Supporting Information

Bioinspired notched Volvox-like nested Z-Scheme heterostructure improves solar energy utilization for highly visible-light-driven hydrogen

production

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Number of figures: 25

Number of tables: 5

Contents

| Supporting Information | S1 |
|------------------------------------|-----|
| Contents | S2 |
| Chemicals | S4 |
| Characterizations | S4 |
| Synthesis of different products | S5 |
| Photocatalytic measurement | S6 |
| Photocatalytic stability test | S7 |
| Apparent quantum efficiency test | S7 |
| Photoelectrochemical measurement | S8 |
| The detection of hydroxyl radicals | S8 |
| Computational details | S8 |
| Figure S1 | S10 |
| Figure S2 | S11 |
| Figure S3 | S12 |
| Figure S4 | S13 |
| Figure S5 | S14 |
| Figure S6 | S15 |
| Figure S7 | S16 |
| Figure S8 | S17 |
| Figure S9 | S18 |
| Figure S10 | S19 |
| Table S1 | S20 |
| Table S2 | S21 |
| Figure S11 | S22 |
| Figure S12 | S23 |
| Figure S13 | S24 |
| Figure S14 | S25 |
| Figure S15 | S26 |
| Figure S16 | S27 |

| Figure S17 | S28 |
|------------|-----|
| Table S3 | S29 |
| Figure S18 | S30 |
| Figure S19 | S31 |
| Table S4 | |
| Table S5 | |
| Figure S20 | |
| Figure S21 | |
| Figure S22 | S36 |
| Figure S23 | |
| Figure S24 | S38 |
| Figure S25 | |
| References | |

Chemicals

Zinc sulphate heptahydrate (ZnSO₄·7H₂O, analytical grade) and absolute ethanol (C₂H₆O, analytical grade) were purchased from Tianjin Deen Chemical Reagent Co., LTD. D(+)-Glucose (C₆H₁₂O₆, analytical grade) was purchased from Sinopharm Group Chemical Reagent Co., LTD. Hydrochloric acid (HCl) was purchased from Luoyang Chemical Reagent Factory. Cadmium chloride hemipentahydrate (CdCl₂·2.5H₂O, analytical grade) was purchased from Alfa Aesar Chemical Co., LTD. Thioacetamide (CH₃CSNH₂, analytical grade), Calcium acetate (Ca(CH₃COO)₂·xH₂O, analytical grade) and lanthanumacetate (La(CH₃COO)₃·xH₂O, analytical grade) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Ultrapure water was used in the experiment.

Characterizations

The morphology and element composition of the products were investigated by using a SU8010 cold field emission scanning electron microscope (FESEM) equipped with an energy spectrometer (EDS). Transmission electron microscope (TEM) and high-resolution TEM (HRTEM) analyses were performed using a JEM-2100 transmission electron microscope equipped with a selected-area electron diffraction (SAED), which was used to investigate the interior structure. Scanning transmission electron microscopy (STEM) images were obtained using a Tecnai F30 (FEI, USA). To prepare the TEM and STEM samples, 5 mL dilute alcohol solution of the products was dripped onto the carbon-coated copper grids. The composition and crystalline structures of the products were characterized on the powder X-ray diffraction (XRD) on a Bruker D8 & Advance X-ray powder diffractometer with graphite monochromatized CuK α (λ =0.15406 nm). X-ray photoelectron spectroscopy (XPS) further investigates the composition of the products. The Fourier transform infrared (FT-IR) spectroscopy was measured using a PerkinElmer Spectrum

400F in the wavenumber range of 4000-400 cm⁻¹. Ultraviolet-visible (UV-vis) spectra were measured by Lambd 950 and the photoluminescence (PL) emission spectra were obtained from a FLS980 fluorescence spectrophotometer. N₂ absorption/desorption isotherms were generated at 77 K using a Micromeritics ASAP 2010 analyzer and the specific surface areas were calculated utilizing the Brunauer-Emmett-Teller (BET) model. The samples were firstly degassed at 350 °C for 6 h before analysis. The pore size distribution was calculated from the adsorption branch of the isotherms using the Barret-Joyner-Halenda (BJH) model. The total pore volume was estimated from the amounts of N₂ adsorbed at a relative pressure (P/P₀) of 0.99.

