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Supporting Information

for

CdZnS nanorods with rich sulfur vacancies for highly efficient photocatalytic hydrogen production

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Experimental Section

1. Material Synthesis

1.1 Chemicals: All the reagents were used as received without further purification. Reaction and stock solutions were prepared by using deionized water provided with a UPT–I–5T ultrapure water system.

1.2 Synthesis of CdS and ZnS nanorods: CdS and ZnS nanorods were prepared by a solvothermal method using ethylenediamine as solvent and structure–directing agent according to previous reported literature.[S1]

1.3 Synthesis of $Cd_{0.6}Zn_{0.4}S$ nanorods: In a typical synthesis procedure, 1.8 mmol $Cd(NO_3)_2 \cdot 4H_2O$, 1.2 mmol $Zn(NO_3)_2 \cdot 6H_2O$ and 9.0 mmol $CS(NH_2)_2$ were dissolved in 30 mL of the mixture of ethylenediamine and water (v:v = 2:1) under constant stirring for 30 min, and transferred into 50 mL Teflon–lined stainless–steel autoclaves. The autoclaves were maintained at 180 °C for 12 h and then cooled to room temperature naturally, and then the precipitate was obtained by centrifugation and washed several times with deionized water and ethanol and vacuum dried at 65 °C overnight. The as–prepared sample was identified as $Cd_{0.6}Zn_{0.4}S$ and denoted as CZS. Pt loading on CZS was synthesized by in situ photo–deposition of 1 wt% Pt on as–prepared CZS NRs using $H_2PtCl_6 \cdot 6H_2O$ aqueous solution.

2. Characterization.

Powder X–ray diffraction (PXRD) patterns were collected using a Rigaku Miniflex 600 X–ray diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm). Scanning electron microscopy (SEM) images were photographed by using a JSM6700–F with a working voltage of 10 kV. Transmission electron microscopy (TEM) and high resolution TEM (HR–TEM) images were recorded by using a FEI Talos F200 working at 200 kV. X–ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Fisher ESCALAB 250Xi spectrometer with Al Kα X–ray source (15 kV, 10 mA). To compensate effects related to charge shifts C 1s peak at 284.6 eV was used as internal standard. Diffuse reflectance spectra (DRS) were recorded on a Shimadzu UV–vis spectrophotometer (UV–2550) with $BaSO_4$ as the background. The photoluminescence (PL) spectra and time–resolved fluorescence emission spectrum were collected on a FLS 980 fluorometer spectrometer at room temperature. Electron spin resonance (ESR) spectra were recorded on a Bruker E500 spectrometer.

3. Photoelectrochemical performance: Photoelectrochemical tests were carried out in a standard three–electrode system on an electrochemical analyzer (Zana, Germany). The counter electrode and reference electrode are Pt and Ag/AgCl, respectively. Aqueous Na_2SO_4 (0.2 M, pH = 6.8) solution was used as the supporting electrolyte. The samples (5.0 mg) were homogeneously dispersed in 1.0 mL ethanol and 50 μL Nafion. The supersonic reaction time was 1 h by dropping slowly on the tin–plated indium (ITO) glass (deposited area was 1.0 cm^2). Mott–Schottky curves were measured in dark at a frequency of 1.0 kHz. The following Mott-Schottky equation is taken to calculate the flat-band potential values (E_{FB}).[S2]

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 e N_D}\left(E - E_{FB} - \frac{k_B T}{e}\right) \qquad (S1)$$

where C is the space charge capacitance in the semiconductor, N_D is the carrier density, e the elemental charge, ε_0 the permittivity of the vacuum, ε the relative permittivity of the semiconductor, E the applied potential, E_{FB} the flat band potential, T the temperature and K_B the Boltzmann constant.

4. Visible–light–driven photocatalytic test: The photocatalytic hydrogen evolution from water splitting was carried out in a top–irradiation glass–closed gas circulation system at ambient temperature. The photocatalyst (5.0 mg) was dispersed in 100 mL of aqueous solution with 0.35 M Na_2S and 0.25 M Na_2SO_3 as sacrificial agent. Prior to visible light irradiation, the reactant system was degassed through the exhaust to ensure that the reaction system was in an anaerobic condition, and then was irradiated by a 300 W Xe lamp with a cutoff filter of 420 nm for H_2 evolution under magnetic stirring. Overall pure water splitting was conducted under the same conditions except without sacrificial agent. The photocatalytic stability was studied using parameters similar to those of photocatalytic activity.

