Supporting Information

Enhanced photocatalytic H_2 evolution over covalent organic framework through assembled NiS cocatalyst

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Section I. Materials and Methods

1. Materials

Anhydrous 1,2-dichlorobenzene (o-DCB), anhydrous n-butanol (n-BuOH) and chloroplatinic acid hexahydrate were purchased from Aladdin Industrial. Tetrahydrofuran (THF), acetone, Sodium sulfide nonahydrate, Sodium Sulfite, L(+)-Ascorbic acid and Nickel(II) acetate tetrahydrate were purchased from Shanghai Chemical Regents Company. Methyl Alcohol, Ethanol, Triethanolamine and Ascorbic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. 1,3,5-Triformylphloroglucinol (Tp) and 4,4'-biphenyldiamine (BD were purchased from Jilin Chinese Academy of Sciences-Yanshen technology Co. Ltd. Ascorbic acid were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals were used without further purification.

2. Characterizations

Powder X-ray diffraction (PXRD) patterns were collected at room temperature on an X-ray diffraction spectrometer (Bruker D8 Advance, Germany) with Cu Kα radiation at λ = 0.154 nm operating at 40 kV and 40 mA.Fourier transform infrared (FT-IR) spectra were recorded on Nicolet 6700 (Thermofsher, USA) Fourier transformation infrared spectrometer.Solid-state CP/MAS ^{13}C NMR spectra were recorded on 400WB AVANCE III (Bruker, Switzerland) plus 400 MHz spectrophotometer at 298 K.High-resolution transmission electron microscopy images were obtained using a JEOL 2100F microscope operated at 200 kV accelerating voltage. The elemental mappings of C, N, O and S atoms were collected using the same transmission electron microscope (operating at 200 kV) under the ADF STEM mode.The chemical compositions of samples were examined using X-ray photoelectron spectroscopy (XPS) with Thermo Scientific K-Alpha+. All the XPS spectra were corrected according to C 1s line at 284.6 eV. Diffuse reflectance UV-visible absorption spectra were collected on a Lambda 750 spectrometer (referenced to barium sulphate). On the basis of the Kubelka-Munk (KM) method and the UV visible diffuse absorption spectra by the following equation:

$$\alpha h\nu = A(h\nu - Eg)^2,$$

the Eg of all samples can be calculated experimentally, where α, A, h, and hν are the absorption coefficient, constant, and Planck's constant, and photon energy, respectively. Photoluminescence (PL) profiles were performed on Fluorescence Spectrophotometer Qm 40 (PTI, USA) with a 350 nm laser excitation source.The lifetimes of fluorescence spectra was examined by FLS1000 (EdinburghInstruments，UK) equipped with a 350 nm laser as the excitation source and employing Time Correlated Single Photon Counting (TCSPC) technique. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was done on a VARIAN VISTA RL simultaneous spectrometer (Agilent Technologies, Santa Clara, California, USA) with a CCD-detector.Nitrogen sorption isotherms were determined at 77 K using the Quantachrome Autosorb-iQ after more than 8 hours of degassing in vacuum at 120 ℃.

3. Methods

3.1 Electrochemical measurements

Electrochemical measurements were measured by CHI760E electrochemical workstation (Chenhua, Shanghai) in a three electrode cell system. The COF powder was ultrasonically dispersed in ethanol for 10 min. Then the dispersion was drop-cast onto the fluorine-doped tine oxide (FTO) conductive glass for the preparation of the working electrode. The Ag/AgCl electrode worked as the reference electrode while the platinum wire worked as the counter electrode. The Mott–Schottky tests were carried out in 0.1 M Na_2SO_4 solution as the supporting electrolyte. All of the potentials were calibrated to the Reversible Hydrogen Electrode (RHE). Photocurrent measurements were performed using a 300 W Xe lamp with a cutoff filter ($\lambda \geq 420$ nm). Electrochemical impedance spectroscopy (EIS) were measured in 0.1 M NaCl solution.

Section II. Supplementary figures and tables

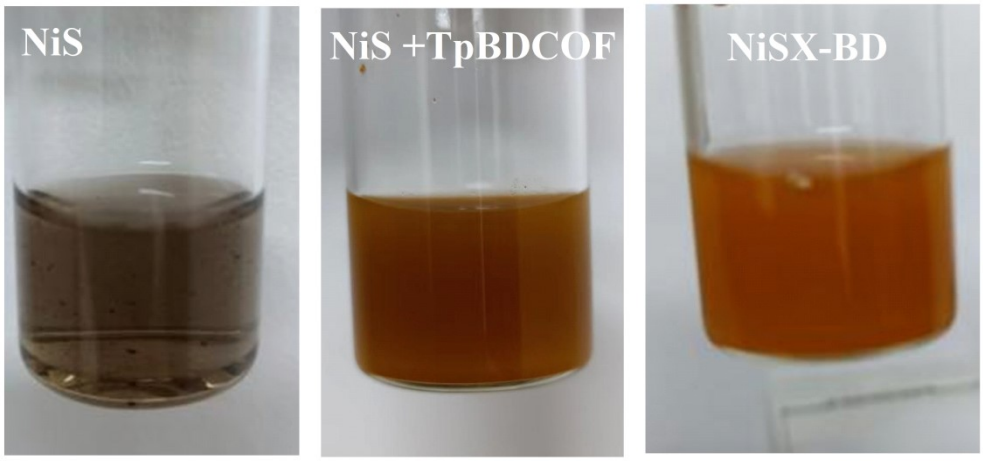

Figure S1. The synthetic experiment of NiSX-BD.

