

SrNbO₂N as a Water-Splitting Photoanode with a Wide Visible Light Absorption Band

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Preparation of SrNbO₂N Particles

Oxide precursors were prepared by the polymerized complex method. In a typical synthesis, NbCl₅ (High Purity Chemicals, 99.9%) and SrCO₃ (Kanto Chemical, 99.9%) were dissolved in a stoichiometric ratio in methanol. Citric acid (Wako Pure Chemicals, 98.0%) and ethylene glycol (Kanto Chemical, 99.5%) were added, and the solution was kept at 473 K overnight to promote polymerization. After becoming a yellow resin, the mixture was pyrolyzed at 623 K, followed by calcination in air at 923 K and 1073 K for 2 h each, with intermediate grinding. The obtained white oxide powder was then nitrated under NH₃ flow (250 mL·min⁻¹) for 15 h at 1123 K. The production of SrNbO₂N was confirmed by X-ray diffraction analysis.

Preparation of SrNbO₂N/FTO Electrodes

The electrodes were prepared by electrophoretic deposition in an acetone solution (50 mL) containing SrNbO₂N powder (40 mg) and iodine (10 mg). Two parallel FTO electrodes were immersed in the solution with a 10–15 mm separation, and a 10 V bias was applied between the two for 3 min under potentiostat control. The SrNbO₂N-coated area was fixed at either 1 cm × 3 cm or ca. 1.5 cm × 4 cm. The as-prepared electrode was once calcined at 673 K for 0.5 h, dropped with 10 mM of NbCl₅ in methanol solution (25 μL for 1 × 3 cm² electrode; 50 μL for 1.5 × 4 cm² electrode), and then dried. After this procedure was repeated 6 times, the electrode was heated in NH₃ flow (20 mL·min⁻¹) at 753 K for 0.5 h.

Preparation of Colloidal IrO₂ and Adsorption

Colloidal IrO₂ was deposited on the surface of the prepared electrodes as a promoter for water oxidation. A colloidal IrO₂ aqueous solution was prepared by hydrolysis of Na₂IrCl₆.^{S1,2} 0.0080 g of Na₂IrCl₆ was dissolved in 50 mL H₂O, and the pH of the solution was adjusted to 11–12 with aqueous NaOH solution (1 M). The solution was heated at 353 K for 0.5 h, and then cooled to room temperature by immersion in an ice-water bath. The pH of the cooled solution was then adjusted slowly to 9 with aqueous HNO₃ solution. Subsequent heating at 353 K for 0.5 h resulted in a deep blue solution containing colloidal IrO₂, which was diluted to 50 mL in total volume.

The adsorption of the as-prepared colloidal IrO₂ was conducted by soaking the SrNbO₂N electrode in a diluted colloidal solution (ca. 15 vol.%) overnight, followed by rinsing with water prior to photoelectrochemical measurements.

Photoelectrochemical Measurements

Photoelectrochemical measurements were carried out with a potentiostat (HSV-110, Hokuto Denko) and an electrochemical cell at room temperature. The cell was made of Pyrex glass, and was a **three-electrode-type system** using **Pt wire** and an **Ag/AgCl electrode** as the counter and reference electrodes, respectively. **A Na₂SO₄ aqueous solution (pH ≈ 6)** was used as the electrolyte, which was saturated with argon gas prior to the electrochemical measurements. The light source was a xenon lamp (300 W) fitted with a cutoff filter to irradiate visible light ($\lambda > 420$ nm). The potential of the photoelectrode is reported against the reversible hydrogen electrode (RHE):

$$E_{\text{RHE}} = E_{\text{AgCl}} + 0.059 \text{ pH} + E^{\circ}_{\text{AgCl}} \quad (E^{\circ}_{\text{AgCl}} = 0.1976 \text{ V at 298 K})$$

Evolved H₂ and O₂ gasses were detected by on-line gas chromatography (Agilent MicroGC G3000 with TCD detector and MS-5A column, argon carrier gas). The experimental setup is schematically illustrated in Figure S1.