Table S1. Typical ZnCdS solid solution photocatalysts for hydrogen evolution

Photocatalyst	**Morphology**	**Light source**	**H_2 evolution rate (μmol h^{-1} g^{-1})[a]**	**Reference**
$Cd_{0.5}Zn_{0.5}S$	Nanorods	$\lambda \geq$ 420nm 300W (Xe)	10970	[S3]
$Cd_{0.6}Zn_{0.4}S$	Nanoparticles	$\lambda >$ 420nm 300W (Xe)	42660	[S4]
$Cd_{0.57}Zn_{0.43}S$	Nanospheres	$\lambda \geq$ 420nm 500W (Xe)	1766	[S5]
$Cd_{0.5}Zn_{0.5}S$	Nanotwins	$\lambda \geq$ 430nm 300W (Xe)	25800	[S6]
$Cd_{0.24}Zn_{0.76}S$	3D nanoflowers	$\lambda >$ 420 nm 300W (Xe)	ca. 9167	[S7]
$Cd_{0.8}Zn_{0.2}S$	Nanocrystals	$\lambda \geq$ 420nm 300W (Xe)	6320	[S8]
$Cd_{0.54}Zn_{0.46}S$	Double–shell hollow nanospheres	$\lambda >$ 420 nm 300W (Xe)	4100	[S9]
$Cd_{0.8}Zn_{0.2}S$–DETA	Nanoflowers	$\lambda >$ 400nm 300W (Xe)	12718	[S10]
$Cd_{0.9}Zn_{0.1}S$	Nanotetrapods	$\lambda >$ 420 nm (Xe)	8040	[S11]
$Cd_{0.5}Zn_{0.5}S$	Porous nanosheets	300W (Xe)	ca.1667	[S12]
$Cd_{0.6}Zn_{0.4}S$	Nanorods	$\lambda \geq$ 420nm 300W (Xe)	59330	**This work**

[a] converted value according the optimized activity in the corresponding literature.

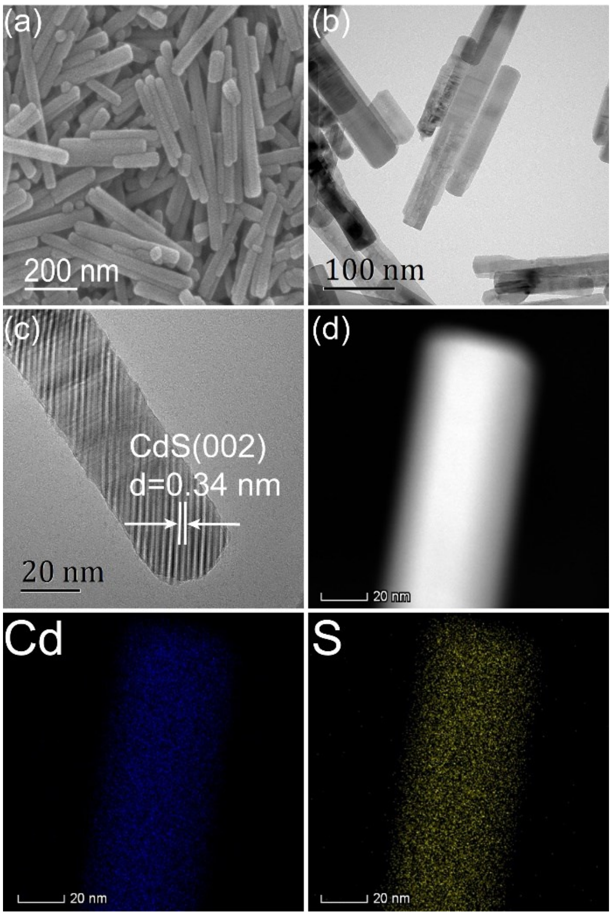

Fig. S1 SEM (a), TEM (b), HRTEM (c) and (d) element mapping of CdS NRs.

