

Supporting Information

Wide Visible-Light-Responsive Tunneled $\text{MgTa}_2\text{O}_{6-x}\text{N}_x$ Photocatalyst for Water Oxidation and Reduction

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1. Experimental details

1.1 Materials and reagents

For the preparation of MgTa_2O_6 , TaCl_5 (99.99%, Alfa Aesar), $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ (96%, Sinopharm Chemical), ethylene glycol (99.0%, Sinopharm Chemical), anhydrous citric acid (99.5%, Sinopharm Chemical) and CH_3OH (99.5%, Bodi Chemical) were used. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (99.5%, Sinopharm Chemical) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99.0%, Sinopharm Chemical) were employed to deposit Pt and CoO_x cocatalysts, respectively. CH_3OH (99.5%, Bodi Chemical) and AgNO_3 (99.9%, Alfa Aesar) were employed as sacrificial electron donor and acceptor, respectively. La_2O_3 (99.95%, Sinopharm Chemical) was applied as a buffer agent. All chemicals were used as-purchased without further purification.

1.2 Preparation of MgTa_2O_6 and $\text{MgTa}_2\text{O}_{6-x}\text{N}_x$ ^{SI}

Typically, TaCl_5 was dissolved in methanol, and then anhydrous citric acid (CA) and ethylene glycol (EG) with the molar ratio of $\text{Ta}/\text{CA}/\text{EG} = 1/15/60$ were added. The reaction mixture was then mechanically stirred until it became transparent, followed by addition of stoichiometric $(\text{MgCO}_3)_4 \cdot \text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$. 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 15 h. The final product was well-crystalline white MgTa_2O_6 powder.

$\text{MgTa}_2\text{O}_{6-x}\text{N}_x$ was prepared by a thermal ammonolysis process. Typically, 2.0 g MgTa_2O_6 was placed in the corundum boat and put into a quartz tube. It was then heated at 1123 K for 15 h under the ammonia flow ($20 \text{ mL} \cdot \text{min}^{-1}$). After naturally cooling to room temperature, the sample was collected and stored in a desiccator for use.

1.3 Deposition of Pt or CoO_x cocatalyst

The 0.4 wt% Pt cocatalyst was deposited by conventional impregnation and subsequent H_2 reduction. Typically, 0.2 g photocatalyst was immersed in a *ca.* 2 mL H_2PtCl_6 aqueous solution, and sonicated for *ca.* 5 min. After the solution was

completely evaporated in a water bath at 353 K, the resulting powder was collected and reduced at 473 K for 1 h under a flow of 5% H₂/Ar (200 mL·min⁻¹).

The deposition of cobalt oxide as water oxidation cocatalyst was referred to the literature.^{S2} Typically, a calculated amount of cobalt nitrate aqueous solution (2 mL) was added to the aqueous suspension containing 0.2 g photocatalyst, 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 NH₃ flow with the flow rate of 20 mL·min⁻¹. The deposited cobalt oxide cocatalyst was denoted as CoO_x here, and the deposited content calculated by cobalt element is 1 wt%.

1.4 Characterizations of catalysts

X-ray diffraction (XRD) measurement was carried out on a Rigaku D/Max-2500/PC powder diffractometer (Cu K α radiation) with operating voltage of 40 kV and operating current of 200 mA. The scan rate of 5°·min⁻¹ or 0.5°·min⁻¹ was applied at a step size of 0.02°. UV-Vis diffuse reflectance spectra (DRS) were recorded on a UV-Vis spectrophotometer (JASCO V-550) equipped with an integrating sphere, and BaSO₄ powder was used as the reference for baseline correction. The morphologies and particle sizes were examined by scanning electron microscopy (SEM; Quanta 200 FEG, FEI). The Brunauer-Emmett-Teller (BET) surface area was measured at 77 K using a Micromeritics ASAP 2000 adsorption analyzer. X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi, a monochromatic Al K α X-ray source) was carried out to check the binding energies of elements and judge the relative positions of valence bands, which the C 1s peak (284.6 eV) was employed for reference. The content of nitrogen dopant was analyzed using a flash elemental analyzer (HORIBA, EMGA-930).

