Supporting Information

Constructing noble-metal-free Z-scheme photocatalytic overall water splitting systems using MoS₂ nanosheets modified CdS as a H₂ evolution photocatalyst

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Scheme S1. Chemical structures of $[Co(bpy)_3](PF_6)_3/[Co(bpy)_3](PF_6)_2$ electron mediator.



Figure S1. XRD patterns of MoS₂/CdS HERs loaded with various amounts of MoS₂.



Figure S2. Raman spectra of bare CdS and 4 wt.% MoS₂/CdS composite.



Figure S3.UV-vis spectra of MoS₂/CdS HEP loaded with various amounts of MoS₂.



Figure S4. SEM image of pure CdS sample.



Figure S5. SEM image of pure MoS₂ sample.



Figure S6. XRD patterns of Co₃O₄/BiVO₄ OEPs loaded with various amounts of Co₃O₄.



Figure S7. UV-vis spectra of Co_3O_4 /BiVO₄ OEPs loaded with various amounts of Co_3O_4 .



Figure S8. SEM image of pure BiVO₄ sample.



Figure S9. SEM image of 1.5 wt.% $Co_3O_4/BiVO_4$ OEP.



Figure S10. TEM image of 1.5 wt.% $Co_3O_4/BiVO_4$ OEP.



Figure S11. Survey XPS spectra of 1.5 wt.% $Co_3O_4/BiVO_4$ composite.



Figure S12. high resolution XPS spectra of Bi 3d.



Figure S13. high resolution XPS spectra of V 2p.



Figure S14. high resolution XPS spectra of O 1s.



Figure S15. high resolution XPS spectra of Co 2p.



Figure S16. GC-MS of decomposition product collected from the reaction mixture after 4 h of visible light irradiation clearly reveals 2,2'-bipyridine (m/z = 156) dissociates from cobalt complexes electron mediator.



Figure 17. Cyclic voltammograms of the $[Co(bpy)_3]^{3+}/[Co(bpy)_3]^{2+}$ redox couple in saturated KCl solution (potential vs. Ag/AgCl).

$$4CdS \xrightarrow{hv} 4CdS(h^+ + e^-)$$
(1)

$$4\text{BiVO}_4 \xrightarrow{n\nu} 4\text{BiVO}_4(h^+ + e^-)$$
(2)

$$4CdS(h^{+} + e^{-}) + MoS_2 \longrightarrow 4CdS(h^{+}) + 4MoS_2(e^{-})$$
(3)

$$4MoS_2(e) + 4H^+ \longrightarrow 4MoS_2 + 2H_2$$
(4)

$$4CdS (h^{+}) + 4[Co(bpy)_{3}]^{2+} \longrightarrow 4CdS + 4[Co(bpy)_{3}]^{3+}$$
(5)

$$4\text{BiVO}_4(h^+ + e^-) + 4\text{Co}_3\text{O}_4 \longrightarrow 4\text{BiVO}_4(e^-) + 4\text{Co}_3\text{O}_4((h^+))$$
(6)

$$4\text{BiVO}_4(e^-) + 4[\text{Co}(\text{bpy})_3]^{3+} \longrightarrow 4\text{BiVO}_4 + 4[\text{Co}(\text{bpy})_3]^{2+}$$
(7)

$$4Co_{3}O_{4}(h^{+}) + 2H_{2}O \longrightarrow 4Co_{3}O_{4} + 4H^{+} + O_{2}$$
(8)

Scheme S2. Summarized transfer routes of photoinduced charge carriers in this Z-scheme system.

Sample	Sample concentration (mg/L)	Mo or Co concentration (mg/L)	$MoS_2 \text{ or } Co_3O_4$ concentration (mg/L)	cocatalyst/photocatalyst ratio (wt%)
4% MoS ₂ /CdS	403	8.87	14.79	3.67
1.5 % Co ₃ O ₄ /BiVO ₄	434	6.24	8.49	1.44

Table S1. Weight ratio of cocatalyst exhibited in 4% MoS_2/CdS and 1.5% $Co_3O_4/BiVO_4$ samples.

Table S2. Comparison of photocatalytic performance for water splitting between the current work and other reported studies.

Entry	H_2 evolution	O ₂ evolution	Light source	Activity $(umol h^{-1})$		Quantum yield	Ref
	photocataryst	prococacaryse		H ₂	0 ₂	(%)	
1	Ru-SrTiO₃:Rh	BiVO ₄	300 W Xe lamp	5.0	2.2		(1)
2	Ru-SrTiO₃:Rh	WO ₃	300 W Xe lamp (λ>420 nm)	5.7	2.4	0.4 (420 nm)	(2)
3	Ru-SrTiO₃:Rh	$AgNbO_3$	300 W Xe lamp (λ>420 nm)	1.9	0.7	0.1 (420 nm)	(2)
4	Ru-SrTiO₃:Rh	Bi ₂ MoO ₆	300 W Xe lamp (λ>420 nm)	12	5.2	0.9 (420 nm)	(2)
5	$Pt-IrO_2/Sm_2Ti_2S_2O_5$	PtO _x /H-Cs- WO₃	300 W Xe lamp (λ>420 nm)	4.06	1.61		(3)
6	Ru-SrTiO₃:Rh	BiVO ₄	300 W Xe lamp (λ>420 nm)	0.5	0.4		(4)
7	Pt/TaON	RuO ₂ /TaON	300 W Xe lamp (λ>420 nm)	10	4	0.1-0.2 (420 nm)	(5)
8	Pt/CaTaO ₂ N	Pt/WO ₃	300 W Xe lamp (λ>420 nm)	5.5	2.5	, , , , , , , , , , , , , , , , , , ,	(6)
9	Pt BaTiO₃:Rh	PtO _x /WO ₃	300 W Xe lamp (λ>420 nm)	1.7	0.6	0.5 (420 nm)	(6)
10	$Pt/H_4Nb_6O_{17}$	PtO ₂ /WO ₃	300 W Xe lamp (λ>420 nm)	2.2	0.9	0.05 (480nm)	(7)
11	Ru-SrTiO₃:Rh	BiVO ₄	300 W Xe lamp (λ>420 nm)	7.9	3.5		(8)
12	Pt-Ba(0.3)-Ta ₃ N₅	PtO _x /WO ₃	300 W Xe lamp	3.2	1.6		(9)
13	Pt-TaON	PtO _x /WO ₃	300 W Xe lamp	15.6	7.5		(10)
14	PRGO(Ru/SrTiO₃:Rh)	BiVO ₄	300 W Xe lamp (λ>420 nm)	3.5	1.4	1.03 (420nm)	(11)
15	Ru-SrTiO₃:Rh	Ir/CoO _x /Ta₃N	300 W Xe lamp (λ>420 nm)	~11.5	~5.5		(12)
16	Ru/SrTiO₃:Rh	BiVO ₄	300 W Xe lamp (λ>420 nm)	13	5.8		(13)
17	Pt/CuGaS₂	CoO _x /BiVO ₄	300 W Xe lamp (λ>420 nm)	3.5	1.7		(14)
21	MoS ₂ /CdS	Co ₂ O ₃ /BiVO ₄	300 W Xe lamp (λ>420 nm)	14.5	7.1	1.04 (420nm)	This work

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