References

- S1. Harriman, A.; Pickering, I. J.; Thomas, J. M.; Christensen, P. A. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2795.
- S2. Le Paven-Thivet, C.; Ishikawa, A.; Ziani, A.; Le Gendre, L.; Yoshida, M.; Kubota, J.; Tessier, F.; Domen, K. *J. Phys. Chem. C* **2009**, *113*, 6156.

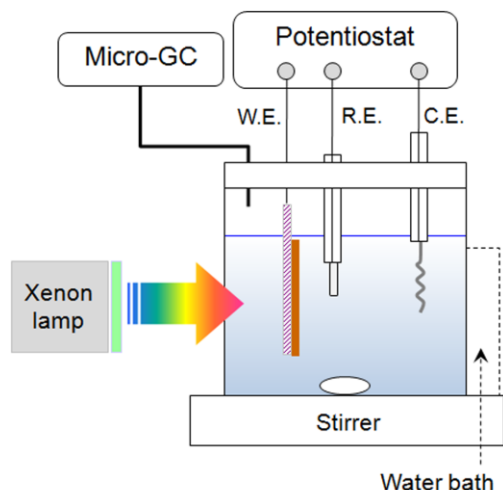


Figure S1. A schematic illustration of the experimental setup for photoelectrochemical water splitting and $\text{H}_2\text{-O}_2$ detection by a micro-GC.

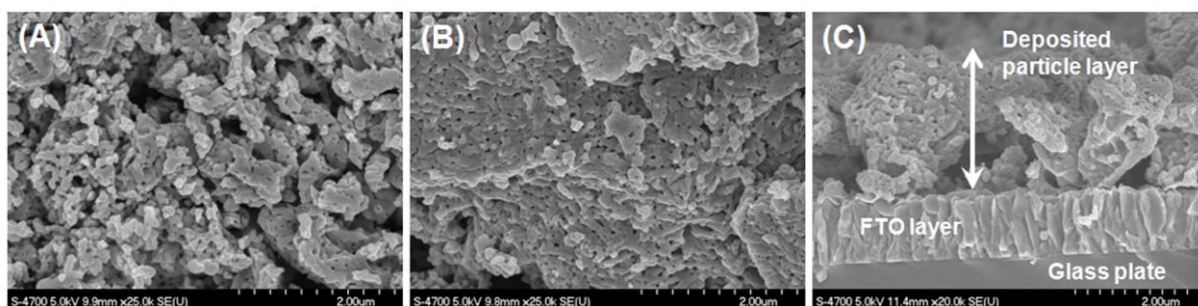


Figure S2. SEM images of $\text{SrNbO}_2\text{N}/\text{FTO}$ electrodes (A) before and (B) after post-necking treatment. (C) indicates the cross section image of (B).

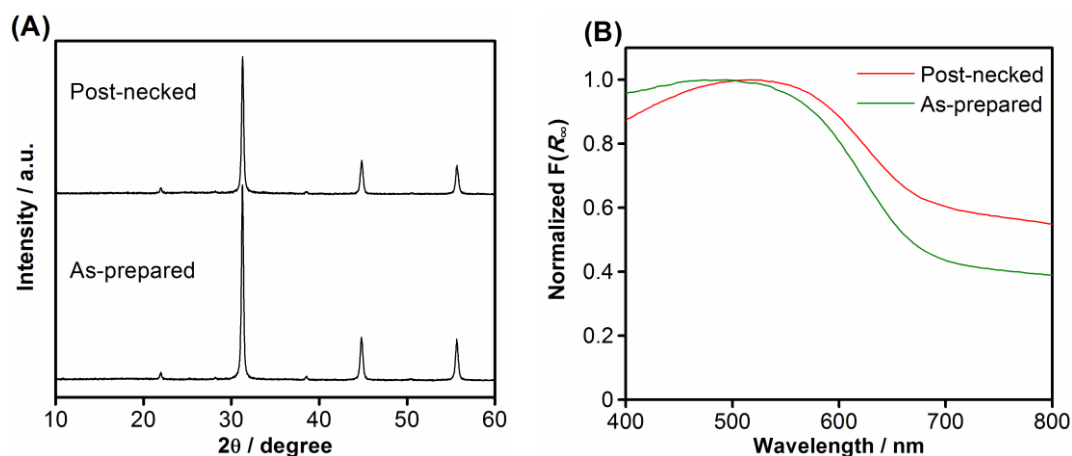


Figure S3. (A) XRD patterns and (B) DRS of SrNbO_2N powder before and after post-necking treatment.

