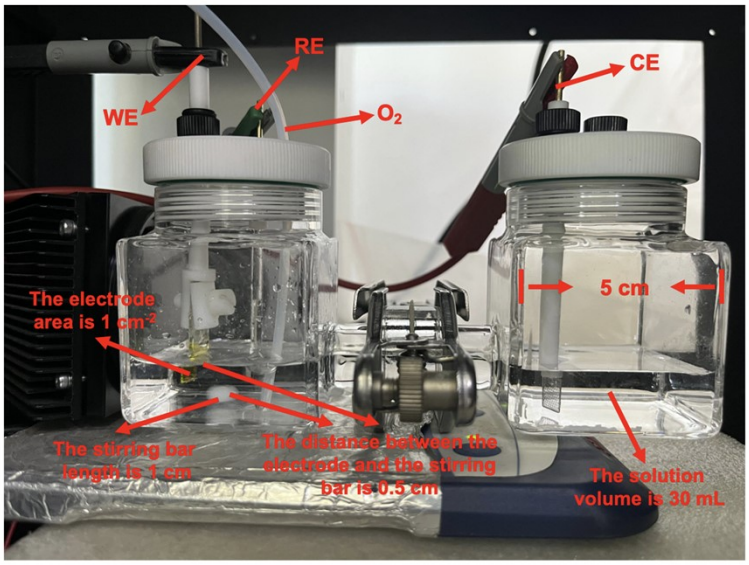
Electronic Supplementary Information for

Multipoint-bridging structure with piezoelectric-induced S-scheme junction for piezoelectrically-enhanced photoelectrochemical H_2O_2 production

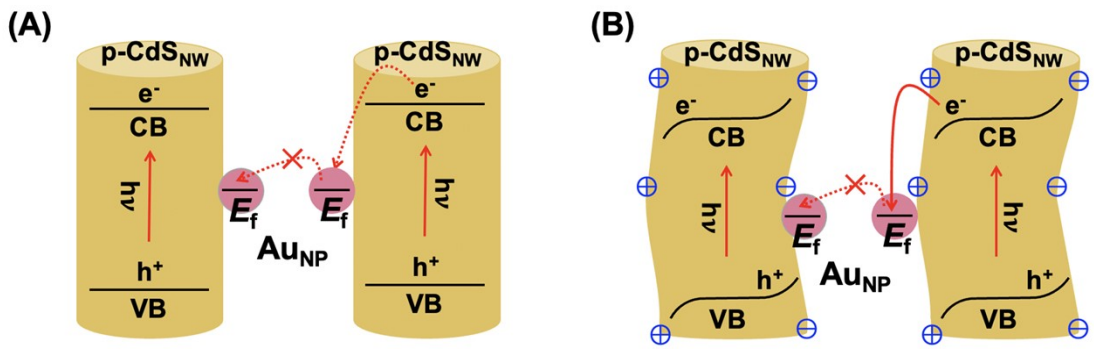
Chenpu Chen, Jun Cheng*

Key Laboratory of Chemical Biology & Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, China

*Corresponding author.
E-mail address: cj1006@hunnu.edu.cn (J. Cheng).



Scheme S1. Device image of the PPEC-ORR. Here, the side length of the PEC cell is 5 cm, the solution volume is 30 mL, the electrode area is 1 cm^{-2}, the stirring bar length is 1 cm, and the distance between the electrode and the stirring bar is 0.5 cm.



Scheme S2. Illustration of the energy band structures and the possible electron-transfer pathways on the Au_{NP}/p-CdS_{NW}/ITO electrode in an unstirred (A) or 1500-rpm-stirred (B) O_2-saturated 0.5 M aqueous Na_2SO_4 under 100 mW cm^{-2} AM 1.5G simulated sunlight illumination. Here, although solution stirring can bend the p-CdS_{NW} to generate piezoelectric charges and interleave the energy band positions of two adjacent p-CdS_{NW}[1], the spatial distance between the p-CdS_{NW} is sufficiently large and there is no transverse electron conductor bridge. Therefore, transverse electron transfer between adjacent p-CdS_{NW} is not possible (dashed arrows).

