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Supporting Information

Cu_2O@COF Core-Shell Catalyst for Electrochemical CO_2 Reduction

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Section 1. General Materials and Methods

Materials: The primary reagents used in this study include o-DCB (1,2 Dichlorobenzene, 99%), anhydrous n-BuOH (nButanol, 99%), Copper (II) Chloride ($CuCl_2$), Boron trifluoride-diethyl ether (BF_3•OEt_2), 2-Vinyl pyridine and L-ascorbic acid were purchased from Sigma Aldrich Chemicals. 4,4',4"(1,3,5-triazine-2,4,6-triyl)trainline (95%), and 4,4',4"-trinitrilotribenzaldehyde were all supplied by BLD pharm. Acetic acid (>99.0%), methanol (MeOH), Ethanol (EtOH), were purchased from Carl Roth. Sodium Hydroxide (NaOH) and 2-Vinylpyridine was purchased from Thermo Fisher Scientific. All chemicals were of analytical grade and used without further purification. Deionized water used during the materials synthesis and for conducting experiments was purified using a Direct-Q 3UV water purification system (Millipore Corp., France).

X-ray powder diffraction (XRD) patterns was collected on a Bruker D8 Advance diffractometer in reflection geometry operating with a Cu Kα anode (λ = 1.54178 Å) operating at 40 kV and 40 mA. Samples were ground and mounted as loose powders onto a Si sample holder. PXRD patterns were collected from 2 to 60 2θ degrees with a step size of 0.02 degrees and an exposure time of 2 seconds per step.

Thermogravimetric analyses (TGA) were performed using a TGA Q500 thermal analysis system under a N_2 atmosphere from room temperature to 800 °C at a ramping rate of 2 °C /min.

Attenuated total reflectance Fourier-transform infrared spectrometry (ATR-FT-IR) was conducted using a PerkinElmer Spectrum Two spectrometer with diamond/ZnSe ATR accessory. All spectra were collected using a $LiTaO_3$ MIR detector over a range of 450 to 4000 cm-1. All spectra were processed using Spectrum 10 software.

Solid-state diffuse reflectance Ultraviolet–visible spectroscopy (UV-vis) spectra of the as prepared pristine COF, Cu_2O NCs and all xCu@COF NCs have been collected on Varian Cary 300 UV-Vis Spectrophotometer.

Field Emission Scanning Electron Microscopy (FESEM) was measured on a ZEISS GeminiSEM500. Cu_2O NCs, COF and all xCu@COF NCs were observed directly without gold coating in nanoVP mode.

High Resolution Transmission Electron Microscopy (HRTEM) images were obtained using a Talos F200S Microscope (Thermo Fisher Scientific) operated at 200 kV. In this microscopy technique, a beam of electrons is transmitted through a specimen to form an image. A Ceta 16M camera (TEM mode) and a HAADF and BF detector (STEM mode; Scanning Transmission Electron Microscopy) were used to capture the images.

The sample was prepared on a 3 mm gold grid (Lacey, 400 mesh) by dropping 10 µl of the sample suspension (acetone-toluene mixture) onto it and air-drying it at room temperature. A Super-X G2 detector equipped with two silicon drift detectors (SDD) was used during the TEM analysis for energy dispersive X-ray spectroscopy (EDS) to determine the elemental composition with counting time of 60 seconds. EDS was also used for chemical characterization with compositional mapping in STEM mode.

Ar sorption measurements were performed at 87 K using an Autosorb-iQ-MP from Quantachrome. Prior to the analysis, the sample was activated at 120 ^{o}C for 24 h. Using the Ar adsorption isotherm, the surface area was calculated over a pressure range 0.05-0.1 = p/p_0 using Brunauer-Emmett-Teller (BET) methods.

Electrode Preparation

The electrodes for H-type cell electrochemical measurements were prepared on 2.5 cm^2 carbon paper (Alfa Aesar, Toray Carbon Paper, GGP-H-60). The stock solutions of as prepared catalysts were drop-casted on each side of the carbon paper to yield 50 µg on the electrode for each catalyst. After that, the electrodes were dried 1 hour in oven to ensure complete evaporation of ethanol.

Electrochemical Experiments

Electrocatalytic measurements were conducted in H-cell by using an Autolab (Metrohm) potentiostat equipped with an ion-exchange membrane (Selemion AMV, AGC) for the separation of the anodic and the cathodic compartments. Furthermore, a leak free Ag/AgCl reference electrode (LF-1, Alvatek) was placed near to working electrode in the cathodic compartment. A platinum gauze electrode (MaTecK, 3,600 mesh cm-2) assisted as the counter-electrode in the anodic compartment. 0.1 M $KHCO_3$ was used as an electrolyte (Alfa Aesar, 99.7–100.5%), was purified with cation exchange resin (Chelex 100 Resin, Bio-Rad) and purged with 99.99% CO_2 for 20 mins. The products were determined for the static CO_2RR by taking an aliquot from electrolyte after every 15 min.

Liquid products were analyzed by using high performance liquid chromatograph (shimadzu prominence), equipped with a refractive index detector and a NUCLEOGEL SUGAR 810 column and, and a liquid GC (Shimadzu 2010 plus), armed with a fused silica capillary column and a flame ionization detector. While, gaseous products were detected ans quantified by online gas chromatography (GC, Agilent 7890B), equipped with the thermal conductivity detector and a flame ionization detector. Each reported data was measured at least three time hence, presented with average values.

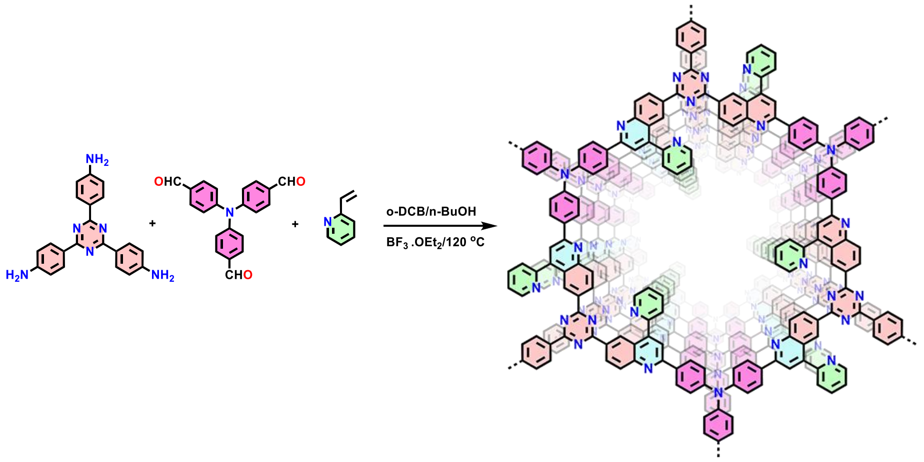
Section 2. Synthesis of Cu_2O, COF and xCu@COF

Synthesis of Cu_2O Nanocubes

Cu_2O nanocube was fabricated by wet chemical reduction method according to the previous report. In a typical synthesis anhydrous $CuCl_2$ (0.171 g) was dissolved into 100 ml water. Then the solution was stirred for 15 minutes. After that, 10 mL NaOH aqueous solution (2.0 M) was then added drop-wise into the above light green solution. After vigorous magnetic stirring for 30 minutes, 10 mL ascorbic acid solution (0.6 M) was added to above made solution. The color of the liquid changed gradually from blue to turbid red. The mixture was aged for 3 h. All procedures were carried out at the temperature of 55 °C under constant vigorous magnetic stirring. The resulting precipitate was collected from the solution by centrifugation at 6,000 r.p.m. for 5 min and washed several times with deionized water and ethanol.

