Supporting Information

Highly efficient noble metal free photocatalytic hydrogen evolution system containing MoP and CdS quantum dots

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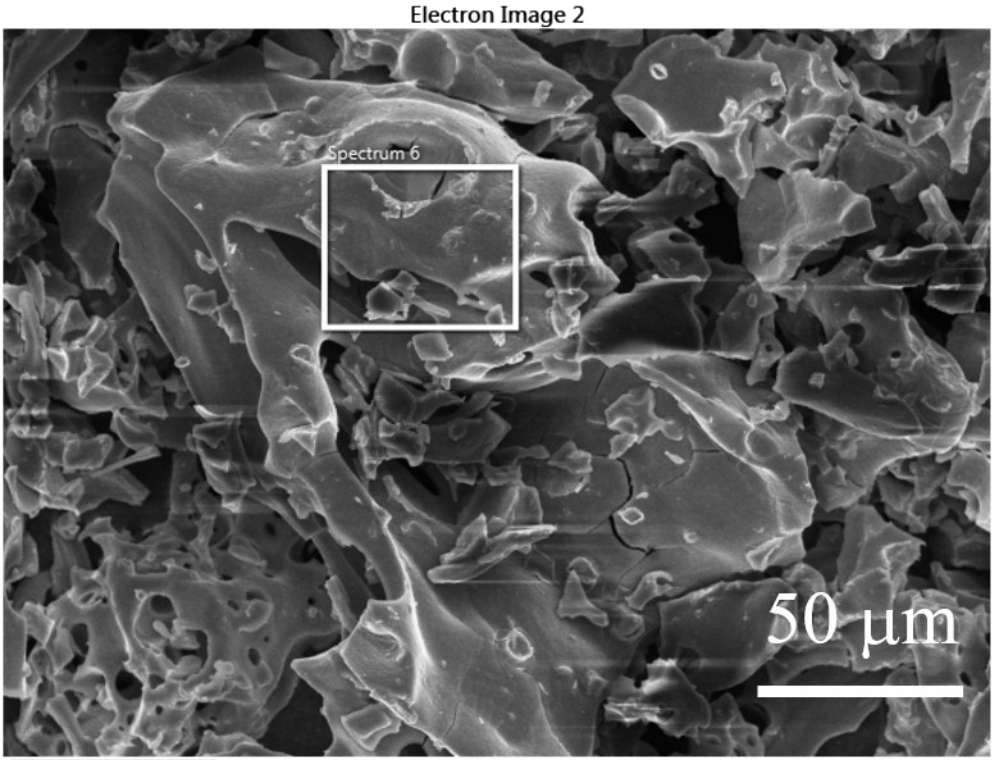

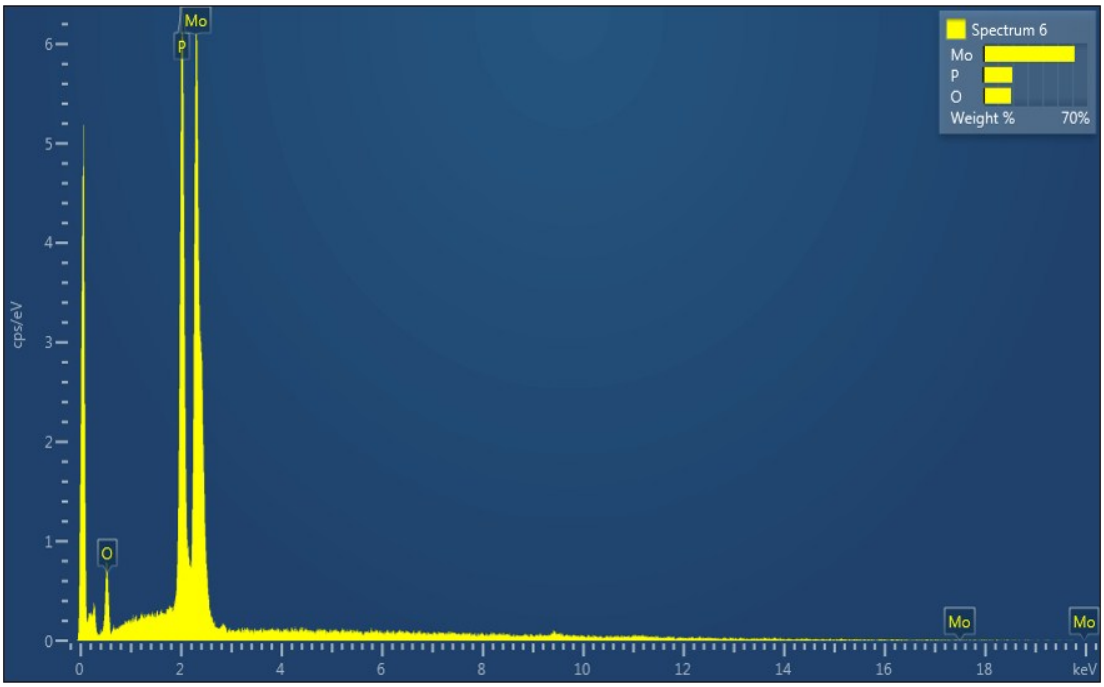

Fig. S1 SEM and EDS spectrum of MoP-2CA-650.