Synthesis of Mother-twin Hollow ZnO

Firstly, 0.86 g ZnSO₄·7H₂O was dissolved in 10 mL deionized water and adjusted with hydrochloric acid until the solution was clarified. And dissolve 8 g $C_6H_{12}O_6$ in 20 mL of deionized water, slowly added to the above clear solution, and continue to stirring for 72 h. Then it is heated in a 50 mL Teflon-lined stainless steel autoclave for 40 h at 180 °C. The black products obtained were washed respectively with deionized water and absolute ethanol 3 times, and dried at 80 °C for 12 h. The black products were heated to 550 °C for 180 min in air at the rate of 2 °C/min. Finally, the white powders were obtained.

Synthesis of Mother-twin Hollow ZnO/CdS

ZnO/CdS heterostructures were synthesized by the *in situ* deposition method. Firstly, 50 mg mother-twin hollow ZnO was dispersed into a 0.1 mmol CdCl₂·2.5H₂O solution stirring for 6 h and then washed with deionized water. After that, the above precipitation was added to a 0.1 mmol CH₃CSNH₂ solution stirring for 6 h and then washed with deionized water to remove the excrescent S²⁻ ions. Finally, the obtained precipitate was washed with deionized water for 3 times and dried at 60 °C for 12 h. The as-prepared ZnO/CdS was labeled as Mother-twin HZC-3, and

the synthesis of other ZnO/CdS samples was similar to that of Mother-twin HZC-3 except that the concentrations of $CdCl_2 \cdot 2.5H_2O$ and CH_3CSNH_2 are different. The amounts of different samples and the corresponding abbreviations are shown in Table S2.

Synthesis of Mother-twin Hollow CaCO₃

Firstly, 0.86 g Ca(CH₃COO)₂·xH₂O was dissolved in 10 mL deionized water and adjusted with hydrochloric acid until the solution was clarified. And dissolve 8 g $C_6H_{12}O_6$ in 20 mL of deionized water, slowly added to the above clear solution, and continue to stirring for 72 h. Then it is heated in a 50 mL Teflon-lined stainless steel autoclave for 40 h at 180 °C. The black products obtained were washed respectively with deionized water and absolute ethanol 3 times, and dried at 80 °C for 12 h. The black products were heated to 550 °C for 180 min in air at the rate of 2 °C/min. Finally, the white powders were obtained.

Synthesis of Mother-twin Hollow La₂O₃

Firstly, $0.53 \text{ g La}(CH_3COO)_3 \cdot xH_2O$ was dissolved in 10 mL deionized water and adjusted with hydrochloric acid until the solution was clarified. And dissolve 8 g $C_6H_{12}O_6$ in 20 mL of deionized water, slowly added to the above clear solution, and continue to stirring for 72 h. Then it is heated in a 50 mL Teflon-lined stainless steel autoclave for 40 h at 180 °C. The black products obtained were washed respectively with deionized water and absolute ethanol 3 times, and dried at 80 °C for 12 h. The black products were heated to 550 °C for 180 min in air at the rate of 2 °C/min. Finally, the white powders were obtained.

Photocatalytic measurement

The photocatalytic H₂-production performance of the samples was evaluated in a top-irradiation quartz cell connected to a closed glass gas circulation system (Labsolar-III, Perfect Light Ltd.) at room temperature and atmospheric pressure. A 300 W Xenon lamp using 420 nm cut-off filter was

used as the solar light source. Different amounts of the photocatalysts (15, 20, 25, 30 and 35 mg) were dispersed in 50 mL of mixed solution (0.25 M Na₂S and 0.35 M Na₂SO₃ as sacrificial agents) in a 100 mL three-necked flask. Before light illumination, the circulation system was pumped by N₂ for 0.5 h to remove air. The power density of light was measured to be 100 mW/cm² using a radiometer (FZ-A, China). The photocatalytic measurement was conducted for 4 h under stirring at a speed of 400 rpm. The amount of hydrogen evolved under irradiation was monitored *via* a gas chromatograph (Shimadzu GC-2014) with Ar as the carrier gas.