Synthesis of COF

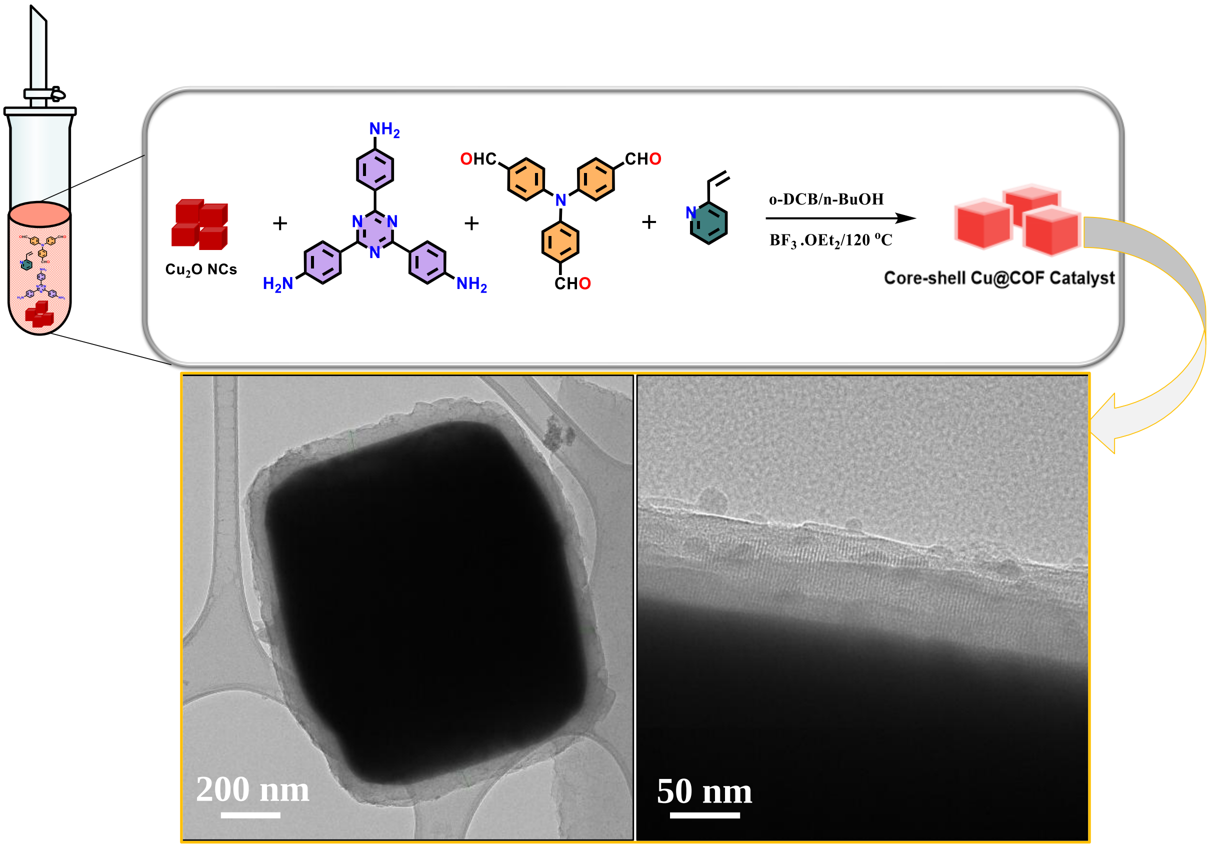
A Pyrex glass Schlenk tube (15 mL) was charged with 2,4,6-Tris(4-aminophenyl) triazine (60 mg, 0.15 mmol), 4,4',4''-trinitrilotribenzaldehyde (56 mg,0.15 mmol), 2-vinylpyridine (60 µL, 0.6 mmol), $BF_3 \cdot OEt_2$ (10 µL, 0.1 mmol) and acetic acid (100 µL, 6M) in o-dichlorobenzene (o-DCB)/n-BuOH (2 / 2 mL). The mixture was first sonicated for 0.5 h to form bulk solid and then shlenk tube flashed frozen at 77 K (liquid N_2 bath) and degassed by three times of freeze-pump-thaw cycles. The internal pressure was evacuated to 10^{-3} mbar. Afterwards, the tube was sealed and heated at 120 °C for 3 days. The bright yellow precipitate was washed with acetone and tetrahydrofuran several times and collected by filtration. Finally, the powder was dried in a normal oven at 80 °C. Yield = 89.7 % (93 mg). Anal. Calcd. (%): C, 81.10; H, 3.89; N, 15.01. Found (%): C, 78.85; H, 5.10; N, 16.05.



Scheme 1. Synthesis of COF via Povarov reaction.

Synthesis of core shell xCu@COF

Core shell Cu@COF nanocubes were simply synthesizes by one pot, wet-chemical process in the Pyrex glass Schlenk tube. COF organic precursors with the different ratios of Cu_2O cubes added to the Schlenk tubes. 3 mL of *n*-BuOH and 3mL of *o*-dichlorobenzene with 2-vinylpyridine (60 µL, 0.6 mmol), $BF_3.OEt_2$ (10 µL, 0.1 mmol) and acetic acid (100 µL, 6M) were also added on the above Schlenk tubes as a solvent. The mixture was sonicated to 30 mins until a homogenous solution was obtained. Schlenk tube underwent degassing and evacuation process three times by freeze-pump-thaw cycles with flashing frozen at 77 K (liquid N_2 bath). After that, the Schlenk tube with internal pressure 10^{-3} mbar were sealed and heated at 120 ºC for 3 days. The red precipitates were washed with solvent mixture (MeOH, DME and Acetone) several times. Finally, the red powder was collected after Soxhlet extraction for 12h and dried at 80ºC for 6h.



Scheme 2. A schematic diagram of the Core- shell xCu@COF electrocatalyst synthesis.

Section S3. FESEM and HRTEM images of Cu_2O, COF and xCu@COFs

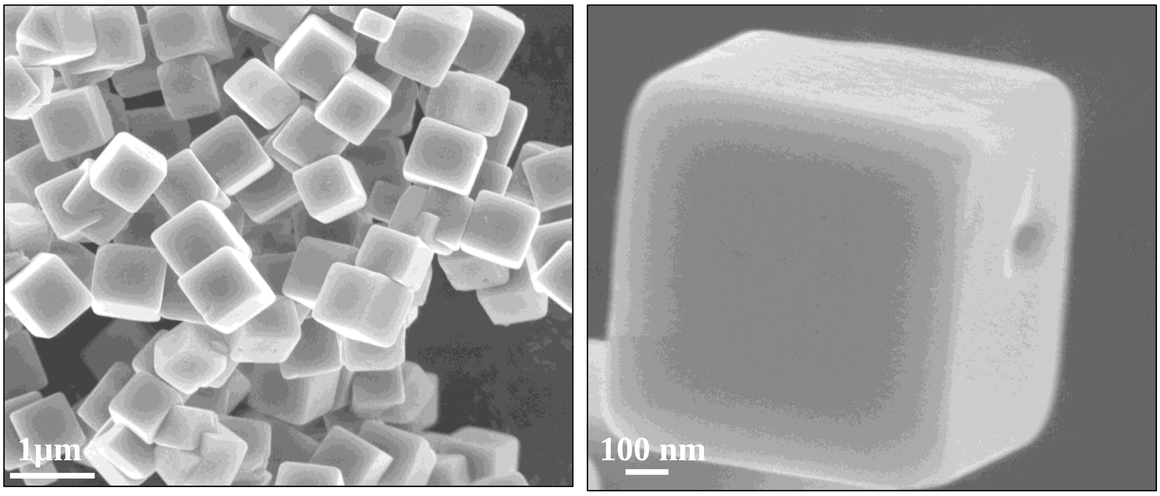


Figure S1. FESEM image of Cu_2O NCs.

