Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.
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Supporting Information

Synthesis of non-noble metal solid solution($Cd_{0.76}Co_{0.17}Mo_{0.07}S$) via MOF precursors for enhanced hydrogen production

Experimental section

Preparation of Mo-MOF

Mo-MOF was prepared by modifying the method reported by Martin[1]. 1.4 g of molybdenum trioxide and 0.664 g of imidazole were dissolved in 100 ml of aqueous solution and refluxed at 80 °C for 12 h. The product was collected and centrifuged, the product was washed twice with aqueous solution and finally dried in a vacuum drying oven at 60 °C for 12 h to obtain a white powder.

Preparation of CdIF-3\ZIF-67

The preparation of CdIF-3 was referred to the work of Zhong *et al*[2] with modifications: 0.7712 g of cadmium nitrate tetrahydrate and 1.642 g of 2-methylimidazole were mixed with 2.8 ml of triethylamine solution and 57 ml of methanol. After sonication for 10 minutes it was poured into an autoclave and reacted at 60 °C for 48 h. The precipitate was collected by centrifugation, washed with methanol, and dried in an oven at 60 °C for 12 h to obtain a white powder. ZIF-67 was prepared according to the work of Chen[3] with modifications: 0.33 g of cobalt nitrate hexahydrate and 0.78 g of 2-methylimidazole were dissolved in 30 ml of methanol and stirred vigorously at room temperature for 6 h. The stirred sample was collected directly from the precipitate by centrifugation, washed with methanol, and dried in an oven at 60 °C for 12 h to give a purple powder.

Preparation of samples for control experiments

Preparation of physical mixed samples: CdCo-MOF and Mo-MOF were directly vulcanized to CdCoS and MoS_2 with ethylenediamine, and then 50 mg and 3.335 mg were placed in 10 ml of ethanol solution and sonicated for 120 min, centrifuged, and then dried for 12 h at 60 °C, to obtain the physical mixed samples, which were labelled as mixed samples.

Sample preparation for vulcanization in alkaline solution as solvent at pH=9: An alkaline solution was prepared by dissolving 30mg of NaOH in 100ml of deionized water, and the pH was measured using acid-base paper at pH=9. 100 mg of CdCo-MOF and 6.67 mg of Mo-MOF were dissolved in 20 ml of the alkaline solution, and a vulcanization reaction was carried out for 8 h at 220 °C. The samples obtained by centrifugal drying were labeled as alkaline samples.

Sample preparation for direct mixed vulcanization of metal raw materials: 200 mg $Cd(NO_3)_2 \cdot 4H_2O$, 55 mg $Co(NO_3)_2 \cdot 6H_2O$, 37 mg MoO_3, and 600 mg of thioacetamide were dissolved in 30 ml of ethylenediamine solution, and vulcanization reaction was carried out at 220 °C for 6 h, and samples obtained after centrifugation and drying were labeled as direct vulcanization samples.

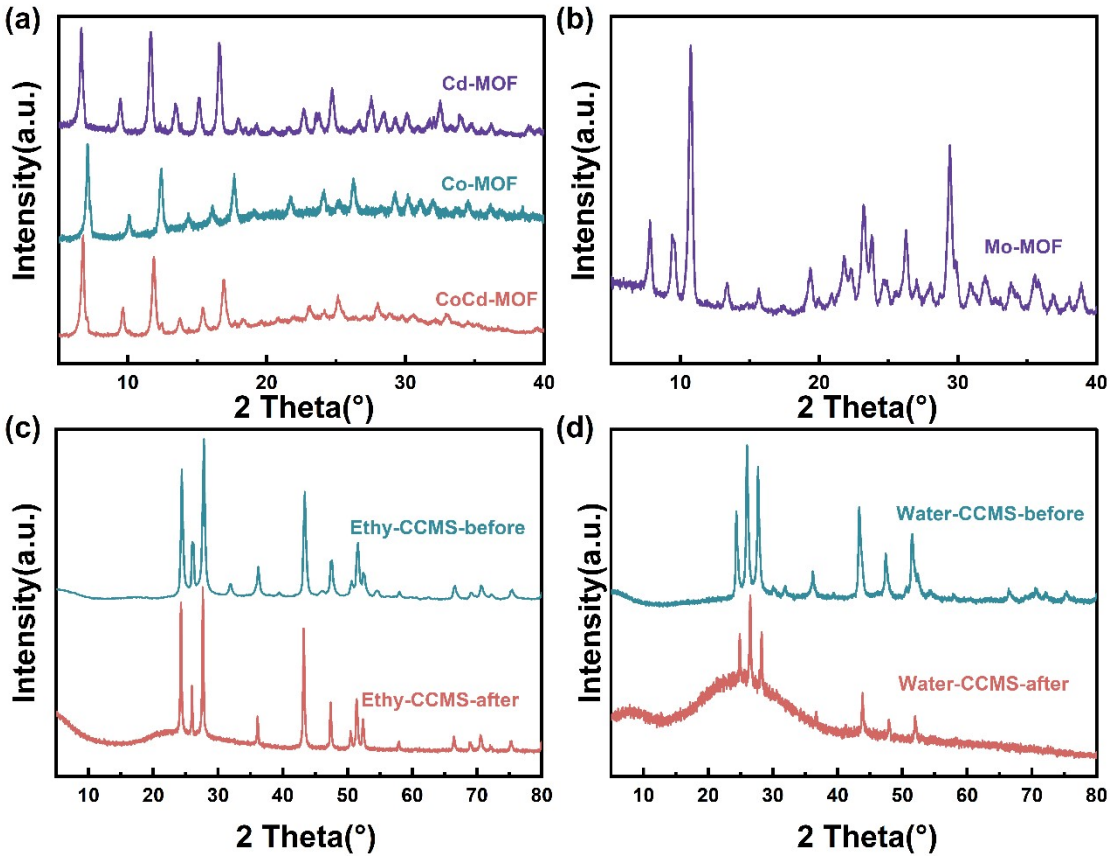

Figure S1. XRD spectra of Cd-MOF\Co-MOF\CdCo-MOF (a) and Mo-MOF (b) ;