Photocatalytic stability test

In the cycle stability test, 25 mg Mother-twin HZC-3 was dispersed into 50 mL mixed solution of 0.25 M Na₂S and 0.35 M Na₂SO₃. The one-cycle activity was tested every 4 h without any condition change. The photocatalyst after every 4 hours of irradiation was collected by centrifugation, then washed, dried and reused for the next photocatalytic cycle.

Apparent quantum efficiency test

The apparent quantum efficiency (AQE) was determined at monochromatic wavelengths of 365 nm (light intensity: 1.5 mW/cm²), 380 nm (light intensity: 2.5 mW/cm²), 400 nm (light intensity: 6.2 mW/cm²) and 420 nm (light intensity: 9.8 mW/cm²), respectively. And the experiments were performed under the same photocatalytic reaction conditions. The AQE is calculated according to the following equation:

 $AQE = \frac{number of reacted electrons}{number of incident photons} \times 100\%$

$$AQE = \frac{nH2 \times NA \times 2}{S \times W \times t \times \lambda /hc} \times \frac{100\%}{100\%}$$

Where nH_2 , h, c and N_A represent the number of H₂ molecules produced by photocatalysis, the Planck constant, the speed of light and Avogadro constant. S, W, t and λ represent the irradiation area, the irradiation intensity, the irradiation time and the monochromatic wavelength, respectively.

Photoelectrochemical measurements

The transient photocurrent response (TPR) and electrochemical impedance spectroscopy (EIS) were measured at room temperature with a CHIE760 electrochemical workstation (Shanghai ChenHua Limited, China). Ag/AgCl (in saturated KCl solution) and Pt wire were used as the reference electrode and the counter electrode, respectively. The working electrode was constructed as follows: 20 mg of photocatalyst, 10 µL of Nafion (5wt.%), and 1 mL of ethanol are uniformly mixed and ground into a slurry, then it was coated on a piece of FTO glass with an active area of ca. 0.5 cm². The obtained working electrodes were dried at room temperature overnight. During the test, the electrode was switched on and off every 5 minutes under a 300 W xenon lamp with using 420 nm cut-off filter and the 0.5 M Na₂SO₄ solution was used as the electrolyte. Electrochemical impedance spectroscopy (EIS) results were measured at an applied voltage of 5 mV on the same system above.

The detection of hydroxyl radicals (•OH)

The test was carried out under the same photocatalytic reaction conditions. During the test, 10 mg sample was dispersed into 25 mL of mixed solutions (0.5 mM terephthalic acid and 2 mM NaOH solution). Before light illumination, the aqueous solution was degassed and bubbled with N_2 for 0.5 h to remove air and ensured that the suspension was under anaerobic conditions. Under light illumination with a 300 W Xenon lamp using 420 nm cut-off filter, 1 mL of the suspension was

centrifuged every 15 minutes. Then the supernatant was collected for the measurement of hydroxyl radicals by a FLS980 fluorescence spectrophotometer with an excitation wavelength of 315 nm.

Computational details

Density functional theory (DFT) was calculated using the Vienna ab initio software package (VASP)¹⁻³ with Projected-augmented wave (PAW) method.^{4,5} The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was selected within the generalized gradient approximation (GGA).⁶ A cutoff energy of 400 eV was used. For the primitive ZnO and primitive CdS, the first Brillouin zone integration was performed using Γ -centered 12 × 12 × 5 and 9 × 9 × 4 Monkhorst-Pack k-point samplings, respectively. For the ZnO/CdS heterojunction, we used Γ - centered 4 \times 2 × 1 k-point samplings for geometry optimization and electronic structure calculations. On-site Coulomb interactions were taken into account through the DFT+U methodology^{7,8} to treat the highly localized Zn 3d states in ZnO, using a parameter of $U = 4.7 \text{ eV}^9$ To accurately describe the vdW interaction, we employed the empirical correction method presented by Grimme (DFT-D3) method.¹⁰ All the structural optimizations were finished until the energy on each atom was less than 1.0×10^{-5} eV and the forces on each atom were less than 0.03 eV·Å⁻¹. After geometry optimization, the average potential profile was calculated to obtain the work functions of CdS (101) and ZnO (101) models (their geometric structures are shown in Figure S2). The work function (Φ) is defined as $\Phi = \text{Evac} - \text{EF}$ (Evac: vacuum energy, EF: Fermi energy).

