

## *Supporting Information*

# **A robust and efficient catalyst of $\text{Cd}_x\text{Zn}_{1-x}\text{Se}$ motivated by the CoP for the photocatalytic hydrogen evolution under the sunlight irradiation**

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## **1. Experimental Section**

### **1.1. General information**

All the chemicals are analytical grade and used as received without further purification.

### **1.2. Preparation of ZnSe-DETA nanobelts**

ZnSe-DETA nanobelt was synthesized using the reported method<sup>1</sup> with a little modification. In a typical procedure, 0.658 g of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  and 0.519 g of  $\text{Na}_2\text{SeO}_3$  were added into the mixing solution containing 16 mL  $\text{H}_2\text{O}$ , 14 mL diethylenetriamine (DETA) and 5 mL  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , then keep magnetic stirring for 30 min to form a transparent solution. Afterwards, the solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave and kept at 160 °C for 12 h. The white samples were collected and washed 3 times with ethanol and water, and dried at 70 °C for 12 h.

### **1.3. Preparation of $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}$ , $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$ , CdSe hollow nanotubes**

These nanobelts were synthesized through selective cation-exchange reaction of ZnSe-DETA with  $\text{Cd}^{2+}$ . For preparation of  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}$  hollow nanobelt, 0.5 mmol of ZnSe-DETA

nanobelt was dispersed in 25 mL ethylene glycol in an ultrasound bath for 30 min and 0.125 mmol  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$  was added under continuous stirring. After 30 min of continuous stirring, the aqueous solution was transferred into a 50 mL Teflon-lined stainless-steel autoclave and heated at 170 °C for 6 h, the yellow precipitates were separated from the solution, and washed several times with ethanol and water, and dried at 40 °C for 12 h. By adjusting the amount of  $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ , cation-exchanged products such as  $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{Se}$  and CdSe hollow nanobelts can be obtained.

#### **1.4. Preparation of $\text{Co}(\text{OH})_2$ nanoparticles**

In a typical procedure, 0.75 g of sodium citrate was dissolved in 100 mL  $\text{H}_2\text{O}$  and 3 g of cobalt nitrate was added into the solution under magnetic stirring. After 30 min of continuous stirring, 25 mL NaOH solution (1 M) was dropped into the solution slowly to form the purple solution and kept stirring for 30 min. Afterwards, the purple products was collected by centrifugation and dried at 40 °C for 12 h.

#### **1.5. Preparation of CoP nanoparticles**

For a typical synthesis,  $\text{NaH}_2\text{PO}_2$  and  $\text{Co}(\text{OH})_2$  were put at two separated positions in a porcelain boat at furnace and the molar ratio for Co to P is 1:10. Subsequently, the samples were heated at 300 °C for 3 h under the protection of  $\text{N}_2$  atmosphere. Finally, the black powders were collected by washing two times with ethanol and dried at 40 °C for 12 h.

#### **1.6. Preparation of $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}/\text{CoP}$ composites**

A mount of  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}$  powder was dispersed into 50 mL  $\text{H}_2\text{O}$  in an ultrasound bath for 60 min, then a proper amount of CoP was added into the suspension under continuous stirring. After 2 h of continuous stirring, the resulting product was collected by centrifugation

and dried at 40 °C for 12 h.

### **1.7. Preparation of Cd<sub>0.25</sub>Zn<sub>0.75</sub>Se /Pt composites**

50 mg Cd<sub>0.25</sub>Zn<sub>0.75</sub>Se powder was dispersed into 50 mL H<sub>2</sub>O in an ultrasound bath for 60 min, then 0.5 mL 1 mg/mL H<sub>2</sub>PtCl<sub>4</sub> solution was added into the suspension under continuous stirring. After 2 h of a 300 W Xe lamp irradiation, the resulting product was collected by centrifugation and dried at 40 °C for 12 h.

### **1.8. Preparation of P25/CoP composites**

50 mg P25 powder was dispersed into 50 mL H<sub>2</sub>O in an ultrasound bath for 60 min, then 2.5 mg CoP was added into the suspension under continuous stirring. After 2 h of continuous stirring, the resulting product was collected by centrifugation and dried at 40 °C for 12 h.

### **1.9. Preparation of P25/Pt composites**

50 mg P25 powder was dispersed into 50 mL H<sub>2</sub>O in an ultrasound bath for 60 min, then 0.5 mL 1 mg/mL H<sub>2</sub>PtCl<sub>4</sub> solution was added into the suspension under continuous stirring. After 2 h of a 300 W Xe lamp irradiation, the resulting product was collected by centrifugation and dried at 40 °C for 12 h.

### **2.0. Preparation of artificial sea water**

The simulated sea water was prepared according to the Mocledon recipe. In a typical procedure, 26.726 g NaCl, 2.26 g MgCl<sub>2</sub>, 3.248 g MgSO<sub>4</sub>, 1.153 g CaCl<sub>2</sub>, 0.721 g KCl, 0.198 g NaHCO<sub>3</sub>, 0.058 g NaBr, 0.058 g H<sub>3</sub>BO<sub>3</sub>, 0.0024 g Na<sub>2</sub>SiO<sub>3</sub>, 0.0015 g Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>, 0.002 g H<sub>3</sub>PO<sub>4</sub>, 0.013 g AlCl<sub>3</sub>, 0.002 g NH<sub>3</sub> and 0.0013 g LiNO<sub>3</sub> were added into 1 L water under stirring. After all the solid dissolved, the artificial sea water was obtained.

### 2.1. Characterizations

X-ray diffraction (XRD) patterns of all samples were collected in the range  $10-80^\circ$  ( $2\theta$ ) using a RigakuD/MAX 2550 diffract meter (Cu K radiation,  $\lambda = 1.5406 \text{ \AA}$ ), operated at 40 kV and 100 mA. The morphologies were characterized by transmission electron microscopy (TEM, JEM2000EX). The surface morphologies were observed by field emission scanning electron microscopy (HITACHI, S4800). The instrument employed for XPS studies was a Perkin-Elmer PHI 5000C ESCA system with Al K $\alpha$  radiation operated at 250 W. The shift of the binding energy due to relative surface charging was corrected using the C1s level at 284.4 eV as an internal standard. Mott-Schottky plots were recorded on an electrochemical workstation (Zahner, Zennium). Measurements were performed on a standard three electrode cell with a working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode as the reference electrode in dark. The working electrode was prepared through a clean fluoride-tin oxide (FTO) deposited with a sample film. The aqueous solution of 0.5 M Na<sub>2</sub>SO<sub>4</sub> purged with nitrogen gas was used as the electrolyte.

### 2.2. Photocatalytic hydrogen evolution

The photocatalytic hydrogen evolution experiments were conducted on an online photocatalytic hydrogen evolution system (Perfectlight, Beijing LabSolar III AG) at ambient temperature (5 °C) using a 300 W Xe lamp equipped with a AM 1.5 solar simulator. 50 mg of catalyst was dispersed in 100 mL of aqueous solution containing Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial reagents, and then the suspension was stirred and vacuumized for 30 min. Hydrogen evolution was observed only under irradiation, being analyzed by an online gas chromatograph (GC7890, Tian Mei, Shanghai, TCD, nitrogen as a carrier gas and 5 Å

molecular sieve column). Once the photocatalytic reaction of a cycle test of 2.5 h was completed, the reactor was replenished with 5 mL  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{SO}_3$  aqueous solution and degassed in vacuum before starting the subsequent cycle. For  $\text{TiO}_2$ -based catalysts, methanol is used as electron donor and the volume ratio of  $\text{H}_2\text{O}$  to methanol is 4:1. The total volume is 100 mL.

The outdoor photocatalytic hydrogen evolution tests under sunlight irradiation were finished in a cuvette. 3 mg  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}/\text{CoP}$  was dispersed in 3 mL aqueous solution containing 1.25 M  $\text{Na}_2\text{S}$  and 1.75 M  $\text{Na}_2\text{SO}_3$  as sacrificial reagents. Then, the cuvette was exposed under sunlight irradiation (06/01/2016, 3:00 pm, Shanghai, China). The photocatalytic sea water splitting tests under sunlight irradiation were conducted by taking place of distilled water with artificial sea water.

