

**Microdroplet assisted hollow ZnCdS@PDA nanocages synergistic confinement
effect for promoting photocatalytic H₂O₂ production**

Chenxi Feng, Lei Zhang*

College of Chemistry, Liaoning University, 66 Chongshan Middle Road, Shenyang Liaoning,
110036, China

*Correspondence author:

Lei Zhang, College of Chemistry, Liaoning University, 66 Chongshan Middle Road, Shenyang

110036, P. R. China.

E-mail address: zhanglei63@126.com; Tel.: +86 24 62207809; Fax: +86 24 62202380.

*Corresponding author. Tel.: +86 024 62207809; Fax: +86 024 62202380.
E-mail address: zhanglei63@126.com (L. Zhang)

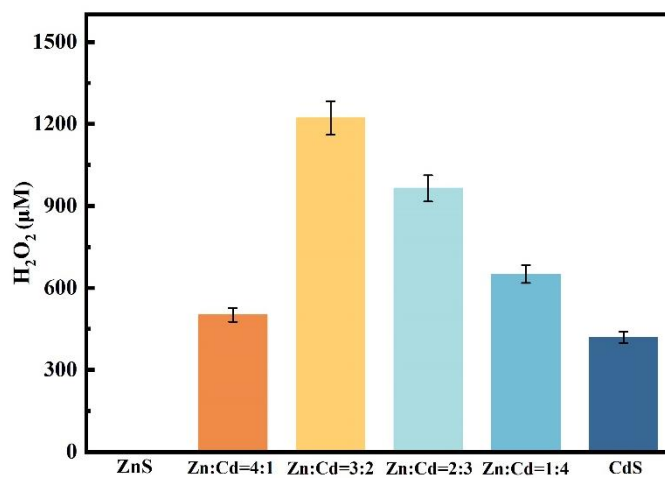


Fig. S1 Photocatalytic H_2O_2 yield of ZnCdS with different ratios of Zn and Cd.

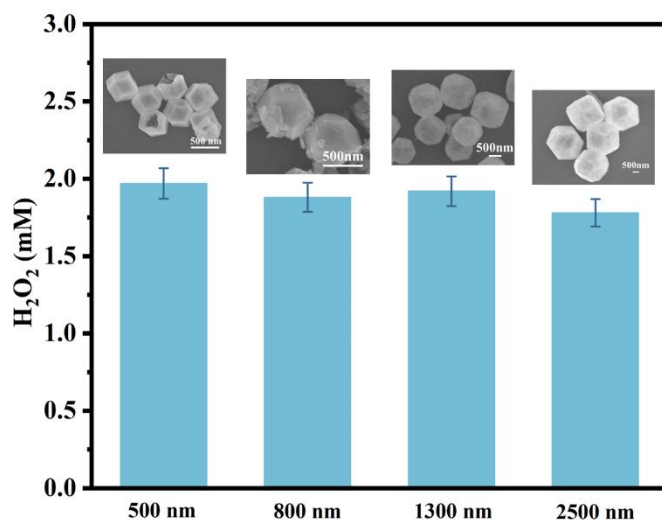


Fig. S2 Effect of different sizes of ZnCdS@PDA on photocatalytic production of H_2O_2 (light reaction for one hour).

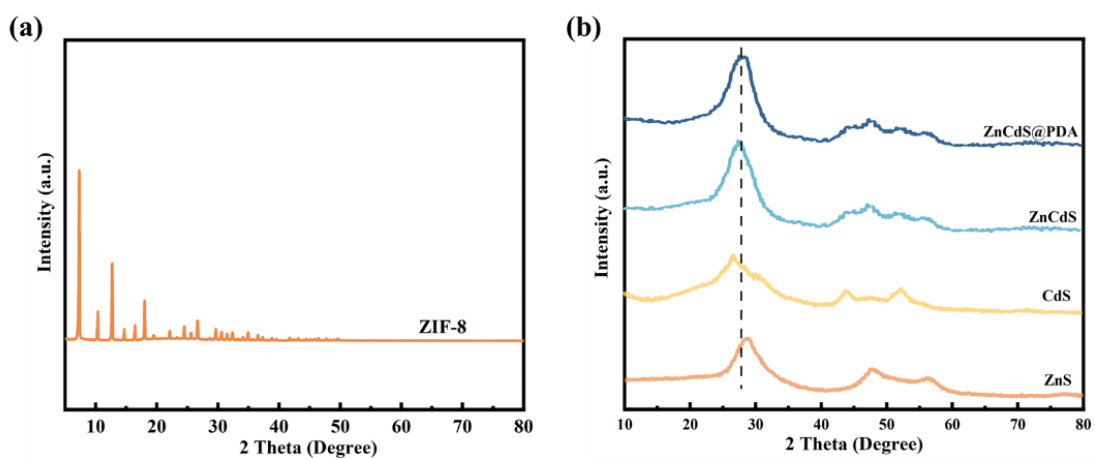


Fig. S3 XRD patterns of ZIF-8 (a), ZnS, CdS, ZnCdS, and ZnCdS@PDA (b).

