

Supplementary Information

Engineering Non-Noble Plasmonic Center in MOF-Derived Z-Scheme Heterojunctions for Enhanced Photoelectrochemical Water Splitting

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Chemical and Materials

Titanium butoxide (TBOT, $\geq 99.0\%$), 2-amino-terephthalic acid (H_2ATA), and Strontium hydroxide octahydrate ($Sr(OH)_2 \cdot 8H_2O$) were purchased from Aladdin Reagent Company (Shanghai, China). The fluorine-doped tin oxide (FTO) conductive substrates were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. Sodium borohydride, ($NaBH_4$, $\geq 98.0\%$), Sodium sulfate (Na_2SO_4 , $\geq 99.0\%$), Acetone, ethanol, methanol, and hydrochloric acid (HCl , $\geq 37.5\%$) were purchased from Beijing Chemical Factory (Beijing, China). Deionized (DI) water was prepared with a resistivity of $18.2\text{ M}\Omega \cdot \text{cm}^{-1}$. All reagents are of analytical grade and were used as received without further purification.

Structure and property characterization

The morphological and structural characterizations of the materials were completed by scanning electron microscopy (Hitachi S4800), and transmission electron microscopy (FEI TalosF200x). X-Ray Diffraction (XRD) was accomplished by using a D8 ADVANCE instrument (Bruker, Germany). UV-Vis diffuse reflectance spectrum (DRS) was characterized on a UV-Vis spectrophotometer (Shimadzu UV-3600). The X-ray photoelectron spectroscopy (XPS) was obtained by taking an XPS analysis (Thermo ESCALAB 250). EPR was obtained by using an EPR spectrometer (Bruker EMXPLUS).

Photoelectrochemical experiments

The PEC measurements were investigated through a three-electrode configuration with the prepared photoanode serving as the working electrode, a platinum slice as the counter electrode, and a saturated Ag/AgCl as the reference electrode. The illumination light was provided by a 300 W xenon lamp, and all of the PEC tests were conducted in $0.5\text{ M Na}_2\text{SO}_4$ (25°C) by using an electrochemical workstation (CHI 660E, Shanghai Chenhua Apparatus Co., China). The potential we measured could be transferred into RHE through the Nernst equation (1) :

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0592 \times \text{pH} + E_{\text{Ag/AgCl}}^0 \quad (1) \quad \text{Where } E_{\text{Ag/AgCl}}^0 = 0.197\text{ V.}$$

DFT calculations and FDTD simulation

In the Density Functional Theory calculations, $3 \times 3 \times 3$ supercells of bulk SrTiO_3 without oxygen vacancy and with oxygen vacancy are built, respectively. Structural optimization was performed by Vienna *Ab-initio* Simulation Package (VASP)^[1] with the projector augmented wave (PAW) method.^[2] The exchange-functional was treated using the Perdew-Burke-Ernzerhof (PBE)^[3] functional. The cut-off energy of the plane-wave basis was set at 450 eV. For the optimization of both geometry and lattice size, the Brillouin zone integration is performed with $2 \times 2 \times 2$ Gamma^[4] k -point sampling. The self-consistent calculations applied a convergence energy threshold of 10^{-5} eV. The equilibrium geometries and lattice constants were optimized with maximum stress on each atom within 0.01 eV/Å. The isosurface level of the electron localization function was set as 5.00 e Å⁻³. The electron localization function was sliced with a scaling bar from 0 to 5 along the face with oxygen vacancy in bulk SrTiO_3 .

The FDTD simulation model with a three-dimensional structure was constructed by aligning the irregular granular R-STO coated on a $\text{TiO}_2/\text{NH}_2\text{-MIL-125}$ nanorod (diameter of TiO_2 : 100 nm). The diameters of R-STO were set at 40–80 nm. A plane-wave source of illumination and frequency-domain field and power monitors were applied to simulate the steady-state behavior and produce the steady-state electric-field data for the plots of electric-field profiles.

