Supporting Information

Engineering Hetero-MOF-derived TiO_2-Co_3O_4 heterojunction decorated with nickel nanoparticles for enhanced photocatalytic activity even in pure water

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1. Experimental Section

1.1 Chemicals: $Ni(NO_3)_2·6H_2O$, $Co(NO_3)_2·6H_2O$, Titanium butoxide ($Ti(OC_4H_9)_4$), N, N-Dimethylformamide (DMF) and polyvinyl pyrrolidone (PVP) were purchased from Shanghai Macklin Biochemical Co., Ltd, China. Sodium borohydride ($NaBH_4$), Hexadecyl trimethyl ammonium bromide (CTAB), P-Phthalic acid (PTA) and 2-Methylimidazole (MIM) were ordered from Shanghai Aladdin Industrial Co., Ltd, China. Ethanol and Methanol could be obtained from Tianjin Fuyu Fine Chemical Co., Ltd, China. All the reagents were analytical grade without further purification. Deionized water was used throughout this study.

1.2 Sample preparation.

1.2.1 Synthesis of MIL-125 (Ti). MIL-125 (Ti) was synthesized by a modified method, 1.49517g PTA and 0.39 mL $Ti(OC_4H_9)_4$ were added into the DMF (15 mL) and ethanol (5 mL) mixture solution. After stirring for 1 h, the mixture was transferred into a 50 mL Teflon-lined autoclave followed by solvothermal treatment at 180 °C for 16 h, and then cooled to room temperature naturally. The treated precipitate was collected by centrifugation and washed thoroughly with DMF and ethanol for two times, respectively. Finally, MIL-125 (Ti) could be obtained after the product was dried at 60 °C overnight.

1.2.2 Synthesis of MIL-125/ZIF-67. In a typical synthesis, 100 mg MIL-125 and 1g PVP were dissolved in 30 mL deionized water under ultrasonication, followed by stirring for 30 min. Then, the obtained mixed solution was rinsed three times with deionized water. Then the precipitates, $Co(NO_3)_2·6H_2O$ and MIM (molar ratio of $Co(NO_3)_2·6H_2O$ to MIM is 1:10.) were dissolved in 30 mL methanol to obtain precipitates. After stirring for 24 h. The precipitates were collected by centrifugation, following by washing with absolute ethanol three times. After the washing treatment, the product was dried at 60 °C overnight, the final products are called MIL-125/ZIF-67.

1.2.3 Synthesis of TiO_2/Co_3O_4. A typical prepared process of TiO_2/Co_3O_4 is as follows: the powder of MIL-125/ZIF-67 was ground for 5 min until smooth and well blended. TiO_2/Co_3O_4 could be obtained after the mixture was calcined at 500 °C for 2 h (the heating rate was 5°C/min) in muffle furnace under air atmosphere. The theoretical molar ratios of Co_3O_4/TiO_2 were 1, 3 , 5, 7 and 10 %, respectively, and the samples were labeled TiO_2/Co_3O_4 1 at%, TiO_2/Co_3O_4 3 at%, TiO_2/Co_3O_4 5 at% (or TiO_2/5at%Co_3O_4), TiO_2/Co_3O_4 7 at% and TiO_2/Co_3O_4 10 at%, respectively. If the single MIL-125 and ZIF-67 was calcined, the pure TiO_2 and Co_3O_4 could be obtained, respectively.

1.2.4 Synthesis of $TiO_2/Co_3O_4/Ni$. Ni nanoparticles were in-situ deposited on TiO_2/Co_3O_4 by photoreduction in the photocatalytic reaction of TiO_2/Co_3O_4 powder and $Ni(NO_3)_2·6H_2O$. The as-synthesized precipitates were washed three times with deionized water, and dried at 60 °C overnight in air, the final products are called $TiO_2/Co_3O_4/Ni$.

1.2.5 Synthesis of TiO_2 by precipitation method. The TiO_2 nanoparticle were synthesized through a precipitation method.[1] In a typical synthesis of procedure, 1 mL $Ti(OC_4H_9)_4$ was firstly added to the 20 mL of isopropyl alcohol, and then 1 mL distilled water was slowly added into the above solution dropwise. After aging under continuous stirring for 30 min, the obtained flocculent precipitate was formed and collected by centrifugation, washed subsequently with distilled water and ethanol for three times respectively. The precipitate was dried in vacuum for some time in order to vaporize most of ethanol and water, and then calcined at 500 °C for 2 h. After heat treatment, the samples were cooled to room temperature, the final product was denoted as TiO_2-P.