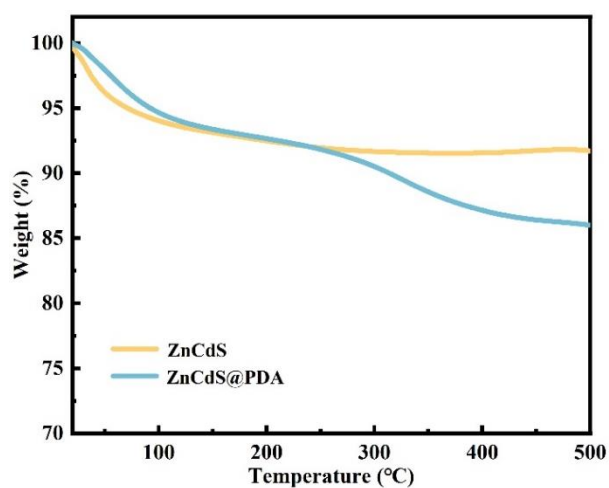


Fig. S4 Thermogravimetry analysis (TGA) curves for ZnCdS and ZnCdS@PDA in air.

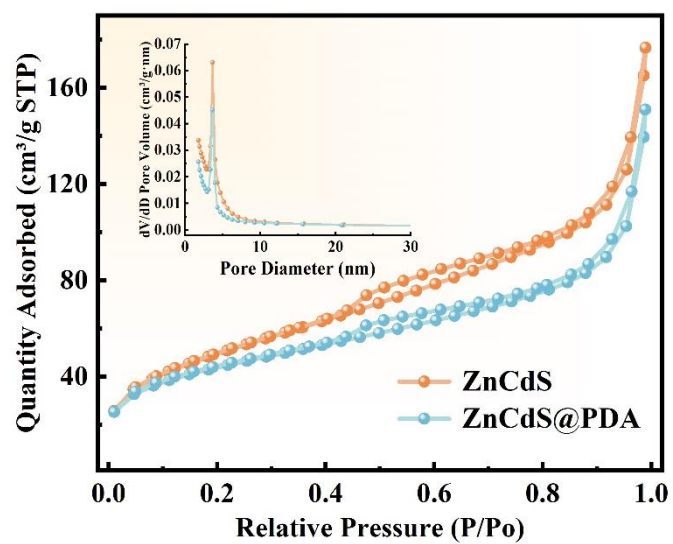


Fig. S5 Adsorption-desorption isotherms (inset: pore size distribution) of ZnCdS and ZnCdS@PDA.