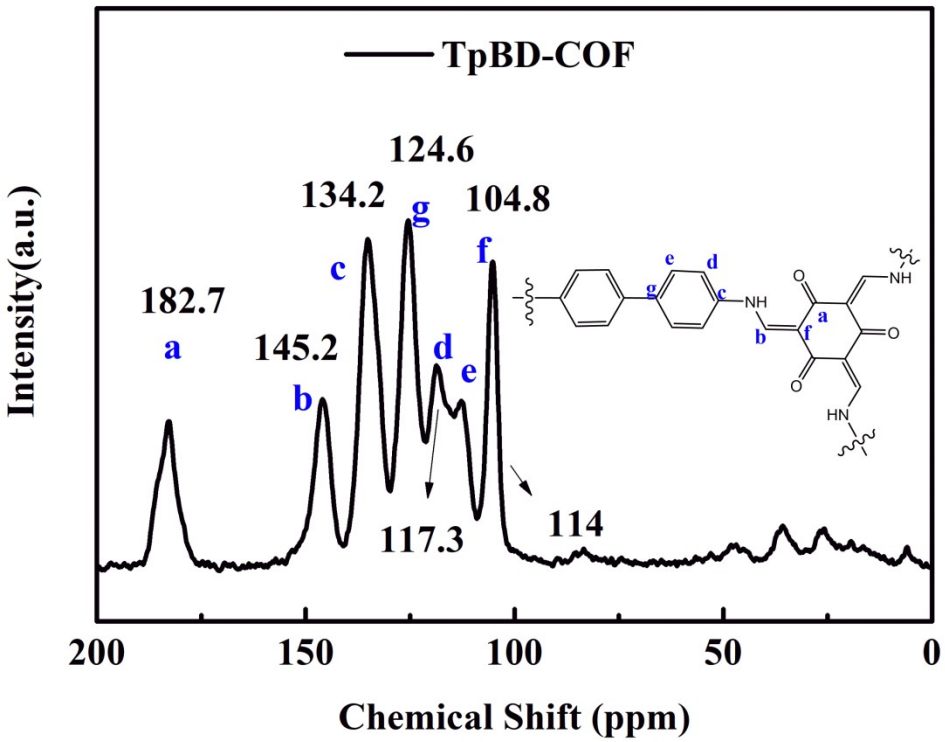

Figure S2. Solid-state ^{13}C NMR spectrum of the TpBD-COF.

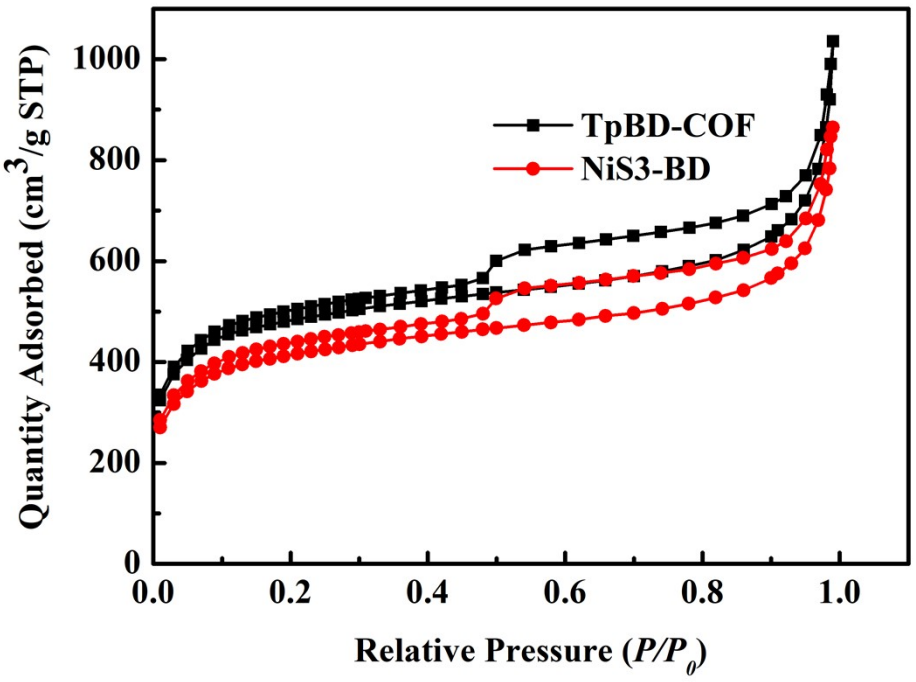

Figure S3. N_2 adsorption (closed circles) and desorption (open circles) isotherms (77 K) of the TpBD-COF and NiS3-BD.