The Gibbs free energy of hydrogen adsorption was calculated according to equation:

$$\Delta \mathbf{G} = \Delta \mathbf{E} + \Delta \mathbf{Z} \mathbf{P} \mathbf{E} - \mathbf{T} \Delta \mathbf{S}$$

Where ΔE is the total energy difference between the reactant and product molecules in the reactions. ΔZPE and T ΔS are the changes in the zero-point energy and the entropic contribution,

respectively. However, ΔZPE and T ΔS of the adsorbed hydrogen are considered negligible and ignored as compared to those obtained for the gaseous phase under ambient conditions.



Figure S1. The structure of the volvox.



Figure S2. Geometric structures of (a) ZnO (101) and (b) CdS (101) surfaces. The gray, red, pink and yellow balls denote Zn, O, Cd and S atoms, respectively.



Figure S3. (a) FESEM, (b) TEM images and (c) the particle size distribution of the CMSs uploaded Zn^{2+} .



Figure S4. STEM and elemental mapping images of the CMSs uploaded Zn^{2+} after hydrothermal time for 1 h (a), 10 h (b) and 40 h (c), respectively.



Figure S5. FESEM and TEM images of (a-d) hollow and (e-h) single-core ZnO.



Figure S6. The particle size distribution of (a) hollow, (b) single-core and (c) dual-core (Mothertwin) of ZnO.



Figure S7. The SEM image of (a) Mother-twin CaCO₃ and (e) La₂O₃; The TEM images of (b) and (c) Mother-twin CaCO₃ and (f) and (g) La₂O₃; The STEM images of (d) Mother-twin CaCO₃ and (h) La₂O₃; XRD patterns of (i) Mother-twin La₂O₃ and (j) Mother-twin CaCO₃.



Figure S8. (a) XRD pattern and (b) FT-IR spectra of Mother-twin HZ.



Figure S9. High-resolution XPS spectra of (a) Zn 2p peaks and (b) O 1s peaks for Mother-twin HZ.



Figure S10. (a) N_2 adsorption-desorption isotherms and (b) pore-size distribution curve of hollow, single-core and dual-core (Mother-twin) ZnO.

| Samples | S_{BET} (m ² ·g ⁻¹) | d _p (nm) | | | |
|-----------------|---|---------------------|-------|-------|-------|
| Hollow ZnO | 32.87 | 8.44 | 14.81 | 27.44 | 43.11 |
| Single-core ZnO | 33.88 | 3.07 | 8.58 | 10.70 | |
| Mother-twin ZnO | 45.82 | 3.84 | 12.80 | | |

Table S1. BET specific surface area and pore sizes of the ZnO with hollow, single-core and dual

 core (Mother-twin) structures, respectively.



Figure S11. (a) XRD patterns and (b) FT-IR spectra at different calcination stages of products obtained during the preparation process of Mother-twin HZ.

| Complex | ZnO | CdCl ₂ ·2.5H ₂ O | CH ₃ CSNH ₂ |
|-------------------|------|--|-----------------------------------|
| Samples | (mg) | (mmol) | (mmol) |
| Mother-twin HZC-1 | 50 | 0.02 | 0.02 |
| Mother-twin HZC-2 | 50 | 0.05 | 0.05 |
| Mother-twin HZC-3 | 50 | 0.10 | 0.10 |
| Mother-twin HZC-4 | 50 | 0.20 | 0.20 |

Table S2. The amounts of precursors in preparing Mother-twin ZnO/CdS.



Figure S12. XRD patterns of Mother-twin HZ, Mother-twin HZC-1, Mother-twin HZC-2 and Mother-twin HZC-4.



Figure S13. FESEM and the particles size distribution of (a) Mother-twin HZC-1, (b) Mother-twin HZC-2, (c) Mother-twin HZC-3 and (d) Mother-twin HZC-4.



Figure S14. TEM of Mother-twin HZC-3.



Figure S15. HRTEM of Mother-twin HZC-3.



Figure S16. XPS spectra of (a) Zn 2p, (b) O 1s, (c) Cd 3d and (d) S 2p of different samples.



