Supplementary Information (SI) for ChemComm.

Supplementary Information

Interfacial regulation of CO_2 electroreduction via CuAu nanoclusters decorated on hierarchically restructured bismuth nanoarchitectures

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Experimental Methods

Chemicals and reagents

Bismuth chloride ($BiCl_3$, 98%, Sigma-Aldrich), tetrachloroauric (III) acid trihydrate ($HAuCl_4.3H_2O$, 99%, Sigma-Aldrich), (R)-4-benzylthiazolidine-2-thione (R-BTT, 97%, Sigma-Aldrich), triethylamine (Et_3N), and acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), methanol (CH_3OH), hydrochloric acid (HCl, 37%) and Copper foam (CuF) substrates were acquired from Xiamen Zopin New Materials Ltd (thickness 2 mm, porosity 95-98%,). Commercial ethanol was used after distillation. DI water from the ultrapure water system Milli-Q. was used.

Pretreatment of metal foams

To get rid of the oxide layer, copper foam was treated first. A piece of copper was sonicated in 3 M HCl for 15 minutes. Next step was removal of any possible organic contaminants; it was cleaned three times with water and then three times with ethanol. These metal foams were used for the deposition or reactions after being vacuum-dried for two hours at 60 °C.

Synthesis of Bi-Based Catalyst

3 mmol of $BiCl_3$ and 5 mL of triethylamine (TEA) were separately dissolved in 25 mL of ultrapure water to obtain homogeneous solutions. The TEA solution was then added dropwise to the $BiCl_3$ solution under vigorous stirring. The resulting mixture was continuously stirred at room temperature for 6 h, followed by centrifugation. Obtained precipitates were then rinsed with water and dried for 5 h at 80 °C in vacuum oven.

The resulting dried powder was named as Bi-complex. This obtained precursor was then annealed in a tubular furnace at 400 °C for 2 h under a N_2 atmosphere, using a ramping rate of 5 °C min^{-1}.

The annealed sample was denoted as An-Bi. An-Bi was then electrochemically reduced using chronoamperometry at −1.0 V for 3 h to induce electrochemical restructuring to form hierarchically restructured bismuth nanoarchitectures (HR-Bi) catalyst.

Synthesis of Fluorescent Cu–Au Alloy Nanoclusters (CuAuNCs)

8 mg of the ligand R-BTT was dissolved in 5 mL of acetonitrile. Subsequently, 10 mg of the copper precursor $Cu(CH_3CN)_4BF_4$ pre-dissolved in 1 mL of acetonitrile was added and the mixture was stirred for 10 min to allow initial complex formation. Separately, 12.74 mg of $HAuCl_4$ was dissolved in 7.96 mL of methanol, and 5 mL of this solution was added to the reaction mixture, resulting in a yellow-colored solution. After stirring for 1–2 min, 6 mL of dichloromethane (DCM) was added, followed by further stirring for 5–10 min. Subsequently, 30 μL of triethylamine was added, causing an immediate color change from yellow to colorless, indicative of reduction and Cu–Au alloy nanocluster formation. After an additional 10 min, 5 mL of methanol was added to reduce the solubility of the nanoclusters and induce aggregation-induced emission (AIE). Within approximately 30 min, bright green, fluorescent precipitates were observed under UV illumination. Continued stirring for several hours led to increased precipitate yield and fluorescence intensity, confirming the successful formation of fluorescent Cu–Au alloy nanoclusters (CuAuNCs). The CuAuNCs were collected by centrifugation, washed three times with acetonitrile and once with methanol to remove residual gold salts, and finally dried under vacuum to obtain the purified product.

Characterization.

SEM images were acquired on a Nova Nano SEM 450 Field Emission Scanning Electron Microscope operating at an accelerating voltage of 10 kV. High-resolution transmission electron microscopy (HRTEM) and transmission electron microscopy-energy dispersive X-ray spectroscopy (TEM-EDX), selected area electron diffraction (SAED), and bright-field and dark-field TEM analyses were performed in a TEM (Tecn F20) G2 30 model with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) studies were performed using Thermo Scientific K-Alpha XPS instrument with Al K_{α} X-ray monochromatic beam. The binding energy data were calibrated relative to the C 1s signal at 284.6 eV. X-ray diffraction (XRD) measurements for the crystallographic study of electrodes were carried out on a Bruker 2D PHASER diffractometer with Cu Kα radiation (l = 1.5418 Å).