1.2.6 Synthesis of TiO_2/Co_3O_4 by precipitation method. In a typical synthesis of procedure, 1 g TiO_2-P, suitable amount of $Co(NO_3)_2\cdot 6H_2O$ and 2 g CTAB were added to the 30 mL of distilled water and stirred until dissolved. Then added ammonia and adjusted PH=6~9. The precipitate was collected after stirring for 2 h, and then washed subsequently with distilled water and ethanol for three times respectively. The precipitate was dried in vacuum for some time in order to vaporize most of ethanol and water, and then calcined at 500 °C for 2 h. After heat treatment, the samples were cooled to room temperature, the final products was abbreviated as TiO_2/Co_3O_4-P.

1.2.7 Synthesis of $TiO_2/Co_3O_4/Ni$ by reduction of $Ni(NO_3)_2$ by $NaBH_4$. The suitable TiO_2/Co_3O_4 P, $NaBH_4$ and $Ni(NO_3)_2\cdot 6H_2O$ were added to the 20 mL ice-distilled water and continued stirring for 30 minutes. The as-synthesized precipitates were washed three times with deionized water, and dried at 60 °C overnight in air, the final product was abbreviated as $TiO_2/Co_3O_4/Ni$-P.

2. Characterization

Powder X-ray diffraction (XRD) patterns were taken by using a Rigaku-miniflex 6 powder X-ray diffractometer equipped with Cu-Ka (λ=0.15406 nm) radiation with a scan rate of 10° min-1 at 2θ ranging from 10° to 80°. Valance band positions of the samples are determined by X-ray photoelectron spectroscopy (XPS), which were recorded on an ESCALAB250XI X-ray photoelectron spectrometer (Thermo Fisher Scientific) using Al Kα radiation, and all binding energies were referred to the C1s peak of 284.8 eV. The content of the metal element was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (ICPOES-730, Agilent). The morphologies of the resultant samples were observed by a transmission electron microscopy (TEM) (JEM-2100, JEOL). The elementary composition of samples was analyzed by the energy dispersive spectrometer (EDS) (JSM-6700F, JEOL) and elemental mapping. Steady photoluminescence (PL) emission spectra were tested by a luminescence spectrophotometer (QM-400, PTI) with 350 nm excitation wavelength. Ultraviolet-visible (UV-vis) diffuse reflectance spectra (DRS) were obtained using a UV–vis spectrophotometer (UV-2600, SHIMADZU).

Electrochemical measurements

The electrochemical experiments were carried out at room temperature using a conventional three-electrode system with a glassy carbon electrode (3 mm in diameter), (sheet resistance 20-25 Ω/square) as the working electrode, a platinum wire as the auxiliary electrode, and an Ag/AgCl electrode as the reference electrode. All the samples were dispersed in deionized water with a concentration of 1.5 mg/mL and deposited on the glassy carbon electrode and dried infrared light irradiation. Na_2SO_4 (0.5 M) solution was used as the supporting electrolyte. The electrocatalytic hydrogen evolution reaction was measured in 1 M KOH solution. EIS and transient photocurrent responses data were recorded using Electrochemical (Bio-Logic SP-150) workstation under a surface power density of about 0.1 mW/cm^2.

3. Photocatalytic Hydrogen Production.

The photocatalytic H_2-production experiments were performed via a photocatalytic H_2-production activity evaluation system (CEL-SPH2N, CEAULight, China) in a 300 mL Pyrex flask, and the openings of the flask were sealed with silicone rubber septum. A 300 W xenon arc lamp, which was positioned 13 cm away from the reaction solution, was used as a all light source to trigger the photocatalytic reaction. The focused intensity on the flask was~200 $mW \cdot cm^{-2}$, which was measured by a FZ-A visible-light radiometer (made in the photoelectric instrument factory of Beijing Normal University, China). In a typical photocatalytic H_2-production experiment, 50 mg of the as-prepared photocatalyst was suspended in 50 mL of mixed aqueous solution containing 10 ml Methanol. Before irradiation, the system was vacuumed for 5 min via the vacuum pump to completely remove the dissolved oxygen and ensure the reactor was in an anaerobic condition. A continuous magnetic stirrer was applied at the bottom of the reactor to keep the photocatalyst particles in suspension during the experiments. H_2 content was analyzed by gas chromatography (GC-7900, CEAULight, China). All glasswares were carefully rinsed with DI water prior to usage. After the reaction, the H_2O_2 amount was determined by a colorimetric titration method based on the formation of a yellow coloured complex Ti^{IV}-H_2O_2, using a UV/Vis spectrophotometer at 410 nm. The apparent quantum efficiencies (AQEs) are presented in Table S2.

