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Size Dependent Selectivity of Cu Nano-Octahedra Catalysts for the Electrochemical Reduction of CO₂ to CH₄

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Experimental Section

Chemicals. All chemicals were used as received. Tri-n-octylphosphine (TOP, 90%) and Copper(I) chloride (CuCl, 99.999%) were purchased from Alfa Aesar. Oleylamine (OLAM, 70%) was purchased from Sigma-Aldrich. Toluene (anhydrous, 99.8%) was purchased from ABCR GmbH.

Synthesis of Cu O_h -NCs with average edge length of 75 nm, 150 nm and 310 nm. The Cu O_h -NCs were synthesized by modifying a previously reported method.¹ CuCl is added to TOP in a vial in a N₂ glove box and this solution is heated at 200°C for 2 hours to form a Cu-TOP complex. In parallel, OLAM is degassed at 80°C for 1 hour in a three-necked flask connected to a Schlenk line, after which the temperature is raised to 335°C. Once this temperature is stable, the hot Cu-TOP solution is rapidly injected into the OLAM and the reaction solution is left to react for a certain time (see Table S1), during which the solution turns reddish-brown. At the end of the synthesis, the heating mantle is withdrawn and the flask is cooled quickly to room temperature using a water bath after which the reaction mixture is transferred to the glovebox for the washing. The 50 mL solution is divided between 2 centrifuge tubes and 25 mL of toluene are added to each tube which is centrifuged at 6000 rpm for 20 minutes. The precipitate in each flask is then redispersed in around 1 mL of toluene for storage. The parameters employed for each size are reported below in Table S1. A detailed study on the synthesis with elucidation of the reaction mechanism will be published elsewhere.

Table S1: Synthesis parameters for the Cu O_h -NCs

Parameter	310 nm	150 nm	75 nm
CuCl (mmol)	4	2	0.25
TOP (mmol)	4	2	1
OLAM (mL)	46	48	49
Reaction volume (mL)	50	50	50
Reaction Temperature (°C)	335	335	335
Reaction Time (min)	30	30	15

Ligand removal. A volume of the toluene solution corresponding to 15 μg of Cu was drop-casted onto 1.4 cm^2 substrate (glass slide for FTIR or glassy carbon for electrochemistry, see below). The substrate was then rinsed with ethanol and then N_2 plasma (80 W) cleaning for 90 seconds before being rinsed with ethanol again to wash away carbonaceous residues.

Structural Characterization. Transmission electron microscopy (TEM) images were acquired on a FEI Tecnai-Spirit at 120 kV. Samples were drop-casted on a copper TEM grid (Ted Pella, Inc.) prior to imaging. Size statistics was performed using the software ImageJ and counting at least 200 particles per sample. The edge length of a triangular face of the octahedra has been referred to as the size of the same. Scanning electron microscopy (SEM) images were acquired on a FEI Teneo, using an inlens (Trinity) detector at a beam energy of 6 keV and a beam current of 25 pA. Samples were prepared on conductive p-doped silicon or glassy carbon substrates. The XRD patterns reported were acquired on a Bruker D8 Advance diffractometer with a $\text{Cu K}\alpha$ source equipped with a Lynxeye one-dimensional detector. The diffractometer operated at 40 kV and 40 mA with a $\text{Cu K}\alpha$ source with wavelength of $\lambda=1.54 \text{ \AA}$.

Surface Characterization. FT-IR was performed using a Perkin Elmer FT-IR spectroscope on silicon chips between $\nu=4000$ and 1000 cm^{-1} . XPS data were collected on a PHI VersaProbe II scanning XPS microprobe (Physical Electronics, Inc) with a monochromatic $\text{Al-K}\alpha$ X-ray source operating at 24.8 W under ultrahigh vacuum conditions. Thin film samples were prepared on glassy carbon substrates. The spectra were referenced at 284.8 eV with the C–C bond of the $\text{C}1\text{s}$ transition.

