Supporting Information

Nitrogen-doped layered oxide $\text{Sr}_5\text{Ta}_4\text{O}_{15-x}\text{N}_x$ for water reduction and oxidation under visible light irradiation

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**Materials and Reagents**

For the preparation of \( \text{Sr}_5\text{Ta}_4\text{O}_{15-x}\text{N}_x \), \( \text{Ba}_5\text{Ta}_4\text{O}_{15-x}\text{N}_x \) and \( \text{Sr}_2\text{Ta}_2\text{O}_{7-x}\text{N}_x \), \( \text{TaCl}_5 \) (99.99%, Alfa Aesar), \( \text{SrCO}_3 \) (99.0%, Sinopharm Chemical), \( \text{BaCO}_3 \) (99.0%, Sinopharm Chemical), ethylene glycol (99.0%, Sinopharm Chemical), anhydrous citric acid (99.5%, Sinopharm Chemical) and \( \text{CH}_3\text{OH} \) (99.5%, Bodi Chemical) were used. \( \text{K}_2\text{IrCl}_6 \) (98.3%, Alfa Aesar), \( \text{Co(NO}_3)_2\cdot6\text{H}_2\text{O} \) (99.0%, Sinopharm Chemical) were employed as precursors of oxygen evolution cocatalysts and \( \left[\text{(NH}_4\right)_2\text{Pt}\left]\text{Cl}_6 \right) \) (98.8%, Alfa Aesar), \( \text{K}_2\text{IrCl}_6 \) (98.3%, Alfa Aesar) and \( \text{Na}_3\text{RhCl}_6\cdot12\text{H}_2\text{O} \) (99.8%, Alfa Aesar) were used as precursors of hydrogen evolution cocatalysts. \( \text{AgNO}_3 \) (99.9%, Alfa Aesar) and \( \text{CH}_3\text{OH} \) (99.5%, Bodi Chemical) were employed as sacrificial electron acceptor and donor, respectively. \( \text{La}_2\text{O}_3 \) (99.95%, Sinopharm Chemical) was applied as a buffer agent. All chemicals were used as-purchased without further purification.

**Preparation of \( \text{Sr}_5\text{Ta}_4\text{O}_{15} \)^{s1}\**

Typically, \( \text{TaCl}_5 \) was dissolved in methanol, and then anhydrous citric acid (CA) and ethylene glycol (EG) with the molar ratio of \( \text{Ta/CA/EG} = 1/15/60 \) were added. The reaction mixture was then mechanically stirred until it showed transparent, followed by addition of stoichiometric \( \text{SrCO}_3 \). Then it was further stirred and kept at 473 K for 5 h to promote polymerization to yield a polymeric gel. The obtained gel was pyrolyzed at 723 K for 4 h to form a powder precursor which was transferred into a muffle furnace for calcination at 1273 K in air for 60 h. The final product was well-crystalline white \( \text{Sr}_5\text{Ta}_4\text{O}_{15} \) powder.

**Deposition of \( \text{CoO}_x \)^{s2}\**

Typically, a calculated amount of cobalt nitrate aqueous solution (2 mL) was added to the aqueous suspension of \( \text{Sr}_5\text{Ta}_4\text{O}_{15-x}\text{N}_x \) (0.2 g), and heated at 353 K in a water-bath. The as-impregnated powder was transferred into a sealed quartz tube and heated at 973 K for 1 h under \( \text{NH}_3 \) flow with the flow rate of 250 mL·min\(^{-1}\). The deposited cobalt oxide cocatalyst was denoted as \( \text{CoO}_x \) here.
Preparation of IrO$_2^{2,3}$

Typically, a given amount of K$_2$IrCl$_6$ was added to a 100 mL deionized water and adjusted the pH value to ca. 12 by KOH (aq.). The reaction mixture was heated in a flask at 353 K until complete dissolution of K$_2$IrCl$_6$. The obtained transparent solution was then cooled to room temperature in an ice-water bath, and the pH value of the cooled solution was adjusted to 8.5-9.5 with diluted HNO$_3$ solution. Further heating at 353 K for 1 h, a deep blue IrO$_2$ colloid solution was finally formed.
Figure S1. SEM image of the synthesized Sr$_5$Ta$_4$O$_{15}$. 
Figure S2. Rate of H\textsubscript{2} evolution on Pt/Sr\textsubscript{5}Ta\textsubscript{4}O\textsubscript{15-x}N\textsubscript{x} samples as a function of platinum content. Reaction condition: 0.15 g catalyst; 150 mL 20 v% methanol solution; 0.15 g La\textsubscript{2}O\textsubscript{3}; 300 W Xe lamp (\(\lambda\geq420\) nm); 5 h irradiation.
**Figure S3.** UV-Vis absorption spectra of the platinum solutions before and after 5 h photodeposition: (A) before photodeposition; (B) after photodeposition.

