Supporting Information

2D Ag modified g-C_3N_4/1D CdS-diethylenetriamine S-scheme heterojunction with enhanced photocatalytic H_2O_2 production

Haoran Chen [a], Junwei Fu [b], Graham Dawson [c], Jinfeng Zhang [a,*], Qingpo Peng [a,*], Kai Dai [a,*]

[a] *Key Laboratory of Green and Precise Synthetic Chemistry and Applications, Ministry of Education, Anhui Province Key Laboratory of Pollutant Sensitive Materials and Environmental Remediation, Huaibei Key Laboratory for Low-Carbon Conversion of Small-Molecule Resources, School of Chemistry and Chemical Engineering, Huaibei Normal University, Huaibei 235000, P. R. China*

[b] *School of Physics, Central South University, Changsha 410083, People's Republic of China;*

[c] *Department of Chemistry and Materials Science, Xi'an Jiaotong Liverpool University, Suzhou 215123, Jiangsu, P. R. China*

* Corresponding authors. Fax: +86-561-3803256

Email address: daikai940@chnu.edu.cn (K. Dai); jfzhang@chnu.edu.cn (J. Zhang); pengqingpo@chnu.edu.cn (Q. Peng)

Photocatalytic performance test

In this experiment, 100 mL single neck flask was used to evaluate photocatalytic performance. The experimental operation steps are as follows: 10 mg catalyst was added to the 100 mL single neck flask with built-in stirring device; 50 mL of deionized water was slowly injected along the inner wall of the flask to ensure that the catalyst is completely immersed in deionized water to form a mixed system. The above catalyst deionized water mixed system is placed in an ultrasonic environment and treated for 5 minutes to achieve uniform dispersion of the catalyst. After ultrasonic treatment, transfer the flask to the constant temperature magnetic stirrer; At the same time, high-purity oxygen is introduced into the flask for purging, and the purging time is controlled to 0.5 h, during which the constant temperature stirring state is maintained. After the completion of the oxygenation operation, the catalyst system in the flask was illuminated with a xenon lamp (wavelength $\lambda \geqslant 400$ nm) for 1 h. After the illumination, immediately stop the mixing operation and high-purity oxygen feeding; 3 mL of the reaction solution is extracted from the flask with an airtight syringe, and the solution is filtered through an inorganic filter head. The filtrate is collected and injected into the cuvette. The filtrate in the above-mentioned cuvette is detected with a UV-Visible spectrophotometer, and its absorbance is determined. 1 mL of oxalic acid solution is added to the cuvette, and the color change of the solution is observed. After the color becomes stable, the absorbance of the solution is measured again using the UV-Visible spectrophotometer. The concentration of H_2O_2 in the system is accurately calculated by combining the data of the two absorbance measurements.

Electrochemical measurements

The number of electrons transferred (n) in the oxygen reduction reaction (ORR) was measured using a rotating ring-disk electrode (RRDE) on a CHI660E electrochemical workstation. The ring potential was maintained at 0.436 V (vs. Ag/AgCl). ORR activity and selectivity were studied under O_2-saturated 0.1 M KOH (pH = 13) conditions with a scan rate of 10 mV/s and a rotation speed of 1600 rpm,

using polarization curves and RRDE measurements. Ag/AgCl, glassy carbon, and carbon rod electrodes served as the reference, working, and counter electrodes, respectively. The catalyst was drop-cast onto the glassy carbon electrode. A catalyst suspension was prepared by dispersing 4 mg of the catalyst in 1000 μL of 0.25% Nafion solution, followed by ethanol dilution to achieve a uniform suspension. The mixture was sonicated for 4 h, and 10 μL of the catalyst slurry was transferred to the glassy carbon electrode (coated area: 0.1256 cm^2). Before RRDE measurements, the electrode was dried under a baking lamp. The value of n was calculated using the equation provided in equation S1.

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}} \quad (S1)$$

To calculate the H_2O_2 selectivity of a catalyst based on the current of a disk electrode and a ring electrode, the formula is given as Equation S2:

$$H_2O_2\% = 200 \times \frac{\frac{I_r}{N}}{I_d + \frac{I_r}{N}} \quad (S2)$$

in which Id is the disk current, and Ir is the ring current. The collection efficiency (*N*) is determined to be 37% in our system.

Characterization

In order to characterize and observe the morphology, structure and microstructure of the samples, the samples were first analyzed by X-ray diffraction (XRD) using an X-ray diffractometer (Panaco, Netherlands) in the ranges of 2θ from 5° to 80°. The functional groups in the samples were detected and analyzed by Fourier transform infrared spectroscopy (FT-IR), and their chemical composition and structure were studied. The optical properties of the materials were analyzed using a photoluminescence spectroscopy (model: FLS920, manufactured in the UK). The morphology of the samples was observed by Scanning electron microscope (SEM). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed at a voltage of 200 kV. The surface morphology

and lattice fringes of the samples were recorded. Lambda 95 Perkin-Elmer spectrometer was used to perform UV-Vis DRS on the powder sample to detect the size of the absorption edge. In addition, the electrochemical workstation (CHI-660D) was used to measure the impedance, Mott–Schottky analysis and transient photoconductivity conductance response tests of the samples. A xenon lamp (Perfect Light) was used as the light source for the photocatalytic reaction.

