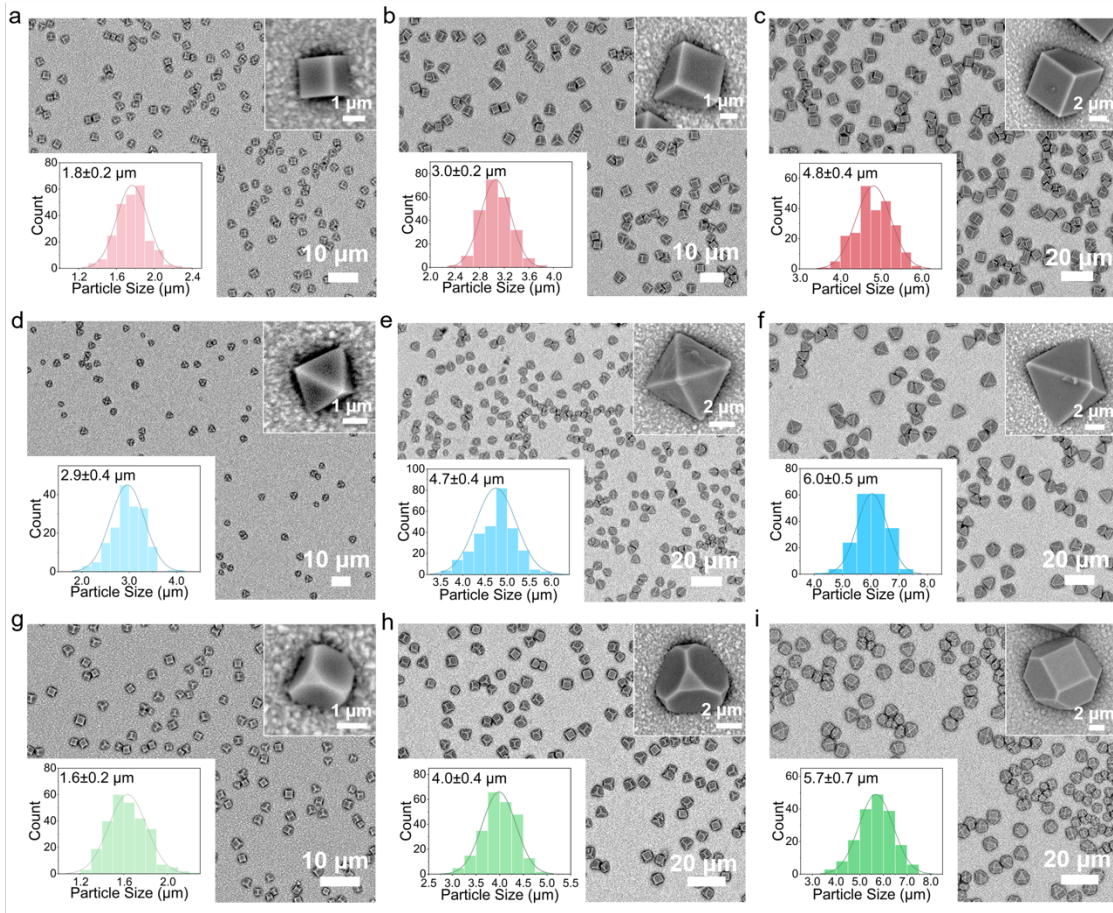


## Supporting Information

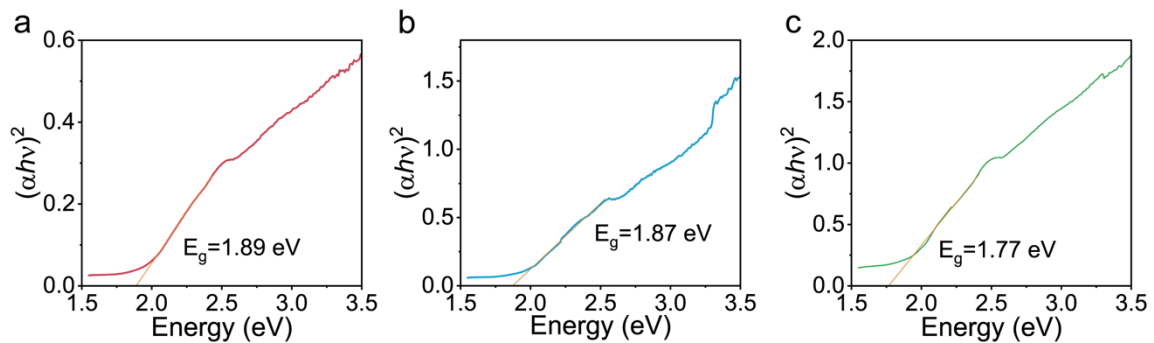
### **Spatial separation of photogenerated charges on anisotropic facets of cuprous oxide**

Tianhui Su, Chunlei Yang, Fushuang Niu, Yanbo Hua, Qinshang Xu, Ke Hu and  
Liming Zhang\*

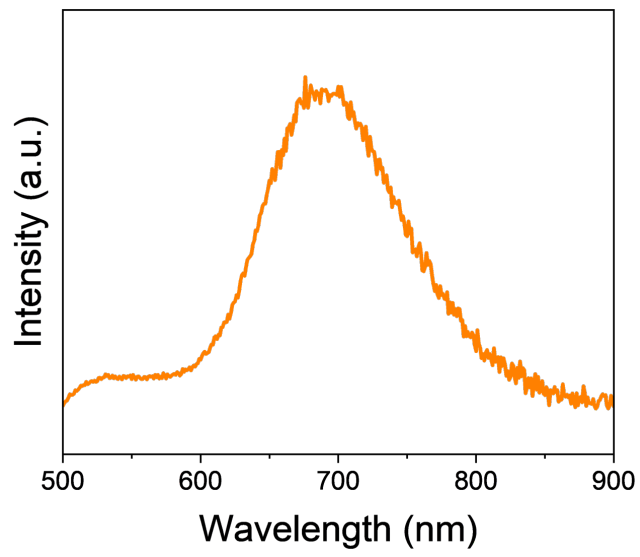
Department of Chemistry, *iChEM* (Collaborative Innovation Center of Chemistry for Energy Materials), Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200438, China  