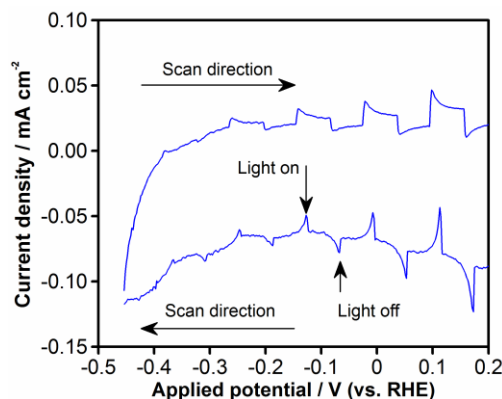


Figure S4. Cyclic voltammogram in aqueous 0.1 M Na_2SO_4 solution ($\text{pH} \approx 6$) under intermittent visible light irradiation ($\lambda > 420 \text{ nm}$) for IrO_2 -modified post-necked SrNbO_2N electrode (2.5 cm^2). Scan rate: $20 \text{ mV} \cdot \text{sec}^{-1}$.

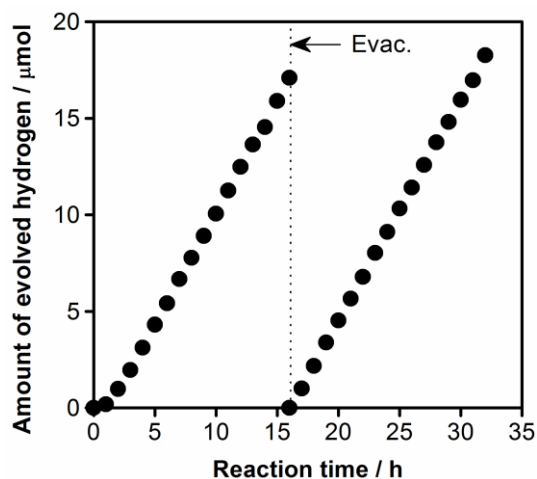


Figure S5. Time course of H_2 evolution from water containing methanol as an electron donor using 1.0 wt% Pt-loaded SrNbO_2N powder under $> 300 \text{ nm}$ irradiation. Reaction conditions: catalyst, 0.1 g; reactant solution, aqueous methanol solution (10 vol.%, 400 mL); light source, high-pressure mercury lamp (450 W); reaction vessel, inner-irradiation type.

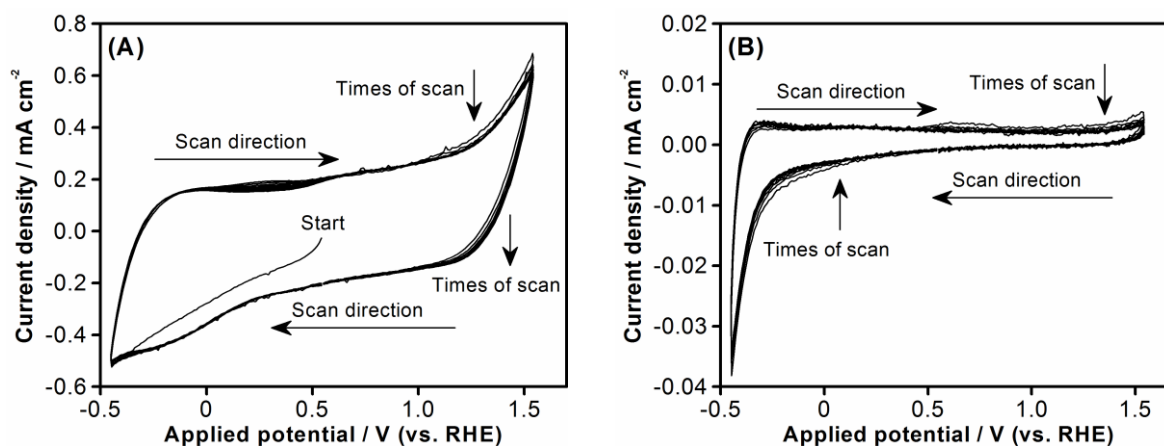


Figure S6. Cyclic voltammogram of (A) IrO_2 -modified post-necked and (B) the as-deposited $\text{SrNbO}_2\text{N}/\text{FTO}$ electrode in the dark condition. Scan rate: $100 \text{ mV} \cdot \text{sec}^{-1}$.

