Supporting Information

Covalent-Organic Framework Based Z-Scheme Heterostructured Noble-Metal-Free Photocatalysts for Visible-Light-Driven Hydrogen Evolution

Yang-Peng Zhang,^a Hong-Liang Tang,^a Hong Dong,^a Meng-Yao Gao,^a Chang-Cheng Li,^a Xiao-Jun Sun,^{*a} Jin-Zhi Wei,^a Yang Qu,^b Zhi-Jun Li,^b and Feng-Ming Zhang^{*a}

^a Key Laboratory of Green Chemical Engineering and Technology of College of Heilongjiang Province, College of Chemical and Environmental Engineering Harbin University of Science and Technology No. 4, Linyuan Road, Harbin 150040 (China).

^b Key Laboratory of Functional Inorganic Materials Chemistry (Heilongjiang University), Ministry of Education, School of Chemistry and Materials Science, International Joint Research Center for Catalytic Technology, Harbin 150080, P. R. China.

Experimental Section

Materials and General Methods. All of reagents and solvents were commercially available and used without further purification besides 1,3,5-triformylphloroglucinol (Tp) which was prepared from Phloroglucinol according to literature method.¹ The composition, structure and texture properties of the materials were investigated by Fourier transform infrared (FT-IR) spectra (Spectrum 100), X-ray powder diffraction (XRD) patterns (Bruker D8 X-ray diffractometer), thermogravimetric analyses (TGA) (SDTA851e), scanning electron microscopy (SEM) micrographs (Hitachi S-4800) and transmission electron microscopy (TEM) experiment (JEM-2100 electron microscope). The N₂ adsorption-desorption isotherms were determined by Micromeritics ASAP 2020 analyzer at 77 K. Before the measurement, the catalysts were degassed at 120°C for 24 h. Optical properties were also studied by diffuse reflectance UV-vis spectroscopy (Lambda 35 spectrometer), photoluminescence spectrum (PL) (SPEX Fluorolog-3 spectrofluorometer with an excitation wavelength of 350 nm) and time-resolved PL of the samples were recorded with FLS1000 Photoluminescence Spectrometer under excitation of nanosecond flashlamp. The electrochemical impedance spectra (EIS), Mott-Schottky plot and photocurrent-time (I-T) profiles was recorded on the CHI660E electrochemical workstation with a standard three-electrode system with the photocatalyst-coated ITO as the working electrode, Pt plate as the counter electrode and a saturated calomel electrode as a reference electrode. A 0.25 M Na₂SO₄ solution was used as the electrolyte. The assynthesized samples (2 mg) were added into 1 mL ethanol and 10 µL Nafion mixed solution, and the working electrodes were prepared by dropping the suspension (200 µL) onto an ITO glass substrate electrode surface and dried at room temperature. A 300 W Xenon lamp with a 420nm cut-off filter was used as the light source during the measurement. The photo responsive signals of the samples were measured under chopped light at 0.5 V. The surface photovoltage spectroscopy (SPS) measurements of the samples were carried out with a home-built apparatus equipped with a lock-in amplifier (SR830) synchronized with a light chopper (SR540). The powder sample was sandwiched between two ITO glass electrodes by which the outer electric field could be employed. The sandwiched electrodes were arranged in an atmospherecontrolled container with a quartz window, and monochromatic light was obtained by passing light from a 500 W xenon lamp (CHF XQ500W, Global xenon lamp power) through a double prism monochromator (SBP300). The SPS signals are the potential barrier change of testing electrode surface between the presence of light and darkness. EPR spectra were recorded on a Bruker EMX-plus electron paramagnetic resonance spectrometer at room temperature under air atmosphere.

Synthesis of α -Fe₂O₃: α -Fe₂O₃ was prepared by a modified method based on a previous report.² FeCl₃·H₂O (0.137 g) was dispersed in H₂O (0.35 mL) and CH₃CH₂OH (5 mL) under magnetic stirring. Then, CH₃COONa (0.4 g) was added into the solution under magnetic stirring. The mixture was then transferred to a Teflon-lined stainless-steel autoclave with a 15 mL capacity and maintained at 180°C for 12 h for solvothermal crystallization. After it cooled down to ambient temperature, the red product was separated by centrifugation, washed with water several times and dried at 80°C overnight yielding the α -Fe₂O₃ hexagonal nanoplates.