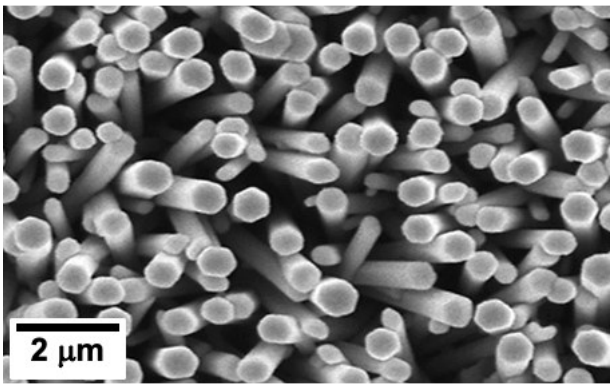


Fig. S1. SEM image of n-CdS_{NW}/ITO electrode.

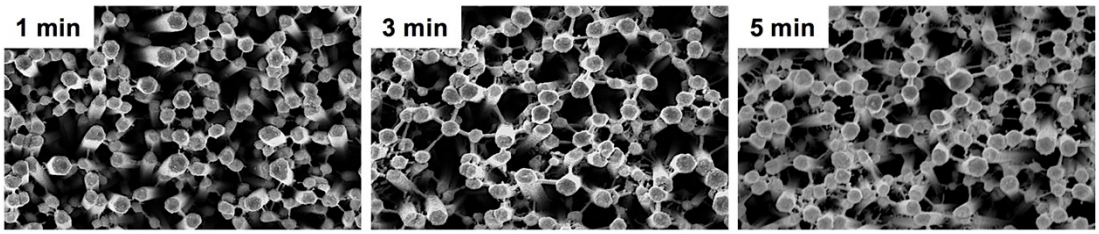


Fig. S2. SEM images of the Au_{NR}/p-CdS_{NW}/ITO electrodes prepared by photodeposition of Au_{NR} at different times.

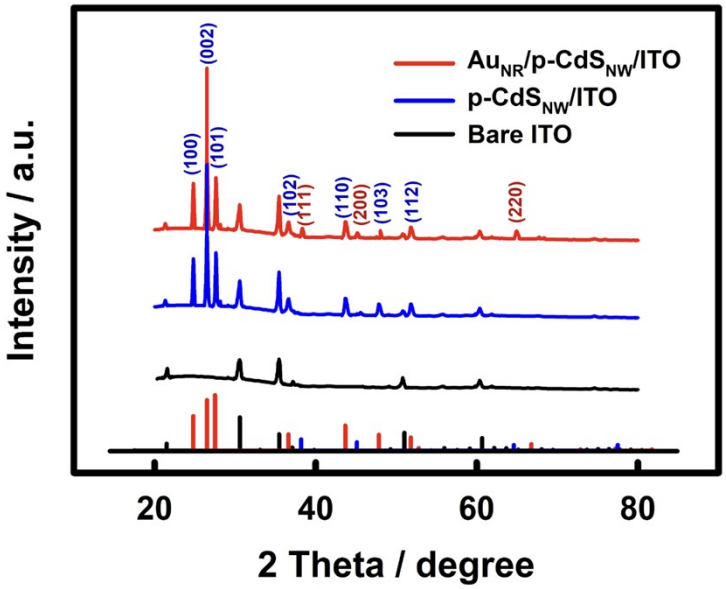


Fig. S3. XRD patterns of the bare ITO, p-CdS_{NW}/ITO and Au_{NR}/p-CdS_{NW}/ITO electrodes.

