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# Self-supported Nanoporous Au<sub>3</sub>Cu Electrode with Enriched Gold on Surface for Efficient Electrochemical Reduction of CO<sub>2</sub>

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Abstract: The key in the electrochemical conversion of CO2 is to develop efficient electrocatalysts with the ease of operation, good conductivity and rich active sites that fulfil the desired reaction direction and selectivity. Herein, an easy oxidative etching of Au<sub>20</sub>Cu<sub>80</sub> alloy has been used to the synthesis of nanoporous Au<sub>3</sub>Cu alloy, representing a facile strategy to tune the electronic properties of the surface and alter the adsorption behaviour of the intermediates. HRTEM, XPS and EXAFS reveal the curved surface of the synthesized nanoporous Au<sub>3</sub>Cu was rich in gold with unsaturated coordination condition, providing fruitful active sites for CO<sub>2</sub> reduction. It can be directly used as self-supported electrode for CO<sub>2</sub> reduction, and exhibits high Faradic efficiency (FE) of 98.12% towards CO at a potential of -0.7 V vs RHE. The FE is 1.47 folds of that over the asmade single nanoporous Au. Density functional theory reveals that \*CO has a relatively long distance on the surface of nanoporous Au<sub>3</sub>Cu, which makes CO easier to desorb from the surface and avoids CO poisoning. The Hirshfeld charge distribution shows that Au atoms have negative charge and Cu atoms exhibit positive charge, respectively, which separately bonds to C atom and O atom in the intermediate of \*COOH through a bidentate mode. This gives the Au<sub>3</sub>Cu the lowest \*COOH adsorption free energy, together with the low desorption energy for CO molecules. This work represents a convenient avenue to engineering the surface over self-supported nanoporous metals with promising applications towards energy catalysis.

### Introduction

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Electrocatalysts is the heart in the design of efficient electrochemical systems with the ability to decrease the kinetic activation barriers and boost the reaction efficiency.<sup>[1]</sup> Great strides including decreasing the size to increase surface area,<sup>[2]</sup> engineering the composition and shape to improve the intrinsic

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activity of the active sites,<sup>[3]</sup> have been made to the development of active electrocatalysts so as to manipulate the transportation of reactants and products on the electrolyte/electrode interface.<sup>[4]</sup> The popular way to get electrodes is to deposit corresponding nanoparticles onto a conductive support.<sup>[5]</sup> The associated issues such as the catalysts lose and aggregate often occur especially enduring long-term reactions.<sup>[6]</sup> On the other hand, the complexity in the system increases the challenge to understand the kinetic process and ascertain the origin of surface catalytic activity. The development of an integrated electrode with good conductivity, high activity and the ease of surface engineering is highly desirable for the fundamental understanding and design of efficient electrocatalytic systems.

Three-dimensional nanoporous metals have the merits of intrinsic conductivity and fruitful nanoscale interconnected ligaments and channels.<sup>[7]</sup> These beneficial micro/nanostructures make intermediate mass/electron transport freely, enabling them to be a class of promising electrocatalysts towards CO<sub>2</sub> reduction reaction (CO<sub>2</sub> RR), <sup>[8]</sup> which is attractive for mitigating warming gas emission and realizing resource utilization. The CO<sub>2</sub> RR products can either be liquid fuels (e.g. ethanol) or gaseous products such as CO for thermo catalytic transformations.<sup>[9]</sup> To date, CO<sub>2</sub> RR has not been a widespread technology because of low energy efficiency and high overpotentials required, a lack of electrocatalytic stability, and unsatisfying selectivity.<sup>[10]</sup> Noble metals such as Au/Ag have been the essential for the electrochemical CO<sub>2</sub> RR to CO. <sup>[5,11]</sup> However, the high cost and earth-deficiency hampers their applications. Various strategies from controlling size to tailoring of the exposed facets, and surface functionalization with molecular decorations have been developed to improve their performances. [12] A class of nanoporous Ag electrode from Jiao's group with intrinsic curved surfaces is capable of reducing CO2 to CO with a 92% faraday efficiency (FE) and a relatively high current density of 18 mA cm<sup>-</sup> <sup>2</sup> at -0.6 V (vs RHE).<sup>[10a]</sup> Zhang et al reported low-coordinated gold atoms are responsible for the enhanced electrocatalytic CO2 RR over porous Au. [13] However, tuning selectivity and suppressing side-reaction of hydrogen evolution with single catalyst is still a challenge because of multistep nature and complexity towards CO<sub>2</sub> RR. Alloying cost-effective Cu with the capacity to convert CO<sub>2</sub> into useful chemical substances is a promising strategy in which the composition and electronic properties of the alloy surface can be finely tuned to alter the reaction intermediate adsorption behavior. <sup>[14]</sup> Developing bimetallic AuCu-based catalysts to break the scaling relationship and stabilize the reaction intermediate to lower the overpotential is beneficial to enhance the reaction activity, selectivity, and stability. <sup>[15]</sup> Open questions still remain regarding the synthesis and scale-up of nanoporous alloys with controlled composition and targeted

