

1 Facet-selective charge carrier transport, deactivation mechanism and  
2 stabilization of a Cu<sub>2</sub>O photo-electro-catalyst

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## Experimental details:

### Material preparation

Cu<sub>2</sub>O was synthesized by a hydrothermal procedure.<sup>1</sup> In a typical procedure, 0.2 M Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O was dissolved in deionized water, and the pH value of the solution was 5.35. Then a controlled amount of glacial acetic acid was added into the Cu(CH<sub>3</sub>COO)<sub>2</sub> solution under magnetic stirring, the pH value was adjusted to 3.55 when the concentration of acetic acid increased to 1.5 M. The transparent solution was transferred into a 100 mL Teflonlined stainless steel autoclave and kept at 200 °C for 10 h. The obtained red precipitates were filtered and washed several times with deionized water and absolute ethanol in turn, finally dried in vacuum oven for 12 h.

For the facet-selective photo-depositions, both reduction and oxidation were carried out at room temperature without pH value adjusted.<sup>2</sup> Normally, 0.50 g Cu<sub>2</sub>O powder and a calculated amount (5 wt%) of SnCl<sub>2</sub> or MnSO<sub>4</sub> precursor were mixed in 100 mL deionized water. The suspension was then irradiated by a 300-W Xe lamp (AM 1.5) under continuous stirring. After 20 min photo-deposition, the suspension was filtered, washed with deionized water for more than three times, and finally dried at 60 °C for overnight. NaIO<sub>3</sub> was added as electron scavenger when depositing MnO<sub>x</sub>.

For Cu<sub>2</sub>O electrodeposition, the films were deposited by electrodeposition from solutions of lactate-stabilized copper sulphate. The deposition substrate was fluorine-doped tin oxide (FTO). The plating bath was 0.2 M CuSO<sub>4</sub> (Tianjin Guangfu) and 0.6 M sodium lactate (Shanghai Dibo) solution in deionized water. The bath pH was adjusted to pH 4.5, 5 and 12 by adding an amount of H<sub>2</sub>SO<sub>4</sub> or KOH. The temperature of the bath was maintained at 30 °C using a water bath with an in situ temperature probe. The Cu<sub>2</sub>O thin films were deposited at 0.37 V vs. RHE for 30 min

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using a potentiostat (IVIUM compactstat) in a three-electrode configuration with a Pt plate counter electrode, and a Ag/AgCl (saturated KCl solution) reference electrode.

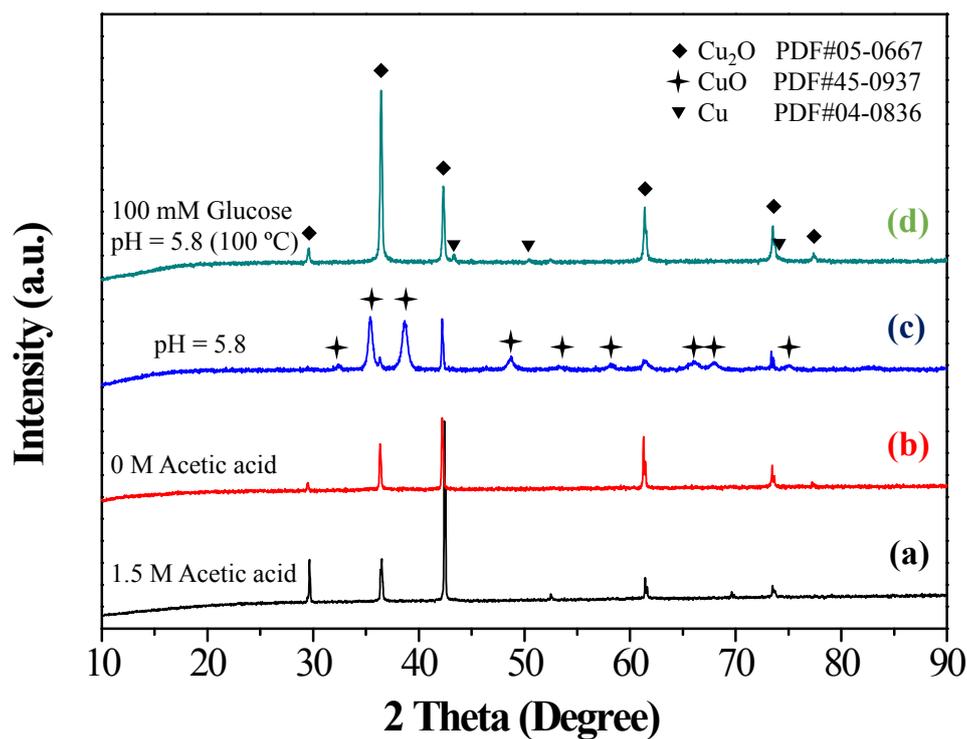
### **Characterization**

X-ray diffraction (XRD) patterns were measured with a D8 Discovery (Bruker) diffractometer, with a Cu K $\alpha$  X-Ray source. The surface morphologies were observed with a field-emission scanning electron microscopy (SEM; Hitachi, S-4800), and energy-dispersive X-ray (EDX) analysis obtained with a Noran System 7 (Thermo). The concentration of copper ions after illumination was measured by an ICP-MS instrument (Agilent 7700X); UV-Visible spectrum was recorded with a spectrometer (Perkinelmer, L750), equipped with an integrating sphere..

