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Supporting Information

The Effects of Annealing Barium Niobium Oxynitride in Argon on Photoelectrochemical Water Oxidation Activity

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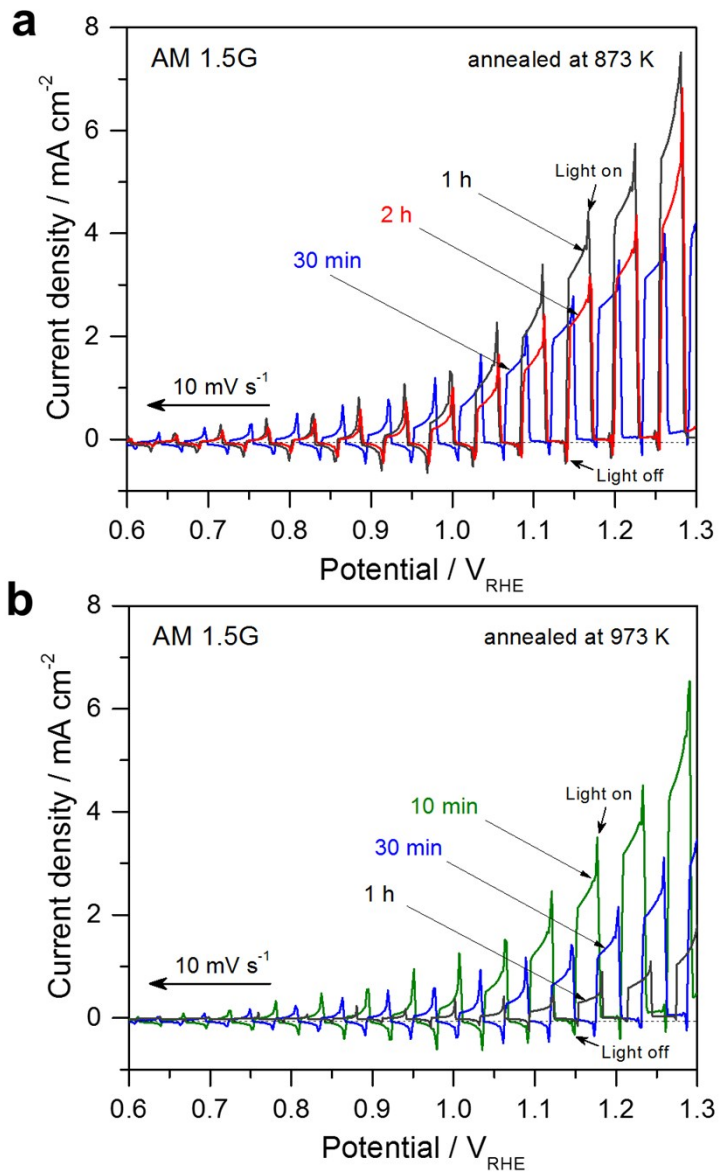

Figure S1. LSV data for $Co(OH)_x$-FeO_x/$BaNbO_2N$ photoanodes as-prepared by nitridation at 1123 K for 15 h and subsequent to annealing in an Ar flow at (a) 873 and (b) 973 K for annealing periods of 10, 30, 60 and 120 min, during PEC water oxidation under chopped AM 1.5G sunlight. The PEC measurements were performed by cathodically sweeping the potential from 0.6 to 1.3 V_{RHE} at a scan rate of 10 mV s^{-1} in a stirred Ar-saturated 0.5 M KBi aqueous electrolyte at pH 13.

