Electronic Supplementary Information

Size- and facet-dependent photoelectrochemical properties of Cu_2O crystals

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Synthesis of size-tunable Cu_2O cubes

To make size-tunable Cu_2O cubes, SDS powder was first dissolved in deionized water, and the solution was sonicated for 10 min. $CuCl_2$ solution was then injected under stirring in a water bath set at 31 ºC. After stirring for 25 min, NaOH solution was introduced. Subsequently, after stirring for 0 sec (immediately), 10 sec, and 20 sec, $NH_2OH{\cdot}HCl$ solution was injected to make *S*-cubes, *M*-cubes, and *L*-cubes, respectively. The mixture was stirred for 20 sec and aged for 50 min to obtain the particles. The precipitate was collected by centrifugation at 6500 rpm and washed with water by repeated centrifugation at 9000 rpm for three times to remove the SDS surfactant. Finally, the particles were preserved in 99% ethanol. The exact reagent concentrations and volumes used are listed in Table S1.

Table S1 Reagent concentrations and volumes used to make various Cu_2O crystals.

	SDS (g)	DI water (mL)	0.1 M $CuCl_2$ (mL)	1 M NaOH (mL)	0.2 M $NH_2OH \cdot HCl$ (mL)
Cubes	**0.348**	**38.2**	**0.4**	**0.8**	**0.6**
CO	**0.348**	**37.4**	**0.4**	**0.8**	**1.4**
Oct	**0.348**	**26.6**	**0.8**	**0.8**	**2.6**
RD	**0.348**	**27.68**	**2**	**0.72**	**0.1 M $NH_2OH \cdot HCl$ (mL)**
					9.6

Synthesis of Cu_2O octahedra and rhombic dodecahedra

The synthesis procedure for Cu_2O octahedra and rhombic dodecahedra is slightly different from that of cubes. The SDS solution was stirred for 5 min in a 31 ºC water bath. Then $CuCl_2$ solution was injected under stirring. After stirring for 10 min and 25 min respectively for octahedra and rhombic dodecahedra, NaOH solution was introduced. After stirring for 4 sec, $NH_2OH{\cdot}HCl$ solution was injected. For octahedra, the mixture was stirred for 10 sec and aged for 25 min. For rhombic dodecahedra, the mixture was stirred for 20 sec and aged for 50 min. The precipitate was collected by centrifugation at 6500 rpm and washed with water by centrifugation at 9000 rpm for three times. Finally, the particles were preserved in 99% ethanol.

Synthesis of Cu_2O cuboctahedra

The synthesis process for Cu_2O cuboctahedra is similar to that of Cu_2O cubes. The SDS solution was sonicated for 10 min. Next, $CuCl_2$ solution was injected under stirring in a 31 ºC water bath. After stirring for 25 min, NaOH solution was introduced. After stirring for 15 sec, $NH_2OH{\cdot}HCl$ solution was injected. The mixture was stirred for 20 sec and aged for 50 min. The precipitate was collected by centrifugation at 6500 rpm and washed with water by centrifugation at 9000 rpm for three times. Finally, the particles were preserved in 99% ethanol.

