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

Composition Effect of Alloy Semiconductors on Pt-tipped $Zn_{1-x}Cd_xSe$ Nanorods for Enhanced Photocatalytic Hydrogen Generation

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Method

Materials. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, ≥99.0%), oleylamine (70%), oleic acid (90%), selenium (Se, 99.99%), octadecene (90%), and cadmium oxide (CdO, 99.99+%) were purchased from Aldrich without further purification.

Preparation of ZnSe nanorods. ZnSe nanorods were synthesized according to the literature.[1] At first, ZnSe nanowires were synthesized by adding 0.20 mmol (0.060 g) $Zn(NO_3)_2 \cdot 6H_2O$ and 30 mL of oleylamine in a 100 mL two-neck flask. The mixture was heated to 110 °C under an inert condition, and kept at the same temperature for 30 min. Then the temperature was raised to 160 °C with injecting 0.20 mmol (0.016 g) Se dissolved in 2.0 mL oleylamine. After the injection, the temperature was cooled to 120 °C and degassed for 10 min. Then the temperature was raised again to 230 °C and kept at the same temperature for 20 min. After the reaction, the reaction mixture was cooled down and the product was precipitated by the addition of methanol with centrifugation at 10,000 rpm for 20 min. The resulting product was dispersed in oleylamine, and kept in a glovebox for 2~4 weeks.

After the aging, the ZnSe nanowires were re-dispersed in oleylamine. Then the solution was heated to 110 °C for 10 min and raised up to 280 °C under an inert condition. The mixture was kept for 60 min at the same temperature. After the reaction, the product was precipitated by adding toluene and methanol with centrifugation at 10,000 rpm. The final product was dispersed in toluene.

Synthesis of $Zn_{1-x}Cd_xSe$ nanorods. For the preparation of $Zn_{1-x}Cd_xSe$ nanorods with various component ratios, the CdO precursor concentration and reaction temperature were changed. For $Zn_{0.75}Cd_{0.25}Se$ nanorods, 0.65 mg of CdO with 10 mL of oleic acid was heated to 130 °C for 30 min, and the quarter amount of the ZnSe nanorods was dispersed in 10 mL of octadecene at 110 °C. Then the ZnSe solution was added to the Cd precursor solution at 270 °C, and the resulting mixture was allowed to stir for 5.5 min. After cooling the mixture, the particles were precipitated by adding toluene and methanol with centrifugation at 10,000 rpm. The final product was dispersed in toluene.

For the other $Zn_{1-x}Cd_xSe$ nanorods, the procedure was identical to that of the $Zn_{0.75}Cd_{0.25}Se$ nanorods except the reaction conditions described in Table S1.

Table S1. Detailed reaction conditions for the synthesis of the $Zn_{1-x}Cd_xSe$ nanorods

Ratio (x)	**0.25**	**0.5**	**0.75**
CdO (mg)	0.65	1.30	3.24
Oleic acid (mL)	10	10	10
Temperature (°C)	270	240	230
Reaction time (min)	5.5	5	4

Synthesis of Pt-tipped $Zn_{1-x}Cd_xSe$ nanorods. To synthesize Pt-tipped $Zn_xCd_{1-x}Se$ nanorods, 0.0064 g of 1,2-hexadecanediol, 0.030 mL of oleylamine, 0.030 mL of oleylamine, and 3.0 mL of phenyl ether were mixed at 80 °C under an inert condition. 0.0015 g of platinum acetylacetonate with the half amount of the $Zn_{1-x}Cd_xSe$ nanorod dispersion in 3.0 mL of dichlorobenzene were stirred at 65 °C in a separate batch. Then the phenyl ether solution was heated to 225 °C and the $Zn_{1-x}Cd_xSe$ nanorod dispersion was added. The reaction mixture was kept at the same temperature for 4 min and immediately quenched using a water bath. After cooling the mixture, the particles were precipitated by adding toluene and methanol with centrifugation at 10,000 rpm. The final product was dispersed in toluene.