Electrochemical experiments

The CO_2R experiments were performed in a two-compartment H-type electrochemical cell with a three-electrode setup. The electrolyte was 0.5 M $KHCO_3$ solution for cathodic compartment and 1 M KOH for anodic compartment separated by a Nafion 117 membrane. $KHCO_3$ solution in cathodic compartment was continuously purged with CO_2 gas. The flow rate of CO_2 was set to 20 cc/min under standard conditions for all the experiments. In conventional 3 electrode setup, synthesized catalysts were used as working electrodes whereas, Pt wire and SCE were used as counter and reference electrodes, respectively. The LSV study was done at a scan rate of 5 mV/s both in Ar and CO_2-saturated environments. Electrochemical impedance spectroscopy (EIS) was carried out to estimate the charge transfer resistance. The electrolyte resistance was measured in a frequency range from 10 MHz to 0.1 Hz with an amplitude of 5 mV.

$$E_{RHE} = E_{Hg2/HgCl2} + 0.244 + 0.059 \times pH \qquad (3)$$

$$E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059 \times pH \qquad (4)$$

The Faradaic efficiency (FE) of the liquid product formate ($HCOO^{-}$) was calculated using equation.

$$FE_{HCOO^-} = \frac{n*F*V*c}{1000*M*Q} \quad (6)$$

where n is the transfer electron number, F is the Faraday efficiency constant (96485 C mol^{-1}), c is the mass concentration of the acid root generated by the reaction (in mg L^{-1}), V is the electrolyte solution volume (in L), M is the molar mass of formic acid (46.03 g mol^{-1}), and Q is the total amount of charge consumed by the entire reaction as monitored by the electrochemical workstation (in coulombs).

The half-cell energy conversion efficiency (CEE, also called cathodic energy efficiency) is calculated using equation

$$CEE_{HCOO^-} = \frac{(1.23 - E_{formate}) * FE_{formate}}{1.23 - E_{cathode}} \quad (7)$$

where $E_{formate}$ of –0.199 V_{RHE} is the standard potential of the formate formation. $FE_{formate}$ is the measured formate Faradaic efficiency. $E_{cathode}$ is the applied potential vs. RHE.

To ensure repeatability and reduce experimental error, every electrochemical measurement was carried out three times.