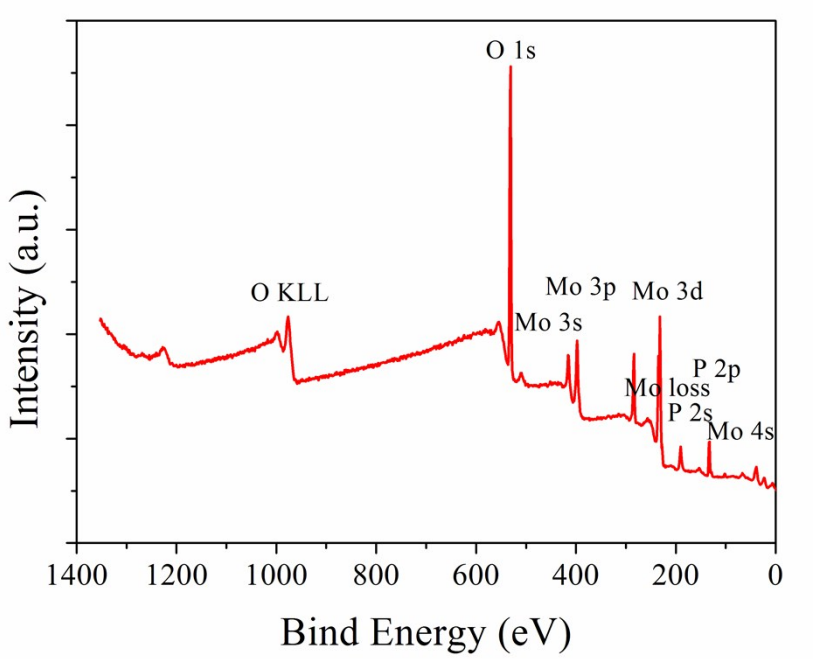

Fig. S2 The XPS survey spectrum of MoP-2CA-650.

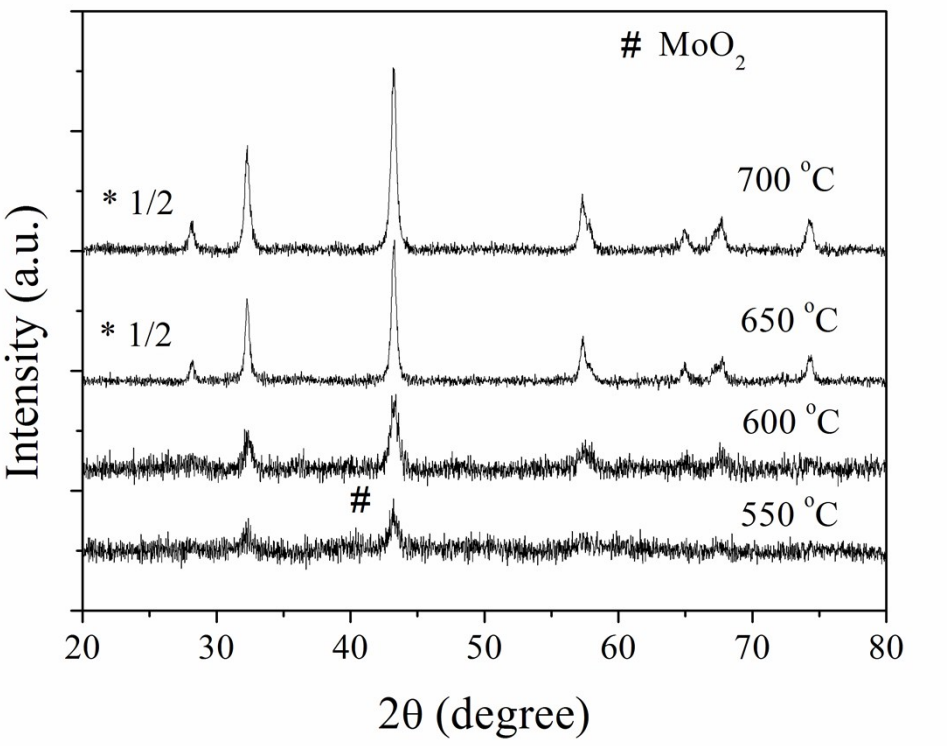

Fig. S3 XRD patterns of MoP-2CA prepared at different temperatures.

