Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Cu(II)-nanoparticle-derived structures under CO_2 reduction conditions: a matter of shape

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Copper Hydroxide Nanocages Synthesis

$Cu(OH)_2$ nanocages were synthesized according to the procedure reported elsewhere1. Briefly, a solution of $CuCl_2$ in ethanol (40 mL, 5.5 mM) was mixed with a solution of polyvinylpyrrolidone (PVP, M_n = 55000), and the resultant mixture was sonicated for 10 min, followed by stirring for 30 min at room temperature. Nanoparticle formation was initiated by a quick addition of a freshly prepared $NaBH_4$ solution (20 mL, 20 mM) to the mixture of $CuCl_2$ and PVP in ethanol under vigorous stirring. The solution color immediately changed to dark brown, the stirring was stopped, and the reaction mixture was aged without agitation for at least 48 h. In this method, the formation of Cu(II)-NCs proceeds through the oxidation of initially formed copper clusters[2]. The final blue colloid of $Cu(OH)_2$ nanocages were purified with ethanol using three centrifugation cycles (7200 g, 10 min), and dispersed in 2 mL of methanol to provide [Cu]=0.085M final concentrated Cu(II)-NCs colloidal solution. Elongated 17±4 nm-wide bundles comprising the structure can be observed in high magnification SEM and TEM images (Figure 1c,d). The formation of these bundles is due to the anisotropic nature of $Cu(OH)_2$, as it consists of complex chains formed through coordination of OH^- and Cu^{2+}, while the bundle organization and the overall size of the particles is dictated by the stabilizing surfactant[3].

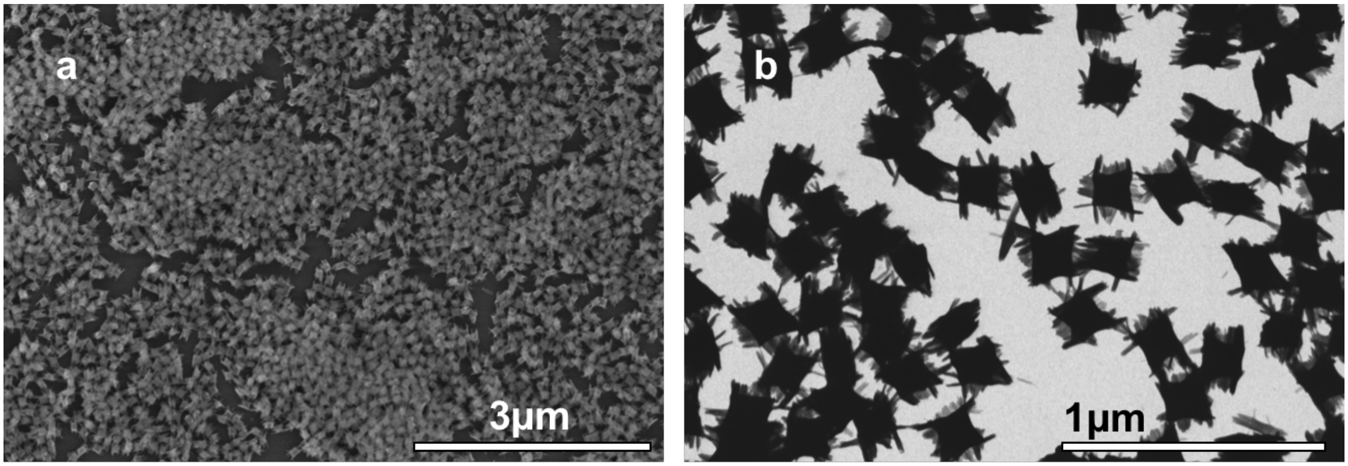

Figure S1. SEM (a) and TEM (b) images of $Cu(OH)_2$ nanocages (Cu(II)-NCs).