Supporting figures

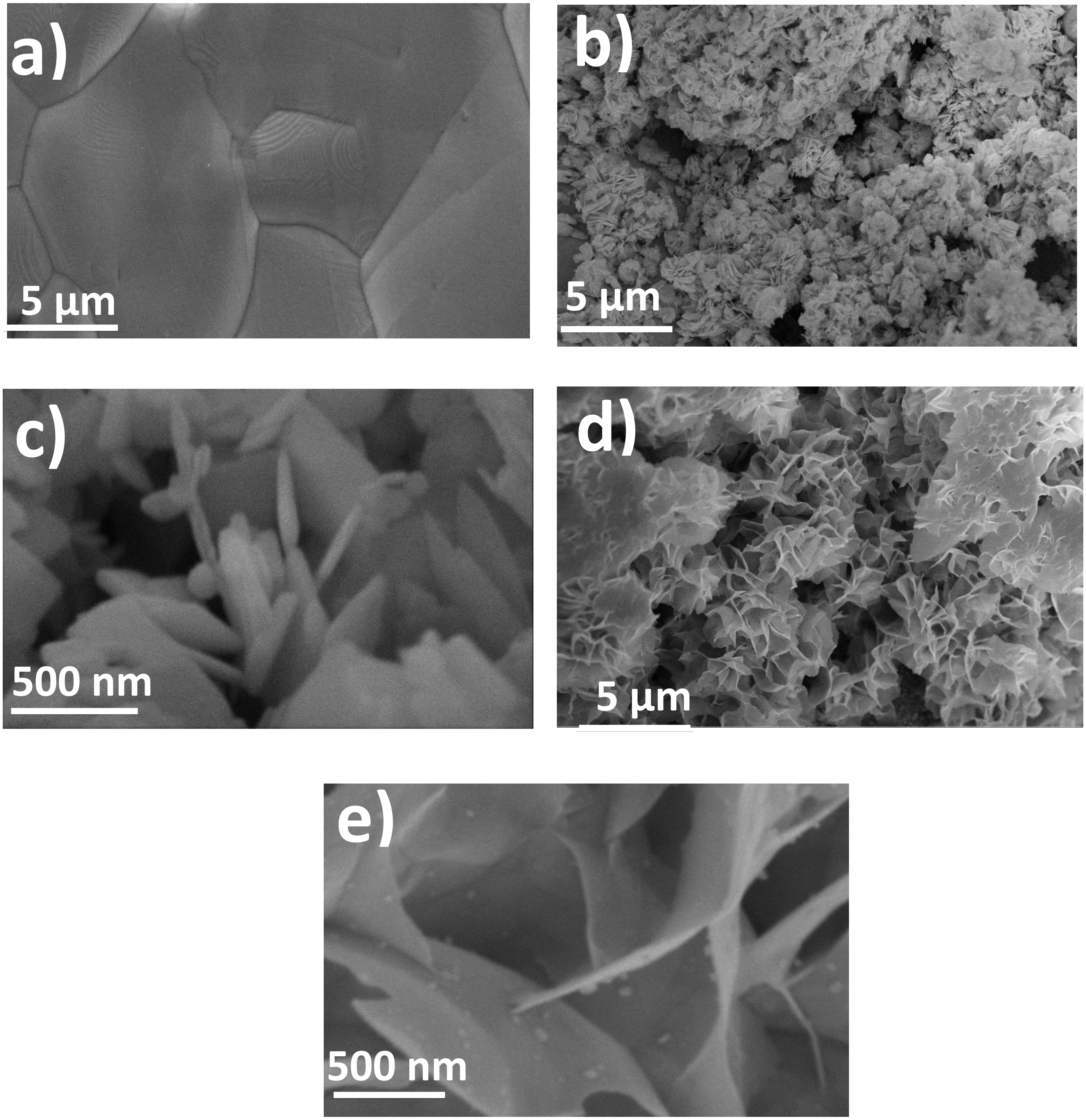

Figure S1 (a) FE-SEM of bare copper foam (b,c) FE-SEM of An-Bi (d,e) FE-SEM of HR-Bi