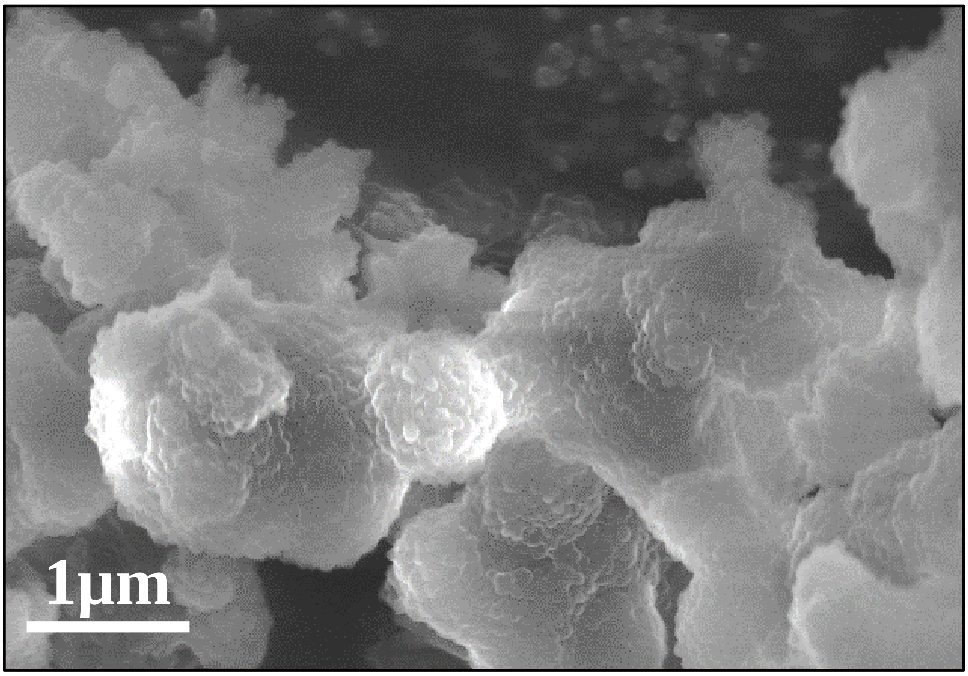


Figure S2. FESEM image of COF.

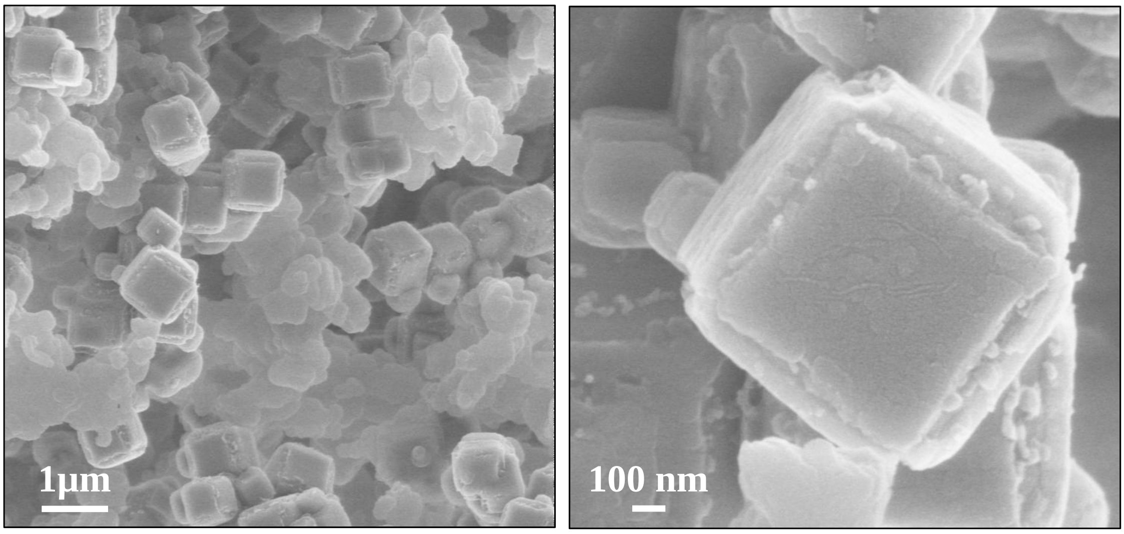


Figure S3. FESEM image of 150Cu@COF**.**

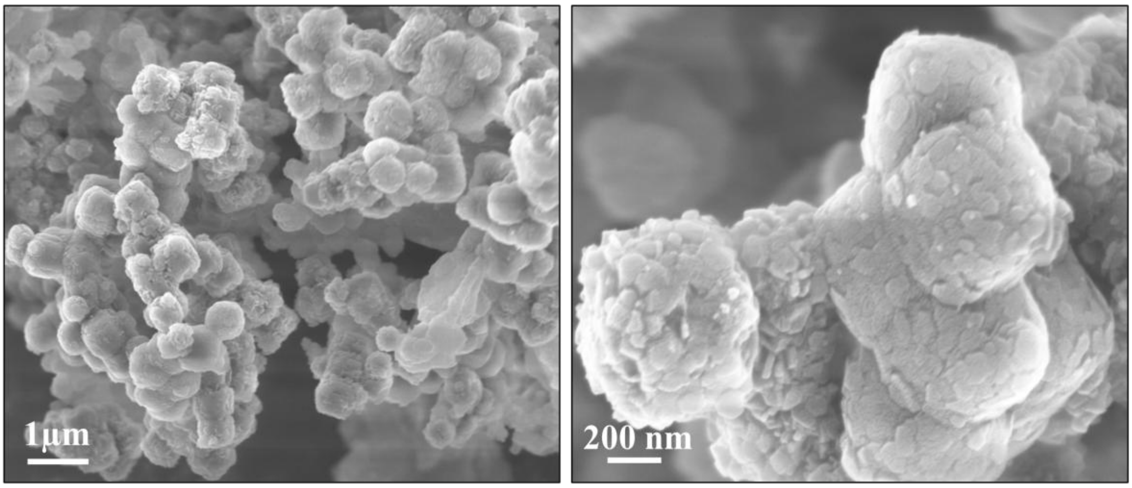


Figure S4. FESEM image of 250Cu@COF.