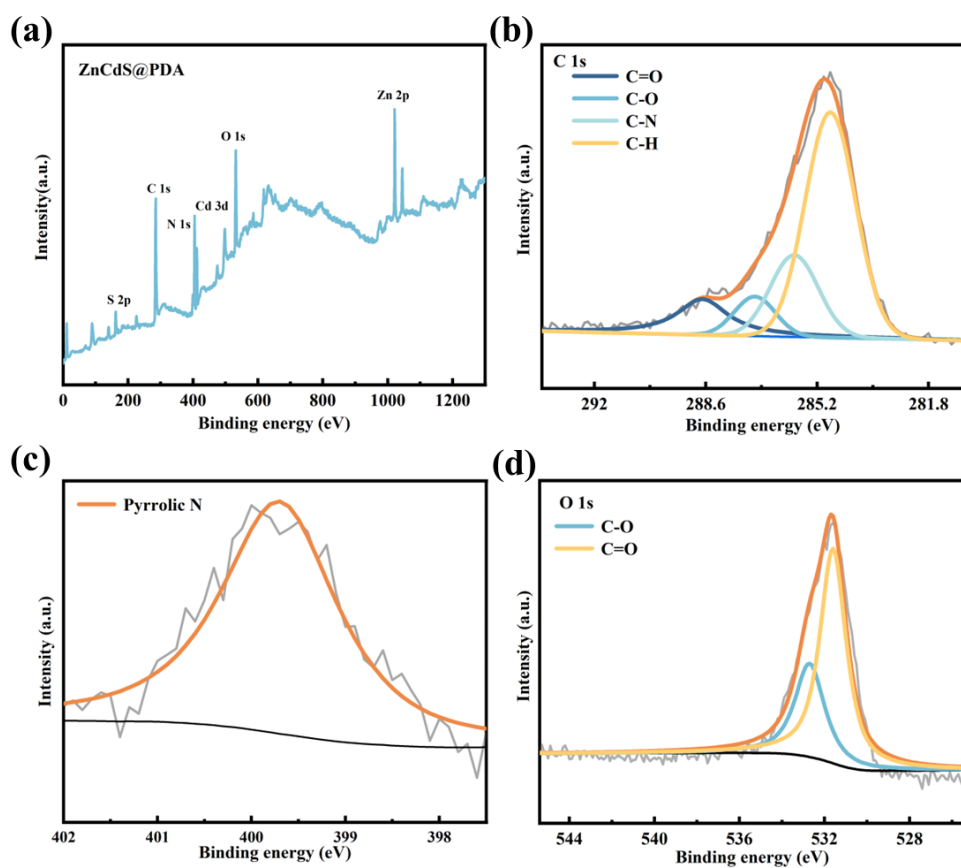


Fig. S6 (a) Wide-scan survey XPS spectrum of ZnCdS@PDA, and (b-d) high-resolution XPS spectra of (b) C1s, (c) Pyrrolic N, (d) O1s for ZnCdS@PDA.

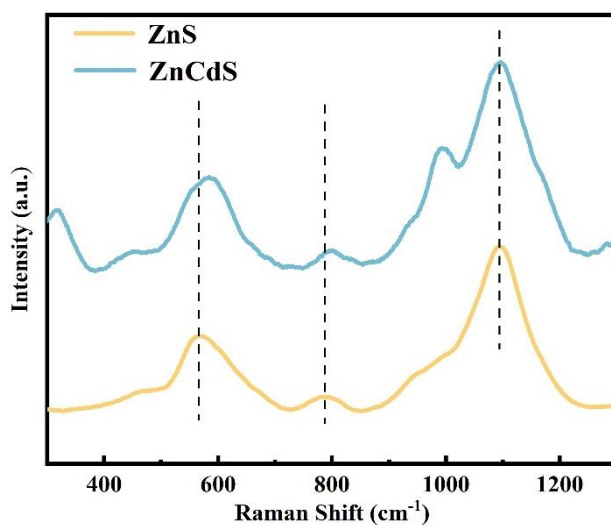


Fig. S7 Raman spectra of the ZnS and ZnCdS.

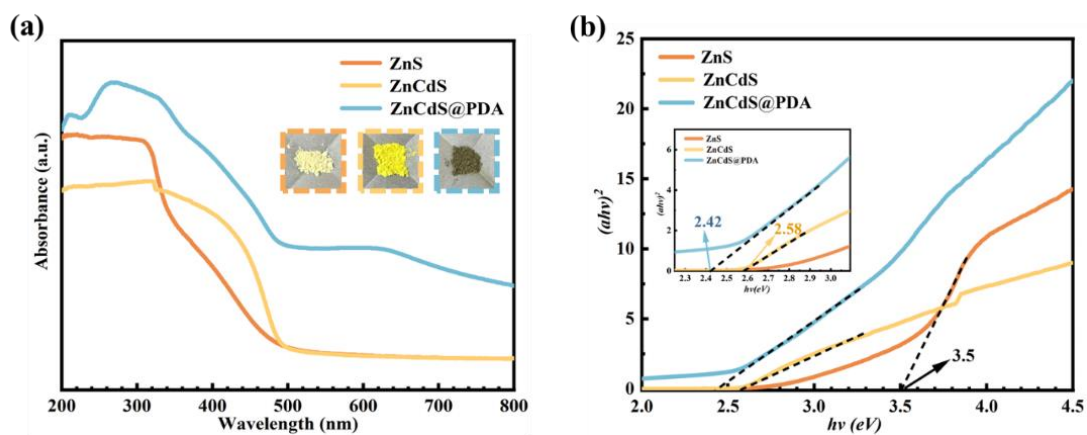


Fig. S8 (a) UV-vis diffuse reflection spectra and (b) Tauc plots of ZnS, ZnCdS, and ZnCdS@PDA.