### **2.3. Photoelectrochemical Tests**

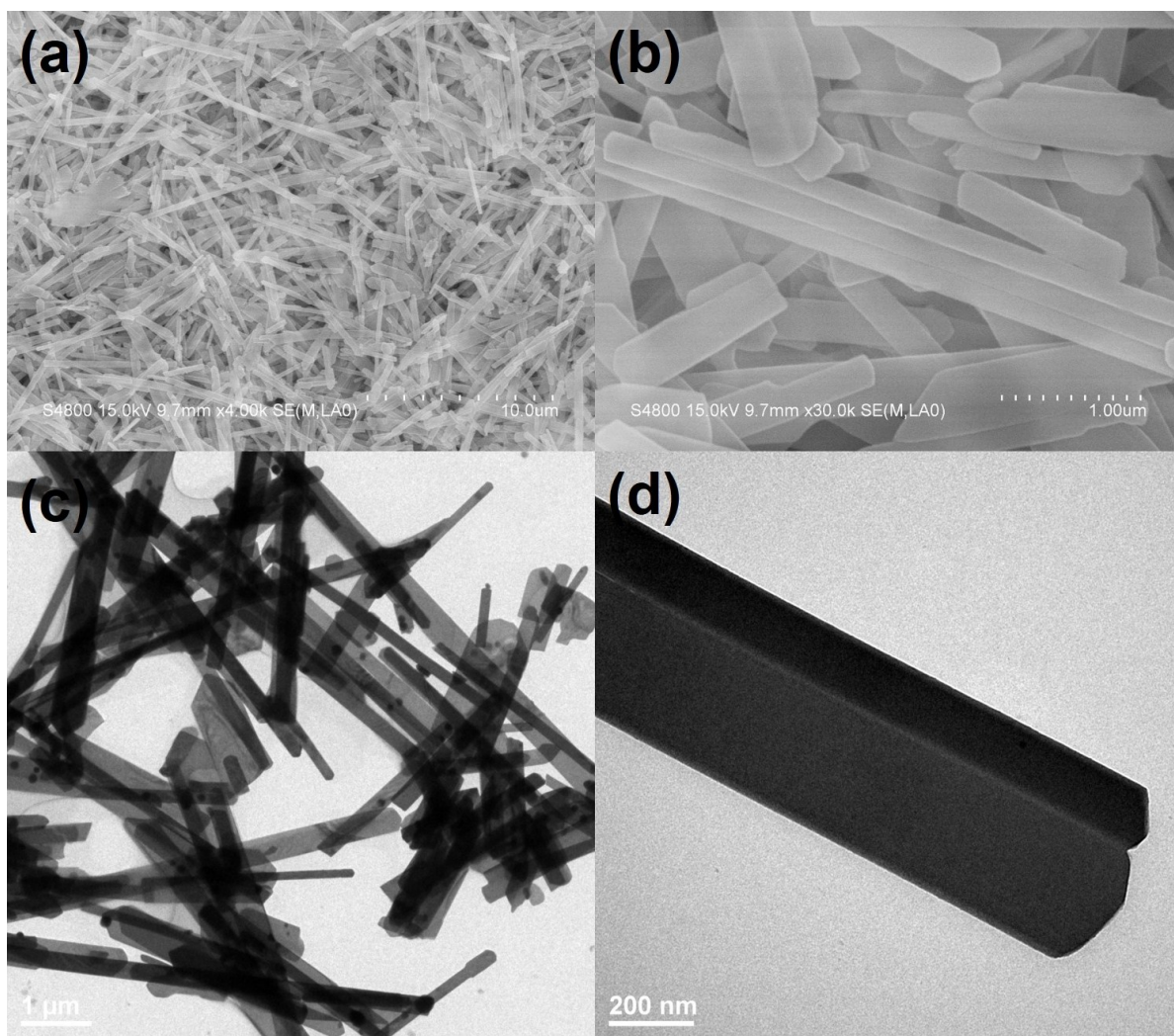
Photocurrent measurements were carried out with an analyzer (Zahner, Zennium) in dark conditions using a standard three electrode cell with a working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode as the reference electrode. A 0.5 M solution of  $\text{Na}_2\text{SO}_4$  was used as the electrolyte. The working electrode was prepared by spreading the 100  $\mu\text{L}$  suspension of FTO glass substrate. The suspension was prepared by dispersing catalyst (10 mg) into a ternary solution containing 100  $\mu\text{L}$  Nafion, 400  $\mu\text{L}$  ethanol and 500  $\mu\text{L}$   $\text{H}_2\text{O}$ . The working electrode was dried at 40 °C. The supporting electrolyte was an aqueous solution of  $\text{Na}_2\text{SO}_4$  (0.5 M) and purged with nitrogen for 30 min before measurement.

### **2.4. Quantum efficiency calculations**

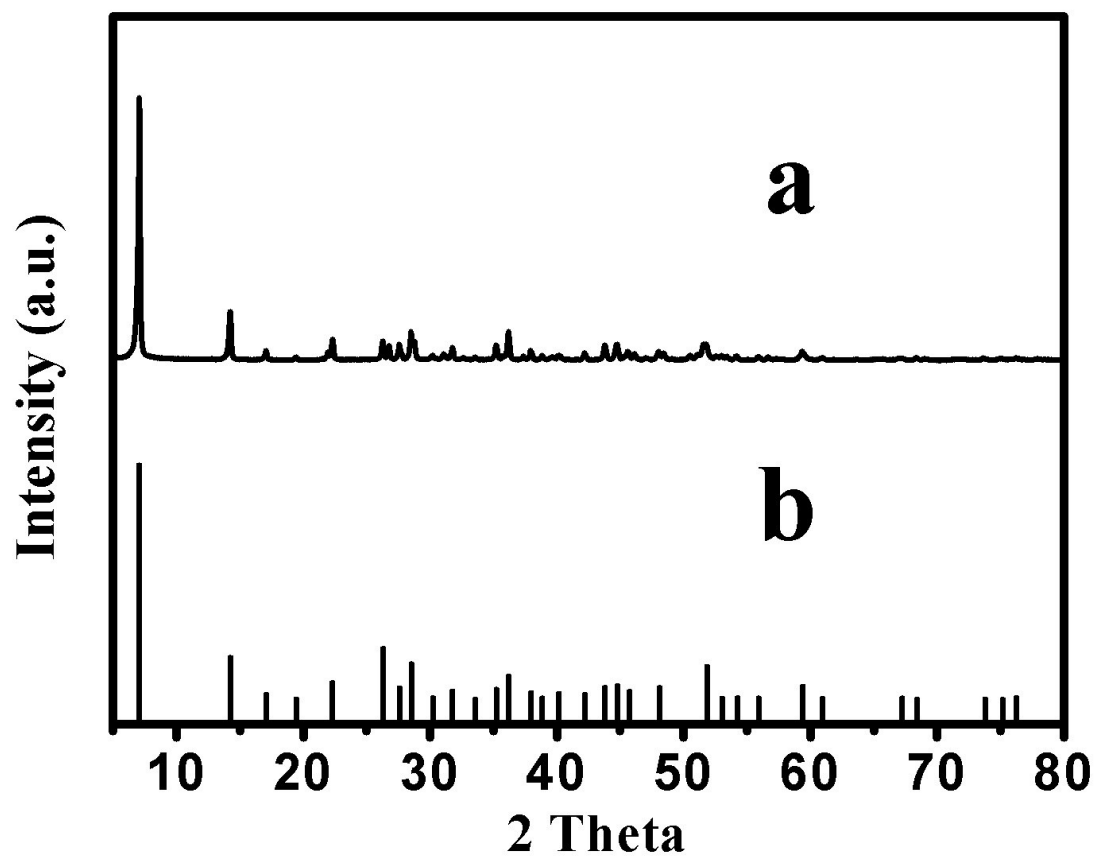
The determination of the quantum efficiency (QE) for hydrogen was performed on an online photocatalytic hydrogen evolution system (Perfectlight, Beijing LabSolarIIIAG) at ambient temperature (5 °C) using a 300 W Xe lamp equipped with  $\lambda \pm 20$  nm band-pass filter. The average intensity of irradiation was determined by a light intensity meter and the irradiation area was 37.9 cm<sup>2</sup>. The number of incident photons (N) was calculated by equation (1). The quantum efficiency is calculated from equation (2).