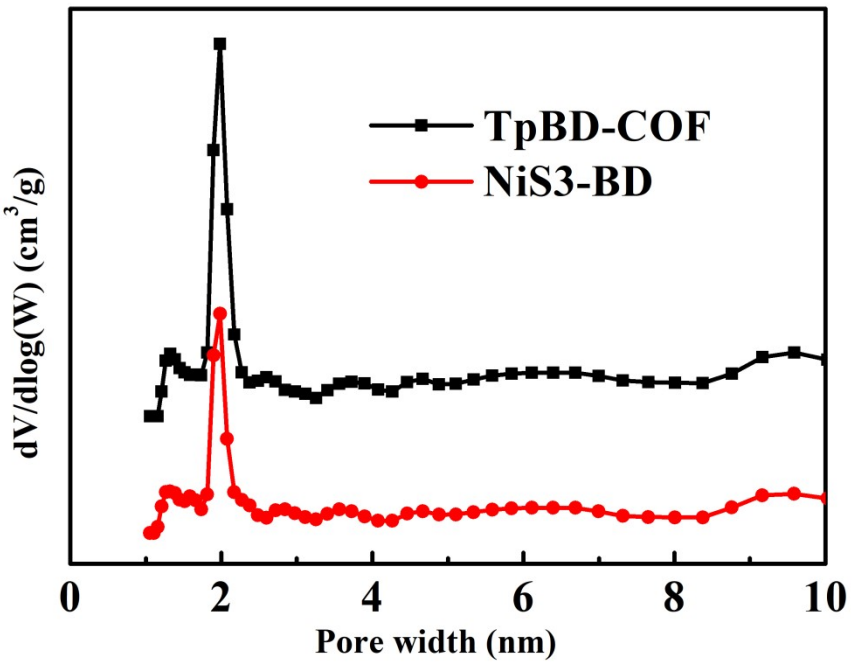

Figure S4. Pore-size distributions of TpBD-COF and NiS3-BD.

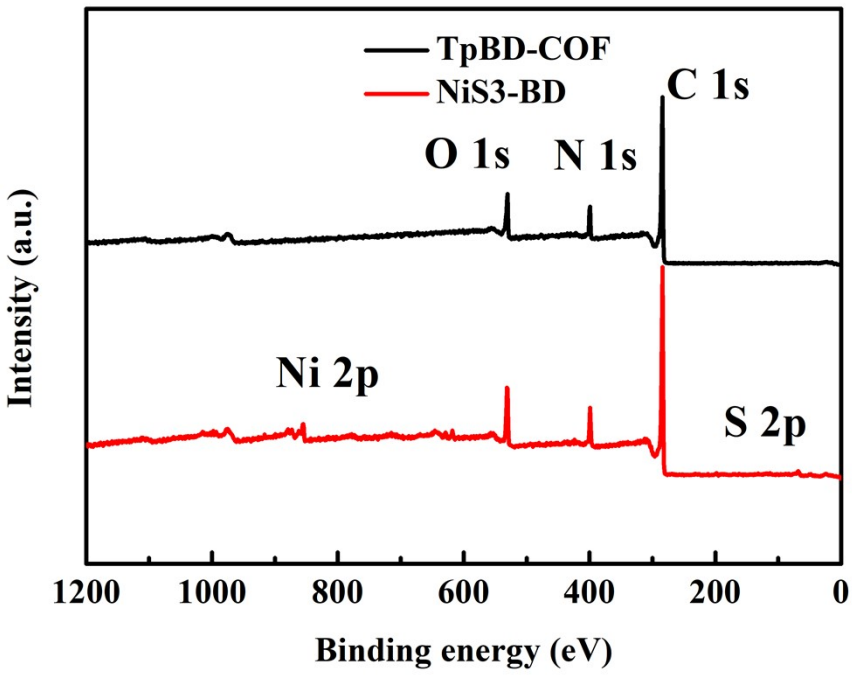

Figure S5. XPS survey spectrum of TpBD-COF and NiS3-BD.

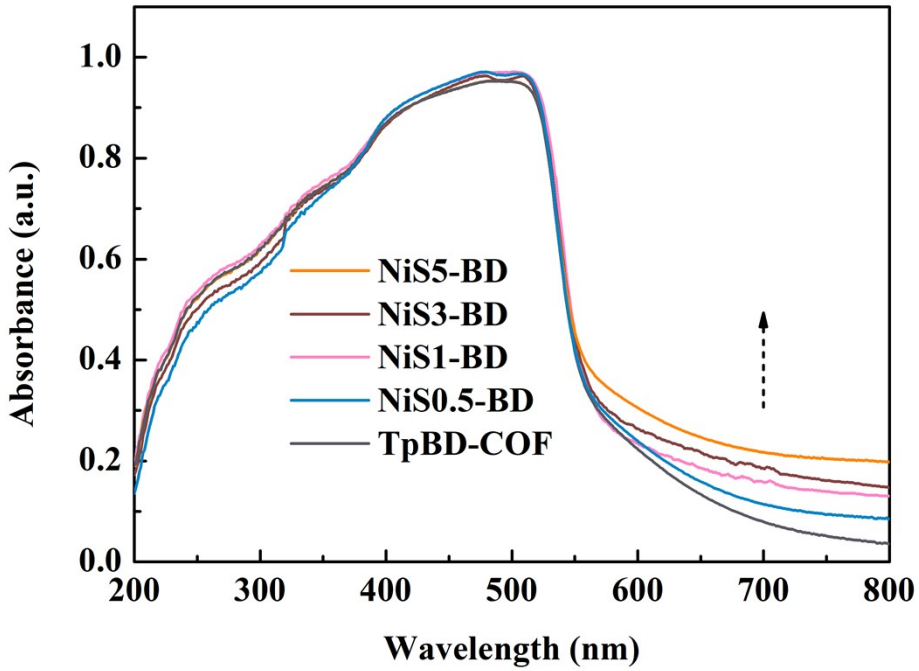

Figure S6. UV-vis diffuse reflectance spectroscopy of TpBD-COF and NiSX-BD.