4. Supporting Figures

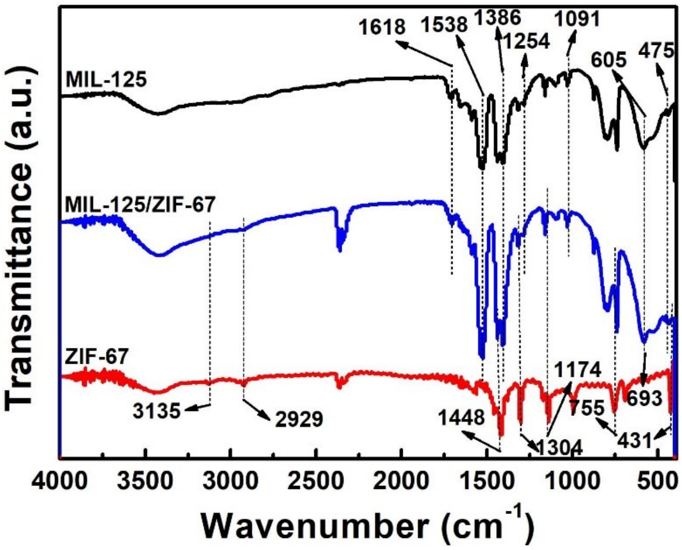

Fig. S1 FT-IR spectrum of the prepared MIL-125, ZIF-67 and MIL-125/ZIF-67.

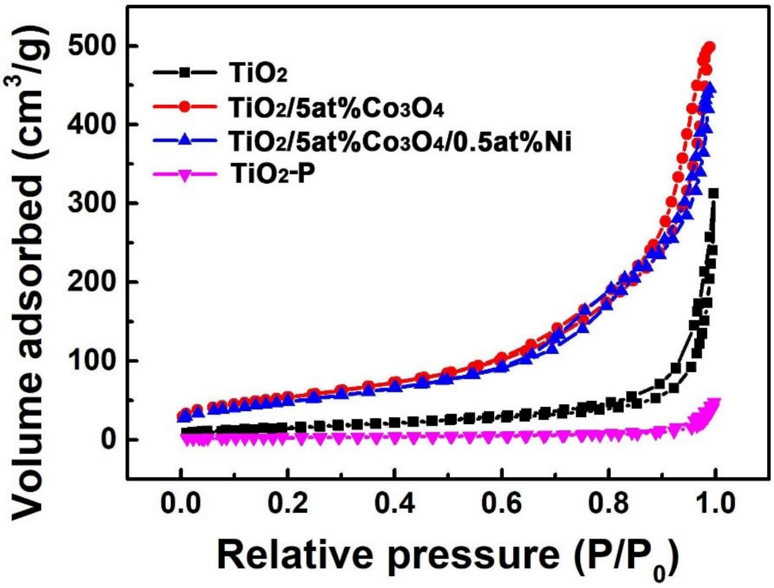

Fig. S2 N_2 adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of TiO_2, TiO_2/5at%Co_3O_4, TiO_2/5at%Co_3O_4/0.5at%Ni and TiO_2-P by precipitation method.

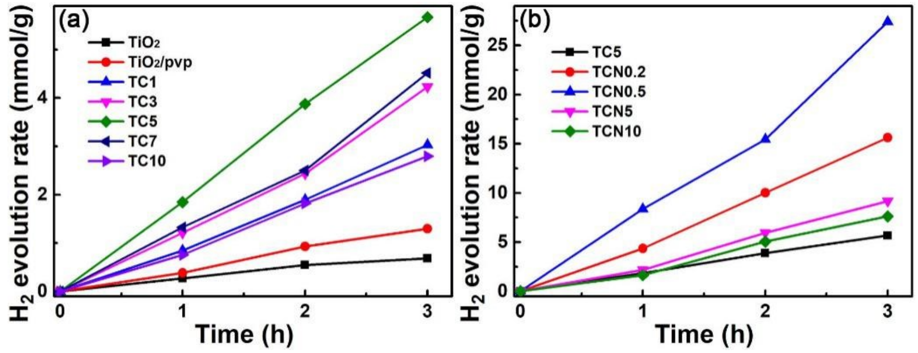

Fig. S3 Photocatalytic H_2 production rate of (a) TiO_2/Co_3O_4 with different amount of Co and (b) TiO_2/Co_3O_4/Ni with different amount of Ni under UV-visible irradiation.