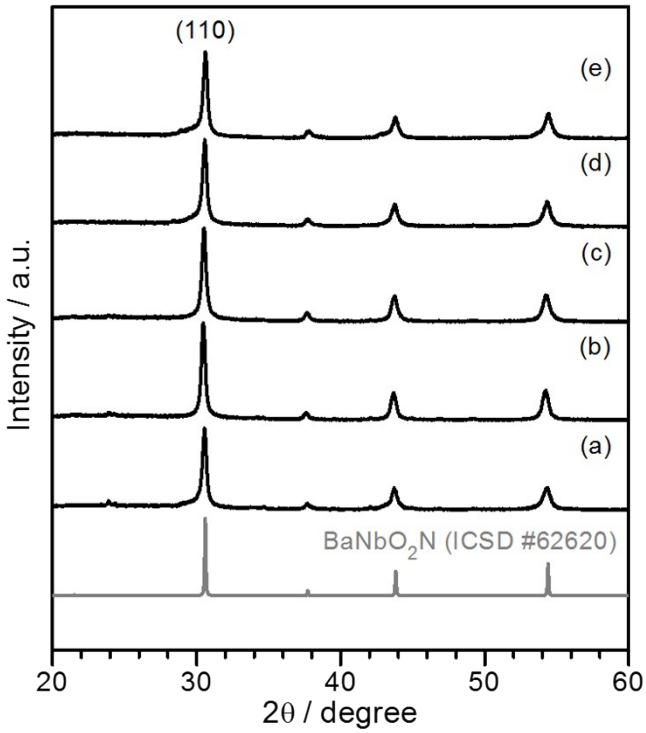

Figure S2. XRD patterns for $BaNbO_2N$ (a) as-prepared by nitridation at 1123 K for 15 h and subsequent to annealing in Ar atmosphere at (b) 773, (c) 873, (d) 973 and (e) 1073 K for 1 h. The full width at half maximum (FWHM) value of 0.34 for the (110) peak was identical for all the conditions, indicating that the bulk crystallinity of $BaNbO_2N$ was maintained after the annealing under Ar.

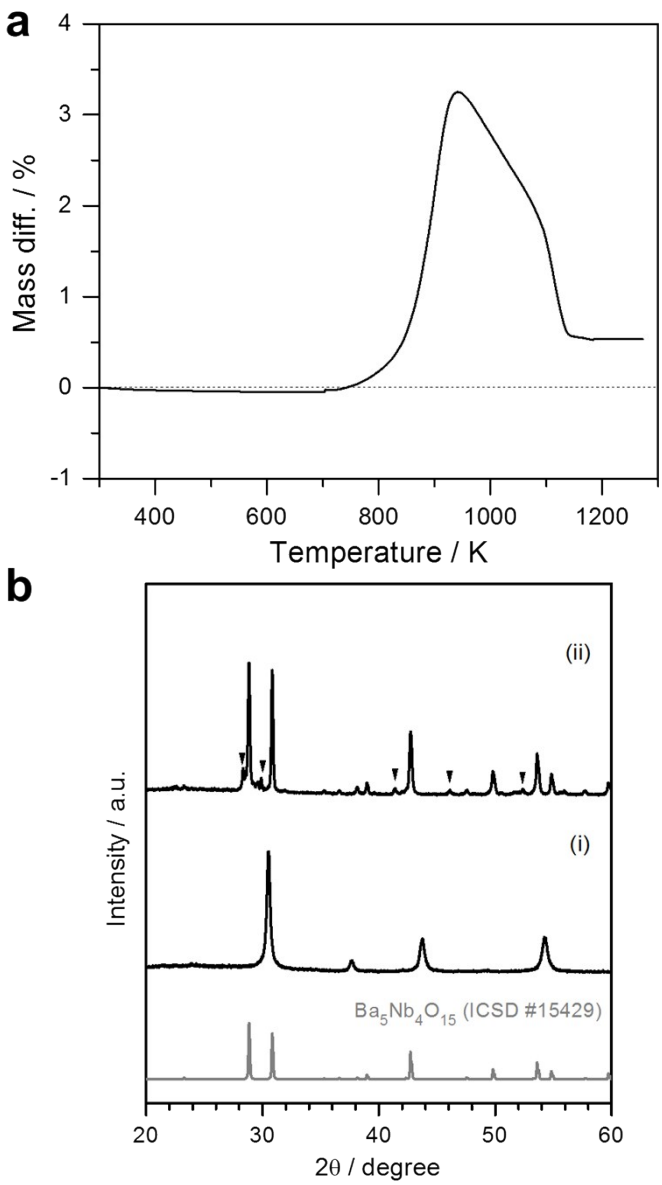

Figure S3. (a) TGA data for $BaNbO_2N$ powder under air flow at a ramp rate of 10 K min^{-1}. The oxynitride powder was prepared by nitridation at 1123 K for 15 h and subsequently annealed in Ar flow at 873 K for 1 h. (b) XRD patterns for (i) $BaNbO_2N$ and (ii) the corresponding powder oxidized after the TGA analysis from 298 to 1273 K in air. Inverted triangles indicate diffraction peaks assignable to Nb_2O_5 (PDF card No. 01-071-0005).