Figure S17. (a) N_2 adsorption-desorption isotherms and (b) pore-size distribution curve of Mothertwin HZC-1, Mother-twin HZC-2, Mother-twin HZC-3 and Mother-twin HZC-4.

| Samples | S_{BET} (m ² ·g ⁻¹) | $d_{\rm p}({\rm nm})$ | | |
|-------------------|---|-----------------------|-------|--------|
| Mother-twin HZC-1 | 59.43 | 3.95 | 22.71 | 103.82 |
| Mother-twin HZC-2 | 70.76 | 3.88 | 23.46 | 93.31 |
| Mother-twin HZC-3 | 81.36 | 3.63 | 23.23 | |
| Mother-twin HZC-4 | 103.04 | 3.60 | 35.35 | 93.51 |

Table S3. BET specific surface area of different samples.



Figure S18. (a) Hydrogen production of Mother-twin HZC-3 sample under 4 h visible light irradiation at different weights, (b) Dependence of the amount of H_2 production on the mass of photocatalysts for Mother-twin HZC with different ZnO/CdS ratios.



Figure S19. (a) Schematic illustration of multiple light reflection effect inside the series of HZ with different interior structures, respectively. (b) Ultraviolet-visible light absorptions of the prepared ZnO hollow spheres with different morphologies (hollow, single-core and dual-core "Mother-twin" structures).

Under the visible-light irradiation, the notched Mother-twin hollow ZnO microspheres possessed the higher light utilization efficiency due to the multiple light reflections within the interior shells of the volvox-like structure (Figure S19a). As shown in Figure S19b, ultraviolet-visible diffuse reflection spectra suggest all ZnO with different structures exhibited ultraviolet absorption. Compared with hollow and single-core ZnO microspheres, Mother-twin HZ exhibited much higher light absorption intensity, further demonstrated that the special Mother-twin structure can enhance light harvest, improving light utilization efficiency.

Table S4. Comparison of simulate sunlight driven H₂ evolution activity over different ZnO based photocatalysts.

| Catalyst | Conditions | Co-catalyst | Sacrificial agent | TOF (mmol·g ⁻¹ ·h ⁻¹) | AQE | Ref. |
|---------------------------------------|----------------------|--|---|---|--------|--------------|
| HZ | 300 W Xe lamp | - | $\begin{array}{c} 0.35 \text{ M} \text{ Na}_2 \text{SO}_3 \\ \text{and} \ 0.25 \text{ M} \text{ Na}_2 \text{S} \end{array}$ | 0.88 | - | This work |
| HZC | 300 W Xe lamp | - | 0.35 M Na ₂ SO ₃ and 0.25 M Na ₂ S | 18.70 | 33.98% | This work |
| ZnO- CdS@Cd | 300 W Xe lamp | Pt | 0.1 M Na ₂ SO ₃ and 0.1 M Na ₂ S | 19.2 | | 11 |
| ZnO- CdS/RGO | 300 W Xe lamp | Pt | 0.1 M Na ₂ SO ₃ and 0.1 M Na ₂ S | 16.8 | | 12 |
| ZnO/CdS- T120 | 300 W Xe lamp | | 0.25 M Na ₂ SO ₃ and 0.35 M Na ₂ S | 1.72 | | 13 |
| CdS/ZnO- 12 | 225 W Xe arc lamp | Pt - | 0.35 M Na ₂ SO ₃ and 0.25 M Na ₂ S | 22.12 3.88 | | 14 |
| CdS/ZnO | 300 W Xe lamp | e. | 0.1 M Na ₂ SO ₃ and 0.1 M Na ₂ S | 0.13 | 19.01% | 15 |
| CdS/ZnO | 300 W Xe lamp | a de la compañía de la | 6.3 g Na ₂ S and 16.8 g Na ₂ SO ₃ | 6.4 | 17.50% | 16 |
| Zn _{0.5} Cd _{0.5} S | AM 1.5G | CoP | 20 vol. % 0.75 M ascorbic acid | 12.18 | 45% | 17 |
| ZCZ-45 | 225 W Xe arc lamp | Pt | $\begin{array}{c} 0.35 \text{ M} \text{ Na}_2 \text{SO}_3 \\ \text{and} \ 0.25 \text{ M} \text{ Na}_2 \text{S} \end{array}$ | 44.70 | - | 18 |
| ZnO/CdS | 350 W Xe lamp | - | $\begin{array}{c} 0.25 \text{ M} \text{ Na}_2 \text{SO}_3 \\ \text{and} \ 0.35 \text{ M} \text{ Na}_2 \text{S} \end{array}$ | 4.13 | - | 19 |
| CdS@ZnO | 300 W Xe lamp | - | 0.2 M Na ₂ SO ₃ and 0.2 M Na ₂ S | 7.94 | - | 20 |
| $Cd_{0.5}Zn_{0.5}S$ | 300 W Xe lamp | P-Pt/PdS - | 0.1 M Na ₂ SO ₃ - Na ₂ S | 70.00 11.00 | 89% | 21 |
| ZnCdS | 300 W Xe lamp | Pt | 0.25 M Na ₂ SO ₃ and 0.35 M Na ₂ S | 33.60 | 25.4% | 22 |
| CdS/ZnS | 300 W Xe lamp | | 0.25 M Na ₂ SO ₃ and 0.35 M Na ₂ S | 14.02 | 2.76% | 23 |
| ZnCdS@D BTCN | 300 W Xe lamp | Pt | 80 mL triethanolamine (10 vol%) | 8.87 | 14.9% | 24 |