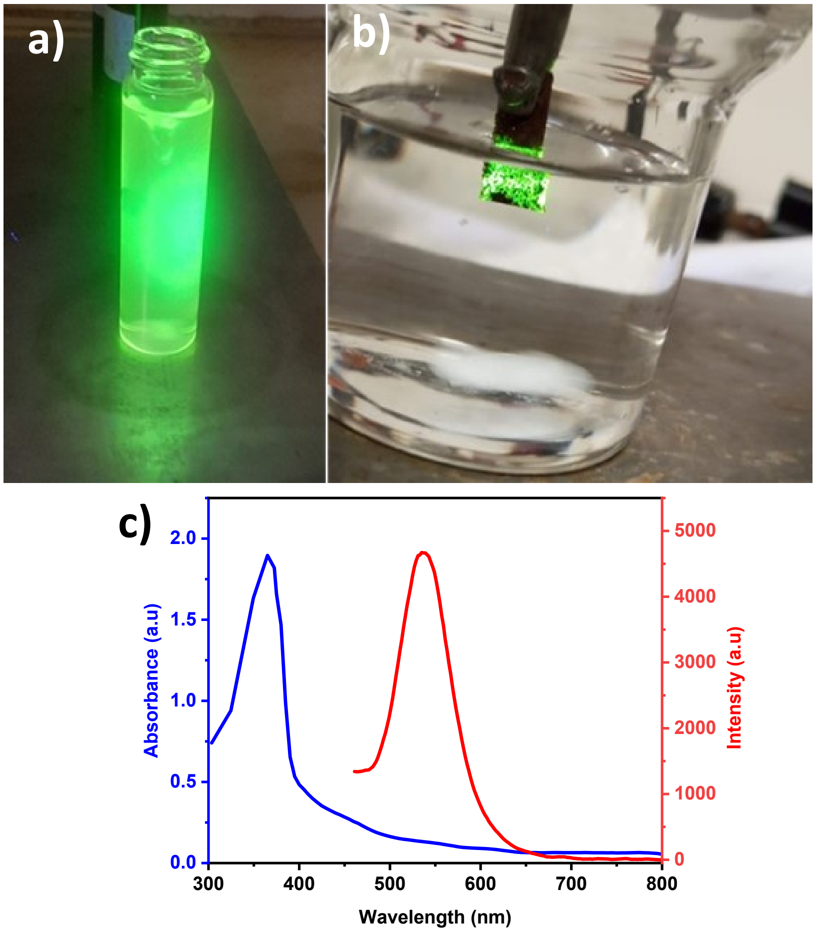

Figure S2 (a) Photoluminescence in CuAuNCs in methanol under UV light, (b) CuAuNCs coated electrode under UV light, (c) UV studies (blue) showing absorbance at 365 nm and PL studies (red) showing emittance at 536 nm.

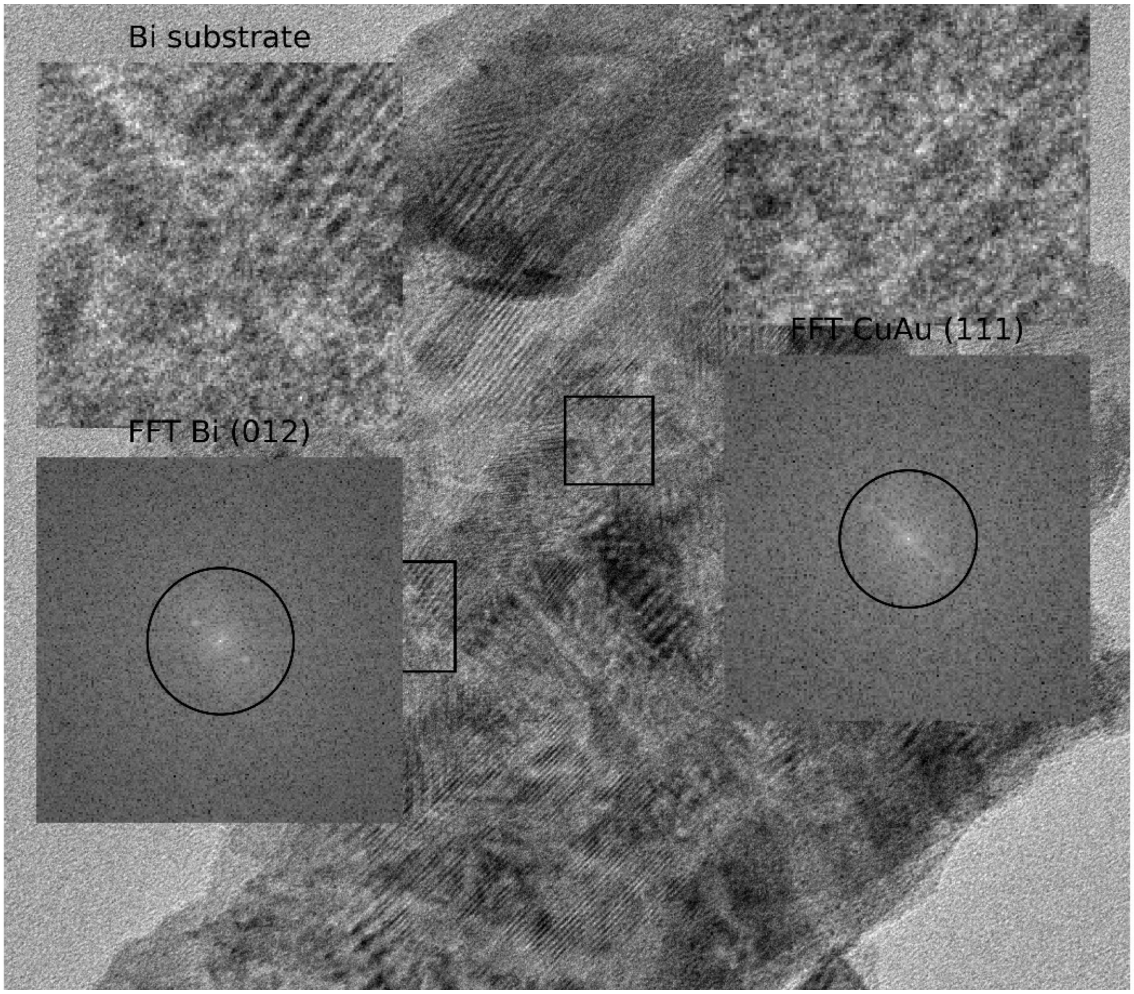

Figure S3 HR-TEM of CuAuNCs/HR-Bi with corresponding FFT showing lattice fringes of 0.224 nm corresponding to CuAu (111) and 0.328 nm assigned to Bi (012), confirming alloy nanocluster formation and crystalline Bi support.