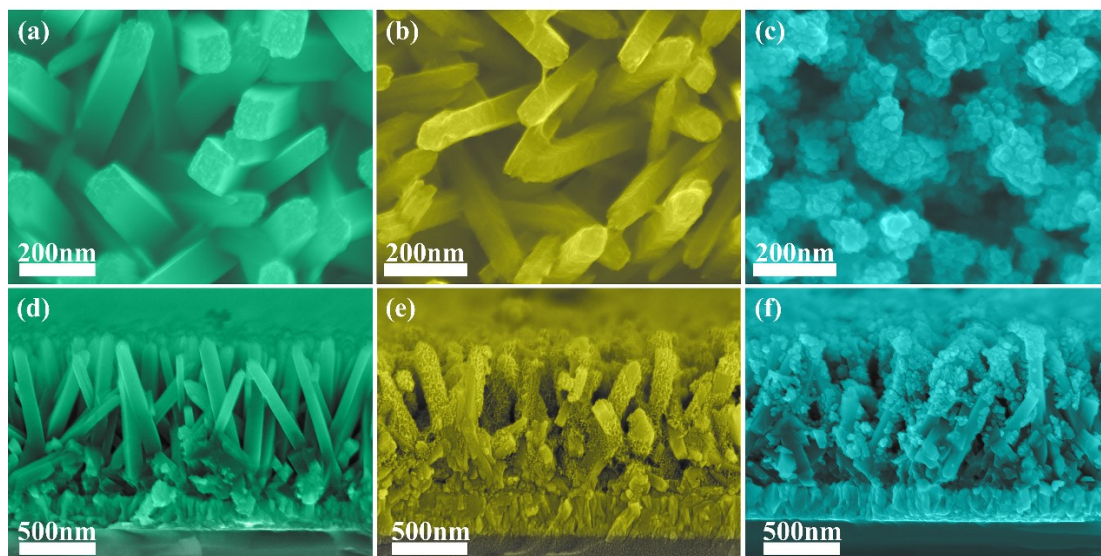


Fig. S1 SEM images of (a) TiO_2 NRs, (b) $\text{TiO}_2@\text{NH}_2\text{-MIL-125}$, (c) $\text{TiO}_2@\text{NH}_2\text{-MIL-125@R-STO}$. Cross-sectional SEM images of (d) TiO_2 NRs, (e) $\text{TiO}_2@\text{NH}_2\text{-MIL-125}$, (f) $\text{TiO}_2@\text{NH}_2\text{-MIL-125@R-STO}$.

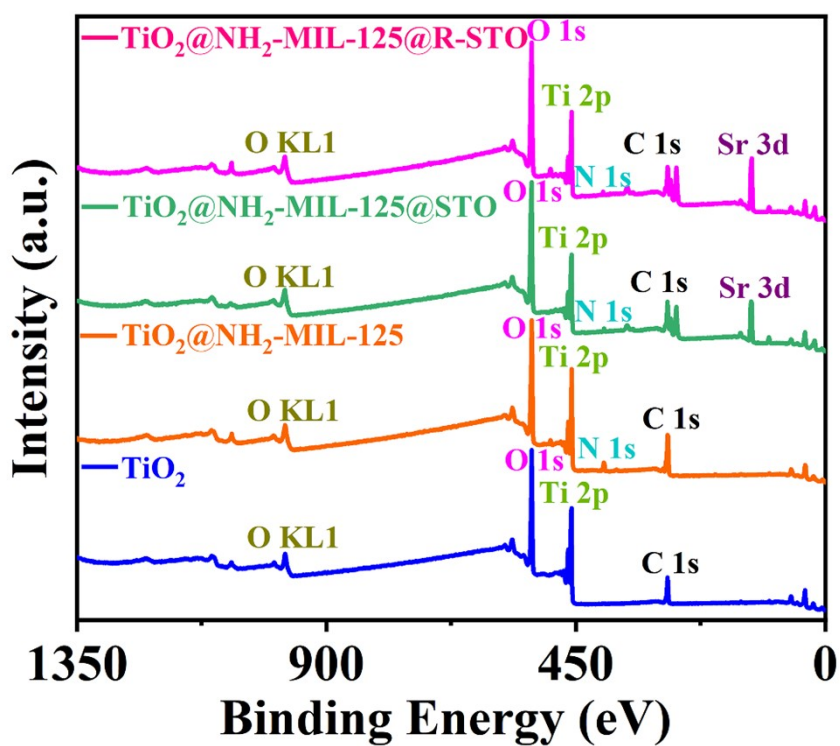


Fig. S2 The full XPS spectra of the samples.

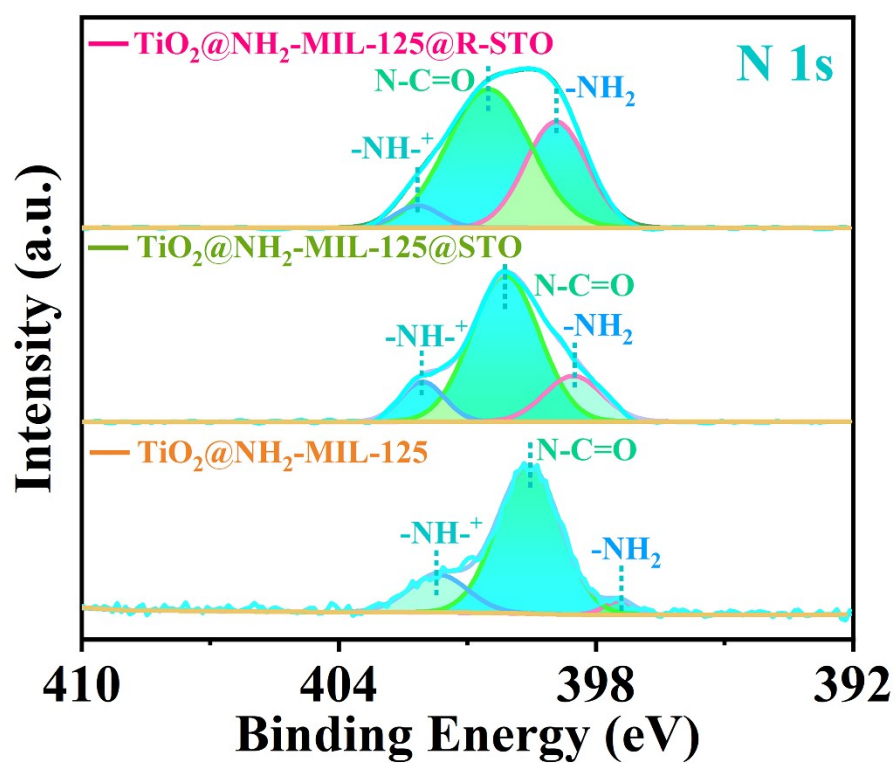


Fig. S3 XPS survey spectra of N 1s.