Vegard's law. Vegard's law is that the lattice parameter of an alloyed solid solution ($A_{1-x}B_x$) approximately equals to the combination of each component's (A or B) lattice parameters at the same temperature as follows:

$$lattice_{A_{1-x}B_x} = (1-x)lattice_A + xlattice_B$$

It is assumed that each component has the identical crystal structure, and x is the mole fraction of the component B in the solution.

Calculation of quantum yields for hydrogen generation reactions. A quantum yield (QY) was calculated by using the following equation:

$$QY(\%) = \frac{n_e}{n_p} \times 100 = \frac{2n_{H_2}}{n_p} \times 100$$

where n_e is the number of electrons participating in the hydrogen generation reaction, n_p is the number of photons absorbed by the light source, and n_{H2} is the number of hydrogen molecules that was generated in the reaction. Because the hydrogen generation reaction is a two-electron reduction process, the n_e is twice of the n_{H2}. The light emitting diode (LED) light used in the reaction is a Thorlabs (405 nm) mounted LED (M405LP1).

Calculation of valence band and conduction band edge positions. To confirm the valence band (VB) and conduction band (CB) edge positions for each sample, the CB edge position was calculated by the following equation: $E_{CB} = \chi - E_c - 1/2E_g$, where E_{CB} is the CB edge potential, and χ is the electronegativity of the semiconductor. It was expressed as the geometric mean of absolute electronegativity of the constituent atoms, where the absolute electronegativity of an individual atom is defined as the arithmetic mean of the atomic electron affinity and the first ionization energy. E_c is the energy of free electrons on the hydrogen scale, of which the value is ~ 4.5 eV, and E_g is the direct bandgap of the semiconductor, which was calculated from the UV-visible spectrum.

Characterization The nanocatalysts were characterized by TEM (Philips F20 Tecnai operated at 200 kV, KAIST). The UV-visible absorption spectra were collected using a Shimadzu UV-3600 spectrophotometer in toluene using a 1-cm quartz cuvette at ambient temperature. The exact composition ratio was estimated using iCAP 6300 Duo inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

Photoelectrochemical characterization. Photoelectrochemical (PEC) characterization was conducted in a three electrode configuration with the metal-semiconductor nanodumbbells/SnO_2/ITO as a working electrode, a Pt wire as a counter electrode, and a Ag/AgCl reference electrode. The 1.0 mg of the sample with the mixture of 0.10 mL of hexane and 0.010 mL of Nafion was loaded dropwise on the electrode. The working electrode area exposed to the electrolyte was 0.28 cm^2, and 150 W Xe lamp (Abet Technologies) was used as a light source for the PEC characterization. In all tests, the lamp intensity on the sample was measured to be 100 mW cm^{-2}. DY2321 potentiostat (Digi-Ivy) was used for all photocurrent responses.

Estimation of electron transfer efficiency to the metal tips. Due to the competitive pathway between the electron scattering by surface traps on the semiconductor and direct electron transfer to the metal tips, the electron transfer efficiency (ε_{ET}) can be described as the following equation:

$$\varepsilon_{ET} = \frac{k_{ET}}{k_{ET} + k_{scat}} = 1 - \frac{k_{scat}}{k_{ET} + k_{scat}}$$

where k_{ET} is the electron transfer rate from the semiconductor to the metal tips, and k_{scat} is the electron scattering rate on the semiconductor. As described, the electron transfer efficiency is determined by two factors, which are all influenced by the electron diffusion rate or mobility of the semiconductor. Basically, the electron transfer process to the metal tips (k_{ET}) is composed of slow electron diffusion along the semiconductor domain (k_{diff}) and the fast electron transfer to the metal tips (k_{metal}), therefore, we modelled the k_{ET} by diffusion constant (D) as $k_{ET} = k_{diff} \times k_{metal} = 4\pi R^{*} D \times k_{metal}$, where R* is the effective radius of semiconductor. According to the electrical mobility equation for diffusion of charged particles, the diffusion constant is proportional to the electron mobility as the following equation:

$$D = \frac{\mu_e k_B T}{e}$$

where e is the electrical charge, k_B is Boltzmann constant, T is the absolute temperature, and μ_e is the electron mobility, which means that the electron transfer rate is proportional to the electron mobility. The electron mobility is also proportional to the scattering time as the below equation:

$$\mu = \frac{q \times \tau_s}{m^*}$$

where m* is an effective mass and τ_s is the average scattering time, which means that electron scattered rate is the result of the electron mobility.