Correspondence to: zhanglm@fudan.edu.cn



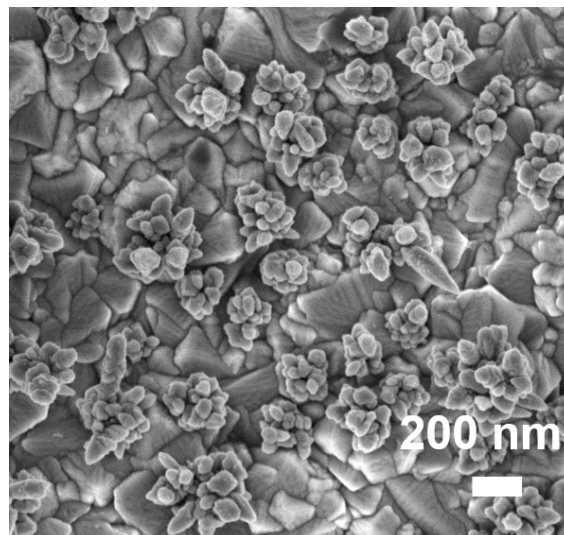
**Figure S1.** Morphology and particle size distribution of as-prepared  $\text{Cu}_2\text{O}$  crystals with different exposed facets. SEM images and particle size distribution of c- $\text{Cu}_2\text{O}$  (a-c), o- $\text{Cu}_2\text{O}$  (d-f) and t- $\text{Cu}_2\text{O}$  (g-i), synthesized under an electrodeposition time of 1 min (a, d, g), 5 min (b, e, h) and 10 min (c, f, i), respectively.