Gradual nanoparticle precursor surface density method for electrode fabrication

To prepare a series of electrodes with different distribution density of the material at the surface, solution regime (a) and spin-coating regime (b) were used:

(a) In the solution regime, a certain volume of the concentrated Cu(II)-NCs solution in methanol was centrifuged to remove methanol and subsequently dried, following redispersion and quick sonication in 50 ml of CO_2-saturated 0.5M $KHCO_3$ to obtain a homogeneous solution. The final concentration of Cu(II)-NCs in the series of experiments varied from [Cu]=0.0001-0.02 M. This solution was transferred into a three-electrode configuration cell with carbon paper (typical working area: 0.5 cm^2), Pt mesh ($2cm^2$), and saturated Ag/AgCl as a working, counter and reference electrodes, respectively. The solution was purged with CO_2 for 15 min, followed by a number of CV scans at 20 mV/s, typically from 0 to -1.2V (using Biologic SP300 electrochemical workstation). After the CV scans, the working electrode was removed from the electrolyte, rinsed thoroughly with deionized water, dried in air, and analyzed using SEM and other characterisation methods, as described below. Variables controlling the material density at the electrode surface in this method included (I) precursor amount added to the electrolyte, as described above; (II) number of CV cycles: increasing the number of cycles resulted in the increase of material density; (III) CV potential range: increasing the range from 0V : -1.2V to 0V : -1.4V resulted in the increase of material density obtained in the same number of CV scans.

(b) In the spin-coating regime, a certain volume (from 20 to 200 μL) of the concentrated Cu(II)-NCs solution in methanol was spin-coated at 3000 rpm on the surface of carbon paper (typical area: 0.5 cm^2), followed by the deposition of 10 μL of 0.5 wt% Nafion 117 solution in methanol. The resultant electrode and dried in a vacuum oven at 50^0C for 10 min. Finally, as-prepared working electrode was immersed into CO_2-saturated 0.5M $KHCO_3$ in a three-electrode configuration cell with Pt mesh ($2cm^2$) and saturated Ag/AgCl as a counter and reference electrodes, respectively. The electrolyte was purged with CO_2 for 15 min, followed by at least 20 CV scans at 20 mV/s, typically from 0 to -1.2V, followed by applying -1.2V for at least 10 min to allow for the system to reach equilibrium and ensure that all Cu(II) was electroreduced. Finally, working electrode was removed from the electrolyte, rinsed thoroughly with deionized water, dried in air, and analyzed using SEM and other characterisation methods, as described below. The variable controlling the material density at the electrode surface in this method was the precursor amount spin-coated on the electrode surface.

Similar general trends in the morphological changes were observed in both solution and spin-coating regime, although the solution regime generally resulted in a more even distribution of structures on the electrode surface.

Material Characterization

Initial Cu(II)-NPs and resultant carbon-paper-supported Cu electrodes were analyzed as-is using scanning transmission electron microscope Hitachi S-5200 and ThermoFisher Scientific K-Alpha X-ray photoelectron spectrometer. For X-ray diffraction analysis, carbon-paper-supported Cu electrodes were crushed into powder using mortar and pestle prior to the analysis using Bruker D8 Advance powder X-ray diffractometer.

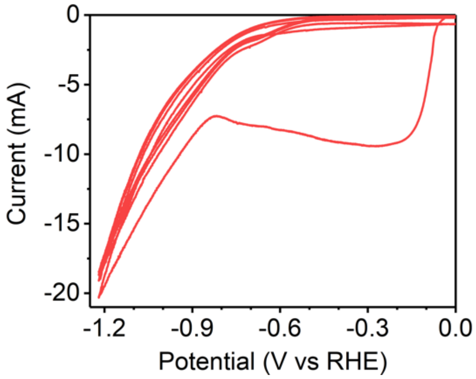

Figure S2. CV plot corresponding to the reduction of dense layer of Cu(II)-NCs spincoated on carbon paper substrate used as a working electrode in CO_2-saturated 0.5M $KHCO_3$ electrolyte. The first scan shows the pronounced reductive feature of $Cu(OH)_2$ between -0.1 and –0.8 V. Scan rate was 20 mV/s.