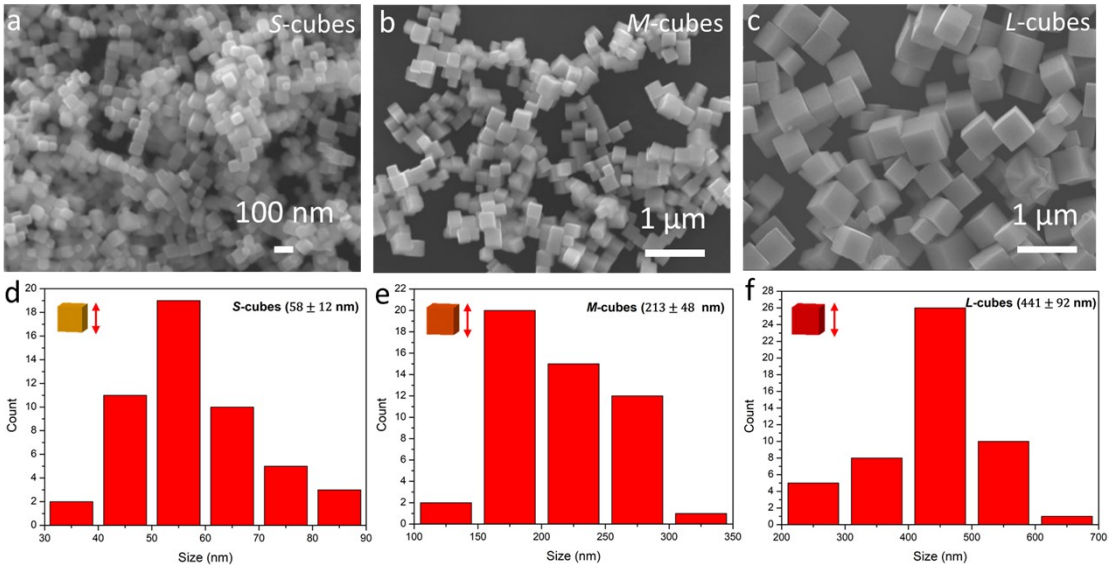

Fig. S1 (a–c) SEM images of the synthesized Cu_2O cubes with different sizes. (d–f) Size distribution histograms of the Cu_2O cubes.

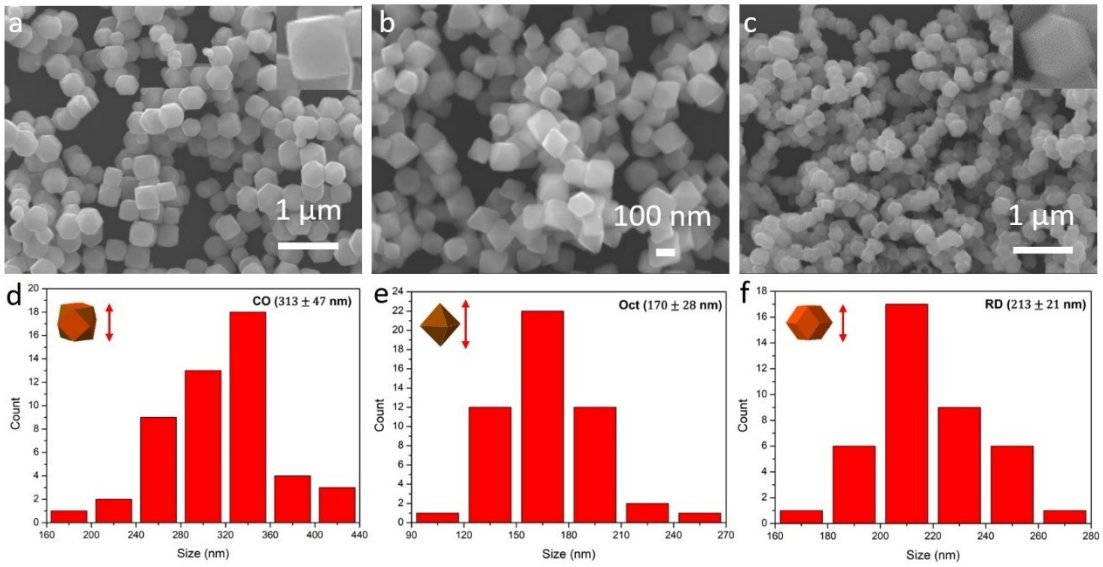

Fig. S2 SEM images of the synthesized Cu_2O (a) cuboctahedra, (b) octahedra, and (c) rhombic dodecahedra and (d–f) their size distribution histograms.

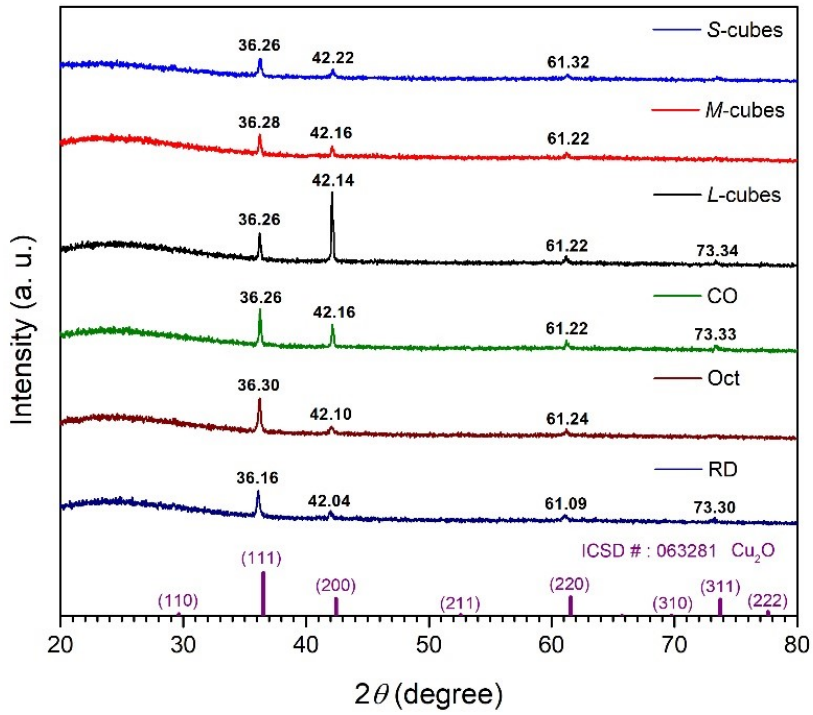

Fig. S3 XRD patterns of different Cu_2O crystals.