Sample Concentration. Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES). ICP-OES was performed on an Agilent 5100 model to determine the Cu concentration. Five standard solutions of Cu were prepared to obtain the calibration curve used to determine the concentrations of the digested nanocrystal solution. The sample solution was prepared by dissolving the nanocrystals in 70% HNO_3 followed by the addition of a specific amount of DI water until the solution reaches the 2% acid content needed for the analysis.

Sample preparation for electrocatalytic measurements. For the CO_2RR tests, 15 μg of Cu O_h -NCs dispersed in toluene were drop-casted onto glassy carbon electrodes. Prior to drop casting, the glassy carbon electrodes underwent a cleaning routine of ultrasonication in acetone, iso-propanol and deionised water, after which they were polished using an Alumina paste (0.5

μm roughness) on a polishing pad. The ligands were there removed from the surface following the treatment reported above.

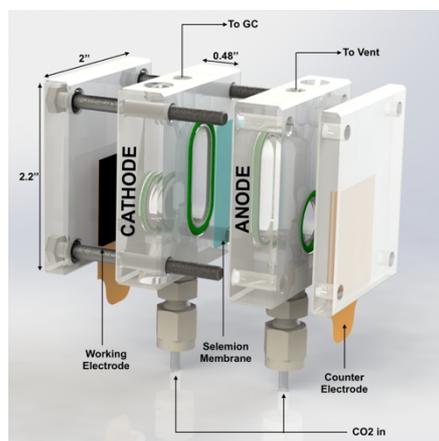
CO₂RR testing. The electrochemical measurements were performed using a Biologic SP-300 potentiostat. Ambient pressure CO₂ electrolysis was carried out in a custom-made gas-tight electrochemical cell made of poly-carbonate and fitted with Buna-N O-rings built in our laboratory.² The configuration of the electrochemical cell (Scheme S1) is such that the working electrode sits parallel with respect to the counter electrode to ensure a uniform potential distribution across the surface. The geometric surface area for both of the electrodes is 1.4 cm². A Selemion AMV anion exchange membrane is used to separate the anodic and cathodic compartments. Each of the compartments in this cell contains a small volume of electrolyte (2 mL each) to concentrate liquid products and therefore increase the detection limits. 0.1 M KHCO₃ solution was used as electrolyte. To make such a solution, a 0.05 M K₂CO₃ solution (purified with Chelex resin to eliminate metallic impurities) was bubbled for 1 h with CO₂. Before starting the CO₂ electrolysis, the electrolyte in the cathodic compartments was purged with CO₂ for at least 15 min. During electrolysis, CO₂ was constantly bubbled through the electrolyte at a flow rate of 5 sccm to prevent depletion of CO₂ in the electrolyte and to allow continuous analysis of gaseous products via a gas chromatograph. The flow rate of CO₂ was controlled with a mass flow controller (Bronkhorst), and the gas was first humidified with water by passing it through a bubbler to minimize evaporation of electrolyte. Platinum foil was used as the counter electrode and Ag/AgCl electrode (leak free series) from Innovative Instruments, Inc. was used as the reference. Voltages were converted to the RHE scale by using a calibrated reference electrode as in the equation below.

$$E(\text{RHE}) = E_{\text{Ag}/\text{AgCl}} + 0.0591 \times \text{pH} + E_{\text{Ag}/\text{AgCl}}^{\circ}$$

Where $E_{\text{Ag}/\text{AgCl}}^{\circ} = 0.206$ V at 298 K and $E_{\text{Ag}/\text{AgCl}}$ is the working potential

Product Analysis. For the analysis of gaseous products, a gas chromatograph (GC, SRI instruments) equipped with a HayeSep D porous polymer column, thermal conductivity detector, and flame ionization detector was used. Ultra-high purity N₂ (99.999%) was used as a carrier gas. The concentration of gaseous products was determined using calibration curves from standard gas mixtures. For liquid product analysis, high-performance liquid

chromatography (HPLC) was carried out on an UltiMate 3000 instrument from Thermo Scientific. During electrolysis, CO₂ was constantly bubbled through the electrolyte to prevent depletion of CO₂ in the electrolyte and to allow continuous analysis of gaseous products via the GC.



