## Supplementary information for

# Morphology-controlled CuO nanoparticles for electroreduction of CO<sub>2</sub> to ethanol

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#### 1. Materials and Instruments

All reagents were used as received.

Potentiostatic electrolysis was performed using a CHI 600a electrochemical Station (Shanghai Chenhua Instruments Company) with the catalysts being loaded on carbon paper (CP, TGP-H-060, Toray).

Liquid phase products were analyzed by Gas Chromatography-Flame Ionization Detector (GC-FID) (SHIMADZU, GC-2014C).

Microstructure and morphology of CuO were analyzed using Hitachi S-4800 field emission Scanning Electron Microscope (FE-SEM).

X-ray diffraction (XRD) patterns were recorded by a Ultima IV X-ray powder diffractometer using Cu K $\alpha$  radiation (k= 1.5406 Å).

 $N_2$  adsorption was carried out at 77 K on a BELSORP-MAX instrument after outgassing the samples for 10 h under vacuum at 573 K.

#### 2. General methods

2.1. Synthesis of CuO nanoparticles

Sample a: 10 mL 0.25 M copper acetate and urea aqueous solution were mixed and

transferred to a Teflon-lined reactor. The reactor was kept in an oven at 130 °C for 1 h. The reaction solution was centrifuged. Dark precipitate was obtained after being washed three times with distilled water and drying at 60 °C for 12 h.

Sample b: The method was the same as sample a except for 0.025 M copper acetate and urea aqueous solution.

Sample c: The method was the same as sample a except that 10 mL 1 M cupric nitrate and sodium carbonate aqueous solution were mixed and the reaction time was 4 h. Sample d and e were synthesized by the methods described in [1].

2.2. Electroreduction of CO<sub>2</sub>

A typical potentiostatic electrolysis was carried out in 0.2 M KI aqueous solution in a divided glass cell under a  $CO_2$  atmosphere, with a CuO loaded carbon paper cathode, a Pt counter electrode and a SCE reference electrode. Each experiment condition was performed for 5 times and the average values were used.



### 3. Characterization of CuO nanoparticles



**Fig. S1** FE-SEM patterns of CuO nanoparticles. (a-1), (a-2): sample a; (b-1), (b-2): sample b; c: sample c; (d-1), (d-2): sample d; (e): sample e.



Fig. S2 b-e: X-ray diffraction (XRD) patterns of CuO nanoparticles after 1 h electrolysis of sample b to e.



**Fig. S3** Current density for CO<sub>2</sub> reduction at various potentials for the electrode loaded with sample a.



Fig. S4 Stability test of sample a, b, c, d and e in electrolysis performed at -1.7 V in 0.2 M KI saturated with 1 atm  $CO_2$ .

#### Reference

1. B.J. Heng, C. Qing, D.M. Sun, B.X. Wang, H. Wang, Y.W. Tang, RSC Adv., 2013, 3, 15719-15726.