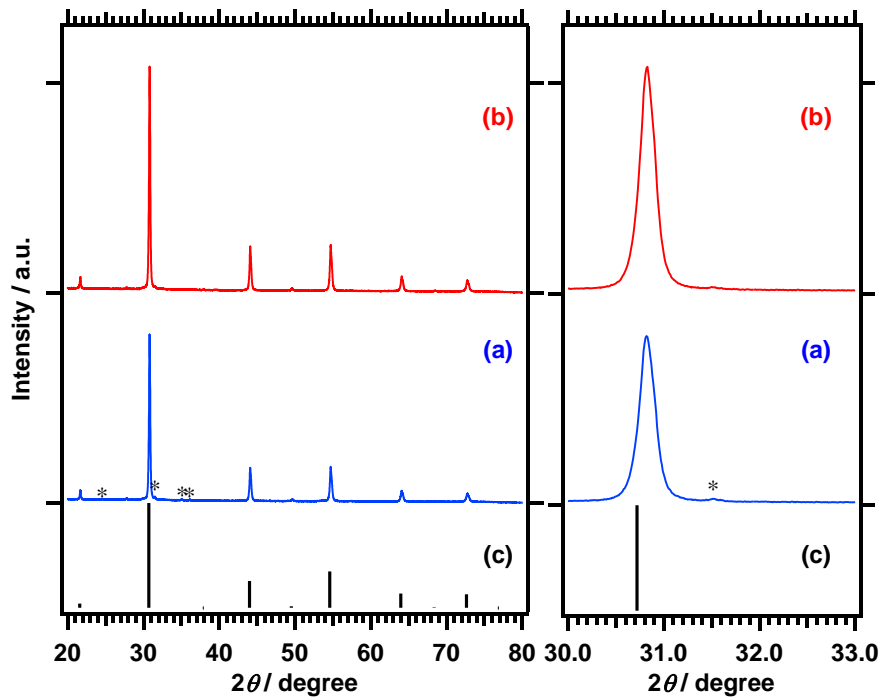


Figure S5. XRD patterns for nitridation products obtained from physical mixtures of Na_2CO_3 , BaCO_3 , ZnO , Ta_2O_5 and NaCl at Na:Ba:Zn:Ta:NaCl molar ratios of (a) 1:3.3:1:3:80 and (b) 1:3.45:1:3:80, along with (c) reference XRD pattern for BaTaO_2N . The precursor mixtures were nitrided at 1173 K. The peaks indicated by an asterisk (*) are attributed to a Ta_3N_5 phase.

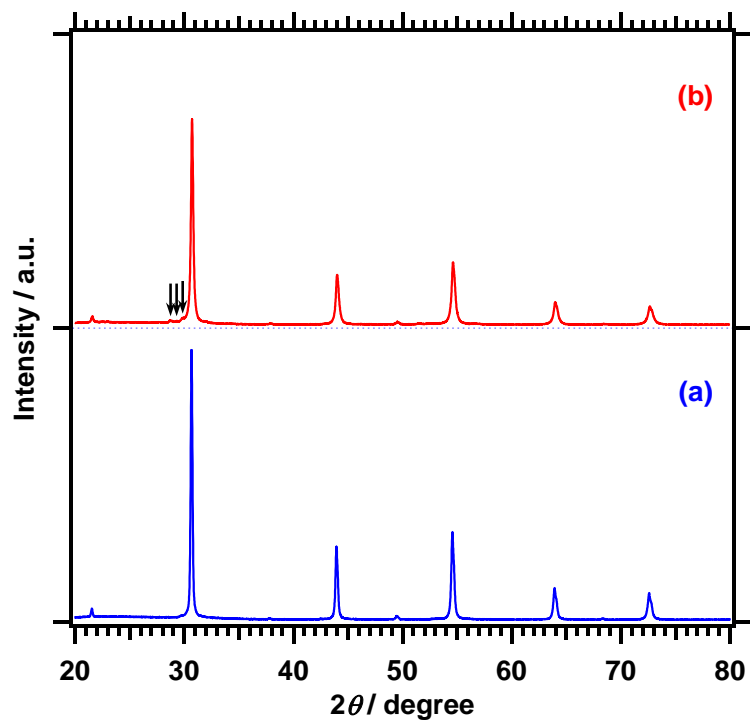


Figure S6. XRD patterns for BaTaO_2N derived from $(\text{Na}_{1/4}\text{Ba}_{3/4})(\text{Zn}_{1/4}\text{Ta}_{3/4})\text{O}_3$ (a) before and (b) after loading of 2 wt% CoO_x by heating under a N_2 flow. Arrows indicate peaks evolved during the CoO_x loading procedure.