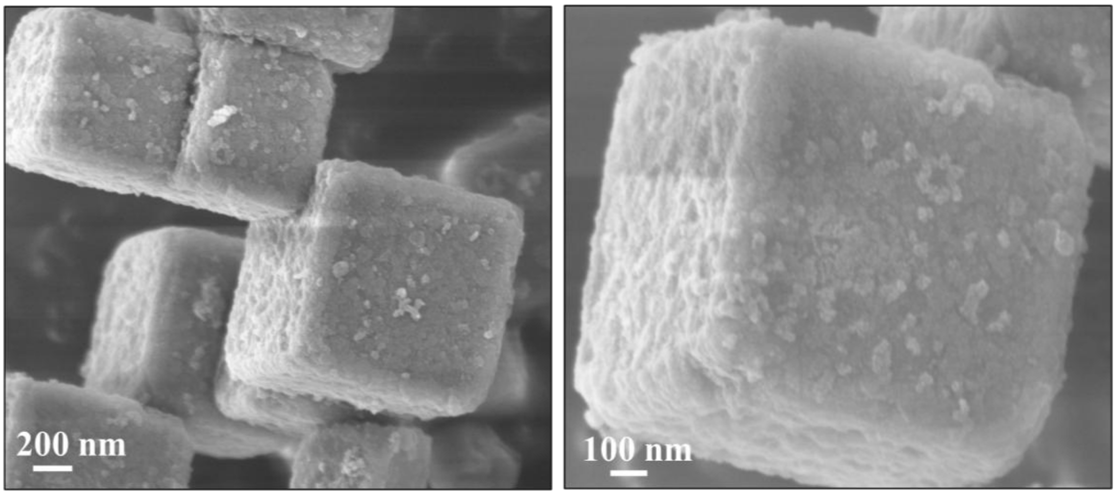


Figure S5. FESEM image of 300Cu@COF.

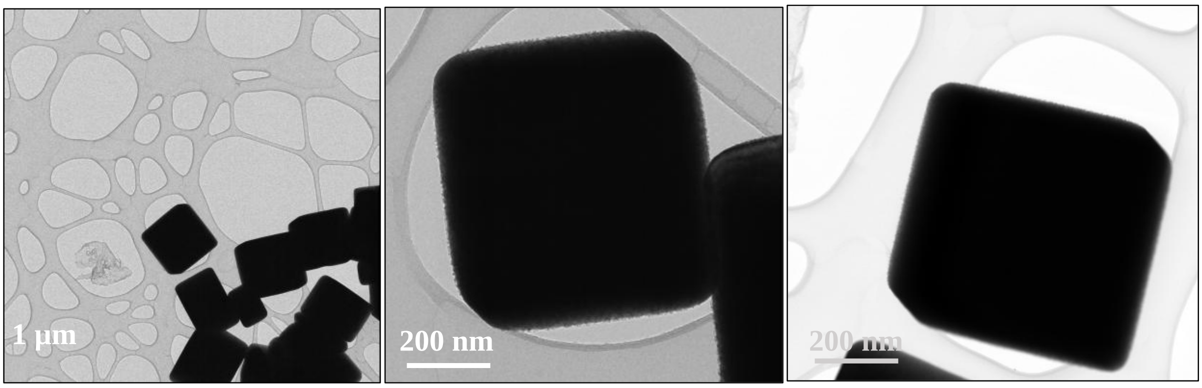


Figure S6. HRTEM image of Cu_2O NCs.

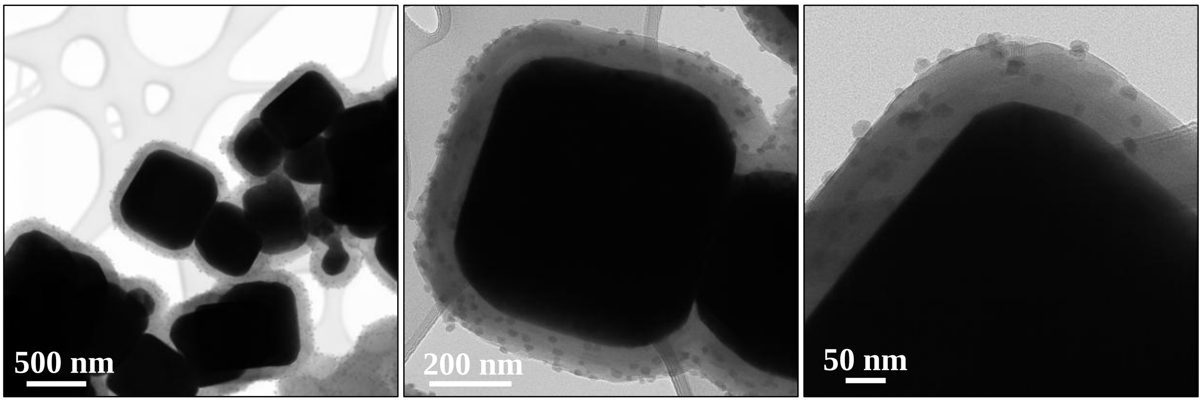


Figure S7. HRTEM image of 150Cu@COF with the shell thickness of 75± 2 nm.

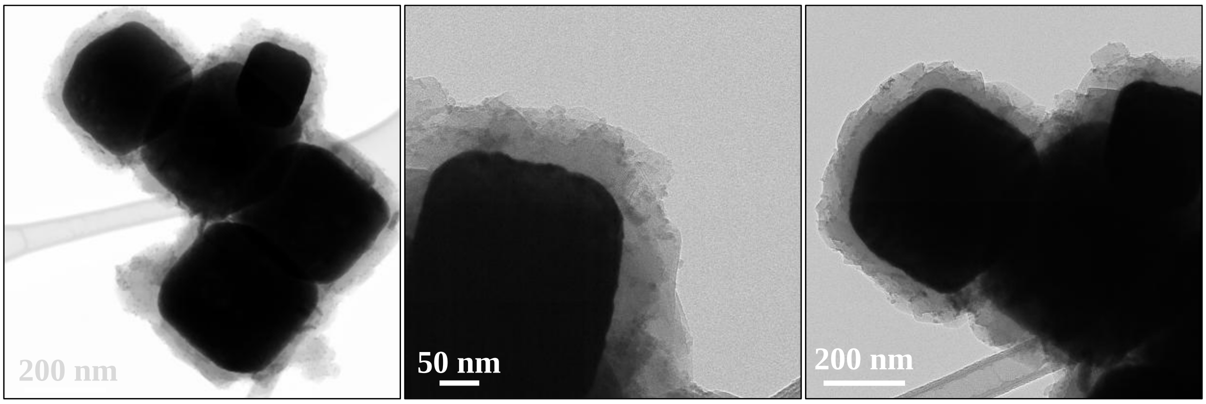


Figure S8. HRTEM image of 200Cu@COF with the shell thickness of 68 ± 3 nm.

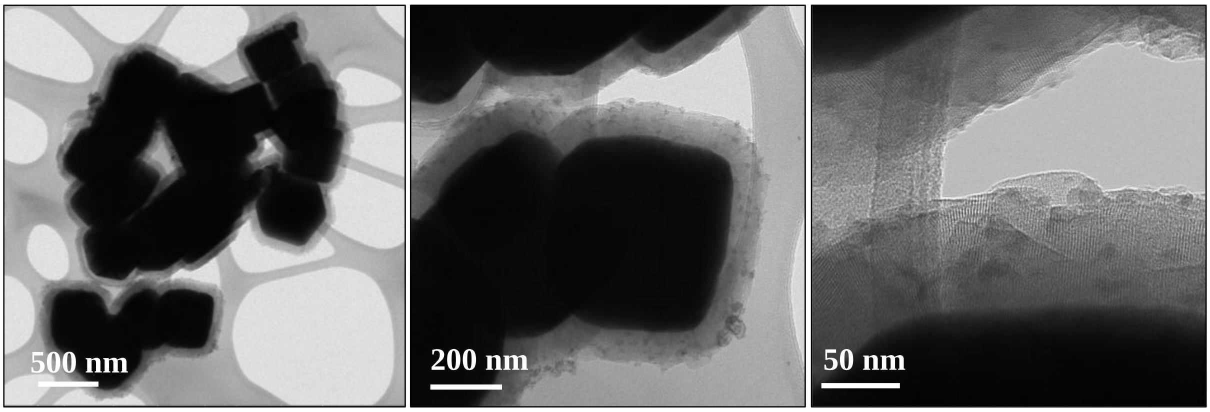


Figure S9. HRTEM image of 250Cu@COF with the shell thickness of 62 ± 4nm.