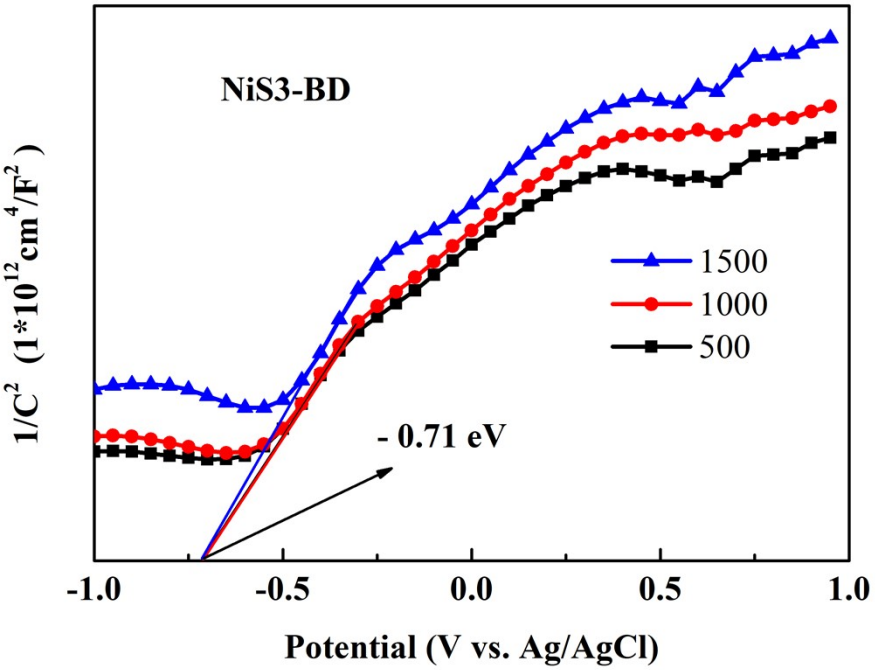

Figure S7. Mott–Schottky plots of the NiS3-BD.

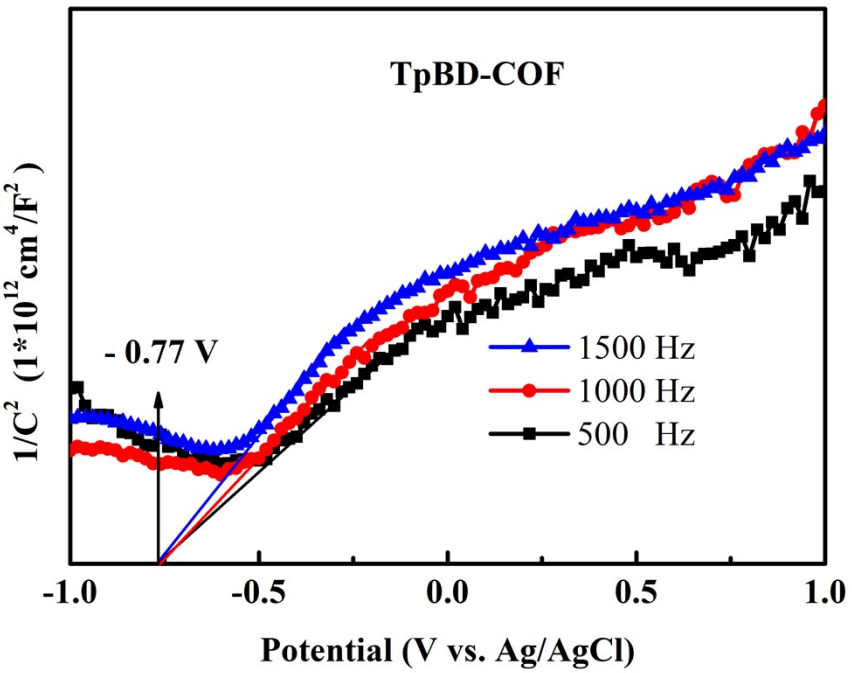

Figure S8. Mott–Schottky plots of the TpBD-COF.