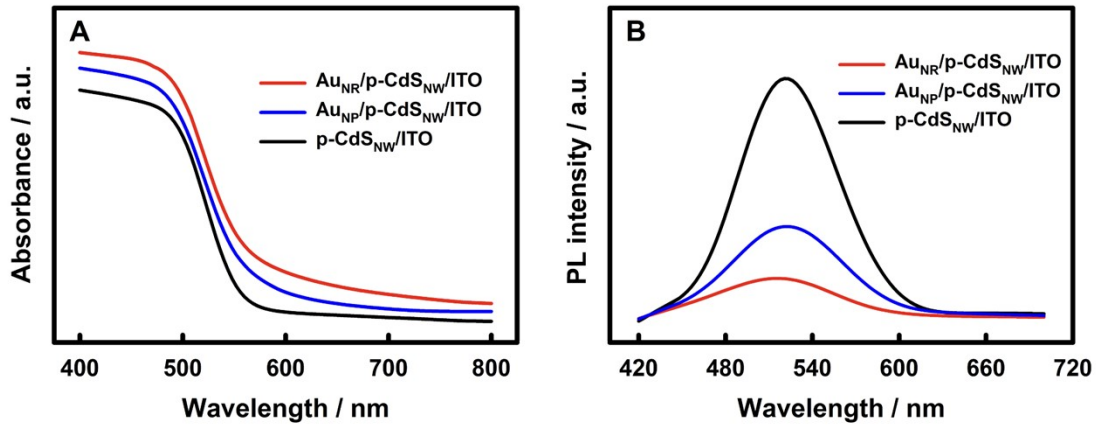


Fig. S4. UV-vis DRS (A) and PL spectra (B) for the p-CdS$_{NW}$/ITO, Au$_{NP}$/p-CdS$_{NW}$/ITO and Au$_{NR}$/p-CdS$_{NW}$/ITO electrodes.

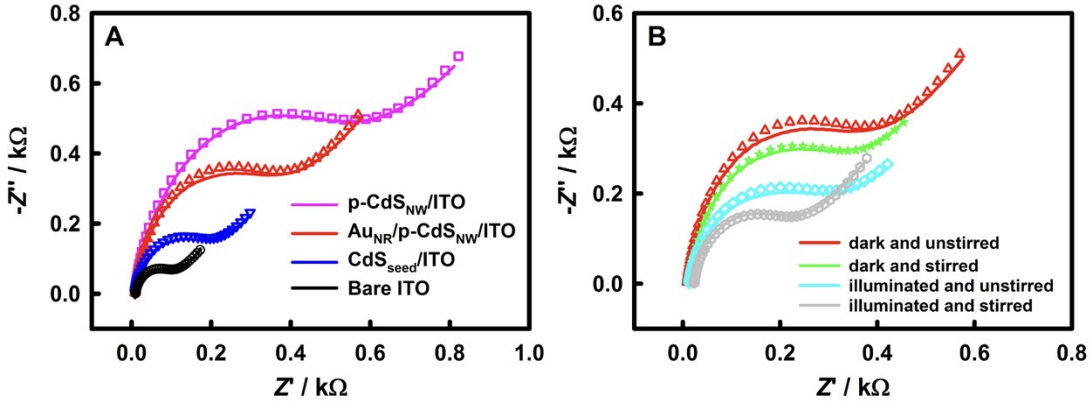


Fig. S5. (A) EIS results of the bare ITO, CdS_{seed}/ITO, p-CdS_{NW}/ITO and Au_{NR}/p-CdS_{NW}/ITO electrodes in 0.5 M aqueous Na_2SO_4 containing 2.0 mM $K_4[Fe(CN)_6]$ under dark and unstirred conditions, (B) EIS results of the Au_{NR}/p-CdS_{NW}/ITO electrode in 0.5 M aqueous Na_2SO_4 containing 2.0 mM $K_4[Fe(CN)_6]$ either without stirring or stirred at 1500 rpm (dark and unstirred; dark and stirred; illuminated and unstirred; or illuminated and stirred).

