Synthesis of CuO nanoparticles

300 μL of glacial acetic acid was added to 90 mL of Cu(NO$_3$)$_2$ aqueous solution (0.02 M) and then heated in a 100 °C oil bath for 20 min. Next, 700 μL of aqueous NaOH (25 wt.%) was quickly injected under vigorous stirring. The reaction was allowed to proceed for 20 min, after which it was cooled down in an ice water mixture. The product was collected by centrifugation at 14000 RPM for 10 min followed by re-dispersion in water and freeze drying.

Synthesis of Au nanoparticles

The synthesis of Au nanoparticles was carried out in two steps, i.e. seed synthesis and seeded growth.

To synthesize Au seeds, 600 μL of freshly-prepared ice-cooled NaBH$_4$ aqueous solution (0.1 M) was quickly injected into 20 mL of HAuCl$_4$ aqueous solution (0.25 mM) containing 0.25 mM trisodium citrate under vigorous stirring. The reaction completed after 2 min of stirring, producing a brownish red colloidal solution. This Au seed colloid was used for the
next step within 10 min to avoid degradation.

The growth solution containing 2.5 mM HAuCl₄ and 80 mM cetyltrimethylammonium bromide (CTAB) in water was prepared ahead of time. To produce Au nanoparticles of desired size, 9 mL of the growth solution was mixed with 500 μL of ascorbic acid aqueous solution (0.1 M) under stirring, and then 10 mL of the Au seed colloid was quickly injected while vigorous stirring was maintained. The reaction completed after 10 min of stirring, yielding a brown colloidal solution.

To remove the excess CTAB in the Au colloidal solution, it was cooled in an ice water mixture for 4 h to let the CTAB oversaturate and precipitate. Then the CTAB precipitate was removed by centrifugation at 8000 RPM for 10 min. Subsequently, minor impurities (i.e. large Au nanoparticles and nanorods) were removed by performing another centrifugation at 14000 RPM for 10 min. The obtained Au nanoparticle colloidal solution was stored at 4 °C. This final suspension contained 0.25 mg mL⁻¹ of Au nanoparticles.

**Structural characterizations**

X-ray diffraction (XRD) data were collected on a Rigaku SmartLab X-ray diffractometer with a Cu target (154 pm wavelength) operated at 44 kV and 40 mA. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy were performed on a PHI VersaProbe II X-ray photoelectron spectrometer with an Al Kα target (1486.7 eV). The energy scale for all spectra was calibrated by fixing the C 1s peak at 284.8 eV. Scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and energy dispersive X-ray spectroscopy (EDS) were performed on a Hitachi SU8230 scanning electron microscope equipped with a Bruker X-Flash 5060FQ EDX detector. Transmission electron microscopy (TEM) was performed on a FEI Tecnai Osiris 200kV TEM.

**Electrochemical measurements**

CO₂ reduction measurements were carried out in a home-made three-electrode H-cell separated by an anion exchange membrane. The data were recorded by a Bio-Logic VMP3 electrochemistry workstation. The electrolyte was 0.5 M KHCO₃ aqueous solution which had
been electrochemically purified by maintaining a current of 150 μA between two parallelly placed Ti sheets in the electrolyte for 24 hours.

The working electrode was prepared by drop-casting a certain amount of catalyst ink on a 1 cm² area of carbon fiber paper (Toray-030, 30% polytetrafluoroethylene). For the Cu catalyst electrode, CuO nanoparticles were dispersed in ethanol by sonication to reach the concentration of 1 mg mL⁻¹, and then 400 μL of the suspension was deposited on carbon fiber paper to reach the mass loading of 0.4 mg cm⁻². For the Cu/Au catalyst electrode, CuO nanoparticles were dispersed in H₂O (2 mg mL⁻¹) and mixed with the Au colloidal solution in a controlled volume ratio for the desired CuO:Au mass ratio. Then, the mixed suspension was loaded on carbon fiber paper, with the mass loading of CuO controlled to be 0.4 mg cm⁻². For the Au catalyst electrode, 1 mL of the Au colloidal solution was mixed with 4 mL of a Vulcan carbon black (FuelCellStore) dispersion (1 mg mL⁻¹ in water) and 17 μL of a Nafion solution (5 wt.%, Sigma-Aldrich) by sonication. Then, 300 μL of the ink was loaded on carbon fiber paper for the mass loading of Au to be 15 μg cm⁻².