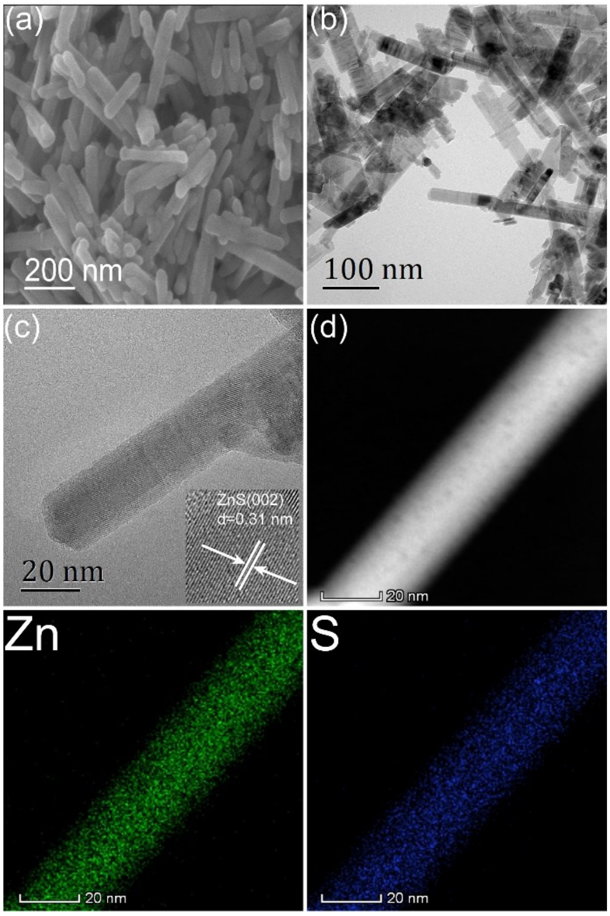

Fig. S2 SEM (a), TEM (b), HRTEM (c) and (d) element mapping of ZnS NRs.