(Discussion) $Ba_{1.02}NbO_{2.79}N_{0.72}$, determined by the elementary analysis data in Table 1, was thermally oxidized in air flow. TGA data in Figure S3 (a) exhibits a typical oxidation trend of oxynitride, exhibiting a mass increase owing to the uptake of O along with the retention of N in the $Ba_{1.02}NbO_{2.79}N_{0.72}$ and a following mass decrease owing to the release of N_2. After the complete oxidation, the total mass of powder was increased approximately by 0.53%, which was consistent

with the expected value, 0.55% calculated by a reaction equation, $10Ba_{1.02}NbO_{2.79}N_{0.72} + 3.65O_2$ (*g*) → $2.04Ba_5Nb_4O_{15} + 0.92Nb_2O_5 + 3.6N_2$ (*g*) ↑. The powder oxidized from $Ba_{1.02}NbO_{2.79}N_{0.72}$ was identified as a mixture of $Ba_5Nb_4O_{15}$ and Nb_2O_5 by the XRD measurement shown in Figure 3S (b). This result demonstrates that the bulk O/N ratio of oxynitride determined by oxygen-nitrogen combustion analysis was accurate.

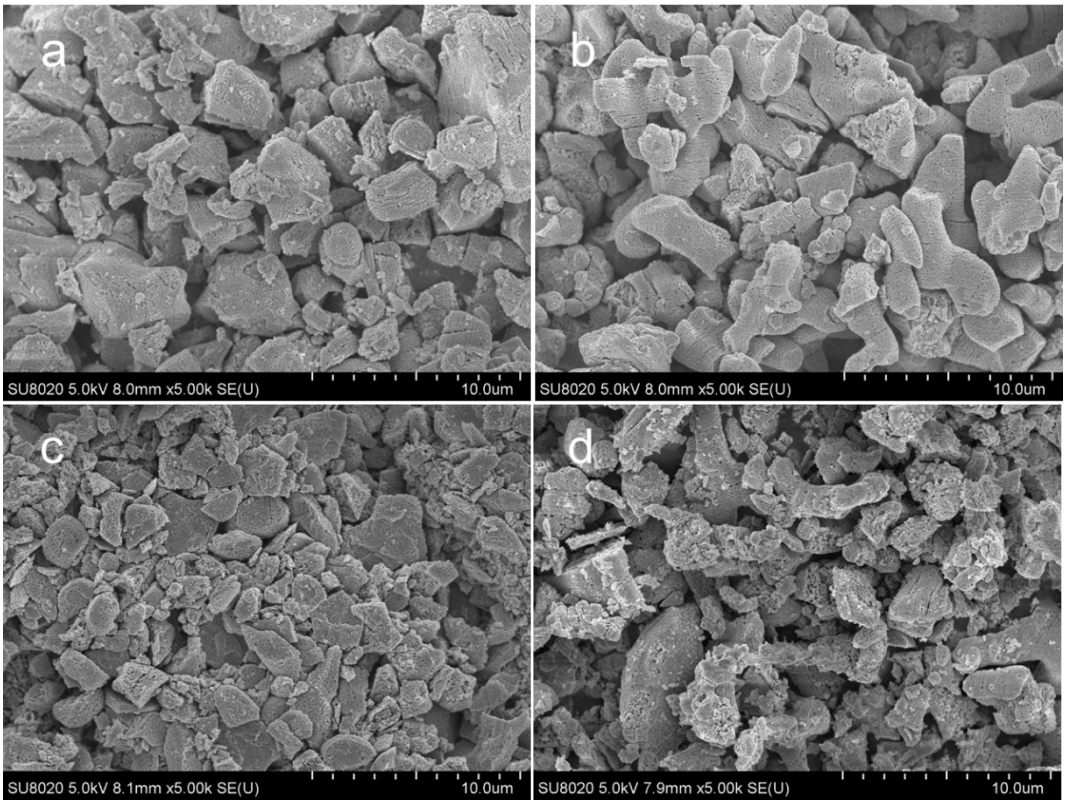

Figure S4. SEM images of $BaNbO_2N$ powder (a) as-prepared by nitridation at 1123 K for 15 h and subsequent to annealing in Ar atmosphere at (b) 873, (c) 973 and (d) 1073 K for 1 h.