XRD spectra of Ethy-CCMS\Water-EEMS before and after the photocatalytic reaction (c)-(d).

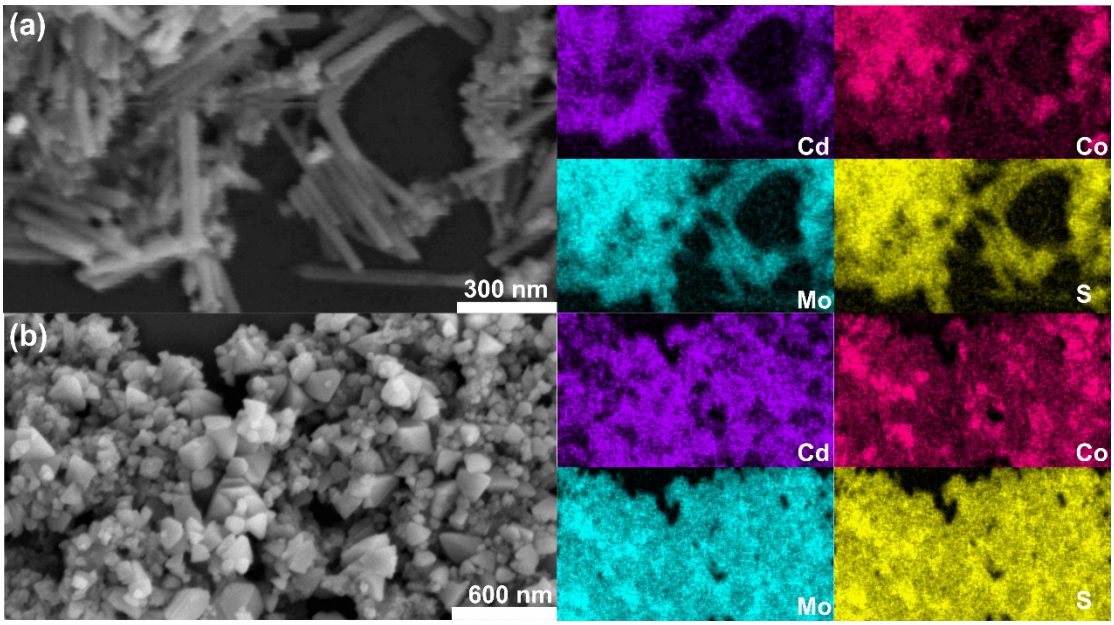

Figure S2. Elemental mapping images of Ethy-CCMS\Water-CCMS (a)-(b).

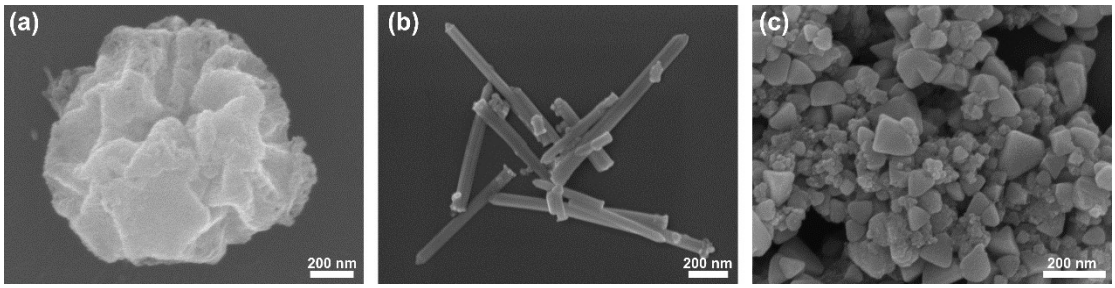

Figure S3. SEM image of (a) CdCo-MOF; (b) Ethy-CCMS ; (c) Water-CCMS.