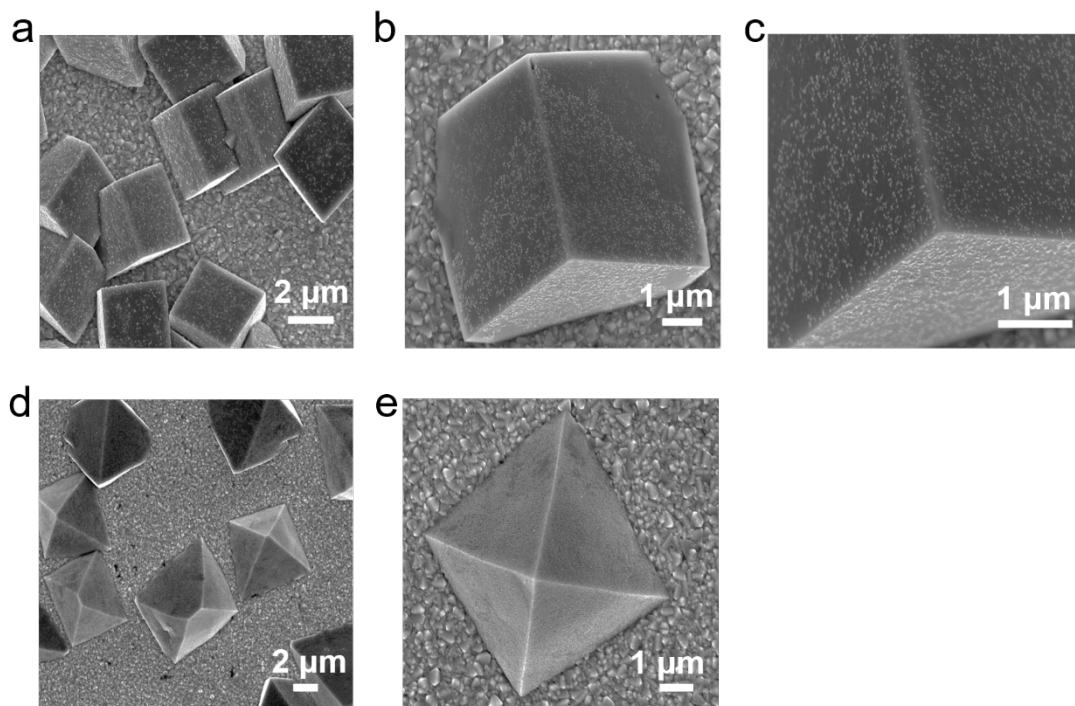
**Figure S2.** Characterization of light absorption properties. Tauc plots of c- $\text{Cu}_2\text{O}$  (a), o- $\text{Cu}_2\text{O}$  (b) and t- $\text{Cu}_2\text{O}$  (c).



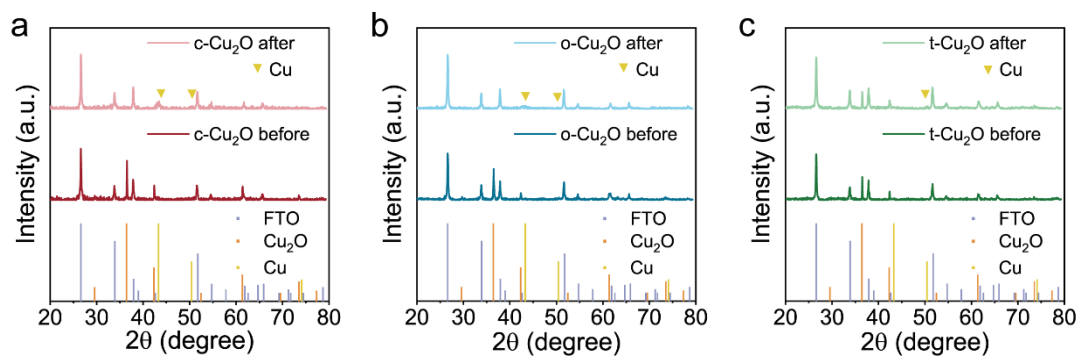
**Figure S3.** Steady state photoluminescence spectrum of as-prepared Cu<sub>2</sub>O.