Scheme 1: Rendering of the H-type liquid cell used in the CO₂RR experiments.

The calculation of FE for gas products was performed using following equation:

$$F = \frac{n \cdot F \cdot C \cdot G \cdot P}{R \cdot T \cdot I}$$

Where, n is the number of electrons transferred to product formation from CO₂ (*i.e.*, 2 for CO, 8 for CH₄ and 12 for C₂H₄) and H₂O (*i.e.*, 2 for H₂); F is the Faraday constant (96485 C.mol⁻¹); C is the measured concentration of the product by GC (in ppm); G is the gas flow rate (ml/min); I is the cell current after subtraction of 75% of the blank glassy carbon signal (in A); P is the pressure (1.01×10⁵ Pa); R is the universal gas constant (8.314 Jmol⁻¹ K⁻¹); T is the temperature (293.15 K)

The FE for liquid products was calculated as follows:

$$FE = \frac{n \cdot F \cdot M \cdot V}{Q}$$

Where, n is the number of electrons transferred to CO₂ to produce a given product (*i.e.*, 2 for formate, 8 for acetate, 10 for ethylene glycol, 12 for ethanol and 18 for 1-propanol); F is the Faraday constant (96485 C mol⁻¹); M is the Molar concentration of the liquid product; V is the liquid volume; Q is the total charge passed over a given time of analysis. All the reported FE and current density data is an average of three measurements with indicated error bars.

Electrochemically active surface area and current normalization.

There exist multiple methods to estimate the Electrochemically Active Surface Area (ECSA) including as the use of a surface roughness factor,³ the geometric surface area of occupied by nanoparticle catalysts,⁴ the ratio of the surface area of the nanoparticles to that of the electrode.⁵ However, so far the most common one relies on the Electrochemical Double Layer (ECDL) capacitance of the electrode and we adhere to the same. The method has been described in literature and it is briefly explained below.^{6,7}

The double layer capacitance is measured by performing cyclic voltammetry on the sample in a potential range where no faradaic processes occur. Hence the measured current is due only to the non-faradaic process of charging of the electrochemical double layer. The difference between the cathodic (i_c) and anodic (i_a) sweeps at a given voltage scales linearly with the scan rate (v), and the slope of the line is equal to the double-layer capacitance C_{DL} .

$$C_{DL} = \frac{i_c - i_a}{v}$$

Using the same method to find the capacitance of a reference electrode, we calculate the surface roughness factor (SRF).

$$SRF = \frac{C_{DL_{sample}}}{C_{DL_{reference}}}$$

Finally, the Normalisation Factor (NF) is calculated using the geometric area of the electrode exposed to the electrolyte.

$$NF = SRF \times Geom. Area$$

The ideal reference sample for the Cu *Oh*-NCs is a flat single crystalline copper surface measured in the same conditions. However, considering our interest in relative intrinsic activities, here we choose the capacitance of the blank glassy carbon ($40 \mu\text{F}/\text{cm}^2$) to determine the SRF. The current is normalized after subtracting 75% of the blank glassy carbon signal.

In Table S1 to S3 below, we report all the values of the measured current density (J), usually referred to as the geometric current density, along with the ECSA-normalized current density

(J_{ECSA}) utilized in this work for the total current and the partial current densities for CO₂RR and HER.