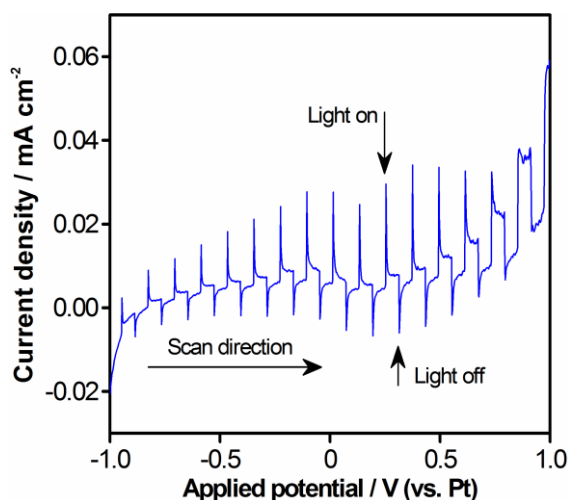


Figure S7. Current-voltage curve in aqueous 0.1 M Na₂SO₄ solution (pH ≈ 6) under intermittent visible light irradiation ($\lambda > 420$ nm) for IrO₂-modified post-necked SrNbO₂N electrode (2.5 cm²) in a two-electrode configuration with a Pt wire cathode. Scan rate: 20 mV·sec⁻¹.

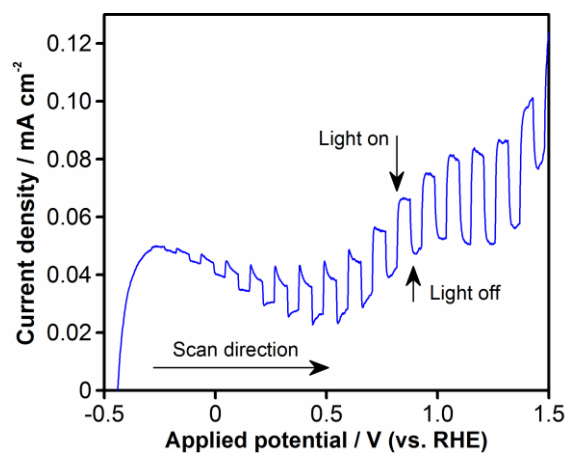


Figure S8. Current-voltage curve in aqueous 0.1 M Na₂SO₄ solution (pH ≈ 6) under intermittent AM1.5 irradiation for IrO₂-modified SrNbO₂N electrode. Scan rate: 20 mV·sec⁻¹.

Table S1. Surface atomic ratios of post-necked SrNbO₂N electrodes before and after photoelectrolysis for 120 min at +1.55 V vs. RHE under visible light ($\lambda > 420$ nm)

| Entry | Electrode | IrO ₂ loading | Surface atomic ratios ^a | | |
|-------|-----------|--------------------------|------------------------------------|------|-------|
| | | | Sr/Nb | N/Nb | Ir/Nb |
| 1 | Before | No | 0.20 | 0.52 | - |
| 2 | After | No | 0.19 | 0.12 | - |
| 3 | Before | Yes | 0.39 | 0.52 | 0.97 |
| 4 | After | Yes | 0.41 | 0.25 | 0.92 |

^a Estimated from the corresponding peak areas normalized by Nb peak.