The reference electrode was Ag/AgCl (sat. KCl) and it was placed in the cathodic compartment of the H-cell; the counting electrode was a graphite rod placed in the anodic compartment. Potentials were calibrated and reported to the RHE scale unless otherwise specified, and 100% iR compensation was applied during every CO₂ reduction measurement.

A galvanostatic procedure was conducted prior to the CO₂ reduction to reduce the CuO nanoparticles and render the Cu or Cu/Au catalyst. Specifically, a 2 mA cathodic current was applied on the working electrode for 30 min under continuous N₂ purging in the cathodic compartment. The total charge passed was 3.7 times that needed to reduce the 0.4 mg of CuO on the electrode, to ensure that the CuO nanoparticles were fully reduced to Cu after this step.

CO₂ was bubbled into the electrolyte continuously at a flow rate of 20 sccm during the CO₂ reduction process. Gas products were analyzed by a gas chromatograph. The gas chromatograph (MG#5, SRI Instruments) was operated with Ar as the carrier gas. The quantification was calibrated by running standard gaseous samples containing known amounts of H₂, CO, CH₄ and C₂H₄.

Liquid products were quantified by conducting ¹H-nuclear magnetic resonance (¹H-NMR)
under the water suppression mode. $^1$H-NMR was collected on a Bruker 400 MHz Broadband Probe NMR spectrometer. 450 μL of the post-electrolysis electrolyte was mixed with 50 μL of an internal standard solution containing 50 mM of potassium benzoate and 10 mM of dimethyl sulfoxide in D$_2$O. By establishing a calibration curve from standard formic acid solutions, formate, which was the only liquid product from CO$_2$ reduction in this study, could be quantified.

Electrochemical surface area (ECSA) was measured in the same electrolyte and cell configuration after electrolysis by performing cyclic voltammetry (CV) between -0.6 and -0.4 V. The scan rate was varied in the range between 20 and 100 mV s$^{-1}$. After plotting the current density vs. the scan rate, relative ECSA was derived from the slope of the line.
Supplementary display items

Figure S1. (a) XRD diagrams of CuO nanoparticles and Au nanoparticles. b) SEM image of CuO nanoparticles. c) STEM image of Au nanoparticles.

Figure S2. Potential-dependent CO\textsubscript{2} reduction performance of Au nanoparticles: (a) Faradaic efficiency and (b) current density.

Figure S3. Potential-dependent current densities for CO\textsubscript{2} reduction catalyzed by (a) Cu and (b) Cu/Au.
Figure S4. $^1$H-NMR spectra of catholyte after CO$_2$ reduction electrolysis at -0.6 V for 1 hour with (a) the Cu catalyst and (b) the Cu/Au catalyst.
Figure S5. (a) XRD diagrams of the Cu and Cu/Au catalysts. (b) TEM image of the Cu/Au catalyst. Some Au nanoparticles are indicated by red arrows. (c) EDS spectrum of the Cu/Au catalyst taken from a 200×200 μm² area. The atomic percentages of Cu and Au were quantified to be 95±1% and 5±1%, respectively. The C and F elements are from carbon fiber paper with polytetrafluoroethylene coating. (d) SEM image and (e, f) the corresponding EDS maps of the Cu/Au catalyst. (g) XPS depth profile of the Cu/Au catalyst.
Figure S6. SEM images of (a) the Cu catalyst and (b) the Cu/Au catalyst. (c) ECSA of Cu and Cu/Au catalysts after performing CO₂ reduction electrolysis for different time at -0.6 V.