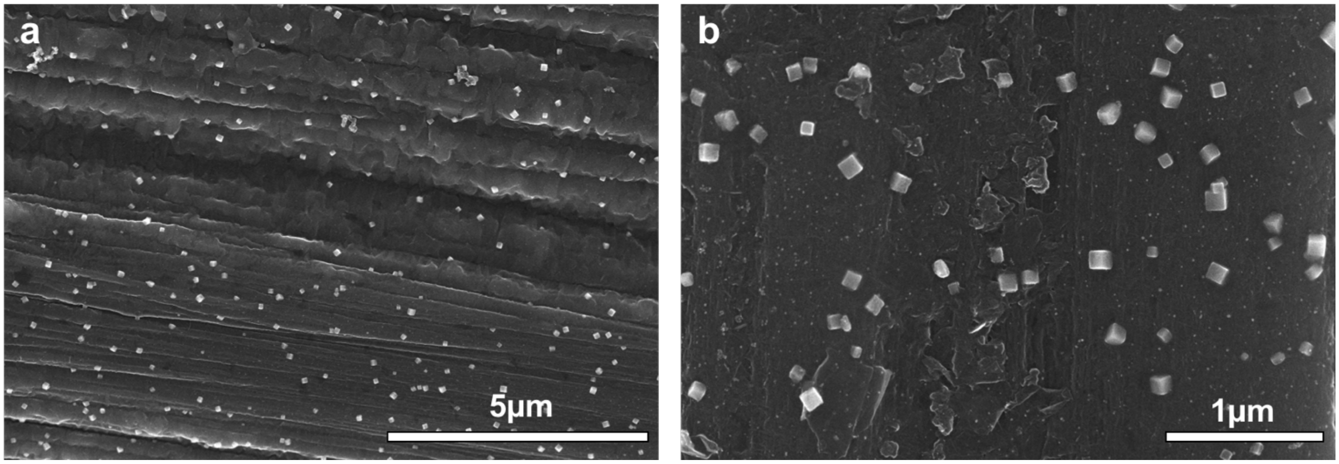

Figure S3. SEM images of Cu nanocubes observed on the surface of carbon paper working electrode after 4 CV cycles at 20 mV/s in CO_2-saturated 0.5M $KHCO_3$ electrolyte containing Cu(II)-NCs ([Cu]=0.0001 M).