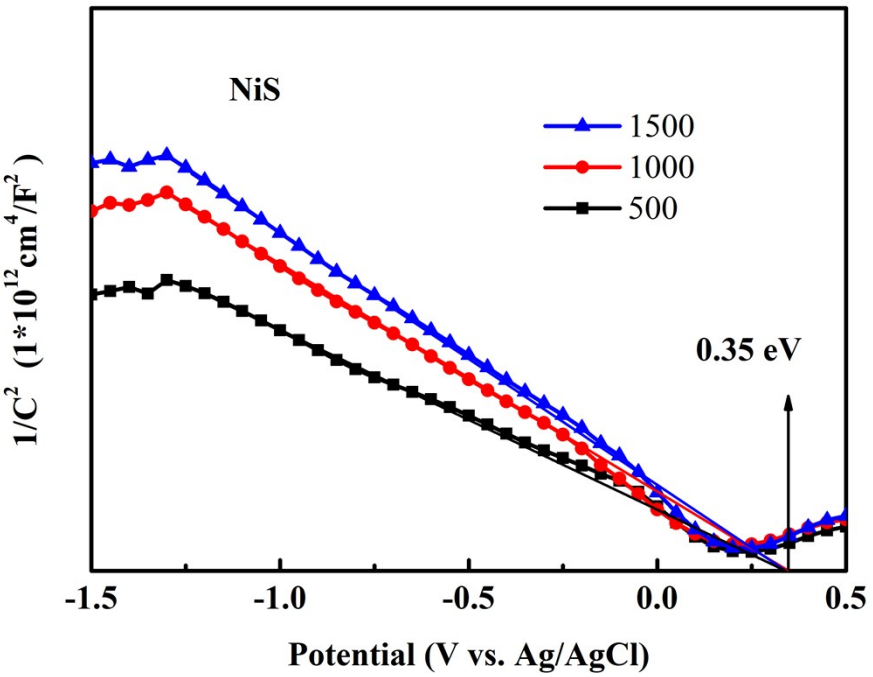

Figure S9. Mott–Schottky plots of the NiS.

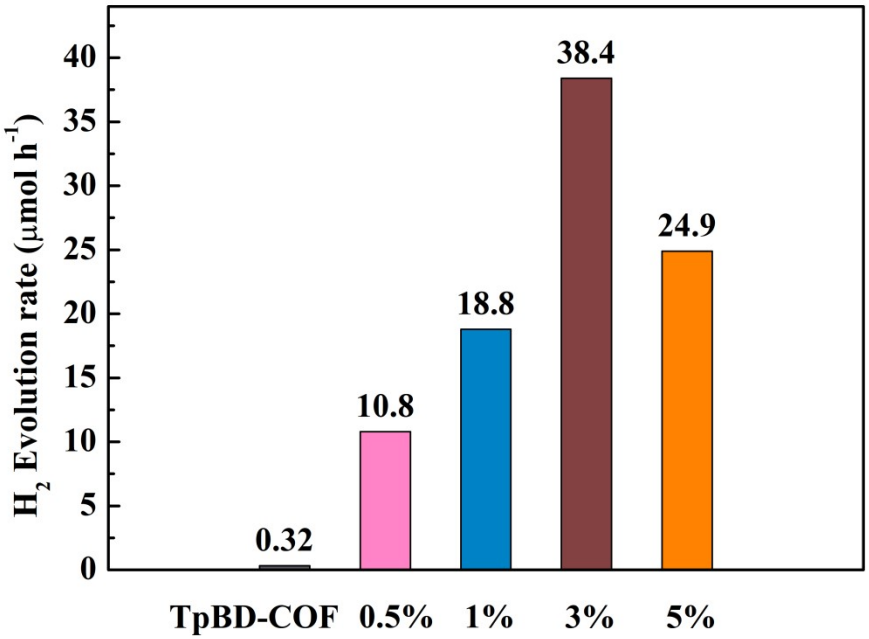

Figure S10. Average photocatalytic H_2 evolution rate of TpBD-COF and NiSX-BD photocatalysts with varying NiS loading.

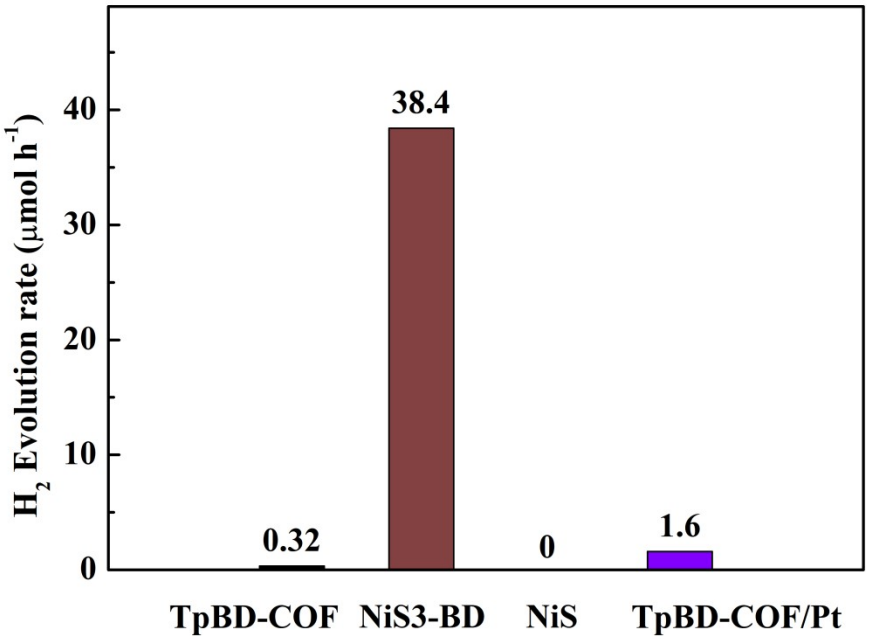

Figure S11. Average photocatalytic H_2 evolution rate of TpBD-COF, NiS3-BD, NiS, and TpBD-COF/Pt.