**Condition:** A desired amount (0.3 wt%) of platinum precursor ([(NH₄)₂Pt]Cl₆) was mixed with the solution containing 20 v% methanol solution (150 mL), 0.15 g Sr₅Ta₄O₁₅₋ₓNₓ, and 0.15 g La₂O₃. Prior to reaction, about 6 mL suspension was withdrew and denoted as sample A. The solution was then evacuated to ensure complete air removal, and irradiated from the top side with a 300 W Xenon lamp using a filtration mirror which was equipped with an optical filter (Hoya, L-42; λ≥420 nm) to cut off the ultraviolet light. After 5 h irradiation, about 6 mL suspension was also withdrawn and remarked as sample B. No H₂ evolution was detected. Sample A and B were centrifuged at the rate of 12000 rpm for 5 min, and their supernatants were measured by UV-Vis absorption spectra. Compared to the Sample A, the disappearance of the absorption peak in the Sample B demonstrates that the platinum precursor has been almost photodeposited on the surface of Sr₅Ta₄O₁₅₋ₓNₓ.
Figure S4. Pt 4d XPS spectra of samples: (a) Pt(Imp.-H2)/Sr5Ta4O15-xNₓ; (b) Pt(P.D.)/Sr5Ta4O15-xNₓ.

Based on the binding energies located at 314.4 and 315.7 eV, the impregnated and photodeposited platinum on the surface of Sr5Ta4O15-xNₓ can be deduced to mainly exist as Pt and PtO, respectively.⁴⁴,⁵⁵
Figure S5. Typical TEM (a, b) and SEM (c, d) images of Pt(P.D.)/Sr$_5$Ta$_4$O$_{15-x}$N$_x$ and Pt(Imp.-H$_2$)/Sr$_5$Ta$_4$O$_{15-x}$N$_x$. 
Figure S6. Representative TEM image of CoO$_x$/Sr$_3$Ta$_4$O$_{15-x}$N$_x$. 
Figure S7. XRD patterns of the Ba$_5$Ta$_4$O$_{15}$ samples before (a) and after thermal ammonia treatment (b).

The XRD patterns of the synthesized Ba$_5$Ta$_4$O$_{15}$ oxide are in good agreement with the standard diffraction patterns of Ba$_5$Ta$_4$O$_{15}$ (PDF#18-0193). After nitrogen doping treatment, the diffraction peaks were maintained.
The XRD patterns of the synthesized Sr$_2$Ta$_2$O$_7$ oxide are in good agreement with the standard diffraction patterns of Sr$_2$Ta$_2$O$_7$ (PDF#30-1304). After nitrogen doping treatment, the diffraction peaks were maintained.
Figure S9. Typical time courses of H₂ evolution for the 0.3 wt% Pt/Bₐ₅Ta₄O₁₅₋ₓNₓ (A) and 0.3 wt% Pt/Sr₂Ta₂O₇₋ₓNₓ (B) under visible light irradiation. Reaction condition: 0.15 g catalyst; 150 mL 20 v% methanol solution; 0.15 g La₂O₃; 300 W Xe lamp (λ≥420 nm).
Figure S10. Typical time courses of O$_2$ evolution for the 1.0 wt% CoO$_x$/Ba$_5$Ta$_4$O$_{15-x}$N$_x$ (A) and 1.0 wt% CoO$_x$/Sr$_2$Ta$_2$O$_{7-x}$N$_x$ (B) under visible light irradiation. Reaction condition: 0.15 g catalyst; 150 mL 0.01 M AgNO$_3$ aqueous solution; 0.15 g La$_2$O$_3$; 300 W Xe lamp ($\lambda \geq$420 nm).
Supplementary References