Therefore, the electron transfer efficiency for each Pt tipped-nanorod can be estimated by using the electron mobilities for both electron transfer and scattering processes.

For the scattering process, we considered two extreme cases. In the case of the ZnSe nanorods, the activity decreased from 0.30 μmol/h to 0.014 μmol/h after the Pt deposition, which meant that most of the electrons were scattered by surface trapping, or k_{scat} is extremely larger than k_{ET}. On the other hand, in the case of CdSe, the activity increased rapidly from 0.11 μmol/h to 7.5 μmol/h, indicating that k_{ET} is extremely larger than k_{scat}. From the above relations, the electron scattering rate is proportional to the electron diffusion constant, which is also proportional to the electron mobility. Consequently, the electron transfer efficiency to the metal tips is ideally 0 for the Pt-tipped ZnSe and 1 for the Pt-tipped CdSe nanorods, and is proportional to the electron mobility for the mixed component of the Pt-tipped $Zn_{1-x}Cd_xSe$ nanorods. Therefore, the electron transfer efficiency can be expressed by the difference of the electron mobility of the sample from that of the ZnSe nanorods with respect to the difference of the electron mobility between the CdSe and ZnSe nanorods as follows:

$$\varepsilon_{ET} = \frac{\mu_x - \mu_{ZnSe}}{\mu_{CdSe} - \mu_{ZnSe}}$$

where x = $Zn_{1-x}Cd_xSe$ (x = 0, 0.25, 0.5, 0.75, and 1).

Reference

1 G. Jia, and U. Banin, *J. Am. Chem. Soc.,* 2014, **136**, 11121

Table S2. Detailed characteristics of the $Zn_{1-x}Cd_xSe$ nanorods.

	EDS (atomic %)	ICP-AES	Length / Diameter (nm)	Size distribution (Length/Diameter) (nm)	One tip/Double tips (%)
ZnSe	$Zn_{0.55}Se_{0.45}$	$Zn_{0.58}Se_{0.52}$	35.92 / 4.78	13.86 / 0.95	43% / 57%
$Zn_{0.75}Cd_{0.25}Se$	$Zn_{0.78}Cd_{0.22}Se$	$Zn_{0.69}Cd_{0.31}Se$	15.62 / 2.94	2.85 / 0.35	38% / 62%
$Zn_{0.5}Cd_{0.5}Se$	$Zn_{0.53}Cd_{0.47}Se$	$Zn_{0.55}Cd_{0.45}Se$	16.03 / 2.52	4.93 / 0.36	37% / 63%
$Zn_{0.25}Cd_{0.75}Se$	$Zn_{0.28}Cd_{0.72}Se$	$Zn_{0.31}Cd_{0.69}Se$	13.93 / 2.84	6.52 / 0.39	40% / 60%
CdSe	$Cd_{0.56}Se_{0.44}$	$Cd_{0.53}Se_{0.47}$	10.96 / 5.25	1.18 / 0.49	45% / 55%