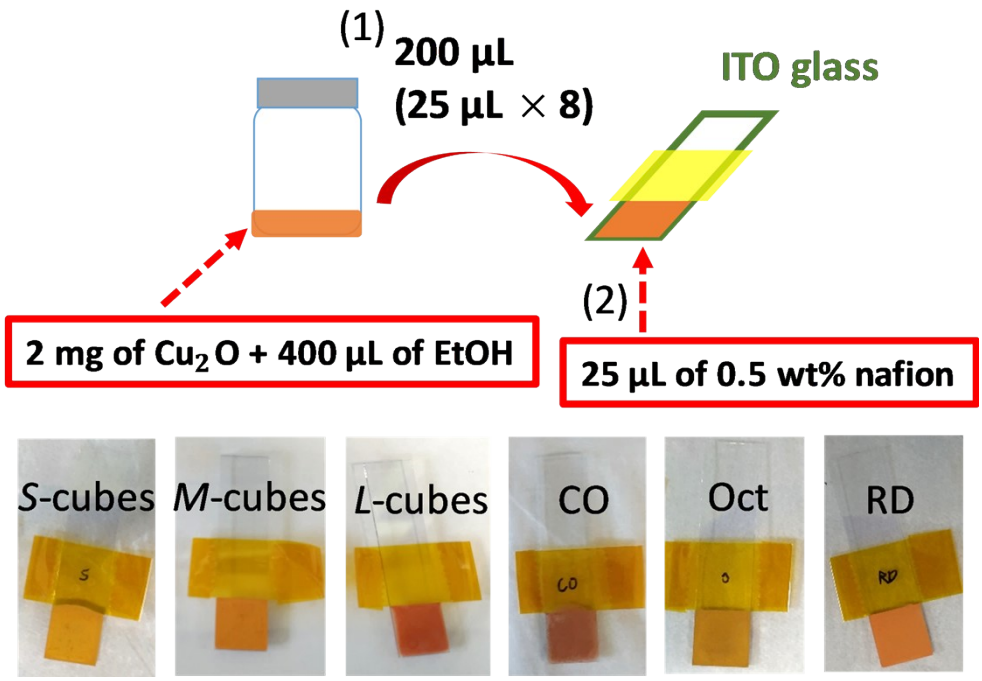

Fig. S4 Illustration of the process to make Cu_2O/ITO photocathodes and photographs of the prepared photocathodes using different Cu_2O crystals.

	Cubes	CO	Oct	RD
L = size				
Volume	L^3	$\frac{5}{6} \times L^3$	$\frac{1}{6} \times L^3$	$\frac{\sqrt{2}}{2} \times L^3$

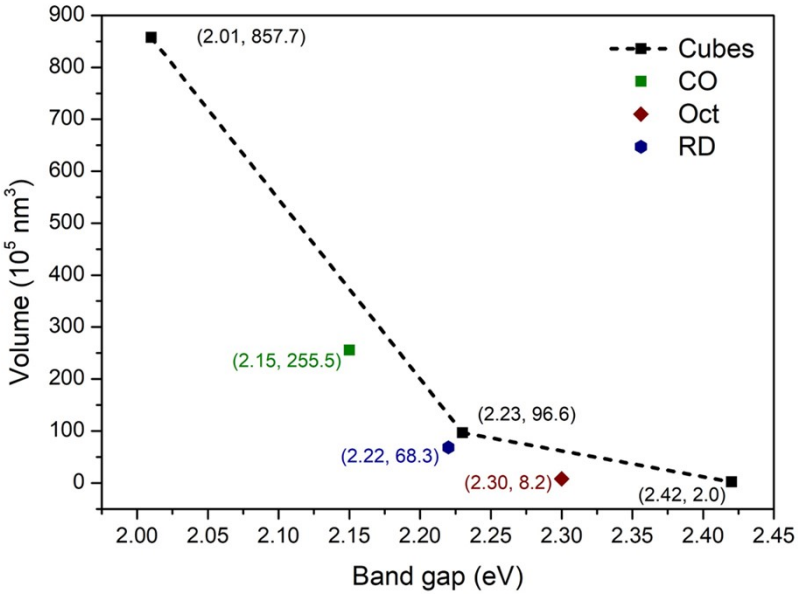

Fig. S5 Determination of the particle volumes and a plot of the particle sizes and their band gaps.

