Supporting Information

Pyrochlore-structural Nd$_2$Ta$_2$O$_5$N$_2$ Photocatalyst with Absorption Edge of over 600 nm for Z-scheme Overall Water Splitting

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1. Experimental section

1.1 Chemical Reagents. Neodymium oxide (Nd$_2$O$_3$) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Tantalum oxide (Ta$_2$O$_5$) and tungsten oxide (WO$_3$) were purchased from High Purity Chemical. Methanol (CH$_3$OH) and chloroplatinic acid hexahydrate (H$_2$PtCl$_6$·6H$_2$O) were produced by Sinopharm Chemical Reagent Co., Ltd. Sodium rhodium chloride dodecahydrate (Na$_3$RhCl$_6$·12H$_2$O) and potassium iodine (KI) were obtained from Alfa Aesar. Potassium chlorine (KCl) was got from Macklin. Ruthenium trichloride (RuCl$_3$) and iridium chloride hexahydrate (H$_2$IrCl$_6$·6H$_2$O) were obtained from Tianjin Heath Biochemical Technology Co., Ltd, Dalian Kaimai Chemical Engineering Co., Ltd. and Tianjin Comiou Chemical Reagent Co., Ltd, respectively. Without special instructions, these reagents were analytically pure. The deionized (DI) water used was 18.2 MΩ.

1.2 Preparation of materials.

1.2.1 Preparation of Nd$_2$Ta$_2$O$_5$N$_2$. Pyrochlore-structural Nd$_2$Ta$_2$O$_5$N$_2$ was
prepared by nitriding NdTaO₄ oxide precursor. Firstly, NdTaO₄ oxide precursor was synthesized by a flux method. Equimolar Nd₂O₃ and Ta₂O₅ were mixed with KCl of equal quality in a mortar. After grinding for 0.5 h in the presence of ethanol, grind for another 0.5 h under dry conditions to ensure uniform mixing. Then, the mixture was transformed into an alumina crucible and heated to 1150 °C for 5 h at a heating rate of 10 °C min⁻¹ in a muffle furnace. After cooling down, the NdTaO₄ oxide precursor was obtained by washing out KCl using DI water. Dry it at 60 °C for 24 h. The NdTaO₄ powder was transferred into an alumina combustion boat and heated to 950 °C at a heating rate of 10 °C min⁻¹ in a tube furnace, reacting for 5 h under the flow of NH₃ (50 ml min⁻¹). After cooling down, Nd₂Ta₂O₅N₂ powder was collected.

1.2.2 Deposition of cocatalysts. For hydrogen evolution, Pt, Ir, Rh and Ru were used as the cocatalyst. The cocatalyst was deposited on Nd₂Ta₂O₅N₂ by impregnation followed by hydrogen reduction method. Typically, Nd₂Ta₂O₅N₂ powder was ultrasonically dispersed in 2 mL H₂O including the calculated amount of metal precursor (H₂PtCl₆·6H₂O, H₂IrCl₆·6H₂O, Na₃RhCl₆·12H₂O or RuCl₃). After drying in a water bath at 80 °C under constant stirring, it was conducted at 200 °C for 1 h under the flow of 5% H₂/95% Ar (V/V) (200 mL min⁻¹). The PtOₓ was deposited on the surface of WO₃ as the cocatalyst for reduction of IO₃⁻ ions in the Z-scheme system.¹ WO₃ was ultrasonically dispersed in 2 mL H₂O including a calculated amount of H₂PtCl₆·6H₂O. After drying at 80 °C, it was calcinated at 550 °C for 0.5 h in a muffle. Then 1% CsCl in a molar ratio of WO₃ was impregnated on 0.5 wt% PtOₓ/WO₃, following calcination at 500 °C for 10 min in a muffle. Finally, the powder was stirring in 1 M H₂SO₄ for 1 h. Wash out the residual H₂SO₄ by DI H₂O and dry the powder.¹ For water oxidation half reaction, CoOₓ was deposited on Nd₂Ta₂O₅N₂ by two-step calcination as cocatalyst.² Nd₂Ta₂O₅N₂ powder was ultrasonically dispersed in 2 mL H₂O including a calculated amount of Co(NO₃)₂·6H₂O. After steaming to dry on 80 °C water bath, it was calcinated at 700 °C for 1 h under the flow of NH₃ (100 mL min⁻¹). When cooling down, the powder was calcinated at 200 °C for 1 h in the air.