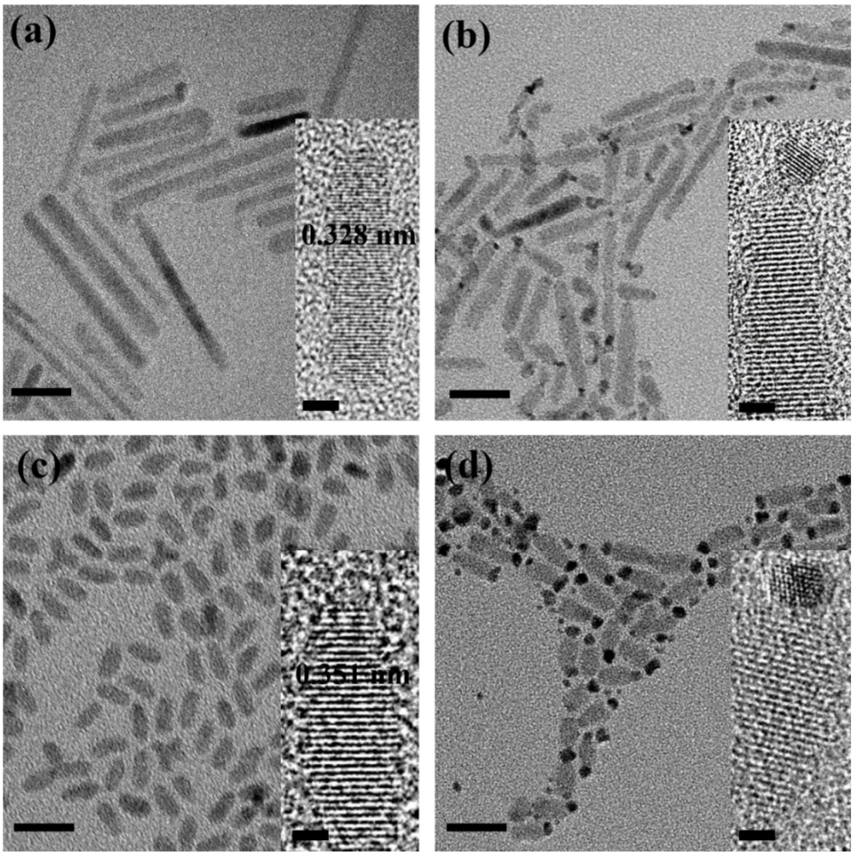

Fig. S1 TEM images of (a) ZnSe, (b) Pt-tipped ZnSe nanorods, (c) CdSe, and (d) Pt-tipped CdSe nanorods. The bars represent 20 nm and (inset) 2 nm.

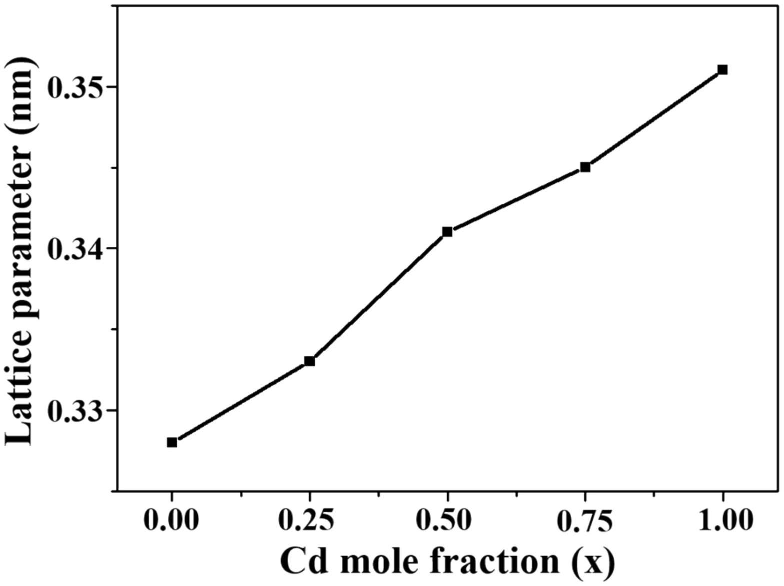

Fig. S2 The lattice parameter values of the $Zn_{1-x}Cd_xSe$ nanorods as a function of the Cd mole fraction (x).

