Electronic Supplementary Information (ESI) for New Journal of Chemistry

In situ growth and activation of an amorphous MoS_x catalyst on Co-containing metal-organic framework nanosheets for highly efficient dye-sensitized H_2 evolution

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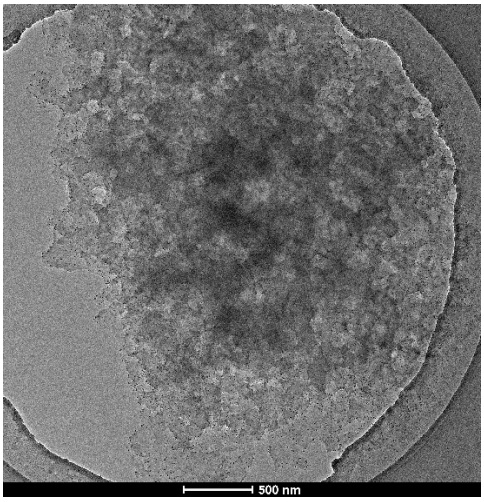

Fig. S1 Low-magnification TEM image of Co-BDC NSs.

Table S1 Zeta potentials of different synthetic systems in TEOA aqueous solution (10%, pH 8).

Sample	Zeta potential (mV)[a]
Co-BDC NSs	-4.69
MoS_4^{2-}	-2.64
Co-BDC NSs/MoS_4^{2-}	-6.54
ErB/MoS_4^{2-}	-1.99
ErB/Co-BDC NSs/MoS_4^{2-}	-3.30

[a]Co-BDC NSs, 0.1mg mL^{-1}; MoS_4^{2-}, 0.1 mM; ErB, 0.1 mM.

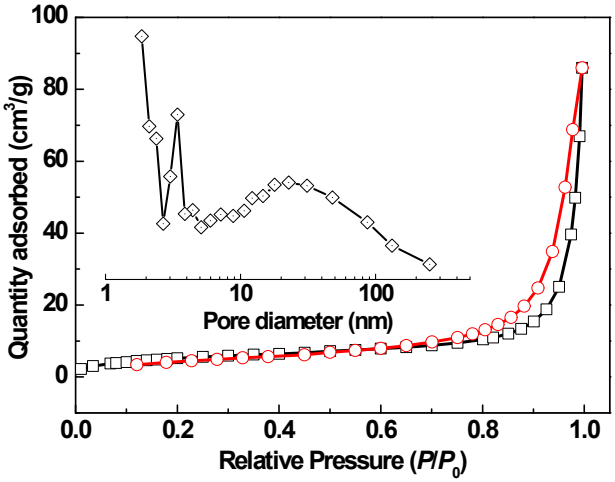

Fig. S2 N_2 adsorption-desorption isotherm and pore size distribution (inset) of Co-BDC NSs

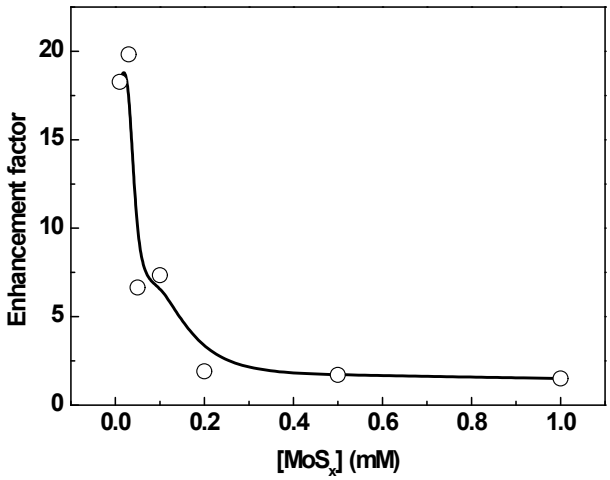

Fig. S3 Enhancement factor of H_2 evolution from ErB-TEOA system by comparing MoS_x and Co-BDC NSs/MoS_x catalysts under visible light irradiation. Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 5 mg; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, λ≥450 nm.