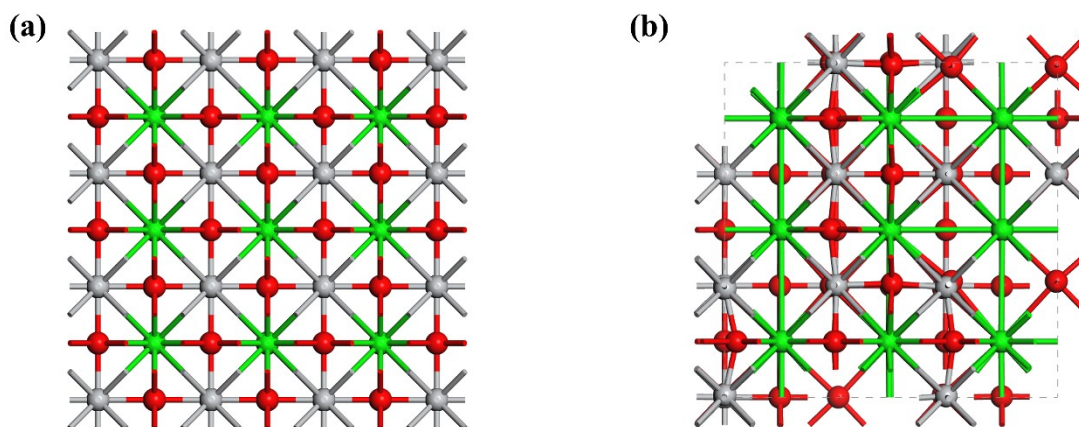


Fig. S4 View of bulk SrTiO_3 without oxygen vacancy (a) and with oxygen vacancy (b). Sr, Ti and O atoms are showed with green, gray and red atoms, respectively.

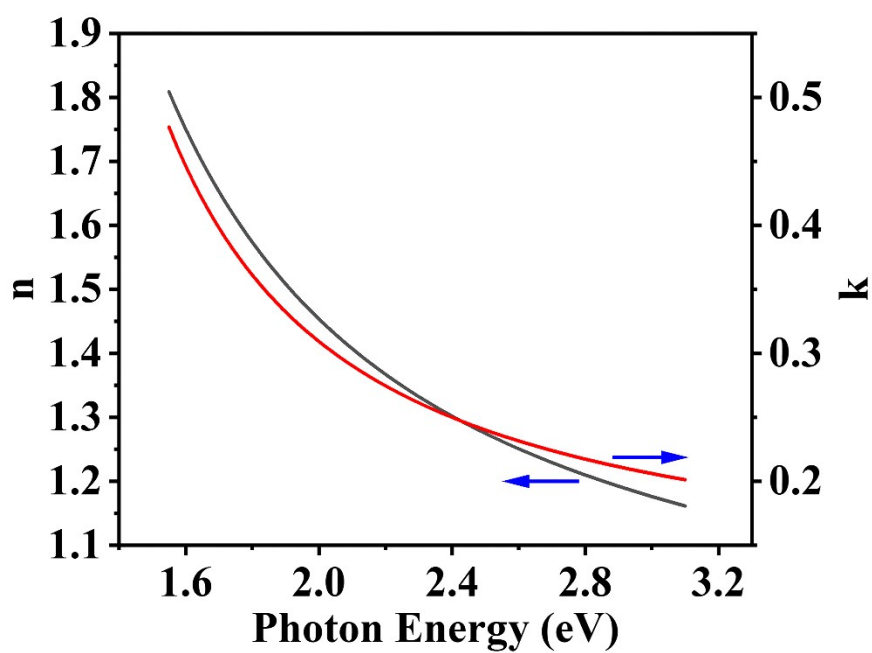


Fig. S5 Refractive index of R-STO measured by an ellipsometer.

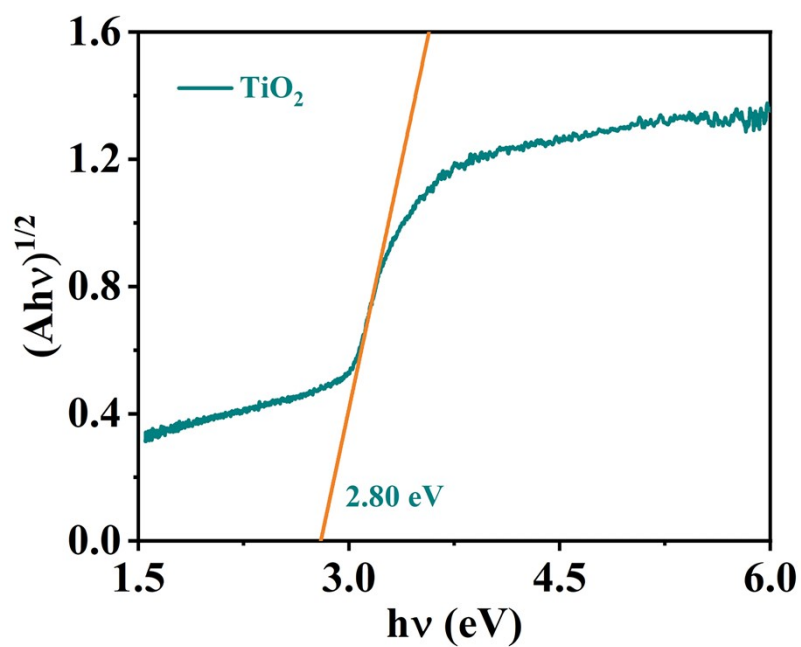


Fig. S6 The Tauc plots of TiO₂ NRs.

