Supporting Information

Prolonged electron lifetime in sulfur vacancies-rich ZnCdS nanocages by interstitial P doping for photocatalytic water reduction

Qiaohong Zhu[a], Zehong Xu[a], Qiuying Yi[a], Muhammad Nasir[b], Mingyang Xing[a], Bocheng Qiu[a,*], and Jinlong Zhang[a,c*]

a. Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, Feringa Nobel Prize Scientist Joint Research Center, School of Chemistry and Molecular Engineering, East China University of Science and Technology, 130 Meilong Road, Shanghai 200237, China.

b. Interdisciplinary Research Centre in Biomedical Materials (IRCBM), COMSATS University Islamabad, Lahore Campus, 1.5 Km Defence Road, Off Raiwind Road, Lahore 54000, Punjab, Pakistan.

c. School of Chemistry & Chemical Engineering, Yancheng Institute of Technology, Yancheng 224051, China

EXPERIMENTAL SECTION

1.1 Chemical materials

All of the reagents were used without further purification.

1.2 Synthesis of ZIF-8 rhombic dodecahedrons

According to the previous reported method[1, 2] to fabricate solid ZIF-8 rhombic dodecahedrons, a mixed solution A of 2-methylimidazole (8 mmol), 1-methylimidazole (0.025 mmol), and methanol (25 mL) was quickly added into a mixed solution B of $Zn(CH_3COO)_2$ (1 mmol) and methanol (25 mL) to form a solution C, and the solution C was kept silence at room temperature for further 24 h after stirring for 2 min. Finally, the products were collected through centrifugation and dried under vacuum condition.

1.3 Synthesis of ZnS nanocages

ZIF-8 rhombic dodecahedrons were used as the templates to fabricate ZnS nanocages. 25 mg ZIF-8, 25 mL ethanol, and 25 μL H_2O were mixed together through ultrasound, thioacetamide (TAA) (150 mg) was then added to form the mixed solution and the solution was heated at the temperature of 55 ^oC 2 h and 75 ^oC 1.5 h, respectively. Finally, the products were collected through centrifugation and dried under vacuum condition.

1.4 Synthesis of ZnCdS nanocages

The ZnCdS nanocages were obtained through a hydrothermal synthesis. After the addition of $Cd(CH_3COO)_2$ into the mixed solution of ZnS nanocages and ethylene glycol, the solution was kept stirring for 30 min, and then was heated at 160 ^oC for 4 h. Finally, the products were collected through centrifugation and dried under vacuum condition.

1.5 Synthesis of P-ZnCdS nanocages

In the phosphatization process[3], 20 mg ZnCdS nanocages and 0.2 g sodium hypophosphite (the mass ratio is 1:10) were placed in the tube furnace with the temperature of 300 ^oC for 2 hours in the N_2 atmosphere, and the resulting sample is collected as P-ZnCdS.

1.6 Characterizations

The X-ray diffraction (XRD) patterns of all samples were collected in the range 10-80° (2θ) using a RigakuD/MAX 2550 diffract meter (Cu K radiation, λ =1.5406 Å), operated at 40 kV and 100 mA. The morphologies were characterized by transmission electron microscope (TEM, JEOL, JEM-1400), high resolution transmission electron microscopy (HRTEM, JEOL, JEM-2100,). The UV-vis absorption was got from a Scan UV-vis spectrophotometer (Varian, Cary 500) furnished with an integrating sphere assembly, using $BaSO_4$ as the reflectance sample. The instrument employed for XPS studies was a Perkin-Elmer PHI 5000C ESCA system with Al Kα radiation operated at 250 W. The shift of the binding energy due to relative surface charging was corrected using the C1s level at 284.8 eV as an internal standard. The photoluminescence (PL) emission spectra of the solid catalysts were also recorded at room temperature (25 °C) using luminescence spectrometry (Cary Eclipse) under the excitation light at 360 nm. The electrochemical experiments were carried out at room temperature in a cell with a standard three-electrode system using an electrochemical analyzer (CHI 660 D electrochemical station, CHI Instruments Inc.). And the electrode consisting of a working electrode (as-prepared samples as the working electrodes with an active area of ca. 0.5 cm^{-2}), a Pt wire as the counter electrode and a saturated Ag/AgCl as the reference electrode was employed.