Table S1. Total Current Density

Size (nm)	Capacitance ($\mu\text{F}/\text{cm}^2$)	Voltage (V)	J (mA/cm^2)	J_{ECSA} (mA/cm^2)
75	157	-1.15	0.785	0.200
		-1.25	1.474	0.375
		-1.35	2.724	0.693
150	100	-1.15	0.738	0.29
		-1.25	1.090	0.43
		-1.35	1.932	0.77
310	183	-1.15	1.673	0.37
		-1.25	2.034	0.44
		-1.35	2.471	0.54

Table S2. Partial Current Density for H₂

Size (nm)	Capacitance ($\mu\text{F}/\text{cm}^2$)	Voltage (V)	J (mA/cm^2)	J_{ECSA} (mA/cm^2)
75	157	-1.15	0.308	0.078
		-1.25	0.331	0.084
		-1.35	1.201	0.306
150	100	-1.15	0.534	0.213
		-1.25	0.450	0.179
		-1.35	1.179	0.470
310	183	-1.15	1.447	0.317
		-1.25	1.708	0.374
		-1.35	1.572	0.344

Table S3. Partial Current Density for CO₂RR

Size (nm)	Capacitance ($\mu\text{F}/\text{cm}^2$)	Voltage (V)	J (mA/cm^2)	J_{ECSA} (mA/cm^2)
75	157	-1.15	0.46	0.12
		-1.25	1.11	0.28
		-1.35	1.04	0.26
150	100	-1.15	0.12	0.05
		-1.25	0.38	0.15
		-1.35	0.40	0.16
310	183	-1.15	0.11	0.02
		-1.25	0.18	0.04
		-1.35	0.75	0.16

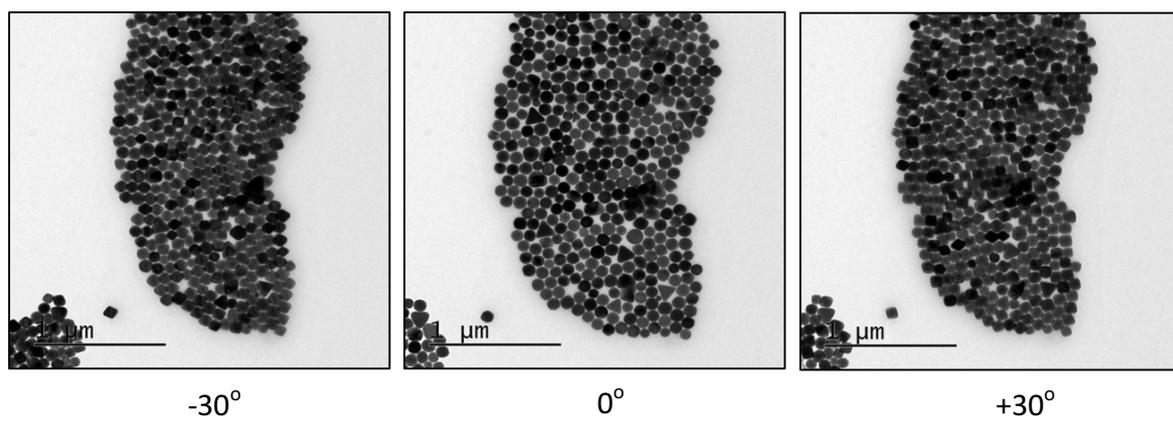


Fig. S1 Tilted TEM to observe different orientations of the smallest sized 75 nm Cu O_h -NCs.