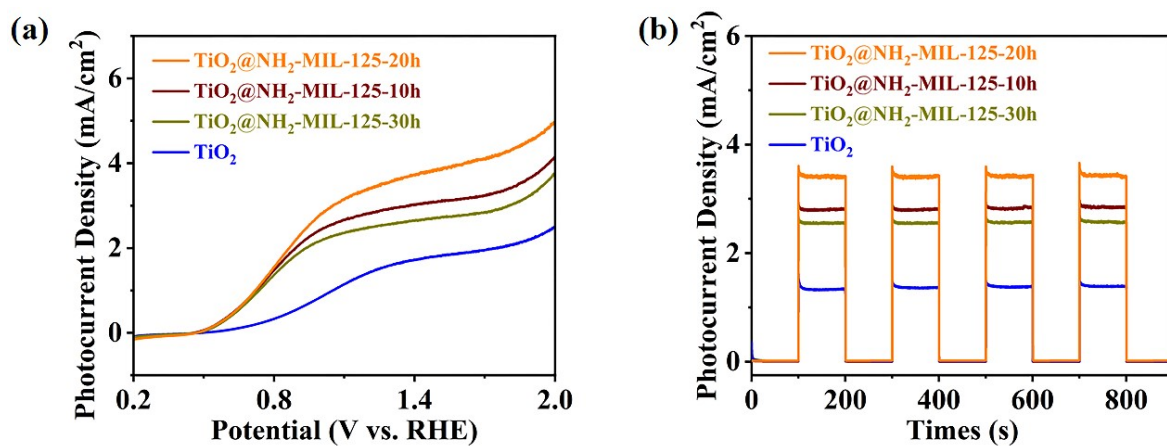


Fig. S7 (a) LSV curves and (b) i-t curves of $\text{TiO}_2@NH_2\text{-MIL-125}$ with different solvothermal reaction time.

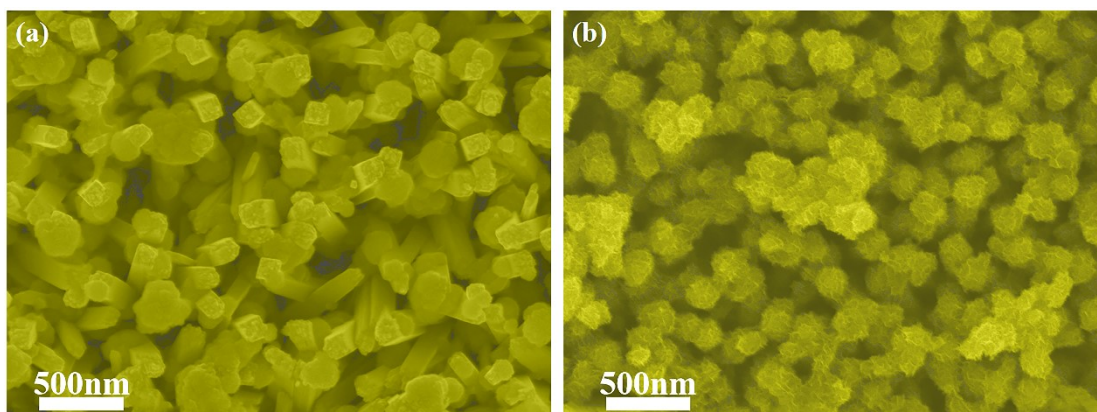


Fig. S8 SEM images of $\text{TiO}_2@NH_2\text{-MIL-125}$ with a solvothermal time of (a) 10 h and (b) 30 h.

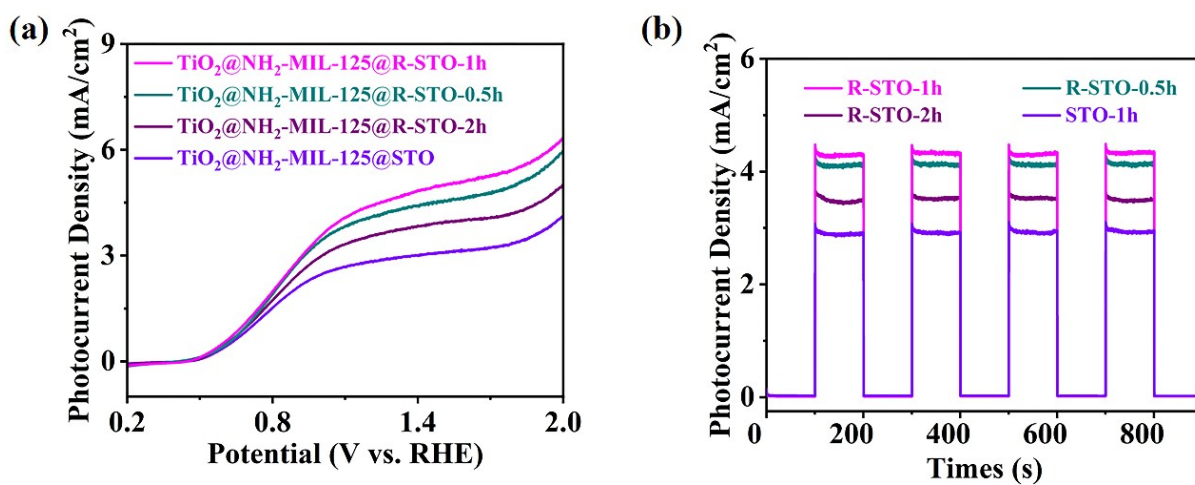


Fig. S9 (a) LSV curves and (b) i-t curves of $\text{TiO}_2@NH_2\text{-MIL-125@R-STO}$ with different reduction times.