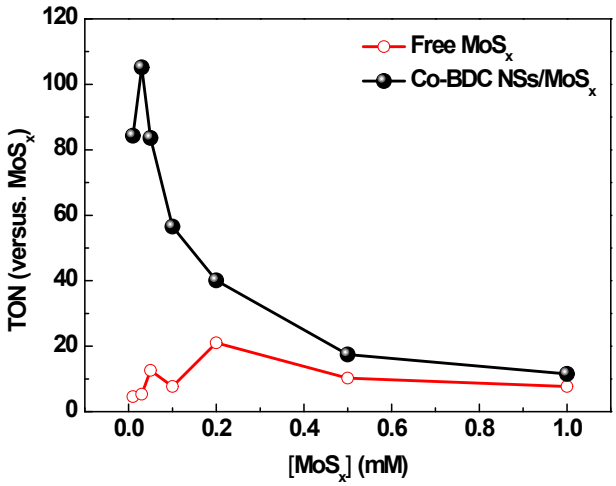

Fig. S4 TONs of H_2 evolution catalyzed by free MoS_x and Co-BDC NSs/MoS_x catalysts as a function of MoS_x concentration after 6 h irradiation. Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 5 mg; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, λ≥450 nm.

Table S2 Photocatalytic H_2 evolution activity of Co-BDC NSs/MoS_x catalyst in this work, in comparison with several representative results with high performance non-noble metal based catalysts from recent publications.

Photocatalytic H_2 evolution system	Light source	H_2 evolution activity ($mmol \cdot h^{-1} \cdot g^{-1}$)	Apparent quantum efficiency (AQE)	TON_{cat}	Ref.

5 mg Co-BDC NSs, 0.03 mM MoS_x, o.1 mM ErB, 10% TEOA, pH=8	30-W white-light LED lamp (λ≥450 nm)	4.8	15% at 500 nm	105.2	This work
10 mg ATP/$Co(OH)_2$, 0.05 mM MoS_x, 0.2 mM ErB, 10% TEOA, pH=8	30-W white-light LED lamp (λ≥450 nm)	16.8	47.7% at 500 nm	363	[1]
5 mg CoAl-LDH NSs, 0.1 mM MoS_x, 0.5 mM ErB, 15% TEOA, pH=8	300-W Xe lamp (λ≥420 nm)	21.5	4.3% at 520 nm	174.2	[2]
10mg GQDs, 8.98×10^{-5} M MoS_x, 5.98×10^{-5} M Co^{2+}, 1 mM ErB, 15% TEOA, pH=7	300-W Xe lamp (λ≥420 nm)	17.4	none	118.0	[3]
100 mg g-C_3N_4, 0.039 mM MoS_x, 0.0125 mM ErB, 0.79 M TEOA, pH=7	400-W High pressure Hg lamp (λ≥420 nm)	0.3	8.3% at 545 nm	32.1	[4]
50 mg MoS_x-rGO/TiO_2 (0.5wt%), 10% methanol	Four LED lamp (3W, 365 nm)	4.1	none	264.4	[5]
10 mg MoS_x/CdS/Co_3O_4, 10% lactic acid	5-W light emitting diode lamp	10.8	none	576.2	[6]
3 mg 0.14 wt%MoS_2QD/Bi_2S_3, 0.5 M Na_2S/Na_2SO_3	500-W Xe arc lamp	17.7	none	24274.3	[7]
100 mg 0.5 wt% MoS_2/PQ, 0.2 M TEOA, pH=7	300-W Xe lamp (λ≥420 nm)	0.08	none	20.4	[8]
20 mg $Zn_{0.2}Cd_{0.8}S$/MoS_2-3%, Na_2S (0.35 M)/Na_2SO_3 (0.25 M)	300-W Xe lamp (λ≥420 nm)	0.4	none	8.8	[9]
20 mg MoS_2/RGO, 0.4 mM EY, 15% TEOA, pH=7	300-W Xe lamp (λ≥420 nm)	1.9	24% at 460 nm	450.8	[10]
50 mg rGO1.5/CdS/MoS_2 (1.5 wt %), 10% lactic acid, pH=11	350-W Xe lamp (λ≥420 nm)	1.9	none	22.7	[11]
$Co(NO_3)_2$+$(NH_4)_2MoS_4$=1 mM, (Co:Mo=4:6), 2 mM ErB, 15% TEOA,	300-W Xe lamp (λ≥420 nm)	53.6	none	100	[12]