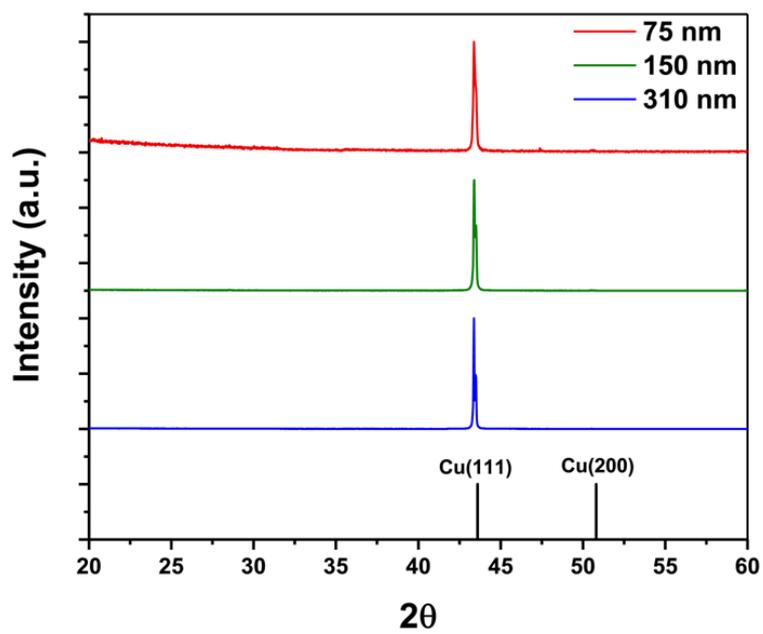


Fig. S2 XRD of the three sizes of Cu O_h -NCs

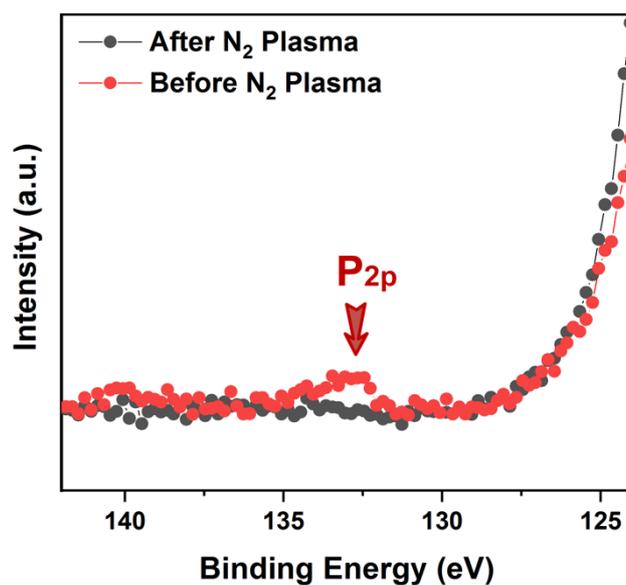


Fig. S3 Representative XPS spectra of the P2p, which is the characteristic element of TOP, after the plasma. The absence of C-H features in the FTIR in Fig. 2 and of the P2p peaks in the XPS confirm that the ligands have been eliminated.

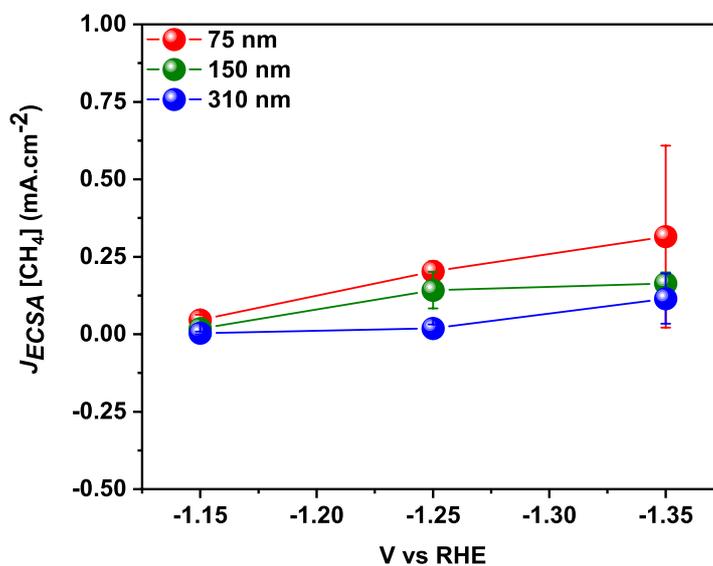


Fig. S4 ECSA-normalized current densities for CH₄ reported for the three sizes of Cu *O_h*-NCs.