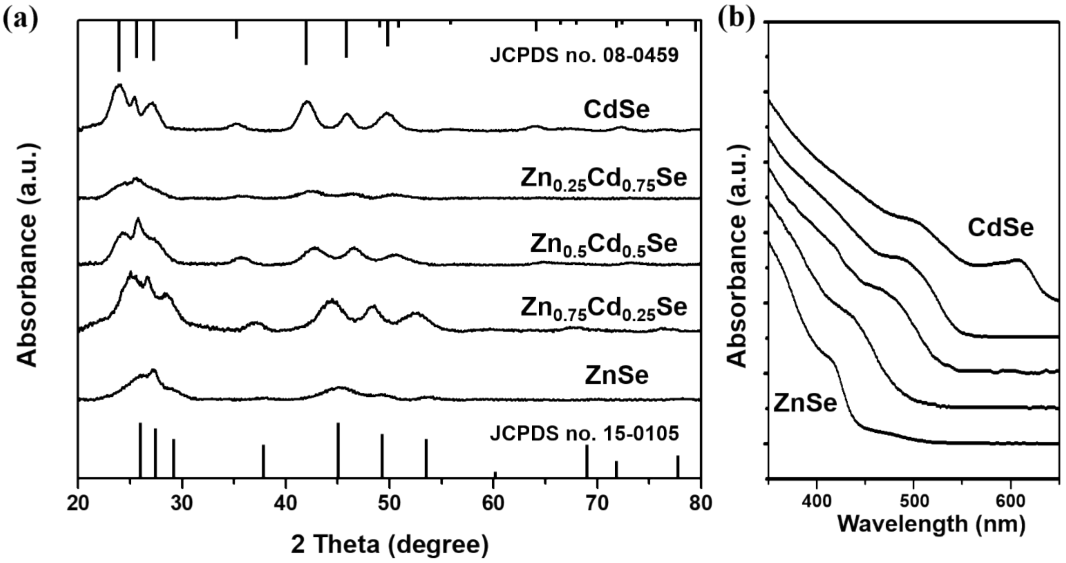

Fig. S3 (a) XRD patterns and (b) UV-visible absorption spectra of the $Zn_{1-x}Cd_xSe$ nanorods (x = 0, 0.25, 0.5, 0.75, and 1).

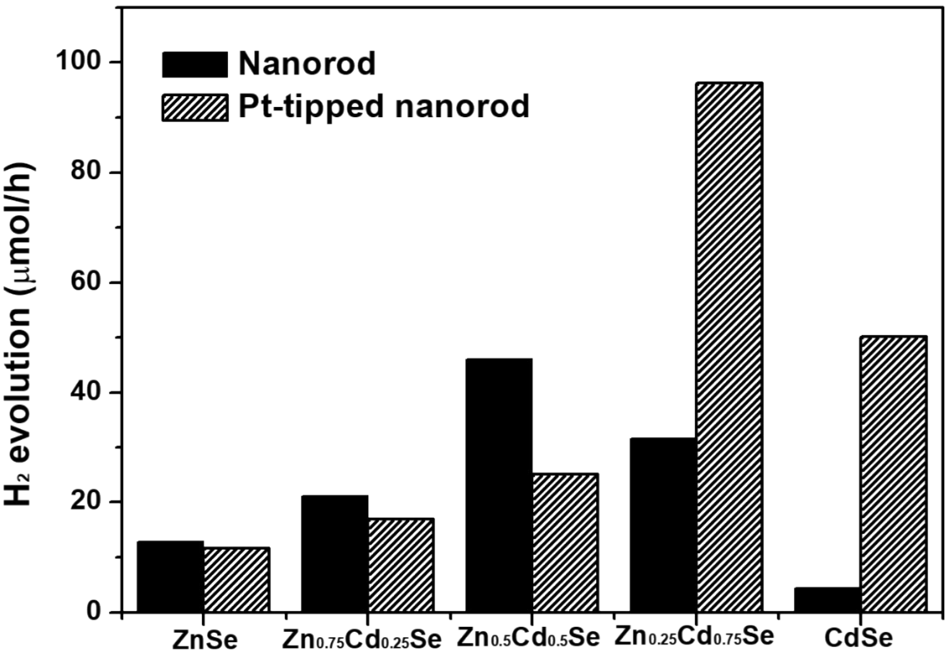

Fig. S4 Photocatalytic hydrogen evolution rates of the $Zn_{1-x}Cd_xSe$ and Pt-tipped nanorods (x = 0, 0.25, 0.5, 0.75, and 1) in a 0.25 M Na_2S/0.35 M Na_2SO_3 aqueous solution by the light irradiation without using a UV filter.

