Atomic Origins of High Electrochemical CO\textsubscript{2} Reduction Efficiency on Nanoporous Gold

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Materials and Methods

Materials. Ethylene glycol (EG, Sigma-Aldrich), poly(diallyldimethylammonium chloride) (PDDA, 20 wt%, MW=200000-350000, Sigma-Aldrich), chloroauric acid trihydrate (HAuCl₄·3H₂O, Sinopharm Chemical Reagent Co. Ltd.), hydrogen nitrate (HNO₃, 65 wt%, Sinopharm Chemical Reagent Co. Ltd.), potassium acid carbonate (KHCO₃, 99.99 wt%, Macklin), 400-nm-thick 12 carat Au₅₀Ag₅₀ leaves (Sepp Leaf Products, Inc.), Nafion solution (5%, DuPont), Toray carbon paper (Toray TGP-H-060, Toray Industries Inc.), Vulcan XC-72 carbon black (Carbot Corp.)

Preparation of NPG Films. NPG films were prepared by dealloying 400-nm-thick 12 carat Au₅₀Ag₅₀ leaves by selectively etching in concentrated HNO₃ (68%) at 50 °C for 40 min [S6]. The as-prepared NPG films were carefully rinsed with ultrapure water for at least 3 times and then floated on ultrapure water for further use.

Synthesis of Au Octahedra: The EG was constantly stirred at 315 rpm with a magnetic stirrer. 5μL 500mM HAuCl₄ and 200μL PDDA were mixed with the EG solution. The resulting mixture was stirred for 30 s and then heated in an oil bath of 200°C without disturbance. After 30 min reaction, the solution was cooled in ice bath. The final products were washed three times by centrifugation (12000 rpm, 10 min) followed by removal of the supernatant and dispersion in water.

Theoretical Calculation. Density functional theory (DFT) calculations were performed with using DMol³ code, which has been widely adopted in published works [S1-3]. The exchange and correlation effects were described by the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional [S4]. All-electron calculations were performed with the double numerical basis sets plus the polarization. The inner electrons were treated by an effective core potential. The Tkatchenko-Scheffler van der Waals correction was utilized in the dispersion-corrected scheme. The spin-unrestricted method was applied for all calculations. The relaxed lattice constant of Au is 4.166 Å. The convergence tolerance of energy was set to be 2 × 10⁻⁵ au, and the geometry optimization were conducted with the maximum force and displacement as 0.004 Ha Å⁻¹ and 0.005 Å, respectively. The real-space global orbital cut-off radius was set to 4.5 Å. The number of 5×5×1 k-points was sampled as the Brillouin zone.
The vacuum space was set to be at least 15 Å. Free-energy changes (ΔG) in electrochemical reaction pathways were calculated according to a published procedure [S5]. ΔG is calculated based on the following equation: $\Delta G = \Delta E + \Delta ZPVE + \int C_p dT - T \Delta S$, where $\Delta E$ is the change in the adsorption energy, $\Delta ZPVE$ and $\Delta S$ are the differences of zero-point vibrational energy and the entropy between the adsorbed state and the gas phase, respectively, $C_p$ is the heat capacity, and $T$ is the system temperature. A vibrational analysis was used to calculate the thermodynamic properties of molecules in the gas phase and adsorbed state.

**Electrochemical Measurements.** An electrochemical station (CHI760D) was used for all CO$_2$ reduction experiments. The platinum gauze and silver chloride electrode (Ag/AgCl) were served as the counter and reference electrodes, respectively. In a typical prepared procedure of the working electrode, the NPG films (1 cm$^2$) were carefully adhered to a carbon paper (1x1.5 cm$^2$) on both sides by the lift-coating method and 20 μL of Nafion ethanol solution (0.5 wt%) was loaded onto a carbon paper electrode with NPG. Using Au octahedra to preparation of one working electrode, three reactions of Au octahedra were mixed with active carbon in 150 μL ethanol solution and 25 μL Nafion solution (5%), sonicated for 30 min to form a homogenous ink. Then, the dispersion was loaded onto a carbon paper electrode with area of 1x1 cm$^2$.

**CO$_2$ Electroc当地oreduction Measurement.** Electrochemical CO$_2$ reduction reactions were performed in a gas-tight two-chamber electrochemical cell separated by the Nafion® 117 film. Each chamber was filled with 30.0 mL 0.5 M KHCO$_3$ solution. Before electrolysis, the electrolyte in the cathodic chamber was bubbled with CO$_2$ gas for at least 30 min. The chronoamperometry was carried out. During electrolysis, CO$_2$ gas was delivered into the cathodic chamber at a rate of 5.00 mL/min and the electrolyte in the cathodic chamber was stirred at a rate of 800 rpm during reaction.

**Product analysis.** The gas mixture was vented directly into a gas chromatography (Fuli GC9790II). High-purity argon was used as the carrier gas. The resulting gas samples were automatically drawn every 20 minutes for measurement. The gas mixtures from electrolysis was detected through a thermal conductivity detector.
(TCD) and a flame ionization detector (FID). Hydrogen and carbon oxide were quantified through TCD, and hydrocarbons (methane, ethane and ethene) were quantified through FID.

**Faradaic Efficiency Calculations.** Calibration gas, with 1% CO and a makeup flow of 5 mL/min, was used as internal standard. The peak of CO was recorded, and the area of CO peak was determined by GC software. The CO evolution rate was determined based on the area of the CO gas peak via internal standard. A stable CO peak was selected for the production rate calculation, which is converted using the calibration to CO production flow rate. Later the flow rate with units of mL/min can be converted to that with units of mole/min using the ideal gas law.

The faradaic efficiency (FE) of NPG catalyst was calculated based on the following Equation:

\[ FE = \frac{\alpha n F}{Q} \]

\( \alpha \): number of electrons required for \( \text{CO}_2 \) reduction reaction (for CO and \( \text{H}_2 \) \( \alpha=2 \))

\( n \): moles of product (measured by GC)

\( F \): Faraday’s constant (96485 C/mol)

\( Q \): total number of electrons measured during this sampling period.
Figure S1. XPS spectra of the NPG film (a) Au 4f and (b) Ag 3d.
Figure S2. EDS spectra of the NPG film.
**Figure S3.** SEM images of NPG before CO$_2$RR.
Figure S4. SEM images of Au octahedra before CO$_2$RR.
**Figure S5.** Fast Fourier transform (FFT) patterns of Fig. 1d.
Figure S6. Free energy diagrams for electrochemical CO$_2$RR to CO on Au(111) and Ag-doped Au(111) surfaces.
Figure S7. (a) The evolution of the anodic peaks during potential cycling at scan rates of 5 mV/s. (b) Faradaic efficiencies for CO and H₂ at various potentials, respectively.
Figure S8. SEM images of NPG after CO$_2$RR.
Figure S9. The stability of NPG for electroreduction reaction in CO₂-saturated 0.5 M KHCO₃ solution for 10 hours at -0.6 V vs. RHE.
Figure S10. The cyclic voltammograms (CVs) evolution of NPG during CO$_2$ electrolysis.
Table S1. Atomic percentage of Au and Ag for NPG measured by EDS and XPS.

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<th>Au</th>
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References