surface catalytic sites. And large void volumes (>70%) easily let them poor mechanical property, challenging their implementation in practice.

In this work, we have achieved a selective synthesis of selfsupported nanoporous Au<sub>3</sub>Cu with gold-enriched surface through controlled oxidative etching of Au<sub>20</sub>Cu<sub>80</sub> alloy under mild condition. The good conductivity and flexibility of the as-preapred nanoporous Au<sub>3</sub>Cu afford it to be used directly as a class of selfsupported efficient electrode, which is capable of reducing CO<sub>2</sub> to CO with the maximum Faradic efficiency (FE) as high as 98.12% with a current density of 12.77 mA cm<sup>-2</sup> at low potential of -0.7 V vs RHE. The value is even higher than reported value <sup>[13]</sup> and selfmade nanoporous gold under similar condition, implying that Cu not only reduce the cost, but also improves the reaction selectivity towards CO. Furthermore, it can maintain a high FE of CO at a wide potential. Density functional theory reveals that the nanoporous Au<sub>3</sub>Cu has the lowest \*COOH adsorption energy, and the decreased energy required for CO desorption. The introduction of Cu makes the Au atom surface more negative charges than the single nanoporous Au, forming a stable doubledentate structure for the \*CO adsorption on the surface of porous Au<sub>3</sub>Cu with a relatively long distance, and leading to the easier desorption of CO. This work presents a convenient avenue to tune the surface engineering of self-supported nanoporous alloys with promising applications towards new energy and environmental catalysis.

### **Results and Discussion**

Figure 1a gives XRD pattern of the as-prepared nanoporous Au<sub>3</sub>Cu. The diffraction peaks at 38.1°, 44.25°, 64.33°, 77.55° and 81.50° can be assigned to the (111), (200), (220), (311) and (222) planes of the face-centered cubic (FCC) structure, demonstrating the successful synthesis of Au<sub>3</sub>Cu. SEM image (Figure 1b) clearly reveals its three-dimensional (3D) bicontinuous nanoporous nature. The zoom-in magnified image in the inset of Figure 1b indicates the ligament and the pore sizes of ~50 nm. For comparison, as can be seen from Figure S2, both nanoporous Au and Cu are also in FCC phase. A thin oxide shell is found on nanopours Cu because of inevitable oxidation in air. [5b] Figure S3a shows that the nanoporous Au has the same structure as the Au<sub>3</sub>Cu. For nanoporous Cu, Figure S3b reveals quasi-twodimensional (2D) nanoporous arrays, possessing 3D networks in the microcosm. The thickness of the nanosheets and the ligament size are ~40 nm and 30 nm, respectively.

As shown in Figure 1c, most ligaments possess positive, negative, and saddle-like surface curvatures, which are different from the nanoparticles with relatively well-defined shape and only convex surface curvature at the corners. <sup>[16]</sup> Furthermore, the interplanar distance from the adjacent lattice fringes in the HRTEM images (Figure 1d) are about 0.24 nm, 0.21 nm and 0.124 nm corresponding to the (111), (200) and (311) planes of FCC Au<sub>3</sub>Cu, respectively. EDX elemental mapping (Figure 1e-h) show that Au and Cu are distributed over the entire ligament. The integration diagram shows that the surface gold content is higher than bulk average content. The linear scan elemental map (Figure

1i) reveals that the gold signals on both sides are stronger than the central region. While the reverse signals occur over Cu, implying the  $Au_3Cu$  surface is enriched in gold.



Figure 1. (a) XRD pattern of the as-prepared Au<sub>3</sub>Cu alloy; (b) Low and high magnification SEM images of nanoporous Au<sub>3</sub>Cu; (c-d) HR-TEM image; (e-h) STEM-EDS elemental mapping of Au<sub>3</sub>Cu; and (i) Line profiles of Au and Cu recorded along the dashed line shown in (e).