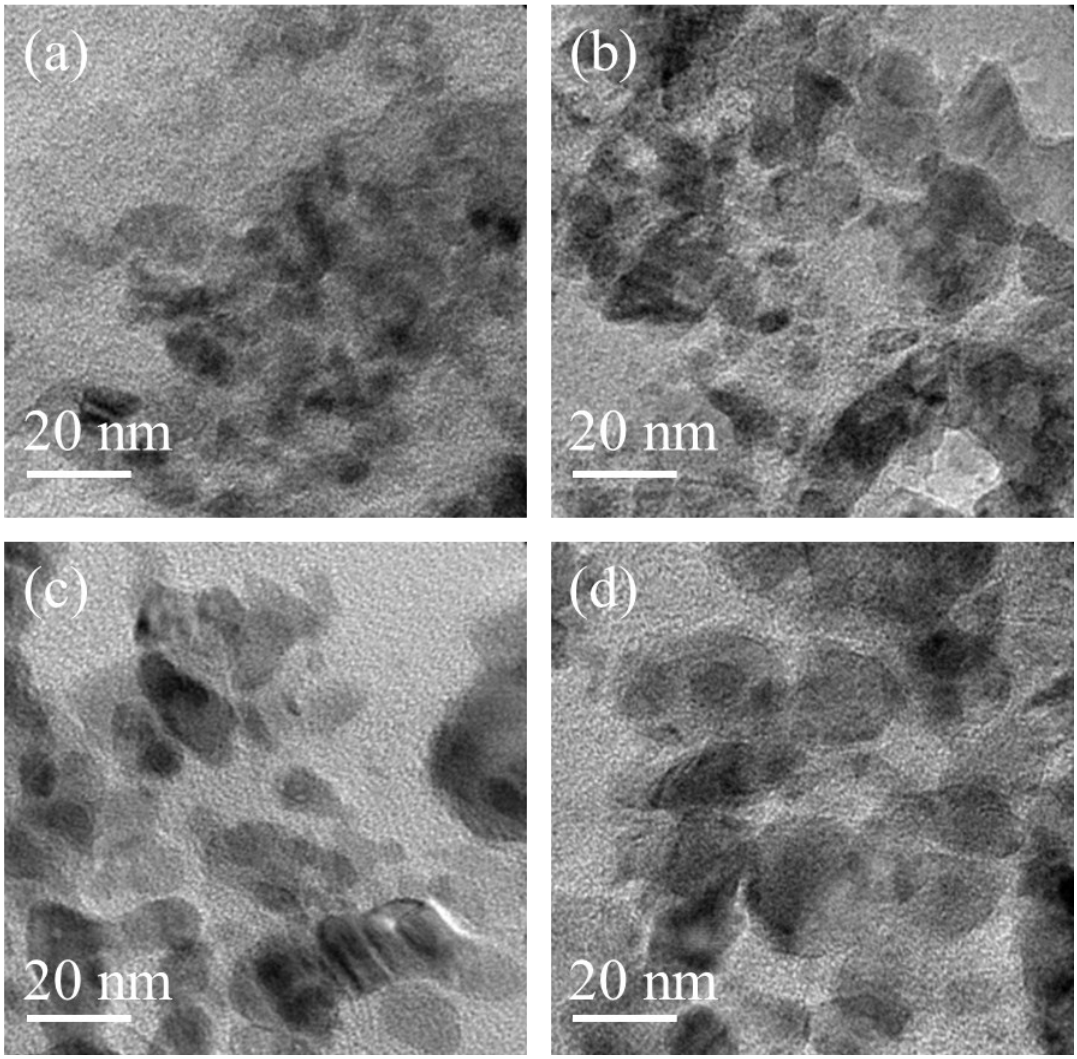

Fig. S4 TEM images of MoP-2CA prepared at different temperatures (a) 550 °C, (b) 600 °C, (c) 650 °C, (d) 700 °C.

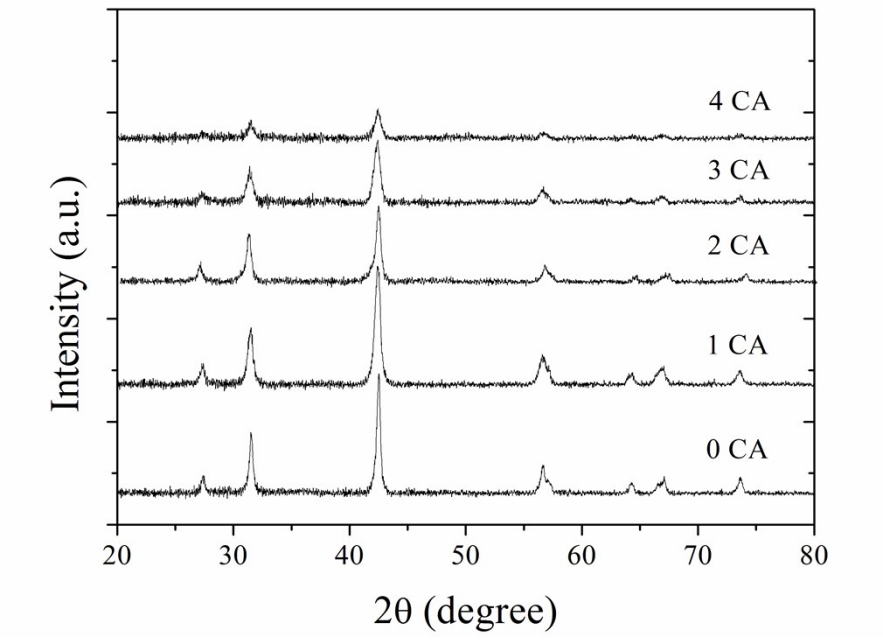

Fig. S5 XRD patterns of MoP prepared at 650 °C with CA:Mo ratio from 0 to 4.