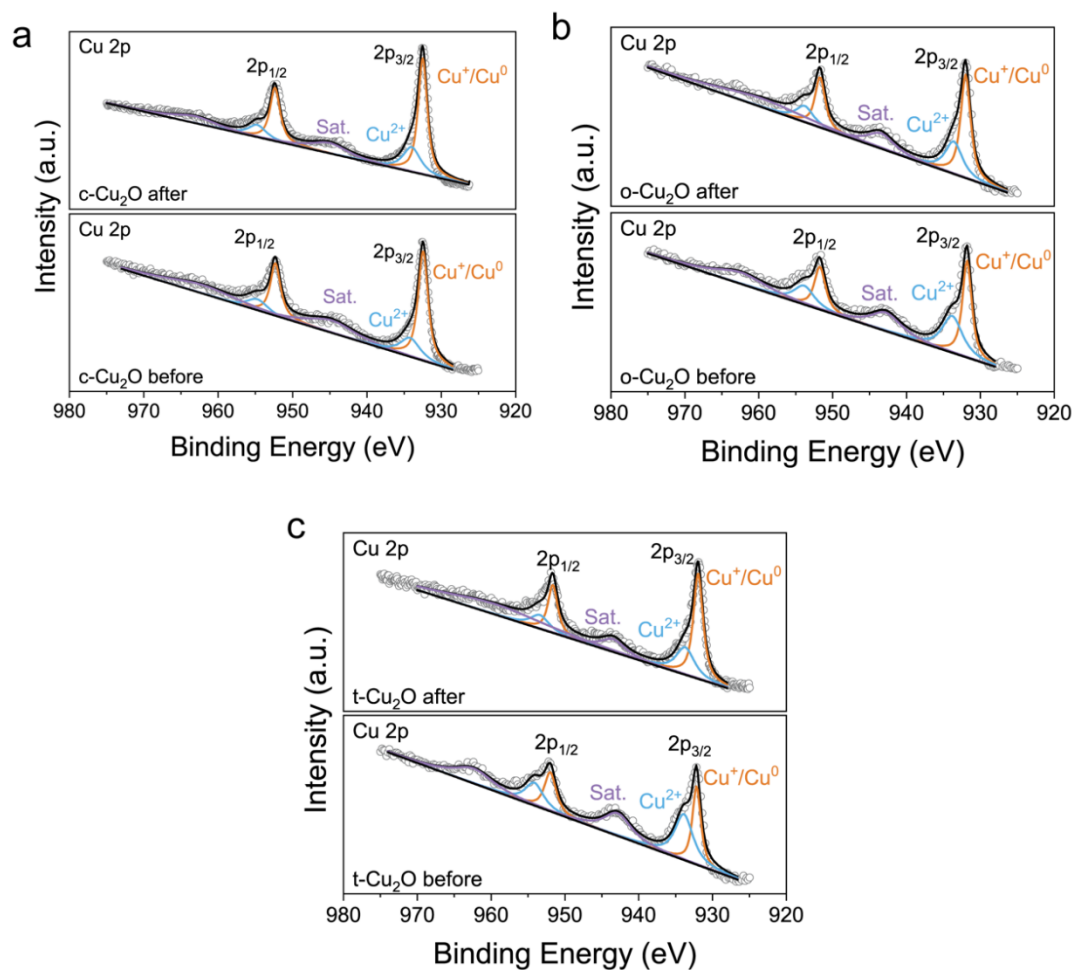
**Figure S4.** The newly formed particles observed on the FTO substrate after reaction in an acid media.



