

Electronic Supporting Information

Insights into *in situ* one-step synthesis of carbon supported nanoparticulate gold-based catalysts for efficient electrocatalytic CO₂ reduction

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1. **Synthesis of Au-SS (synthesized without carbon black support).**

6 mL HAuCl₄ solution (1 g HAuCl₄•3H₂O dissolved in 100 mL H₂O) and 0.20 g CTAC were added in 80 ml H₂O and stirred. A solution prepared by 0.105 g Na₂S•9H₂O dissolved in 10 g water (Na₂S/HAuCl₄ (mol/mol) = 3) was then added fast under vigorous stirring. The obtained suspension was stirred at 60 °C for 4 h, the precipitate was filtered and purified using ethanol and water to remove excess CTAC and unreacted reagents. The wet precipitate was directly dispersed in ethanol ultrasonically and dropped on lacey support film grids for TEM observation. The obtained sample was denoted as Au-SS, where SS is short for sodium sulfide. The TEM image of Au-SS is shown in Fig. S3.

2. **Synthesis of SF-Au-SS/C (synthesized without CTAC surfactant).**

6 mL HAuCl₄ solution (1 g HAuCl₄•3H₂O dissolved in 100 mL H₂O) were added in 80 ml H₂O, and then 60 mg Vulcan XC-72R carbon black was added and stirred. The suspension was sonicated for 20 min and then stirred at 60 °C. A solution prepared by 0.105 g Na₂S•9H₂O dissolved in 10 g water (Na₂S/HAuCl₄ (mol/mol) = 3) was then added fast under vigorous stirring. After the suspension was stirred at 60 °C for 4 h, the precipitate was filtered and purified using ethanol and water to remove unreacted reagents and dried in a vacuum oven at 60 °C overnight. The obtained sample was denoted as SF-Au-SS/C, where SF is short for “surfactant free”, and SS is short for sodium sulfide. XRD pattern and TEM image of SF-Au-SS/C are shown in Fig. S4.

3. **Synthesis of L-Au-UR/C (synthesized with low Au loading)**

1 mL HAuCl₄ solution (1 g HAuCl₄•3H₂O dissolved in 100 mL H₂O) and 0.20 g CTAC were added in 80 ml H₂O, and then 60 mg Vulcan XC-72R carbon black was added and stirred. 0.146 g urea was added into the suspension (urea/HAuCl₄ (mol/mol) = 100:1) and the obtained mixture was heated at 80 °C for 8 h under stirring (pH increases). The precipitate was filtered and purified using ethanol and water to remove excess CTAC and unreacted reagents and dried in a vacuum oven at 60 °C overnight. The obtained sample was denoted as L-Au-SS/C, where L represents low Au loading, and SS is short for sodium sulfide. XRD pattern and TEM image of L-Au-SS/C are shown in Fig. S7.

4. Procedure for the calculation of the Faradaic efficiency (FE)

Gaseous products were analyzed using a gas chromatograph (GC). The outlet gas from the catholyte was injected into the GC through a sampling loop. The calculation of Faradaic efficiency (FE) was carried out follow this:

For CO

$$FE_{CO}(\%) = \frac{Q_{CO}}{Q_{tot}} = \frac{NFGv_{CO}p_0}{RT_0i} \times 100\%$$

And for H₂

$$FE_{H_2}(\%) = \frac{Q_{H_2}}{Q_{tot}} = \frac{NFGv_{H_2}p_0}{RT_0i} \times 100\%$$

where:

v_{CO} (vol%) is the volume concentration of CO;

v_{H_2} (vol%) is the volume concentration of H₂;

G (ml/min) is the gas flow rate;

i (mA) is the steady-state cell current;

p_0 is the atmosphere pressure at 0 °C, $p_0 = 1.01 \times 10^5$ Pa;

$T_0 = 273.15$ K;

N is the number of electrons required to form a molecule of CO or H₂, $N = 2$;

F is the Faraday constant, $F = 96485$ C • mol⁻¹;

R = 8.314 J • mol⁻¹ • K⁻¹.

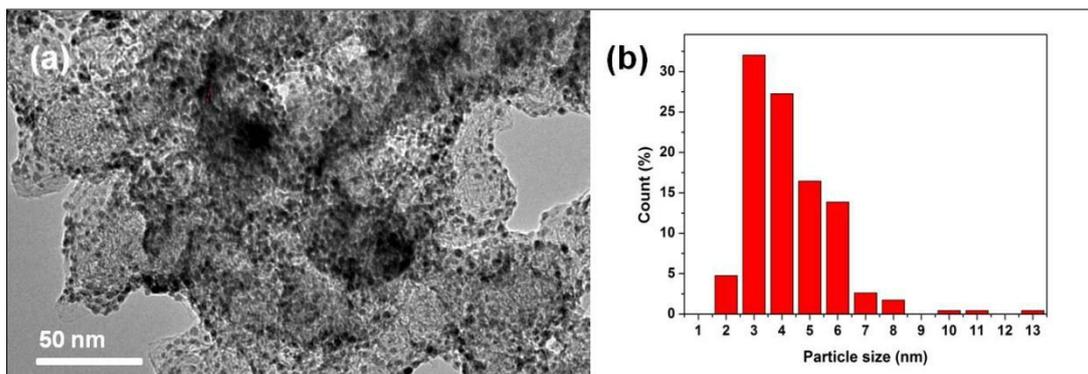


Fig. S1 (a) TEM image of Au-SS/C and (b) the corresponding histogram of the particle size distribution.

