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Electronic Supplementary Information

Photoelectrodes based on 2D Opals Assembled from Cu-Delafossite Double-Shelled Microspheres for Enhanced Photoelectrochemical Response

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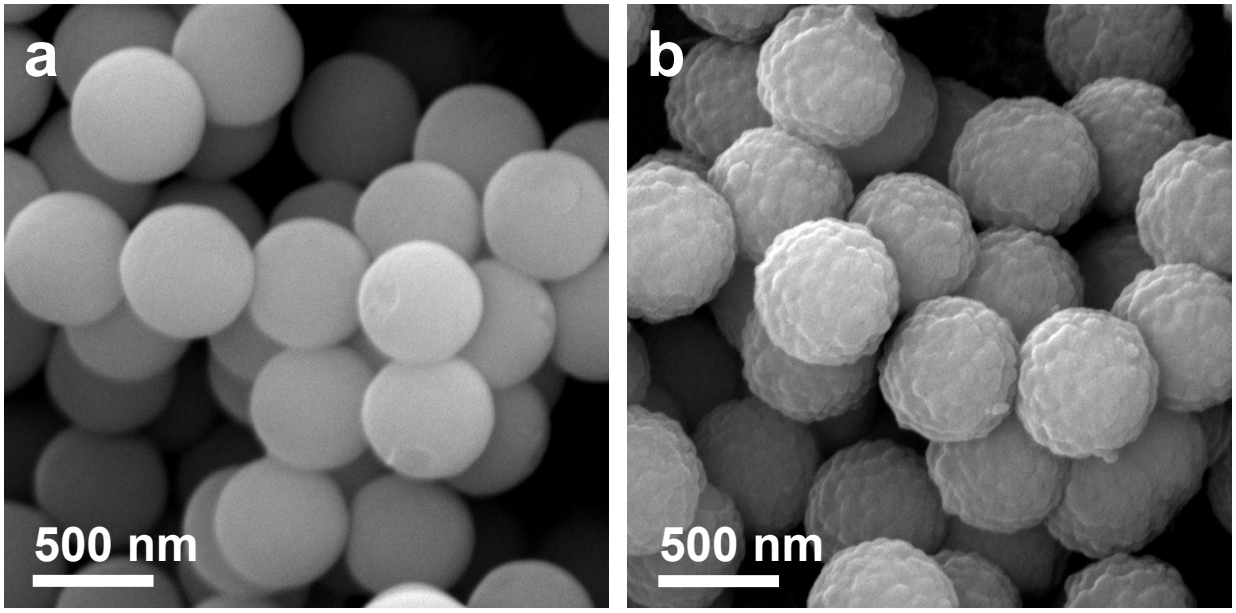

Fig. S1 SEM images of (a) 560-nm-sized SiO_2 microspheres and (b) polydopamine-coated silica (SiO_2@PDA) microspheres.

