

## Electronic Supplementary Information

### Experimental

BaNbO<sub>2</sub>N was prepared by nitriding Ba<sub>5</sub>Nb<sub>4</sub>O<sub>15</sub> under an NH<sub>3</sub> flow. Ba<sub>5</sub>Nb<sub>4</sub>O<sub>15</sub> was prepared by calcining a mixture of BaCO<sub>3</sub> (Kanto, 99.0%) and Nb<sub>2</sub>O<sub>5</sub> (Kanto, 99.95%), to which NaCl (Wako, 99.5%) was added as a flux. The sample was heated at 10 K min<sup>-1</sup> to 1173 K unless otherwise noted, held at the target temperature for 5 h, cooled to 1073 K at 0.5 K min<sup>-1</sup> and subsequently to 923 K at 1 K min<sup>-1</sup>. Finally, the sample was allowed to cool naturally and rinsed with copious amounts of distilled water three times to remove the NaCl flux. BaCO<sub>3</sub> was added to Ba<sub>5</sub>Nb<sub>4</sub>O<sub>15</sub> before nitridation to suppress the possible generation of niobium oxynitride as a by-product.<sup>1</sup> The precursor was nitrided at 1202 K for 15 h under an ammonia flow of 200 mL min<sup>-1</sup>. Excessive Ba species were generated upon conversion of the oxide precursor into BaNbO<sub>2</sub>N and were dissolved by aqua regia. A BaNbO<sub>2</sub>N sample was suspended for 15 s in aqua regia freshly prepared from nitric acid (Wako, 60 wt%) and hydrochloric acid (Wako, 35–37 wt%) at a volumetric ratio of 1:3. The suspension was immediately diluted with distilled water, filtrated, and rinsed with copious amounts of distilled water. The collected powder samples were analysed by X-ray powder diffraction (XRD; RINT-Ultima III, Rigaku; Cu K $\alpha$ ), UV-visible diffuse reflectance spectroscopy (DRS; V-670, JASCO), scanning electron microscopy (SEM; S-4700, Hitachi), and energy-dispersive X-ray spectroscopy (EDX; EMAX-7000, Horiba).

Prior to the photocatalytic reactions, BaNbO<sub>2</sub>N was modified with nanoparticles of CoO<sub>x</sub> or

Pt, which served as cocatalysts for oxygen and hydrogen evolution, respectively.  $\text{CoO}_x$  was loaded by impregnation from an aqueous  $\text{Co}(\text{NO}_3)_2$  solution followed by nitridation treatment at 773 K for 1 h under an  $\text{NH}_3$  flow ( $200 \text{ mL min}^{-1}$ ). Pt was loaded by impregnation from an aqueous  $\text{H}_2\text{PtCl}_6$  solution and subsequent hydrogen reduction treatment at 573 K for 1 h. Photocatalytic reactions were carried out using a closed-circulation system. Typically,  $\text{BaNbO}_2\text{N}$  powder (0.20 g) was suspended in 200 mL of 50 mM aqueous  $\text{AgNO}_3$  solution containing  $\text{La}_2\text{O}_3$  (0.20 g) as a pH buffer for oxygen evolution and 200 mL of 80 vol% aqueous methanol solution for hydrogen evolution. During the oxygen evolution reaction, pH of the solution becomes lower because  $\text{Ag}^+$  is reduced and  $\text{H}^+$  is released from  $\text{H}_2\text{O}$ .  $\text{La}_2\text{O}_3$  with weak basicity stabilized the pH of the reaction solution at around 8. Note that  $\text{La}_2\text{O}_3$  and  $\text{La}(\text{OH})_3$  do not absorb visible light or show photocatalytic activity under visible light. The reaction vessel was evacuated sufficiently to remove air before initiation of irradiation. The light source used was a 300 W Xe lamp equipped with cutoff filters (Hoya, L42 (cutoff wavelength = 410 nm), O560 (540 nm), R64 (620 nm), R70 (680 nm), R72 (700 nm), and IR76N (740 nm)). The cutoff wavelength was defined as the wavelength at which the transmittance fell to below 1%. Evolved gases were analysed by a gas chromatograph (Shimadzu, GC-8A, TCD, Ar carrier, MS5A column).