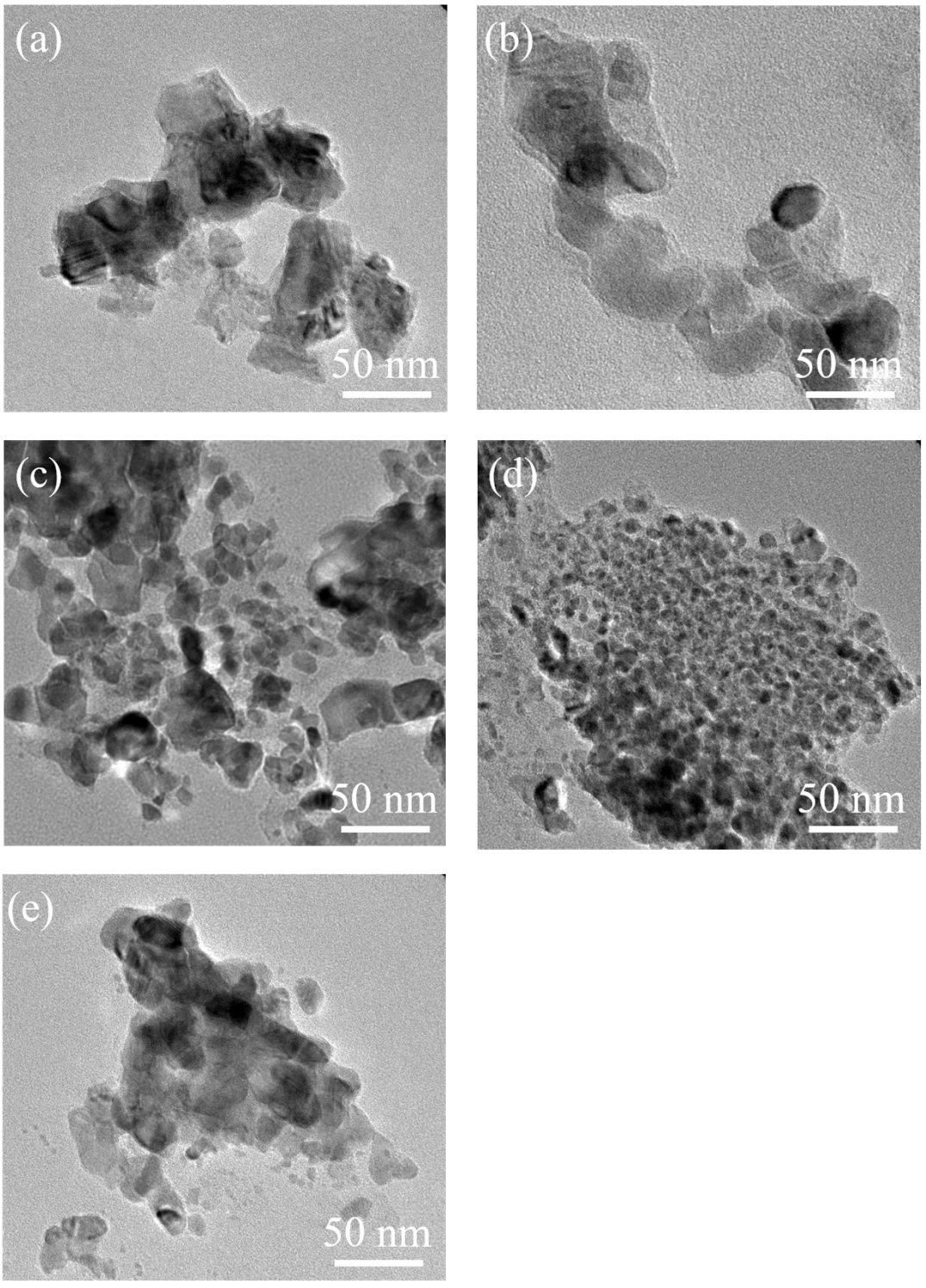

Fig. S6 TEM images of MoP prepared at 650 °C with (a) 0CA, (b) 1CA, (c) 2CA, (d) 3CA and (e) 4CA.

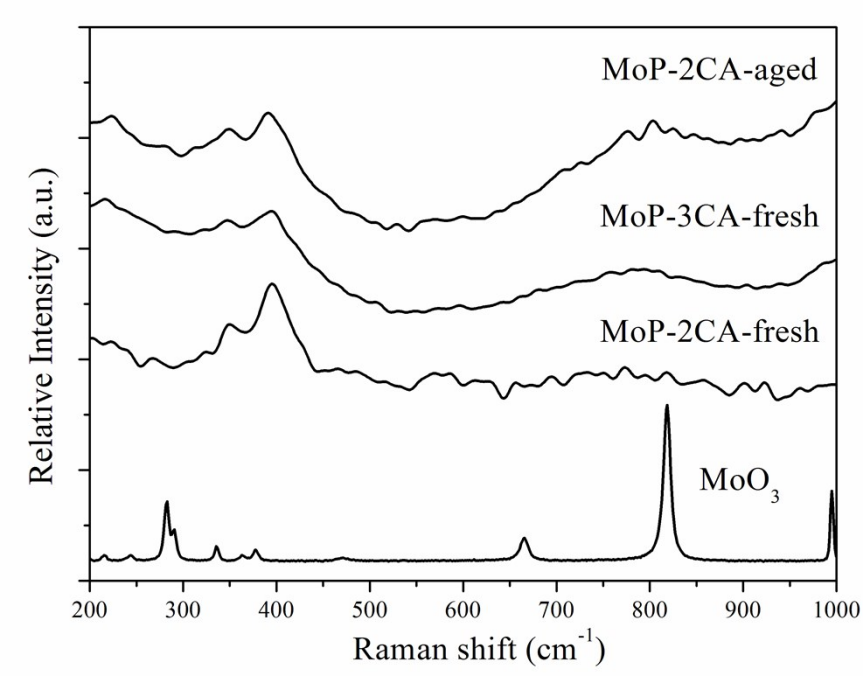

Fig. S7 Raman spectra of different samples recorded at 633 nm (MoP-2CA-aged refers to MoP-2CA stored at ambient condition for 0.5 year).

