

## Supplementary Information for “The Importance of Surface Morphology in Controlling the Selectivity of Polycrystalline Copper for CO<sub>2</sub> Electroreduction”

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### 1 Experimental Details

#### 1.1 Electrochemical Measurement

The electrochemical reactions were carried out in a classical three-electrode cell, which was made of Pyrex glass, using copper as a working electrode, the Hg/HgSO<sub>4</sub> as a reference electrode (in 0.6 M K<sub>2</sub>SO<sub>4</sub>, 0.66 V vs. NHE), and the counter electrode of Pt. The cells of the working electrode and the counter electrode were separated by a solid membrane of commercial Nafion®117, whereby residual protons were exchanged with K<sup>+</sup> in 0.1M KClO<sub>4</sub> prior to the experiments, so that the oxygen produced on the counter electrode would not affect the electroreduction of CO<sub>2</sub> on the working electrode. To saturate the electrolyte with CO<sub>2</sub> and improve the diffusion of gases in the liquid, gas circulation was driven by a diaphragm pump (KNF, NMP830). The electrolyte was potassium perchlorate (Alrich, 99.99%) of 0.1 M and purified through pre-electrolysis method, by applying a bias of -1.0 V on the substitute Pt wire. The pH value was measured by Orion 720. Cyclic voltammetry (CV) and chronoamperometry (CA) were performed using a numeric potentiostat (Biologic VMP2) controlled via the EC-Lab software. The overpotentials related to CVs for the formation of nanoparticles as well as for the CVs obtained during electrochemical characterization of the surfaces are corrected for ohmic drop between the working and the reference electrode after a series of experimentally determined value for ohmic resistance of 10±2 Ω. Each electrochemical reaction of CO<sub>2</sub> proceeded for 15 min, by applying a bias of -1.1 V vs. RHE on the working electrode. The working electrode was immersed in 15 ml of electrolyte with 39 ml of gas phase volume. A 250-µl sample of gas after the reaction was analyzed by a gas chromatograph (Agilent 6890), equipped with a thermal conductivity detector (TCD) through HP-Molecular Sieve 5A and flame ionization detector (FID) through HP-PLOT Q. The products in liquid phase were analyzed through high-performance liquid chromatography (Agilent 1200) with a BioRad HPX-87H column. The experiments were repeated three times to determine the uncertainty of the results.

#### 1.2 Physical Characterization

The surface morphology of the catalyst samples was characterized using scanning electron microscopy (SEM, FEGSEM 200F digital scanning microscope). X-ray

photoelectron spectroscopy (XPS) was employed to determine the surface composition. The XPS system (Sigma Probe, Thermo Scientific) used a monochromated Al K $\alpha$  source for incident radiation and a six-channel detector for measurement of photoelectrons. Charge compensation was utilized during measurement, and base pressure was maintained at  $< 5.0 \times 10^{-9}$  torr. Spectra were calibrated to the C 1s peak at 284.5 eV.

### 1.3 Electronic Structure Calculation

Density functional theory calculations were carried out using a plane-wave pseudopotential implementation<sup>1, 2</sup> and the revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional<sup>3</sup> in the ASE environment with the Dacapo calculator. The free energy of a proton-electron pair at 0 V vs RHE was calculated by its equivalence to gaseous H<sub>2</sub> with the computational hydrogen electrode model, as was demonstrated for the oxygen reduction reaction.<sup>4</sup> The conversion of electronic energies to free energies, the effect of solvation, and the effect of electric fields were handled in a manner identical to that in a previous study that examined CO<sub>2</sub> reduction at copper electrodes.<sup>5</sup>

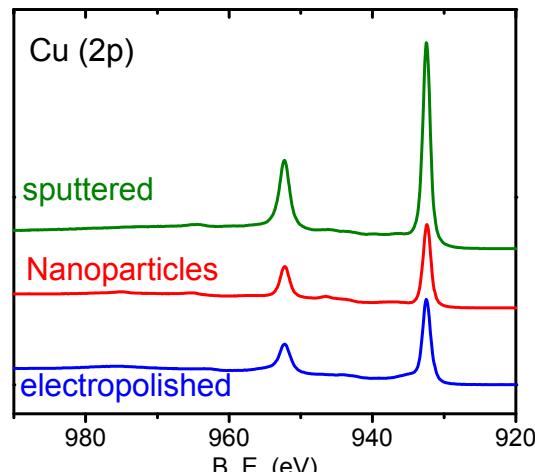
## 2 Additional Data

Fig S1 Photos of Sample A (electropolished surface) in the left and Sample B (nanoparticles covered surface) in the right.