1.5 Photocatalytic reactions

The photocatalytic reactions were carried out in a Pyrex top-irradiation-type reaction vessel connected to a closed gas circulation system. A 150 mL aqueous solution containing 0.15 g photocatalyst was adopted, and 0.01 M AgNO₃ or 20 v% methanol was used as scavengers for photocatalytic water oxidation or reduction,

respectively. 0.15 g La_2O_3 was added to maintain the pH value of the reaction solution, which was measured at *ca.* 8.5. Prior to photoirradiation, the reaction mixture was evacuated to ensure complete air removal, and then 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; $\lambda \geq 420$ nm) to cut off the light in the ultraviolet region. A flow of cooling water was used to maintain the reaction suspension at room temperature. The evolved gases were analyzed by gas chromatography (Agilent; GC-7890A, MS-5A column, TCD, Ar carrier).

1.6 Electrochemical analysis

For the Mott-Schottky (M-S) measurement, $\text{MgTa}_2\text{O}_{6-x}\text{N}_x$ particles was deposited on FTO conducting glass by the electrophoretic deposition (EPD). Typically, the EPD was carried out in an acetone solution (50 mL) containing powder sample (50 mg) and iodine (20 mg), which was dispersed by sonication for 20 min. The FTO electrode was immersed, paralleling with the Pt electrode, and the distance between these two electrodes was 5 cm. 20 V was applied for 1 min using a potentiostat (ITECH IT6834), then the prepared electrodes were calcined in air at 673 K for 0.5 h. The area of the electrode was fixed to 0.36 cm^2 by insulating cement. The M-S measurement was carried out on a Princeton Applied Research PARSTAT 2273, using 0.5 M Na_2SO_4 aqueous solution as electrolyte with pH value of 8.5 adjusted by NaOH. The frequency and amplitude of AC potential were 1 kHz and 0.01 V, respectively.

2. Results of characterizations

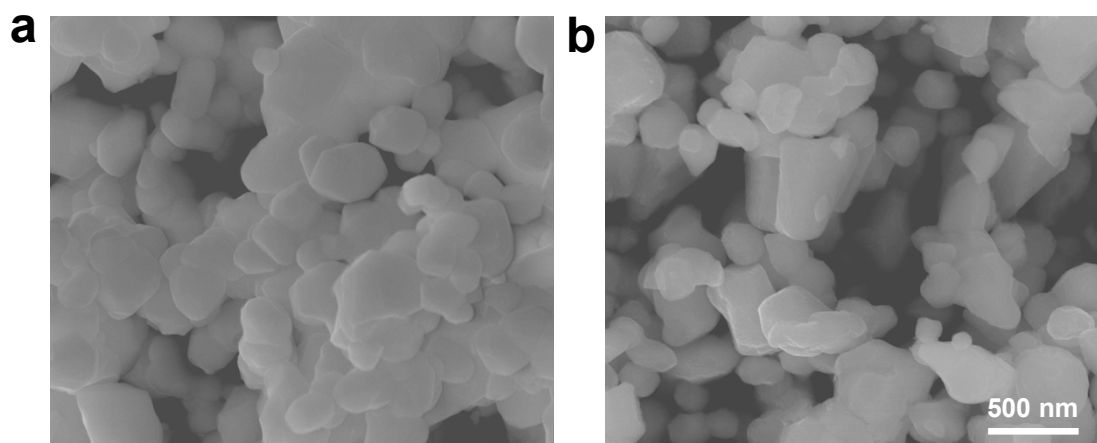


Fig. S1. SEM images of MgTa₂O₆ (a) and MgTa₂O_{6-x}N_x (b) samples.