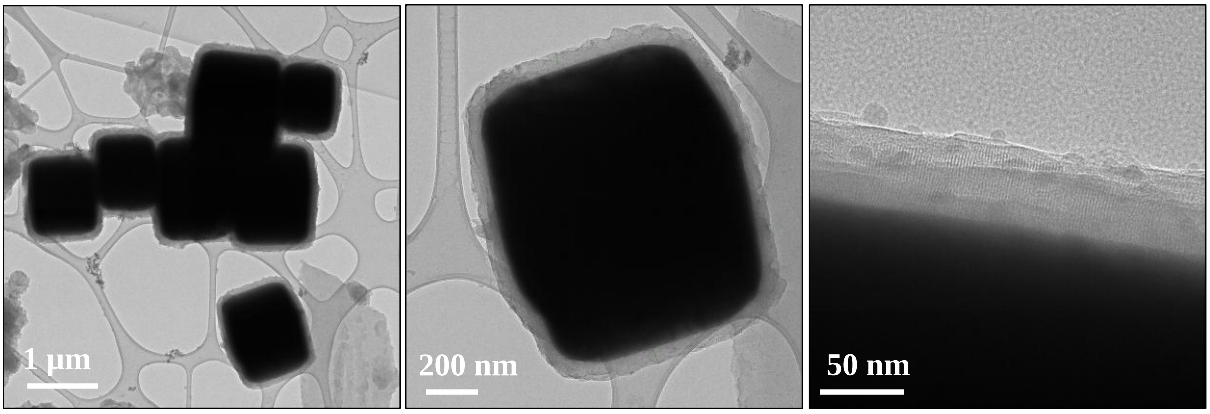


Figure S10. HRTEM image of 300Cu@COF with the shell thickness of 55 ± 2nm.

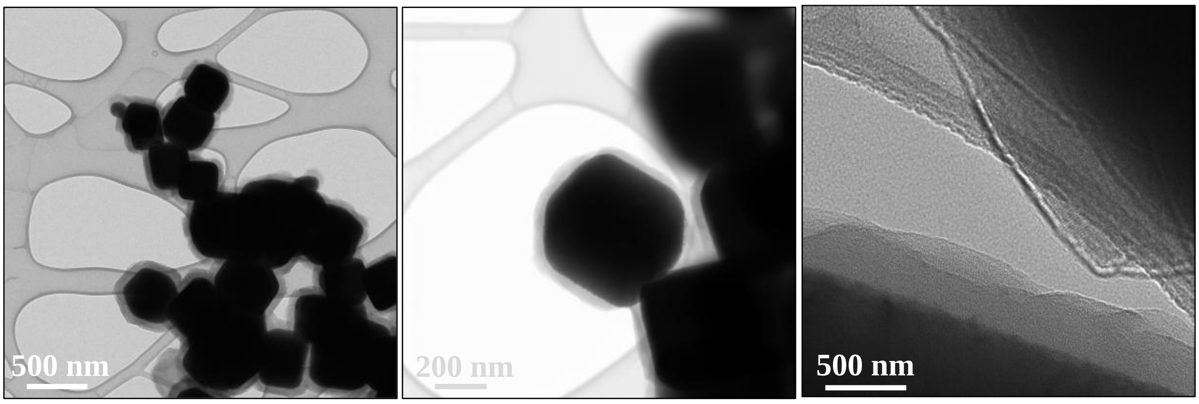


Figure S11. HRTEM image of 350Cu@COF with the shell thickness of 51 ± 2nm.

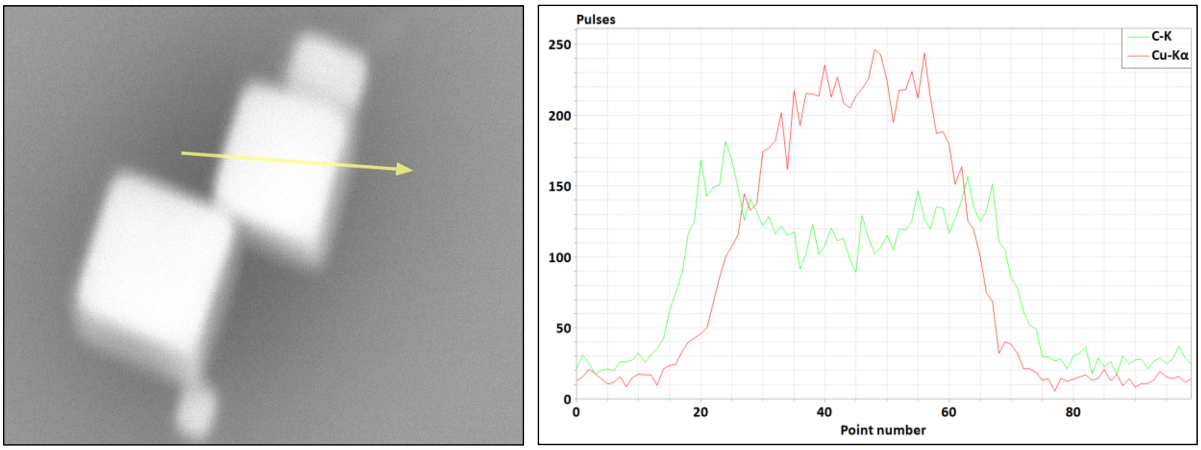


Figure S12. Line scanning Cu_2O NCs, COF and 300Cu@COF NCs.

Section S4. XPS spectrum of Cu_2O, Cu_2O@COFs

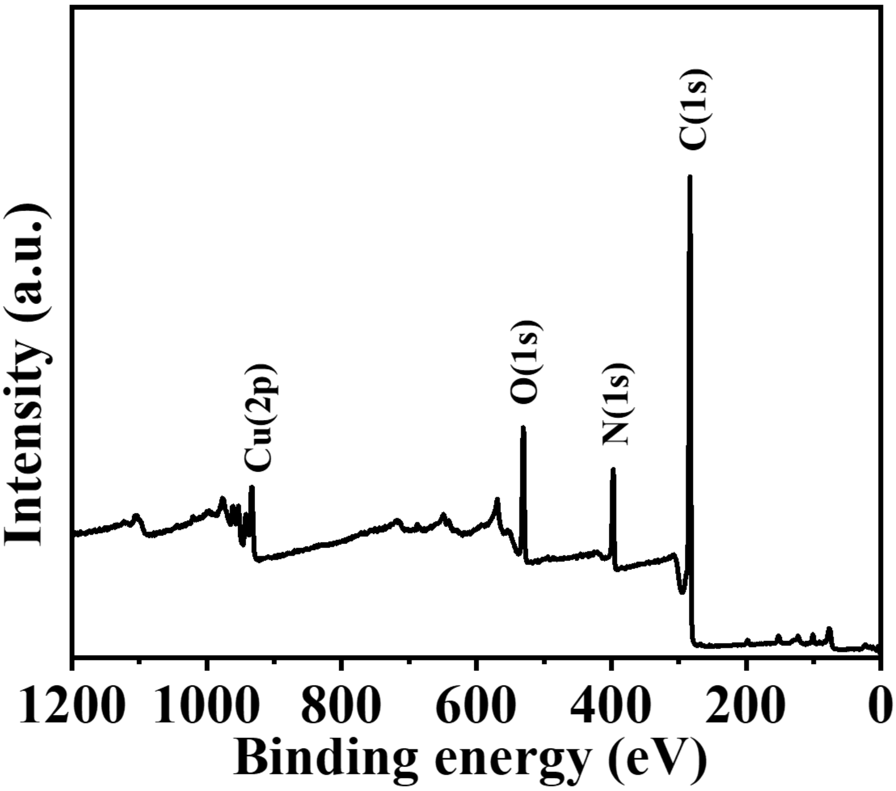


Figure S13. XPS survey spectrum of 300Cu@COF.