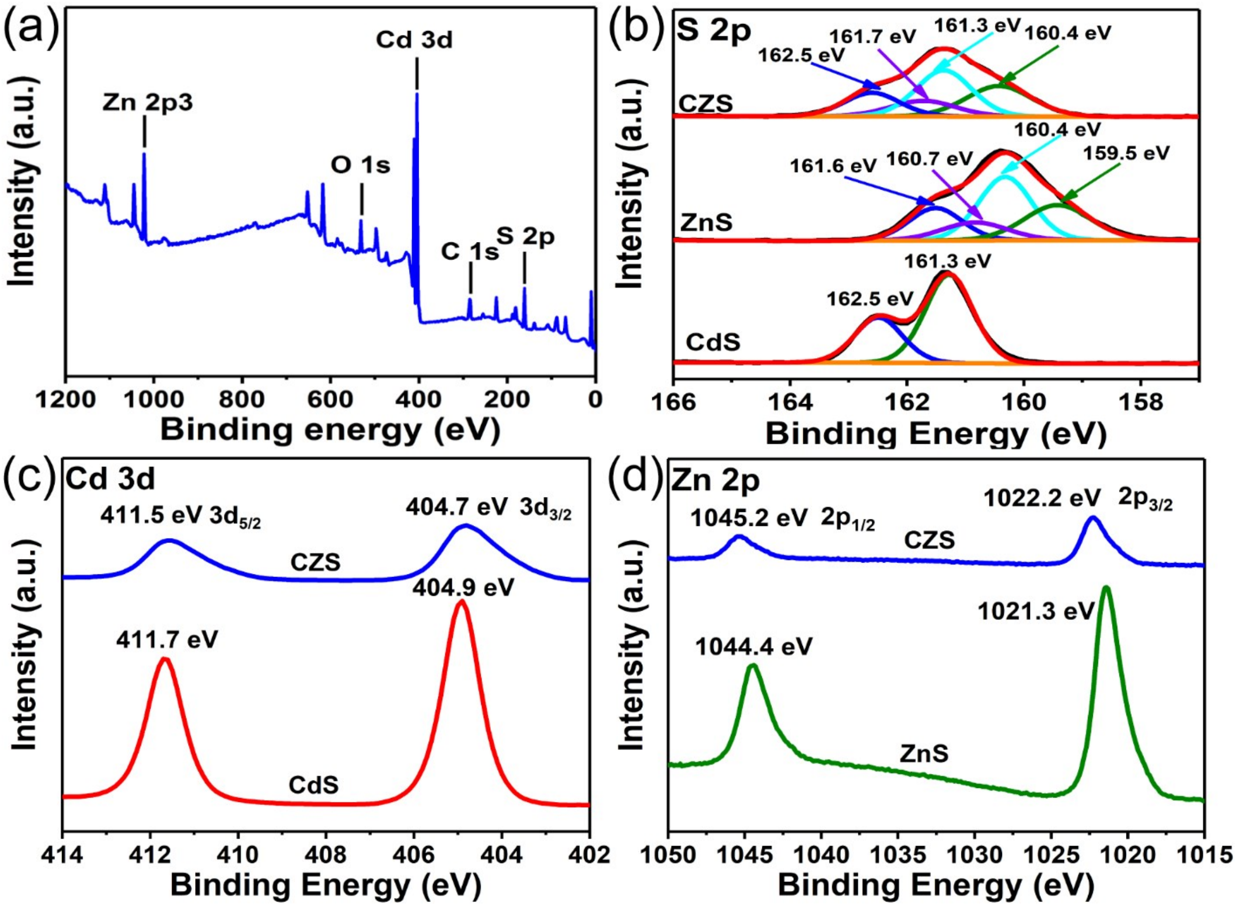

Fig. S3 XPS spectrum of survey for CZS NRs (a), XPS spectra of (b) S 2p (c) Cd 3d and (d) Zn 2p of CdS, ZnS and CZS NRs.

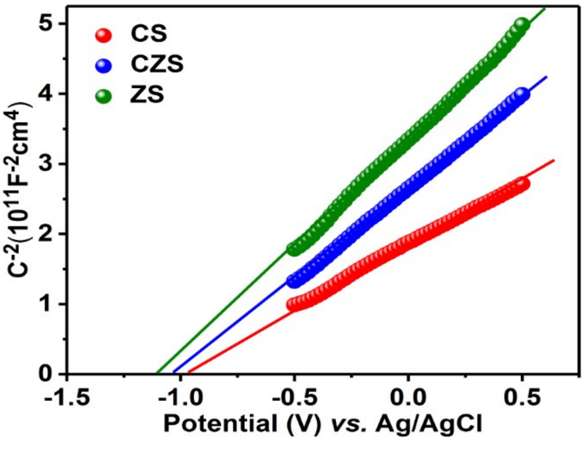

Fig. S4 Mott–Schottky plots of CdS, ZnS and CZS NRs.

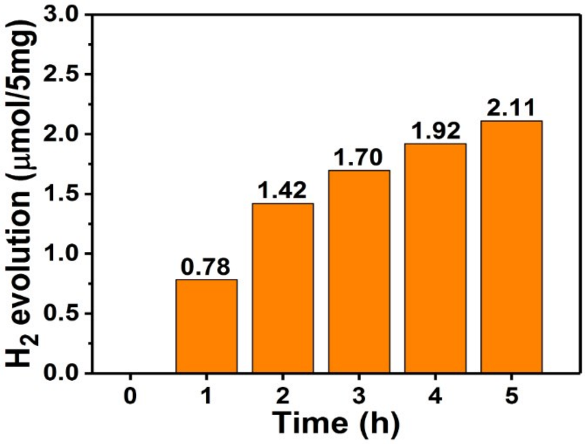

Fig. S5 Time courses of H_2 evolution for 1.0% Pt/CZS in pure water without sacrificial agents under visible light. (Reaction condition: distilled water (pH = 7.0, 100 mL) 300 W Xe–lamp equipped with cut–off filter (λ ≥ 420 nm).)