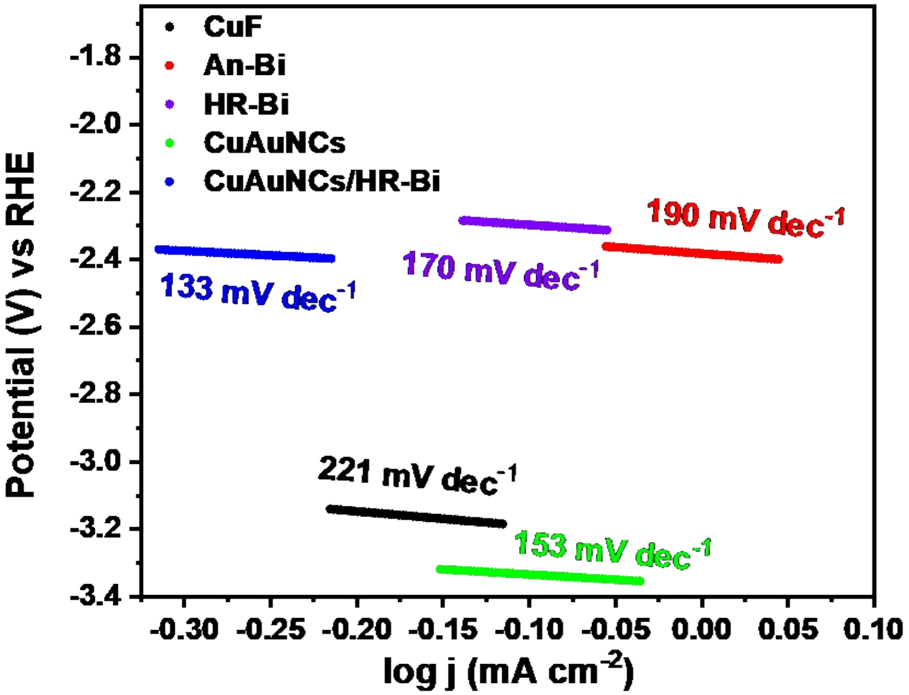

Figure S4 Tafel slope of catalysts showing reaction kinetics of CO_2RR.