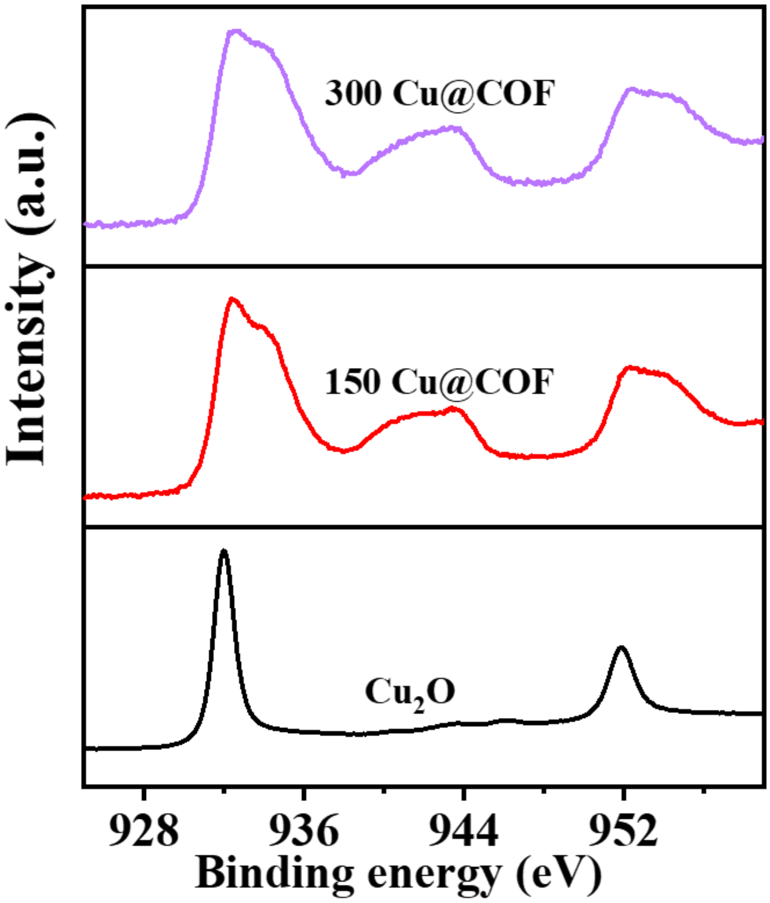


Figure S14. Cu(2p) XPS spectrum of Cu_2O and 150-300 Cu@COF.

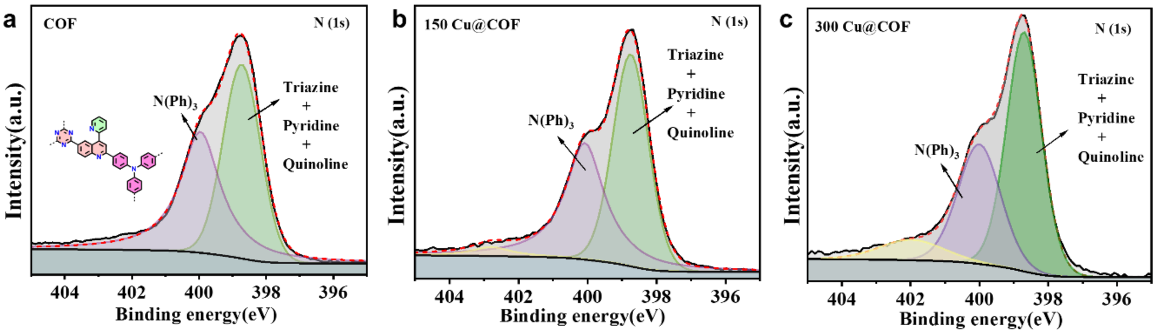


Figure S15. N(1s) XPS spectra of COF and xCu@COF electrocatalysts.

Catalyst	SA_{BET}
Cu_2O	132 m^2/g
350Cu@COF	386 m^2/g
300Cu@COF	334 m^2/g
250Cu@COF	414 m^2/g
200Cu@COF	579 m^2/g
150Cu@COF	710 m^2/g
COF	1720 m^2/g

Table S16: BET surface area of Cu_2O NCs, COF and core-shell xCu@COF electrocatalysts measured at 77 K.

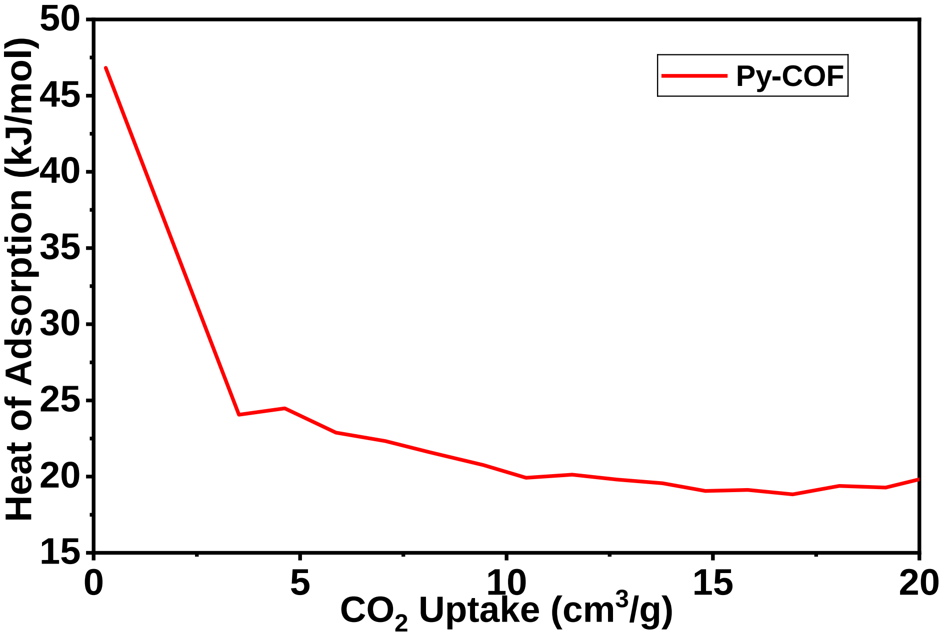


Figure S17: Isosteric heat of CO_2 adsorption (Qst) of Py-COF derived from adsorption isotherms collected at 273 and 298 K.