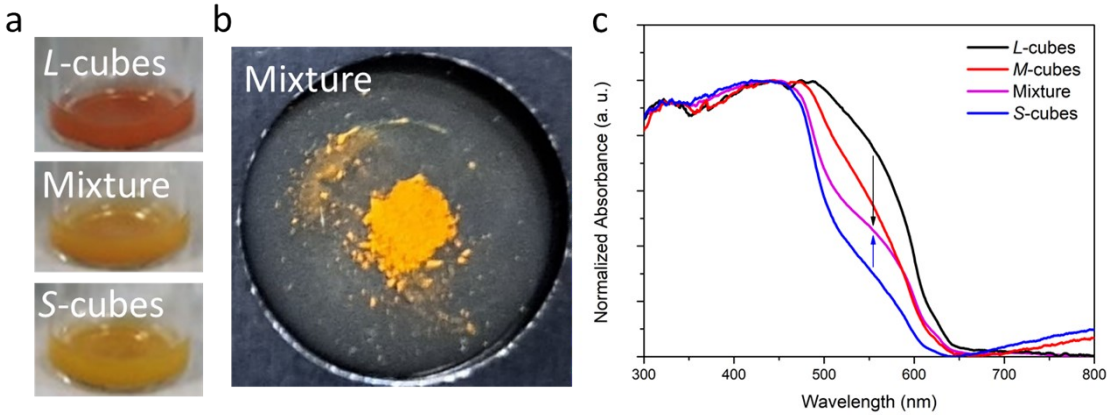

Fig. S6 Photographs of (a) Cu_2O cube dispersions and (b) the mixed powder with large and small cubes. (c) Diffuse reflectance spectra of Cu_2O cubes.

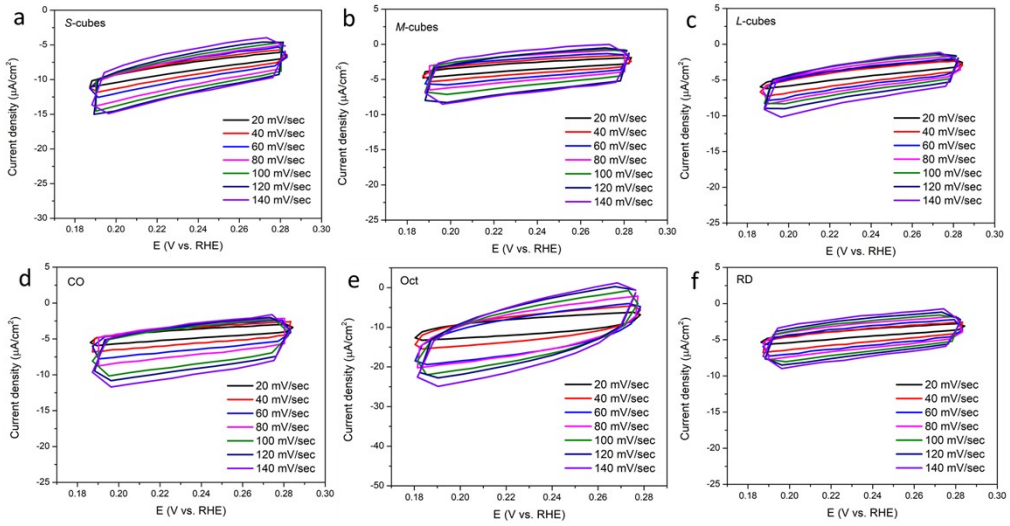

Fig. S7 CV curves for electrochemically active surface area determination.