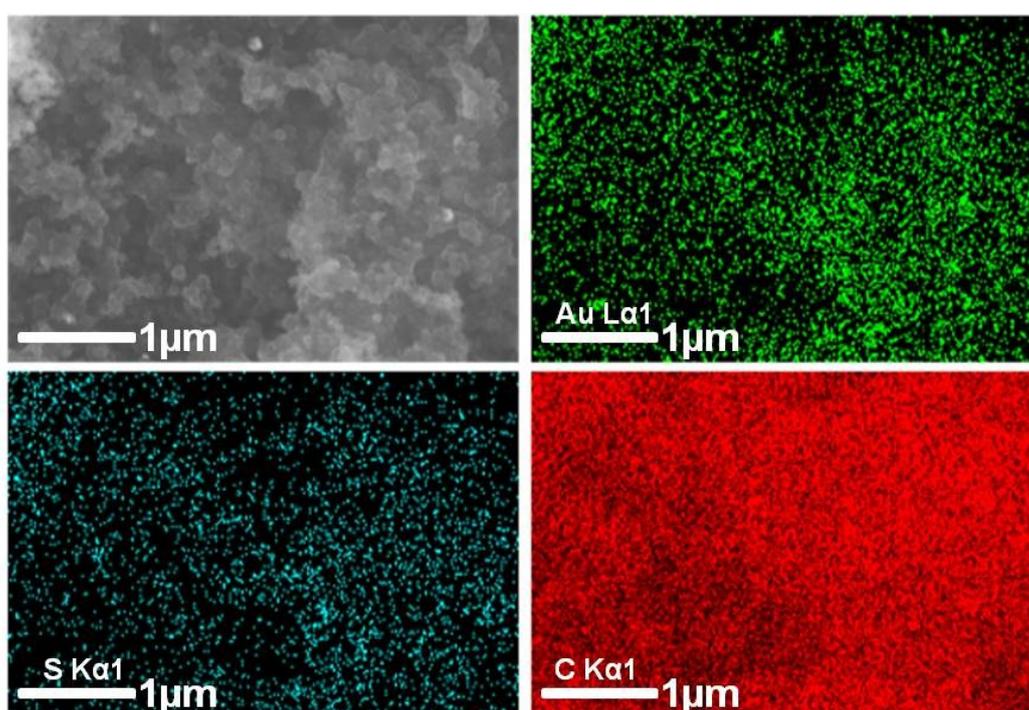


Fig. S2 SEM image and EDX mapping of Au-SS/C

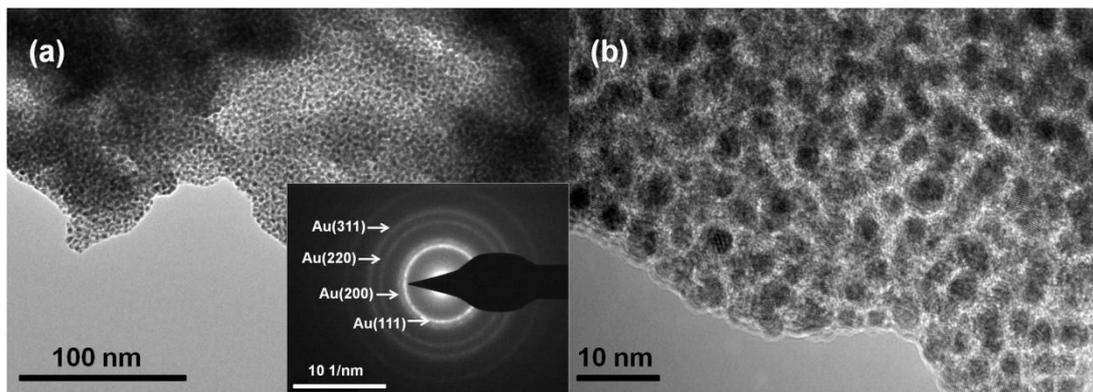


Fig. S3 (a) Low and (b) high magnification TEM images and (inset in a) the corresponding SAED pattern of Au-SS (synthesized without carbon black).