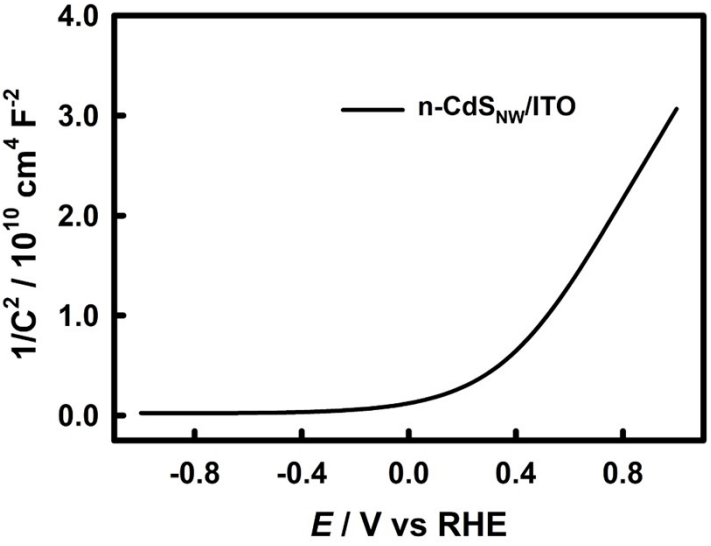


Fig. S6. Mott-Schottky curve for the n-CdS_{NW}/ITO electrode.

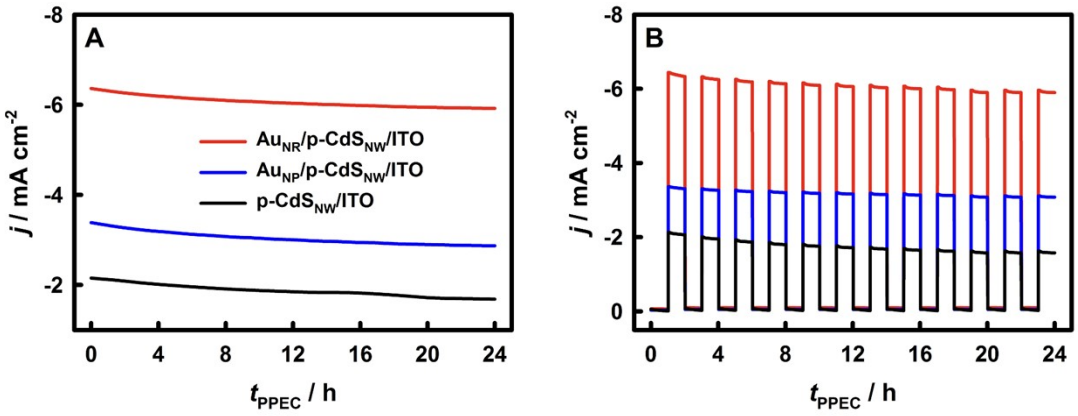


Fig. S7. (A) *j-t* curves under continuous light illumination and (B) *j-t* curves under chopped-light illumination (1 h switch time) of the Au_{NR}/p-CdS_{NW}/ITO, Au_{NP}/p-CdS_{NW}/ITO and p-CdS_{NW}/ITO electrodes at 0.4 V vs RHE in O_2-saturated 0.5 M aqueous Na_2SO_4 stirred at 1500 rpm under 100 mW cm^{-2} Xe lamp illumination.