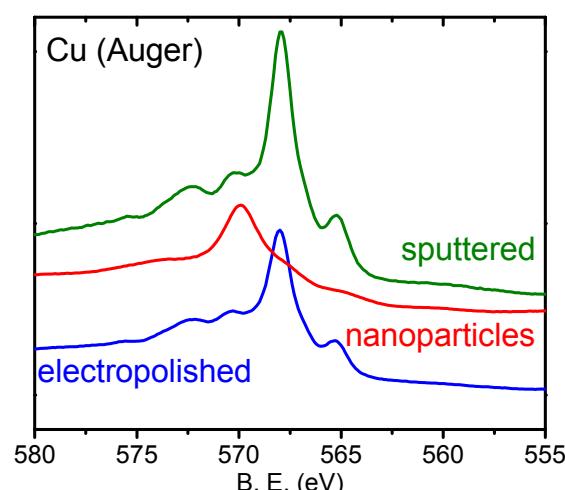


Fig S2

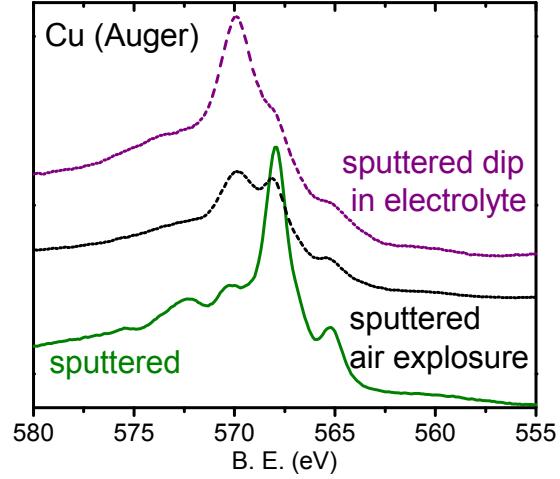
Cu 2p and Cu Auger spectra of copper electrode by XPS: (a) Cu(2p) peak of electropolished, nanoparticles cover and sputter samples (b) Auger peak for a sputter sample, sputter sample after air exposure and sputter sample after immersion in  $\text{KClO}_4$ , where we can see  $\text{Cu}_2\text{O}$  is formed when copper is exposed to air and when is immersed in electrolyte. . The electropolished and nanoparticles covered samples were took out of electrochemical cell, immersed in N2-saturated DI water and transferred to XPS chamber.



(a)



(b)



(c)

Fig S3  
Scanning Electron Microscopy for the copper electrode after 24 hour of reaction

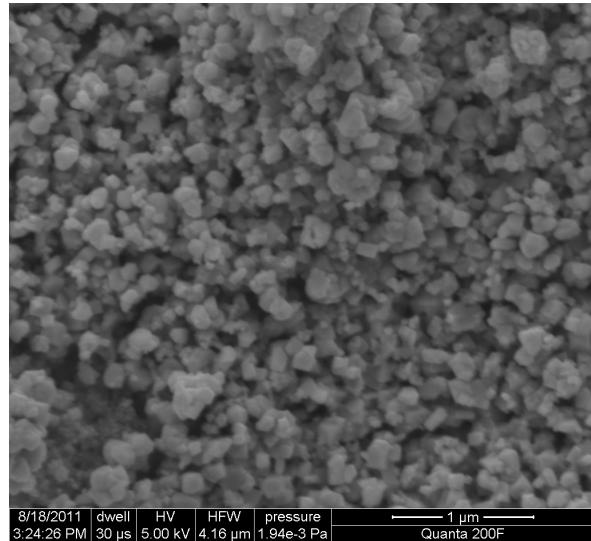


Fig S3

Calculated free energies of for the hydrogen evolution reaction on the (211), (111), and (100) surfaces of the Cu fcc crystal. See also Duran *et al.*<sup>6</sup>