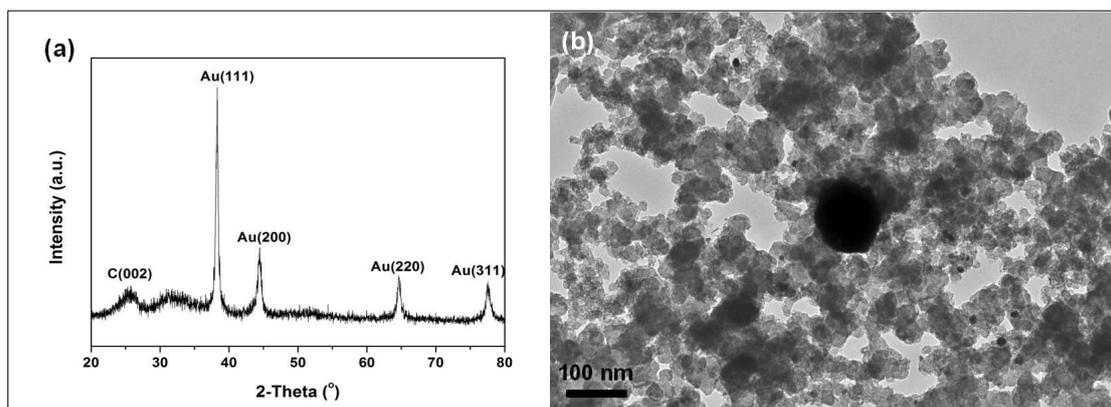


Fig. S4 (a) XRD pattern and (b) TEM image of SF-Au-SS/C (synthesized without CTAC surfactant)

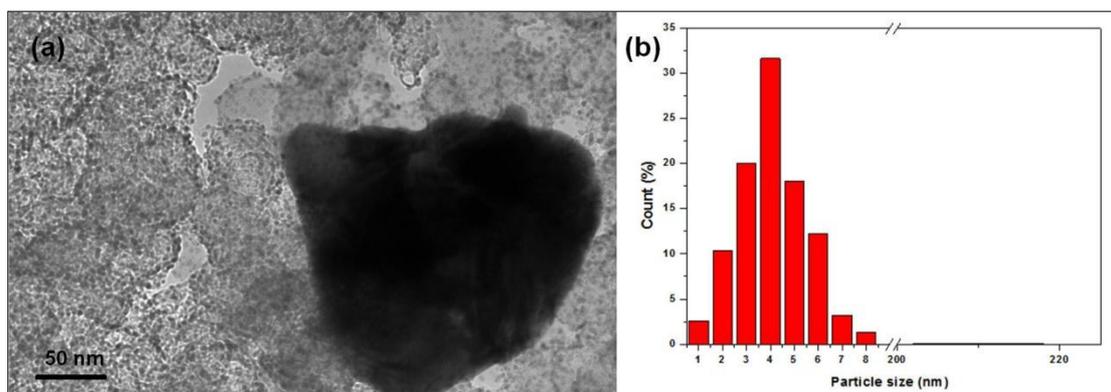


Fig. S5 (a) TEM image of Au-UR/C and (b) the corresponding histogram of the particle size distribution. A large particle is surrounded by many small nanoparticles.

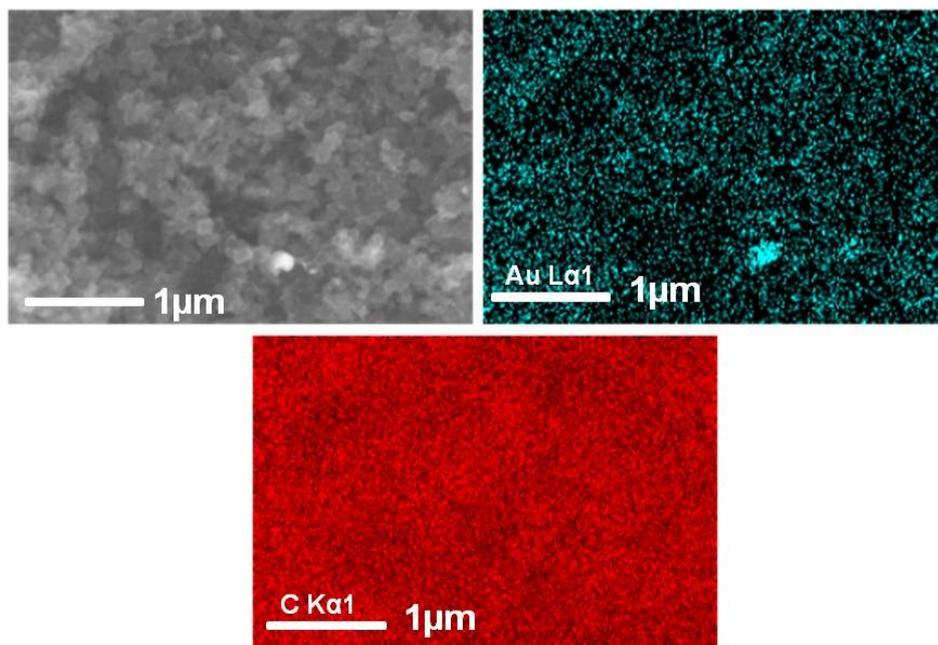


Fig. S6 SEM image and EDX mapping of Au-UR/C.

