Electronic Supplementary Information for

Multipoint-bridging structure with piezoelectric-induced S-scheme junction for piezoelectrically-enhanced photoelectrochemical H₂O₂ 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 AuNP/p-CdSNW/ITO electrode in an unstirred (A) or 1500-rpm-stirred (B) O$_2$-saturated 0.5 M aqueous Na$_2$SO$_4$ under 100 mW cm$^{-2}$ AM 1.5G simulated sunlight illumination. Here, although solution stirring can bend the p-CdSNW to generate piezoelectric charges and interleave the energy band positions of two adjacent p-CdSNW$^1$, the spatial distance between the p-CdSNW is sufficiently large and there is no transverse electron conductor bridge. Therefore, transverse electron transfer between adjacent p-CdSNW is not possible (dashed arrows).
Fig. S1. SEM image of n-CdS\textsubscript{NW}/ITO electrode.
Fig. S2. SEM images of the AuNR/p-CdS NW/ITO electrodes prepared by photodeposition of AuNR 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\textsubscript{NW}/ITO, Au\textsubscript{NR}/p-CdS\textsubscript{NW}/ITO and Au\textsubscript{NR}/p-CdS\textsubscript{NW}/ITO electrodes.
Fig. S5. (A) EIS results of the bare ITO, CdS NW/ITO, p-CdS NW/ITO and Au NR/p-CdS NW/ITO electrodes in 0.5 M aqueous Na₂SO₄ containing 2.0 mM K₄[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 Na₂SO₄ containing 2.0 mM K₄[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$_{NR}$/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$_2$SO$_4$ 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$_2$O$_2$ redox reaction for standard (A, a series of prepared standard H$_2$O$_2$ solutions) or sample (B, the photocathode solution after different PPEC-ORR time) H$_2$O$_2$ solutions. The insets show the linear relationship of the peak absorbance at 330 nm versus H$_2$O$_2$ concentration ($c_{H2O2}$) or PPEC-ORR time ($t_{PPEC}$). Photocurrent density (C) and H$_2$O$_2$ 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$_2$SO$_4$ stirred at 1500 rpm under 100 mW cm$^{-2}$ AM 1.5G simulated sunlight illumination. Here, the molar concentration of H$_2$O$_2$ generated by PPEC and ORR is determined by UV-vis spectrophotometry of Fe$^{3+}$ based on the FeSO$_4$-H$_2$O$_2$ redox reaction. The molar concentration of Fe$^{3+}$ ($c_{Fe3+}$) produced after the FeSO$_4$-H$_2$O$_2$ redox reaction can be calculated according to the Lambert-Beer law.

The corresponding molar quantity of H$_2$O$_2$ ($n$) can be obtained by UV-vis spectrophotometry of Fe$^{3+}$ based on the FeSO$_4$-H$_2$O$_2$ 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$_2$O$_2$ 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 ($\eta$) is calculated according to $\eta = Q'/Q \times 100\%$. 
At 60 min in Fig. S8B, we obtain \( n = 108.9 \, \mu\text{mol} \), \( Q' = 21.01 \, \text{C} \), and \( Q = 22.07 \, \text{C} \), so \( \eta = 95.2\% \).
Reference