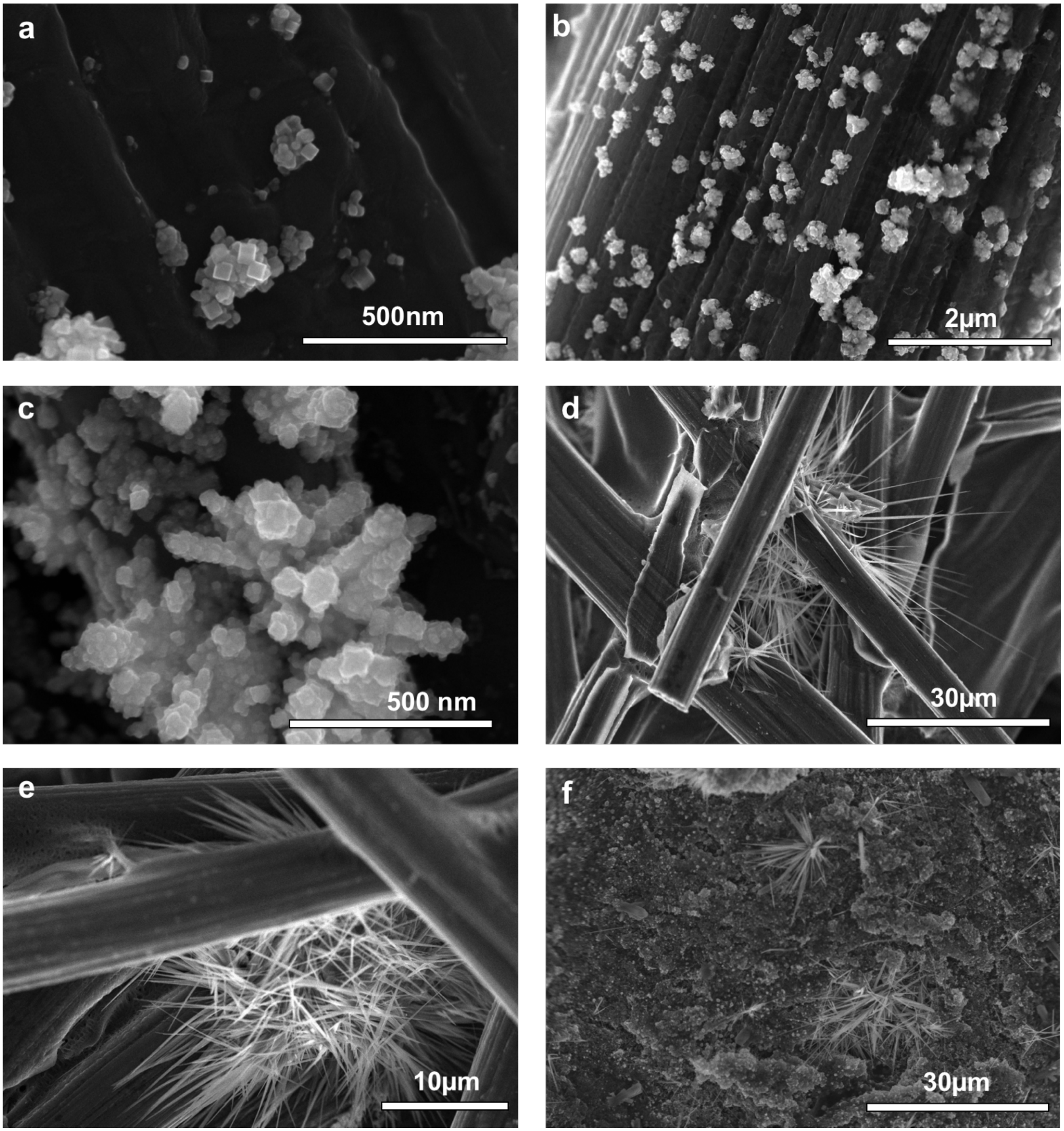

Figure S4. SEM images of Cu nanostructures observed on the surface of carbon paper working electrode at different densities of precursor Cu(II)-NCs in CO_2-saturated 0.5M $KHCO_3$ electrolyte. (a) after 4 CV cycles at 20 mV/s in the electrolyte containing Cu(II)-NCs at [Cu]=0.001 M. (b) after 20 CV cycles at 20 mV/s in the electrolyte containing Cu(II)-NCs at [Cu]=0.001 M. (c) after 20 CV cycles at 20 mV/s with Cu(II)-NCs directly spin-coated on the working electrode (20 µL, [Cu]=0.085 M, 3000 rpm). (d,e) after 20 CV cycles at 20 mV/s in the electrolyte containing Cu(II)-NCs at [Cu]=0.02M. (f) after 20 CV cycles at 20 mV/s with Cu(II)-NCs directly spin-coated on the gas diffusion working electrode (Sigracet purchased from Fuel Cell Store) containing carbon black and PTFE particles (200 µL, [Cu]=0.085 M, 3000 rpm).