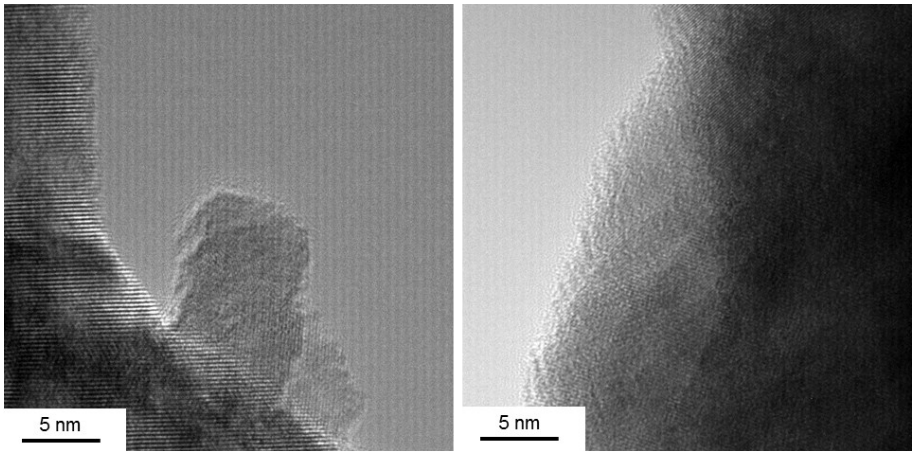

Figure S5. HRTEM images of a $BaNbO_2N$ particle as-prepared by nitridation at 1123 K for 15 h and subsequent to annealing in Ar atmosphere at 773 K for 1 h.