Synthesis of α -Fe₂O₃/TpPa-2 hybrid material: A vacuum valve measuring o.d×i.d. = 19×8 mm² and length 65 mm was charged with Tp (21 mg, 0.1 mmol), 2,5dimethylparaphenylenediamine (Pa-2) (20 mg, 0.15 mmol) and α -Fe₂O₃, wherein different weight ratios of α -Fe₂O₃/TpPa-2 hybrid materials ranging from 0 to 70% (referred to TpPa-2-COF proportion) were synthesized and named TpPa-2-COF, α -Fe₂O₃/TpPa-2-COF (1:9), α -Fe₂O₃/TpPa-2-COF (2:8), α -Fe₂O₃/TpPa-2-COF (3:7), α -Fe₂O₃/TpPa-2-COF (4:6), α -Fe₂O₃/TpPa-2-COF (5:5), α -Fe₂O₃/TpPa-2-COF (6:4) and α -Fe₂O₃/TpPa-2-COF (7:3), respectively. The above mixture was suspended in a solution containing mesitylene (1.5 mL), dioxane (1.5 mL) and aqueous acetic acid (0.5 mL, 3 M). This solution was then sonicated for 30 min in order to form a homogenous solution. Afterwards, the vacuum valve was flash frozen in a liquid N₂ bath (77 K) and degassed by three freeze-pump-thaw cycles, sealed under vacuum, and then heated at 120 °C for 3 days. The products were collected by filtering and washed with anhydrous THF (50 mL) for three times. The powders collected were dried at 180 °C for 12 h under vacuum to afford different weight ratios of α -Fe₂O₃/TpPa-2-COF hybrid materials.

Photocatalytic hydrogen evolution: All photocatalytic experiments were conducted in a 500 mL Pyrex reaction vessel via a photocatalytic H_2 evolution activity evaluation system, where the photoreaction temperature was kept at a constant temperature (4°C) with circulating water through a thermostat. For each experiment, 10 mg of the photocatalyst was suspended in PBS buffer solution (50 mL of 0.1 M solution at pH = 7) containing 100 mg of sodium ascorbate (SA) as sacrificial electron donor, and then the above mixed solution was dispersed in the ultrasound bath for 30 min. The reaction solution was constantly stirred to maintain the entire mixture homogeneous. To thoroughly remove the air inside and make sure that the reaction system was under anaerobic conditions, the whole system was vacuumed for at least 30 min with vacuum bump before irradiation using a 300 W Xenon lamp with a 420 nm cutoff filter. The above reaction solution was stirred for 5 h and irradiated. The hydrogen evolved was determined by a GC112A gas chromatograph with TCD detector. The photocatalytic stability was performed for 25 h in the same processing parameters except that the sacrificial regent was renewed for every 5 h in the aerobic condition.



Figure S1. The XRD patterns of α -Fe₂O₃.



Figure S2. The FT-IR Spectra of as-synthesized samples.



Figure S3. The TGA curves of the as-synthesized samples.



Figure S4. The N₂ adsorption and desorption isotherms of the as-synthesized samples.



Figure S5. The SEM image of α -Fe₂O₃.



Figure S6. The EDS spectra of α -Fe₂O₃/TpPa-2-COF (3:7) hybrid material.



Figure S7. The Mott-Schottky plots of TpPa-2-COF at three different frequencies.



Figure S8. The PXRD patterns of α -Fe₂O₃/TpPa-2-COF (3:7) hybrid material before and after photocatalysis.



Figure S9. The FT-IR spectrum of α -Fe₂O₃/TpPa-2-COF (3:7) hybrid material after photocatalysis.



Figure S10. The SEM image of α -Fe₂O₃/TpPa-2-COF (3:7) hybrid material after photocatalysis.



Figure S11. The TEM and HRTEM images of α -Fe₂O₃/TpPa-2-COF (3:7) hybrid material after photocatalysis.