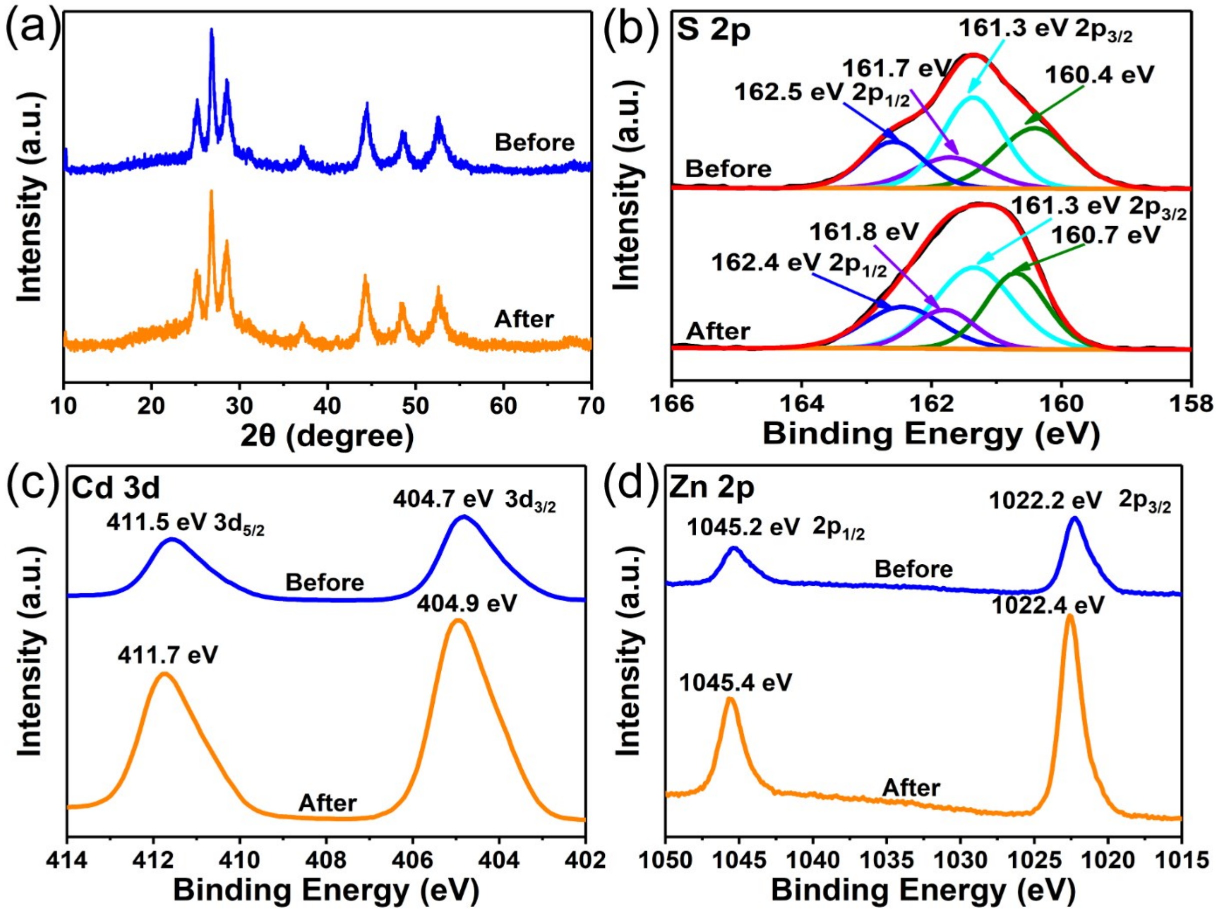

Fig. S6 (a) XRD patterns and XPS spectra of (b) S 2p (c) Cd 3d and (d) Zn 2p of CZS NRs before and after the long–term photocatalytic reaction.

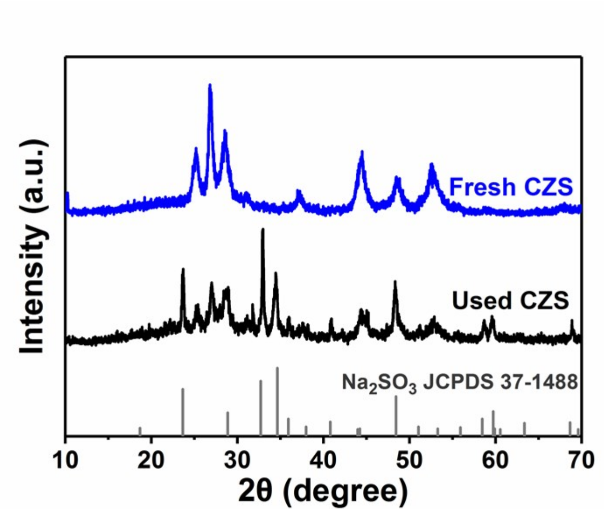

Fig. S7 XRD patterns of CZS NRs before irradiation and unwashed after irradiation for 10 hours.

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