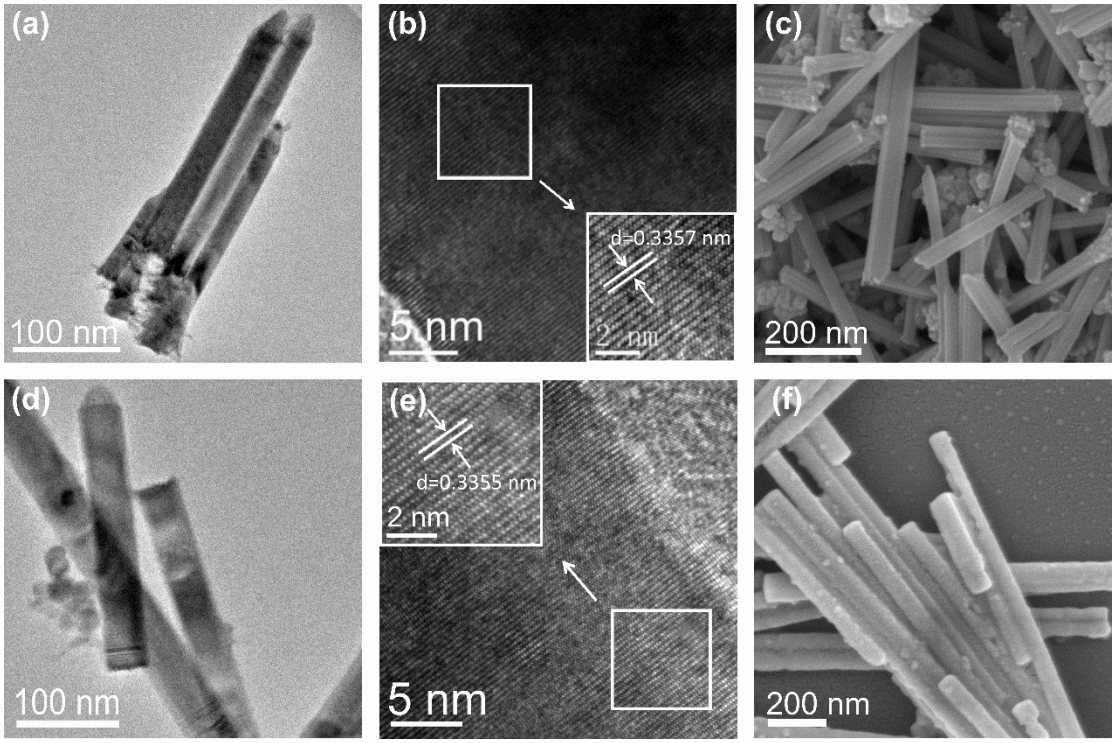

Figure S4. (a) (b) TEM image of Ethy-CCMS before photocatalytic reaction; (c) SEM image of Ethy-CCMS before photocatalytic reaction; (d) (e) TEM image of Ethy-CCMS after photocatalytic reaction; (f) SEM image of Ethy-CCMS after photocatalytic reaction.

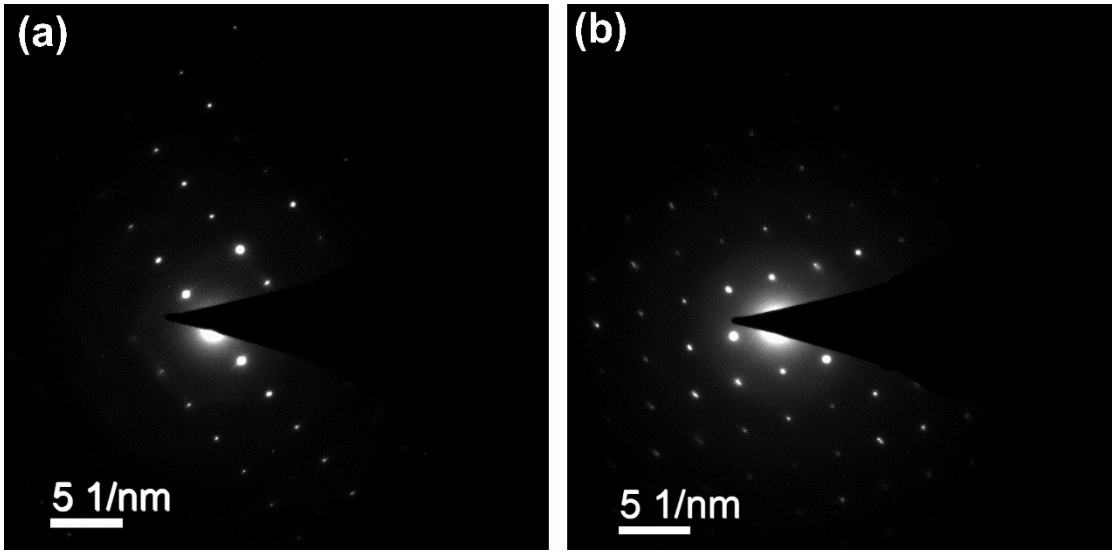

Figure S5. Selected electron diffraction maps (SAED): (a) Ethy-CCMS; (b) Water-CCMS.

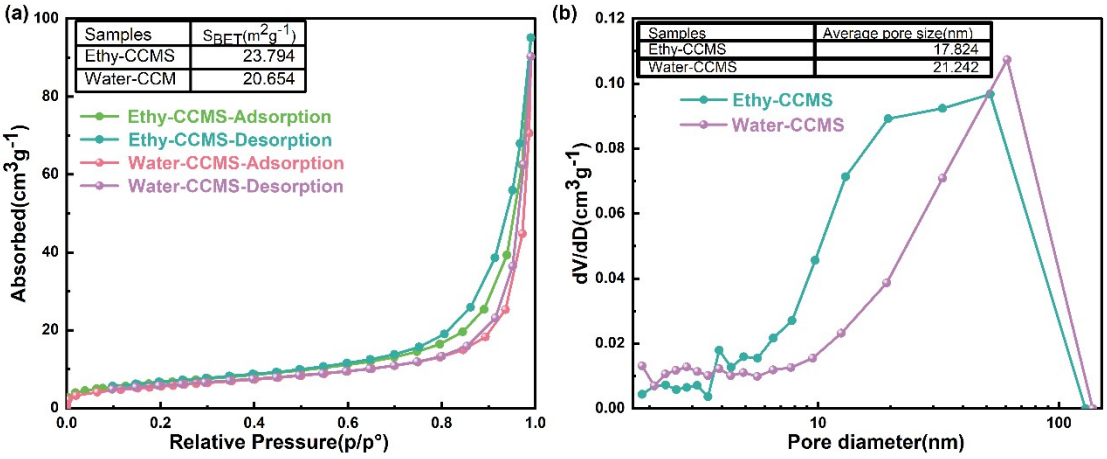

Figure S6. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution plots for Ethy\Water-CCMS.