Figure S7. Cyclic voltammograms of (a) Cu, (b) Cu/Au-A and (c) Cu/Au-B in CO/N₂-saturated 0.5 M KHCO₃. Scan rate: 20 mV s⁻¹.

Figure S8. Cu 2p XPS spectra of Cu, Cu₂O and CuO references.
Figure S9. XPS/Auger spectra of the Cu and Cu/Au catalysts after 4 and 7 hours of CO$_2$ reduction at -0.6 V: (a-b) Cu 2p; (c-d) Cu LMM; (e) Au 4f. The samples were transferred into the XPS spectrometer without exposure to air.
Table S1. Comparison of performance with the state-of-the-art formate-selective CO₂ reduction electrocatalysts. The Cu-primary ones are colored in green.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Electrolyte</th>
<th>Best FE (formate)</th>
<th>Best formate-producing Potential (vs. RHE)</th>
<th>Partial current density of formate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Au</td>
<td>0.5 M KHCO₃</td>
<td>81%</td>
<td>-0.6 V</td>
<td>10.4 mA cm⁻²</td>
<td>This work</td>
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<td>Sulfur-modified Cu</td>
<td>0.1 M KHCO₃</td>
<td>80%</td>
<td>-0.8 V</td>
<td>8 mA cm⁻²</td>
<td>1</td>
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<td>AC-CuSₓ</td>
<td>0.1 M KHCO₃</td>
<td>75%</td>
<td>-0.85 V</td>
<td>5 mA cm⁻²</td>
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<td>Thick Cu₂O films</td>
<td>0.5 M NaHCO₃</td>
<td>33%</td>
<td>-0.5 V</td>
<td>0.89 mA cm⁻²</td>
<td>3</td>
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<tr>
<td>Cu nanofoams</td>
<td>0.1 M KHCO₃</td>
<td>37%</td>
<td>-0.9 V</td>
<td>3.7 mA cm⁻²</td>
<td>4</td>
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<td>Cu-CDots</td>
<td>0.5 M KHCO₃</td>
<td>68%</td>
<td>-0.7 V</td>
<td>2.9 mA cm⁻²</td>
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<td>CuSn₃</td>
<td>0.1 M KHCO₃</td>
<td>95%</td>
<td>-0.5 V</td>
<td>33 mA cm⁻²</td>
<td>6</td>
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<tr>
<td>Sn(S)/Au</td>
<td>0.1 M KHCO₃</td>
<td>93%</td>
<td>-0.75</td>
<td>51 mA cm⁻²</td>
<td>7</td>
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<tr>
<td>Sn</td>
<td>0.1 M KHCO₃</td>
<td>70%</td>
<td>-0.9 V</td>
<td>6 mA cm⁻²</td>
<td>8</td>
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<tr>
<td>Partially oxidized Co</td>
<td>0.1 M Na₂SO₄</td>
<td>90%</td>
<td>-0.19 V</td>
<td>9.54 mA cm⁻²</td>
<td>9</td>
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<td>nanolayers</td>
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<td>Ag/SnOₓ</td>
<td>0.5 M KHCO₃</td>
<td>83%</td>
<td>-1.0 V</td>
<td>6.6 mA cm⁻²</td>
<td>10</td>
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<tr>
<td>Oxide-derived Pb</td>
<td>0.5 M NaHCO₃</td>
<td>95%</td>
<td>-1.05 V</td>
<td>1 mA cm⁻²</td>
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<tr>
<td>Bi nanosheets</td>
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<td>95%</td>
<td>-0.83 V</td>
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<tr>
<td>Cu-doped Bi</td>
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<td>90%</td>
<td>-1.2 V</td>
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<td>CuBi₂ microspheres</td>
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<td>95%</td>
<td>-0.93 V</td>
<td>6.2 mA cm⁻²</td>
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<td>CuOₓ/SnO₂-CNT</td>
<td>0.1 M KHCO₃</td>
<td>77%</td>
<td>-0.99 V</td>
<td>4.0 mA cm⁻²</td>
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References