$$N = \frac{E\lambda}{hc} \quad (1)$$

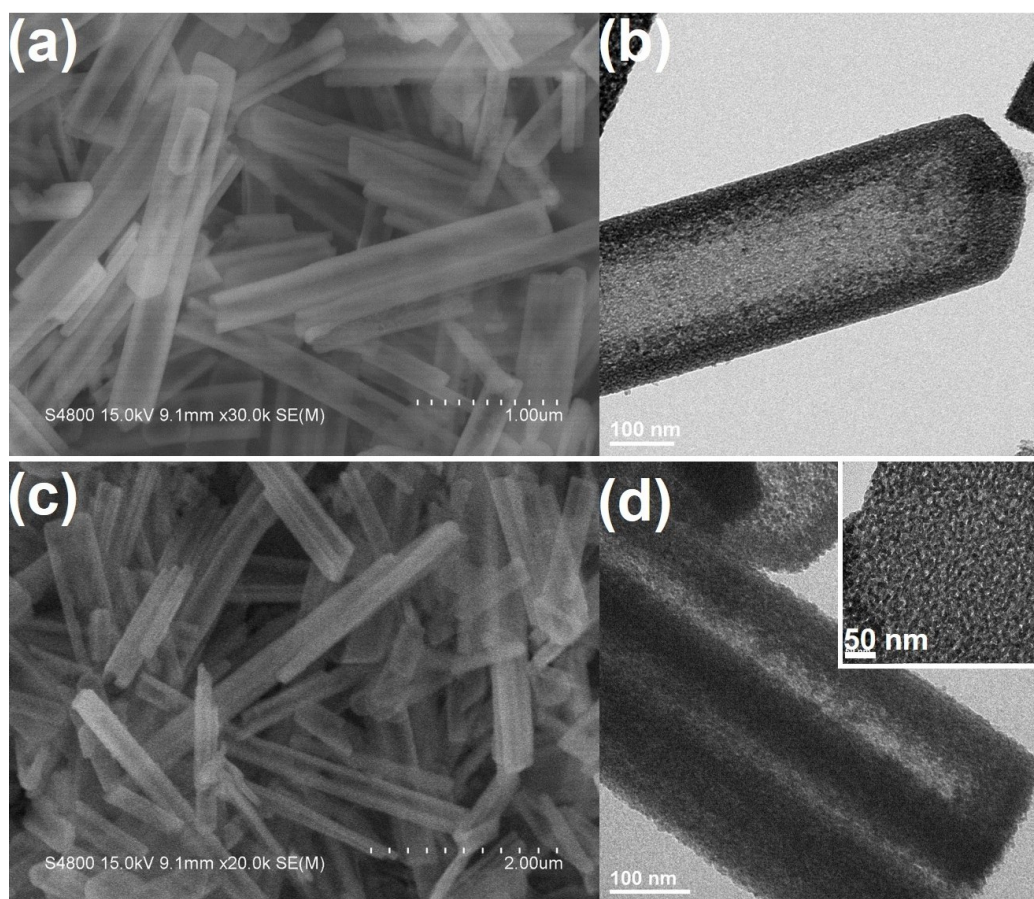
$$QE = \frac{2 * \text{the number of the evolved H}_2 \text{ molecules}}{\text{The number of incident photons}} \quad (2)$$



**Fig. S1** (a, b)SEM and (c, d) TEM images of ZnSe-DETA.



**Fig. S2.** XRD patterns (a) of ZnSe-DETA in this work. The stick pattern (b) is the simulated XRD pattern from the Rietveld refinement and the parameters of ZnSe-DETA reported by Yu et al.<sup>1</sup>



**Fig. S3.** SEM and TEM images of  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}$  (a, b) and  $\text{CdSe}$  (c, d).

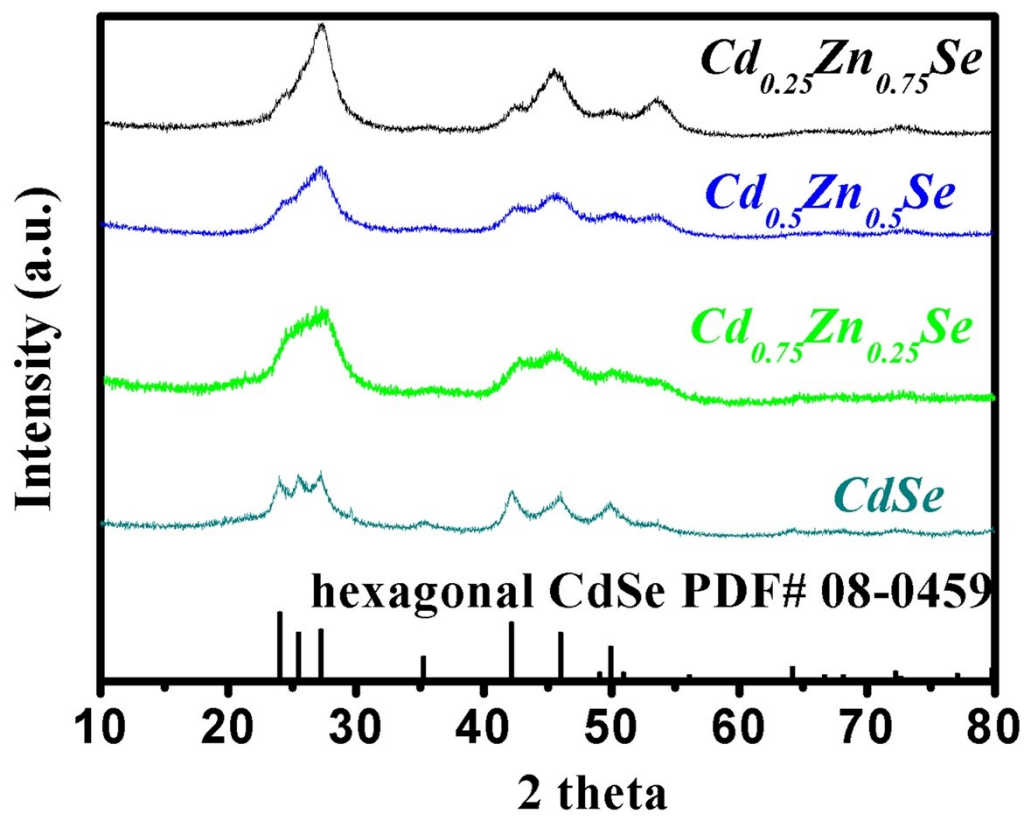
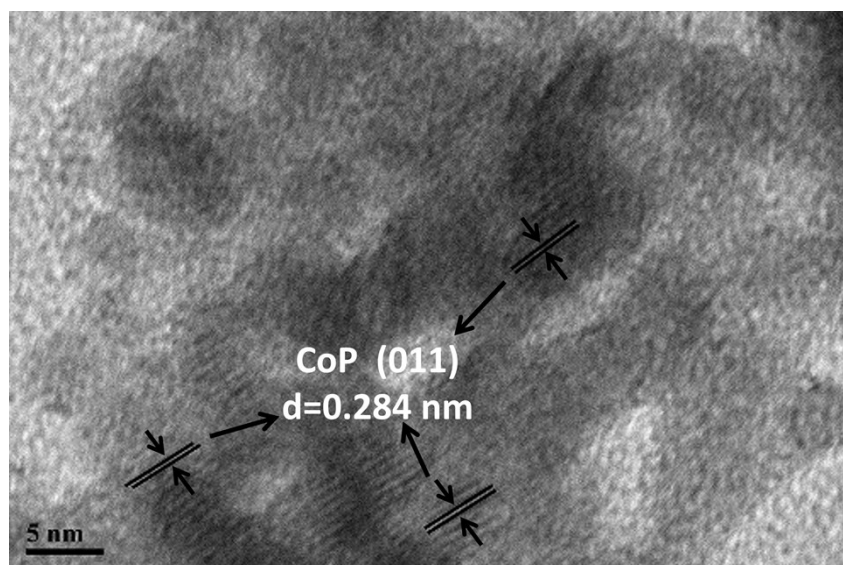


Fig. S4. XRD patterns of different samples.