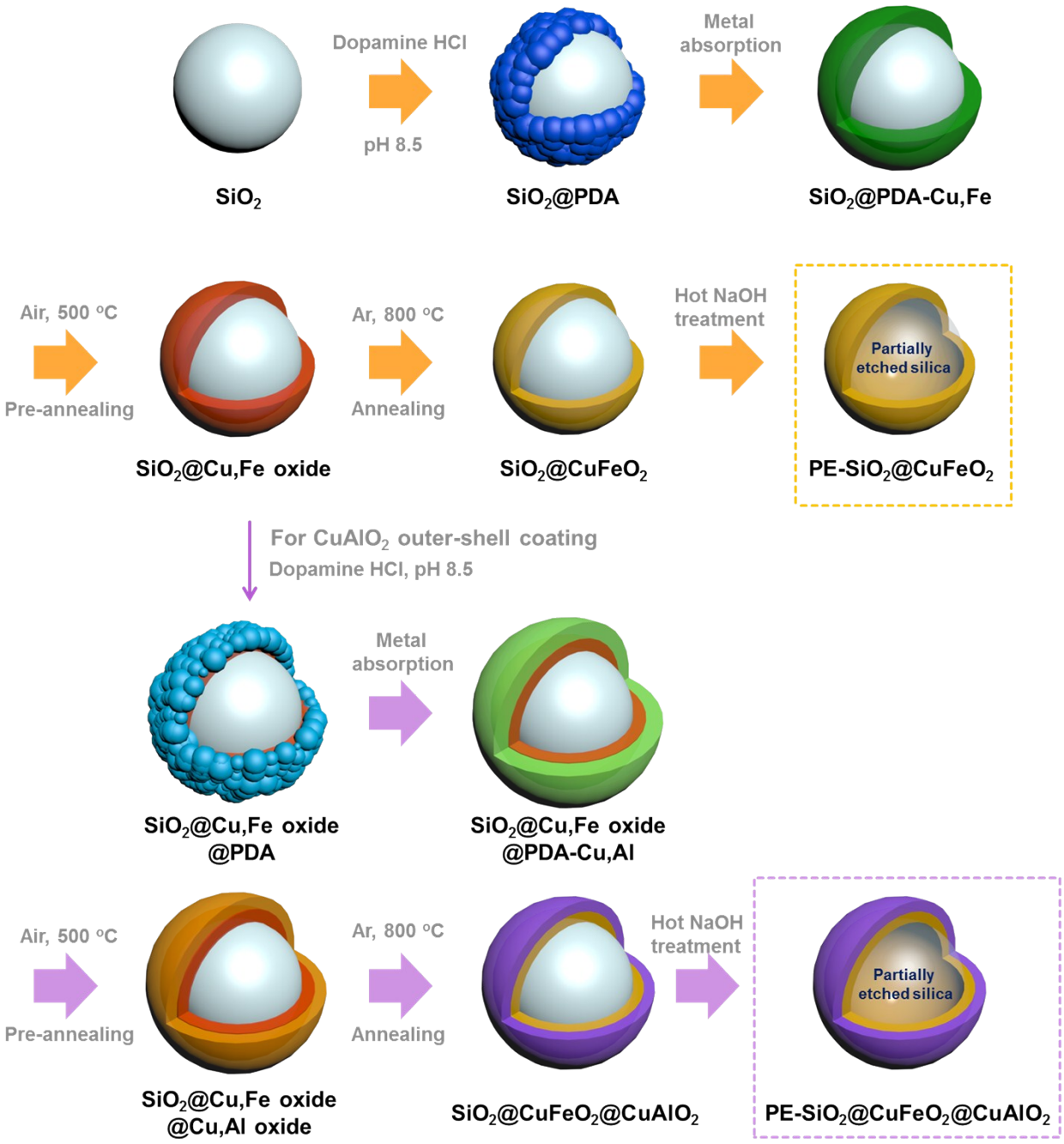

Fig. S2 Schematic illustration of the synthesis of Cu-delafossite single or double-shelled microspheres (*i.e.,* PE-SiO_2@$CuFeO_2$ and PE-SiO_2@$CuFeO_2$@$CuAlO_2$).