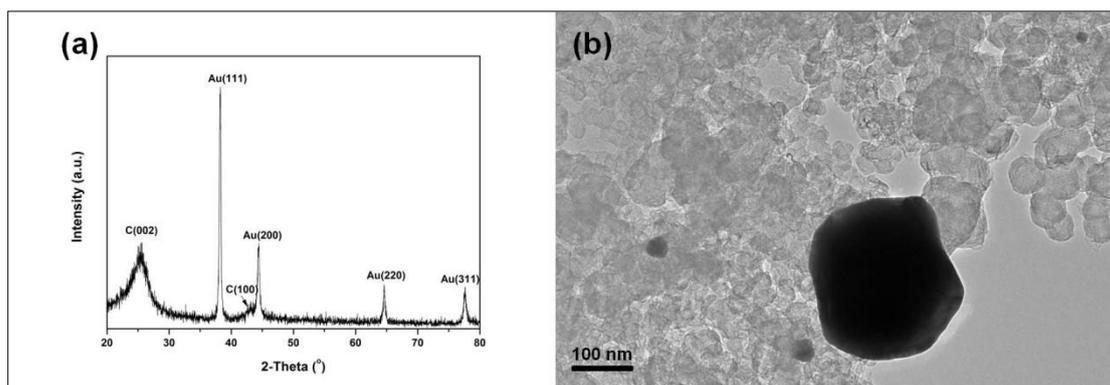


Fig. S7 (a) XRD and (b) TEM image of L-Au-UR/C (HAuCl_4/C (wt/wt) = 1/6)

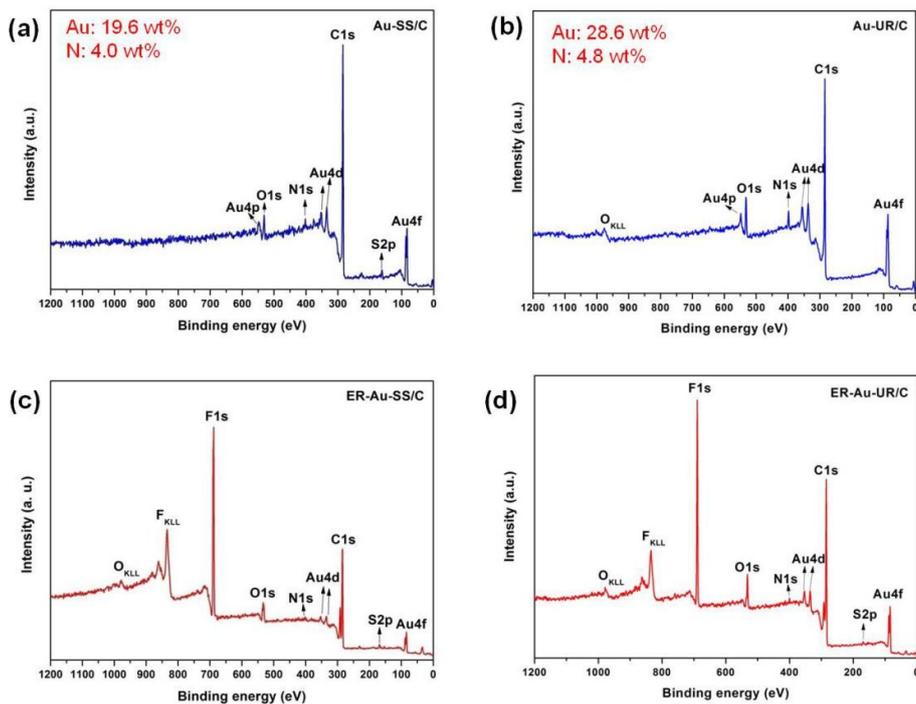


Fig. S8 XPS spectra of (a) Au-SS/C, (b) Au-UR/C, (c)ER-Au-SS/C and (d) ER-Au-UR/C. Nafion composed of the elements carbon, oxygen, sulfur and fluorine can interfere the corresponding XPS peaks of ER-Au-SS/C and ER-Au-UR/C.

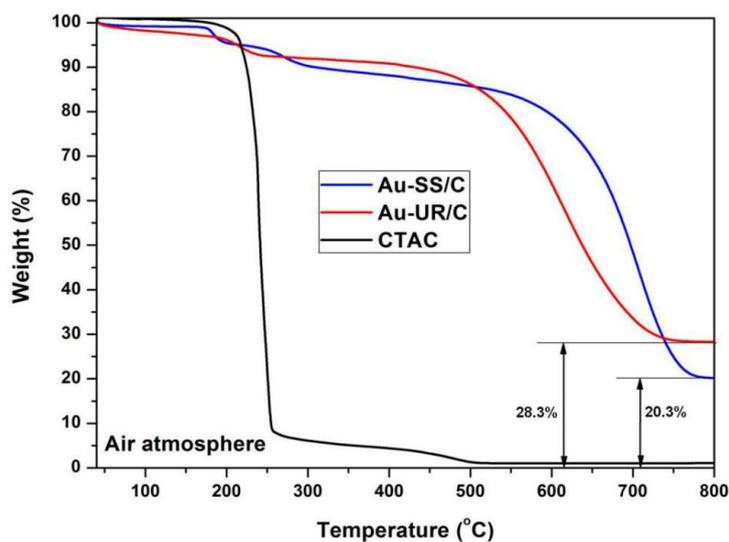


Fig. S9 TGA curves of Au-SS/C, Au-UR/C and CTAC measured at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air atmosphere.