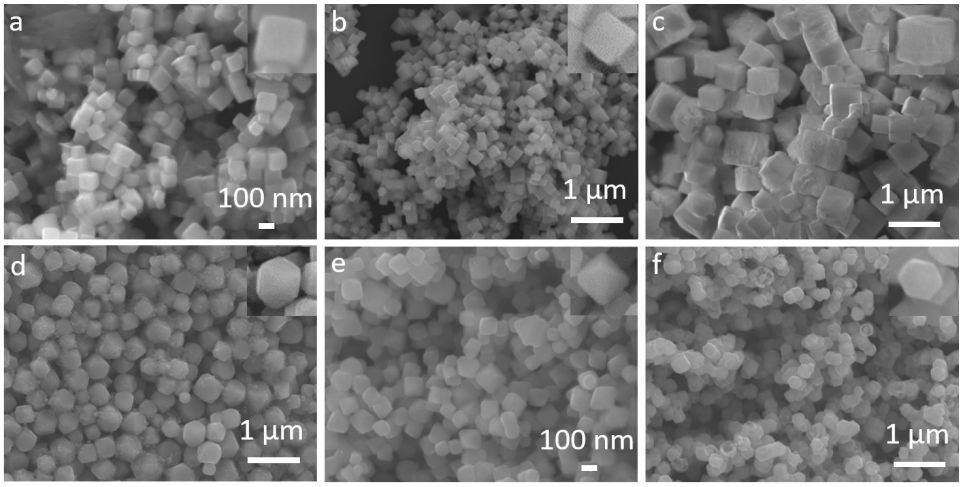

Fig. S8 SEM images of Cu_2O (a) small cubes, (b) medium cubes, (c) large cubes, (d) cuboctahedra, (e) octahedra, and (f) rhombic dodecahedra after photoelectrochemical measurements.

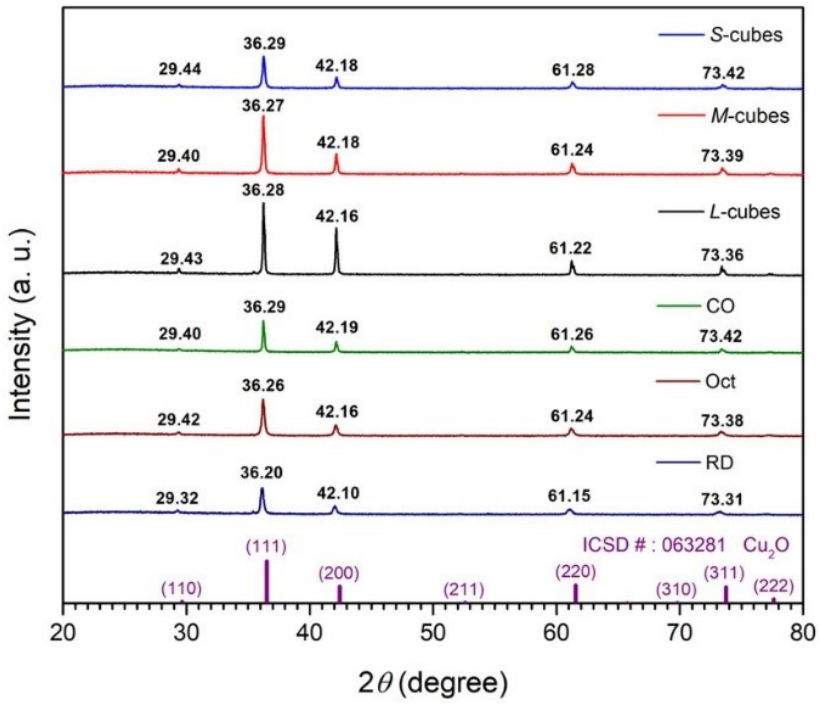

Fig. S9 XRD patterns of Cu_2O crystals after the photoelectrochemical measurements.