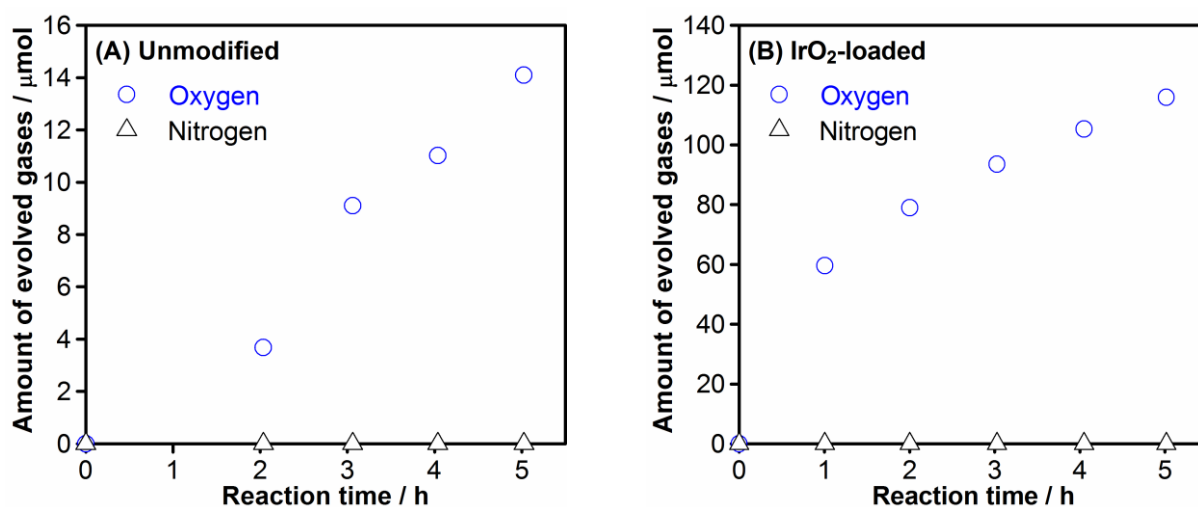


Figure S9. Time courses of O₂ evolution on (A) unmodified and (B) IrO₂-loaded SrNbO₂N under visible light ($\lambda > 420$ nm) from a silver nitrate solution. Reaction conditions: catalyst, 0.1 g (0.2 g La₂O₃ as a buffer); reactant solution, aqueous silver nitrate solution (0.01 M, 100 mL); light source, xenon lamp (300 W) with cutoff filter; reaction vessel, top-irradiation type. The rate of O₂ evolution (especially in IrO₂-loaded sample) decreased gradually with reaction time, due to the photodeposition of metallic Ag particles on the catalyst surface.

