Supplementary Information

Na/Mo co-doped $PbTiO_3$ for efficient photocatalytic water oxidation and Z-scheme overall water splitting under visible light

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Experimental section

Preparation of Mo doped $PbTiO_3$, Na/Mo co-doped $PbTiO_3$ and $PbMoO_4$: A series of Na/Mo co-doped samples were synthesized via a molten salt method.[1] Briefly, the powder of PbO (Sinopharm; 99.5%), TiO_2 (Aldrich; Anatase; 99%) Na_2CO_3 (Sinopharm; 99.5%) and MoO_3 (Aladdin; 99.9%) were added to an agate mortar with at a molar ratio of (100-x) : (100-x) : x : x/2 (x = 0, 2.5, 5 ,7.5, 10, 15) and ground in acetone for 10 min. Then NaCl flux was added according to a solute concentration of 5 mol% and ground for another 20 min. The mixture was transferred to an alumina crucible and heated at 1000 ^oC for 1h in a muffle furnace in air and was naturally cooled to room temperature. The resultants were washed with hot deionized water for several times to remove the flux and then dried at 60 ^oC overnight. The products were denoted as PTO and PTONM-x (x = 2.5, 5 ,7.5, 10, 15). Mo doped PTO (PTOM) was prepared in a similar process without Na_2CO_3 addition, and the products were denoted as PTOM-x (x = 2.5, 5 ,7.5, 10). Similarly, 5 mol% Na doped PTO (PTON-5) was prepared in a similar process without MoO_3 addition. $PoMoO_4$ (PMO) was prepared via solid state method according to a previous report.[2] Specifically, stoichiometric PbO and MoO_3 were ground thoroughly and then calcined in a muffle furnace at 1000 ^oC for 6h. Single domain $PbTiO_3$ (PTOSD) was prepared by a hydrothermal method according to previous reports.[3, 4]

Cocatalyst modulation: RuO_2 for water oxidation reaction was loaded through a thermal impregnation method. Typically, 300 mg photocatalyst was added to 3 mL $RuCl_3$ aqueous solution (3 mg in reference to RuO_2) which was stirred at 80 ^oC for 3 h. The resultant dry powder was then calcined at 350 ^oC for 1 h. $RhCrO_x$ for water reduction was loaded through a photodeposition process. Typically, 300 mg photocatalyst was ultrasonically dispersed in 100mL methanol aqueous solution (20 vol %). Then $Na_3RhCl_3 \cdot 6H_2O$ (3 mL, 1 mg mL^{-1} referred to Rh content) and K_2CrO_4 (4.5 mL, 1 mg mL^{-1} referred to Cr_2O_3 content) aqueous solutions were added into the solution as the cocatalyst precursors. The resulting mixture was irradiated with a Xe

lamp for 3 h under magnetic stirring.

Photocatalytic reactions: Photocatalytic reactions were carried out in a commercial system (Beijing Perfectlight Technology Co., Ltd., Labsolar-6A). During the test process, the reaction temperature was kept at around 10 ^{o}C using a circulating water. For water oxidation process, 100 mg photocatalyst modified with RuO_2 was dispersed into100 mL 2 mM $FeCl_3$ aqueous solution. The suspension was irradiated using a 300 W Xe lamp (Beijing Perfectlight Technology Co., Ltd., PLS-SXE-300UV) with a 420 nm cut-off filter.

For Z-scheme water splitting system, 50 mg RuO_2/PTONM-10 and 50 mg single domain $RhCrO_x$/PTO were dispersed into 100 mL deionized water and then 16.2 mg $FeCl_3$ was added to the reaction vessel as the redox mediator. The suspension was irradiated using a 300 W Xe lamp (Beijing Perfectlight Technology Co., Ltd., PLS-SXE-300UV) with a 420 nm cut-off filter.