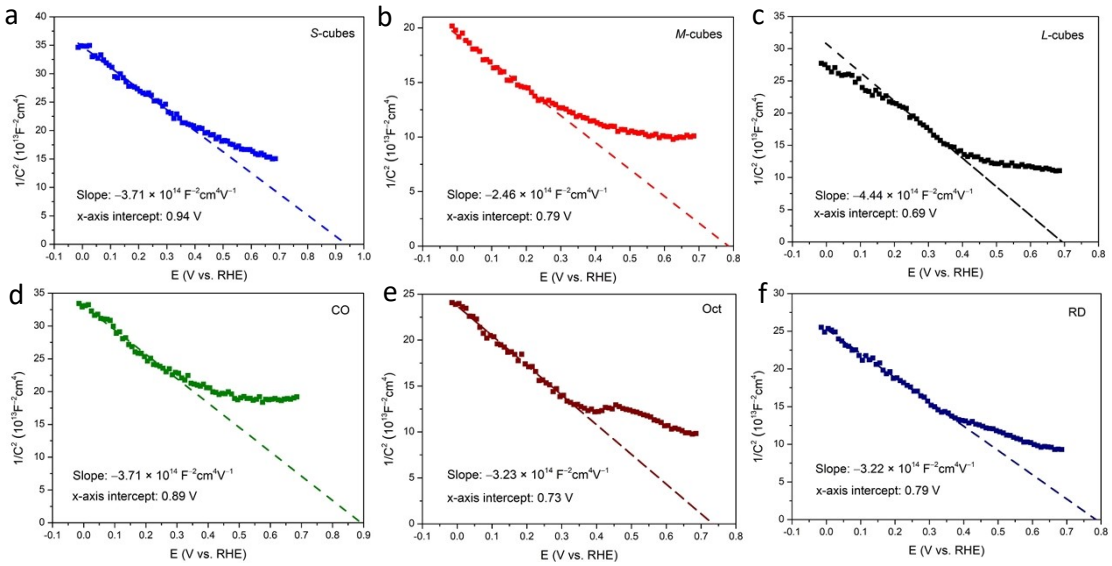

Fig. S10 Mott–Schottky plots of Cu_2O (a) small cubes, (b) medium cubes, (c) large cubes, (d) cuboctahedra, (e) octahedra, and (f) rhombic dodecahedra. The slope and x-axis intercept of each line are provided.

Table S2 Calculations for the determination of conduction band and valence band energies.

Equations	Parameters	*S*-cubes	*M*-cubes	*L*-cubes	CO	Oct	RD
$E_{fb} = E_0 + \frac{k_B T}{e}$	E_0 (V vs. RHE)	0.94	0.79	0.69	0.89	0.73	0.79
	E_{fb} (V vs. RHE)	0.96	0.81	0.72	0.92	0.76	0.81
$N_A = \frac{-2}{slope \times e\varepsilon\varepsilon_0}$	Slope (10^{14} $\mathrm{F^{-2}cm^4V^{-1}}$)	-3.71	-2.46	-4.44	-3.71	-3.23	-3.22
	N_{A} (10^{16} $\mathrm{cm^{-3}}$)	5.01	7.54	4.19	5.01	5.75	5.77
$E_V = E_{fb} + \frac{k_B T}{e} ln \frac{N_V}{N_A}$	$N_{\mathrm{V}} = \frac{2(2\pi m \times k_{\mathrm{B}} T)^{3/2}}{h^3}$	$1.11 \times 10^{19}\ cm^{-3}$					
	E_V (V vs. RHE)	1.10	0.94	0.86	1.06	0.89	0.95
$E_C = E_V + E_g$	E_g (eV)	2.42	2.23	2.01	2.15	2.30	2.22
	E_C (V vs. RHE)	-1.32	-1.31	-1.15	-1.09	-1.41	-1.27