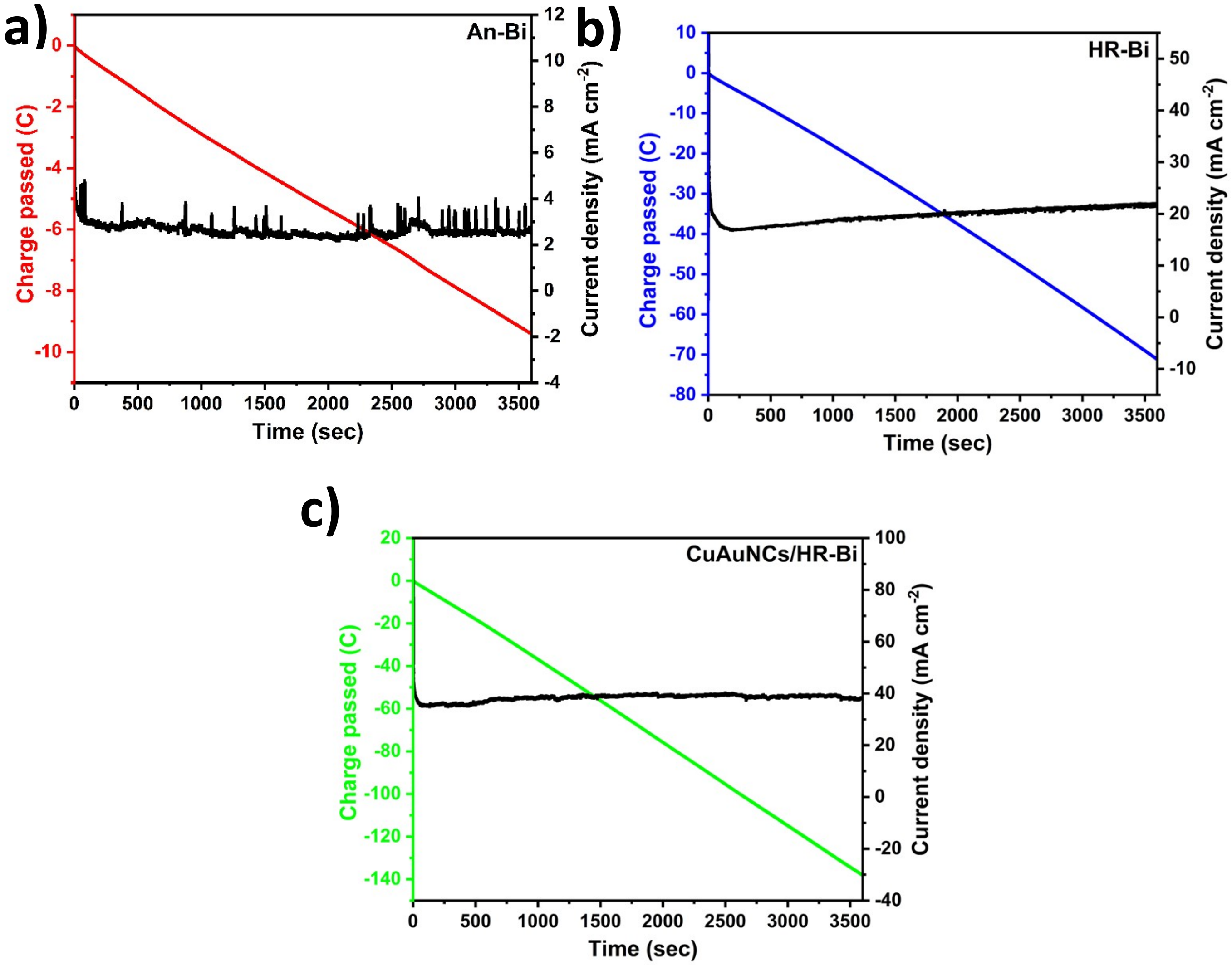

Figure S5 Controlled potential coulometry test for CO_2 reduction using (a) An-Bi (b) HR-Bi and (c) CuAuNCs/HR-Bi as cathode in 0.5 M $KHCO_3$.

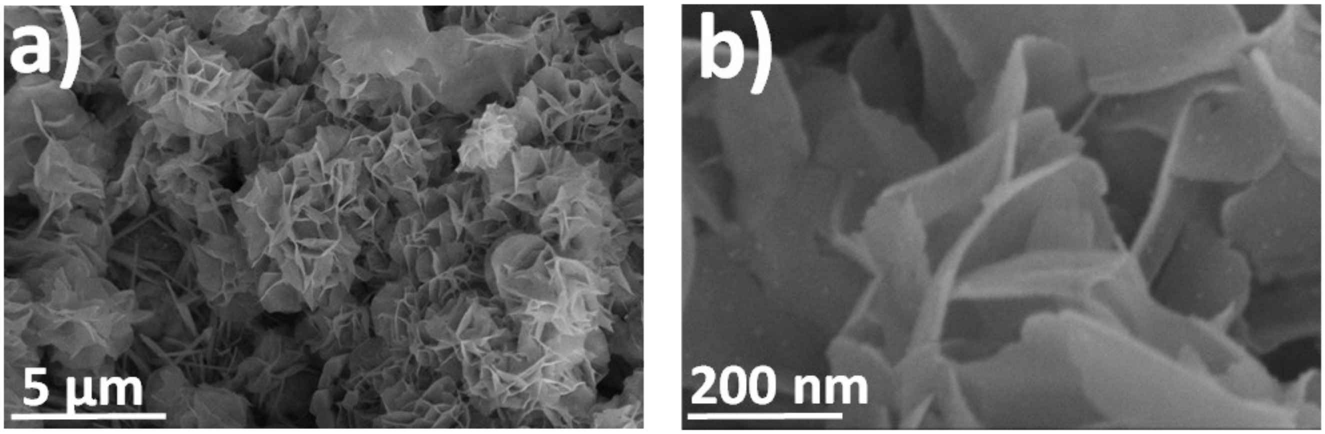

Figure S6 FE-SEM of CuAuNCs/HR-Bi after electrochemical activity.