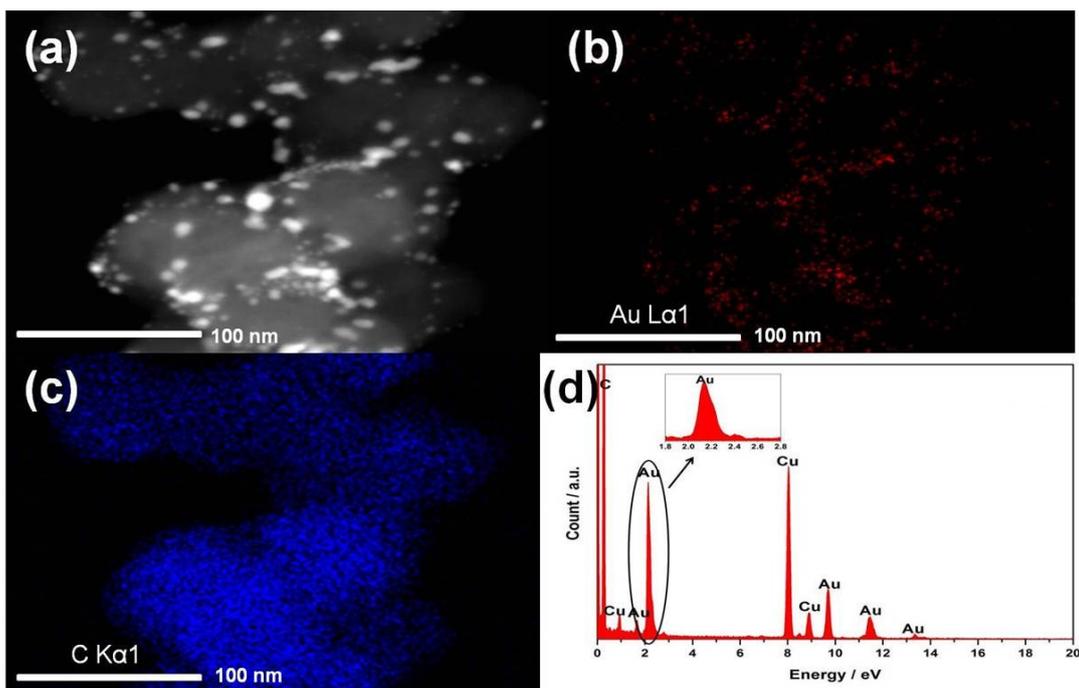


Fig. S10 (a,b,c) STEM-EDX mapping and (d) EDX spectrum of ER-Au-SS/C.

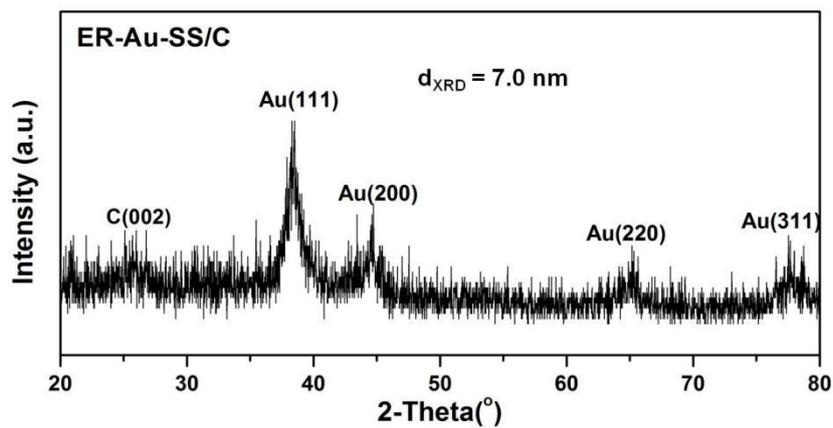


Fig. S11 XRD pattern of ER-Au-SS/C. Crystalline size is calculated from the Au (220) peak of XRD pattern.