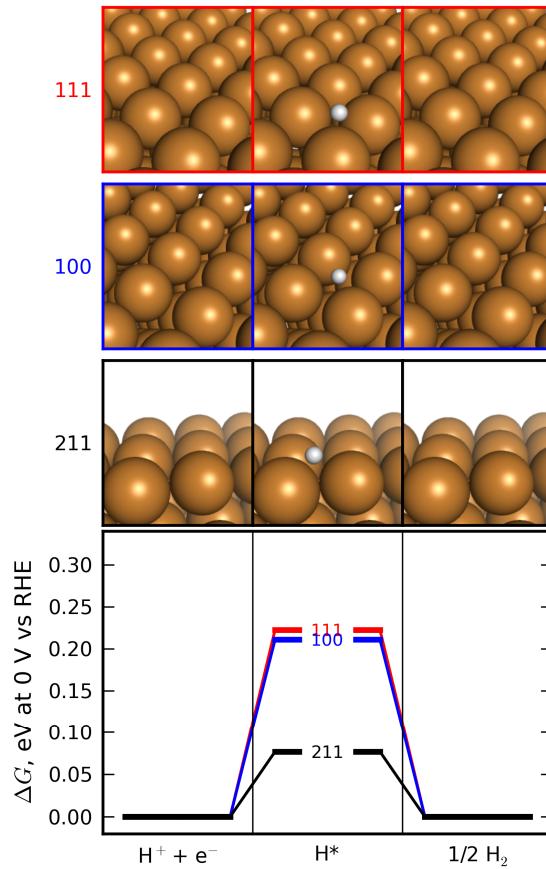
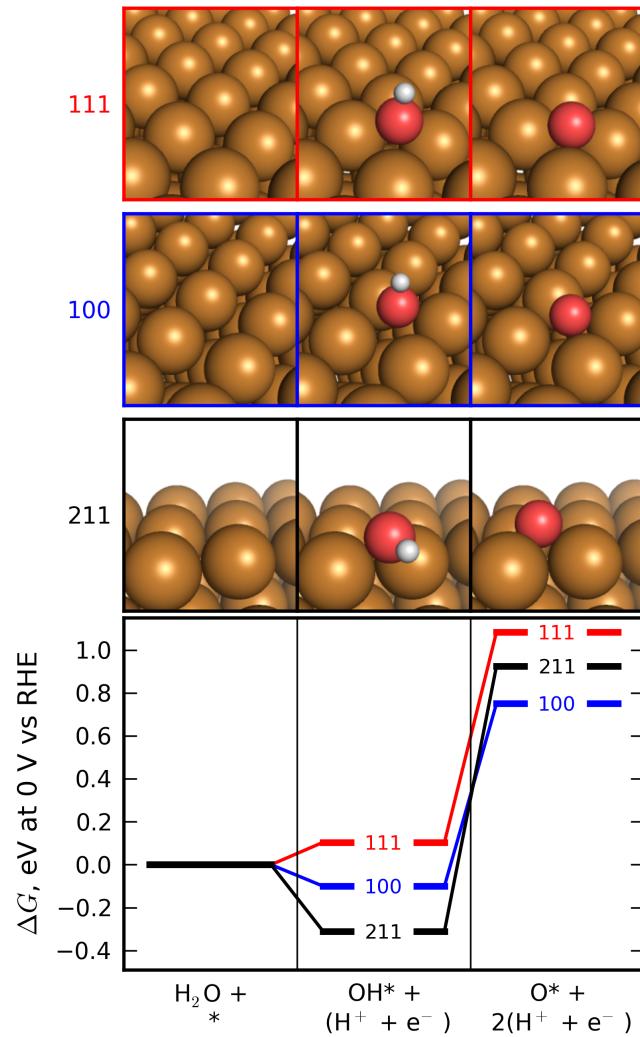


Fig S4

Calculated free energies of water oxidation on the (211), (100), and (111) facets of the Cu crystal at 0 V vs RHE. According to these calculations, a potential of -0.31 V vs RHE is necessary to reduce the step (211) sites to enable hydrogen evolution.



Reference

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