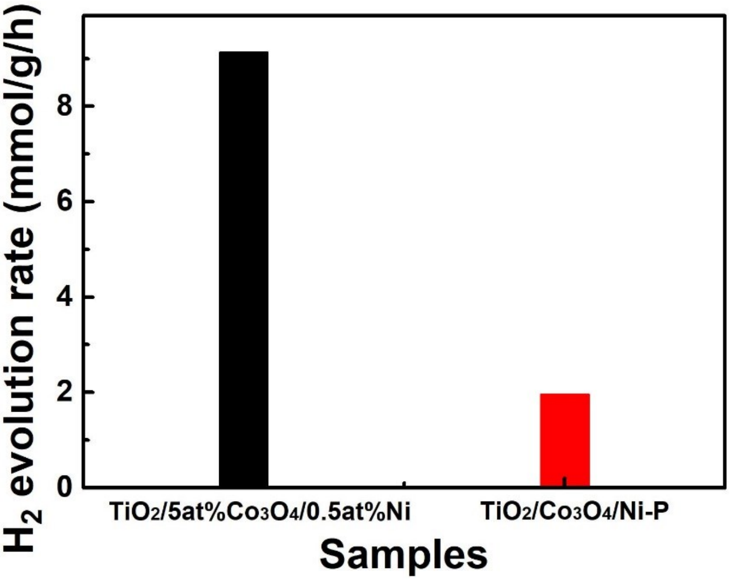

Fig. S4 The photocatalytic activities of TiO_2/5at%Co_3O_4/0.5at%Ni and TiO_2/Co_3O_4/Ni-P by precipitation method.

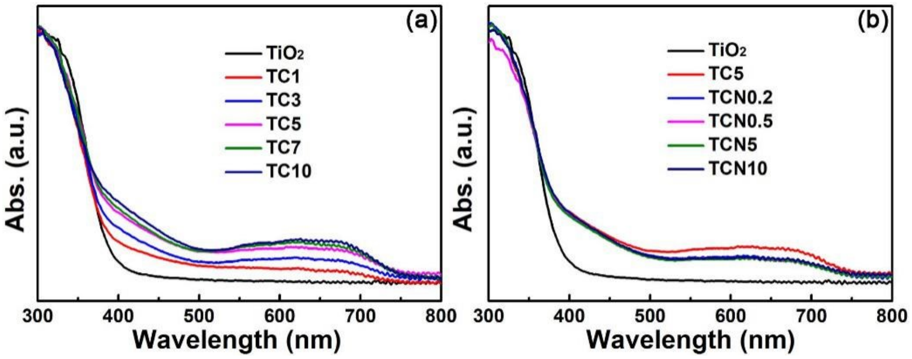

Fig. S5 UV-vis diffuse absorption spectra of (a) TiO_2/Co_3O_4 with different amount of Co and (b) $TiO_2/Co_3O_4/Ni$ with different amount of Ni.

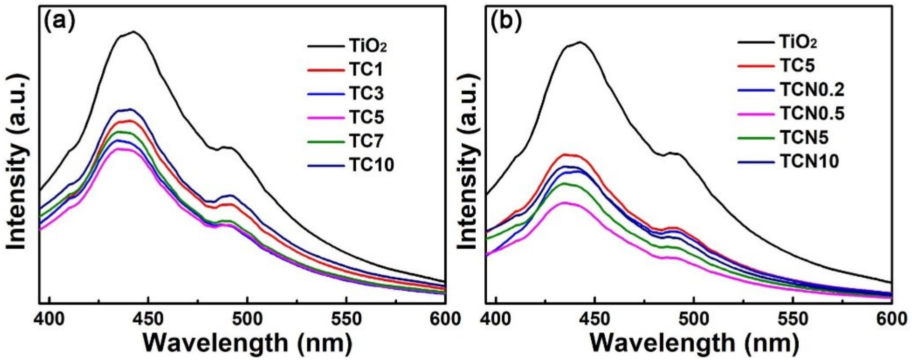

Fig. S6 Photoluminescence spectra of (a) TiO_2/Co_3O_4 with different amount of Co and (b) $TiO_2/Co_3O_4/Ni$ with different amount of Ni.