pH=9					
100 mg TiO2, 0.119 mM $(NH_4)_2MoS_4$, 0.78 mM EY, 10% TEOA, pH=10.7	1000-W Xe arc lamp (AM 1.5 G filter)	1.6	none	8.1	[13]
50 mg MoS_x/CdS-0.2 wt%, 10% lactic acid	300-W Xe lamp (λ≥400 nm)	8.1	none	1515	[14]
4 mM MoS_x, 2 mM ErB, 10% TEOA, pH=8.1	300-W Xe lamp (λ≥420 nm)	9.6	none	25	[15]
17 mg $[Mo_3S_{13}]^{2-}$/MIL-125-NH_2 (0.82 wt%), MeCN:TEA:H_2O=79:16:5	300-W Xe lamp (λ≥420 nm)	2.1	11.8% at 450 nm	2157.5	[16]
17 mg 1T-MoS_2/MIL-125-NH_2 (0.82 wt%), MeCN:TEA:H_2O=79:16:5	300-W Xe lamp (λ≥420 nm)	1.5	5.8% at 450 nm	340.5	[16]
10 μM $[Mo_3S_{13}]^{2-}$, 100 μM $Ru(bpy)_3Cl_2$, CH_3CN:H_2O=9:1, 100 mM H_2A	300-W Xe lamp (λ≥420 nm)	14.5	none	1570	[17]
40 mg CdS/WS_x (12 wt%), 10% lactic solution	300-W Xe lamp (λ≥420 nm)	19.0	14.7% at 420 nm	253.7	[18]
NiS_x/graphene (46.7 wt%), 1 mM EY, 10% TEOA, pH=7,	300-W Xe lamp (λ≥420 nm)	12.4	32.5% at 430 nm	18.5	[19]
100 mg $Cd_{0.5}Zn_{0.5}S$/NiS_x, Na_2S (0.35 M)/Na_2SO_4 (0.25 M)	Xe lamp (λ≥430 nm)	44.6	95% at 425 nm	18374.5	[20]
200 mg NiS_x/C_3N_4 (5 wt%), 20% TEOA	300-W Xe lamp (λ≥420 nm)	2.0	3.2% at 405 nm	59.2	[21]
50 mg a-MoSx/gC3N4, 10% lactic acid	3W-LED (λ≥420 nm)	0.3	none	8.7	[22]
50 mg $Ni(OH)_2$/g-C_3N_4 (0.5 mol%), 10% TEOA	350-W Xe arc lamp (λ≥400 nm)	0.2	1.1% at 420 nm	16.78	[23]

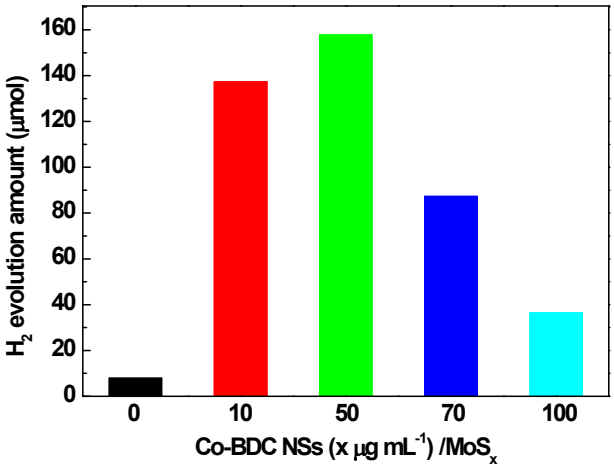

Fig. S5 H_2 evolution amounts over different Co-BDC NSs/MoS_x catalysts sensitized by ErB (0.1 mM) from TEOA solution, where different concentrations Co-BDC NSs were added. Reaction conditions: MoS_x, 0.03 mM; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, λ≥450 nm.