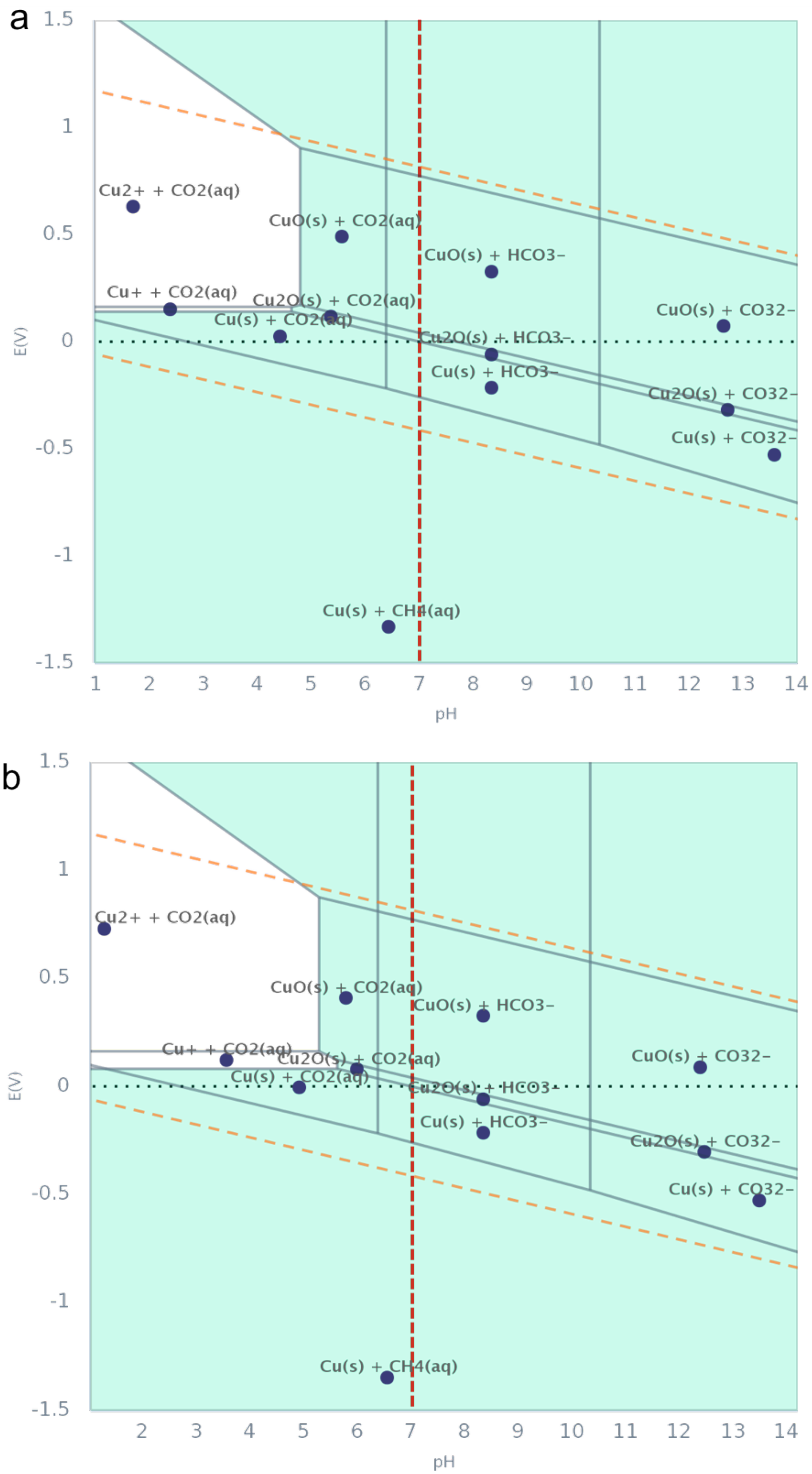

Figure S5. Pourbaix diagrams of Cu phases at 0.001 M (a) and 0.0001 M (b) copper concentration in bicarbonate aqueous solution. Obtained using "Pourbaix diagram" app by Materials Project[4].