Calculation of band structure: First-principles calculations on the electronic properties of pure PTO and doped PTO were performed with density-function theory (DFT) as implemented in VASP (Vienna *ab initio* simulation package).[5-7] The electron-ion interaction was represented by the projector-augmented wave (PAW) method and the electron exchange and correlation were described with the generalized gradient approximation of PBE and GGA+U methods, with plane wave up to an energy cutoff of 600 eV. The U values are 5.0 and 4.38 for Ti and Mo, respectively.[8] For the calculations of pure PTO, the PTO unit cell was used. And for the calculations of doped PTO, a 2×2×2 PTO supercell was used, in which a Ti atom was replaced by a Mo atom ($PbTi_{0.875}Mo_{0.125}O_3$) or a Pb atom was replaced by a Na atom ($Pb_{0.875}Na_{0.125}TiO_3$). The Brillouin zone were sampled by the gamma-centered Monkhorst-Pack k-points meshes of 9×9×9 and 4×4×4 for the pure and doped PTO models, respectively. The electronic and structural ground states of all interested models were optimized by relaxing all degrees of freedom, with the convergence criteria for energy and force are 10^{-5} eV and 0.02 eV/Å, respectively.

Characterization: Scanning electron microscopy (SEM) was taken on a field emission FEI NanoSEM430. Energy dispersive X-ray spectroscopy (EDS) images from scanning TEM high-angle annular dark field (STEM-HAADF) were performed on the Tecnai F20 electron microscopes. X-ray diffraction patterns were recorded on a diffractometer (D/max, 2400) fitted with Cu Kα (λ=1.54050Å) radiation over the 2θ ranges from 5° to 85°. Raman spectra were recorded on HR800 Raman spectroscopy. X-ray photoelectron spectra (XPS) data were captured on X-ray photoelectron spectroscopy (XPS) (Thermo Escalab250, a monochromatic Al Ka X-ray source). All binding energies were referenced to the C 1s peak (284.6 eV) arising from the adventitious carbon. The optical absorption spectra of the samples were collected on a UV-visible spectrophotometer (JASCO V-550) from 200 to 900 nm.

Measurement of apparent quantum yield (AQY): The AQY was calculated using the following expression:

$$AQY = \frac{The\ amount\ of\ O_2 \times 4}{Photon\ Flux(m^{-2}) \times A \times t}$$

where, the amount of O_2 was obtained during photocatalytic overall water splitting process (μmol), photon flux is photons per unit area per unit time (μmol s^{-1} m^{-2}), A is the area through which the photons pass (m^2) and t is irradiation time (μmol).

Mott-Schottky (MS) analysis: The MS data were collected based on using three electrode configurations, in which the prepared photoelectrodes, Ag/AgCl electrode, and Pt foil were used as the working, reference, and counter electrodes, respectively. The tests were carried out in a quartz cell containing 0.5 mol L^{-1} Na_2SO_4 (pH = 7) aqueous solutions. Impedance data at 1000 Hz with 10 mV amplitude in a voltage range from -1.0 V to -0.1 V vs. RHE were used to extract capacitance for the MS analysis.

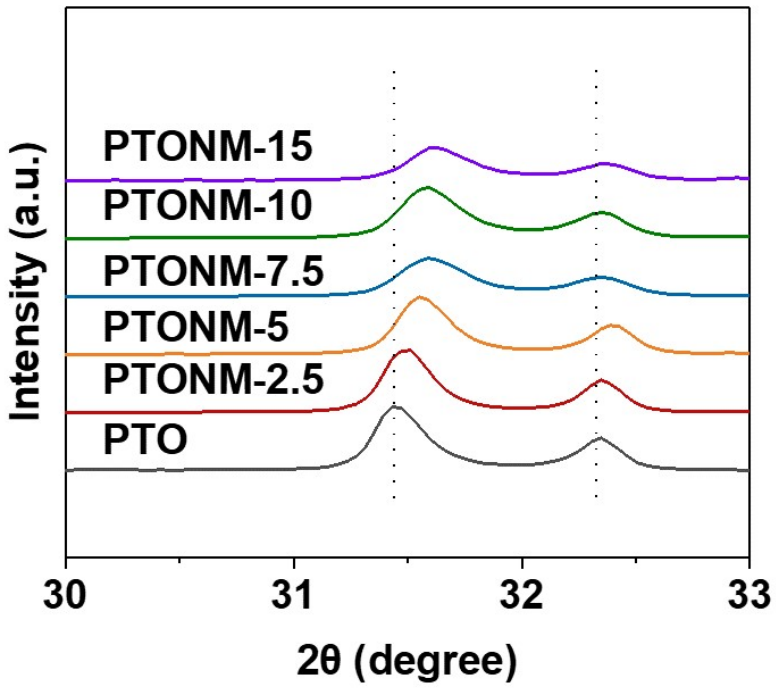

Figure S1. Enlarged XRD patterns of PTO and PTONM-x (x = 2.5, 5, 7.5, 10, 15).