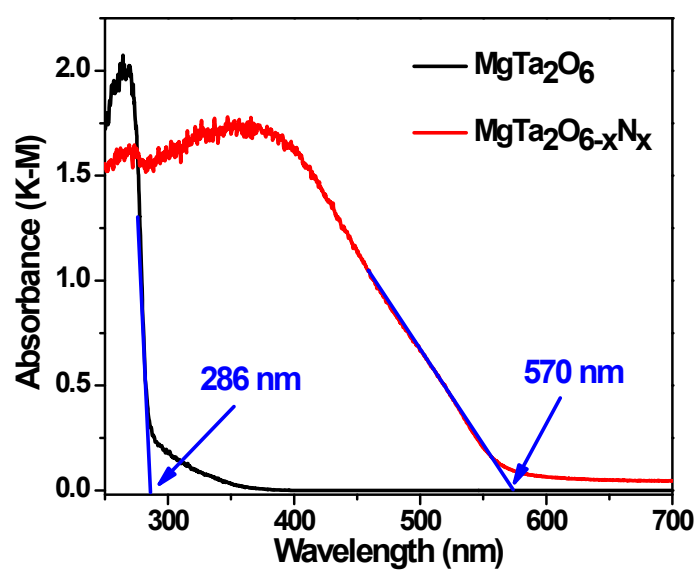


Fig. S2. UV-Vis DRS of MgTa₂O₆ and MgTa₂O_{6-x}N_x samples.

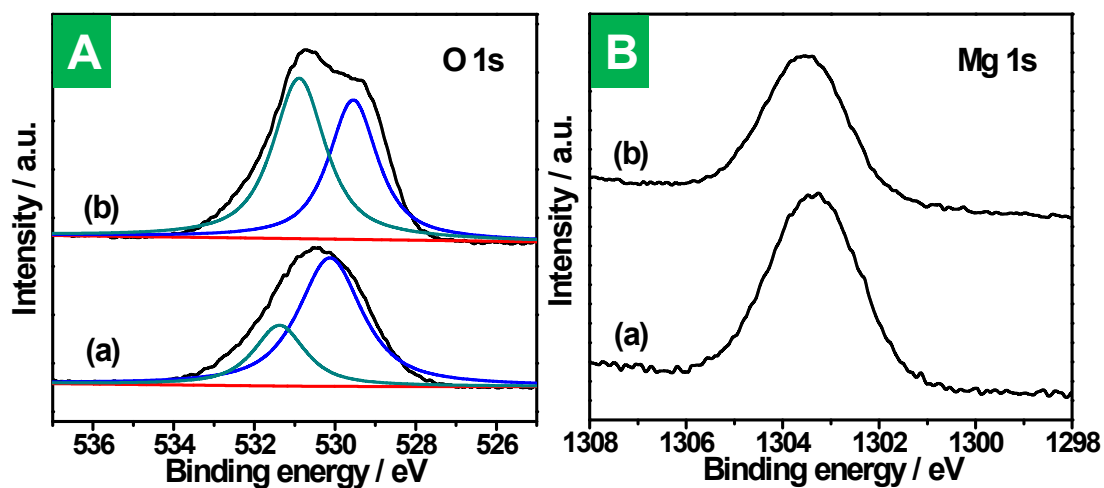


Fig. S3. XPS spectra of O 1s (A) and Mg 1s (B) measured on MgTa₂O₆ (a) and MgTa₂O_{6-x}N_x (b) samples.