1.7 Photocatalytic H_2 measurement

To assess the photocatalytic performance of materials, photocatalytic H_2 evolution reaction was measured on an online photocatalytic hydrogen evolution system (Beijing Perfectlight, LabSolarIIIAG). For H_2 evolution, 20 mg catalyst was dispersed in 100 mL aqueous solution (containing 0.45 M Na_2S and 0.45 M Na_2SO_3 as sacrificial agent). The system was vacuumized for 30 min to remove any residual air in solution before light irradiation. Photocatalytic H_2 evolution was then carried out by irradiating the solution using a 300 W Xenon lamp equipped with AM 1.5 air mass filter. The gaseous product was analyzed by gas chromatography equipped with a thermal conductive detector (TCD) and a 5Å molecular sieve column, using Argon as the carrier gas.

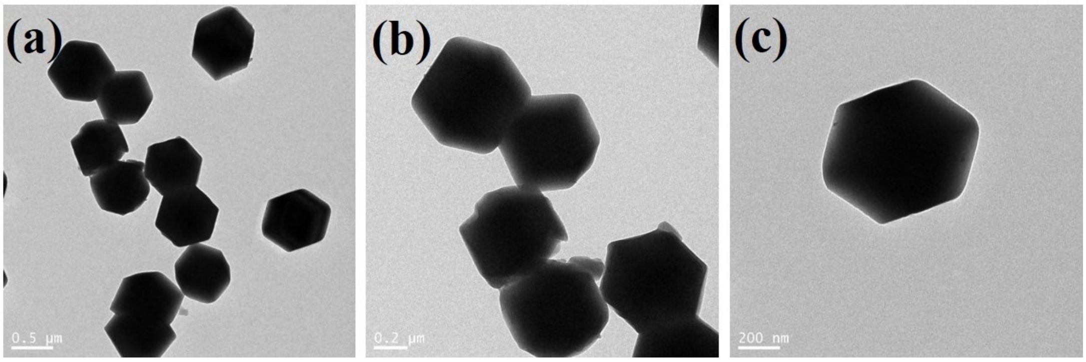

Figure S1. (a-c) TEM images of ZIF-8 rhombic dodecahedrons.

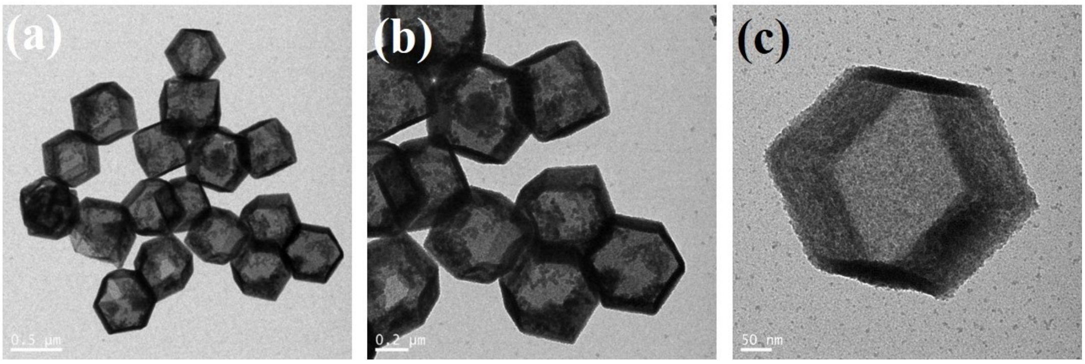

Figure S2. (a-c) TEM images of ZnS nanocages.