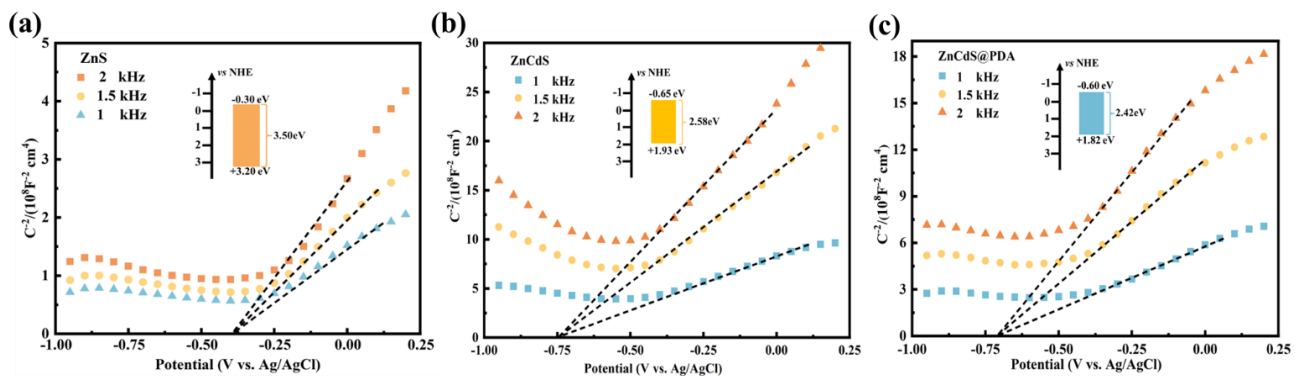


Fig. S9 Mott-Schottky plots of ZnS (a), ZnCdS (b), and ZnCdS@PDA (c).

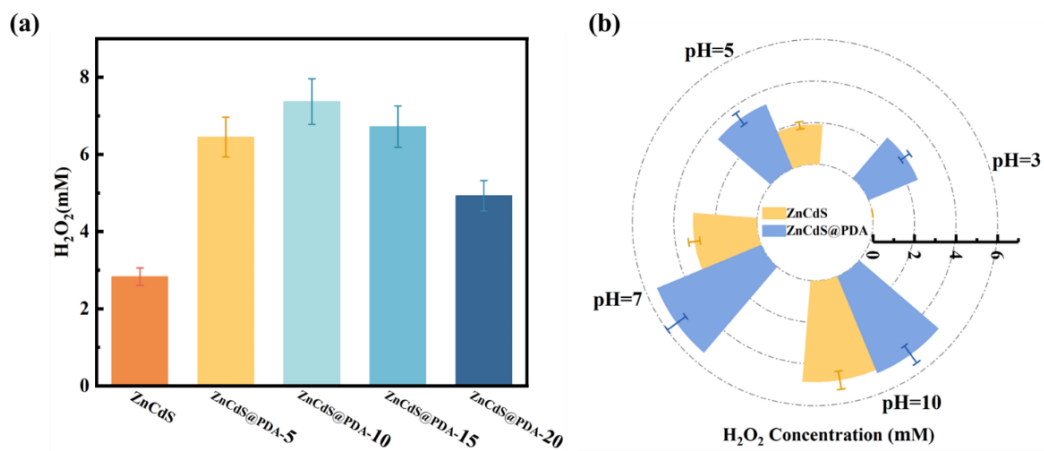


Fig. S10 (a) Photocatalytic H₂O₂ production by ZnCdS and ZnCdS@PDA-X (X = 5, 10, 15 and 20), (b) concentration of H₂O₂ production for ZnCdS and ZnCdS@PDA under different pH conditions.