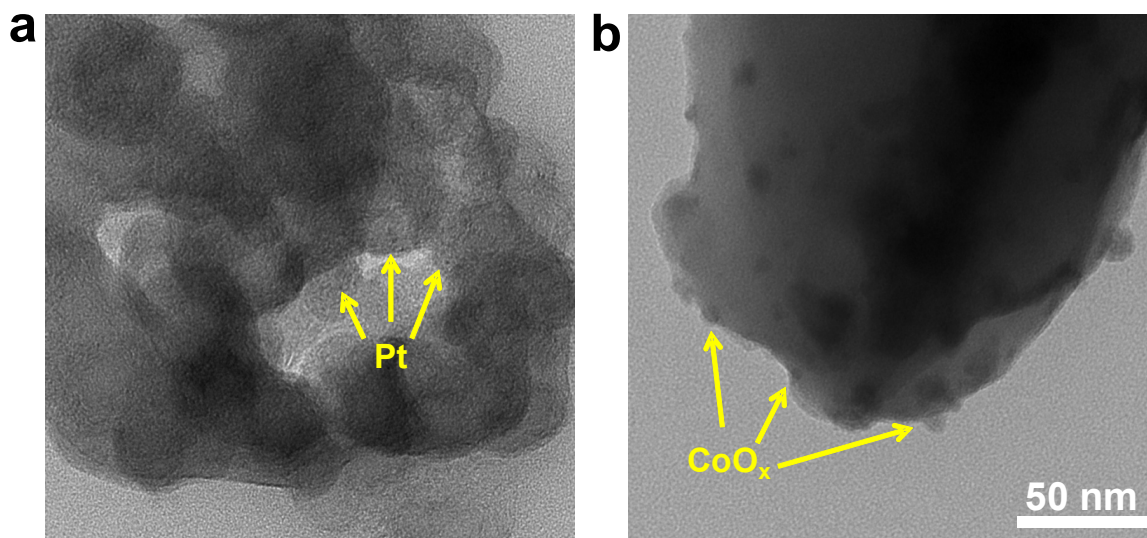


Fig. S4. Typical TEM images of samples: (a) 0.4 wt% Pt/MgTa₂O_{6-x}N_x; (b) 1.0 wt% CoO_x/MgTa₂O_{6-x}N_x.

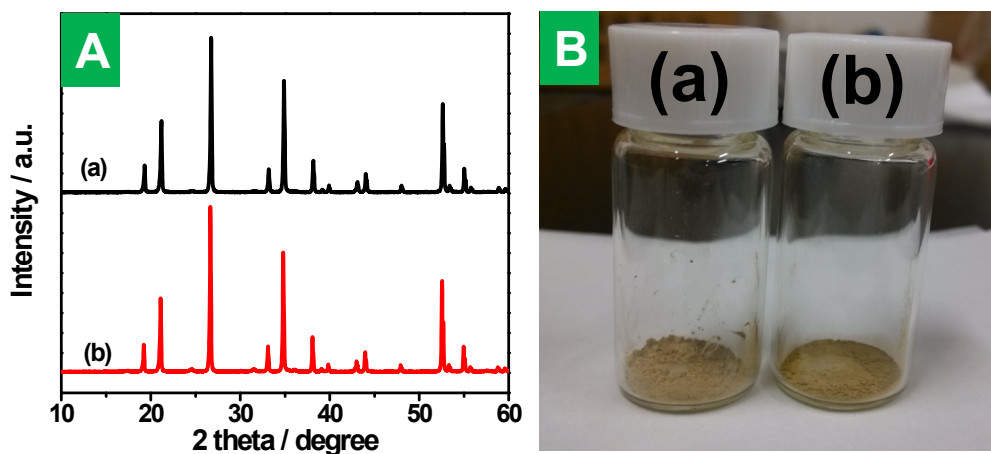


Fig. S5. XRD patterns (A) and photo (B) of 0.4 wt% Pt/MgTa₂O_{6-x}N_x samples before (a) and after (b) photocatalytic hydrogen evolution reaction. The reacted photocatalyst was centrifuged to remove the reactant solution, and washed with HCl aqueous solution (pH = 1) for 30 min to dissolve the La₂O₃ residue. Finally, the sample was obtained by centrifugation, washed with several times and dried in a furnace at 353 K overnight.

Supplementary References

- [S1] K. Yoshioka, V. Petrykin, M. Kakihana, H. Kato and A. Kudo, *J. Catal.* 2005, **232**, 102.
- [S2] F. X. Zhang, A. Yamakata, K. Maeda, Y. Moriya, T. Takata, J. Kubota, K. Teshima, S. Oishi and K. Domen, *J. Am. Chem. Soc.* 2012, **134**, 8348.