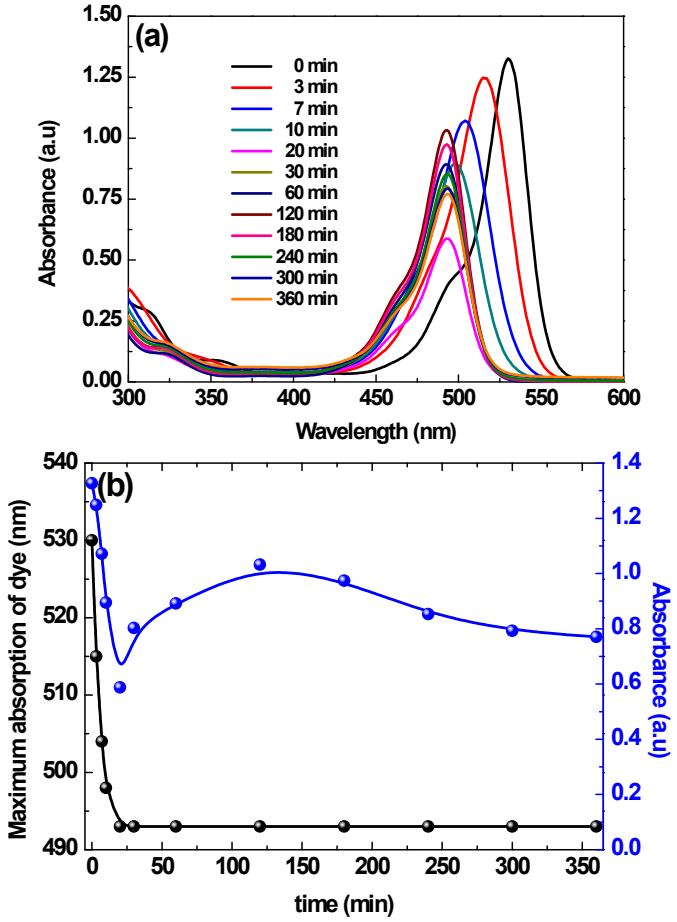

Fig. S6 (a) UV-vis absorption spectra of ErB in TEOA solution during the photocatalytic H_2 reaction from ErB-sensitized Co-BDC NSs/MoS_x as a function of light irradiation time. (b) The variations of maximum wavelength and absorbance of ErB during the photocatalytic H_2 reaction as a function of light irradiation time.

Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 5 mg; MoS_x, 0.03 mM; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, λ≥450 nm.

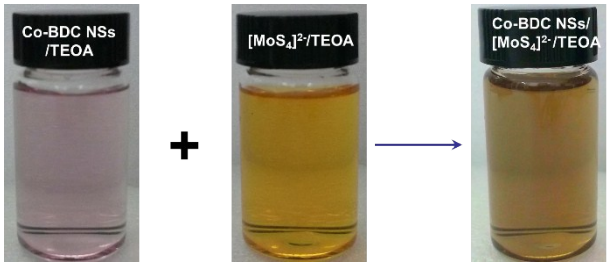

Fig. S7 Digital photos of Co-BDC NSs, $[MoS_4]^{2-}$, and Co-BDC NSs/$[MoS_4]^{2-}$ mixture in TEOA.

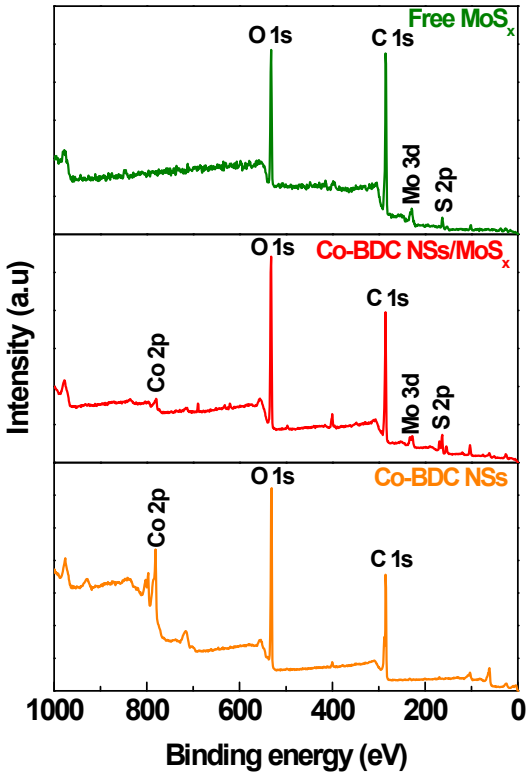

Fig. S8 XPS survey spectra of free MoS_x, Co-BDC NSs, and Co-BDC NSs/MoS_x catalysts.

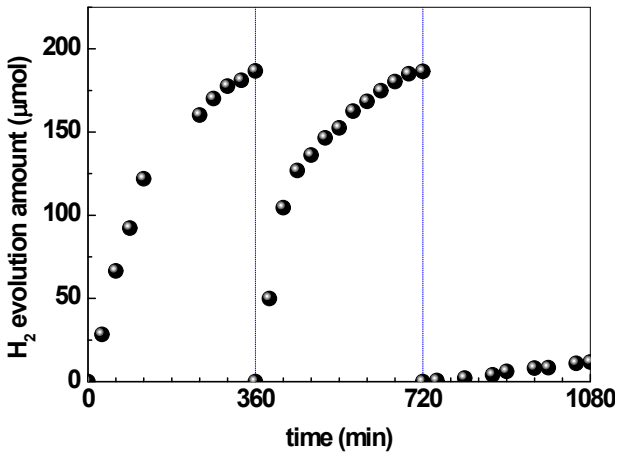

Fig. S9 The stability of photocatalytic H_2 evolution over Co-BDC NSs/MoS_x catalysts from ErB-TEOA system. Reaction conditions: ErB, 0.1 mM; Co-BDC NSs, 15 mg; MoS_x, 0.09 mM; 100 mL TEOA solution, 10%, pH 8; 30-W LED lamp, $\lambda \geq 450$ nm.

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