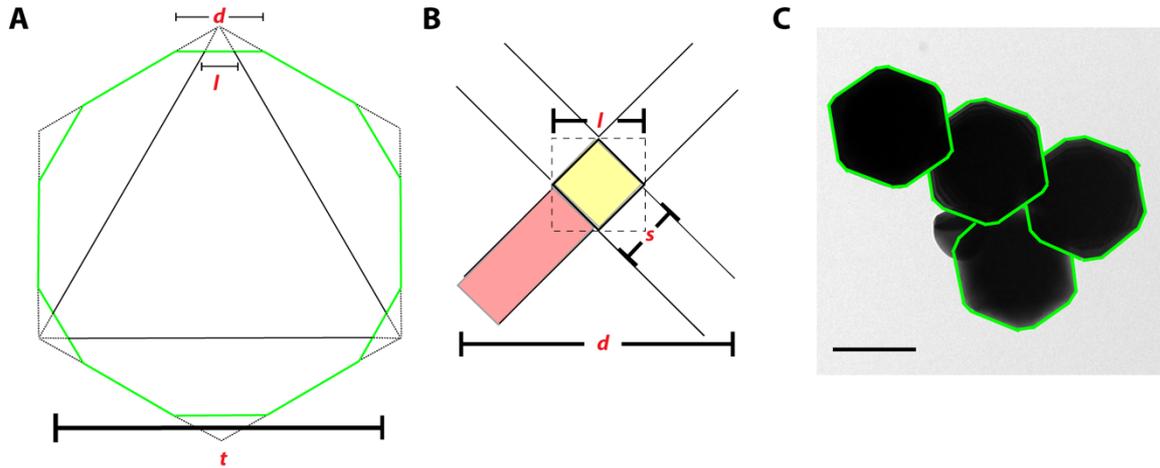


Fig. S5 (A) Schematic of an octahedron viewed from the [111] axis. The green perimeter indicates the truncated octahedron. (B) Enlarged view (A) from the [100] viewing axis with {110} in red and {100} in yellow. (C) Example of the geometric fitting on the 310 nm Cu O_h-NC (scale bar is 250 nm). Geometric fits on 30 NCs for each size were used to estimate the {100}/{111} and {110}/{111}.

The method for the calculations is described below:

The uniform contrast of the NCs prevents us from directly measuring the size of each facet. Hence, we rely on the visible outermost edges that are truncated hexagons. d is the measured length of the truncated corner of the hexagon. t is the base of the truncated triangular facet.

A simple geometrical calculation gives us the length l of the short end of the polygon formed as a result of the truncation of a triangular face.

$$l = \frac{d}{3}$$

The {100} facet exposed at the corner is approximated to be a square, whose side s is given by

$$s = \frac{l}{\sqrt{2}}$$

Having quantified the l and s , the areas of each of the facets are estimated in the following manner

$$t \cdot t \cdot \frac{\sqrt{3}}{4} \cdot 8 = \text{total area } \{111\} \text{ per octahedron}$$

$$s \cdot t \cdot 12 = \text{total area } \{110\} \text{ per octahedron}$$

$$s \cdot s \cdot 6 = \text{total area } \{100\} \text{ per octahedron}$$

Table S4. Calculated {100}/{111} and {110}/{111} ratios for the three sizes of Cu O_h-NCs