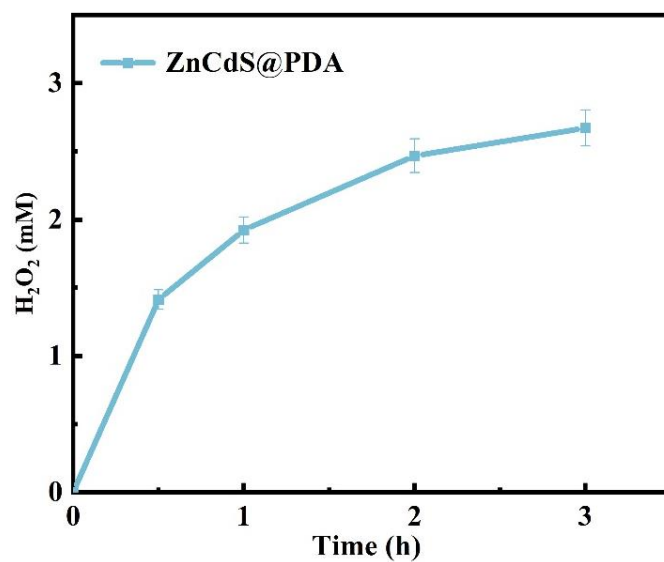


Fig. S11 H₂O₂ yield of ZnCdS@PDA in bulk solution

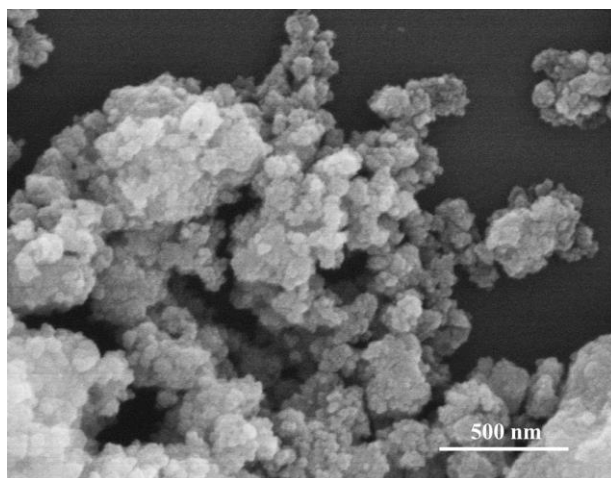


Fig. S12 SEM images for ZnCdS@PDA-p.

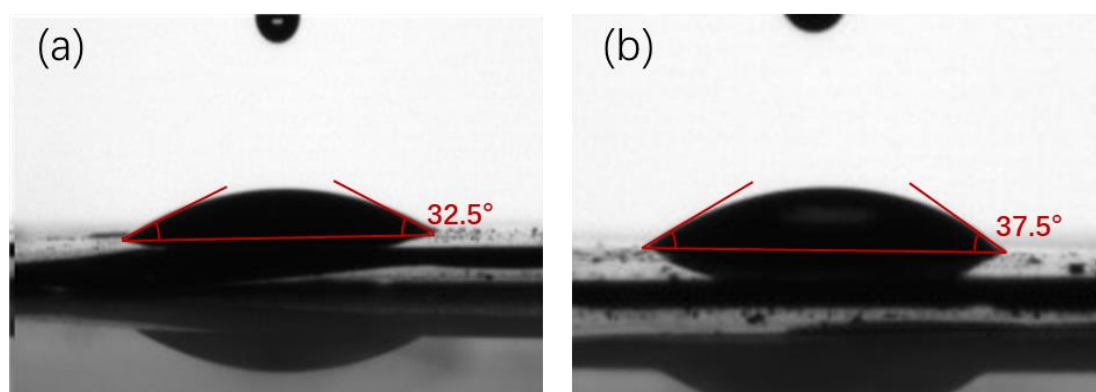


Fig. S13 Image of the contact angle between (a) ZnCdS@PDA and (b) ZnCdS@PDA-p.

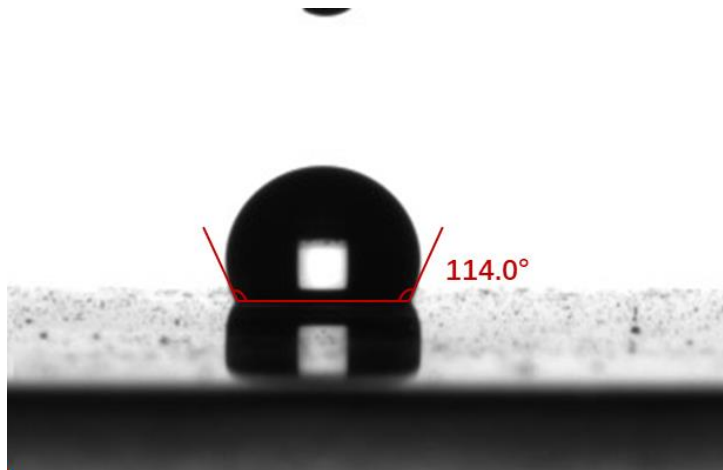


Fig. S14 Contact angle image of a hydrophobic glass panel.