Figure S12. XPS spectra of Fe 2p region of α -Fe₂O₃/TpPa-2-COF (3:7) hybrid

material before and after photocatalytic reaction.



Figure S13. DMPO spin-trapping EPR spectra of α -Fe₂O₃, TpPa-2-COF, and α -Fe₂O₃/TpPa-2-COF (3:7) without light irradiation.

Apparent Quantum Efficiency (AQE) calculation process:

 $N = \frac{E\lambda}{hc}$ $AQE = \frac{the number of reacted electrons}{the number of incident photons} \times 100\%$ $= \frac{2 \times the number of evoled H_2 molecules}{N} \times 100\%$

h is Plank constant = $6.62606957 \times 10^{-34}$ J·S, *c* is velocity of light = 2.99792458×10^{8} m·S⁻¹.

Calculation of band edge of α -Fe₂O₃

 α -Fe₂O₃ material: The valence band (VB) and conduction band (CB) positions of α -

Fe₂O₃ were calculated by the following equations:³⁻⁵

$$X = (X_{Fe}^{2} * X_{O}^{3})^{1/(2+3)}$$
$$E_{CB} = X - E - 1/2E_{g}$$
$$E_{VB} = E_{CB} + E_{g}$$

where E_{CB} is the CB edge potential, E_{VB} is the VB edge potential, and X is the absolute electronegativity of the semiconductor, expressed as the geometric mean of

the absolute electronegativity of the constituent atoms, which is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy; E is the energy of free electron on the hydrogen scale (4.5 eV) and E_g is the band gap of the semiconductor. Hence, the values of X, E_g , E_{CB} , and E_{VB} of the α -Fe₂O₃ samples are shown in Supplementary Table 1. Accordingly, α -Fe₂O₃ has the E_{CB} and E_{VB} of 0.31 eV and 2.375 eV, respectively.

Sample	$X_{Fe} (eV)$	X ₀ (eV)	X (eV)	E _g (eV)	E _{CB}	E _{VB}
α-Fe ₂ O ₃	4.06	7.45	5.84	2.065	0.31	2.375

Catalyst	Cocatalyst	Sacrificial agent	Light source	Activity	Ref.
Catalyst				(µmol·g ⁻¹ ·h ⁻¹)	
α -Fe ₂ O ₃ /g-C ₃ N ₄	Pt	TEOA	λ>420 nm	398.0	6
α -Fe ₂ O ₃ /g-C ₃ N ₄	Pt	TEOA	λ>400 nm	31400	7
Ni(OH) ₂ /g-C ₃ N ₄		TEOA	λ>400 nm	87	8
BP/RP	Со	no	λ>420 nm	2960	9
Cd _{0.5} Zn _{0.5} S/BiVO ₄	Pt	Na ₂ S/Na ₂ SO ₃	λ>420 nm	2350	10
CdS/Co ₉ S ₈		Na ₂ S/Na ₂ SO ₃	AM 1.5	1061.3	11
CdS/CoS ₂		ascorbic acid	AM 1.5	5540	12
CdS/polyimide	Pt	lactic acid	λ>420 nm	613	13
Fe ₂ O ₃ /g-C ₃ N ₄	Pt	TEOA	λ>420 nm	584	14
g-C ₃ N ₄ /Bi ₄ NbO ₈ Cl	Pt	lactic acid	λ>420 nm	287.71	15
g-C ₃ N ₄ -CuInS ₂		Na ₂ S/Na ₂ SO ₃	λ>420 nm	1290	16
g-C ₃ N ₄ /WO ₃	Pt	TEOA	λ>420 nm	3120	17
ZnO/CdS		Na ₂ S/Na ₂ SO ₃	350 W Xe	4143	18
			lamp		
$g-C_3N_4/\alpha$ -Fe ₂ O ₃	Pt	TEOA	λ>420 nm	2066.2	19
α -Fe ₂ O ₃ /g-C ₃ N ₄	Pt	TEOA	λ>400 nm	77.6	20
α-Fe ₂ O ₃ /TpPa-2-COF		Sodium	λ>420 nm	3770	This
		ascorbate			work

 Table S1. Summary of representative direct Z-scheme photocatalysts in water splitting.

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