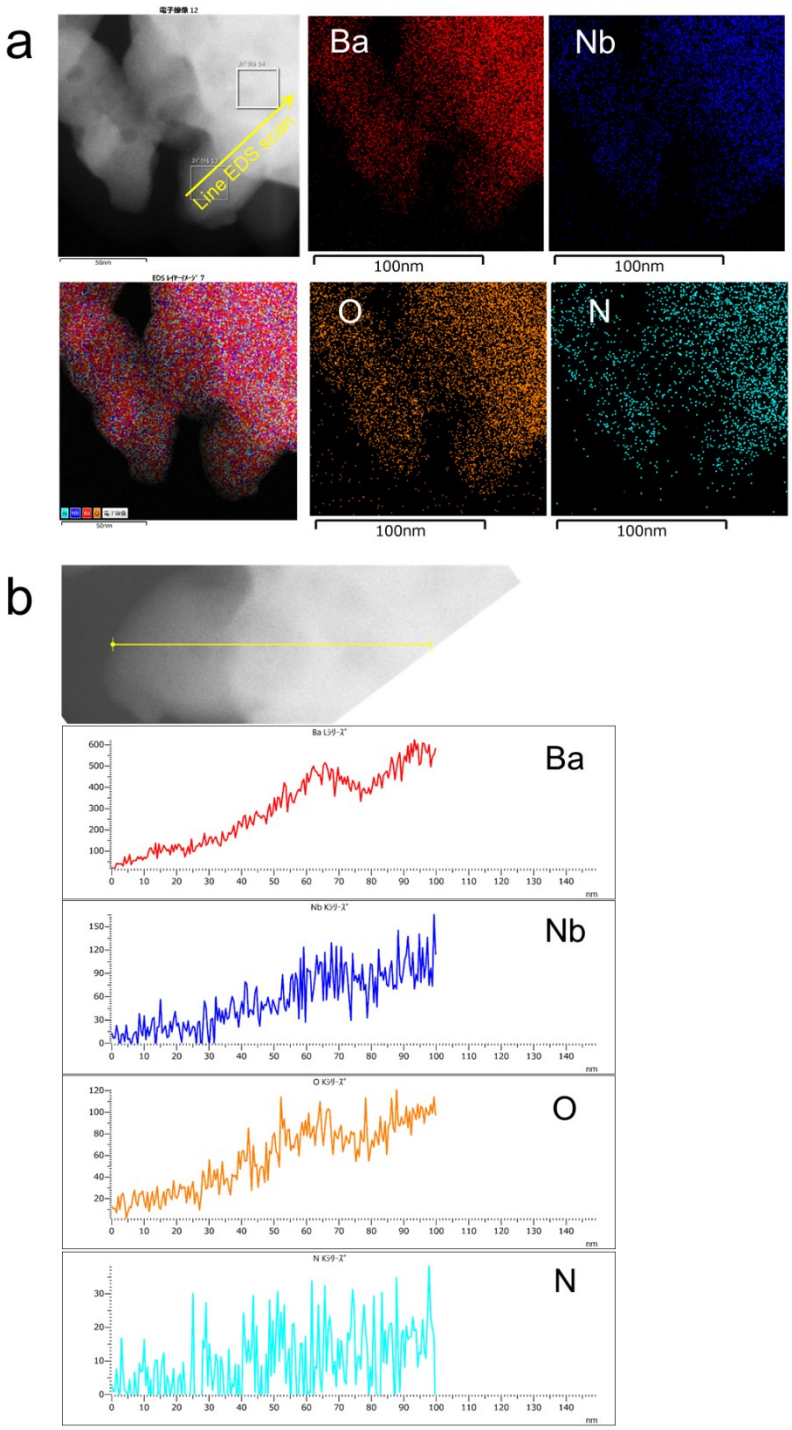

Figure S6. (a) STEM image and the corresponding EDS spectra of a $BaNbO_2N$ particle as-prepared by nitridation at 1123 K for 15 h and subsequent to annealing in Ar at 873 K for 1 h. (b) Line EDS spectra of Ba L-series, Nb K-series, O K-series and N K-series on the $BaNbO_2N$ particle. The scan direction of line EDS was shown in the STEM image of (a).

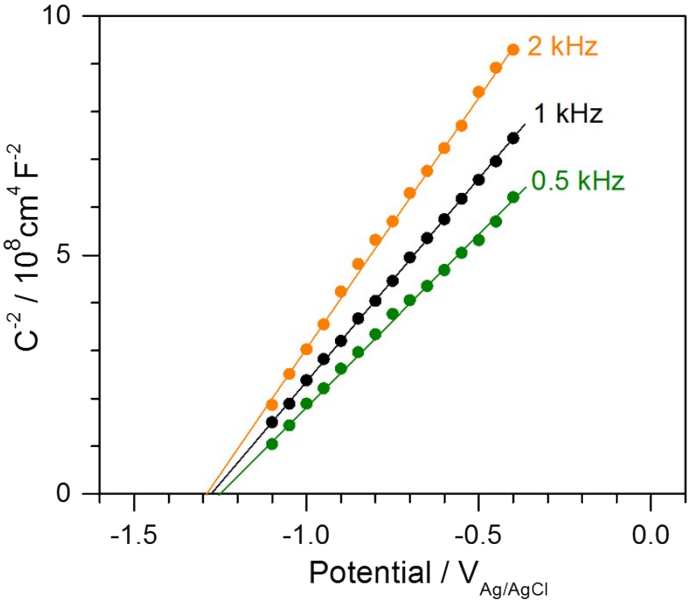

Figure S7. Mott-Schottky plots for bare $BaNbO_2N$ photoanodes at different frequencies such as 0.5, 1 and 2 kHz. $BaNbO_2N$ powder was prepared by nitridation at 1123 K for 15 h and subsequent to annealing in Ar at 873 K for 1 h. The measurements were performed in an Ar-saturated 0.5 M aqueous KBi electrolyte at pH 13 under dark conditions. The plots were recorded by cathodically sweeping the potential with an AC amplitude of 15 mV.