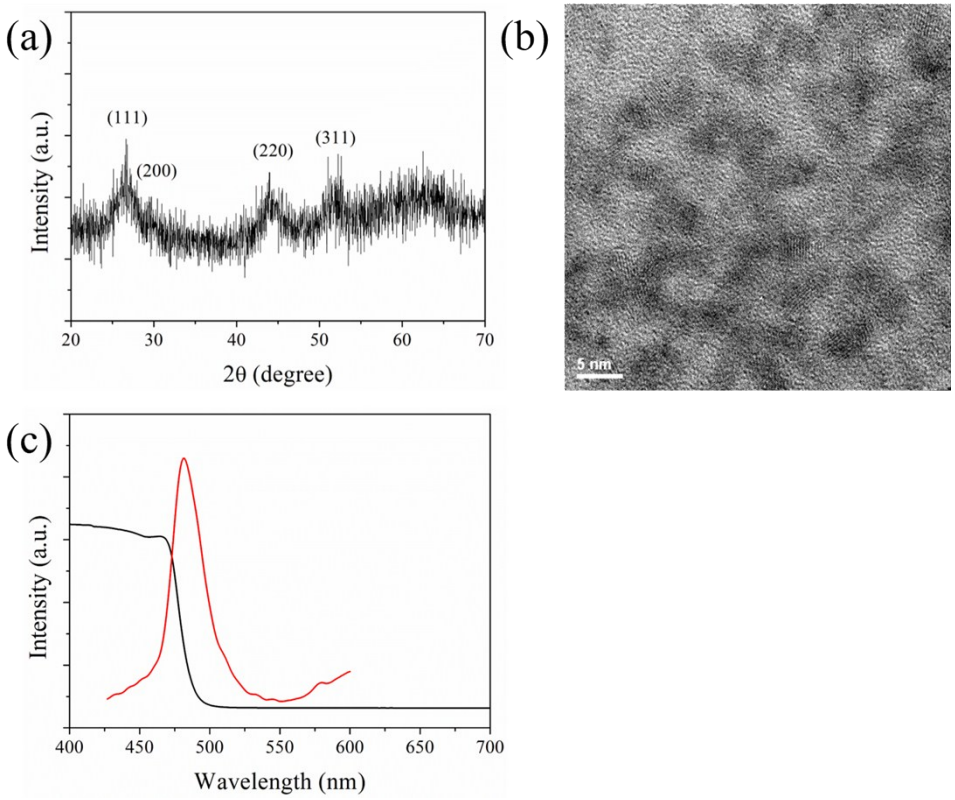

Fig. S8 (a) XRD patterns, (b) TEM image and (c) UV-vis and PL spectra of as prepared CdS QDs.

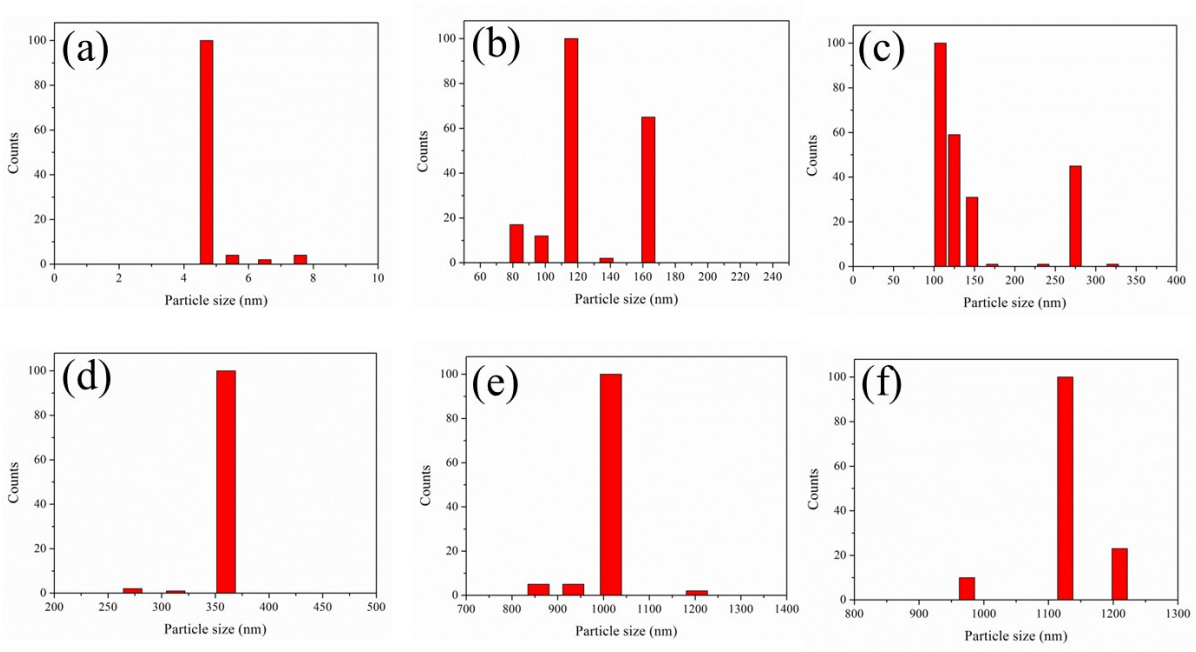

Fig. S9 Particle size distribution of (a) CdS QDs, (b) MoP, (c) CdS/MoP in water, and CdS/MoP in LA solution (d) pH 1, (e) pH 3, (f) pH 6.

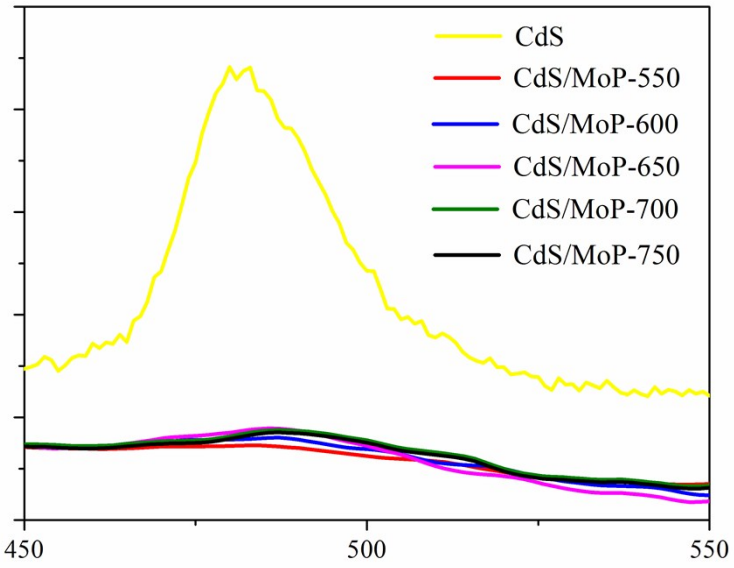

Fig. S10 PL emission spectra of various samples at an excitation wavelength of 360 nm at 77 K.