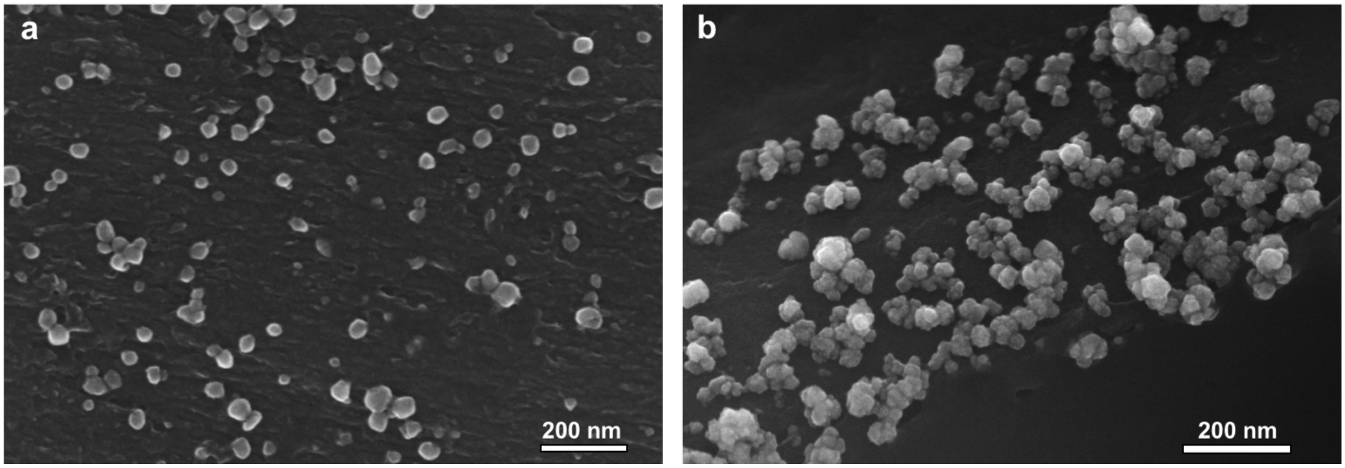

Figure S6. SEM images of Cu nanostructures observed on the surface of carbon paper working electrode at different densities of precursor Cu(II)-NCs in Ar-saturated 0.5M $KHCO_3$ electrolyte containing Cu(II)-NCs at [Cu]=0.0001 M (a) and [Cu]=0.001 M (b).