**Fig. S5.** HRTEM image of CoP.

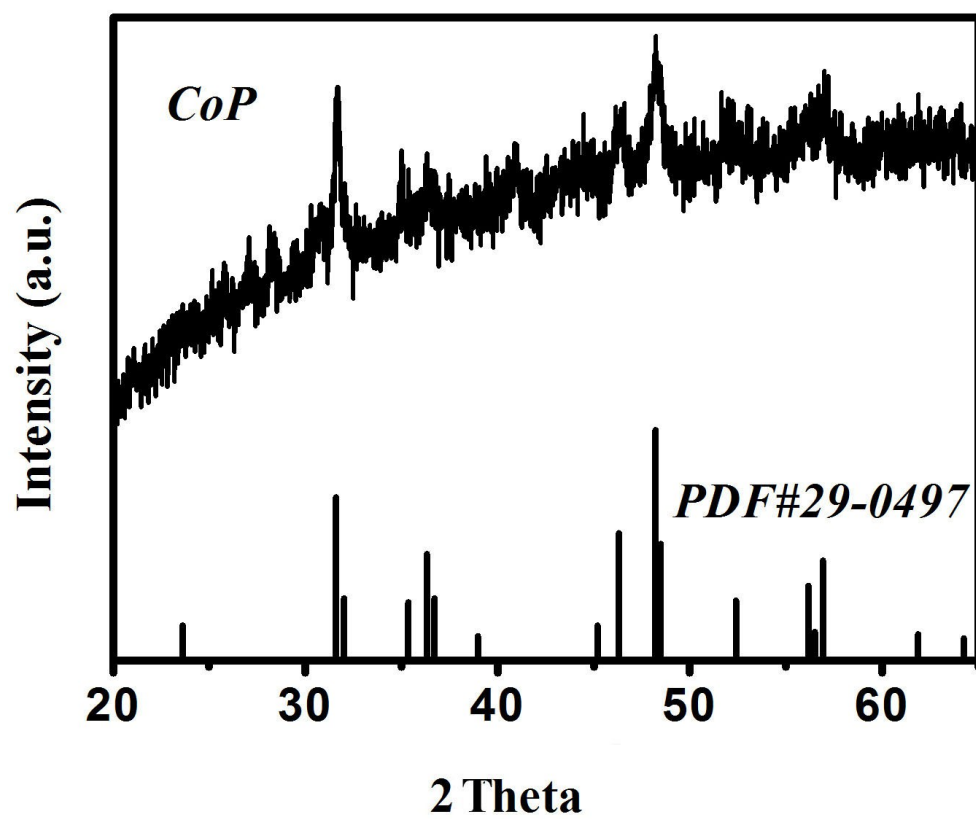
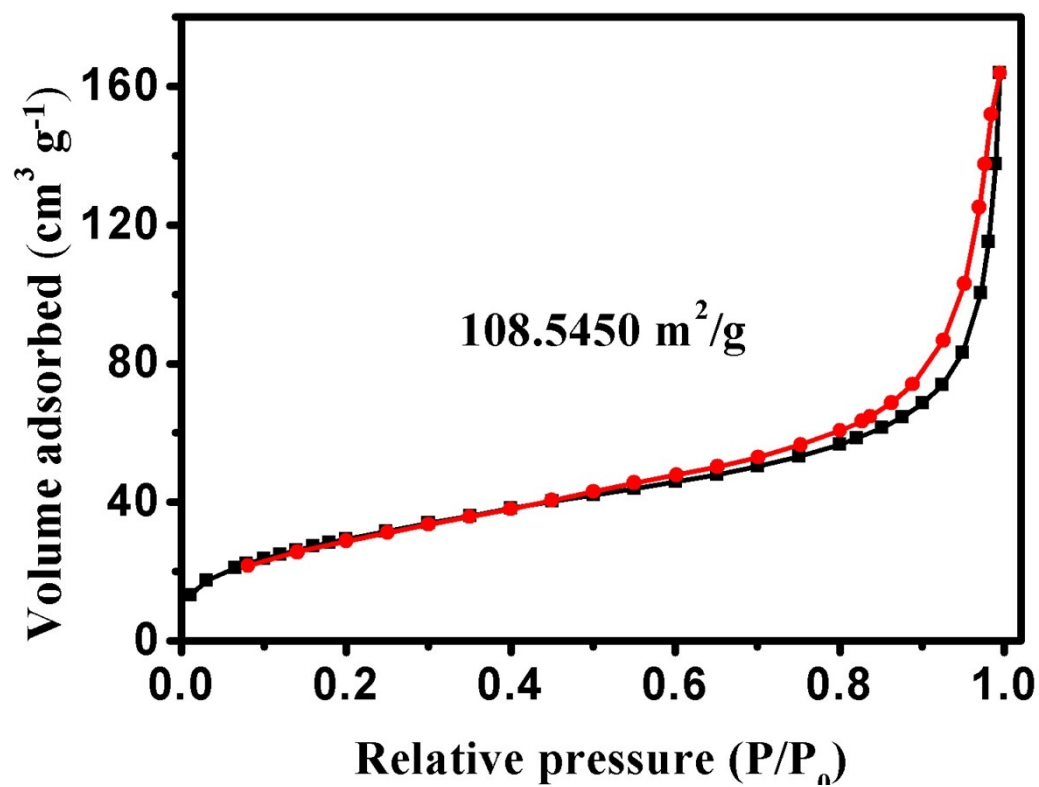
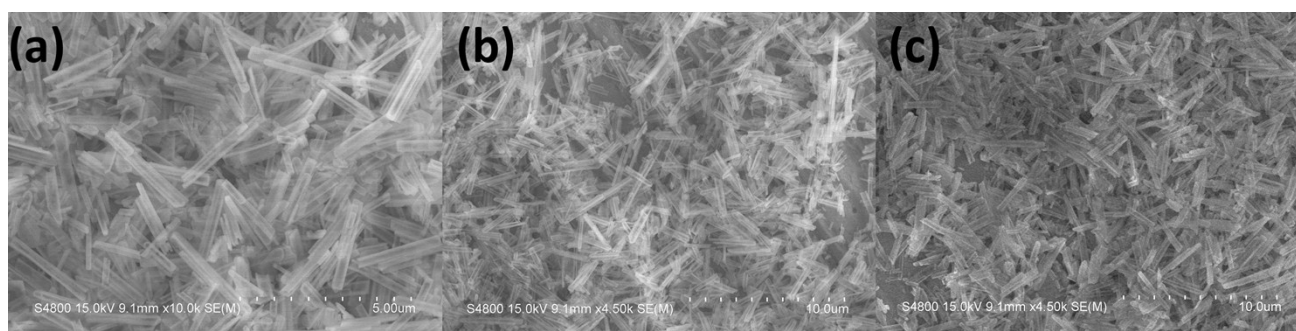


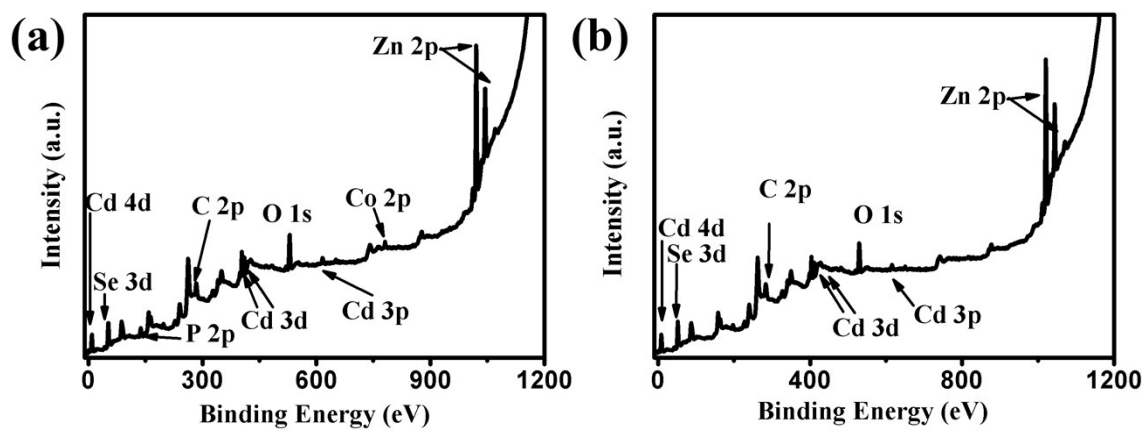
Fig. S6. XRD patterns of CoP.



**Fig. S7.** Nitrogen adsorption-desorption curves of Cd<sub>0.25</sub>Zn<sub>0.75</sub>Se/CoP.



**Fig. S8.** SEM images of (a)  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}/\text{CoP}$  (1 wt%),  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}/\text{CoP}$  (5 wt%) and  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}/\text{CoP}$  (10 wt%).



**Fig S9.** The XPS spectra of  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}/\text{CoP}$  (a) and  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}$  (b).