1.3 Characterization. Powder X-ray diffraction (XRD) was carried out on a SmartLab X-ray diffractometer (Cu Kα radiation, λ = 1.5418 Å). The diffraction date
for two theta ranging from $10^\circ$ to $80^\circ$ were recorded at the speed of $20^\circ$ per minute. High-quality data was collected with $0.01^\circ$ per step to conduct the Rietveld refinement. The XRD refinement was performed on a General Structure Analysis System (GSAS) software.\textsuperscript{3} Morphology and element distribution mapping were recorded on a JSM-7900F field emission scanning electron microscope (SEM) and a HT7700 transmission electron microscopy (TEM). X-ray photoelectron spectroscopy (XPS) was employed to acquire valence states of elements on an ESCALAB Xi + X-ray photoelectron spectrometer (Al Kα X-ray, $h\nu = 1486.6$ eV). The surface area was calculated from $N_2$ adsorption–desorption experiment on a Quadrasorb evo. Ultraviolet-visible (UV-vis) diffuse reflectance absorption spectroscopy (DRS) was characterized on a JASCOV-650 UV-vis diffuse reflectance spectrometer with BaSO$_4$ powder as background. And the wavelength of switching the light source from the tungsten lamp to deuterium lamp is 323 nm.

1.4 Computational details. All first-principles calculations were carried out based on the density functional theory (DFT) and the Perdew-Burke-Eznerhof generalized gradient approximation (PBE-GGA).\textsuperscript{4, 5} The projector augmented wave (PAW)\textsuperscript{6, 7} scheme as incorporated in the Vienna Ab initio Simulation Package (VASP)\textsuperscript{8, 9} was used, and a plane-wave expansion for the basis set with a cutoff energy of 500 eV was employed. The convergence criteria for the force and electronic self-consistent iteration were set to 0.02 eV·Å$^{-1}$ and $1.0\times10^{-5}$ eV, respectively. The Brillouin zone was sampled by a Monkhorst-Pack\textsuperscript{10} of $3 \times 3 \times 3$ K-point grid for bulk Nd$_2$Ta$_2$O$_5$N$_2$. The PBE + $U$ approach was employed to accurately describe the electron states of $f$ and $d$ electrons, and the $U$ values for Nd 4$f$ and Ta 5$d$ states were chosen as 6.0 eV and 4.5 eV according to the previous reports\textsuperscript{11, 12}, respectively.

1.5 Photocatalytic Performance. The photocatalytic reaction was carried out in a typical Pyrex top-illuminated reactor. The reactor was connected with a gas circulation system and a gas chromatography system. A certain amount of the sample was ultrasonically dispersed in the aqueous solution (20 vol% methanol for H$_2$ evolving half reaction, 10 mM AgNO$_3$ for O$_2$ evolving half reaction and 1 mM KI for Z-scheme overall water splitting). The air in the reactor was completely removed by
pumping before photocatalytic reaction. The solution was maintained at 15 °C by circulating cold water during the reaction. A 300 W Xenon lamp was employed as the light source with a filter to cut off ultraviolet light. The amount of gas evolution was detected by a thermal conductivity detector in a gas chromatography (GC-2014, Shimadzu). The apparent quantum efficiency (AQE) at 420 nm was calculated by the equation AQE = \((AR/I) \times 100\%\), where A represents a coefficient (2 for \(\text{H}_2\) evolution), R represents the evolution rate of \(\text{H}_2\) in the initial one hour irradiation in a proton reduction reaction and I represents the absorption rate of incident photons. The total number of incident photons at a monochromatic wavelength of 420 nm was measured to be \(1.50 \times 10^{20}\) photons h\(^{-1}\).

1.6 Electrochemical and photoelectrochemical analysis. Mott-Schottky measurements were performed on a Princeton electrochemical workstation in 0.5 M \(\text{Na}_2\text{SO}_4\). For the preparation of the working electrode, 10 mg sample was ultrasonically dispersed in 1 mL ethanol with 10 \(\mu\)L 5 \text{wt}\% nafion solution. The suspension was dropped on a 1×2 cm\(^2\) fluorine-doped tin oxide (FTO) conductive glass. Then the as-prepared electrode was heated at 450 °C for 1 h under \(\text{N}_2\) atmosphere. A Pt sheet was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The current-potential curve was performed in 0.5 M \(\text{Na}_2\text{SO}_4\) solution with a scan speed of 2 mV S\(^{-1}\) and switched between dark and light irradiation every 10 s.
2. Results of characterizations

Fig. S1 XRD patterns of as-prepared NdTaO$_4$ and Nd$_2$Ta$_2$O$_5$N$_2$.