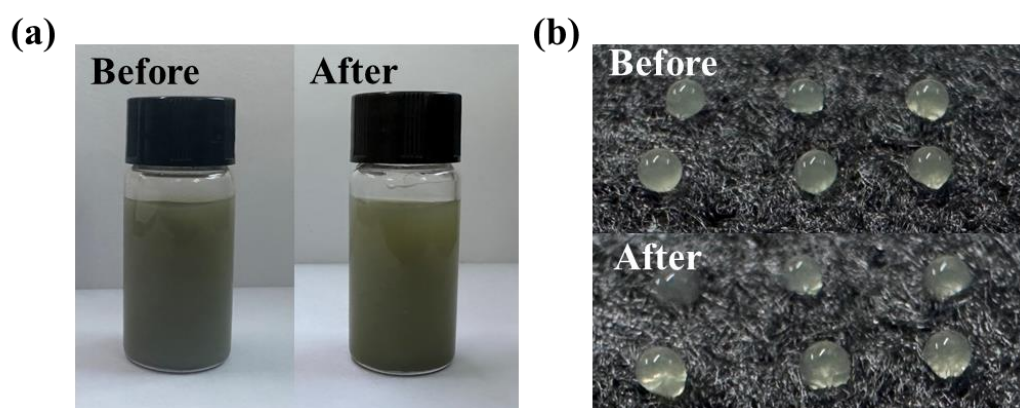


Fig. S15 Dispersion stability of ZnCdS@PDA in bulk (a) and microdroplets (b).

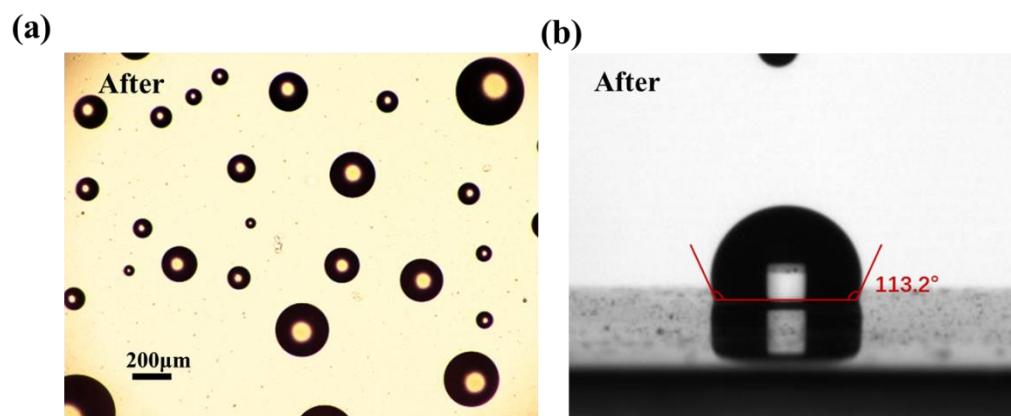


Fig. S16 (a) Microscopic and (b) contact angle images of the stability of microdroplets after a period of time.

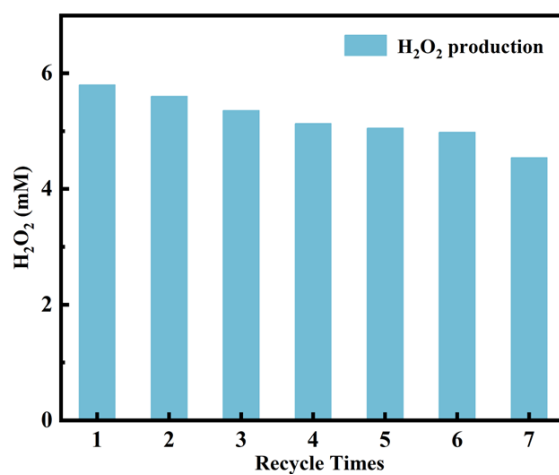


Fig. S17 Recycle experiment of ZnCdS@PDA.