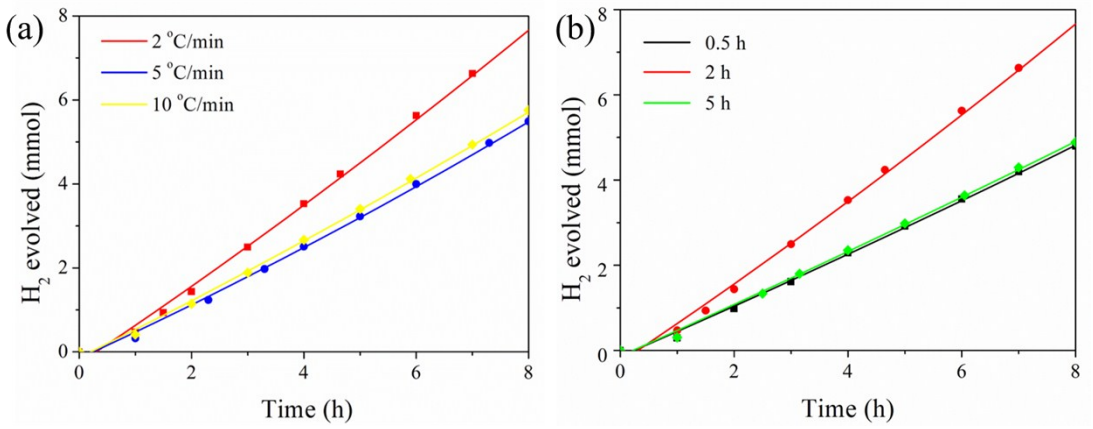

Fig. S11 Time course of H_2 evolution using MoP-2CA-600 samples with (a) different ramping rate; (b) different calcination duration.

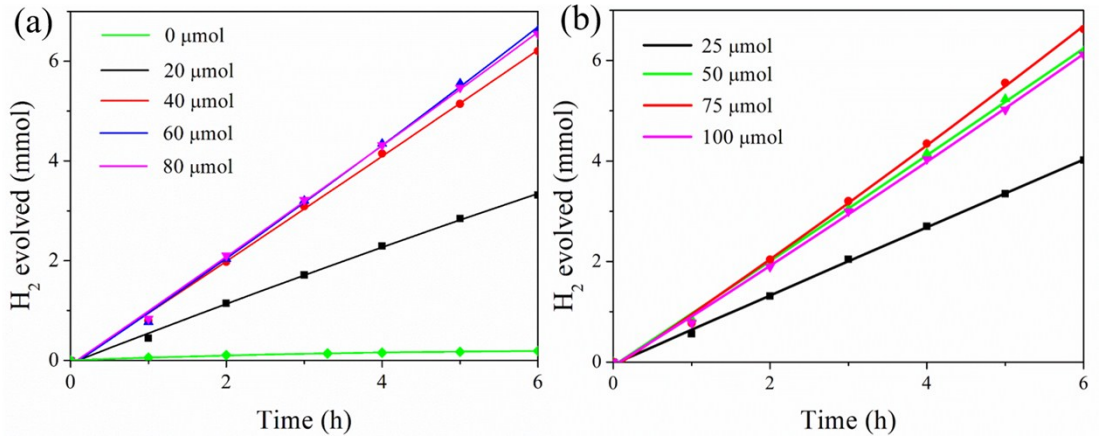

Fig. S12 Time course of H_2 evolution with (a) different amount of MoP while the amount of CdS QDs was fixed at 50 μmol; (b) different amount of CdS QDs while the amount of MoP was fixed at 60 μmol.

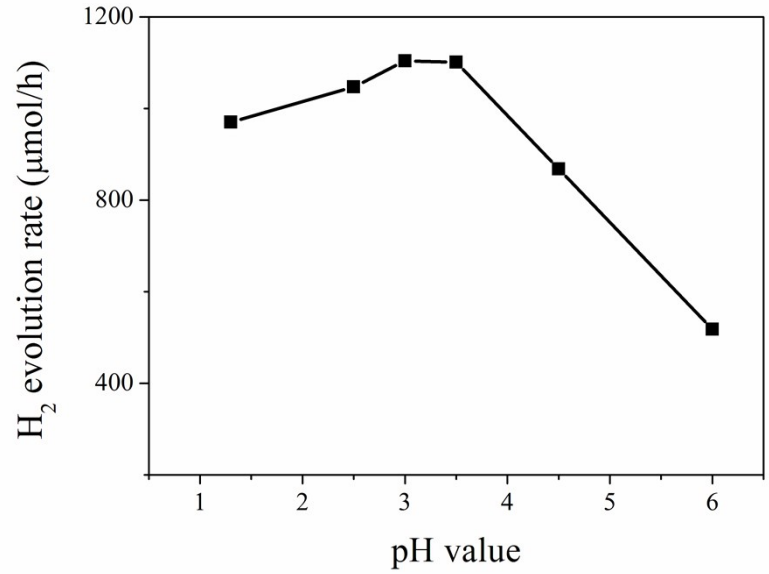

Fig. S13 H_2 evolution rate of CdS/MoP-600 at different pH values of the reaction solution.