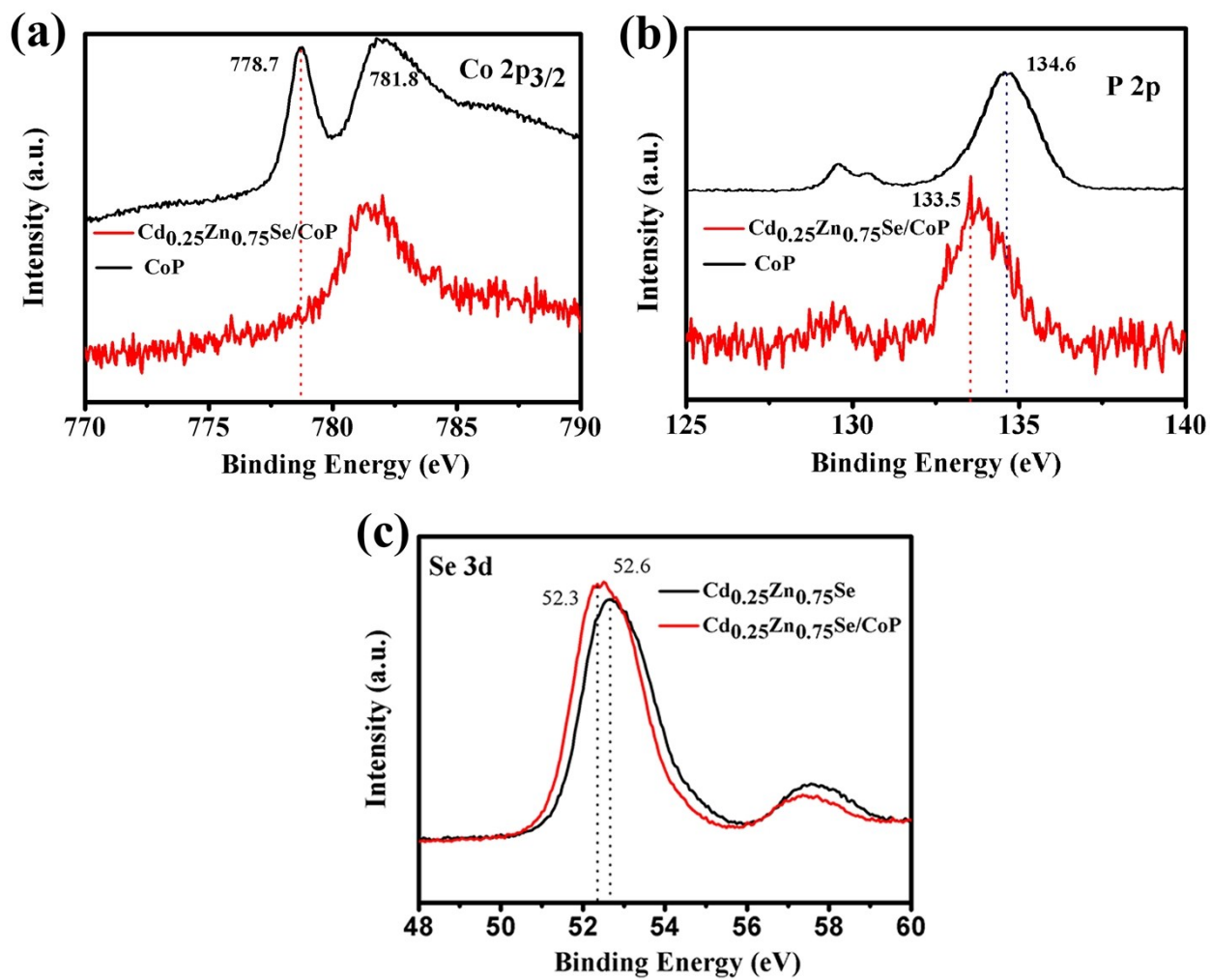
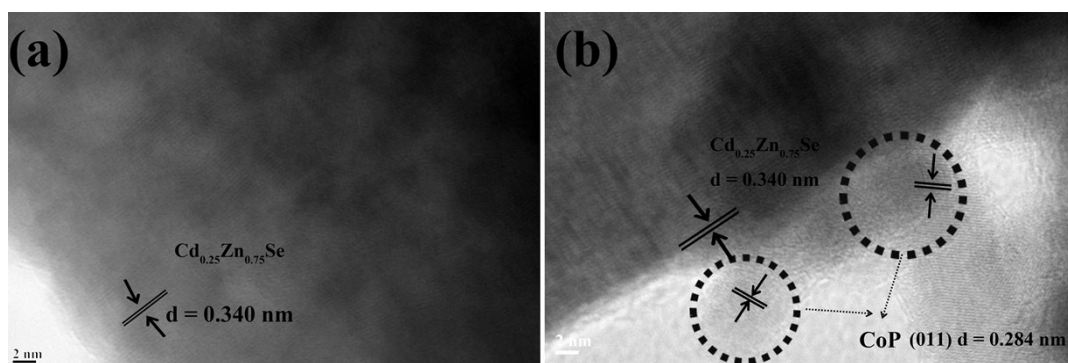
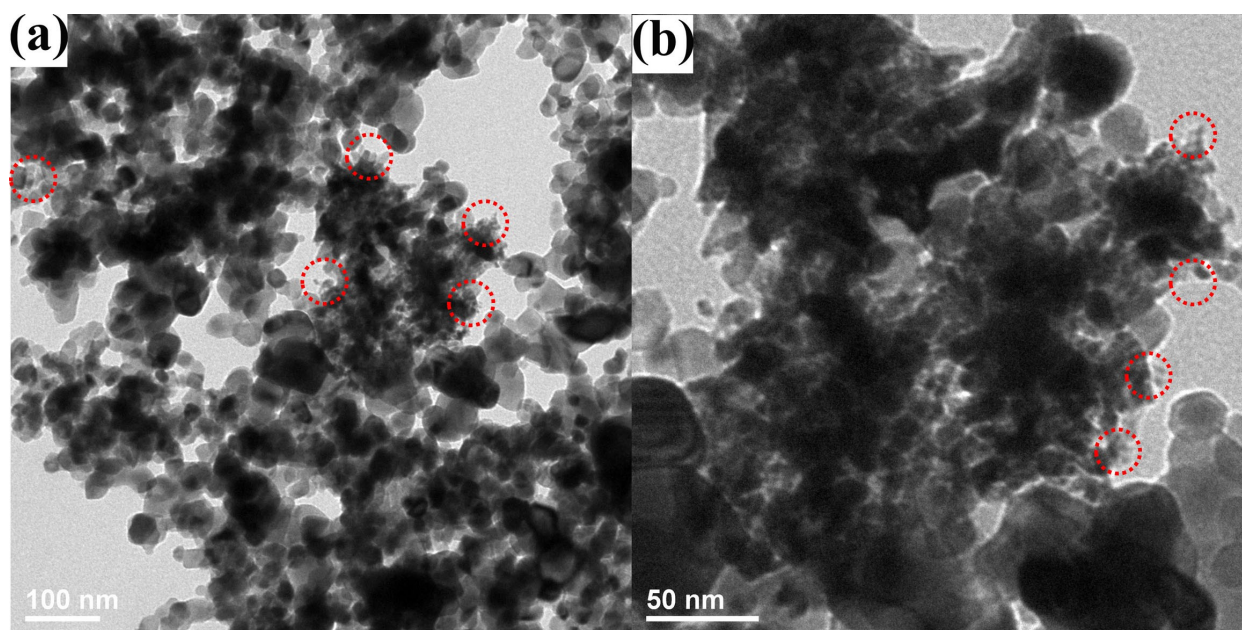


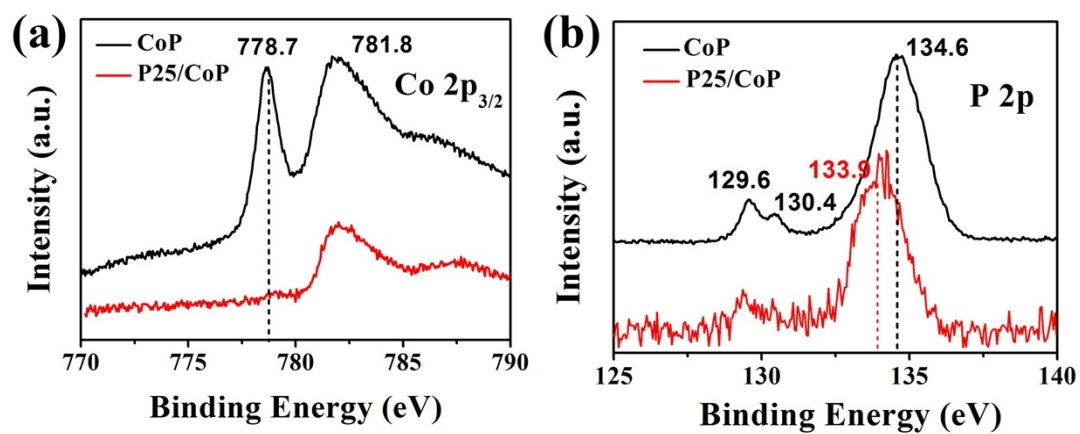
Fig. S10. XPS spectra of different samples.