Size (nm)	{100}/{111}	{110}/{111}
75	0.012	0.21
150	0.004	0.19
310	0.002	0.07

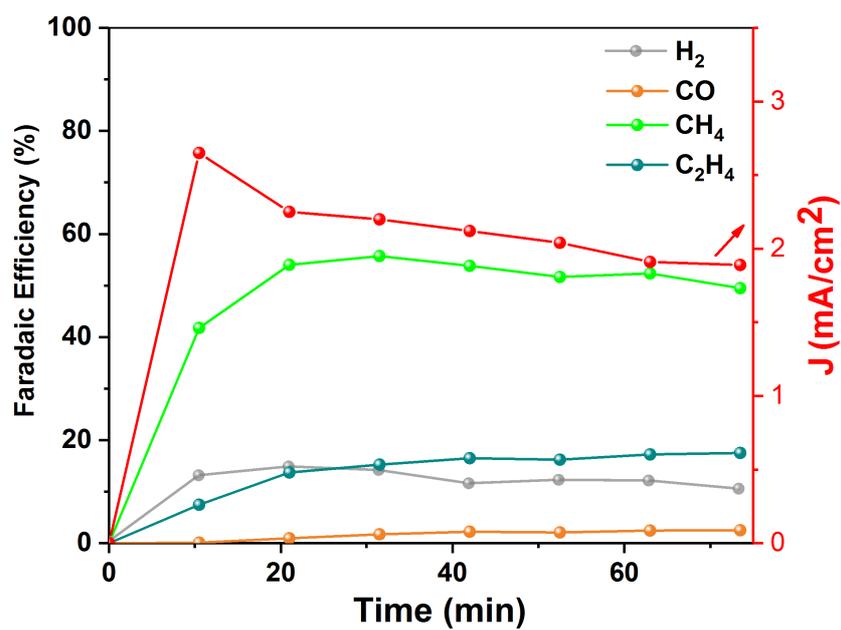


Fig. S6 Measured current density and Faradaic efficiencies of gaseous products from CO₂RR over the 75 nm O_h-Cu NC at -1.25 V vs RHE in CO₂ saturated 0.1 M KHCO₃.

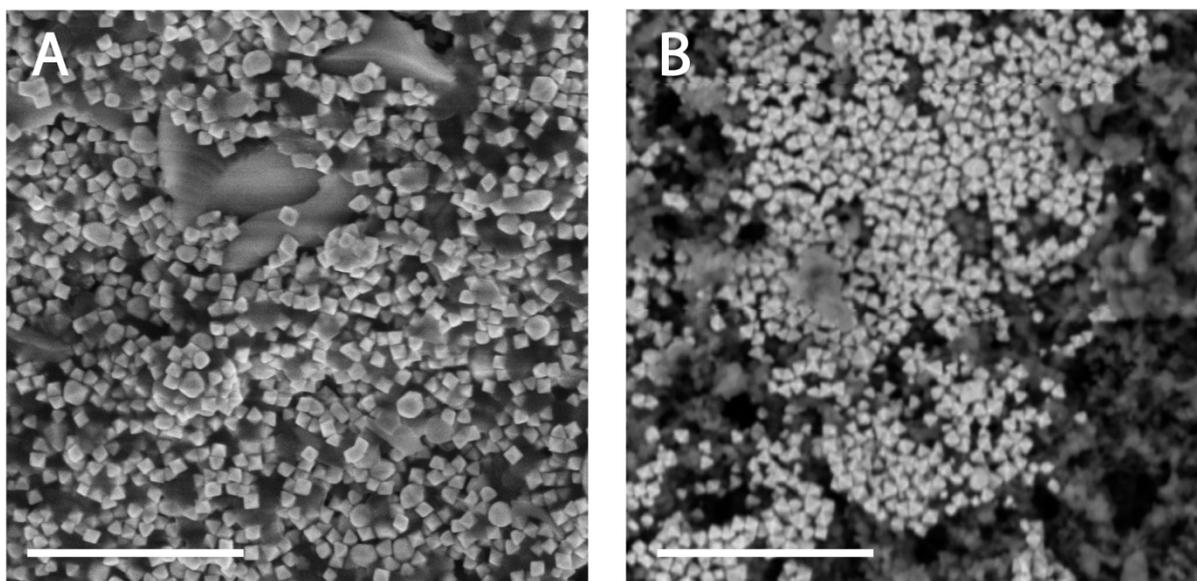


Fig. S7 SEM images of the 150 nm Cu O_h-NCs deposited onto carbon paper with a loading of 50 $\mu\text{g}/\text{cm}^2$: (A) before electrolysis and (B) after CO₂RR performed in an alkaline electrolyzer at -300 mA/cm² in 1M KOH for 80 minutes. Scale bar is 2 μm

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