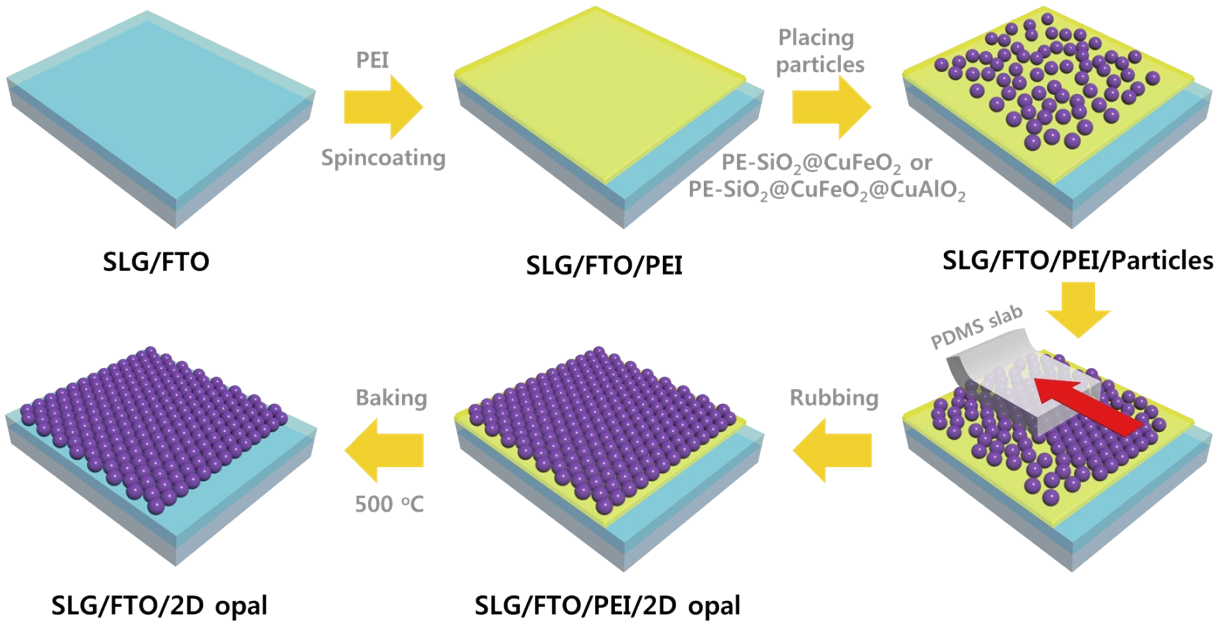

Fig. S3 Schematic of the procedure for fabricating a 2D opal-structured Cu-delafossite single or double-shelled photocathode by a dry-rubbing method.

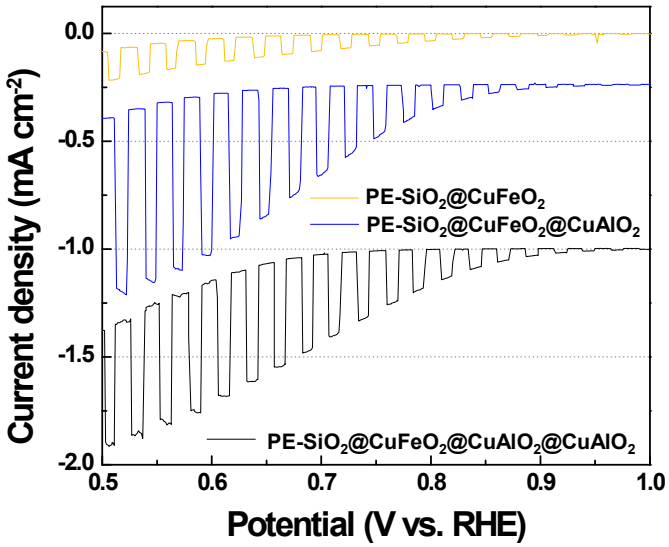

Fig. S4 Linear sweep voltammograms of 2D opal photocathodes composed of microspheres with single- or double-shell and double-shell with thicker outer-shell in 1 M NaOH solution, under chopped illumination. The sweep rate was 5 mV s^{-1}, and the scan was performed in the cathodic direction. PE-SiO_2@$CuFeO_2$@$CuAlO_2$@$CuAlO_2$ represents thicker outer-shelled microspheres with dual-coating of $CuAlO_2$.

Table S1. Comparison of photocurrent density of previous CuFeO2 based photocathodes and double-shelled photocathode

Photocurrent density (mA cm^{-2})[a]	Reference
1.09	This work (PE-SiO_2@$CuFeO_2$@$CuAlO_2$)
1.2	Prévot et al. *Journal of Materials Chemistry A* **4**, 3018 (2016) ($CuAlO_2$-$CuFeO_2$ *host-guest*)
0.4	Jang et al. *Chemistry of Materials* **28**, 6054 (2016) (Oxygen intercalated $CuFeO_2$)
0.16	Read et al. *The Journal of Physical Chemistry Letters* **3**, 1872 (2012) ($CuFeO_2$ thin film)

[a]The photocurrent density was measured using 1 sun chopped illumination, O_2-saturated 1 M NaOH electrolyte, and 0.6 V *vs*. RHE.