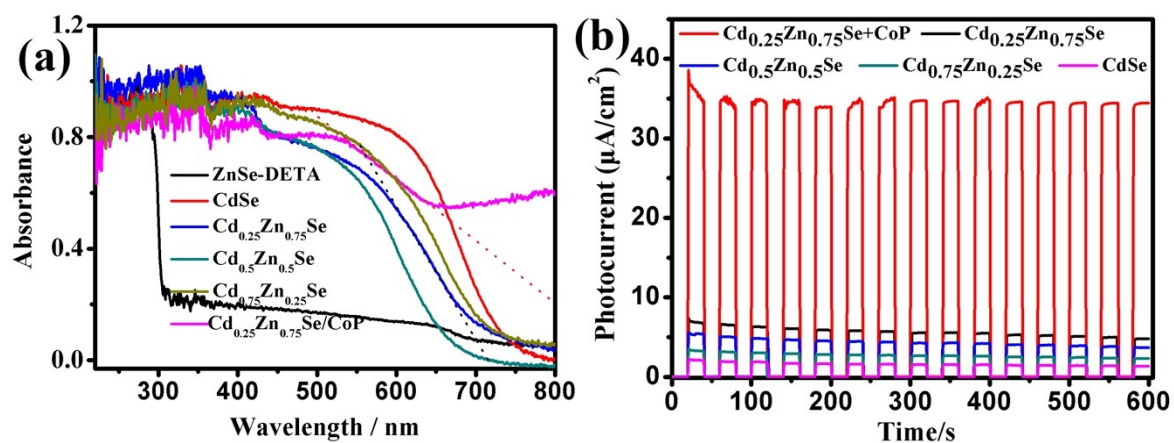
**Fig. S11** The HRTEM images of  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}$  (a) and  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}/\text{CoP}$  (b)



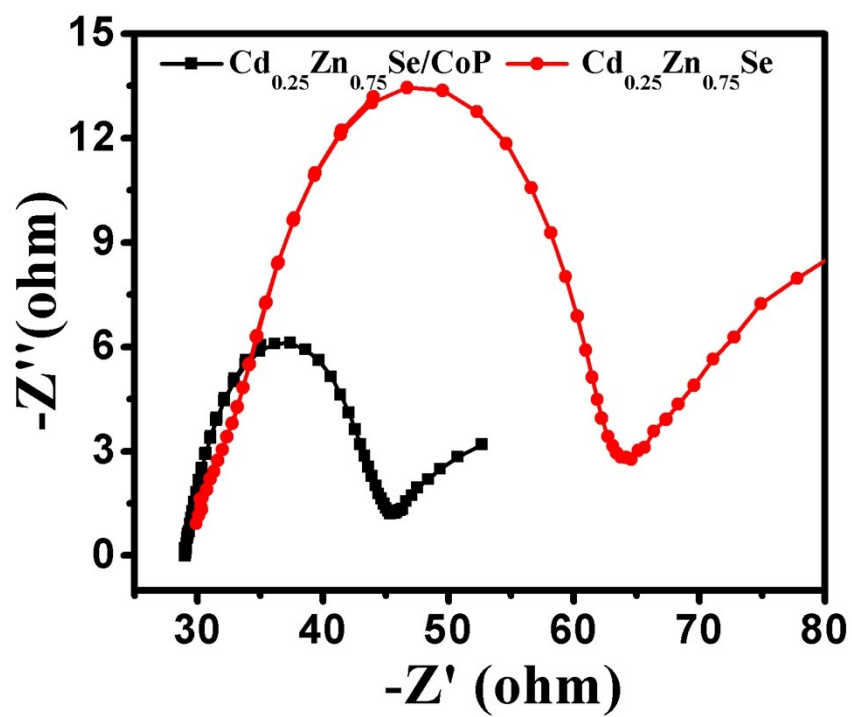
**Fig. S12.** TEM images of P25/CoP (red circles refer to CoP nanoparticles ).



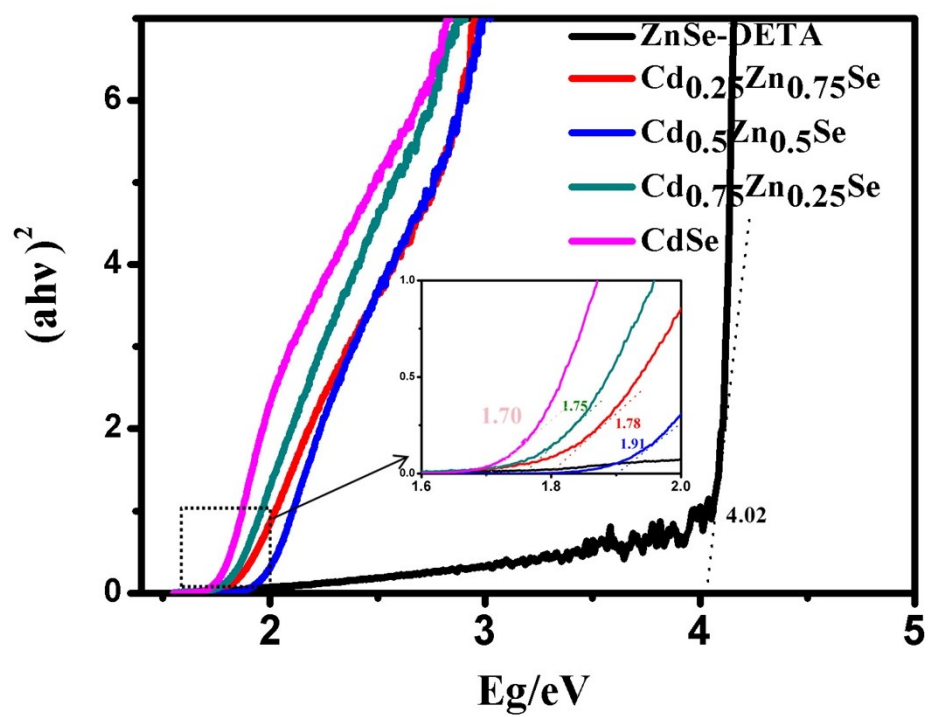
**Fig. S13.** (a) Co 2p XPS spectra of CoP before and after loading with P25. (b) P 2p XPS spectra of CoP before and after loading with P25.



**Fig. S14.** (a) UV-DRS spectra of different samples; (b) Transient photocurrent responses of different samples (under 300 W Xe lamp irradiation with AM 1.5 filter).



**Fig. S15.** EIS Nyquist plots of  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se/CoP}$  and  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se}$  under AM 1.5G irradiation.