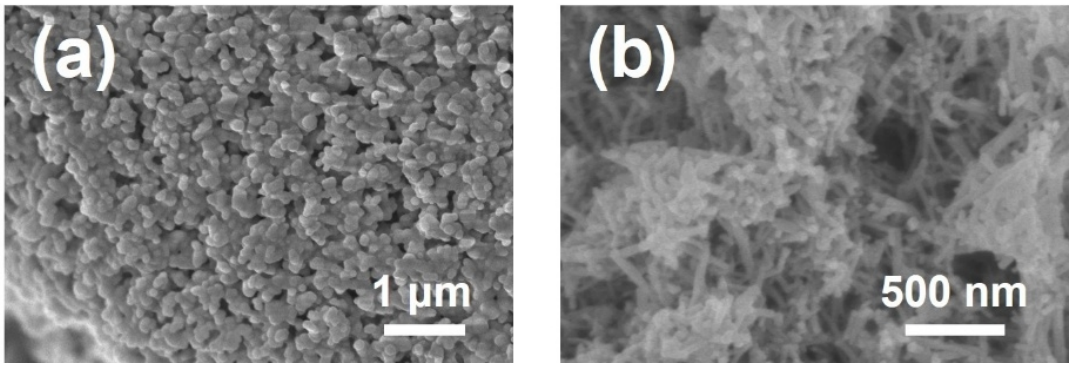

Fig. S1. SEM images of (a) CdS, (b) CdS-D.

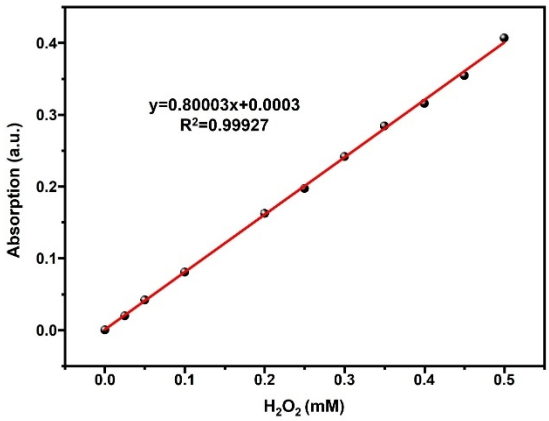

Fig. S2. The standard curve of absorption intensity and H_2O_2 concentration.

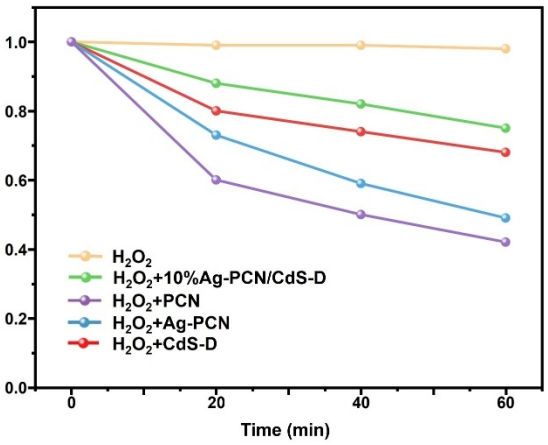

Fig. S3. Decomposition curve of H_2O_2 under light irradiation and Ar atmosphere (H_2O_2 initial concentration: 1 mm).

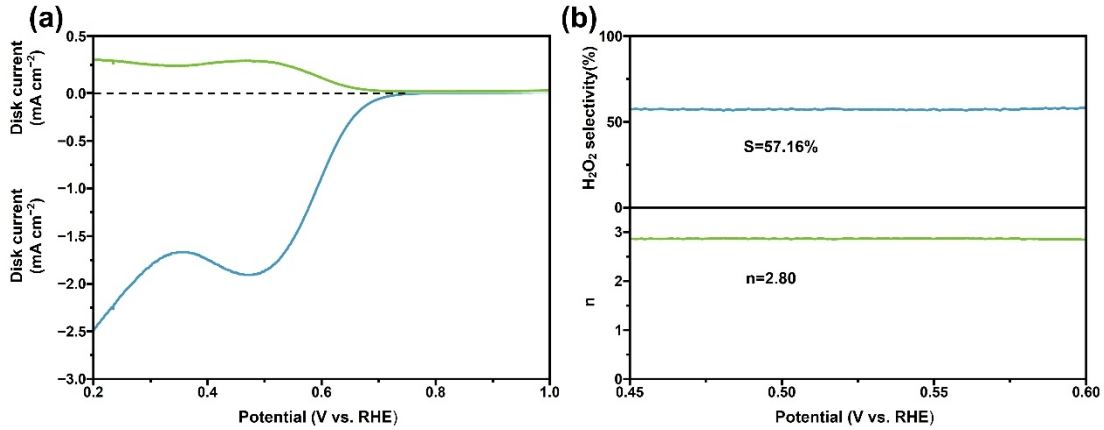

Fig. S4. (a) RRDE polarization curves of 10%Ag-PCN/CdS-D in 0.1 M KOH (pH =13). (b) Calculation of electron transfer number and H_2O_2 selectivity at different potentials from RRDE data for 10%Ag-PCN/CdS-D.