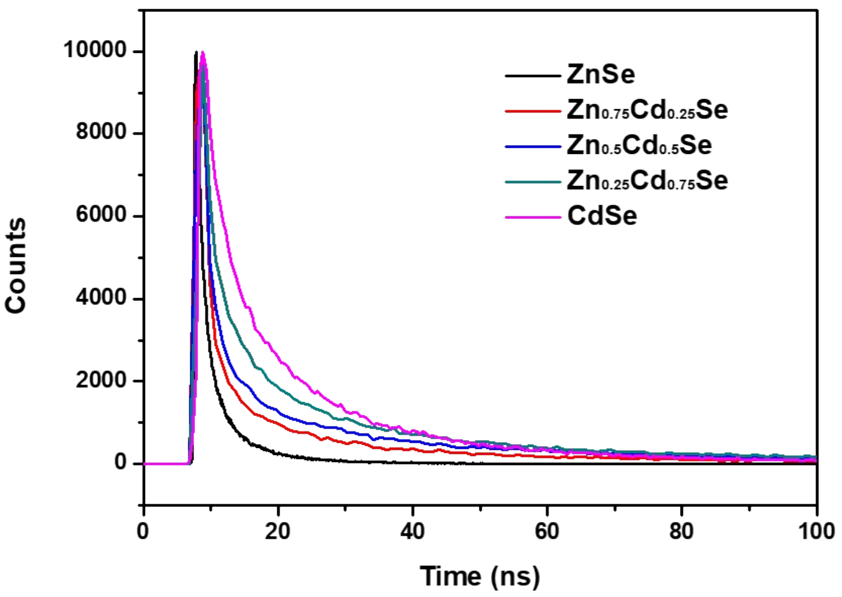

Fig. S5 Time-correlated single photon counting (TCSPC) analysis of $Zn_{1-x}Cd_xSe$ nanorod. The fitting parameters by triexponential kinetics (τ_1, τ_2, and τ_3) were 1.93, and 8.10 ns for ZnSe, 2.37, 18.47 and 101.4 ns for $Zn_{0.75}Cd_{0.25}Se$, 3.10, 25.17, and 117.5 ns for $Zn_{0.5}Cd_{0.5}Se$, 5.65, 32.67, and 118.4 ns for $Zn_{0.25}Cd_{0.75}Se$, and 13.51, and 40.21 ns for CdSe, respectively. These triexpotential kinetics were assigned to be exciton radiative recombination, quenching processes by the local environment, and carrier trapping at defect sites.[37] The intensity-average lifetimes (<τ>) were calculated to be 3.24, 8.85, 12.17, 17.95 and 17.20 ns for $Zn_{1-x}Cd_xSe$ nanorods (x = 0, 0.25, 0.5, 0.75, 1.0), respectively.

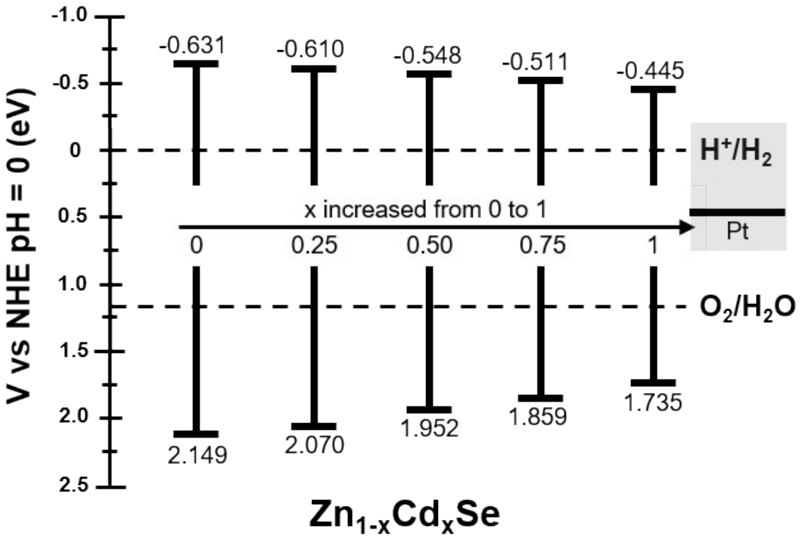

Fig. S6 Valence and conduction band edge potentials of the $Zn_{1-x}Cd_xSe$ nanorods (x = 0, 0.25, 0.5, 0.75, and 1).