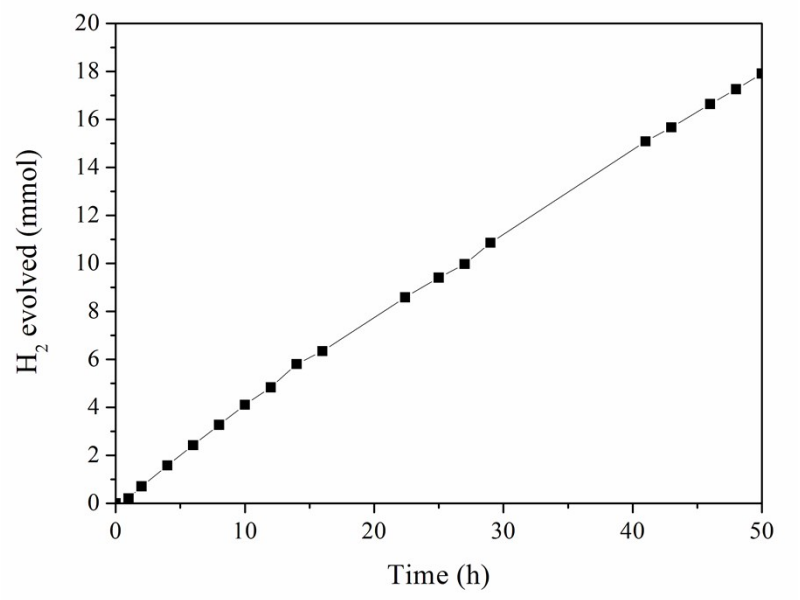

Fig. S14 Long duration irradiation test using 10.8 mg CdS and 2 mg MoP in 20 vol% lactic acid solution.

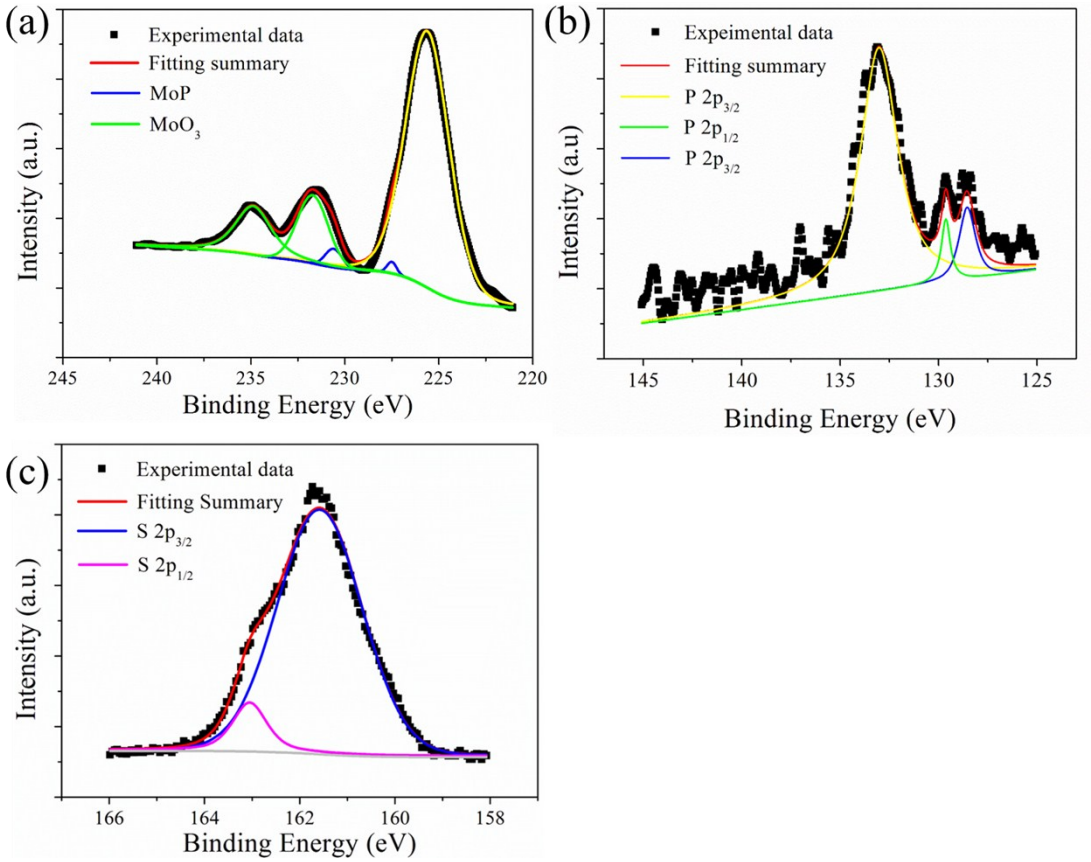

Fig. S15 High resolution XPS spectra of (a) Mo, (b) P and (c) S in the MoP/CdS QDs after photoreaction.

Exfoliation of MoS_2: Commercial MoS_2 was purchased from Sigma-Aldrich (powder, <2μm,

99%). The exfoliation of MoS_2 was conducted using probe sonicator mentioned in the experimental section. A certain amount of MoS_2 (50 mg) was ground and dispersed in N-methyl-pyrrolidone (99.8%, Sigma-Aldrich, 50 mL). The suspension was then ultrasonicated using the probe sonicator at 80% power for 2 h. After this process, the suspension was centrifuged at 3000 rpm for 45 min to isolate the unexfoliated MoS_2. The supernatant containing few-layered MoS_2 nanosheets was collected and subsequently the nanosheets were obtained by centrifugation at 12000 rpm and dried under vacuum overnight.