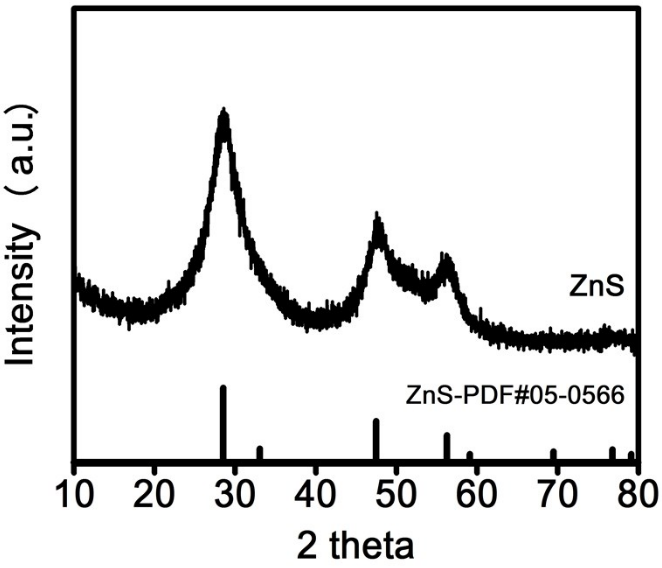

Figure S3. XRD pattern of ZnS nanocages.

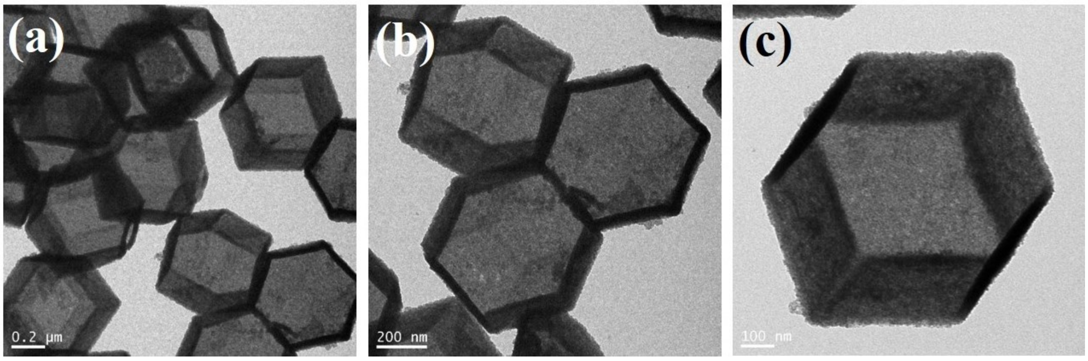

Figure S4. (a-c) TEM images of ZnCdS nanocages.

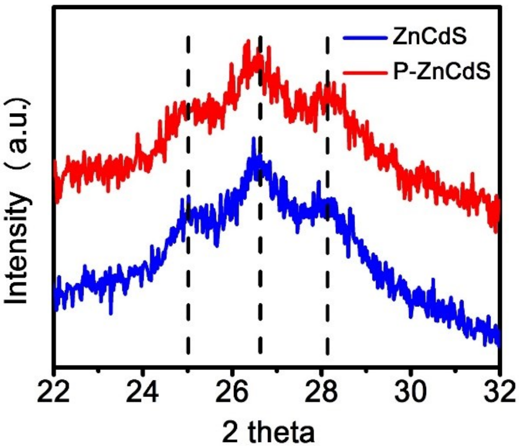

Figure S5. XRD patterns of ZnCdS and P-ZnCdS in the range of 22° to 32°.

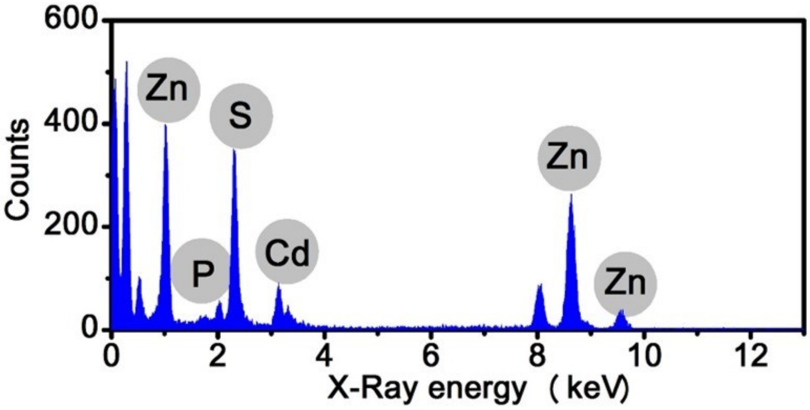

Figure S6. EDX spectrum of P-ZnCdS nanocages.