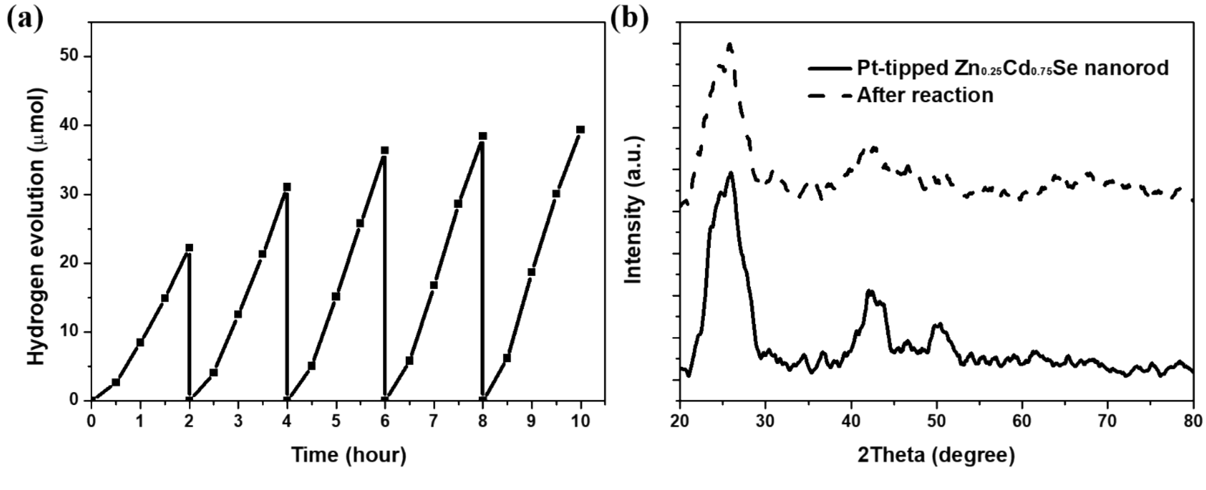

Fig. S7 (a) The amount of hydrogen evolution using Pt-tipped $Zn_{0.25}Cd_{0.75}Se$ nanorods under the identical reaction conditions. N_2 purging was performed at the beginning of every 2-h reaction. (b) XRD spectra of the Pt-tipped $Zn_{0.25}Cd_{0.75}Se$ nanorods before and after the repetitive hydrogen evolution reactions.