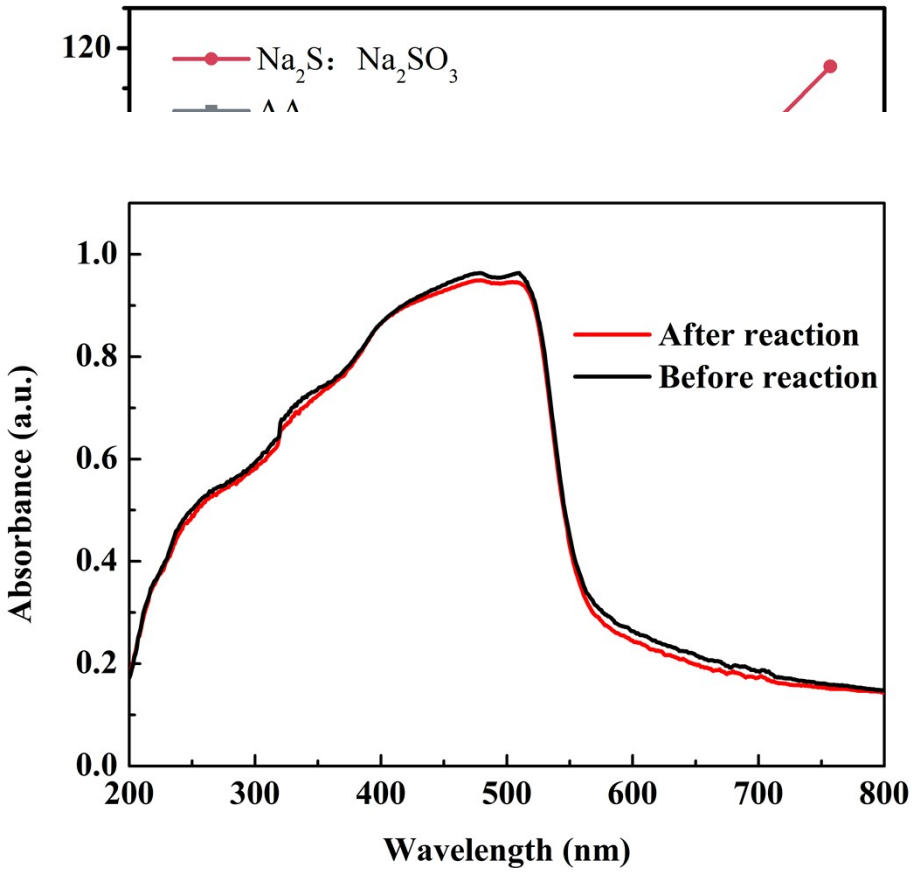

Figure S12. Photocatalytic hydrogen production performance of NiS3-BD measured in the presence of different hole scavengers.

Figure S13. FT-IR spectra of NiS3-BD before (black) and after 18h (red) photocatalytic process.

Figure S14. UV-vis diffuse reflectance spectroscopy of NiS3-BD before (black) and after 18h (red) photocatalytic process measured in the solid state.

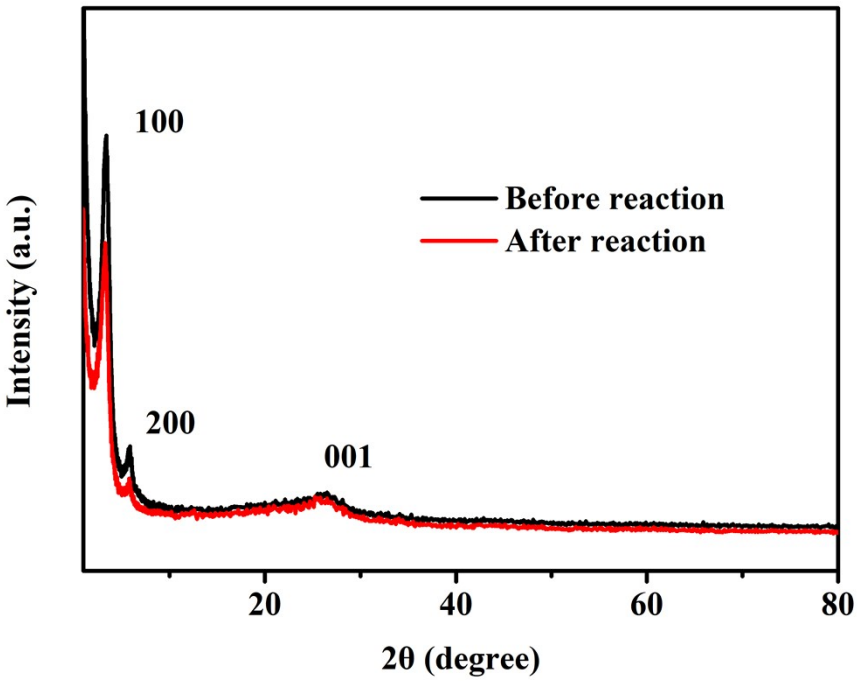

Figure S15. Experimental powder X-ray diffraction pattern of the raw NiS3-BD (black), and the NiS3-BD photocatalyst after 18 h hydrogen evolution experiment under visible light (red).