Table S1 Cell parameters fitting from XRD patterns.

Mo	a	c	c/a	V
PTO	3.9058	4.1432	1.060781	63.20565
PTONM-2.5	3.90632	4.1323	1.05785	63.05615
PTONM-5	3.90504	4.12355	1.055956	62.88141
PTONM-7.5	3.90846	4.1093	1.051385	62.77391
PTONM-10	3.90683	4.10365	1.050378	62.63533

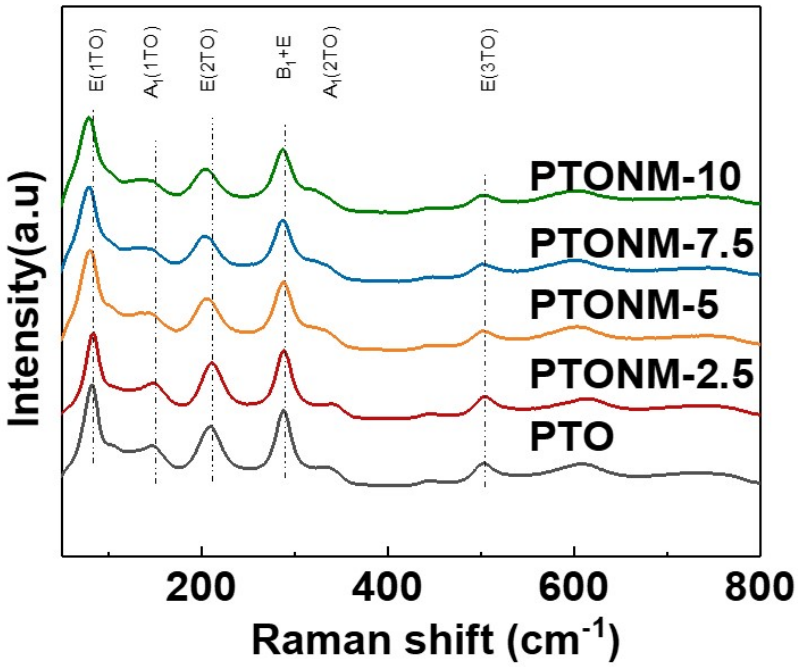

Figure S2. Raman spectra of PTO and PTONM-x (x = 2.5, 5, 7.5, 10).

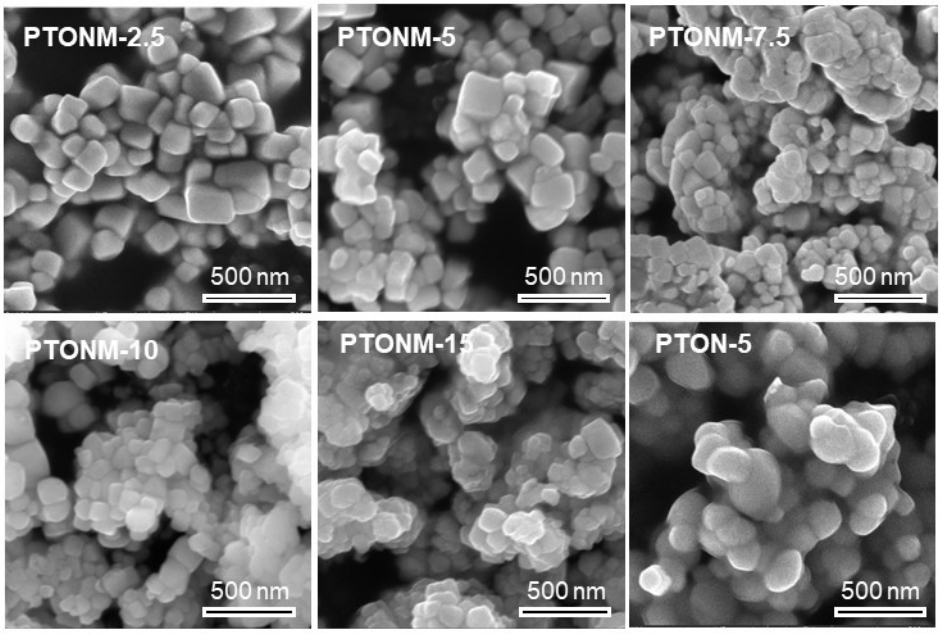

Figure S3. SEM images of PTONM-x (x = 2.5, 5, 7.5, 10, 15) and PTON-5.