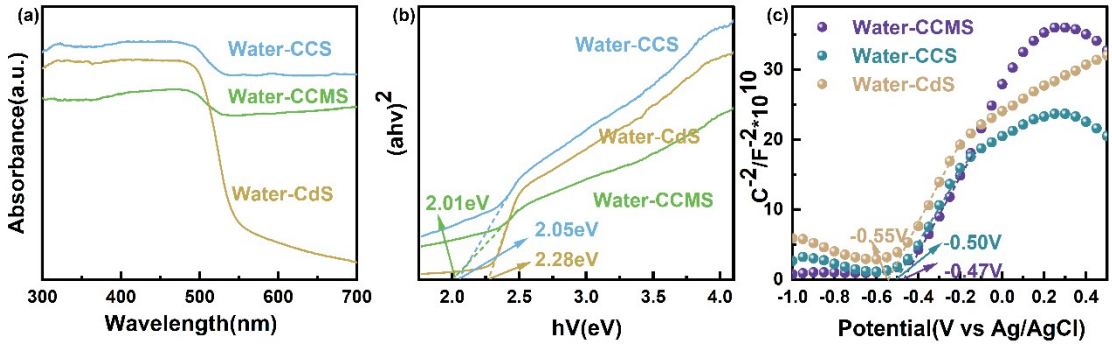

Figure S7. (a) UV-vias; (b) Tauc plots; (c) Mott-Schottky spectra of the Water-CCMS

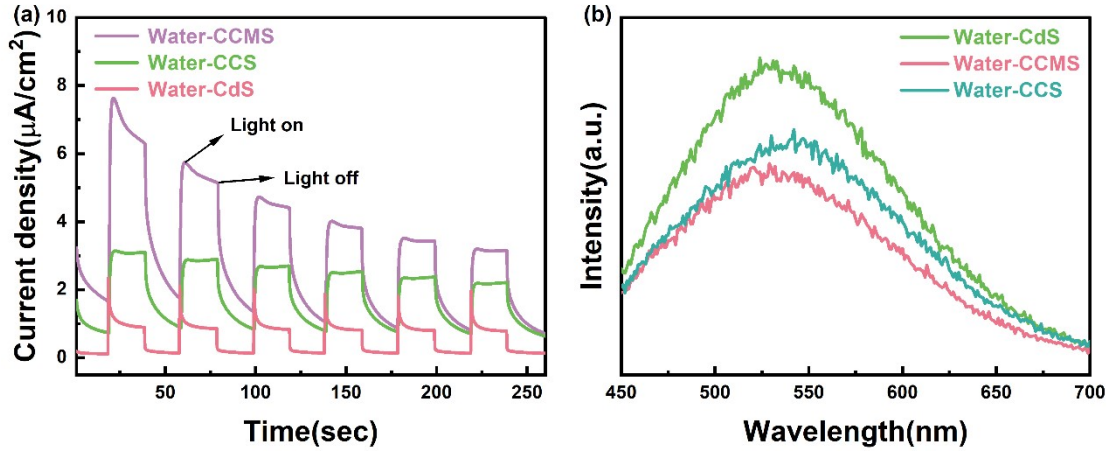

Figure S8. (a) Transition photocurrent spectra; (b) Photoluminescence spectra of the Water-CCMS.