**Fig. S16.** Curve of Kubelka-Munk function plotted against the photon energy.

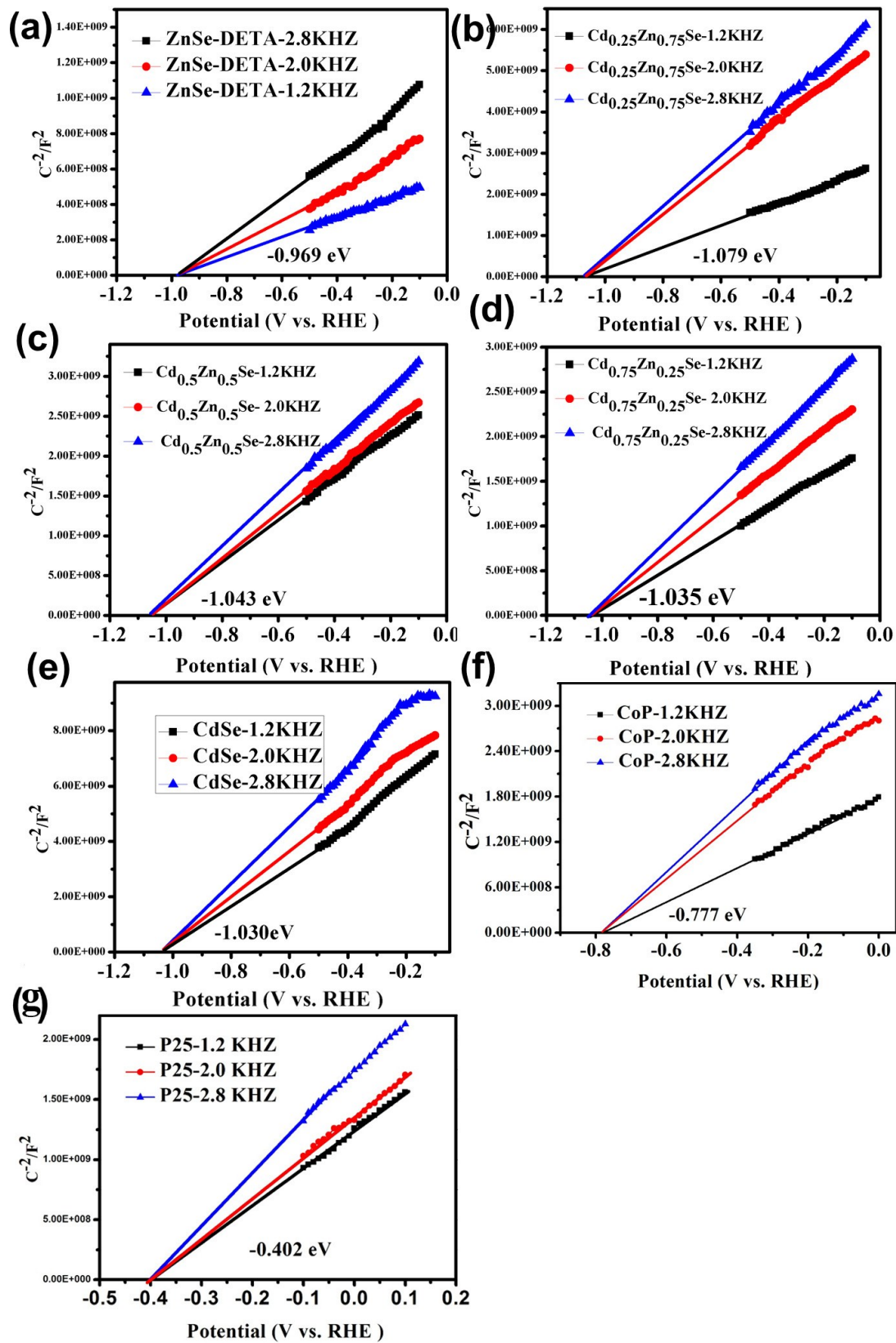
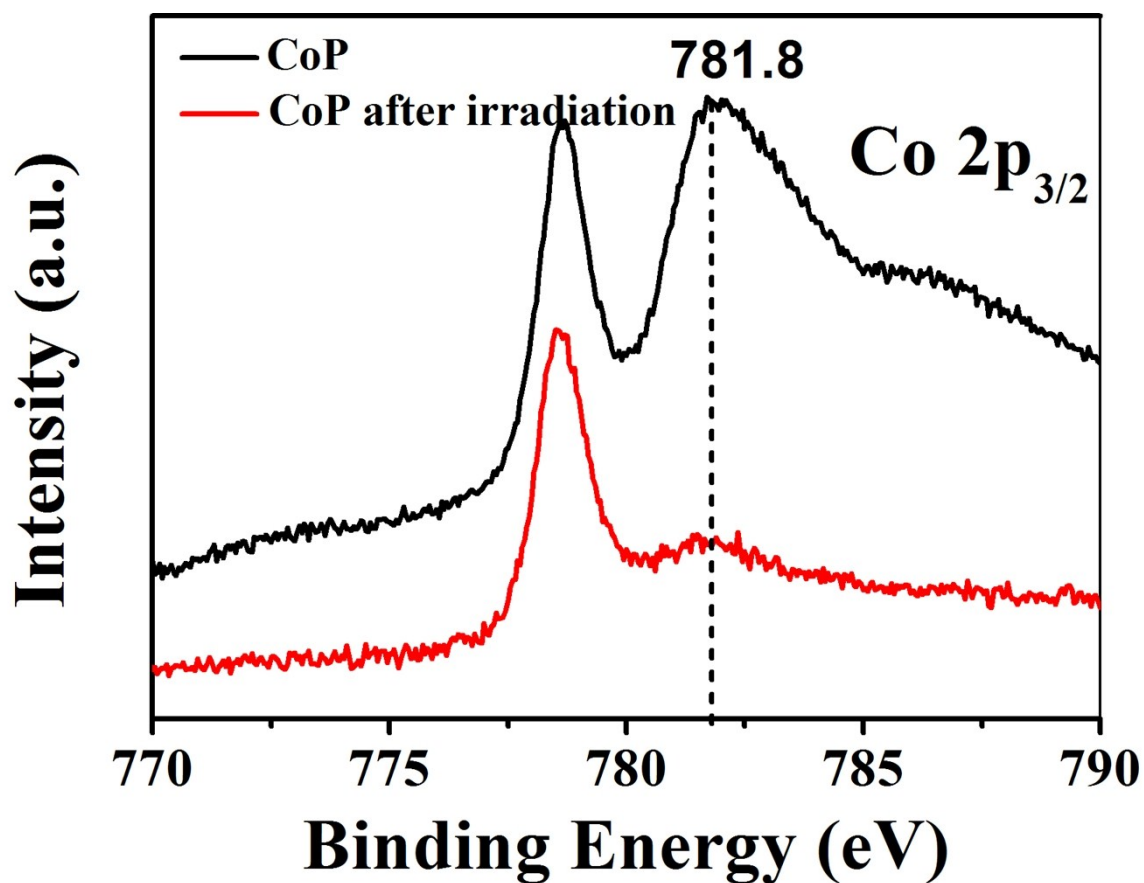
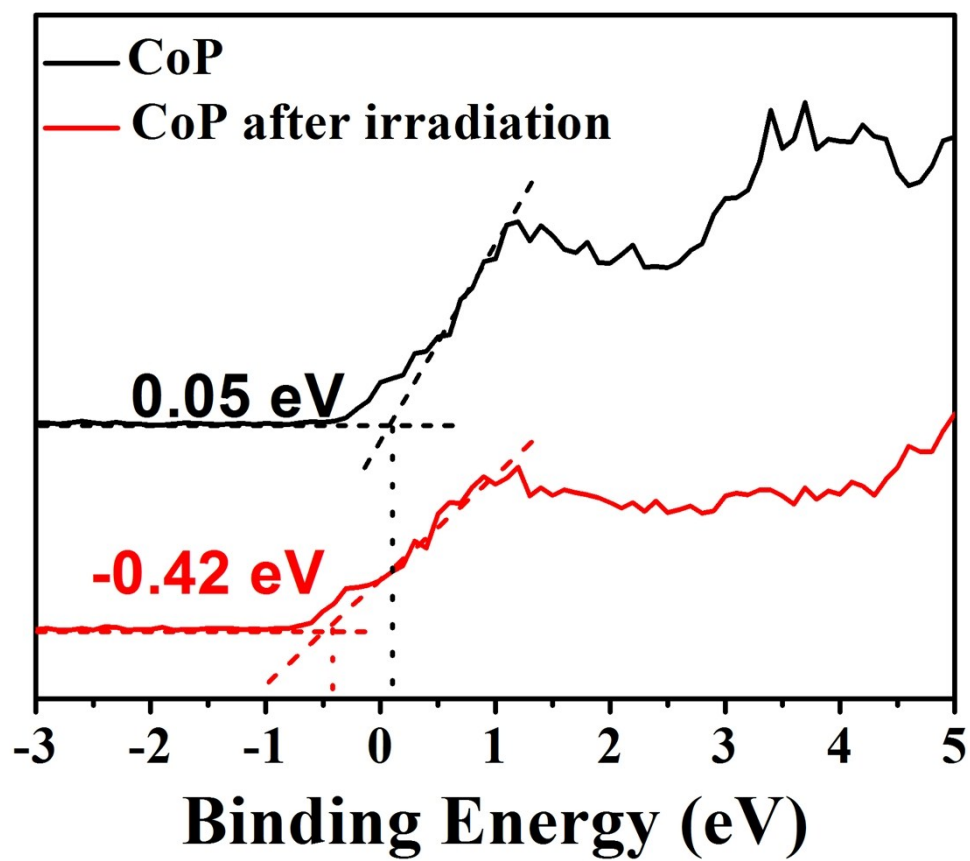