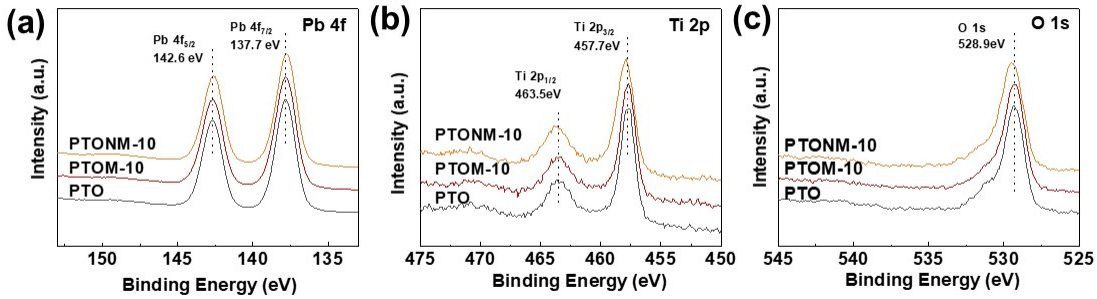

Figure S4 XPS spectra of Pb 4f, Ti 2p and O 1s in PTO, PTOM-10 and PTONM-10.

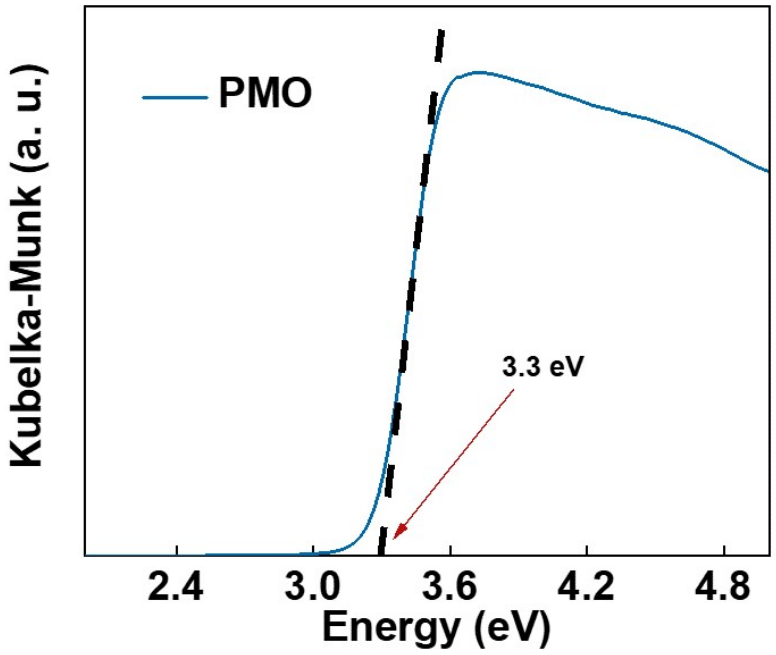

Figure S5 Kubelka-Munk curve of PMO.