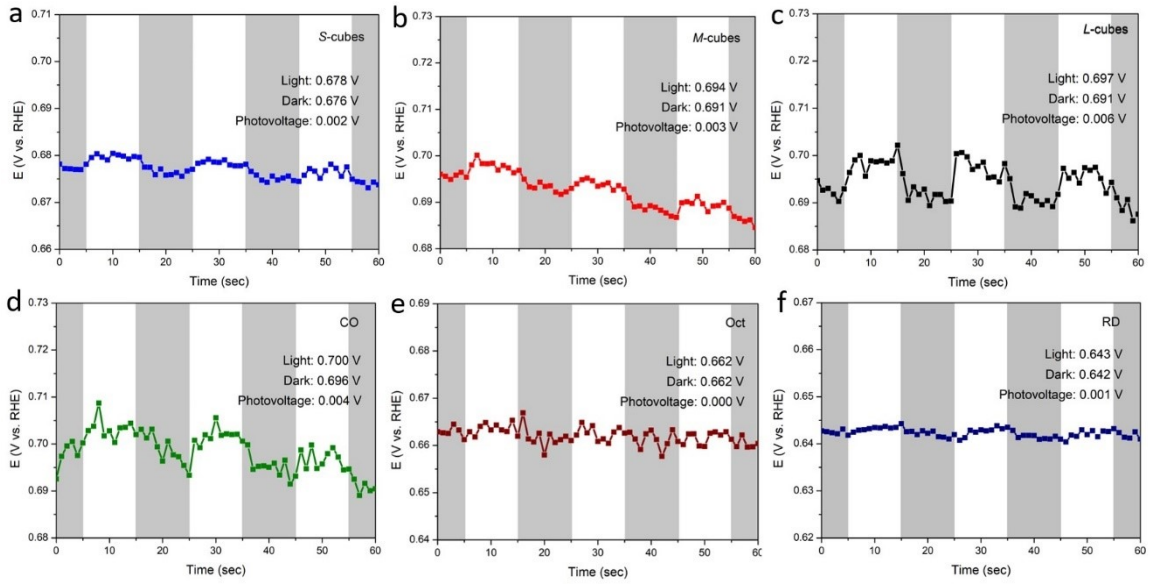

Fig. S11 Chopped-light open-circuit potential measurements of Cu_2O (a) small cubes, (b) medium cubes, (c) large cubes, (d) cuboctahedra, (e) octahedra, and (f) rhombic dodecahedra. Standard deviation of small cubes, medium cubes, and rhombic dodecahedra is 0.001 V. Standard deviation of large cubes and octahedra is 0.002 V. Standard deviation of cuboctahedra is 0.003 V.

Table S3 Photovoltages and build-in potentials of different Cu_2O crystals.

Equations	Parameters	*S*-cubes	*M*-cubes	*L*-cubes	CO	Oct	RD
$E_{ph,OC} = E_{OC}^{light} - E_{OC}^{dark}$	E_{OC}^{light} (V vs. RHE)	0.678	0.694	0.697	0.700	0.662	0.643
	E_{OC}^{dark} (V vs. RHE)	0.676	0.691	0.691	0.696	0.662	0.642
	$E_{ph,OC}$ (V)	0.002	0.003	0.006	0.004	-	0.001
$E_{bi} = E_{fb} - E_{OC}^{dark}$	E_{fb} (V vs. RHE)	0.96	0.81	0.72	0.92	0.76	0.81
	E_{bi} (V)	0.28	0.12	0.03	0.22	0.10	0.17

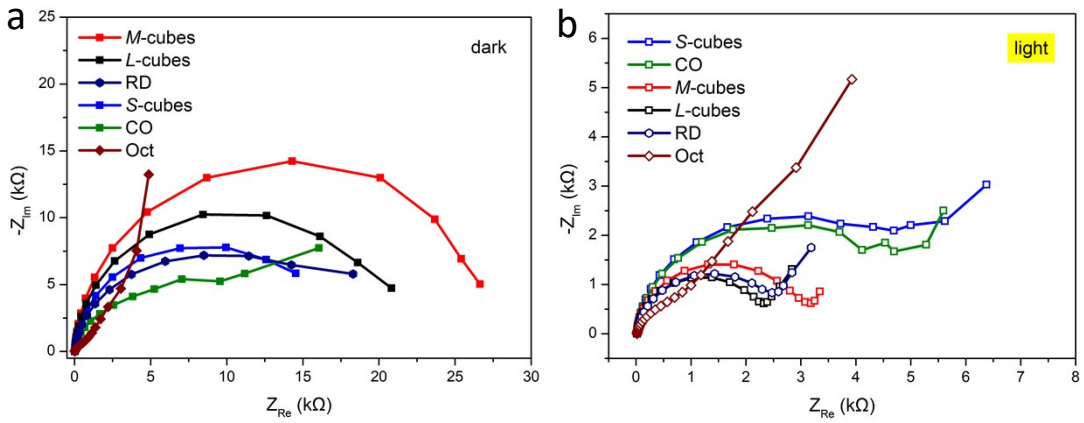

Fig. S12 Nyquist plots from EIS measurements of Cu_2O crystals (a) in the dark and (b) under back-side illumination.