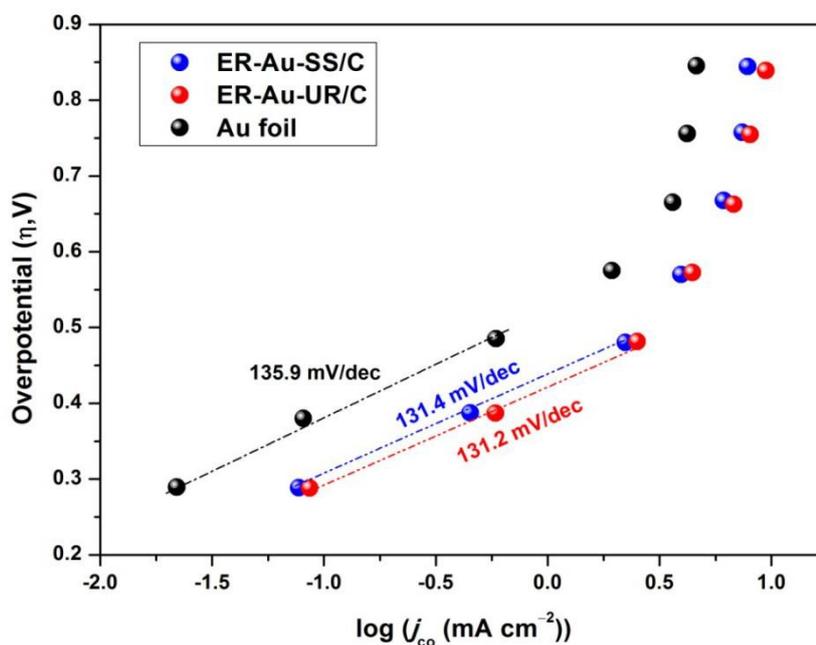


Fig. S12 Tafel plot at different overpotentials η (iR-corrected) as a function with the CO partial current density j_{CO} , on ER-Au-SS/C, ER-Au-UR/C and Au foil.

Table S1 Kinetic data of ER-Au-SS/C, ER-Au-UR/C and Au foil for electroreduction of CO_2 to CO.

Catalyst	Tafel slope (mV dec ⁻¹)	Exchange current density (mA cm ⁻²)
ER-Au-SS/C	131.4	5.07E-3
ER-Au-UR/C	131.2	6.69E-3
Au foil	135.9	1.47E-3

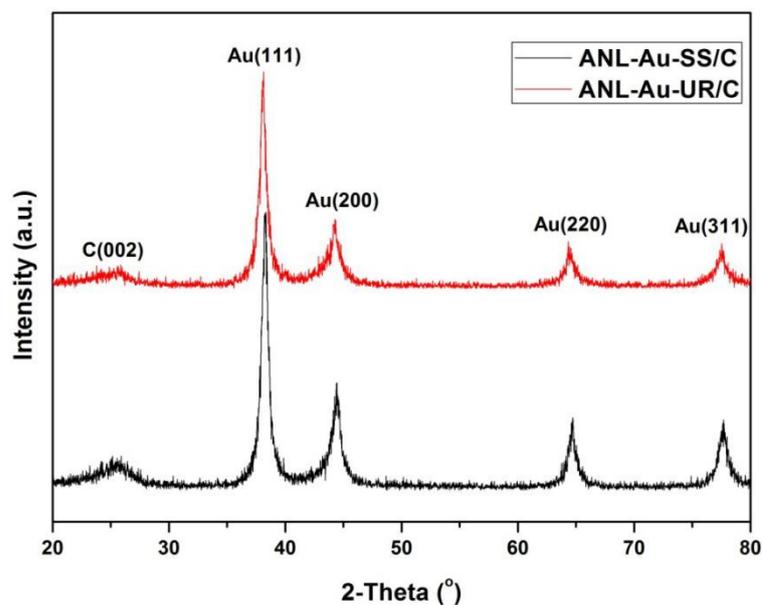


Fig. S13 XRD patterns of ANL-Au-SS/C and ANL-Au-UR/C.