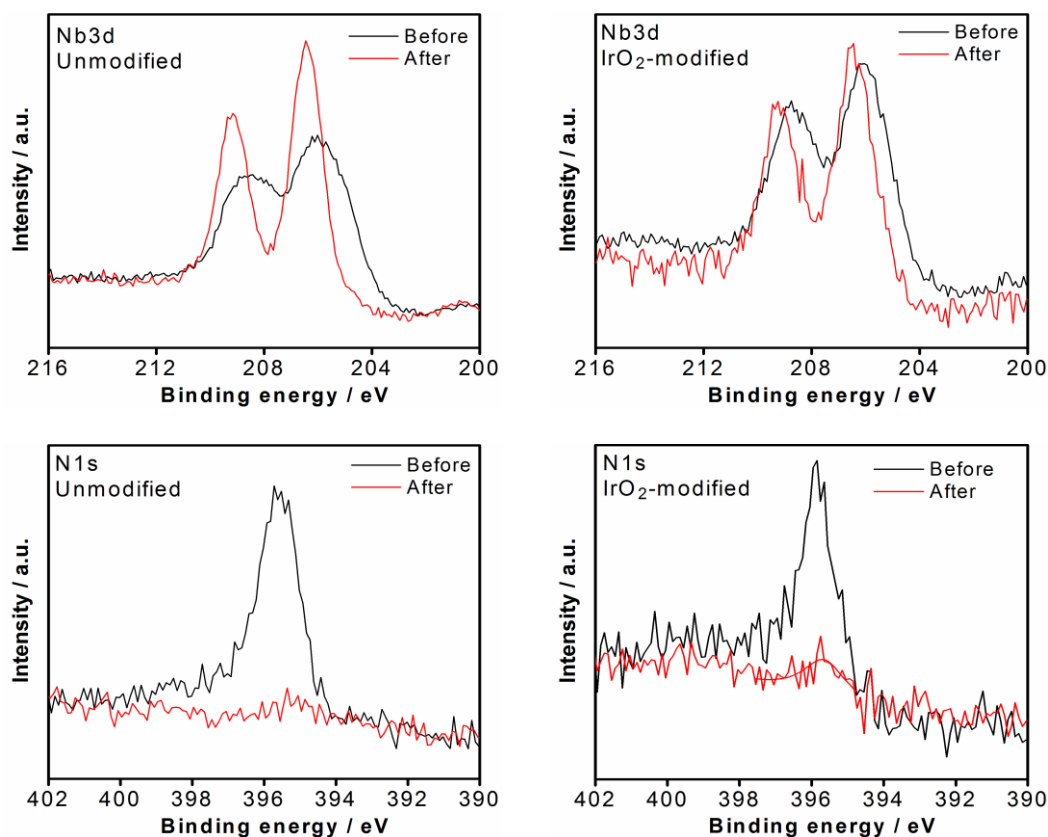


Figure S10. XPS spectra for Nb3d and N1s of post-necked SrNbO₂N electrodes with and without modifying IrO₂ colloids. The binding energies determined by XPS were corrected in reference to the Sn 3d peak (486.4 eV) derived from FTO for each sample.

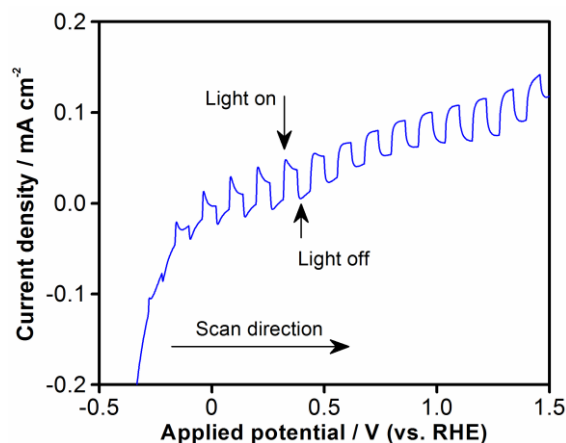


Figure S11. Current-voltage curve in aqueous 0.1 M Na_2SO_4 solution ($\text{pH} \approx 6$) under intermittent visible light irradiation ($\lambda > 420 \text{ nm}$) for IrO_2 -modified SrNbO_2N electrode that was in prior used for photoelectrolysis at 1.55 V vs. RHE for 120 min. Scan rate: $20 \text{ mV}\cdot\text{sec}^{-1}$.

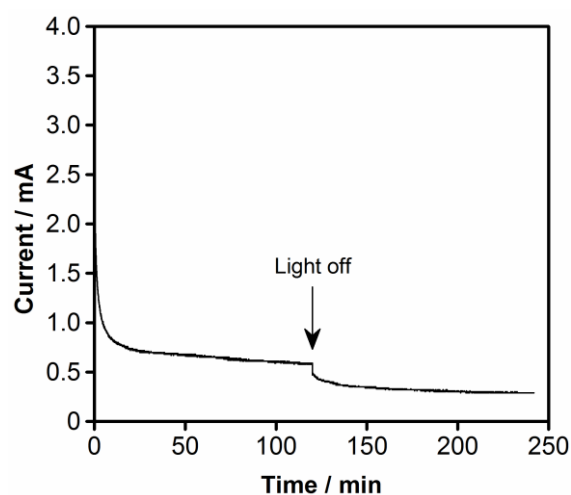


Figure S12. Current-time curve in aqueous 0.5 M Na_2SO_4 solution ($\text{pH} \approx 6$) for IrO_2 -modified post-necked SrNbO_2N electrodes (6 cm^2) at +1.55 V vs. RHE under visible light ($\lambda > 420 \text{ nm}$).