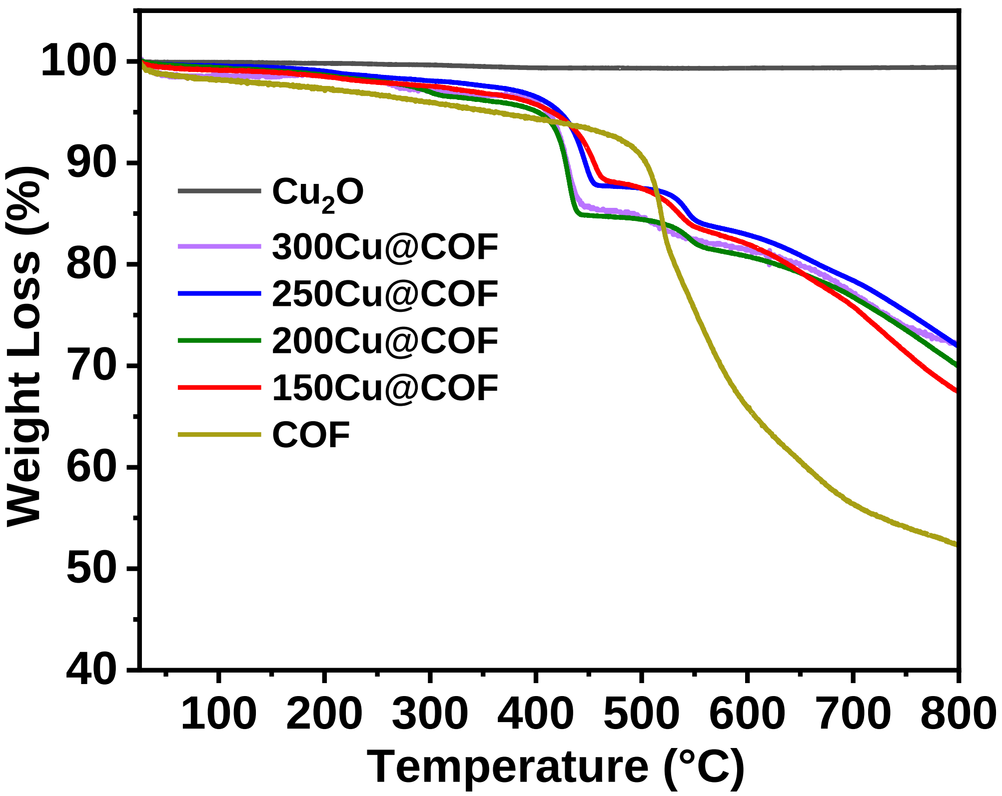


Figure S18. TGA of Cu_2O, COF and core-shell xCu@COF electrocatalysts.

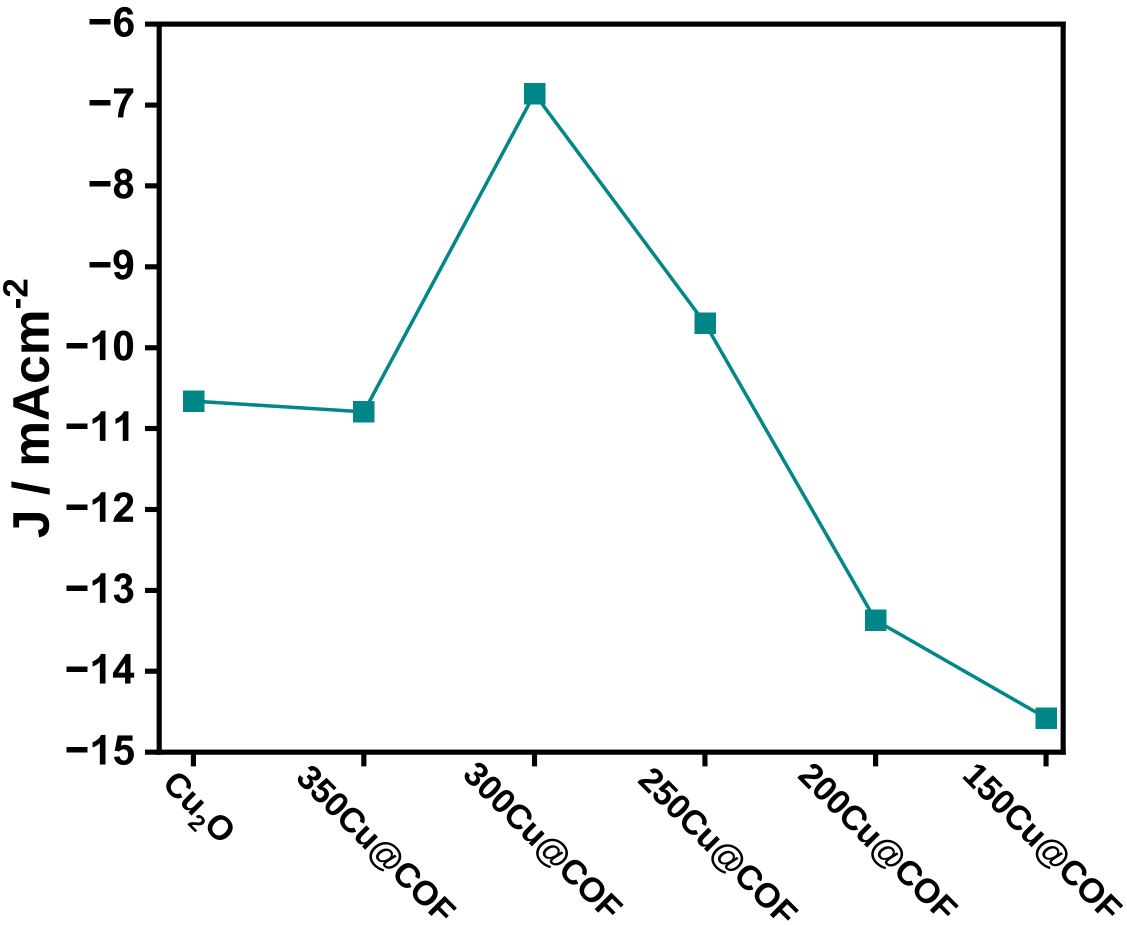


Figure S19. Current densities of core-shell xCu@COF electrocatalysts.