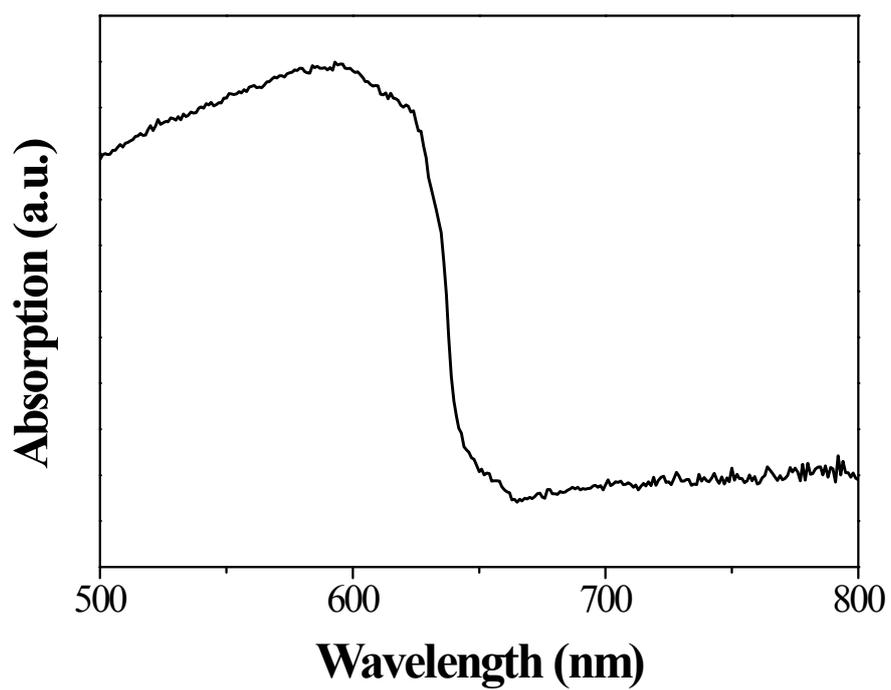
Photoelectrochemical response measurements were carried out using a three-electrode setup, with a platinum counter-electrode and a Ag/AgCl/KCl(sat.) reference electrode ( $E = 0.210$  V vs NHE). All the potentials in this work are converted using the reversible hydrogen electrode (RHE) as the reference electrode, according to the following equation:<sup>3</sup>

