

## Supporting Information

### 1. Characterization

X-ray diffractometer (XRD, Rigaku, Smart LAB SE) was used to obtain crystalline phase of the samples. The morphology was characterized by scanning electron microscope (SEM, Sigma) and transmission electron microscopy (TEM, FEI Talos F200X). X-ray photoelectron spectrometry (XPS, Kratos, AXIS NOVA) was employed to obtain the surface elemental components and their states. UV-vis diffuse reflection spectrophotometry (UV-vis DRS, Shimadzu, UV-3600) was used to reveal the light absorption features. Steady state photoluminescence spectra were measured by a fluorescence spectrophotometer (PL, Hitachi, F7000).

### 2. Photoelectrochemical performance

3 mg catalyst was highly dispersed into 3 mL water, then 1 mL of suspension was dripped onto a FTO conductive glass, and dried at ambient condition as working electrode. Transient current density, electrochemical impedance spectroscopy (EIS), cyclic voltammetry curve (CV) as well as Mott-Schottky (MS) were measured in 0.5 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution (pH=7). The reference and counter electrode are Hg/HgCl<sub>2</sub> and Pt wire, respectively.

### 3. Photocatalytic H<sub>2</sub> evolution experiments

The experiments were executed in a jacketed reactor in a sealed vacuum environment at 30 °C maintained by flowing circulating water. Specifically, 10 mg of photocatalyst was added into 100 mL TEOA aqueous solution (20 v%). The reactor was irradiated under a 300 W Xe lamp. The amount of H<sub>2</sub> was measured via gas chromatography.

Photocatalytic H<sub>2</sub> production experiment with 365 nm band-pass filter can be performed to measure the apparent quantum efficiency (AQE), which can be calculated from the formula as follows.

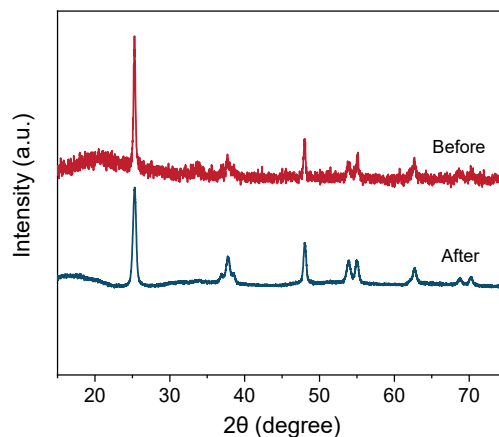
$$\begin{aligned} \text{AQE} &= \frac{2 \times \text{the number of evolved H}_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\% \\ &= \frac{2 \times n(\text{H}_2) \times N_A \times h \times c}{ISt\lambda} \times 100\% \end{aligned}$$

Where  $N_A$  represents Avogadro constant at  $6.022 \times 10^{23} \text{ mol}^{-1}$ ;  $I$  is the energy density of incident light ( $\text{W}/\text{m}^2$ );  $S$  represents irradiation area at  $0.00385 \text{ m}^2$ ;  $t$  denoted illumination time(s);  $h$  represents the Planck constant at  $6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ ;  $\lambda$  is wavelength of incident light at  $3.65 \times 10^{-7} \text{ m}$ ;  $c$  represents the speed of light at  $3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1}$ .

#### 4. Active species capture experiment

First, 0.32 g NaOH and 0.3322 g terephthalic acid (TA) are dispersed in the 400 mL of deionized water. 10 mg photocatalyst was dispersed into 100 mL of above solution. Subsequently, the solution was irradiated under a 300 W Xe lamp, and 3 mL of liquid was filtered and collected at 10 min intervals. The obtained solution was measured by a fluorescence spectrophotometer (PL, Hitachi, F7000) and the signal of  $\text{TA}\cdot\text{OH}^-$  can be observed at 425 nm.

Electron spin resonance (ESR) experiment was used to further reveal the existence of hydroxyl radical ( $\cdot\text{OH}$ ). The 5,5-dimethyl-1-pyrroline (DMPO) was applied as scavengers to determine  $\cdot\text{OH}$  in ultrapure water.



**Fig. S1.** XRD pattern of 15%- $\text{Co}_{0.85}\text{Se}/\text{TiO}_2$  composite before and after use.

**Table S1.** Comparison of various cobalt selenides as electrocatalysts.

Catalysts	Electrolyte	capacity	Overpotential (mV) at 10 mA cm <sup>-2</sup> ( $\eta_{10}$ , HER/OER)	Reference
Co <sub>0.85</sub> Se/CNTS	/	194 mAh·g <sup>-1</sup> (1000 mA·g <sup>-1</sup> )	/	[1]
Co <sub>0.85</sub> Se/rGO	/	460 mAh·g <sup>-1</sup> (500 mA·g <sup>-1</sup> )	/	[2]
Co <sub>0.85</sub> Se@N-doped rGO	/	400.8 mAh·g <sup>-1</sup> (10 A·g <sup>-1</sup> )	/	[3]
MWCNTs/Co <sub>0.85</sub> Se	0.5 M H <sub>2</sub> SO <sub>4</sub>	/	266	[4]
FeCoSe <sub>2</sub> /Co <sub>0.85</sub> Se	1.0 M KOH	/	330	[5]
Co <sub>0.85</sub> Se-NC/C	1.0 M KOH	/	298	[6]
Co <sub>0.85</sub> Se	1.0 M KOH	/	243	[7]
Co <sub>3</sub> O <sub>4</sub> /Co <sub>0.85</sub> Se/Co <sub>9</sub> Se <sub>8</sub>	1.0 M KOH	/	360	[8]
Co <sub>0.85</sub> Se spheres	1.0 M KOH	/	290	[9]

**Table. S2.** Related reports of TiO<sub>2</sub> photocatalyst in the literature.

Photocatalyst	Solution	Light source	HER	Ref.
NiO/TiO <sub>2</sub>	20 v% methanol	300 W Xe lamp	1549.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[10]
WO <sub>3</sub> /TiO <sub>2</sub> /rGO	20 v% methanol	350 W Xe lamp	245.8 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[11]
CoS@TiO <sub>2</sub>	10 v% lactic acid	150 W Xe lamp	194.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[12]
CoP/TiO <sub>2</sub>	10 v% methanol	300 W Xe lamp	604 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[13]
TiO <sub>2</sub> /BiYO <sub>3</sub>	20 v% methanol	300 W Xe lamp	634.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[14]
CuPc/TiO <sub>2</sub>	40 v% methanol	300 W Xe lamp ( $\lambda > 420$ nm)	95 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[15]
Cu <sub>3</sub> P/TiO <sub>2</sub>	30 v% methanol	300 W Xe lamp	607.5 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[16]
BP/TiO <sub>2</sub>	17 v% methanol	300 W Xe lamp	112 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	[17]

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