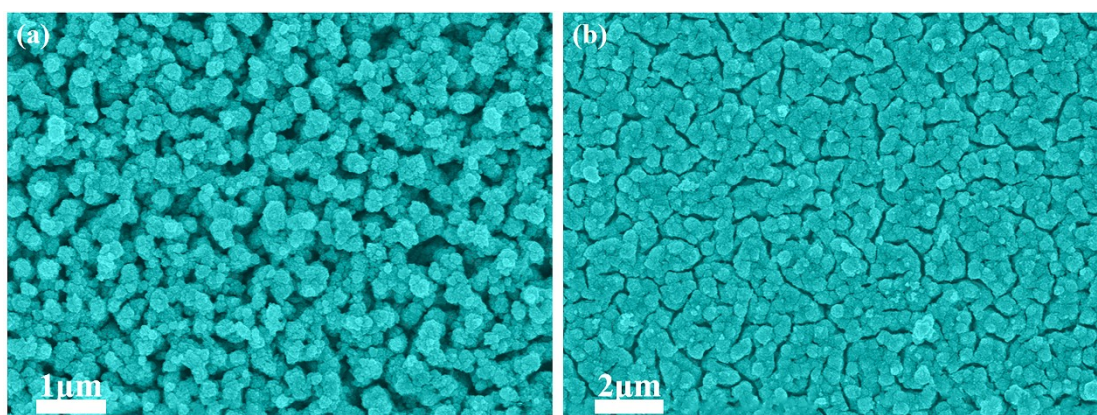


Fig. S10 SEM images of $\text{TiO}_2@\text{NH}_2\text{-MIL-125@R-STO}$ with reduction time of (a) 0.5 h and (b) 2 h.

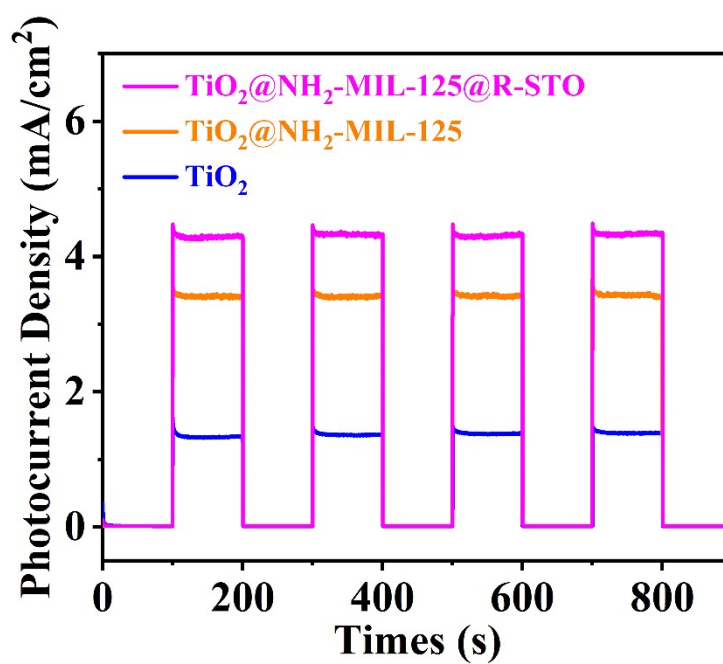


Fig. S11 I-t curves of TiO_2 , $\text{TiO}_2@\text{NH}_2\text{-MIL-125}$, and $\text{TiO}_2@\text{NH}_2\text{-MIL-125@R-STO}$ under illumination at 1.23 V (vs. RHE).

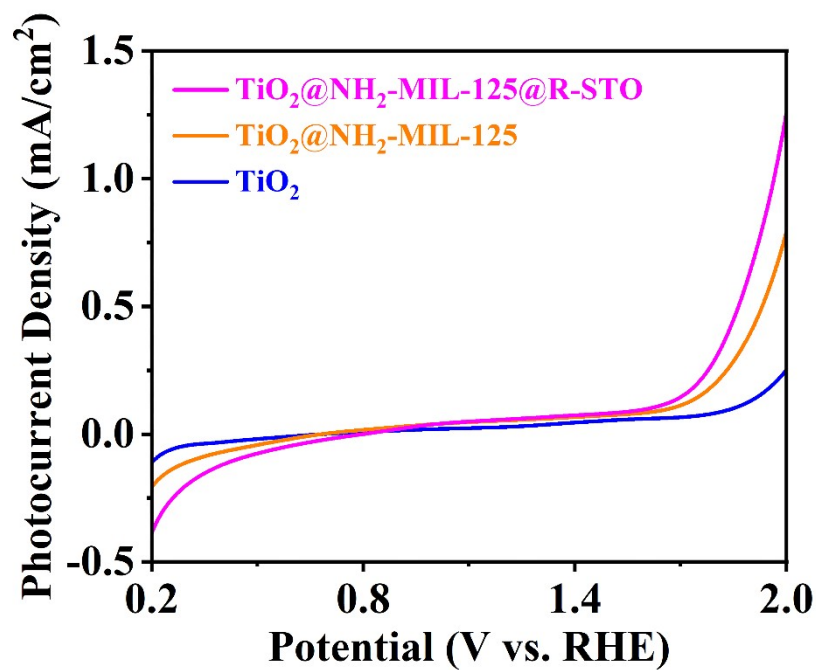


Fig. S12 LSV curves of TiO_2 , $\text{TiO}_2@\text{NH}_2\text{-MIL-125}$, and $\text{TiO}_2@\text{NH}_2\text{-MIL-125@R-STO}$ in dark.