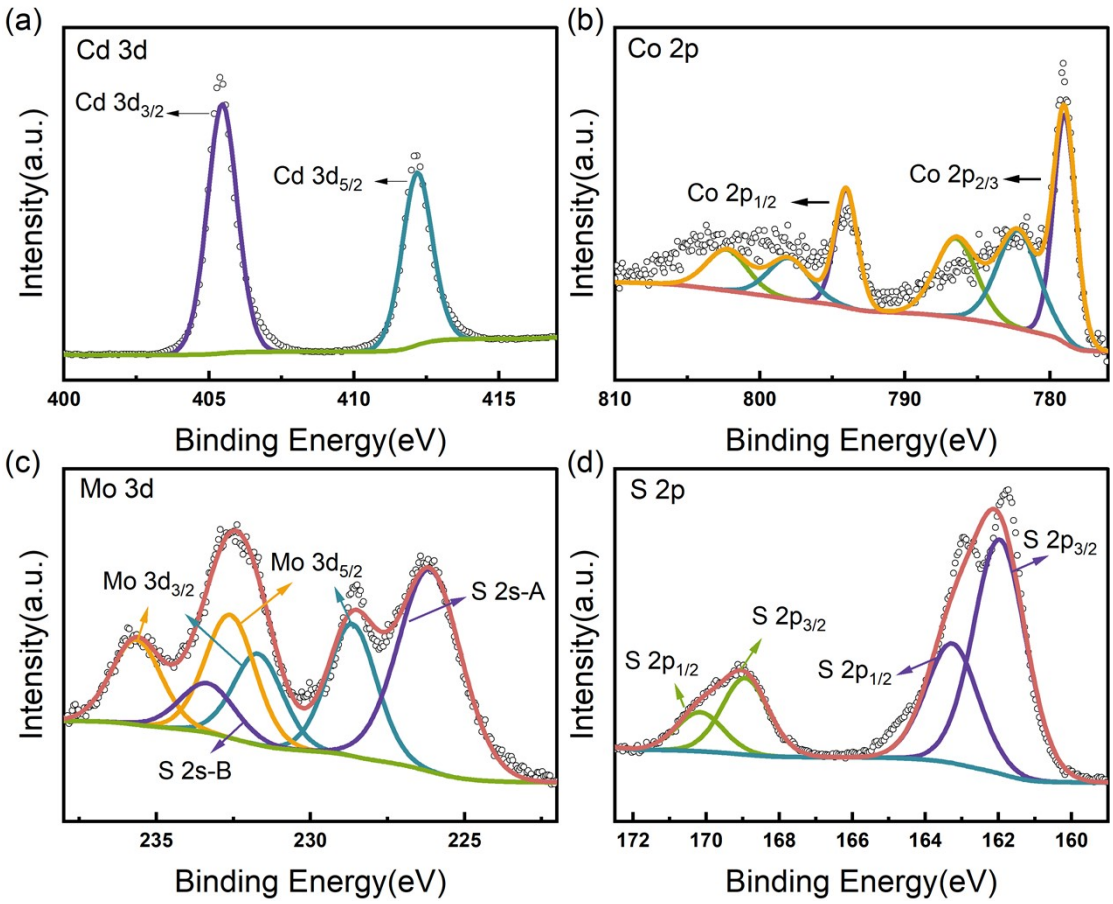

Figure S9. (a)-(d) XPS spectra of Cd, Co, Mo, S of the Water-CCMS

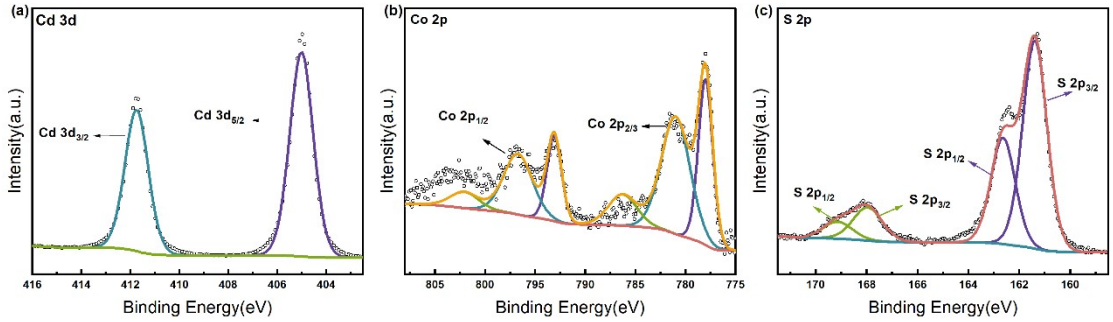

Figure S10. (a)-(c) XPS spectra of Cd, Co, Mo, S of the Ethy-CCS.

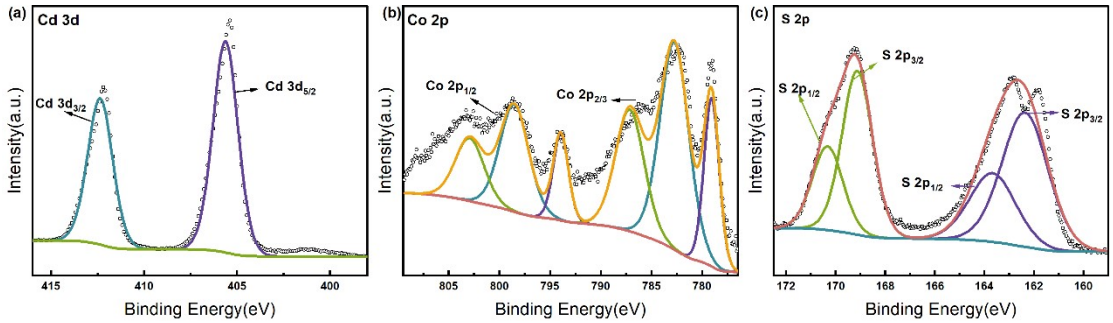

Figure S11. (a)-(c) XPS spectra of Cd, Co, Mo, S of the Water-CCS.