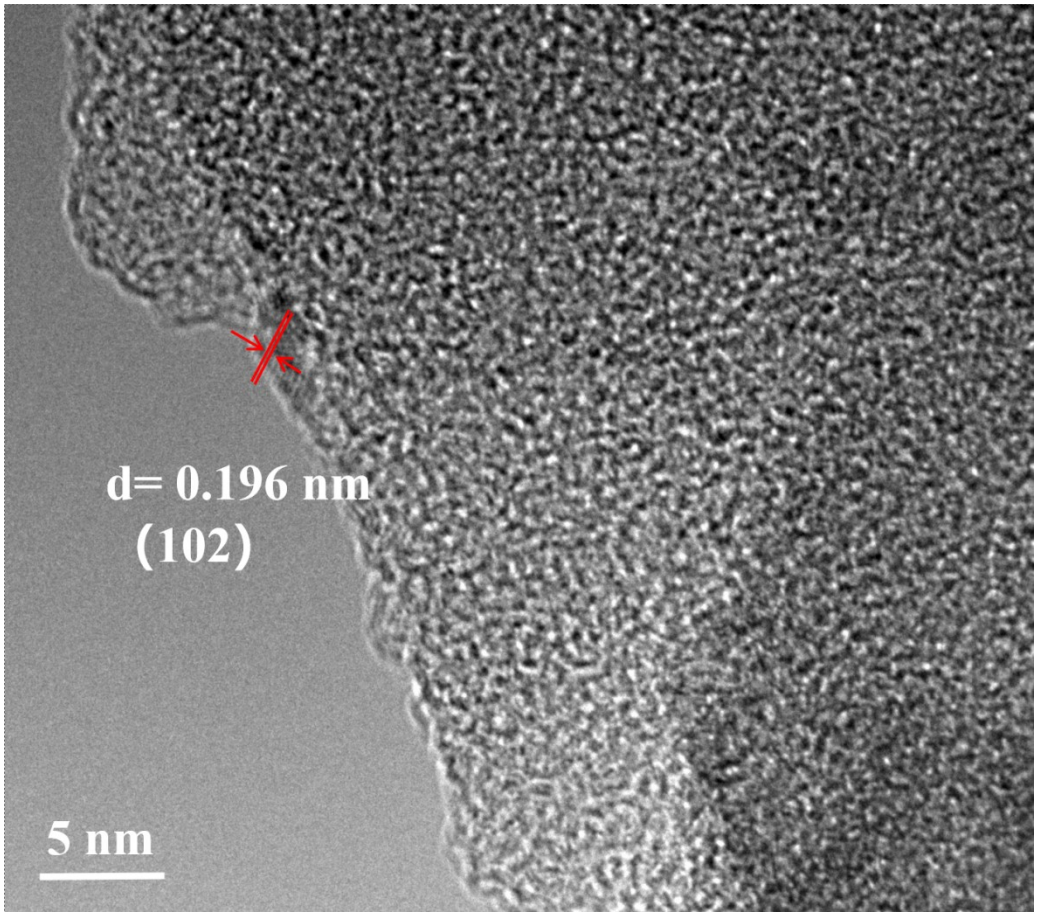

Figure S16. HR TEM image of NiS3-BD after photocatalytic reaction.