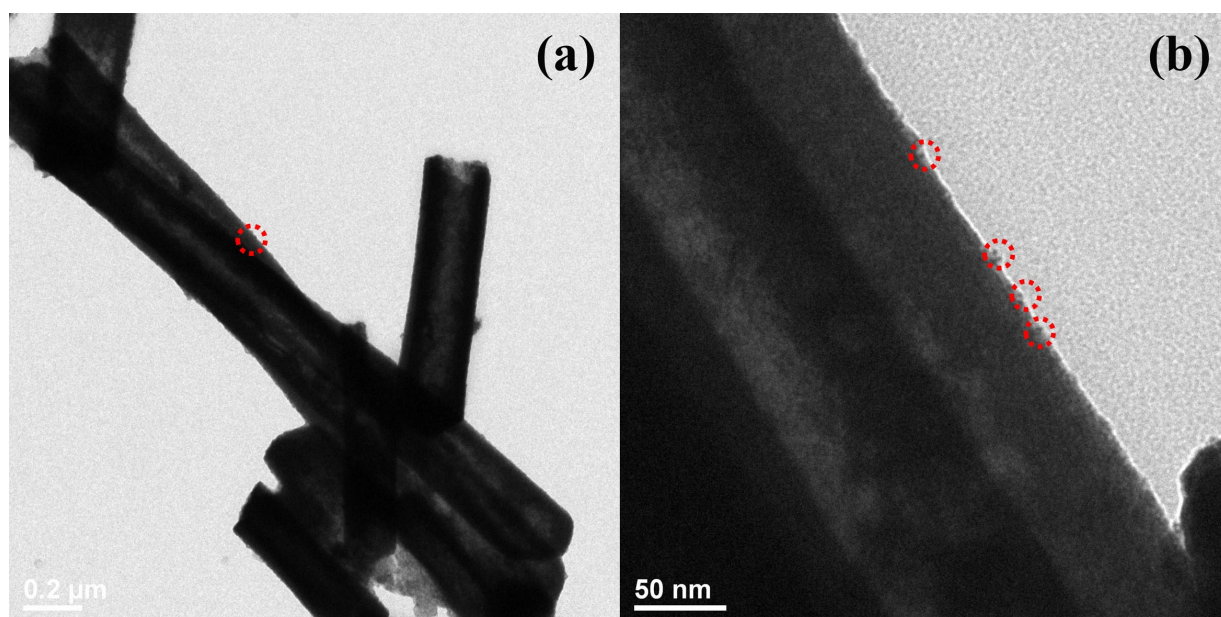
Fig. S17. Mott-Schottky plots of different samples.



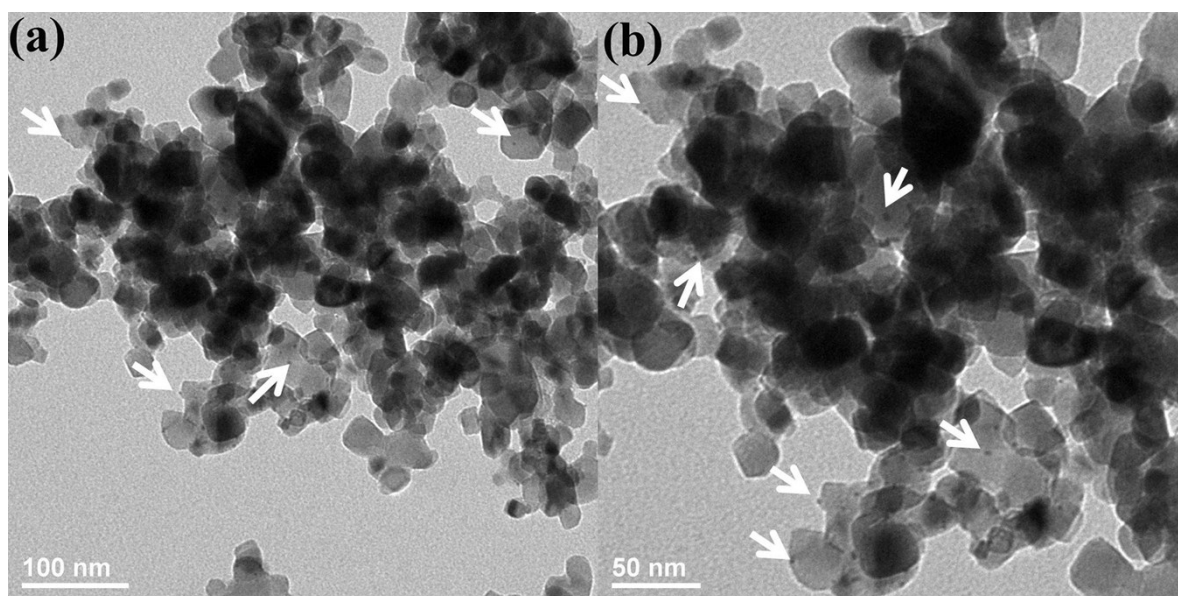
**Fig. S18.** Co 2p XPS spectra of CoP before and after the solar light irradiation (the decrease intensity of the characteristic peak at 781.8 eV of oxidation Co indicates some reduction reaction occurring on Co under the light irradiation).



**Fig. S19.** XPS valence band spectra of CoP before and after light irradiation.



**Fig. S2o.** The TEM images of  $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Se/Pt}$  (red circles refer to Pt nanoparticles ).



**Fig. S21.** The TEM images of P25/Pt (white arrows refer to Pt nanoparticles ).

**Table S1. Experimental preparation details.**

| Samples                                  | mole of ZnSe-DETA | mole of CdCl <sub>2</sub> | n <sub>Zn</sub> /n <sub>Cd</sub> (ICP) |
|------------------------------------------|-------------------|---------------------------|----------------------------------------|
| Cd <sub>0.25</sub> Zn <sub>0.75</sub> Se | 0.500 mmol        | 0.125 mmol                | 2.92                                   |
| Cd <sub>0.5</sub> Zn <sub>0.5</sub> Se   | 0.500 mmol        | 0.250 mmol                | 0.95                                   |
| Cd <sub>0.75</sub> Zn <sub>0.25</sub> Se | 0.500 mmol        | 0.375 mmol                | 0.32                                   |
| CdSe                                     | 0.500 mmol        | 0.500 mmol                |                                        |

ICP results are in good agreement with the theoretical results.

**Table S2. Bandgaps of different semiconductors.**

| Samples                                  | Bandgaps (eV) | aCB (eV) | bVB (eV) |
|------------------------------------------|---------------|----------|----------|
| ZnSe-DETA                                | 4.020         | -0.969   | 3.051    |
| Cd <sub>0.25</sub> Zn <sub>0.75</sub> Se | 1.780         | -1.079   | 0.701    |
| Cd <sub>0.5</sub> Zn <sub>0.5</sub> Se   | 1.910         | -1.043   | 0.867    |
| Cd <sub>0.75</sub> Zn <sub>0.25</sub> Se | 1.750         | -1.035   | 0.715    |
| CdSe                                     | 1.700         | -1.030   | 0.670    |
| CoP                                      | 0.827         | -0.777   | c0.050   |
| P25                                      | 2.962         | -0.402   | c2.560   |

a: Conduction Band; b: Valence Band, which were obtained by “Bandgap” minus “CB”; c: VB was obtained by the XPS results.

**Movie S1.** The movie of catalyst splitting pure water under sunlight irradiation.

The irradiation started from 13:00 pm and the intensity of solar light is highest in the day.

Location: Shanghai, China, Dec 29, 2015.

**Movie S2.** The movie of catalyst splitting pure water under simulated solar light irradiation.

In order to observe hydrogen bubbles obviously, we design a device to export the excess gas due to the increasing system pressure caused by the hydrogen from water splitting. With the absence of catalyst, we cannot observe the bubbles in the beaker, which rules out the effect of gas expansion resulted by the heat of Xe lamp irradiation. With the addition of catalyst, we can clearly observe the bubbles in the beaker.

**Movie S3.** The movie of catalyst splitting artificial seawater under sunlight irradiation.

The irradiation started from 15:10 pm and the intensity of solar light is relatively low in the day.

Location: Shanghai, China, Jan 8, 2016.

## References:

1. W. Yao, S.-H. Yu, X. Huang, J. Jiang, L. Q. Zhao, L. Pan and J. Li, *Adv.Mater.*, 2005, **17**, 2799-2802.