Table S2. Photocurrent densities of Cu-delafossite-based 2D opal photocathodes with/without hot NaOH treatment

Assembled microsphere	Photocurrent density (mA cm^{-2})[a]
SiO_2@$CuFeO_2$	0.30
PE-SiO_2@$CuFeO_2$	0.12
SiO_2@$CuFeO_2$@$CuAlO_2$	0.19
PE-SiO_2@$CuFeO_2$@$CuAlO_2$	1.09

[a]Photocurrent density was measured under 1 sun chopped illumination, in 1 M NaOH electrolyte at +0.6 V *vs.* RHE.

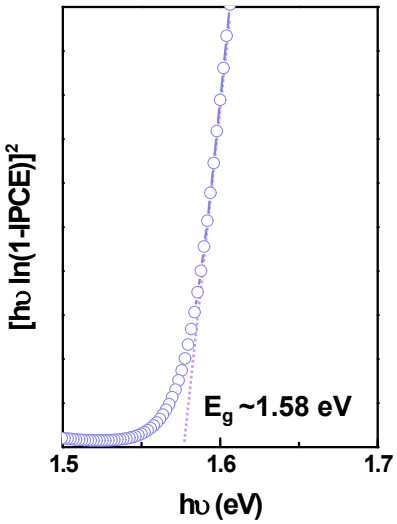

Fig. S5 Plot of $[hv \ln(1 - IPCE)]^2$ versus photon energy (hv/eV) to determine the bandgap of the PE-SiO_2@$CuFeO_2$@$CuAlO_2$ microsphere. The bandgap of $CuFeO_2$ is extrapolated to 1.58 eV.

Table S3. Resistance and capacitance parameters obtained by fitting the Nyquist plots in Figure 5c using a simple equivalent circuit model (inset). Nyquist plots of the 2D opal photocathodes were obtained under simulated solar light illumination in oxygen-saturated 1 M NaOH solution.

Assembled microsphere type	R_s (Ω cm^2)	R_1 (Ω cm^2)	CPE_1 (F cm^{-2})
PE-SiO_2@$CuFeO_2$	3.55	12992	1.93×10^{-5}
PE-SiO_2@$CuFeO_2$@$CuAlO_2$	1.91	1754	2.65×10^{-5}

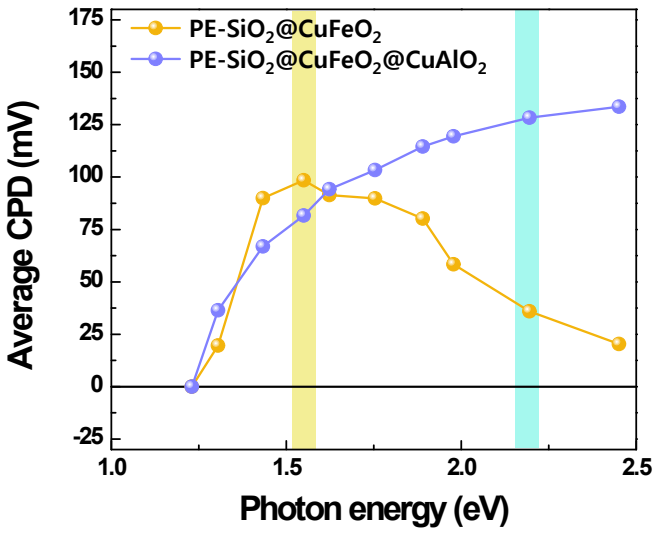

Fig. S6 Surface photovoltage spectra of single and double-shelled photocathodes depending on the photon energy. Surface photovoltage spectra were obtained from the average of each CPD map as a function of the incident photon energy. The CPD maps were obtained from KPFM analysis using monochromators for wavelengths ranging from 506 to 1008 nm. The yellow region indicates the wavelength (800 nm, near the bandgap of $CuFeO_2$) of the irradiated light. The blue region represents the photon energy associated with the PSB.