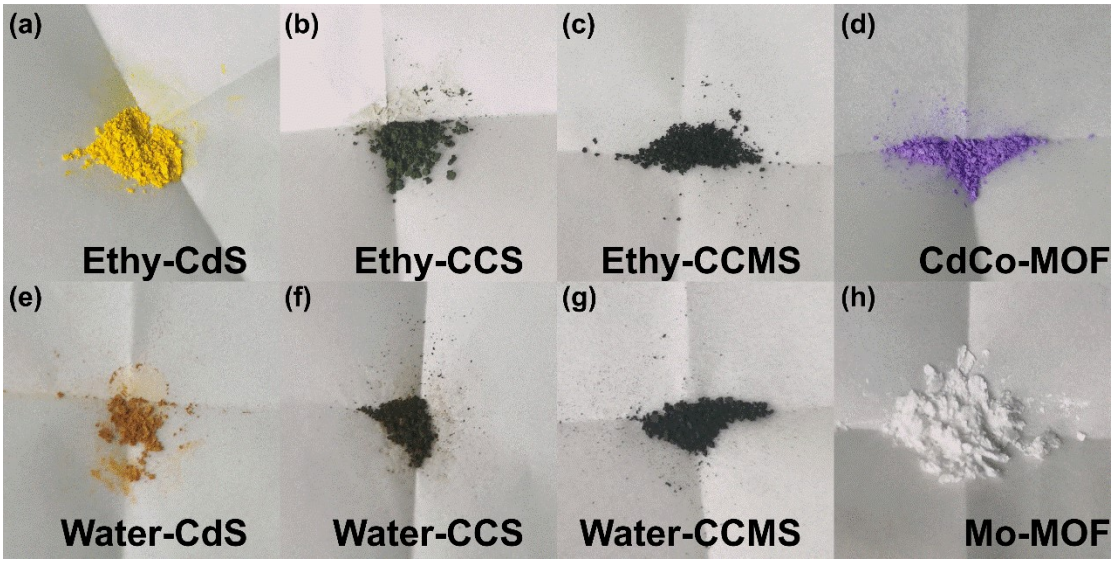

Figure S12. (a)-(h) Photo of Ethy-CdS, Ethy-CCS, Ethy-CCMS, CdCo-MOF, Water-CdS, Water-CCS, Water-CCMS, Mo-MO in daylight.

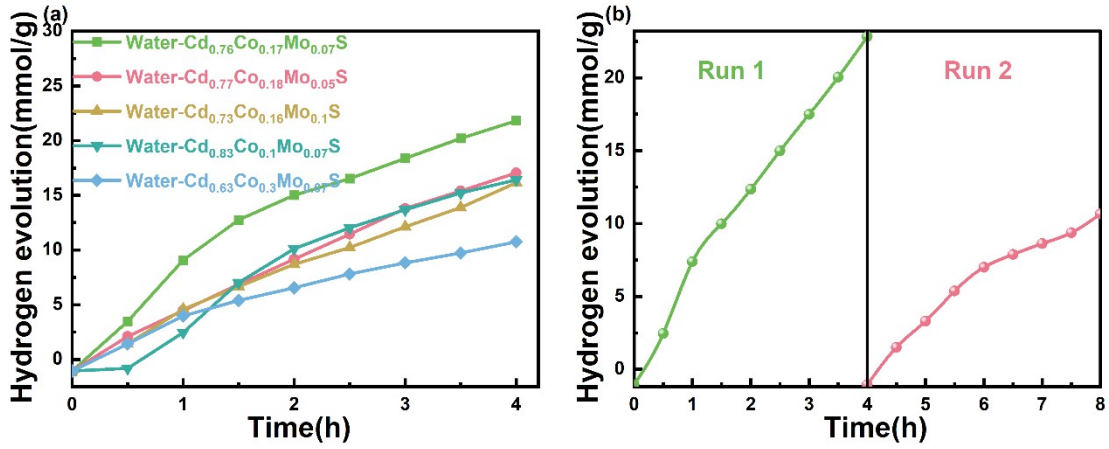

Figure S13. Hydrogen evolution rate of (a) Series of samples with different ratios of elements in water environment；(b) Cyclic hydrogen production efficiency of Water-CCMS.