| λ (nm) | 365 | 380 | 400 | 420 |
|---------|-------|-------|------|------|
| AQE (%) | 33.98 | 28.34 | 4.97 | 2.39 |

Table S5. AQE over the Mother-twin HZC-3 at different wavelengths.



Figure S20. (a) XRD pattern, (b) FESEM and (c) TEM images of Mother-twin HZC-3 after photocatalytic hydrogen production.



Figure S21. (a, c, e) XRD patterns and (b, d, f) FESEM images of Mother-twin HZC-1, Mother-twin HZC-2 and Mother-twin HZC-4 after photocatalytic H₂ production.



Figure S22. UV-vis absorption spectra of samples with Mother-twin hollow structure.



Figure S23. Tauc plot for optical-band-gap determination of HZC-1, HZC-2, HZC-3 and HZC-4, respectively.



Figure S24. Nyquist plots of electrochemical impedance spectra of HZC-1, HZC-2, HZC-3 and HZC-4, respectively.



Figure S25. Valence band spectrum of (a) ZnO and (b) CdS.

References

(1) Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15-50.

(2) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B.* **1996**, *54*, 11169-11186.

(3) Kresse, G.; Hafner, J. Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal-Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B.* **1994**, *49*, 14251-14269.

(4) Blöchl, P. E. Projector Augmented-Wave Method. Phys. Rev. B. 1994, 50, 17953-17979.

(5) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B.* **1999**, *59*, 1758-1775.

(6) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

(7) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B.* **1998**, *57*, 1505-1509.

(8) Wang, L.; Maxisch, T.; Ceder, G. Oxidation Energies of Transition Metal Oxides within the GGA+U Framework. *Phys. Rev. B.* **2006**, *73*, 195107.

(9) Sun G.; Xiao B.; Zheng H.; Shi J.; Mao S.; He C.; Li Z.; Cheng Y. Ascorbic Acid Functionalized CdS–ZnO Core–Shell Nanorods with Hydrogen Spillover for Greatly Enhanced Photocatalytic H₂ Evolution and Outstanding Photostability. *J. Mater. Chem. A.* **2021**, *9*, 9735-9744.

(10) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465.

(11) Wang, X.; Liu, G.; Wang, L.; Chen, Z.; Lu, G. Q.; Cheng, H. -M. ZnO-CdS@Cd Heterostructure for Effective Photocatalytic Hydrogen Generation. *Adv. Energy Mater.* 2011, *2*, 42-46.

(12) Wang, X.; Yuan, B.; Xie, Z.; Wang, D.; Zhang, R. ZnS-CdS/Graphene Oxide Heterostructures Prepared by a Light Irradiation-Assisted Method for Effective Photocatalytic Hydrogen Generation. J. Colloid Interf. Sci. 2015, 446, 150-154.

(13) Zhao, H.; Dong, Y.; Jiang, P.; Wang, G.; Miao, H.; Wu, R.; Kong, L.; Zhang, J.; Zhang, C. Light-Assisted Preparation of a ZnO/CdS Nanocomposite for Enhanced Photocatalytic H₂

Evolution: An Insight into Importance of in Situ Generated ZnS. *ACS Sustain. Chem. Eng.* **2015**, *3*, 969-977.