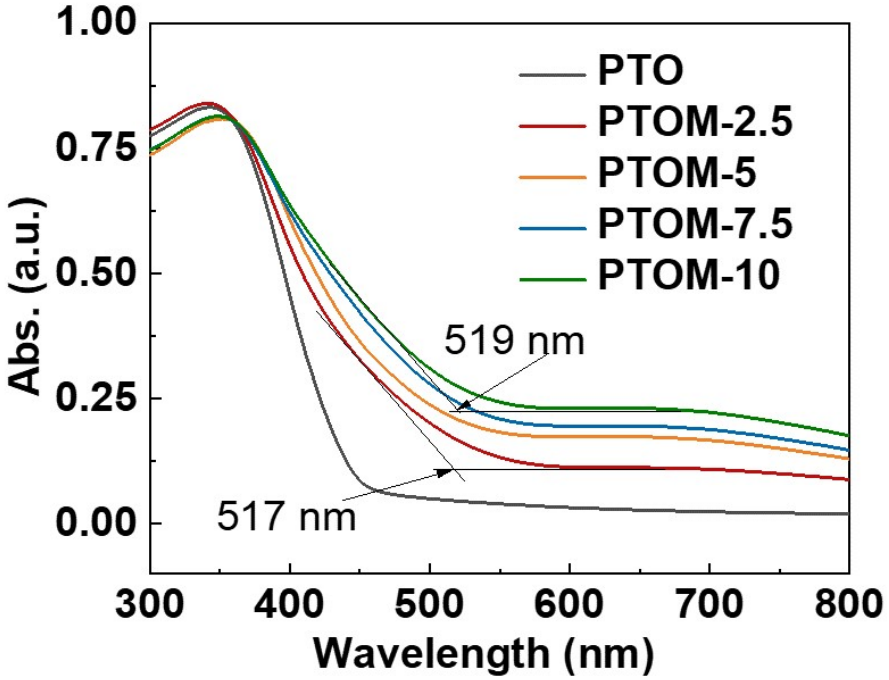

Figure S6 UV-visible diffuse reflectance spectrum of PTO doped with different amount of Mo.

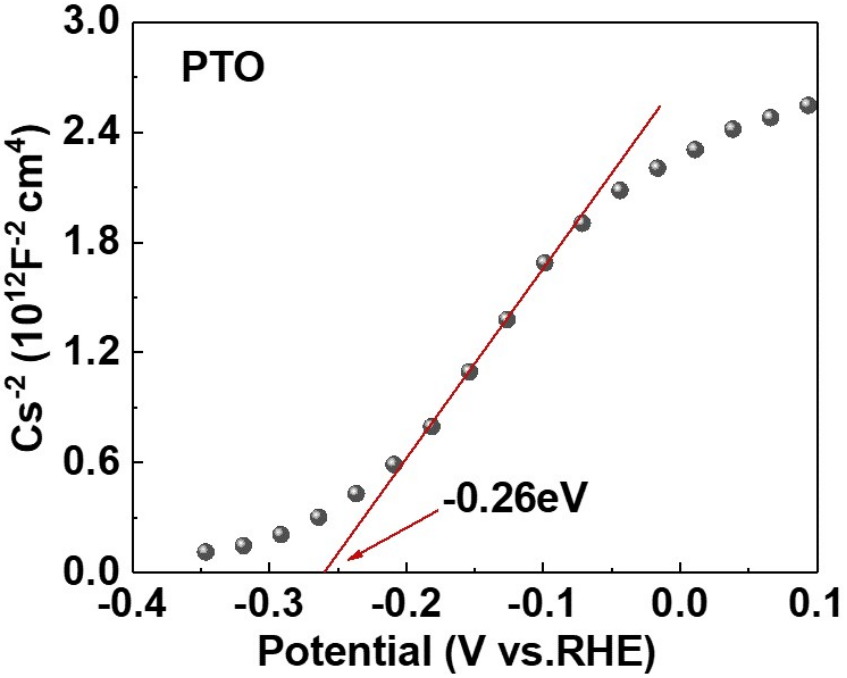

Figure S7 Mott-Schottky plot of PTO.

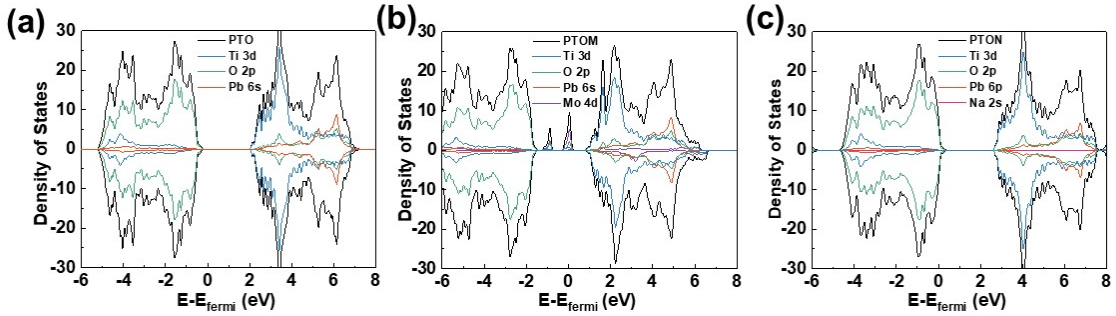

Figure S8 Density of states (DOS) projection of (a) pristine PTO, (b) PTOM and (c) PTON.