To quantify ORR selectivity, a rotating ring-disk electrode (RRDE) experiment was performed. The 10%Ag-PCN/CdS-D composite showed a continuous increase in disk current below 0.4 V vs RHE. Analysis of ring and disk currents indicated a 57.16% selectivity toward H_2O_2 formation with an average electron transfer number (n) of 2.80.

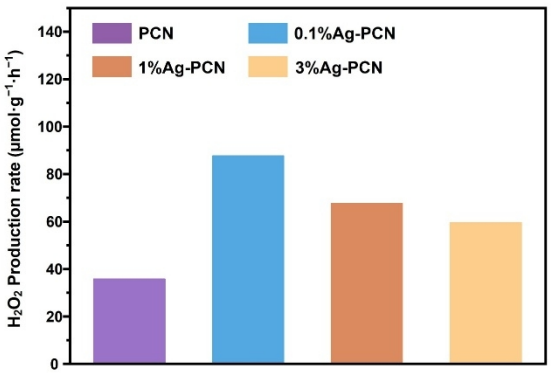

Fig. S5. Photocatalytic H_2O_2 performance of samples.

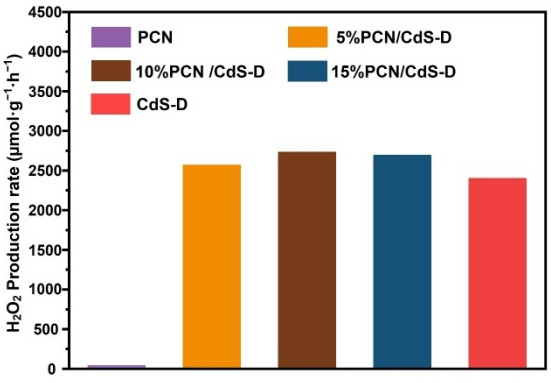

Fig. S6. Photocatalytic H_2O_2 performance of samples.

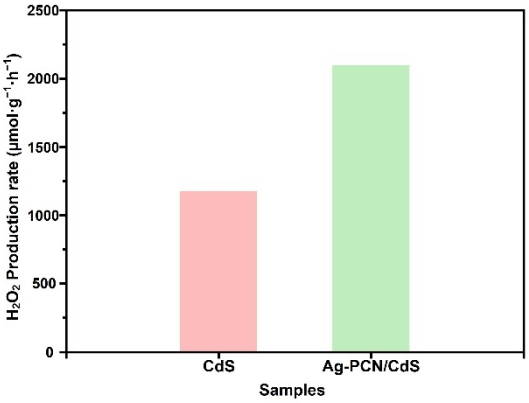

Fig. S7. Photocatalytic activity plots of CdS and Ag-PCN/CdS.

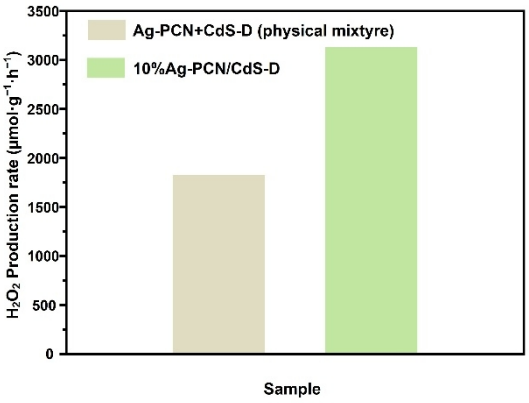

Fig. S8. Photocatalytic H_2O_2 performance of 10%Ag-PCN/CdS-D (physical mixture) and 10%Ag-PCN/CdS-D. The mass ratio of physical mixture of Ag-PCN and CdS-D is 1:9.

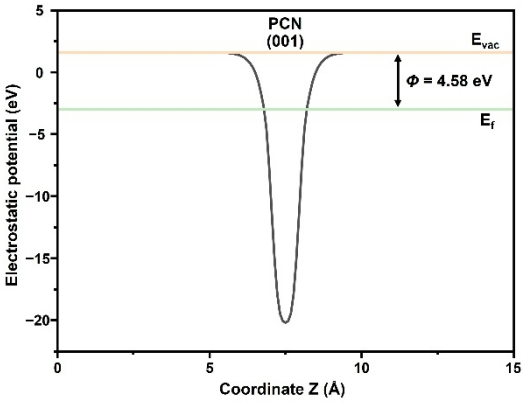

Fig. S9. Electrostatic potentials of PCN.