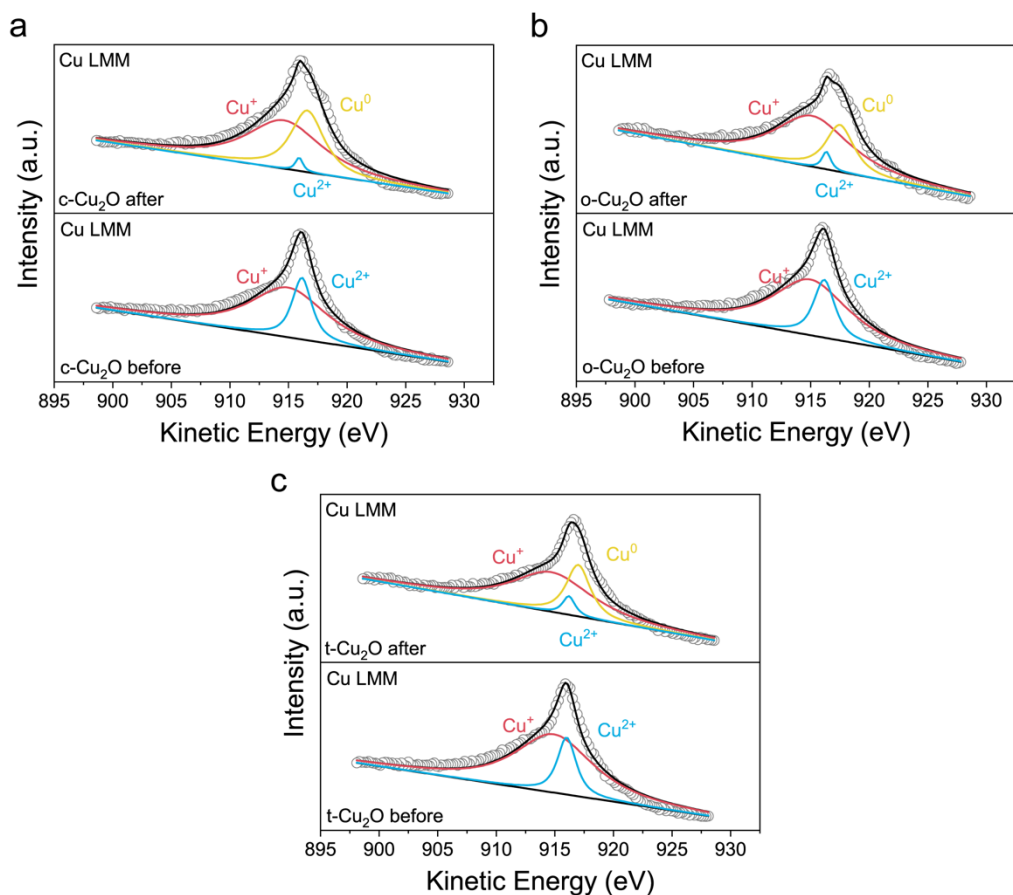
**Figure S5.** Morphology evolution of  $\text{Cu}_2\text{O}$  in a neutral electrolyte. SEM images of c- $\text{Cu}_2\text{O}$  (a-c), o- $\text{Cu}_2\text{O}$  (d-e) after photoelectrocatalysis at 0 V vs. RHE for 3 min in 1 M  $\text{Na}_2\text{SO}_4$ .



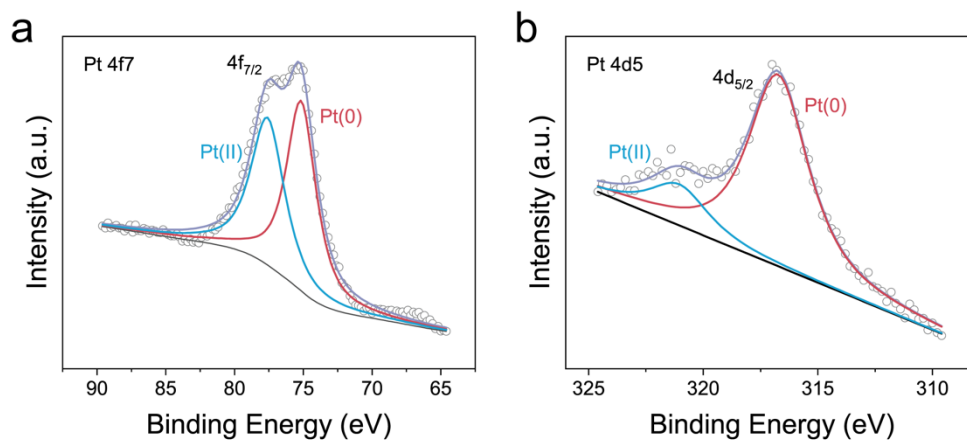
**Figure S6.** Comparison of  $\text{Cu}_2\text{O}$  before and after HER. X-ray diffraction patterns of c- $\text{Cu}_2\text{O}$  (a), o- $\text{Cu}_2\text{O}$  (b) and t- $\text{Cu}_2\text{O}$  (c) before and after HER. Reactions were carried out under 0 V vs. RHE for 30 min in 1 M  $\text{Na}_2\text{SO}_4$ .