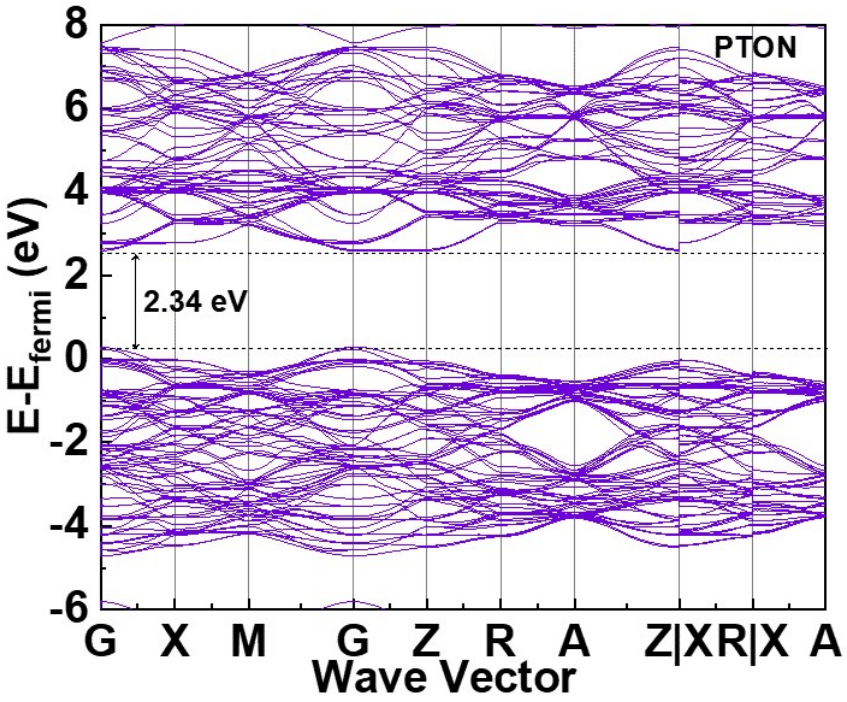

Figure S9 Band structure of PTON.

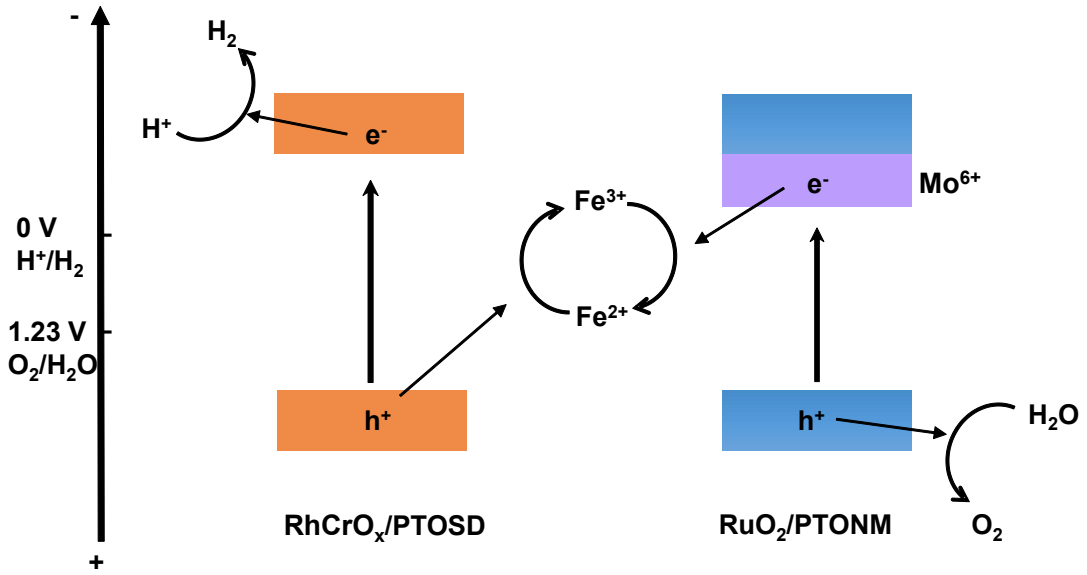

Figure S10 Schematic diagram of the Z-scheme system.

Notes and references

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