Preparation of amorphous MoS_3: the preparation was conducted following the method developed by our group[S1]. Typically, 2.0 mmol of $(NH_4)_2MoS_4$ and 0.2 g of PVP were dissolved in 75 mL of deionized water. 1.0 mL of thioacetic acid was added to the solution before it was transferred into a Teflon-lined autoclave with a capacity of 120 mL. The mixture was subjected to hydrothermal treatment at 200 ^oC for 12 h. After cooling to room temperature, the obtained brown color suspension was mixed with 300 mL of acetone and kept still over night for the precipitation of the solid particles. The dark brown colored solid was washed thoroughly with acetone and centrifuged several times before being dried at room temperature to obtain PVP-modified MoS_3 nanoparticles.

Table S1 Brunaur-Emmett-Teller (BET) surface areas of different MoP samples.

sample	**specific surface area (m^2/g)**
2CA-550	6.6
2CA-600	18.2
2CA-650	19.8
2CA-700	15.1
0CA-650	8.8
1CA-650	7.3
3CA-650	32.5
4CA-650	43.5

Table S2 Comparison of representative metal phosphide containing photocatalytic H_2

evolution systems.

Photocatalyst	Light source	Sacrificial agent	H_2 evolution Activity	Quantum efficiency	Ref
MoP/CdS QDs	300 W Xe, >420 nm	Lactic Acid	1.1 mmol/h	45%	This work
FeP/TiO_2	200 W Hg(Xe) arc, >365 nm	MeOH-H_2O	1.9 μmol/mg/h	8.7%	S2
P_{HIV}/CoP	500 W Xe, >420 nm	TEOA	160.7 μmol[a]	--	S3
CoP/CdS	30 × 3W WLED source, >420 nm	Lactic Acid	251 μmol/h	25.1%	S4
Ni_2P/CdS	30 × 3W WLED source, >420 nm	Lactic Acid	143 μmol/h	14.3%	S4
Cu_3P/CdS	30 × 3W WLED source, >420 nm	Lactic Acid	77 μmol/h	7.7%	S4
Ni_2P/CdS NRs	30 × 3W WLED source, >420 nm	Lactic Acid	130 μmol/h[b]	--	S5
Ni_2P/CdS NRs	300 W Xe, >420 nm	Na_2S-Na_2SO_3	1.2 mmol/mg/h	41%	S6
Co_2P/CdS NRs	30 × 3W WLED source, >420 nm	DL-mandelic acid	15 umol/h	6.8%	S7
Cu_3P/CdS NRs	300 W Xe, >420 nm	Na_2S-Na_2SO_3	184 μmol/mg/h	25%	S8
MoP/CdS NRs	300 W Xe, >420 nm	Lactic Acid	163 μmol/mg/h	16.7%	S9
MoS_2/CdS	300 W Xe, >420 nm	Lactic Acid	1.28 mmol/h	28.1	S10
MoS_2/CdS	300 W Xe, >420 nm	Lactic Acid	1.31 mmol/h	--	S11
MoS_3-CdS/CdSe NRs	500 W Hg/Xe arc, 450 nm	TEOA	10 umol/h	10%	S12

a: H_2 evolution measured in 40 min.

b: Calculated by the H_2 evolved in the first 2 h.

Table S3 The intensity of monochromatic irradiation and amount of evolve H_2 under monochromatic light irradiation.

	Left	Right	Front	Back	Center	Average	Average (mW)	Evolved H_2 in 1 hour (μmol)
420 nm	0.82	0.96	0.67	0.9	0.89	0.85	0.85	82
	0.86	0.97	0.72	0.85	0.8	0.84		
	0.85	0.99	0.75	0.92	0.73	0.85		
440 nm	1.25	1.35	1.28	1.06	1	1.19	1.19	117
	1.11	1.39	1.26	1.16	1.07	1.20		
	1.13	1.39	1.24	1.16	1.05	1.19		
460 nm	1.29	1.52	1.35	1.13	1.36	1.33	1.35	154
	1.28	1.5	1.37	1.24	1.46	1.37		
	1.29	1.5	1.36	1.23	1.44	1.36		
480 nm	0.33	0.33	0.39	0.3	0.62	0.39	0.4	33
	0.35	0.33	0.39	0.29	0.63	0.4		
	0.29	0.35	0.4	0.31	0.62	0.39		
500 nm	0.9	1.07	0.98	0.87	1.03	0.97	0.98	2.7
	0.92	1.07	0.97	0.9	1.02	0.98		
	0.95	1.08	0.98	0.86	1.03	0.98		

At 460 nm monochromatic light irradiation, the total photo energy in 1 hour is calculated as:

$$\text{Photo energy} = \frac{1.35 \times 3.14 \times 3 \times 3 \times 3600}{3.14 \times 0.5 \times 0.5} = 175 \text{ J}$$

Where

1) photo energy: the energy of all photons at 460 nm wavelength irradiated on the surface of the reaction solution in the reactor with a diameter of 60 mm in 1 hour;

Numerator:

2) 1.35 mW: average intensity of irradiation
3) 3 cm: radius of the surface of the reactor
4) 3600 s: equivalent to 1 hour

Denominator:

5) area of the silicon photodiode

The energy of one photon at 460 nm wavelength is $\frac{6.62\text{x}10^{-34} \text{ x } 3\text{x}10^{8}}{460\text{x}10^{-9}} = 4.3\times10^{-19}$ J.

So the total amount of incident photons in 1 hour is $\frac{175\text{x}10^{6}}{4.3\text{x}10^{-19} \text{ x } 6.02\text{x}10^{23}} = 672.3$ μmol

$$\text{Apparent quantum efficiency} = \frac{2 \times \textit{the number of evolved hydrogen molecules}}{\textit{the number of incident photons}} \times 100\% =$$

$$\frac{2 \times 154}{672.3} \times 100\% = 45.8\%$$

Apparent quantum efficiency under other monochromatic light irradiation can be calculated using the same method.

Reference:

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