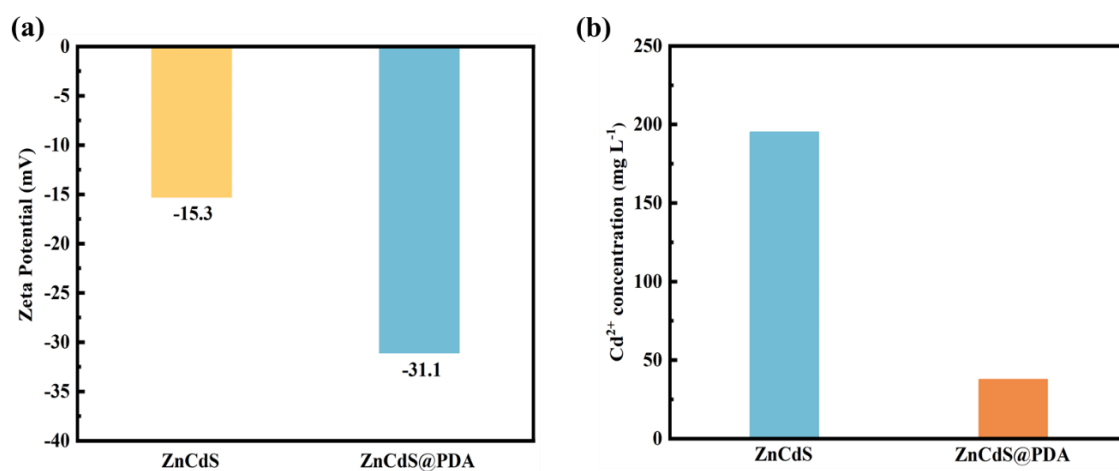


Fig. S18 Zeta potential (a) and ICP (b) comparison data for ZnCdS and ZnCdS@PDA.

Table 1 Atomic percentages of ZnS and ZnCdS calculated using XPS

Atomic % [←]	S [←]	Zn [←]	Cd [←]	S: (Zn+Cd) [←]
ZnS [←]	48.54 [←]	51.46 [←]	0 [←]	0.94: 1 [←]
ZnCdS [←]	48.03 [←]	30.38 [←]	21.59 [←]	0.92: 1 [←]

EXPERIMENTAL SECTION

Bulk phase photocatalytic H₂O₂ production

The bulk phase photocatalytic activity was tested by a 100 W Xenon lamp with a 420 nm filter. The irradiated surface area is $4.23 \times 10^{-3} \text{ m}^2$. For a typical reaction, 20 mg catalyst was dispersed in 20 mL deionized water (pH = 7) to form a reaction suspension. The suspension was stirred and purged with O₂ for 0.5 h before irradiation. The hydrogen peroxide concentration was analyzed via iodometric titration method.

Preparation of superhydrophobic substrate

Prepare a n-hexane solution of 2.5 wt% polydimethylsiloxane, wherein the polydimethylsiloxane prepolymer is in a mass ratio of 10:1 to the curing agent, then mix it well and set aside (1). The superhydrophobic glass pane (thickness 2 mm, diameter 3 cm) was prepared by submersing the pre-cleaned glass pane into the as-prepared suspensions, and then dried under 120 °C for 4 h.

Microdroplets generation and photocatalytic H₂O₂ production

For comparison with bulk phase photocatalytic activity, 2 mg ZCS-PDA catalyst was dispersed in 2 mL deionized water (pH = 7) to form a microdroplet precursor solution through ultrasonic treatment 2 h. A volume of microdroplet precursor solution (2, 1, and 0.5 μL) was pipetted onto an ultra-hydrophobic glass plate to form an array of microdroplets. To make it easier, an ultra-fine spray bottle was applied to generate a large number of smaller microdroplets with air as the nebulizing gas under constant gas pressure, and then microdroplets were sprayed on a prepared superhydrophobic glass sheet.

The microdroplet photocatalysis was performed through placing the generated microdroplets in an airtight custom-designed environmental chamber under high relative humidity conditions. The reaction temperature was maintained at room temperature by using a circulating condensed water around the reaction chamber. The high-humidity gas flow was obtained by passing the fresh O₂ through a bottle containing 80 vol% deionized water. Before the photocatalytic experiment started, the closed chamber was first energized with high humidity O₂ for 30 min to maintain a sufficient oxygen atmosphere and to ensure a constant microdroplets size. After the pre-designed irradiation time, the microdroplets were gathered and quantificationally diluted using deionized water for H₂O₂ determination. The hydrogen peroxide concentration was analyzed via iodometric titration method.

Characterization of catalyst

Morphology of the photocatalysts were characterized by a field emission scanning electron microscope (SEM, S4800, Hitachi Co., Japan) and transmission electron microscope (TEM, 2100F, JEOL Co., Japan). Characterization of photocatalysts with Powder Xray diffraction (XRD) patterns collected on D8 advanced Diffractometer (Bruker Co., Germany) using Cu-K α radiation ($\lambda = 0.1542$ nm), X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi, Thermo Electron Co., America), electron spin resonance (ESR, ER200-SRC, Bruker Co., Germany), Fourier transform infrared spectroscopy (FTIR, PerkinElmer Co., America). Photoluminescence (PL) spectra of the samples were collected on a fluorescence spectrometer (RF-5301PC, SHIMADZU, Japan). Mott-Schottky plot, electrochemical impedance spectroscopy (EIS), and time-resolved photocurrent were carried out on a computer-controlled electrochemical workstation (CHI 660D, Shanghai ChenHua Instruments Co., China) in a threeelectrode configuration with the as-prepared materials (3 mg) on fluorine-doped tin