For measurements of the dependence of the  $\text{O}_2$  evolution rates on the cutoff wavelength of the incident light, an additional cutoff filter was inserted besides the L42 filter. The apparent quantum efficiency for water oxidation was measured under illumination monochromated with a

band pass filter (Asahi Spectra, PB0119, central wavelength: 640 nm, full width at half maximum: 60 nm). A L42 cutoff filter was also inserted to avoid possible transmission of shorter-wavelength photons. The apparent quantum efficiency was estimated using

$$\text{AQY (\%)} = A \cdot R / I \times 100$$

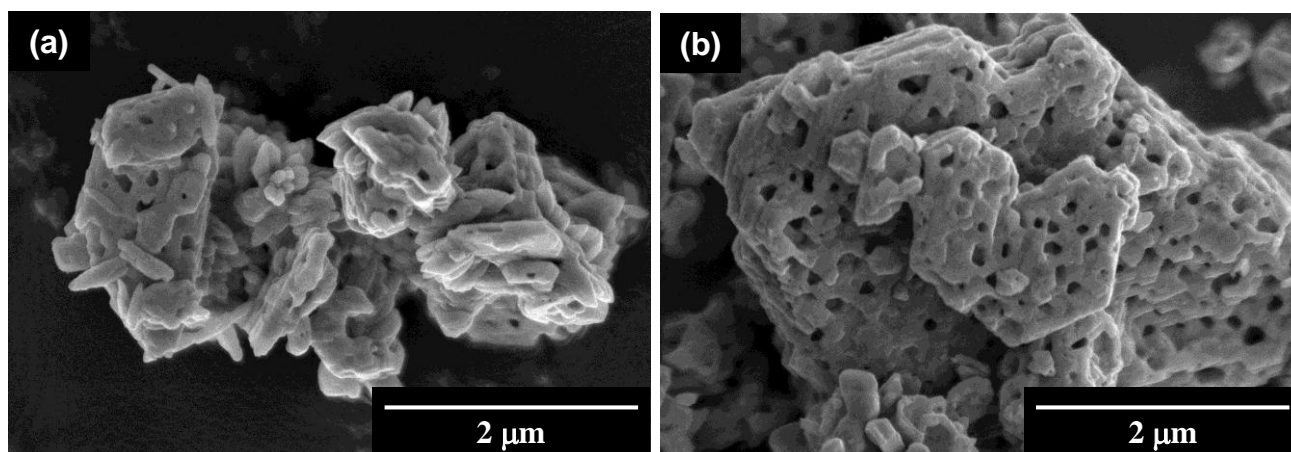
where  $A$ ,  $R$ , and  $I$  denote the number of electrons involved in oxygen evolution (four), the oxygen evolution rate, and the rate of incident photons, respectively. The power spectrum of incident photons was measured using a grating spectroradiometer (AM1.5G, EKO Instruments Co., Ltd., LS-100). The detector was placed at the level of the reaction solution and moved across the centre of the reactor. The total number of photons was calculated to be  $7.9 \times 10^{21}$  photon  $\text{h}^{-1}$  by integrating the intensity radially.

Photoanodes of  $\text{BaNbO}_2\text{N}$  decorated with  $\text{CoO}_x$  (2 wt%) were fabricated by the particle transfer method.<sup>2</sup>  $\text{CoO}_x/\text{BaNbO}_2\text{N}$  powder suspended in 2-propanol was dropped on a glass plate to pile up the photocatalyst powder. After the solvent was evaporated, thin layers of Nb and Ti were sputtered on the surface as contact and conductor layers, respectively, by radio-frequency (RF) magnetron sputtering at an Ar pressure of  $1 \times 10^{-1}$  Pa. The contact and conductor layers were deposited at an RF power of 200 W, at 573 K for 15 min and at 373 K for 3 h, respectively. The sputtered film was transferred onto another glass plate using adhesives and ultrasonicated sufficiently to remove photocatalyst particles loosely attached to the metal layers. Finally, an electrical contact was established between the metal layers and a conductive wire using In solder. The