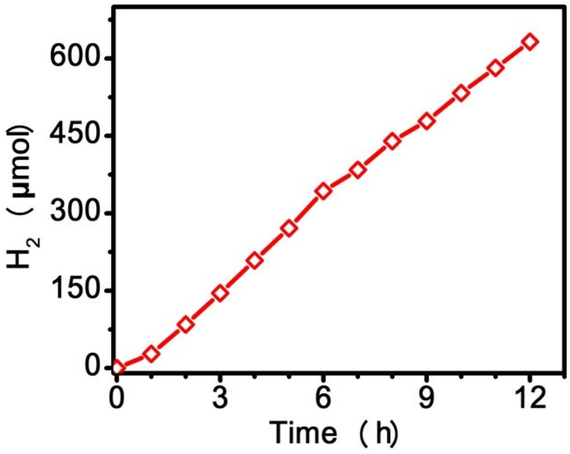

Figure S7. Stability of P-ZnCdS nanocages for H_2 evolution.

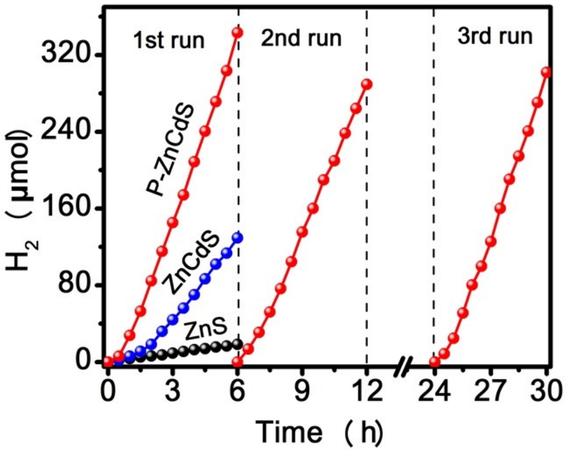

Figure S8. Cyclic photocatalytic HER of P-ZnCdS.

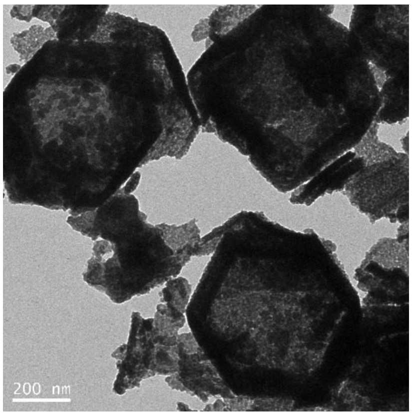

Figure S9. TEM image of P-ZnCdS nanocages after photocatalytic HER.

Table S1. XPS data analysis of P-ZnCdS before and after reaction (atomic%).

	Zn	Cd	S	P
Before reaction	25.11%	26.58%	43.23%	5.02%
After reaction	24.46%	25.47%	44.63%	5.43%

References:

1. W. Zhan, Q. Kuang, J. Zhou, X. Kong, Z. Xie and L. Zheng, Semiconductor@metal–organic framework core–shell heterostructures: a case of ZnO@ ZIF-8 nanorods with selective photoelectrochemical response. *J. Am. Chem. Soc*, 2013, **135**, 1926-1933.
2. J. Chen, J. Chen and Y. Li, Hollow ZnCdS dodecahedral cages for highly efficient visible-light-driven hydrogen generation. *J. Mater. Chem. A*, 2017, **5**, 24116-24125.
3. B. Qiu, Q. Zhu, M. Xing and J. Zhang, A robust and efficient catalyst of $Cd_xZn_{1-x}Se$ motivated by CoP for photocatalytic hydrogen evolution under sunlight irradiation. *Chem. Commun.*, 2017, **53**, 897-900.