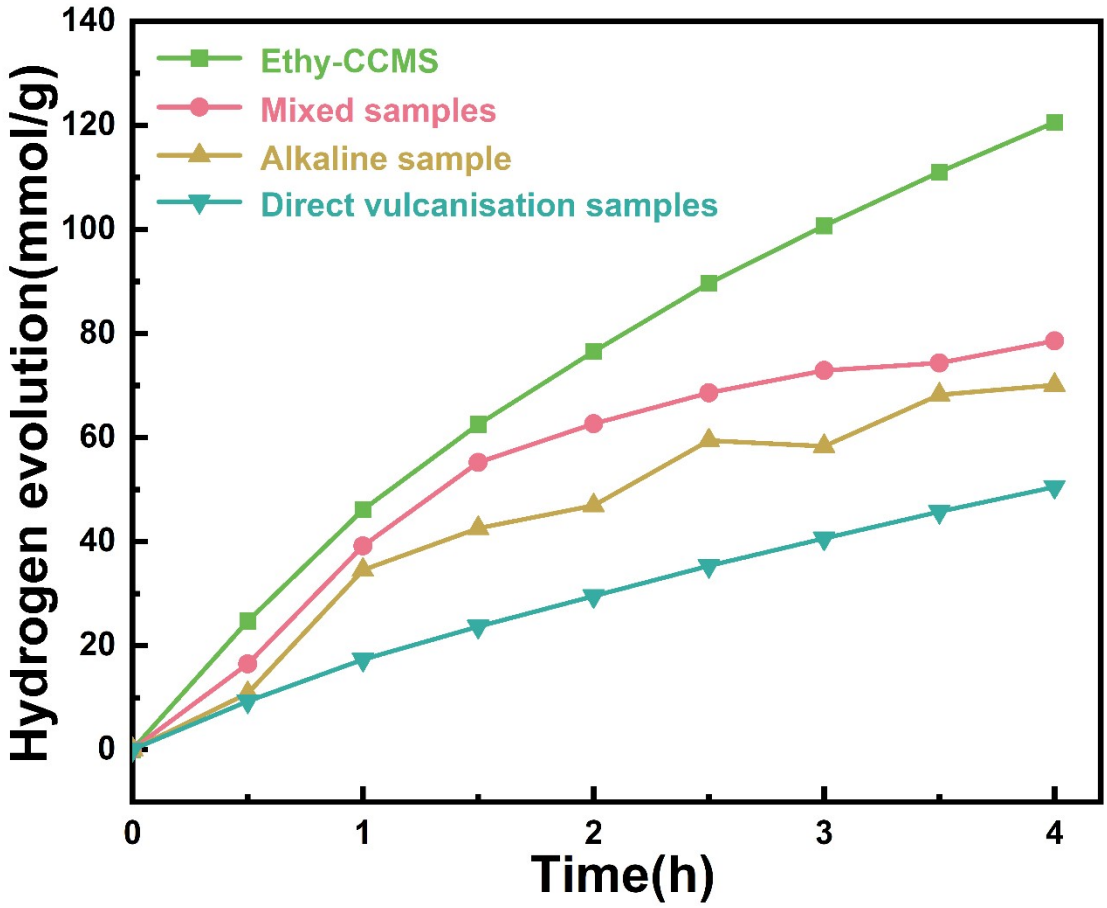

Figure S14. Hydrogen evolution rates for Ethy-CCMS, physically mixed samples, alkaline solution sulphide samples and raw material direct sulphide samples.

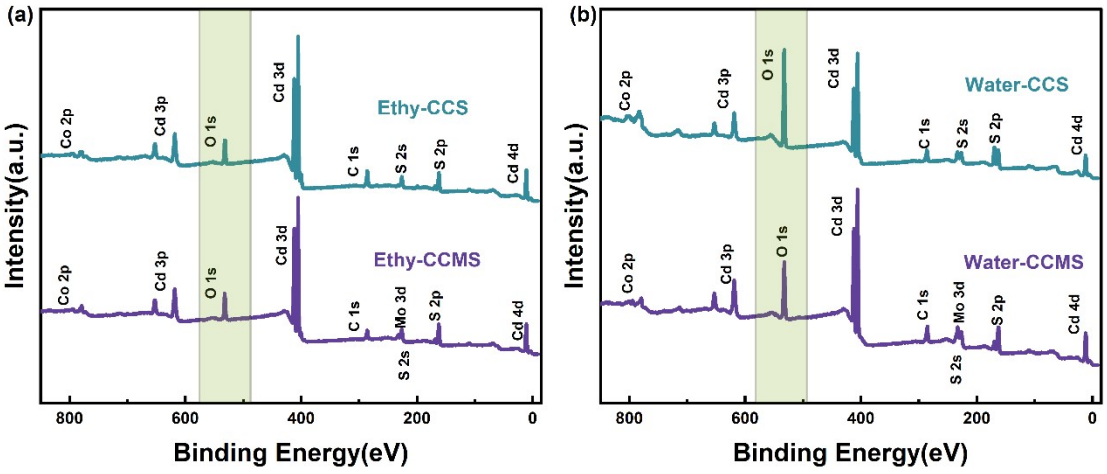

Figure S15. XPS analysis of Survey spectrum of Ethy-CCS\Ethy-CCMS and Water-CCS\Water-CCMS.