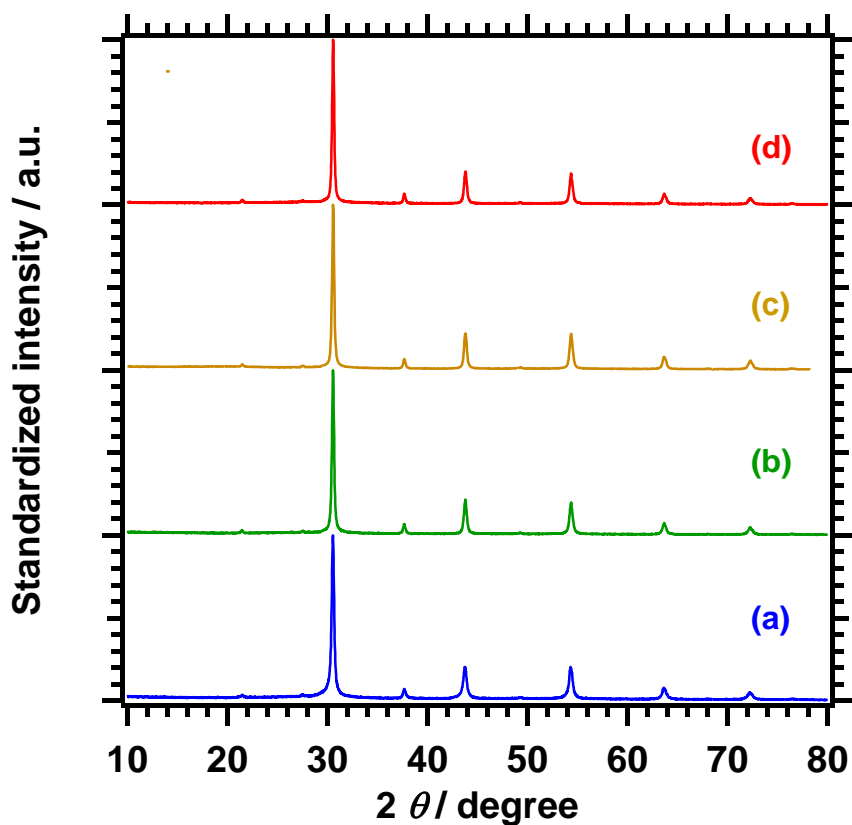
photoelectrochemical performance was measured in the three-electrode configuration under intermittent illumination from a solar simulator (SAN-EI ELECTRIC CO.,LTD., XES-40S1). A Pt wire and a Ag/AgCl electrode were used as counter and reference electrodes, respectively. The potential of the BaNbO<sub>2</sub>N photoanodes was swept at 10 mV s<sup>-1</sup>.

## References

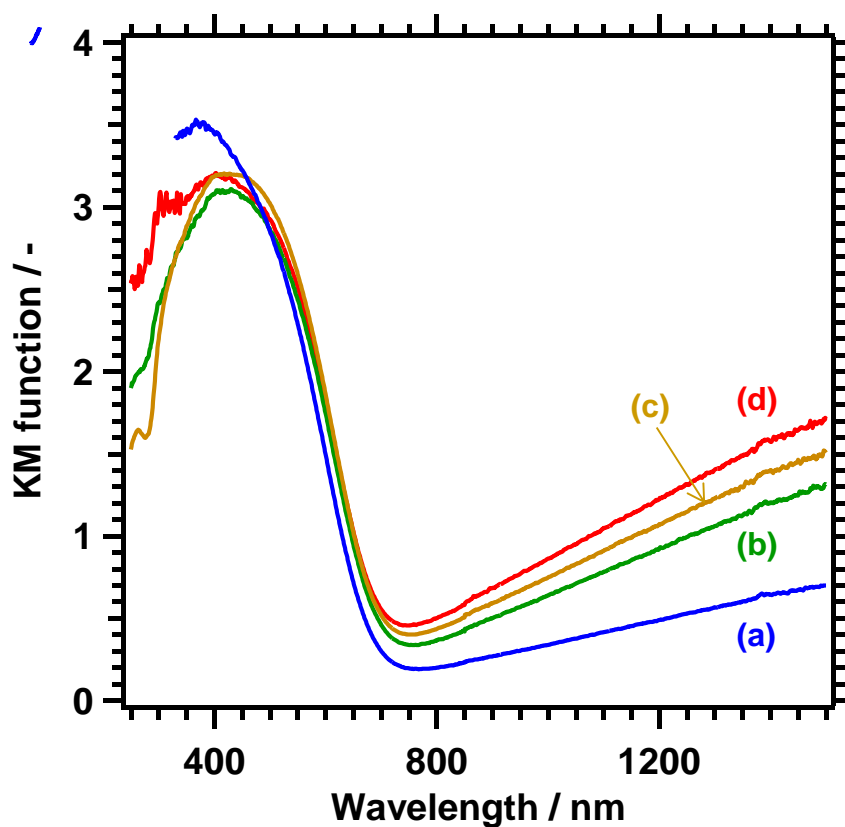
1. B. Siritanaratkul, K. Maeda, T. Hisatomi, and K. Domen, *ChemSusChem*, 2011, **4**, 74–78.
2. T. Minegishi, N. Nishimura, J. Kubota, and K. Domen, *Chem. Sci.*, 2013, **4**, 1120–1124.