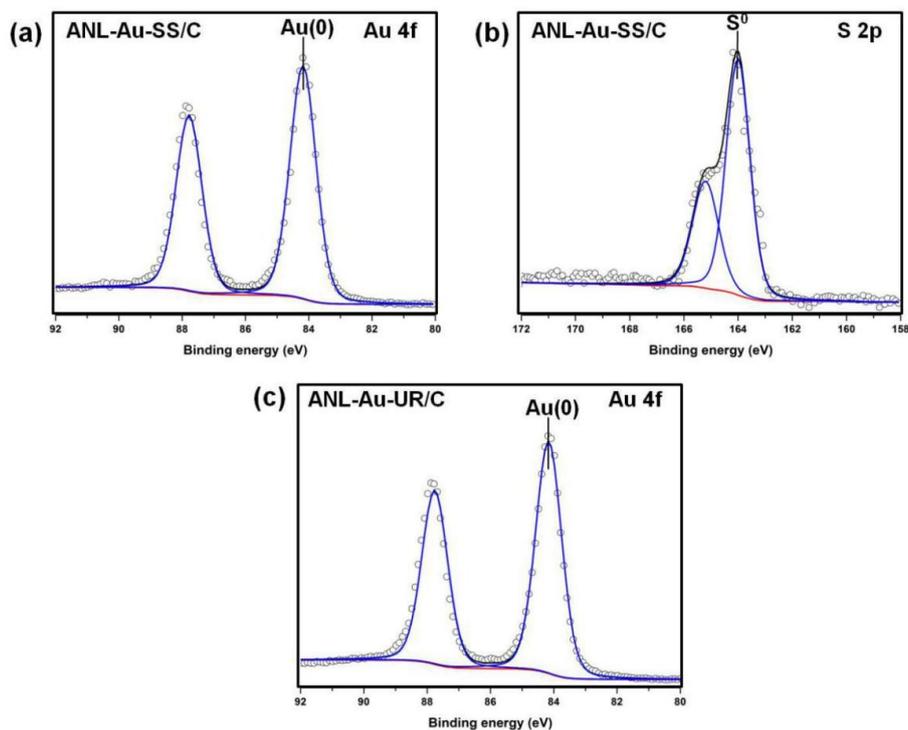


Fig. S14 X-ray photoelectron (a) Au 4f and (b) S 2p spectra of ANL-Au-SS/C, and (c) Au 4f spectrum of ANL-Au-UR/C. The open circles represent the experimental data and the solid line represents the fitted data.

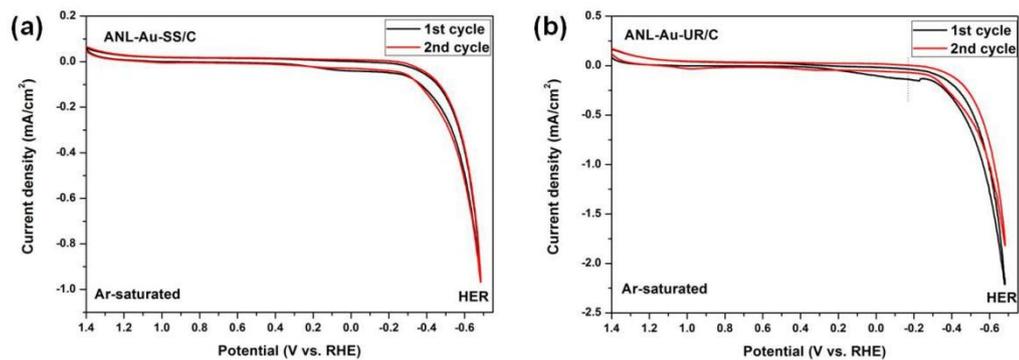


Fig. S15 The first and second cycle in cyclic voltammograms obtained with (a) ANL-Au-SS/C and (b) ANL-Au-UR/C modified electrodes in Ar-saturated 0.1 M KHCO₃ aqueous electrolyte under stirring. In each case the potential scans were initiated at 1.4 V and continued with 10 mV s⁻¹ scan rate to cathodic direction.

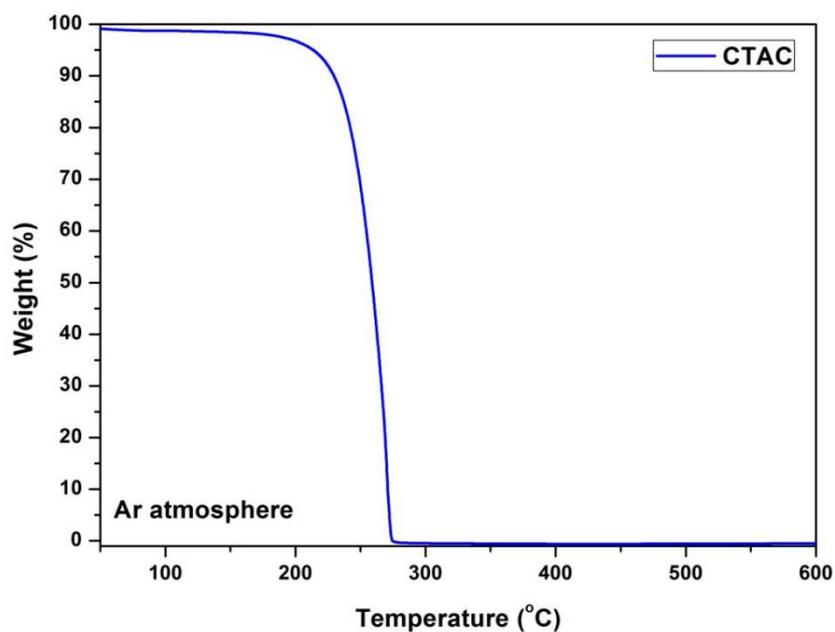


Fig. S16 TGA curve of CTAC measured at a heating rate of 10 °C min⁻¹ in Ar atmosphere.