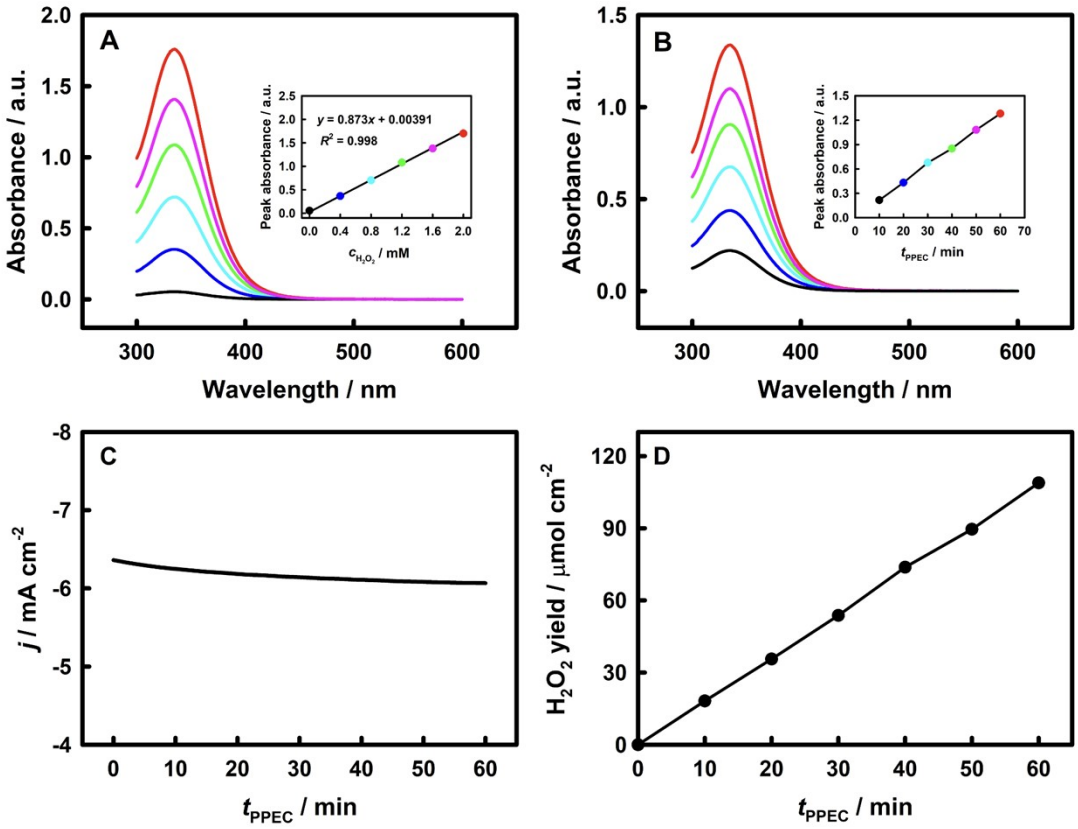


Fig. S8. UV-vis absorption spectra of Fe^{3+} generated by the $FeSO_4$-H_2O_2 redox reaction for standard (A, a series of prepared standard H_2O_2 solutions) or sample (B, the photocathode solution after different PPEC-ORR time) H_2O_2 solutions. The insets show the linear relationship of the peak absorbance at 330 nm versus H_2O_2 concentration (c_{H2O2}) or PPEC-ORR time (t_{PPEC}). Photocurrent density (C) and H_2O_2 yield (D) on the Au_{NR}/p-CdS_{NW}/ITO electrode at 0.4 V vs RHE in O_2-saturated 0.5 M aqueous Na_2SO_4 stirred at 1500 rpm under 100 mW cm^{-2} AM 1.5G simulated sunlight illumination. Here, the molar concentration of H_2O_2 generated by PPEC and ORR is determined by UV-vis spectrophotometry of Fe^{3+} based on the $FeSO_4$-H_2O_2 redox reaction. The molar concentration of Fe^{3+} (c_{Fe3+}) produced after the $FeSO_4$-H_2O_2 redox reaction can be calculated according to the Lambert-Beer law.

The corresponding molar quantity of H_2O_2 (n) can be obtained by UV-vis spectrophotometry of Fe^{3+} based on the $FeSO_4$-H_2O_2 redox reaction $2Fe^{2+} + H_2O_2 + 2H^+ = 2Fe^{3+} + 2H_2O$. The electric charge ($Q$') corresponding to the ORR generation of n mol H_2O_2 can be obtained from the Faraday law of electrolysis, $Q' = zFn$, where z is the number of electrons transferred during ORR ($z = 2$) and F is the Faraday constant (96485.3 C mol^{-1}). The Faraday efficiency (η) is calculated according to $\eta = Q'/Q \times 100\%$.

At 60 min in Fig. S8B, we obtain n = 108.9 μmol, Q' = 21.01 C, and Q = 22.07 C, so η = 95.2%.

Reference

1. L. Pan, S. C. Sun, Y. Chen, P. H. Wang, J. Y. Wang, X. W. Zhang, J. J. Zou and Z. L. Wang, *Adv. Energy Mater.*, 2020, **10**, 2000214.