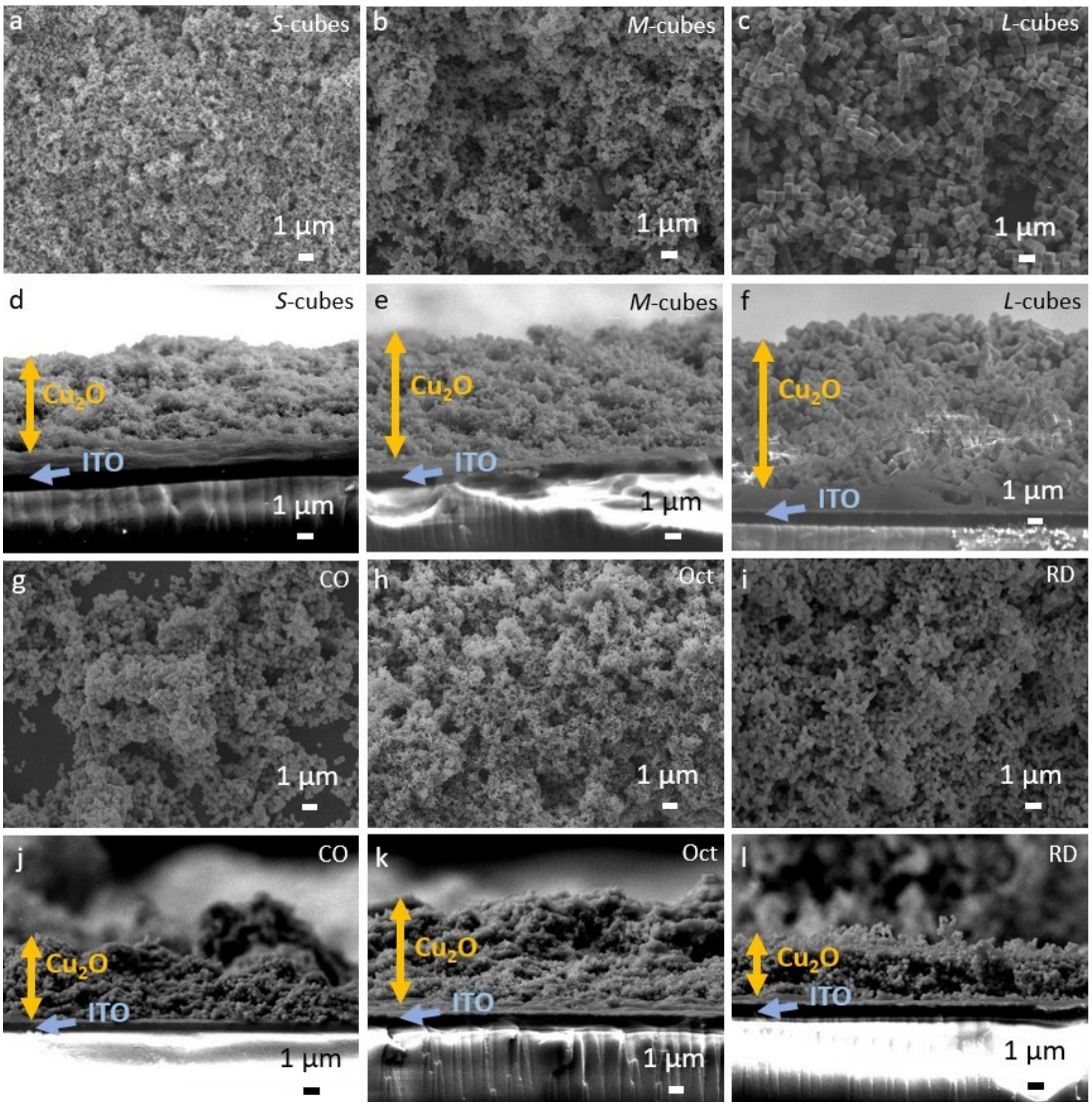

Fig. S13 SEM images of (a–c, g–i) the top views and (d–f, j–l) cross-sectional views of Cu_2O/ITO photocathodes.

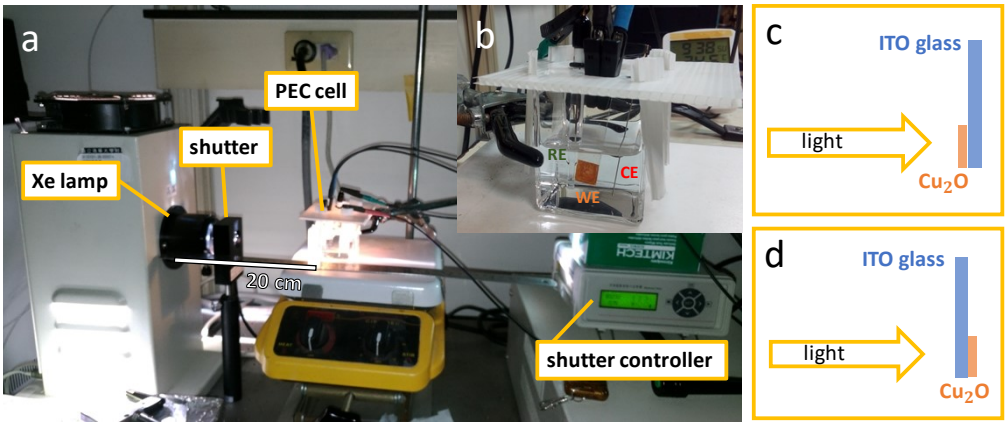

Fig. S14 (a) Setup for the photoelectrochemical experiments. (b) Photograph of the reaction cell. (c, d) Drawings of the (c) front-side and (d) back-side light illumination directions.