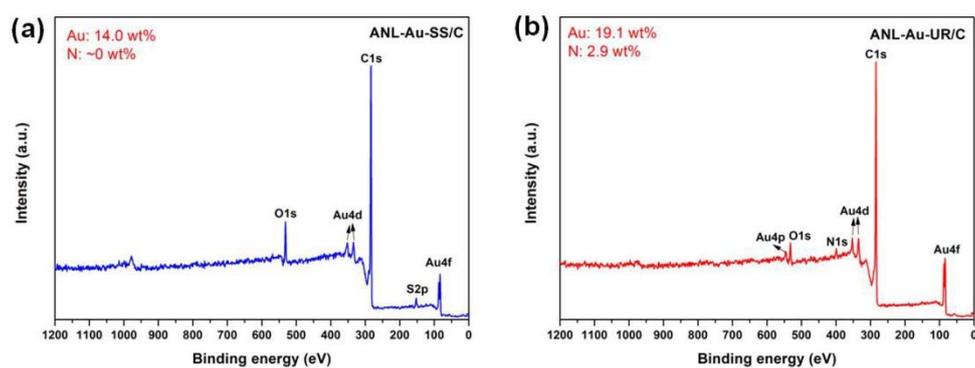


Fig. S17 XPS spectra of (a) ANL-Au-SS/C and (b) ANL-Au-UR/C. The Au loadings calculated from XPS spectra are largely lower than that from TGA, indicating the largely decreased Au surface area.

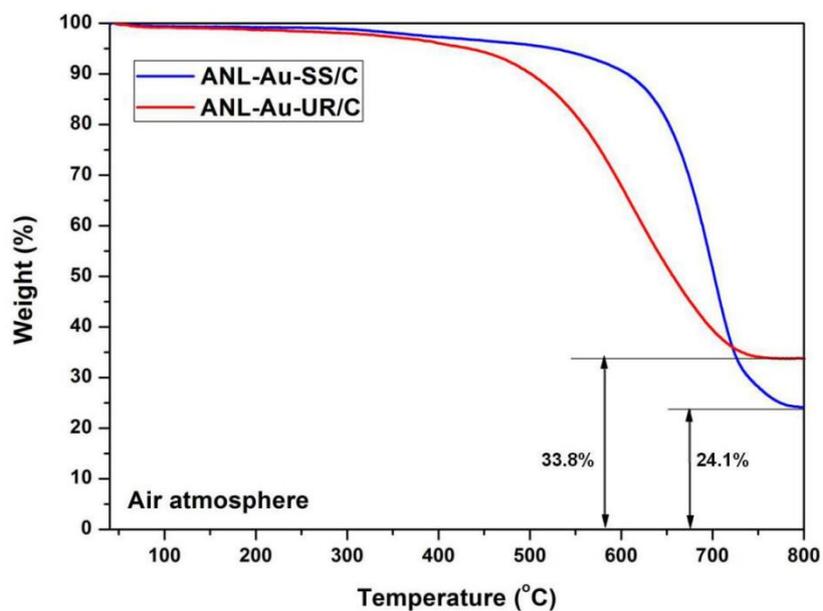


Fig. S18 TGA curves of ANL-Au-SS/C and ANL-Au-UR/C measured at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ in air atmosphere.

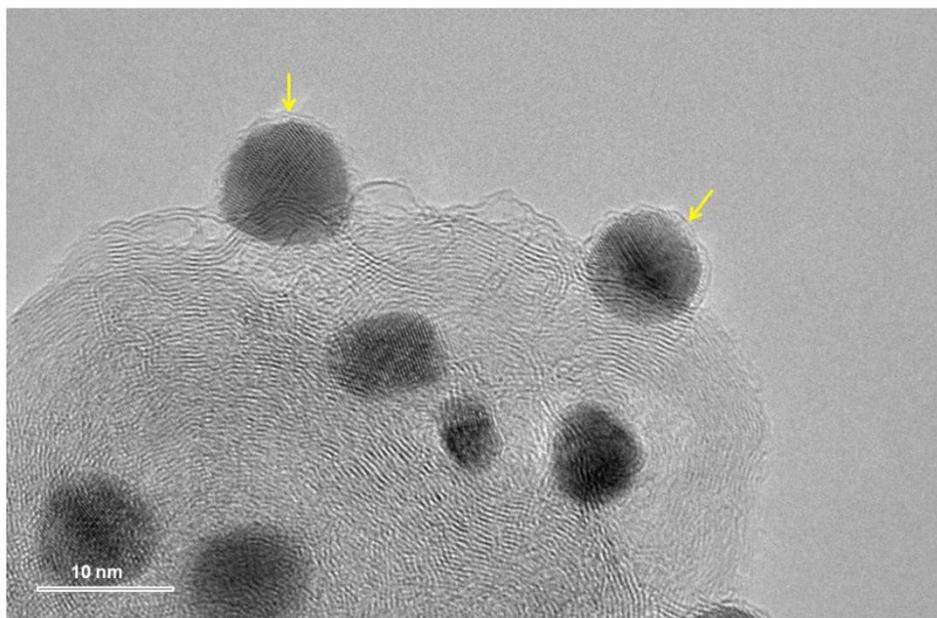


Fig. S19 Enlarged TEM image of ANL-Au-UR/C. Some gold nanocrystals are covered by a 0.5 nm thick light-contrast shell (yellow arrows) that likely corresponds to the carbon phase.