Table S1 Atomic coordinate information obtained from Rietveid refinement

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Fig. S2 SEM image of NdTaO₄.

Fig. S3 (a) SEM image of mixture Nd₂Ta₂O₅N₂ and NdTaO₄. The energy dispersive X-ray spectrum (EDS) of position 1 (b) and position 2 (c) (inset: mass percentage of Nd, Ta, O and N).

To rule out the possibility that the N signal is from the background, the mechanical mixture of Nd₂Ta₂O₅N₂ and NdTaO₄ was prepared for the comparison. As shown in Fig. 1c and Fig. S2, the morphologies of Nd₂Ta₂O₅N₂ and NdTaO₄ are different. So it is easy to distinguish between Nd₂Ta₂O₅N₂ and NdTaO₄ in the mixture. The energy dispersive X-ray spectrums (EDS) of the positions from different morphologies were analyzed. As shown in Fig. S3b and c, the N element content is
5.3 wt% in position 1 (Nd$_2$Ta$_2$O$_5$N$_2$), while in position 2 (NaTaO$_4$) is only 0.2 wt%, which indicates the N signal from Nd$_2$Ta$_2$O$_5$N$_2$ is not from the background.

Fig. S4 N$_2$ adsorption–desorption isotherms of Nd$_2$Ta$_2$O$_5$N$_2$.

There was no obvious capillary coagulation effect from the N$_2$ adsorption and desorption result shown in Fig. S4. So it is considered that those pores in Nd$_2$Ta$_2$O$_5$N$_2$ (Fig. 1c) are macroporous architectures.

Fig. S5 XPS survey spectrum of Nd$_2$Ta$_2$O$_5$N$_2$. 
Fig. S6 High-resolution XPS spectra of Ta 4f (a), O 1s (b) and N 1s (c) of Nd$_2$Ta$_2$O$_5$N$_2$.

Fig. S7 Rate of H$_2$ evolution on Pt/Nd$_2$Ta$_2$O$_5$N$_2$ as a function of Pt loading amount (calculated with metal amount).

Conditions: 150 mg photocatalyst, 120 mL H$_2$O, 30 mL CH$_3$OH, 300 W Xe lamp with a cutoff filter (λ ≥ 420 nm).
Fig. S8 Time course of H\textsubscript{2} evolved on Nd\textsubscript{2}Ta\textsubscript{2}O\textsubscript{5}N\textsubscript{2} with different kinds of cocatalyst loaded. The loading amount is 1 wt\%.

Conditions: 150 mg photocatalyst, 120 mL H\textsubscript{2}O, 30 mL CH\textsubscript{3}OH, 300 W Xe lamp with a cutoff filter (\(\lambda \geq 420\) nm).

Fig. S9 XRD patterns of (a) Nd\textsubscript{2}Ta\textsubscript{2}O\textsubscript{5}N\textsubscript{2}, (b) 1 wt\% Pt/Nd\textsubscript{2}Ta\textsubscript{2}O\textsubscript{5}N\textsubscript{2} and (c) 1 wt\% Pt/Nd\textsubscript{2}Ta\textsubscript{2}O\textsubscript{5}N\textsubscript{2} after photocatalytic proton reduction reaction for 5 h.
Fig. S10 TEM image of 1 wt% Pt/Nd₂Ta₂O₅N₂.

Fig. S11 High-resolution XPS spectra of Pt 4f of 1 wt% Pt/Nd₂Ta₂O₅N₂.
Fig. S12 Photocatalytic performance of O$_2$ evolution. (a) Rate of O$_2$ evolution on CoO$_x$/Nd$_2$Ta$_2$O$_5$N$_2$ as a function of CoO$_x$ loading amount (calculated with metal amount); (b) Time course of O$_2$ evolved with 1.5 wt% CoO$_x$ loading on Nd$_2$Ta$_2$O$_5$N$_2$.

Reaction condition: 150 mg photocatalyst; 150 mL H$_2$O; 1.5 mmol AgNO$_3$; 0.15 g La$_2$O$_3$; 300 W Xe lamp with a cutoff filter ($\lambda \geq 420$ nm).

Fig. S13 Current-potential curve of Nd$_2$Ta$_2$O$_5$N$_2$ and 1.5 wt% CoO$_x$/Nd$_2$Ta$_2$O$_5$N$_2$

Condition: 0.5 M Na$_2$SO$_4$ aqueous solution, chopped irradiation under visible light ($\lambda \geq 420$ nm).
Notes and References