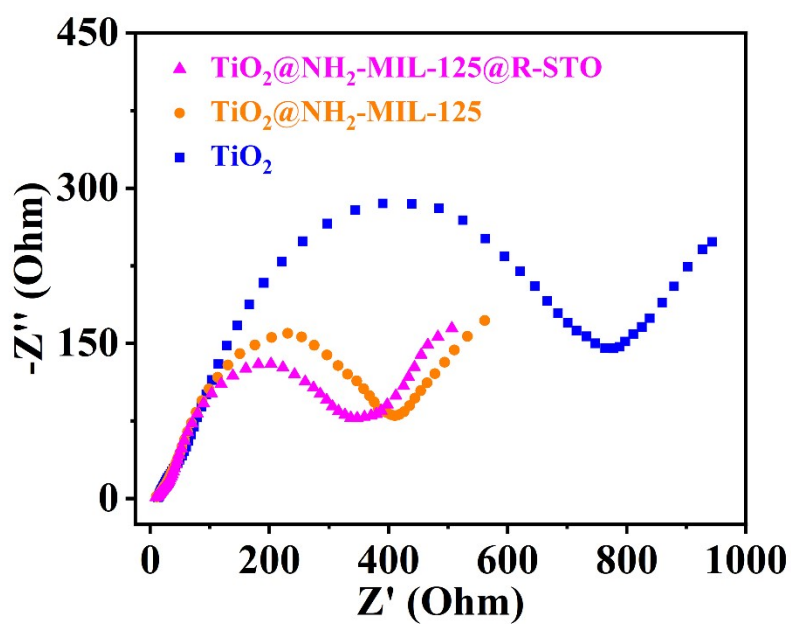


Fig. S13 Nyquist plots of TiO_2 , $\text{TiO}_2@\text{NH}_2\text{-MIL-125}$, and $\text{TiO}_2@\text{NH}_2\text{-MIL-125@R-STO}$ under illumination.

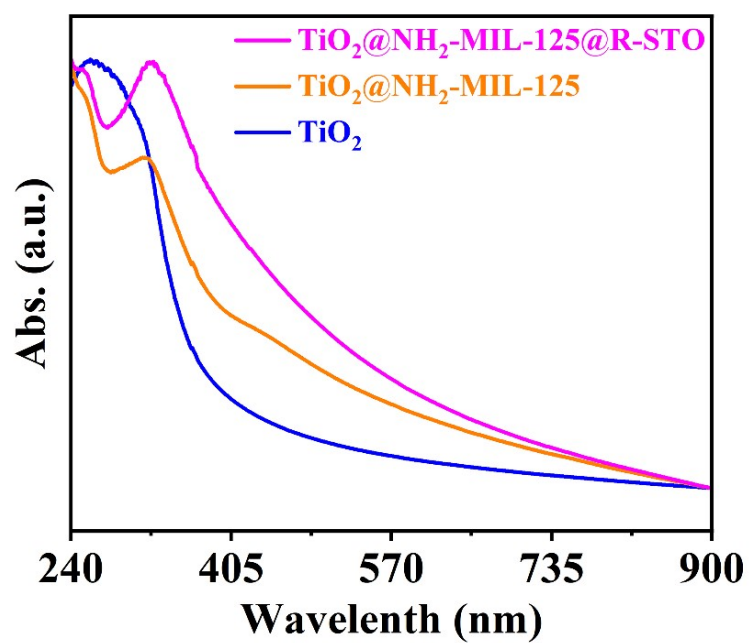


Fig. S14 UV-Vis absorption spectra of TiO_2 NRs, $\text{TiO}_2@NH_2\text{-MIL-125}$, $\text{TiO}_2@NH_2\text{-MIL-125@R-STO}$ photoanodes.

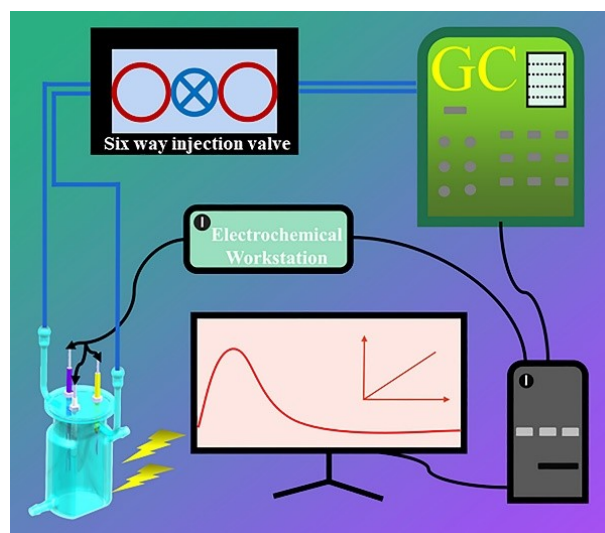


Fig. S15 The schematic diagram of the PEC reaction system.