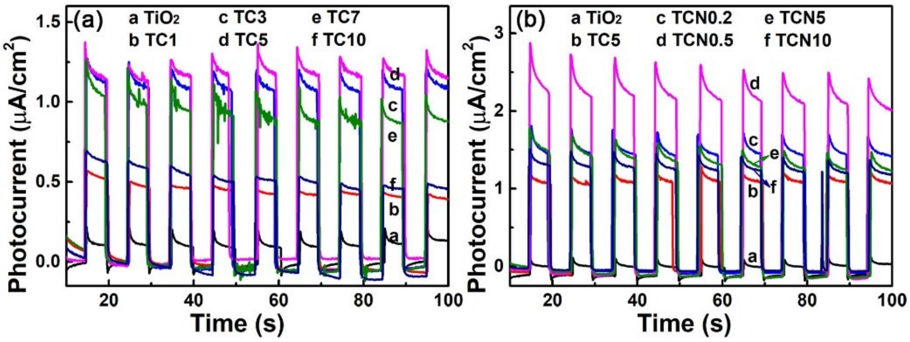

Fig. S7 Transient photocurrent responses of (a) TiO_2/Co_3O_4 with different amount of Co and (b) $TiO_2/Co_3O_4/Ni$ with different amount of Ni.

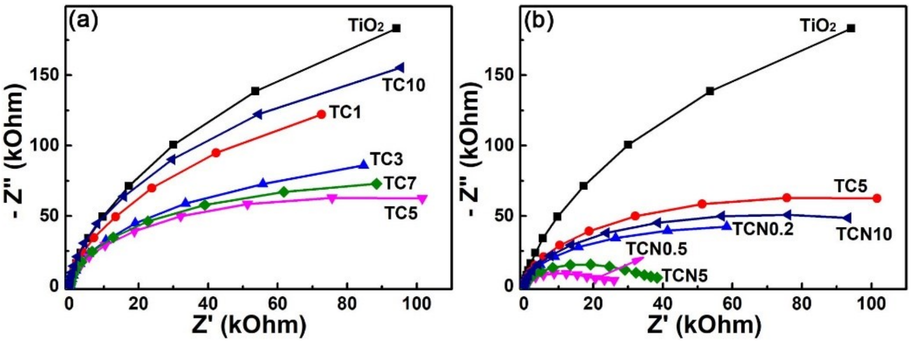

Fig. S8 The Nyquist plots of (a) TiO_2/Co_3O_4 with different amount of Co and (b) $TiO_2/Co_3O_4/Ni$ with different amount of Ni.

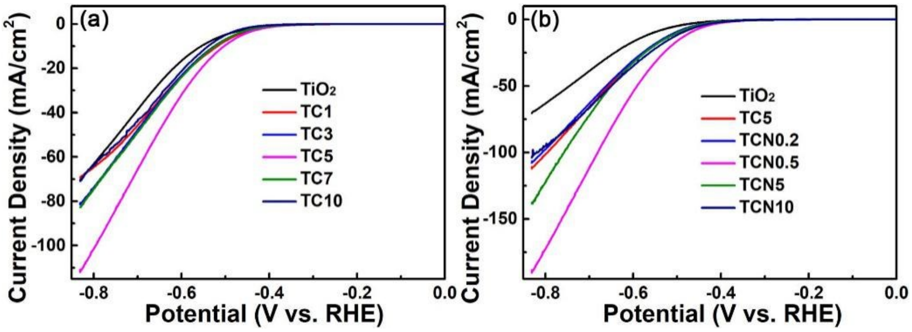

Fig. S9 Electrocatalytic HER of (a) TiO_2/Co_3O_4 with different amount of Co and (b) $TiO_2/Co_3O_4/Ni$ with different amount of Ni.

