Electronic supplementary Information

Biomimic electron transport via multi redox shuttles from photosystem II to photoelectrochemical cell for solar water splitting

Zhen Li^{a,b}, Wangyin Wang^a, Chunmei Ding^a, Zhiliang Wang^{a,b}, Shichao Liao^{a,b}, Can Li^a*

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences; Dalian National Laboratory for Clean Energy, Collaborative Innovation Center of Chemistry for Energy Materials (*i*ChEM), Dalian, 116023, China;

^b University of Chinese Academy of Sciences, Beijing 100049, China

* E-mail of corresponding author: <u>canli@dicp.ac.cn</u>



Figure S1 Double-reciprocal plots of the O_2 evolution activity with DMBQ (a) and ferricyanide (b) as electron acceptors. According to the Lineweaver-Burk Double-reciprocal plot method, an equation is obtained:

$$\frac{1}{V} = \frac{K_m}{V_{max}} \times \frac{1}{[S]} + \frac{1}{V_{max}}$$

In our study, V, [S], V_{max} and K_m are denoted as the O₂ evolution rate (µmol O₂ (mg of Chl)⁻¹ h⁻¹), concentration of electron acceptor (mmol L⁻¹), maximum reaction rate (µmol O₂ (mg of Chl)⁻¹ h⁻¹) and Michaelis-Menten constant (mmol L⁻¹).



Figure S2 Spectra of light in three wavelength regions. Blue: 400-500 nm, green: 500-600 nm, red: 600-700 nm. The light is provided by the halogen lamp equipped with different combinations of long-pass and short-pass filters.



Figure S3 SEM images of CdS/FTO. (a) Morphology of CdS/FTO before reaction (inserted: section image of CdS/FTO). (b) Morphology of CdS/FTO after PEC reaction.



Figure S4 Performance of the CdS-based two-electrode cell. (a) The photocurrent in chronoamperometry test during the H₂ production process with 20 mM K₄Fe(CN)₆ as donor. (b) UV-Vis absorption of the anodic solution before and after PEC reaction in (a) for 1 h. (c) The photocurrent in chronoamperometry test with 10 mM K₄Fe(CN)₆ or DMBQH₂ as electron donor. Light source: 300W Xenon lamp (>420 nm), 100 mW cm⁻².



Figure S5 XRD patterns of CdS electrodes before reaction (a) and after reaction for 1h (b). The PEC hydrogen evolution reaction was conducted in the CdS-based twoelectrode cell with 20 mM $Fe(CN)_6^{4-}$ as electron donor to CdS photoanode. The peak data in standard PDF card of hexagonal CdS and tetragonal SnO₂ are given in the figure for comparison.



Figure S6 V_{OC} of the galvanic cell dependent on the ratios of the redox ions and the corresponding discharging current. (a) 1 mM DMBQH₂, 1 mM DMBQ, 5 mM Fe(CN)₆³⁻, change the concentration of Fe(CN)₆⁴⁻: 10 mM, 5 mM, 2.5 mM, 1.25 mM. (b) 5 mM Fe(CN)₆³⁻, 5 mM Fe(CN)₆⁴⁻, 1 mM DMBQH₂, change the concentration of DMBQ: 2 mM, 1 mM, 0.5 mM, 0.25 mM. (c) The corresponding discharging current of (a). (d) The corresponding discharging current of (b).

Nernst equation in this galvanic cell:

 $E = E^{0} + (RT/nF)ln(C_{ox}/C_{re}) = E^{0} + 0.059 lg(C_{ox}/C_{re})$

 $E_{DMBQ/DMBQH_2} = E_{DMBQ/DMBQH_2}^0 + 0.059 lg(C_{DMBQ}/C_{DMBQH_2})$

 $E_{Fe(CN)_6^{3-/4-}} = E_{Fe(CN)_6^{3-/4-0}} + 0.059 lg(C_{Fe(CN)_6^{3-}}/C_{Fe(CN)_6^{4-}})$