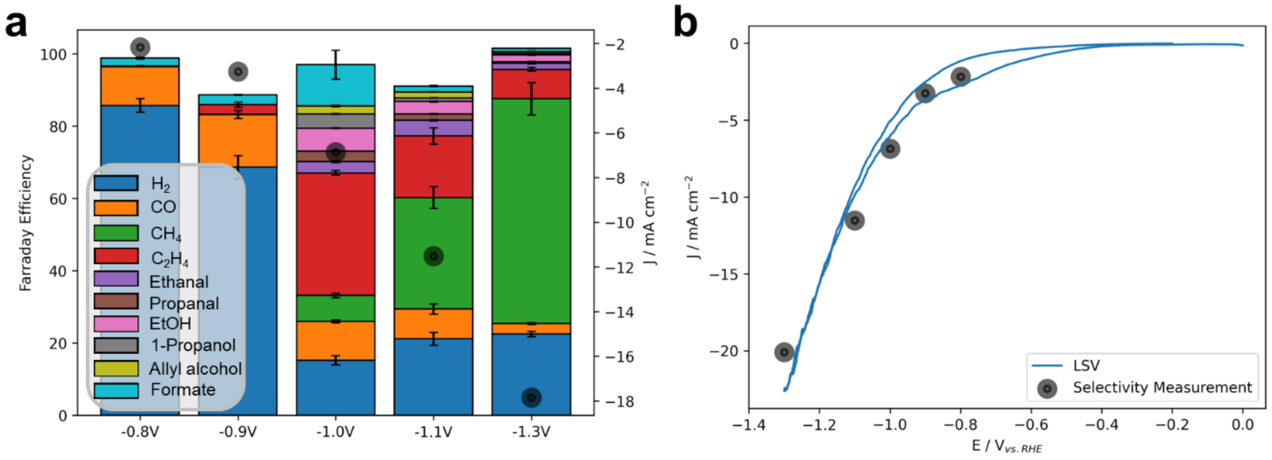
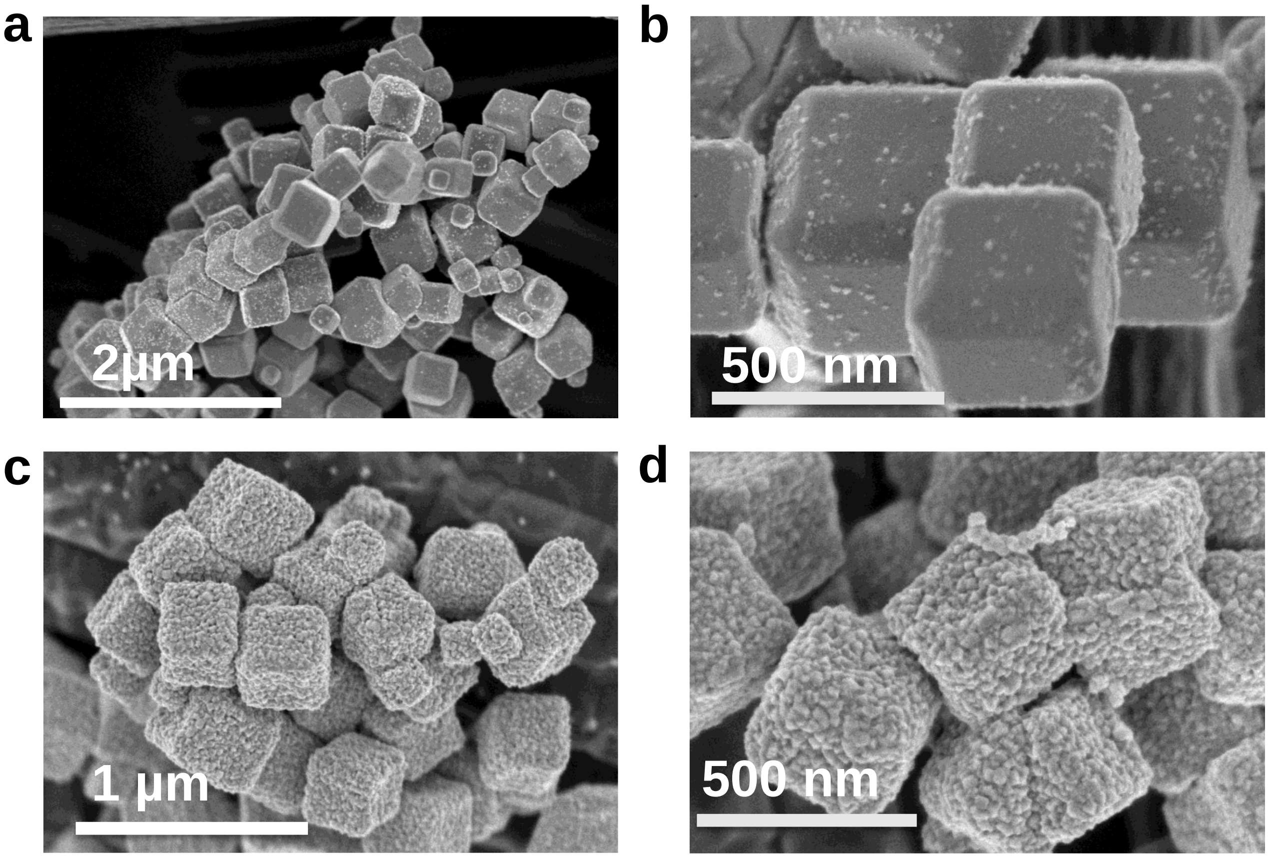
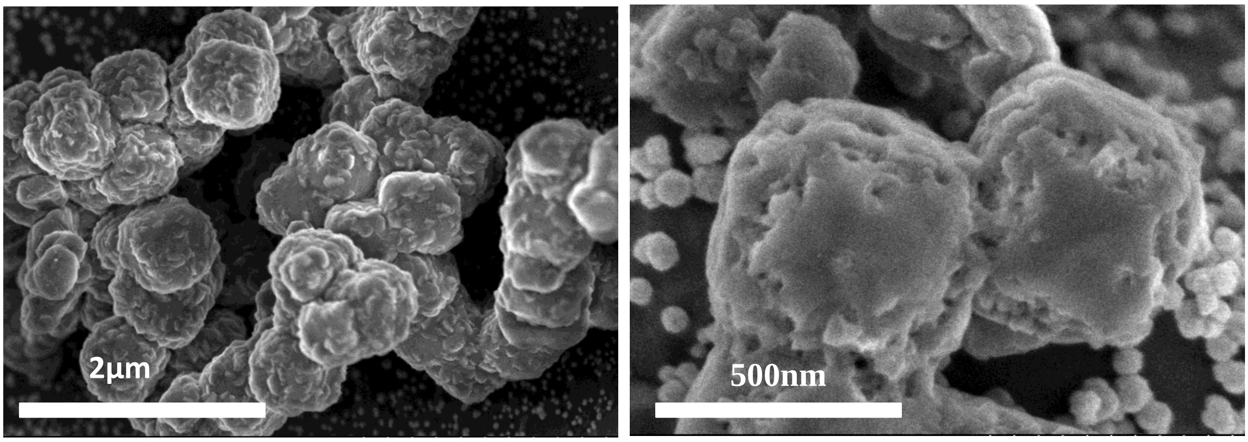


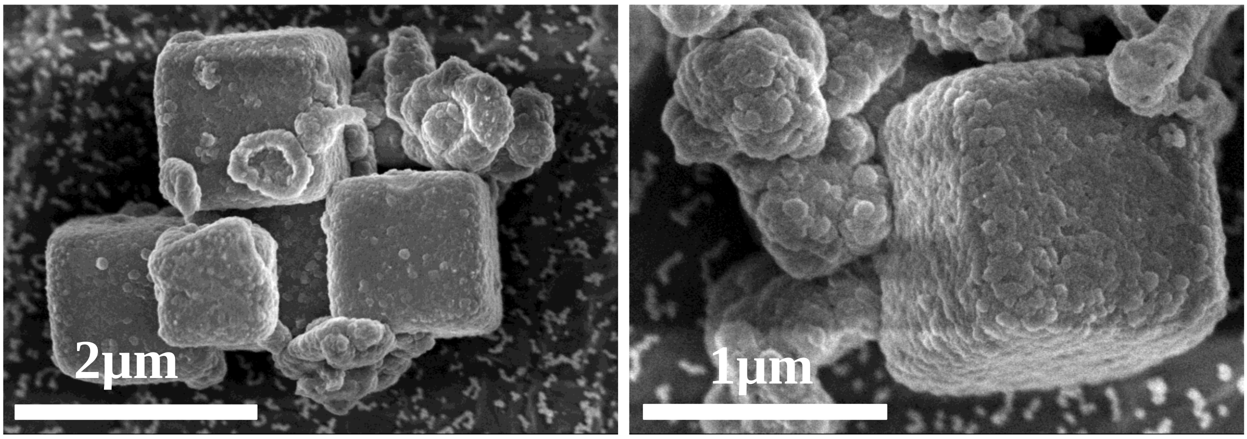
Figure S20. (a) Faradaic efficiencies and current densities at different potentials (–0.8 to –1.3 V vs RHE). (b) Linear sweep voltammetry (LSV) curve, showing the catalytic current response as a function of applied potential of core-shell 300Cu@COF.



S21. SEM images of Cu_2O (a-b) before and (c-d) after electrocatalytic reaction.



S22. SEM images of 150Cu@COF after electrocatalytic reaction.



S23. SEM images of 300Cu@COF after electrocatalytic reaction.