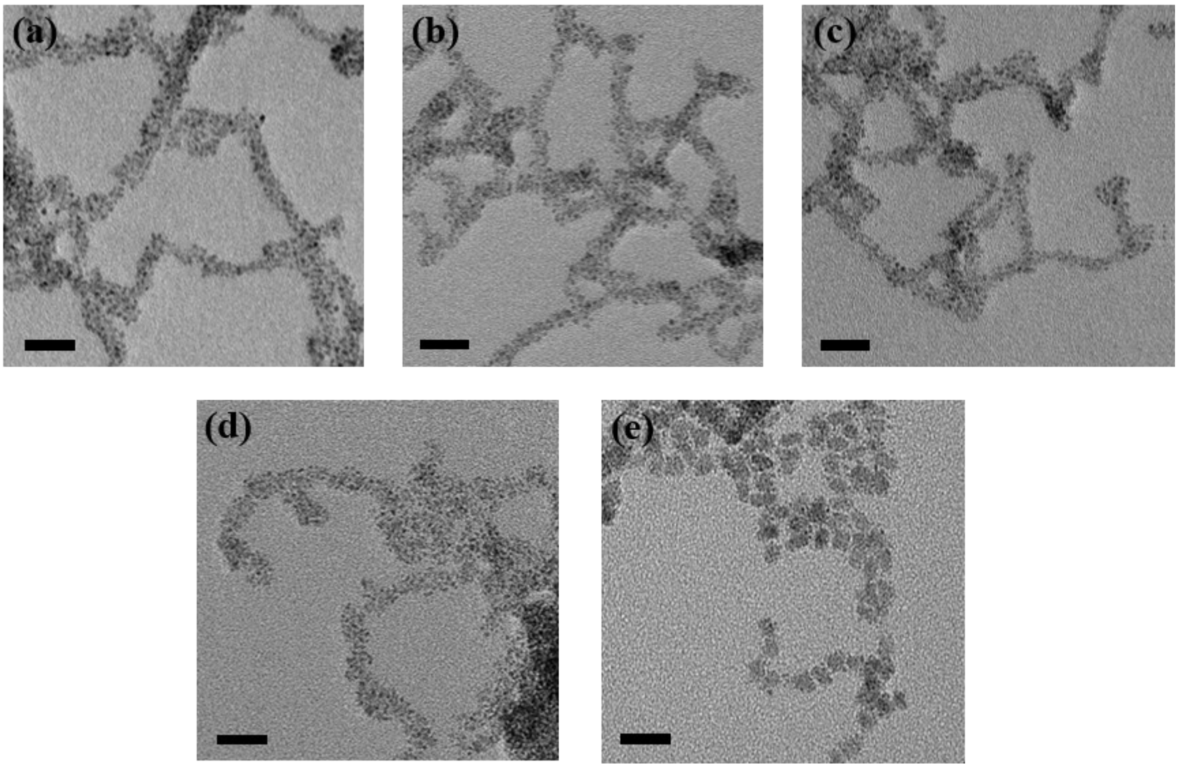

Fig. S8 TEM images of Pt-photodeposited (a) ZnSe, (b) $Zn_{0.75}Cd_{0.25}Se$, (c) $Zn_{0.5}Cd_{0.5}Se$, (d) $Zn_{0.25}Cd_{0.75}Se$, and (e) CdSe nanorods. The bars represent 20 nm.

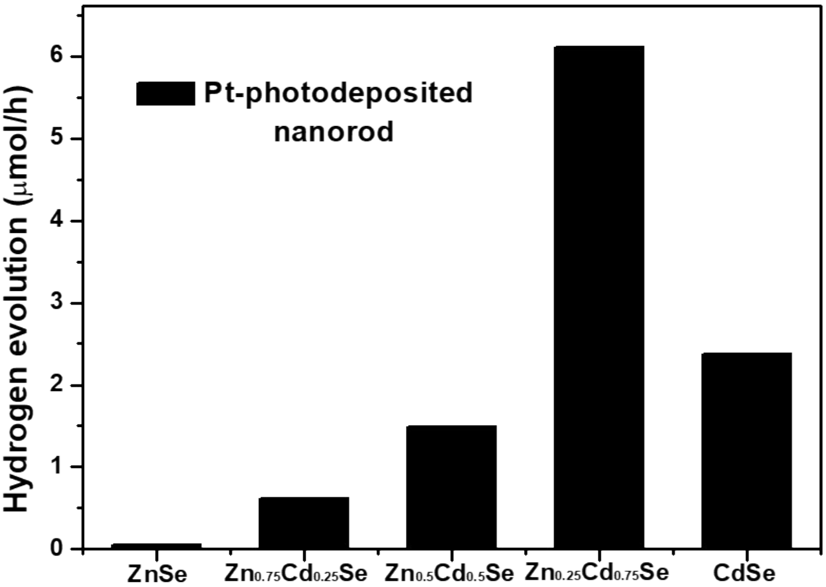

Fig. S9 Photocatalytic hydrogen evolution rates of the Pt-photodeposited $Zn_{1-x}Cd_xSe$ nanorods ($x = 0, 0.25, 0.5, 0.75$, and 1) in a 0.25 M Na_2S/0.35 M Na_2SO_3 aqueous solution under visible light ($\lambda > 400$ nm) irradiation.