 $V_{oc} = E_{Fe(CN)_6^{3-/4-}} - E_{DMBQ/DMBQH_2}$

= $V^0 + 0.059 lg (C_{Fe(CN)_6^3} \cdot C_{DMBQH_2} / C_{Fe(CN)_6^4} \cdot C_{DMBQ})$



Figure S7 Performance of the graphite-based galvanic cell. (a) The discharging current in chronoamperometry test, 2 mM $Fe(CN)_6^{3-}$, 1 mM DMBQH₂. (b) UV-Vis absorption of $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ before and after reaction. (c) UV-Vis absorption of DMBQ/DMBQH₂ before and after reaction.



Figure S8 Water splitting induced by the half reactions. (a) Water splitting induced by water oxidation. Concentrations of redox mediators: 0 mM $Fe(CN)_6^{4-}$ / 5 mM $Fe(CN)_6^{3-}$ and 2 mM DMBQ / 2 mM DMBQH₂. (b) Water splitting induced by hydrogen production. Concentrations of redox mediators: 10 mM $Fe(CN)_6^{4-}$ / 5 mM $Fe(CN)_6^{3-}$ and 0 mM DMBQ / 2 mM DMBQH₂. PSII: 22 µg Chl mL⁻¹. Light source: AM 1.5G, 100 mW cm⁻². Applied bias: 0 V.



Figure S9 Time courses of H₂ and O₂ evolution in the PSII-CdS hybrid PEC cell. Concentrations of redox mediators: 10 mM K₄Fe(CN)₆ / 5 mM K₃Fe(CN)₆ and 2 mM DMBQ / 2 mM DMBQH₂; PSII: 22 μ g Chl mL⁻¹, 45 mL; Light source: AM 1.5G simulator, 100 mW cm⁻².



Figure S10 Scheme and performance of the simple mixed cell. (a) Scheme of the simple mixed cell. (b) The current dependent on the addition of PSII samples in the mixed cell comprising CdS electrode, 10 mM $Fe(CN)_6^{4-} / 5$ mM $Fe(CN)_6^{3-}$ and 2 mM DMBQ / 2 mM DMBQH₂. The small vertical arrows represent the addition of 0.15 mg Chl of PSII every time.



Figure S11 Currents in the hybrid cell (red line) and the single galvanic cell (black line). The concentrations of the redox mediators: $10 \text{ mM Fe}(\text{CN})_6^{4-} / 5 \text{ mM Fe}(\text{CN})_6^{3-}$ and 2 mM DMBQ / 2 mM DMBQH₂. Light source: AM 1.5G solar simulator, 100 mW cm⁻². The experiments were carried out under chopped light.



Figure S12 The tandem light absorption and the corresponding PSII activity. (a) Light spectral distributions through the hybrid cell. Black: the full AM 1.5G spectrum reaching to Cell B; Red: the Cell B-filtered light spectrum reaching to Cell A; Blue: the light spectrum through the whole tandem system. (b) Water oxidation activity of PSII with or without CdS/FTO as light filter. Light intensity of the full spectrum to CdS/FTO plate is 100 mW cm⁻². PSII: 10µg Chl mL⁻¹; DMBQ: 2 mM.



Figure S13 Scheme of the re-assembled solar energy storage battery

Electron acceptor	Linear fitting equation	K _m	V _{max}
DMBQ	y = 0.00194 + 0.00161 x	0.83	515
K ₃ Fe(CN) ₆	y = 0.00874 + 0.01948 x	2.23	114

Table S1 Kinetic data of O_2 evolution by PSII with different electron acceptors. The unit of K_m and V_{max} is mmol L⁻¹ and µmol O_2 (mg of Chl)⁻¹ h⁻¹ separately. V_{max} is the maximum O_2 evolution rate which can be reached, and K_m indicates the concentration of the electron acceptor required when the activity is up to half of the V_{max} value, reflecting the affinity between PSII and the electron acceptor.