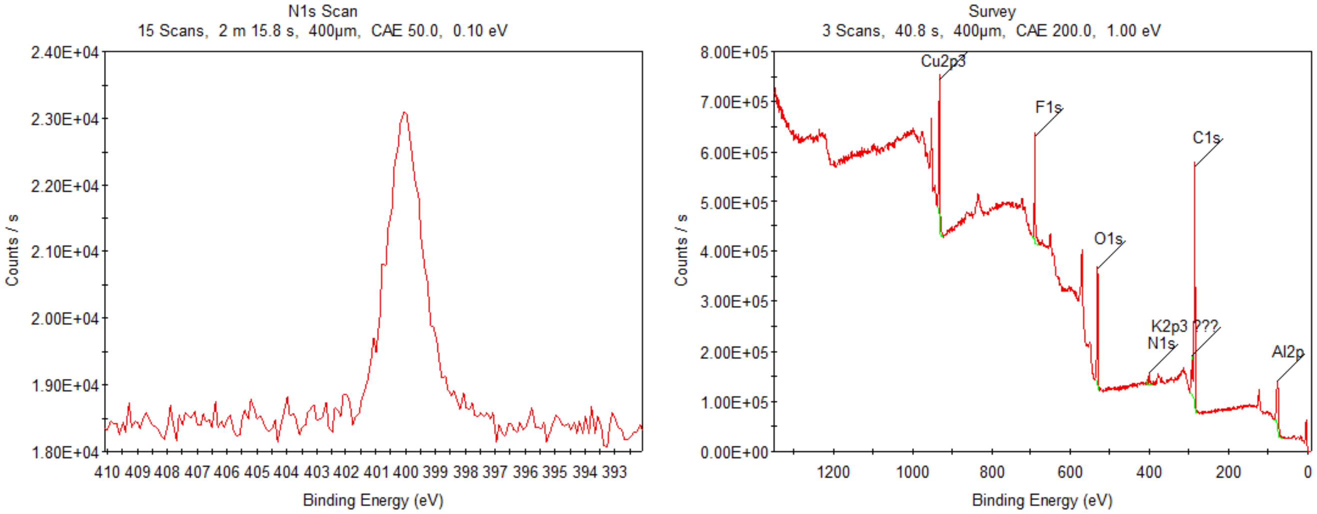

Figure S7. N1s (left) and Survey XPS of Cu nanostructures on the surface of carbon paper obtained by Cu(II)-NCs electroreduction (20 CV cycles, 20 mV/s) in CO_2-saturated 0.5M $KHCO_3$ electrolyte containing Cu(II)-NCs at [Cu]=0.02M. Residual N content is due to the presence of PVP stabilizer at the nanoparticle surface.

CO_2 electroreduction tests and product analysis

The electrocatalytic activity of the obtained electrode with high density of material was evaluated by performing constant-potential electrolysis at ambient temperature. All CO_2 electroreduction experiments were performed using a three-electrode system connected to an electrochemical workstation (Biologic SP300). Saturated Ag/AgCl and Pt mesh were used as a reference and counter electrodes, respectively. The electrolyte was 0.5M $KHCO_3$, saturated with CO_2. The experiments were performed in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion 117). The CO_2 gas was delivered into the cathodic compartment at a rate of 20 sccm and vented directly into the gas-sampling loop of a gas chromatograph (MG5, SRI Instruments). The chromatograph was equipped with a packed MolSieve 5A column and a packed Haysep D column. Argon (Praxair, 99.999%) was used as a carrier gas. A flame ionization detector, equipped with a methanizer, was used to qualify CO, methane, and ethylene yields, and a thermal conductivity detector was used to quantify hydrogen yield. Concentration of liquid products was analyzed using Bruker 500 MHz nuclear magnetic resonance spectrometer. In a typical experiment, 0.8 mL sample of the electrolyte after 1 hour of electrolysis was mixed with 0.1 mL D_2O and 2×10^{-7} M dimethyl sulfoxide solution in water, used as an internal standard. 1D ^{1}H spectra were measured using water suppression technique.