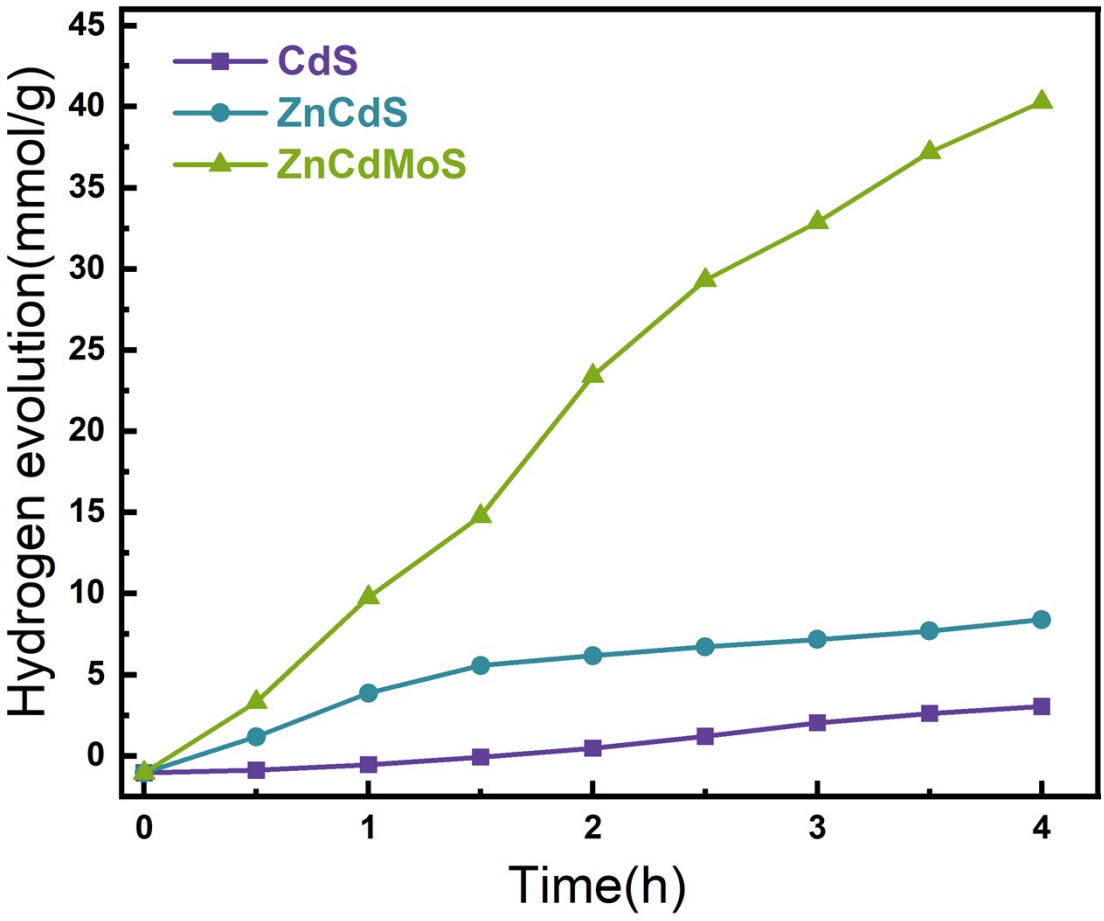

Figure S16. Hydrogen evolution rate of three precursor sulfide products, CdIF3, ZnCd-MOF, ZnCd-MOF with Mo-MOF.

Table S1. XPS results of elemental contents of Samples

Samples	Cd (at%)	Co (at%)	Mo (at%)	S (at%)	O (at%)
Ethy-CCS	18.13	2.36	\	21.99	16.45
Ethy-CCMS	21.97	3.07	1.44	29.22	18.09
Water-CCS	9.44	5.73	\	26.14	42.86
Water-CCMS	14.19	2.63	3.06	25.67	30.03

Table S2. ICP-AES results of elemental contents of Samples

Samples	Cd (mol%)	Co (mol%)	Mo (mol%)
Ethy-CCMS	41.32	16.55	2.19
Water-CCMS	48.48	19.18	5.05

Table 3. Comparison of the H_2-production rates of CdS composite photocatalysts for water splitting

Photocatalyst	Irradiation source	Reaction conditions	Nobel metal cocatalyst	Activity $mmolg^{-1}h^{-1}$	Ref
Ethy-$Cd_{0.76}Cd_{0.17}Mo_{0.07}S$	300 W Xe lamp(λ>420 nm)	10 mg catalyst 50 mL 10 vol% lactic acid aqueous	\	30.14	This work
CdS/PBC	300 W Xe lamp(λ>420 nm)	25 mg catalyst 50 mL 0.35M Na_2S and 0.25M Na_2SO_3 aqueous	\	14.67	[4]
MoS_2-CdS/GDY-10%	300 W Xe lamp(λ>420 nm)	100mg catalyst 100 mL 0.35 M Na_2S and 0.25M Na_2SO_3 aqueous	\	17.99	[5]
MoS_2-tipped CdS nanorod	300 W Xe lamp(AM 1.5)	100 mg catalyst 60ml supernatant collected from plastic pretreatment	\	6.68	[6]
CdS@CoS/WS_2	300 W Xe lamp(λ>420 nm)	100 mg catalyst 100mL of 25 vol% methanol/H_2O solution	\	10.62	[7]
CdS/PT	350 W Xe lamp(λ>420 nm)	10 mg catalyst 80 mL 10 vol% lactic acid aqueous solution	Pt	9.28	[8]
P-MoS_2/CdS	300 W Xe lamp(λ>420 nm)	10 mg catalyst 100 mL 0.35M Na_2S and 0.25M Na_2SO_3 aqueous	\	5.89	[9]
MoS_2/CdS	300 W Xe lamp(λ>420 nm)	20 mg catalyst 100 mL 20 vol% lactic acid aqueous solution	\	15.5	[10]
CdS@MoS_2	300 W Xe lamp(λ>420 nm)	20 mg catalyst 100mL 10 vol% lactic acid aqueous solution	\	15.26	[11]
MoS_2/CdS	300 W Xe lamp(λ>420 nm)	50 mg catalyst 100mL 10 vol% lactic acid aqueous solution	\	10.672	[12]
CdS/Co_9S_8	300 W Xe lamp(AM 1.5)	20 mg catalyst 100 mL $Na2_S$ and Na_2SO_3 aqueous	\	1.06	[13]

5%CoP/CdS-P	30x3 W Xe lamp(λ>420 nm)	5mg catalyst 20 mL water	\	0.231	[14]
b-TiO_2/MoS_2/CdS	300 W Xe lamp(λ>400 nm)	20 mg catalyst 100mL 10 vol% lactic acid aqueous solution	\	9	[15]
M-t-CdS Nrs	300 W Xe lamp(AM 1.5)	30 mg catalyst 90mL 28.6 vol% lactic acid aqueous solution	\	8.44	[16]
$MoS_{0.2}$/CdS-N	300 W Xe lamp(λ>400 nm)	50 mg catalyst 100mL 10 vol% lactic acid aqueous solution	\	10.1	[17]

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