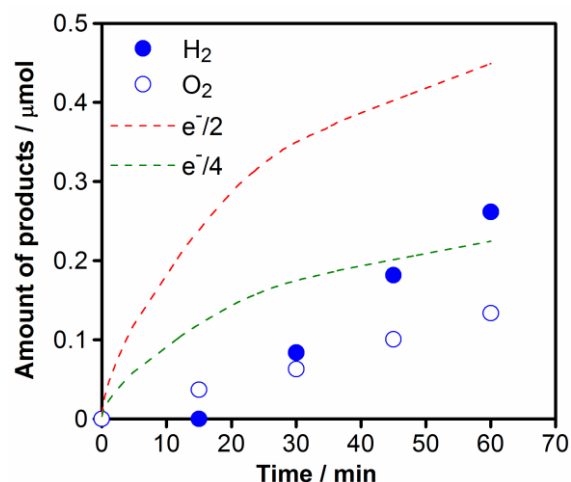


Figure S13. Time course of gas evolution in photoelectrochemical water splitting using post-necked SrNbO_2N electrodes (6 cm^2) modified with colloidal IrO_2 recorded at +1.0 V vs. RHE in aqueous 0.5 M Na_2SO_4 solution ($\text{pH} \approx 6$) under visible light ($\lambda > 420 \text{ nm}$).

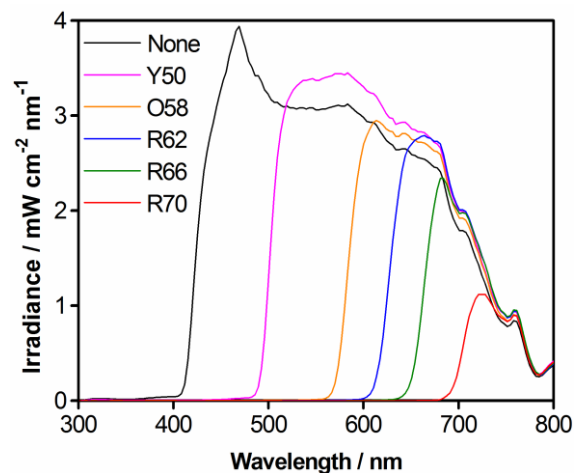


Figure S14. Spectral feature of a 300 W Xe lamp fitted with a CM-1 cold mirror and a L42 cutoff filter, further equipped with different cutoff filters of Y50, O58, R62, R66 and R70.

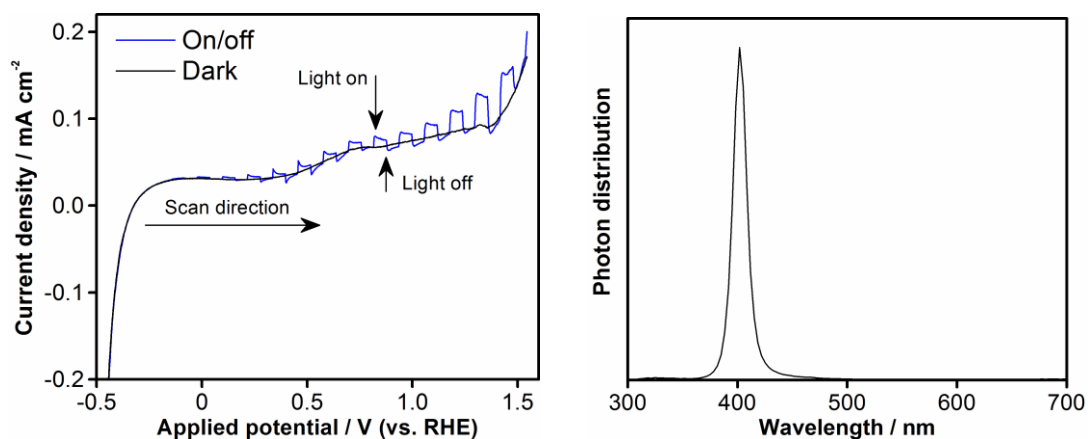


Figure S15. (Left) Current-voltage curves in aqueous 0.5 M Na_2SO_4 solution ($\text{pH} \approx 6$) under intermittent irradiation of monochromatized light ($\lambda = 400 \text{ nm}$, $12.4 \text{ mW}\cdot\text{cm}^{-2}$) for IrO_2 -modified SrNbO_2N electrodes (6 cm^2). Scan rate: $20 \text{ mV}\cdot\text{sec}^{-1}$. (Right) A spectrum of the light source used for the current-voltage measurement.