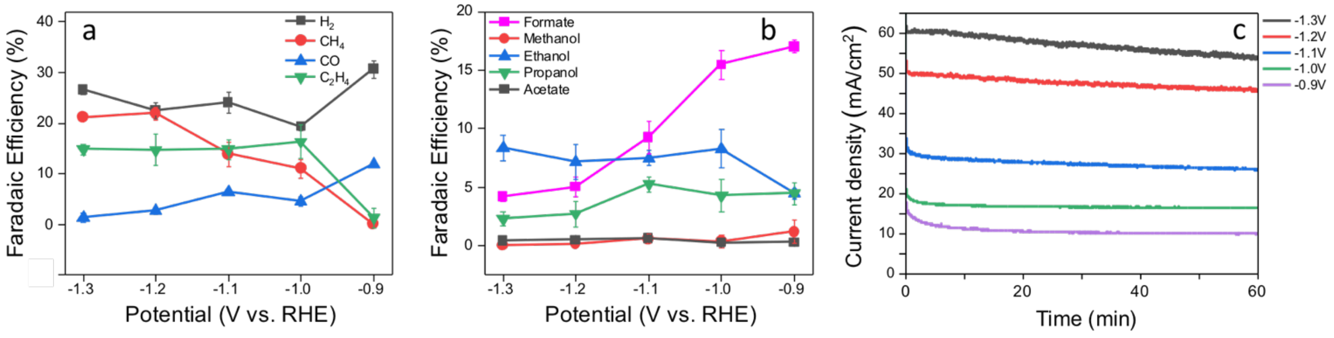

Figure S8. CO_2RR performance in 0.5M $KHCO_3$ electrolyte. Cu microurchines were obtained by Cu(II)-NCs electroreduction (20 CV cycles, 20 mV/s) in CO_2-saturated 0.5M $KHCO_3$ electrolyte containing Cu(II)-NCs at [Cu]=0.02M. (a,b) FE of gas (a) and liquid (b) products obtained after 1h of electrolysis. (c) Geometric current densities of the catalysts over 1h of operation at different applied potentials (from -0.9V to -1.3V vs RHE).

The electrochemically active surface area (ECSA) of the carbon paper-supported copper catalysts were measured using a double layer capacitance method in 0.1 M $HClO_4$ electrolyte[5]. Cyclic voltammetry scans were recorded in the potential range from -0.05 to 0.2 V vs RHE. The roughness of the catalysts were compared to electrochemically polished Cu foil whose surface area is defined as 1. ECSA-normalized current densities of the NCs and Mus at -1.1V vs RHE presented below (corresponding FE of the major products are shown in Table 1 of the main text).

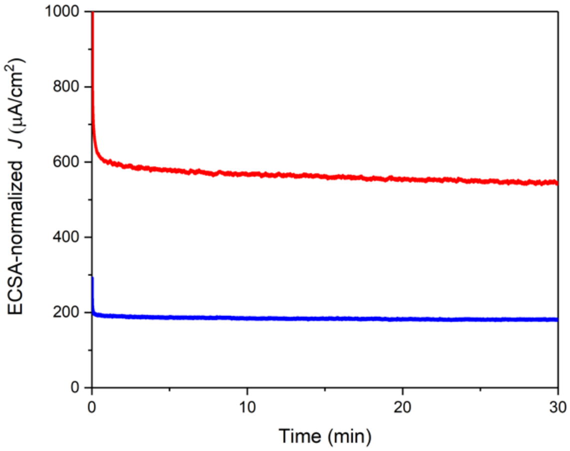

Figure S9. ECSA-normalized current density (J) comparison of NCs (blue) and MUs (red) during CO_2RR in 0.5M $KHCO_3$ electrolyte. FEs of the major products for NCs and MUs are shown in Table 1 of the main text.

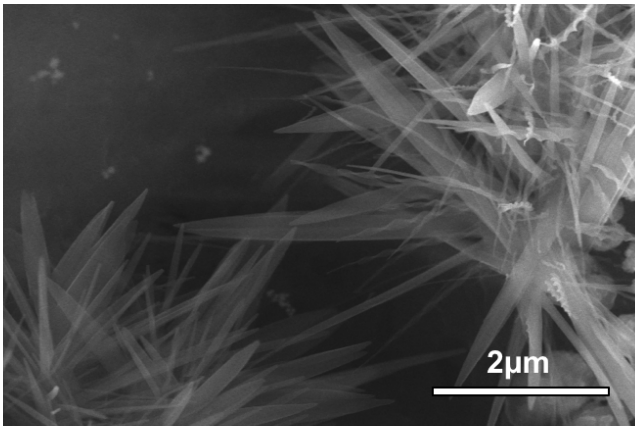

Figure S10. SEM images of degraded Cu microurchines observed on the working electrode surface after 1 hour of CO_2RR electrolysis in 0.5M $KHCO_3$ at -1.3V vs RHE (See Fig. S9c). The electrode was prepared from reduction of Cu(II)-NCs directly spin-coated on the working electrode (20 μL, [Cu]=0.085 M, 3000 rpm) in CO_2-saturated 0.5M $KHCO_3$ electrolyte using 20 CV cycles at 20 mV/s.

References

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