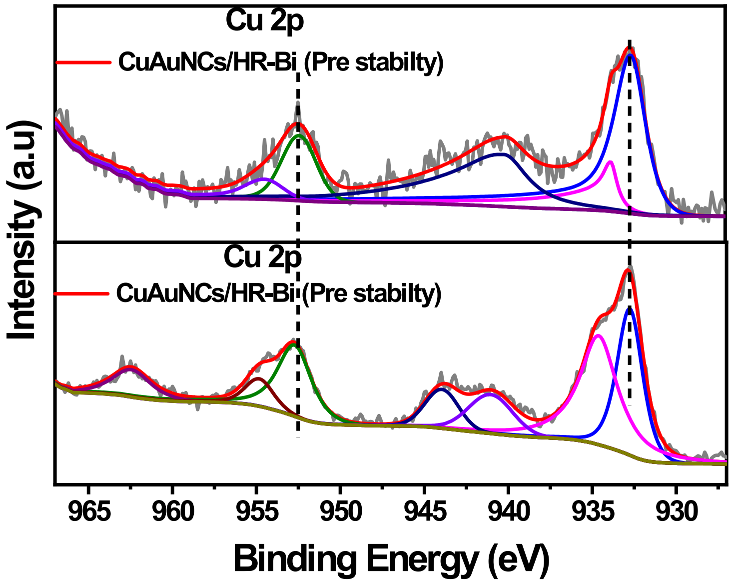

Figure S7 Cu 2p XPS spectra of catalyst CuAuNCs/HR-Bi before and after electrochemical activity.

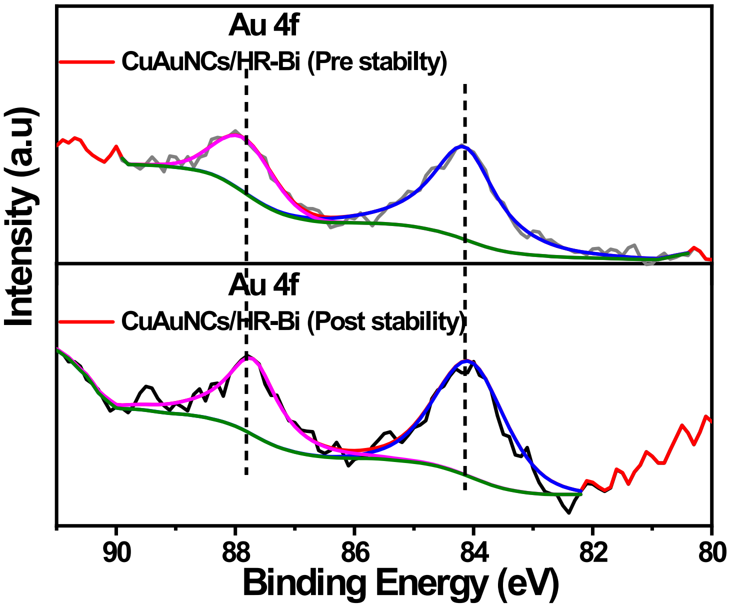

Figure S8 Au 4f XPS spectra of catalyst CuAuNCs/HR-Bi before and after electrochemical activity.

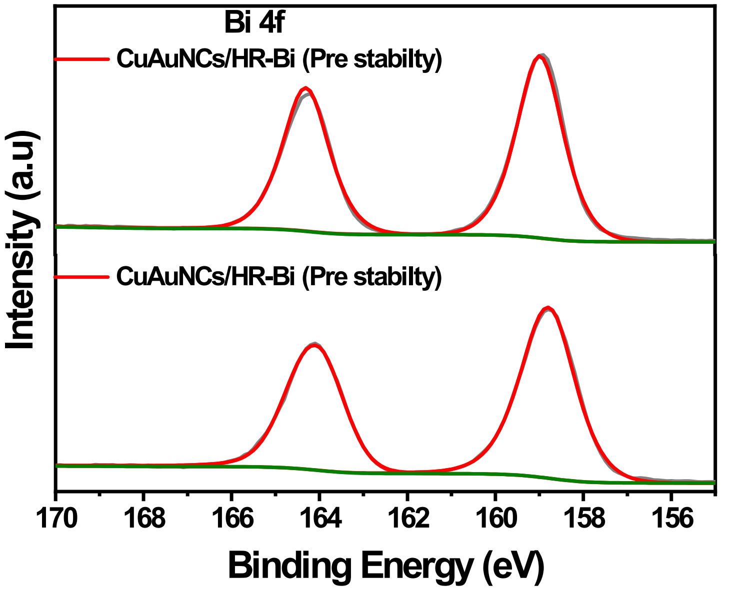

Figure S9 Bi 4f XPS spectra of catalyst CuAuNCs/HR-Bi before and after electrochemical activity.