$$E(RHE) = E(Ag/AgCl) + 0.21 + 0.059 \times pH \quad (1)$$

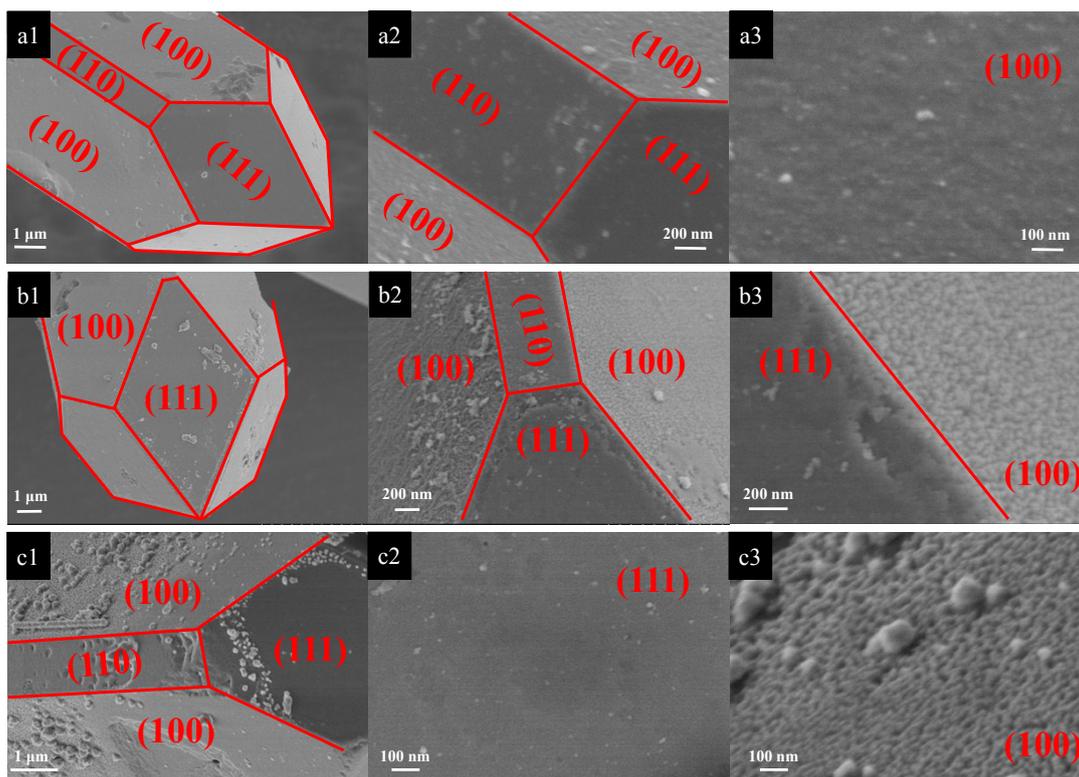
The surface area of the film in contact with the electrolyte (0.5 M Na<sub>2</sub>SO<sub>4</sub>) was 1.0 cm<sup>2</sup>. The electrochemical behaviour was monitored with an IVIUM compactstat, while the light was provided by a 300 W Xenon-arc lamp, calibrated to provide 1 sun (100 mW·cm<sup>-2</sup>) of AM 1.5 illumination to the sample.<sup>4,5</sup>



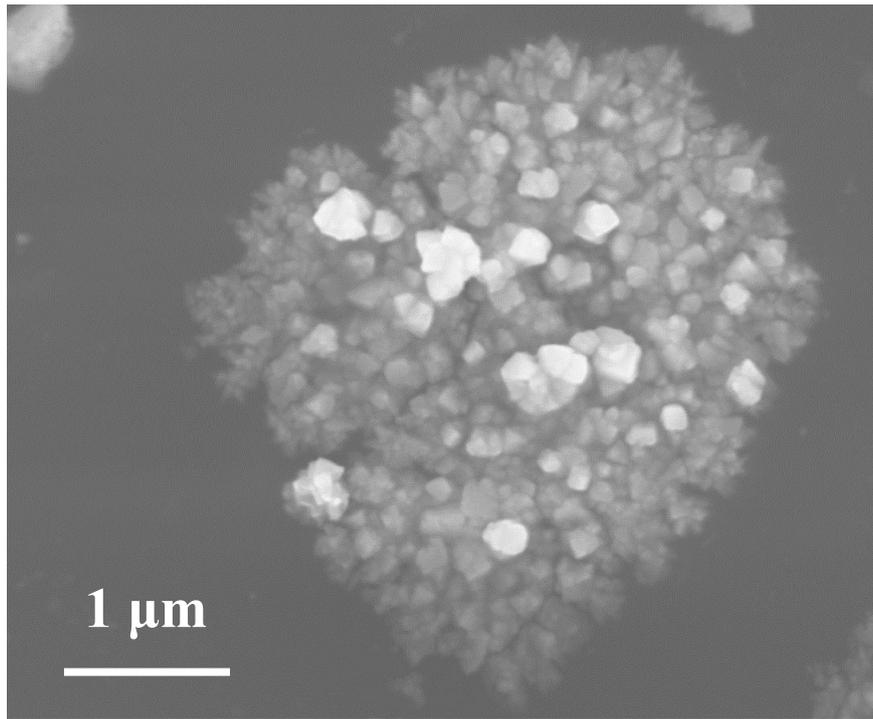
**Figure S1.** XRD patterns of the Cu<sub>2</sub>O microcrystals synthesized in different conditions: (a) 0.2 M copper acetate, 1.5 M acetic acid, pH 3.55, 200 °C; (b) 0.2 M copper acetate, 0 M acetic acid, pH 5.35, 200 °C; (c) 0.2 M copper acetate, 1.5 M acetic acid, pH 5.8 (by adding NaOH), 200 °C; (d) 0.2 M copper acetate, 1.5 M acetic acid, 100 mM glucose, pH 5.8 (by adding NaOH), 100 °C.



**Figure S2.** UV-Vis absorption spectrum of the as-prepared Cu<sub>2</sub>O microcrystals.



**Figure S3.** SEM images of the Cu<sub>2</sub>O microcrystals (a) before illumination; (b) after 0.5 h illumination; (c) after 1 h illumination.



**Figure S4.** SEM image of the electrodeposited metallic Cu particles on a carbon film from the solution during the photo-catalytic reaction.

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## References:

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