oxide (FTO, $2 \times 2 \text{ cm}^2$) as the working electrode, the Pt wire as the counter electrode, the Ag/AgCl as the reference electrode, and 0.10 M Na_2SO_4 as electrolyte. UV-vis diffuse reflectance spectra (DRS) were performed with UV-Vis DRS (UV2550, Shimadzu, UV-2600). Adsorption amount of the samples was collected on a programmed temperature rise chemisorption analyzer (BELCAT-A, Japan).

Characterization of microdroplets

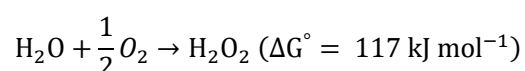
The contact angle of microdroplets and hydrophobic glass plate were measured using an optical contact angle meter (Kruss DSA100, Germany). Size of microdroplets were observed using an optical microscope. Raman spectra were obtained with an Renishaw in Via Raman spectrometer (Renishaw Trading Co., Ltd). Microdroplets containing 4 M NaSCN and 500 μL of as synthesized Au nanoparticles suspension were used for interfacial electric field measurements at low temperature and high humidity. The Raman spectra was measured for 2 times at a wavelength of 532 nm, with a laser power of 2.5 mW. The electric field strength (E) is calculated from the following conversion equation (eq. S1) (2):

$$E = (\Delta\nu(\text{C}\equiv\text{N})/0.36) \times 10^6 \text{ [(V/cm)/cm}^{-1}] \quad (\text{eq. S1})$$

where $\Delta\nu(\text{C}\equiv\text{N})$ is the difference value of detected Raman shift of $\nu(\text{C}\equiv\text{N})$ between microdroplet interior and air-water interface.

Determination of solar-to-chemical conversion (SCC) efficiency

The free energy for H_2O_2 formation:



The total input energy:

$$E_{\text{solar}} (W) = \text{irradiance} (W \text{ m}^{-2}) \times \text{irradiated area} (\text{m}^2) \quad (\text{eq. S2})$$

The determination of SCC:

$$\text{SCC efficiency (\%)} = \frac{[\Delta G \text{ for H}_2\text{O}_2 \text{ generation (J mol}^{-1}\text{)]} \times [\text{H}_2\text{O}_2 \text{ formed (mol)}]}{[\text{total input energy (W)}] \times [\text{reaction time (s)}]} \quad (\text{eq. S3})$$

According to eq. S3, the free energy for H₂O₂ generation is 117 kJ·mol⁻¹. The irradiance of simulated solar source is 100 mW·cm⁻², while the irradiated area is 4.23 × 10⁻³ m².

Determination of diffusion coefficient (D/r_0^2) of O₂

The diffusion coefficient (D/r_0^2) of O₂ can be calculated according to the following formula:

$$\frac{Q_t - Q_0}{Q_\infty - Q_0} = \frac{6}{r_0} \sqrt{\frac{Dt}{\pi}} \quad (\text{eq. S4})$$

where Q_t , Q_∞ and Q_0 are the amounts adsorbed at time t , at time of sorption equilibrium and at time $t = 0$, respectively.

Assuming that O₂ diffusion of the catalyst follows *Fick's law* and using the linear form of this equation to investigate the O₂ diffusion coefficient on the catalysts (3).

The test method of electron transfer number (n)

The electron transfer number (n) can be calculated according to the following formula:

$$n = \frac{4I_d}{I_d + I_r/N} \quad (\text{eq. S5})$$

Where I_d and I_r represent the current of disk and ring, respectively. N is the rotating disk-ring electrode (RRDE) collection efficiency. The averaged collection efficiency N is 0.37.

References

- (1) X. Liu, X. Zhang, Q. Chen, Y. Pan, C. Liu and C. Shen, *Chemical Engineering Journal*, 2021, **406**.
- (2) K. Li, Q. Ge, Y. Liu, L. Wang, K. Gong, J. Liu, L. Xie, W. Wang, X. Ruan and L. Zhang, *Energy & Environmental Science*, 2023, **16**, 1135-1145.
- (3) L. Zhao, B. Shen, J. Gao and C. Xu, *Journal of Catalysis*, 2008, **258**, 228-234.