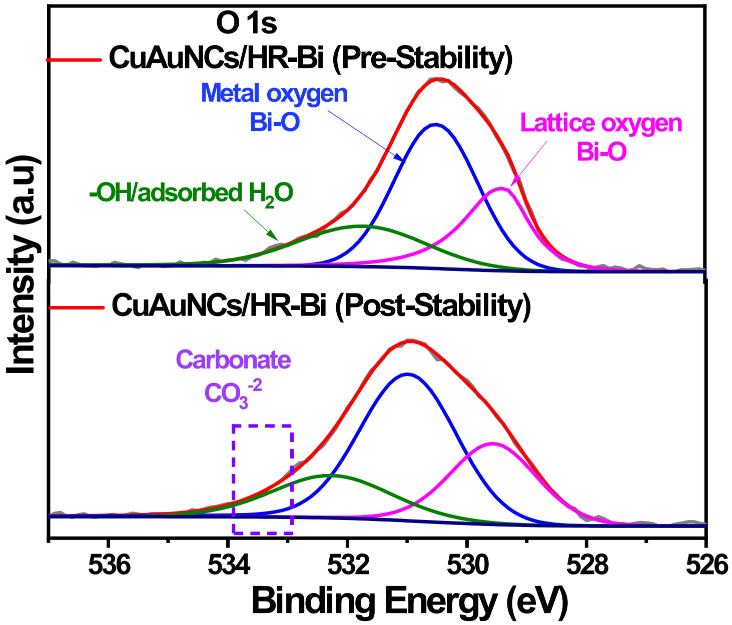

Figure S10 O 1s XPS spectra of catalyst CuAuNCs/HR-Bi before and after electrochemical activity.

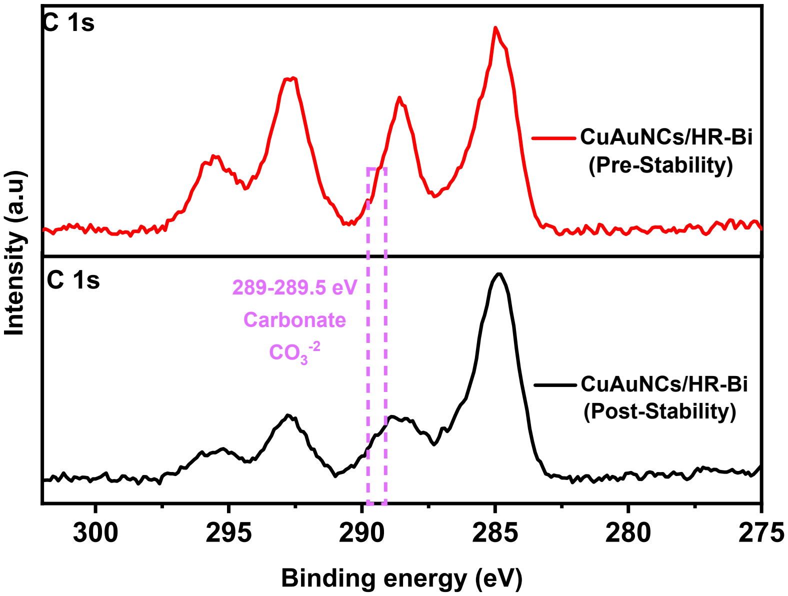

Figure S11 C 1s XPS spectra of catalyst CuAuNCs/HR-Bi before and after electrochemical activity.

Table S1. The concentration (ppm) of Au, Bi and Cu in electrolyte after stability of catalyst CuAuNCs/HR-Bi obtained by ICP analysis.

Sample label	**Au (ppm)**	**Bi (ppm)**	**Cu (ppm)**
Electrolyte (CuAuNCs/HR-Bi)	0.169 ppm	1.081 ppm	0.777 ppm