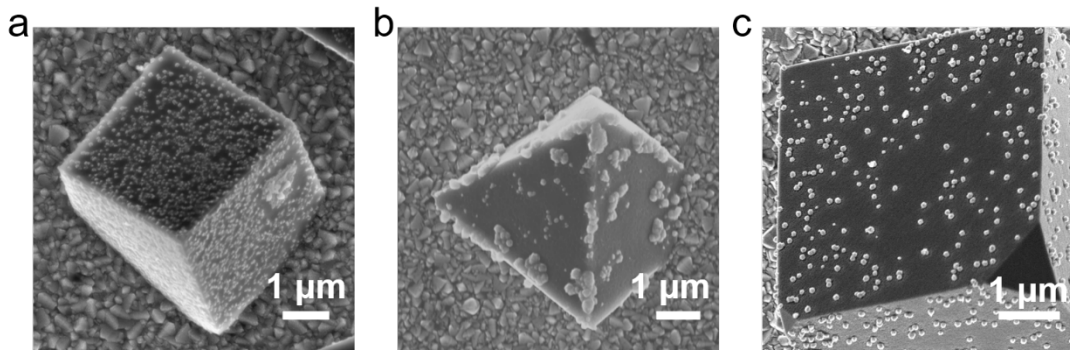
**Figure S7.** X-ray photoelectron spectrum of c-Cu<sub>2</sub>O (a), o-Cu<sub>2</sub>O (b) and t-Cu<sub>2</sub>O (c) before and after HER. Reactions were carried out under 0 V vs. RHE for 30 min in 1 M Na<sub>2</sub>SO<sub>4</sub>.



**Figure S8.** Cu LMM Auger electron spectra of c-Cu<sub>2</sub>O (a), o-Cu<sub>2</sub>O (b) and t-Cu<sub>2</sub>O (c) before and after HER. Reactions were carried out under 0 V vs. RHE for 30 min in 1 M Na<sub>2</sub>SO<sub>4</sub>.



**Figure S9.** XPS spectra after photodeposition of Pt. The peak for Pt(II) can be attributed to the incomplete reduction of H<sub>2</sub>PtCl<sub>6</sub>. Since the precursor of Pt photodeposition is H<sub>2</sub>PtCl<sub>6</sub> with Pt(IV), the presence of Pt(II) still can demonstrate the occurrence of Pt(IV) reduction process by photogenerated electrons.



**Figure S10.** SEM images of c-Cu<sub>2</sub>O(a), o-Cu<sub>2</sub>O(b) and t-Cu<sub>2</sub>O(c) after Pt photodeposition.

**Table S1.** Fitting parameters of biexponential PL decay.

Sample	Decay lifetime (ns)		Amplitude		Average lifetime (ns)
	$\tau_1$	$\tau_2$	$A_1$	$A_2$	$\tau$
c-Cu <sub>2</sub> O	141.0538	1618.694	0.54753	0.32342	1428.731
o-Cu <sub>2</sub> O	87.92246	1381.479	0.54537	0.39306	1276.519
t-Cu <sub>2</sub> O	241.5337	1990.808	0.59169	0.29374	1647.265