(14) Ma, D.; Shi, J.; Zou, Y.; Fan, Z.; Ji, X.; Niu, C. Highly Efficient Photocatalyst Based on a CdS Quantum Dots/ZnO Nanosheets 0D/2D Heterojunction for Hydrogen Evolution from Water Splitting. *ACS Appl. Mater. Interfaces.* **2017**, *9*, 25377-25386.

(15) Xie, Y.; Yang, Y.; Wang, G.; Liu, G. Oxygen Vacancies Promoted Interfacial Charge Carrier Transfer of CdS/ZnO Heterostructure for Photocatalytic Hydrogen Generation. *J. Colloid Interf. Sci.* **2017**, *503*, 198-204.

(16) Guo, X.; Chen, Y.; Qin, Z.; Su, J.; Guo, L. Facet-Selective Growth of CdS Nanorods on ZnO Microrods: Intergrowth Effect for Improved Photocatalytic Performance. *ChemCatChem*, **2017**, *10*, 153-158.

(17) Wang, P.; Zhan, S.; Wang, H.; Xia, Y.; Hou, Q.; Zhou, Q.; Li, Y.; Ramasamy Rajesh Kumar. Cobalt Phosphide Nanowires as Efficient Co-Catalyst for Photocatalytic Hydrogen Evolution over Zn_{0.5}Cd_{0.5}S. *Appl. Catal. B-Environ.* **2018**, *230*, 210-219.

(18) Shi, J.; Ma, D.; Zou,Y.; Fan, Z.; Shi, J.; Cheng, L.; Ji, X.; Niu, C. Rational Construction of Multiple Interfaces in Ternary Heterostructure for Efficient Spatial Separation and Transfer of Photogenerated Carriers in the Application of Photocatalytic Hydrogen Evolution. *J. Power Sources*, **2018**, *379*, 249-260.

(19) Wang, S.; Zhu, B.; Liu, M.; Zhang, L.; Yu, J.; Zhou, M. Direct Z-scheme ZnO/CdS Hierarchical Photocatalyst for Enhanced Photocatalytic H₂-Production Activity. *Appl. Catal. B-Environ.* **2019**, *243*, 19-26.

(20) Yi, L.; Dong, R.; Ma, Y.; Liu, W.; Zhu, A.; Tan, P.; Bian, Y.; Xiong, X.; Li, E.; Pan, J. Improved Photocatalytic Hydrogen Evolution by Facet Engineering of Core-Shell Structural CdS@ZnO. *Int. J. Hydrogen Energy*, **2019**, *44*, 25599-25606.

(21) Khan, K.; Tao, X.; Shi, M.; Zeng, B.; Feng, Z.; Li, C.; Li, R., Visible-Light-Driven Photocatalytic Hydrogen Production on Cd_{0.9}Zn_{0.5}S Nanorods with an Apparent Quantum Efficiency Exceeding 80%. *Adv. Funct. Mater.* **2020**, *30* (42), 2003731.

(22) Ha, E.; Ruan, S.; Li, D.; Zhu, Y.; Chen, Y.; Qiu, J.; Chen, Z.; Xu, T.; Su, J.; Wang, L.; Hu, J., Surface disorder engineering in ZnCdS for cocatalyst free visible light driven hydrogen production. *Nano Res.* **2021**, *15* (2), 996-1002.

(23) Zhang, D.; Teng, J.; Yang, H.; Fang, Z.; Song, K.; Wang, L.; Hou, H.; Lu, X.; Bowen, C. R.; Yang, W., Air - condition process for scalable fabrication of CdS/ZnS 1D/2D heterojunctions toward efficient and stable photocatalytic hydrogen production. *Carbon Energy*, **2022**, 1-14.

(24) Li, H.; Tao, S.; Wan, S.; Qiu, G.; Long, Q.; Yu, J.; Cao, S., S-scheme heterojunction of ZnCdS nanospheres and dibenzothiophene modified graphite carbon nitride for enhanced H2 production. *Chinese J. Catal.* **2023**, *46*, 167-176.