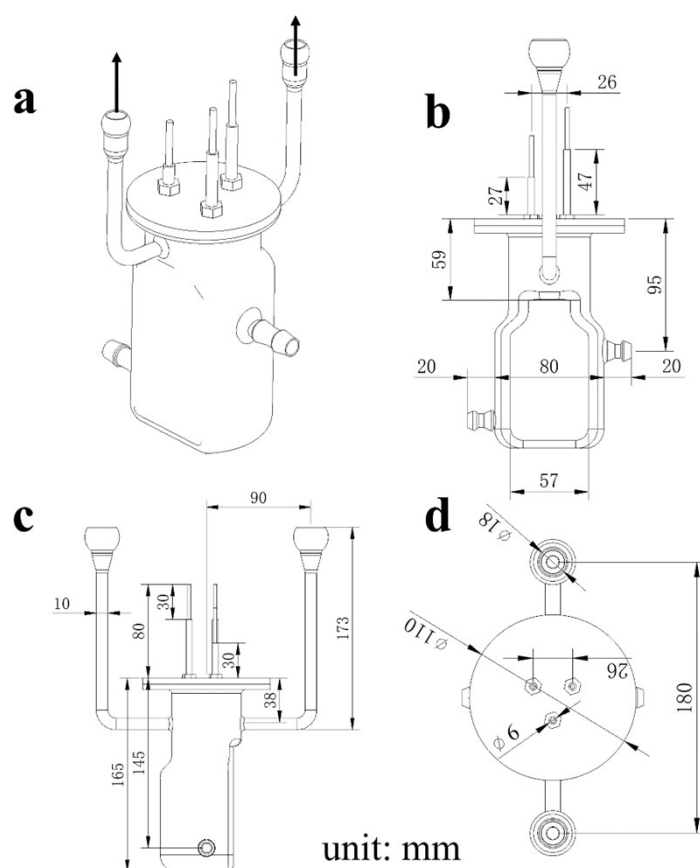


Fig. S16 The size of the home-made reaction cell.

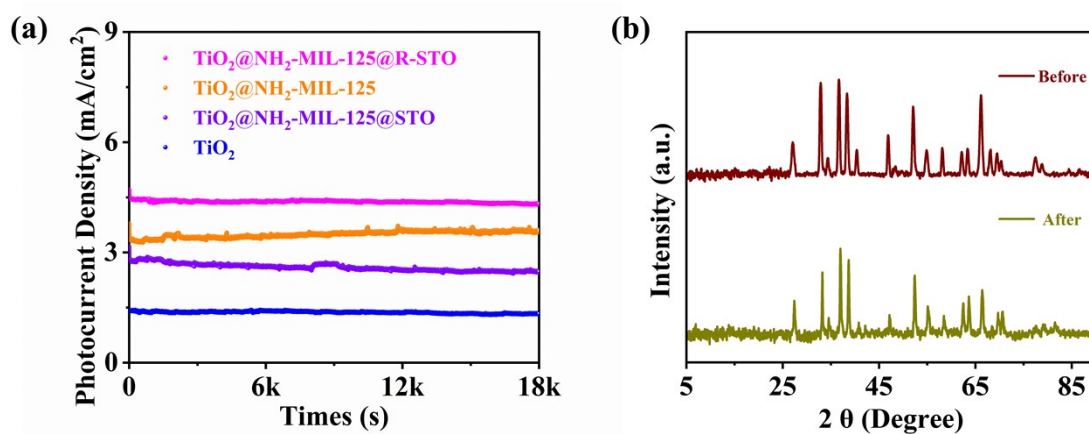


Fig. S17 The stability of TiO_2 , $\text{TiO}_2@\text{NH}_2\text{-MIL-125}$, $\text{TiO}_2@\text{NH}_2\text{-MIL-125}@\text{STO}$ and $\text{TiO}_2@\text{NH}_2\text{-MIL-125}@\text{R-STO}$. (b) The PXRD of $\text{TiO}_2@\text{NH}_2\text{-MIL-125}@\text{R-STO}$ before and after PEC water splitting for 5h.

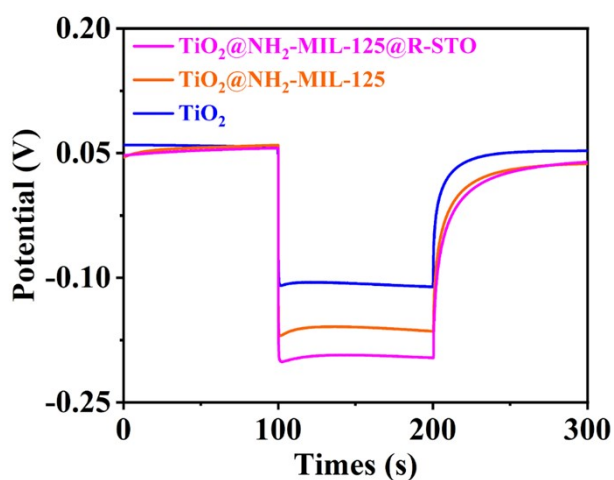


Fig. S18 Open-Circuit Photo-Voltage (OCP) curves of TiO_2 , $\text{TiO}_2@NH_2\text{-MIL-125}$, and $\text{TiO}_2@NH_2\text{-MIL-125@R-STO}$.