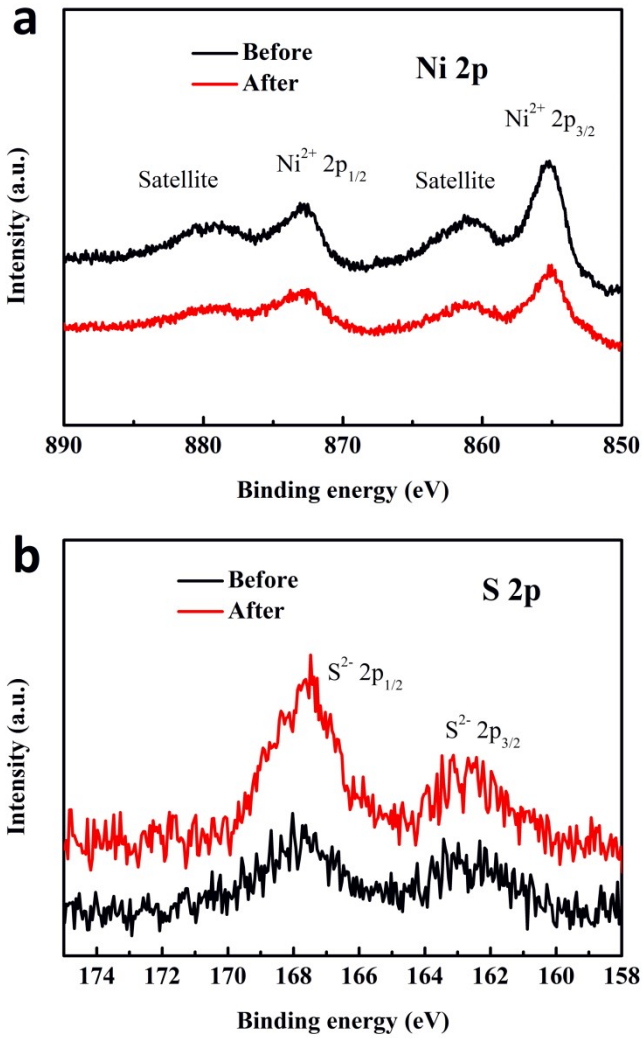

Figure S17. XPS of the NiS3-BD after the photocatalytic hydrogen production： a) Ni 2p peak; b) S 2p peak.

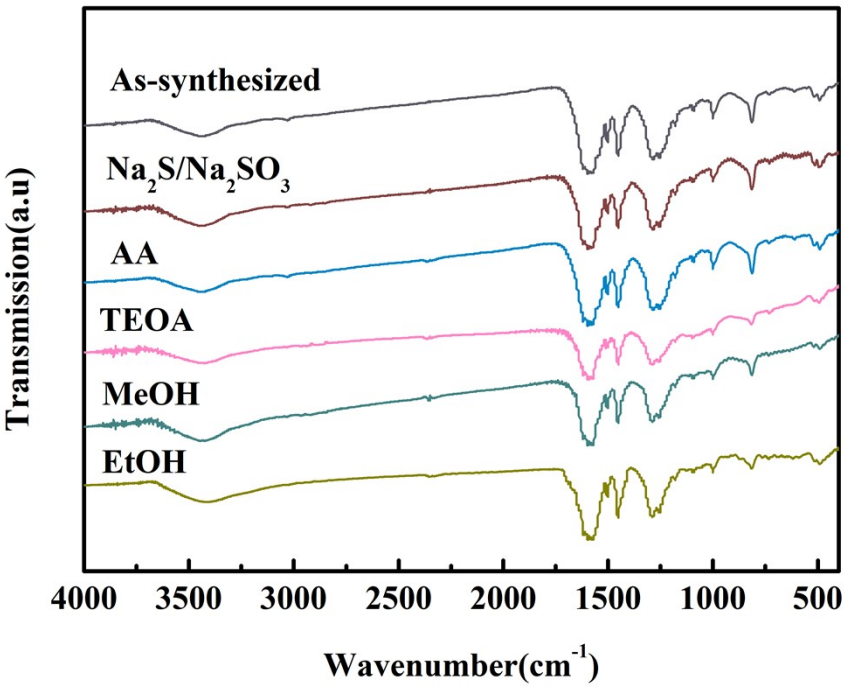

Figure S18. FT-IR spectra of the TpBD-COF and immersed in solution with different sacrificial agents for 2 days.

Table S1. ICP-AES of NiSX-BD.

	NiS0.5-BD	NiS1-BD	NiS3-BD	NiS5-BD
Ni wt%	0.31	0.62	1.91	3.14
S wt%	0.17	0.33	1.01	1.69

Table S2. Summary of H_2 evolution activity of photocatalyts.

Catalyst	**Co-catalyst**	**SED**	**Illumination**	**Activity, μmol g^{-1} h^{-1}**	**AQE 420 nm**	**Ref**
TpBD-COF	**NiS**	**Na_2S/ Na_2SO_3**	**> 420 nm**	**3840**	**0.24%**	**This work**
g-C_3N_4/CdS	NiS	TEOA	> 420 nm	2563	-	[1]
TMC/NiS-1.5	NiS	LA	Xe lamp	638	-	[2]
$Ni(OH)_2$-2.5%/TpPa-2	$Ni(OH)_2$	SA	> 420 nm	1895.99	-	[3]
TpPa-1-COF	MoS_2	AA	> 420 nm	5585	0.76%	[4]
SnS_2/TpPa-1-COF	-	AA	> 420 nm	2474	0.23%	[5]
FS-COF	Pt	AA	> 420 nm	10100	3.2%	[6]
N_2-COF	Co-1[a]	TEOA	AM1.5	782	0.16%	[7]
N_2-COF	Co-2[b]	TEOA	AM1.5	414	-	[7]
N_2-COF	Co-1	TEOA	AM1.5	100	-	[7]
N_2-COF	Co-1	TEOA	AM1.5	163	-	[7]
COF-42	Co-1	TEOA	AM1.5	233	-	[7]
CdS-COF	Pt	LA	> 420 nm	3678	4.2	[8]
Tp(BT0.05TP0.95)-COF	Pt	AA	> 420 nm	9840	2.34%	[9]
SP^2-COF_{ERDN}	Pt	TEOA	> 420 nm	2120	0.47%	[10]
TpDTz COF	NiME	TEOA	AM 1.5	941	0.2%	[11]

AA: Ascorbic Acid, SA: Sodium ascorbate, TEOA: Triethanolamine, LA: lactic acid:
Co-1[a]: $[Co(dmgH)_2pyCl]$, Co-2[b]: $[Co(dmgBF_2)_2(OH_2)_2]$.

References

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