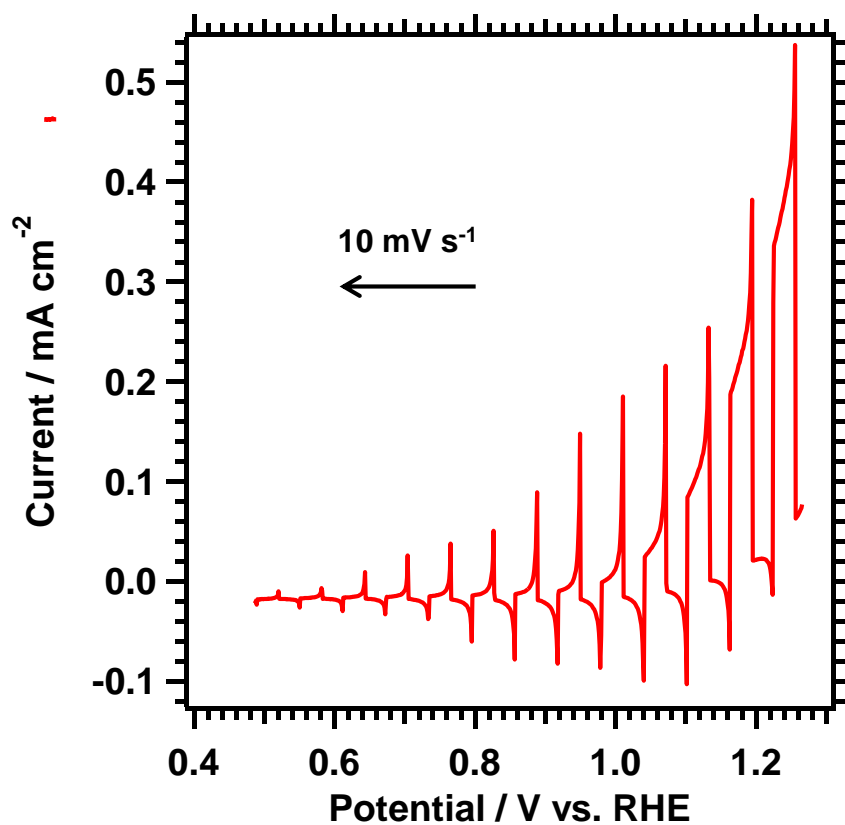
**Figure S1.** SEM images of BaNbO<sub>2</sub>N (a) before and (b) after a 15-second treatment with aqua regia. BaNbO<sub>2</sub>N was prepared at a Ba/Nb ratio of 2.00.



**Figure S2.** XRD patterns for aqua-regia-treated BaNbO<sub>2</sub>N, nitrided from Ba<sub>5</sub>Nb<sub>4</sub>O<sub>15</sub> mixed with various amounts of BaCO<sub>3</sub>. The Ba/Nb ratio during nitridation was (a) 1.25, (b) 1.50, (c) 1.75, and (d) 2.00.



**Figure S3.** UV-Vis diffuse reflectance spectra of aqua-regia-treated  $\text{BaNbO}_2\text{N}$  nitrided from  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  mixed with various amounts of  $\text{BaCO}_3$ . The Ba/Nb ratio during nitridation was (a) 1.25, (b) 1.50, (c) 1.75, and (d) 2.00.



**Figure S4.** Current-potential curve for 2 wt% CoO<sub>x</sub>/BaNbO<sub>2</sub>N photoanode prepared by the particle transfer method with a Nb contact layer and a Ti conductor layer. Light source, a solar simulator (SAN-EI ELECTRIC CO.,LTD., XES-40S1); electrolyte solution, 0.1 M aqueous NaOH solution (pH 13); scan rate, 10 mV s<sup>-1</sup>.