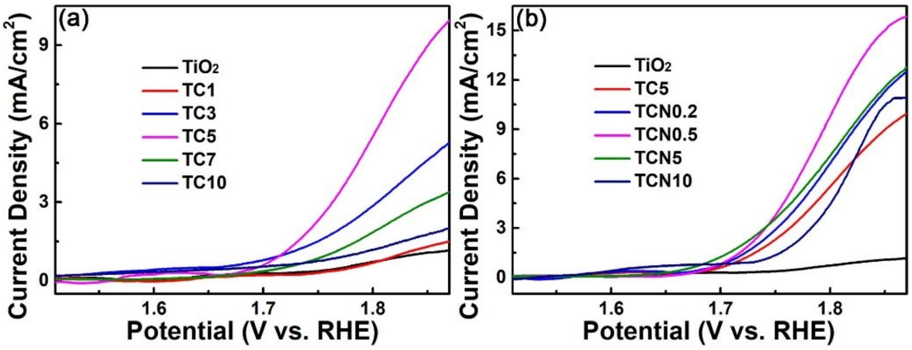

Fig. S10 Electrocatalytic OER of (a) TiO_2/Co_3O_4 with different amount of Co and (b) $TiO_2/Co_3O_4/Ni$ with different amount of Ni.

Table S1 The Co and Ni contents in the as-prepared samples of TCN0.4, TCN0.8 and TCN1 measured by ICP-OES.

Samples	TCN0.4	TCN0.8	TCN1
Co content (at%)	1.18	1.24	1.21
Ni content (at%)	0.24	0.39	0.47

Table S2. Calculated apparent quantum efficiency (AQE) of TiO_2/5at%Co_3O_4/0.5at%Ni samples at different wavelengths.

Wavelength (nm)	H_2 Evolved (μmol)	Light Intensity (mW)	AQY (%)
365	9.23	8.6	19.57
420	5.68	13.1	6.84
475	2.82	18.4	2.65
550	0.8	20.3	0.48
650	0.17	16.5	0.09

λ=365 nm

$$N = \frac{E\lambda}{hc} = \frac{8.6 \times 10^{-3} \times 3600 \times 365 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 5.68 \times 10^{19}$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 9.23 \times 10^{-6}}{5.68 \times 10^{19}} = 19.57\%$$

λ=420 nm

$$N = \frac{E\lambda}{hc} = \frac{13.1 \times 10^{-3} \times 3600 \times 420 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 9.96 \times 10^{19}$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 5.68 \times 10^{-6}}{9.96 \times 10^{19}} = 6.84\%$$

λ=475 nm

$$N = \frac{E\lambda}{hc} = \frac{18.4 \times 10^{-3} \times 3600 \times 475 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.58 \times 10^{20}$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 2.82 \times 10^{-6}}{1.58 \times 10^{20}} = 2.65\%$$

λ=550 nm

$$N = \frac{E\lambda}{hc} = \frac{20.3 \times 10^{-3} \times 3600 \times 550 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 2.02 \times 10^{20}$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 0.8 \times 10^{-6}}{2.02 \times 10^{20}} = 0.48\%$$

λ=650 nm

$$N = \frac{E\lambda}{hc} = \frac{16.5 \times 10^{-3} \times 3600 \times 650 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} = 1.94 \times 10^{20}$$

$$AQE = \frac{the\ number\ of\ reacted\ electrons}{the\ number\ of\ incident\ photons} \times 100\%$$

$$= \frac{2 \times the\ number\ of\ evolved\ H_2\ molecules}{N} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 0.17 \times 10^{-6}}{1.94 \times 10^{20}} = 0.09\%$$

Table. S3. Comparison of photocatalytic performances over the developed photocatalysts with the other photocatalysts reported.

Photocatalysts	Solvents	H_2 evolution rate (μmol/g/h)	Ref.
TiO_2/5at%Co_3O_4/0.5at%Ni	pure water	122.67	This wok
TiO_2/Co_3O_4 quantum dots	pure water	41.8	2
Rutile TiO_2	pure water	56.6	3
Ru/TiO_2	pure water	40.78	4
Au/TiO_2	pure water	116.54	4
TiO_2/C_3N_4	pure water	251	5
TiO_2/g-C_3N_4	pure water	374.2	6
TiO_2 nanobelts	pure water	614	7
Anatase TiO_2	pure water	850	8
Rutile TiO_2	pure water	1229	9

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