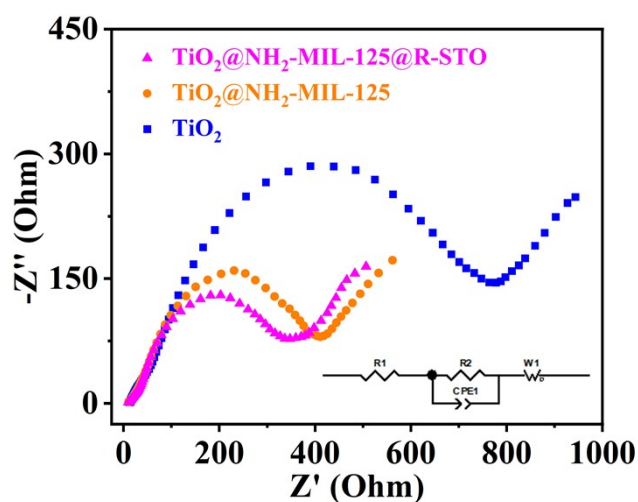


Fig. S19 Bode-Phase plots of TiO_2 , $\text{TiO}_2@NH_2\text{-MIL-125}$, and $\text{TiO}_2@NH_2\text{-MIL-125@R-STO}$ (Insert: the equivalent circuit model corresponding to the EIS).

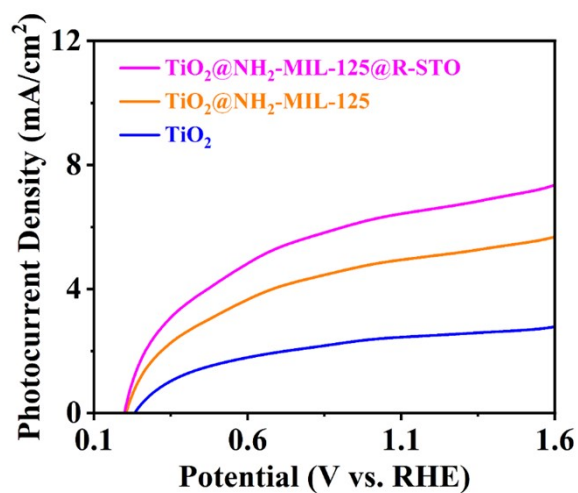


Fig. S20 LSV plots of the samples in 0.5 M $\text{Na}_2\text{SO}_3/\text{Na}_2\text{SO}_4$.

Equation S1 :

$$\eta = [j(E_{\text{rev}}^{\theta} - |V|)]/J_{\text{light}}$$

where η is the photoconversion efficiency, j is the photocurrent density ($\text{mA} \cdot \text{cm}^{-2}$), E_{rev}^{θ} is the standard reversible potential (1.23 V vs. RHE), V and J_{light} are applied potential and incident light intensity, respectively.^[5]

Equation S2 :

$$J_{\text{abs}} = \int_{300}^{\lambda_e} \frac{\lambda}{1240} \times N_p(\lambda) \times \text{LHE}(\lambda) d\lambda$$

$$\text{LHE}(\lambda) = 1 - 10^{-A(\lambda)}$$

Where λ is the wavelength (nm), λ_e is the absorption edge wavelength of photoanodes, $N_p(\lambda)$ is the photo flux ($\text{mA} \cdot \text{cm}^{-2}$), and $A(\lambda)$ is the absorbance at wavelength λ .^[6]

Table S1. Comparison of the PEC catalytic performance of the catalysts under light irradiation.

	Material	Current density (mA/cm^2)	Electrolyte	Ref.
1	Acac-PEG decorated PbCrO_4	$3.15 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	0.5 M PBS	[7]
2	$\text{Ta}:\text{Fe}_2\text{O}_3/\text{Fe}_2\text{O}_3/\text{FTO}$	$1.93 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	1M KOH	[8]
3	$\text{Ti}-\text{Fe}_2\text{O}_3$ MCs	$2.5 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	1M NaOH	[9]
4	$\text{In}_2\text{S}_3/\text{TiO}_2$	$2.74 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	1M NaOH	[10]
4	$\text{CsTaWO}_{6-x}\text{N}_x$	$\sim 2.5 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	0.5 M K_2HPO_4	[11]
5	$\text{Li}_{0.2}\text{TiO}_2$	$1.87 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	1M NaOH	[12]
6	pnp- SnS_2	$3.28 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	0.5 M Na_2SO_4	[13]
7	$\text{BVO}/\text{F}_x\text{N}_{4-x}\text{-H}$	$3.65 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	1M KOH	[14]
8	$\text{Fe}_2\text{TiO}_5\text{-TiO}_2$	$\sim 0.3 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	1M NaOH	[15]
9	$\text{BiVO}_4/\text{TiO}_2$	$1.7 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	0.5M K-Pi /1M Na_2SO_3	[16]
10	CQDs-H/ TiO_2	$3.0 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	1 M KOH	[17]
11	$\text{TiO}_2/\text{NH}_2\text{-MIL-125@R-STO}$	$4.4 \text{ mA}/\text{cm}^2$ at $1.23 V_{\text{RHE}}$	0.5 M Na_2SO_4	This work

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