Figure 2. XPS spectra of (a) Au 4f region and (b) Cu 2p region.

XPS was applied to characterize the surface composition and oxidation state of nanoporous Au<sub>3</sub>Cu in detail. Figure 2a, b are the high-resolution spectra of Au 4f and Cu 2p regions over Au<sub>3</sub>Cu. Au 4f spectrum exhibits binding energy (B.E.) peaks of 4f<sub>7/2</sub> and 4f<sub>5/2</sub> at 84.5 eV, and 88.2 eV, respectively, coinciding with the state of metallic Au. The band positions have a slight shift to the high energy direction compared to pure nanoporous Au because of the electronic interaction between Au and Cu in the alloy. The surface Au content is 77.95%, confirming the gold is rich on the surface. In Cu 2p region, the peaks at 932.7 eV and 952.6 eV are assigned to the binding energies of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$ , indicating the existence of Cu (0). In addition, the remaining small peaks at 934.48 eV and 953.78 eV can be assigned to CuO, which come from an inevitable oxidation of the sample in air. <sup>[17]</sup> In comparison with pure nanoporous Cu, the band positions have a significant negative shift, demonstrating that the surface copper

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(content of 22.05%) has a little bonding with surface gold. <sup>[12b]</sup> For the cross-section, the ratio of Au is decreased to 72.88%, while is lower than the surface. The B.E. of Au  $4f_{7/2}$  and  $4f_{5/2}$  shifts to the higher energy direction, compared to those for single nanoporous Au. Correspondingly, the B.E. of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  moves to the opposite direction. It is reasonable to infer that the valence electrons transfer from Cu atom to Au atom due to their different electronic negativity, resulting in the interatomic charges are redistributed. A decrease in B. E. over Cu atom reflects the downshift of d-band center, weakening chemisorption of oxygencontaining species, e.g.,  $CO_{ads}$  and  $OH_{ads}$ , on the surface. <sup>[5a, 18]</sup>

To gain insights into the surface coordination environments of the nanoporous Au<sub>3</sub>Cu, the XANES spectra was collected form Au<sub>3</sub>Cu at Au L<sub>3</sub> edge. As shown in Figure 3a, edge positions of Au in the XANES profile of Au<sub>3</sub>Cu has similar edge shape to that of reference Au foil, indicating its full Au (0) state. <sup>[19]</sup> Additionally, it has a small increase in intensity above the Au foil in the region from 11920 eV - 11950 eV. This region is where the "white line" absorption occurs, indicating increased electron density over the d-band of Au. The magnitude of the change in the white line is consistent with those over bulk AuCu alloys. <sup>[20]</sup> The edge position has a slight shift towards high photon energies compared with Au foil. The phenomenon at the two edges are caused by the electron transfer from Cu to Au, which is consistent with the XPS analyses. The loss of electrons in the Cu d-band is compensated by gaining s-p bands. [21] The EXAFS with the data-fitting in R space was carried out to determine the short-range local coordination structure including distances (R) and coordination number (CN) around the gold atoms. As revealed in Figure 3b and Table S1, three peaks in the range of 2.2-3.5 Å can be assigned to the contribution from metallic Au-Au with a CN number of 7.3. Figure S4 presents EXAFS data of nanoporous Au<sub>3</sub>Cu, showing the coordination environment surrounding Au and Cu. The Au L<sub>3</sub>edge of nanoporous Au<sub>3</sub>Cu exhibits a larger first-shell scattering amplitude, which can be attributed to the stronger constructive interference of photoelectron scattering. The lower CN for gold indicated that Au atoms are relatively unsaturated compared to Cu, resulted from gold enriched at the surface.



Figure 3. X-ray fine absorption spectroscopy of  $Au_3Cu$ . (a) XANES spectra; (b) EXAFS spectra at the Au  $L_3$ -edge.

The as-synthesized nanoporous  $Au_3Cu$  can be directly applied as electrode for  $CO_2$  RR. Figure 4a gives the linear sweep voltammetry (LSV) curve in the  $N_2$  and  $CO_2$  atmosphere over nanoporous Au, Cu and Au<sub>3</sub>Cu, respectively. The applied potential was in a range of 0 ~ -1.4 V (vs. RHE) at a sweep rate of 50 mV/s, A quite difference was observed among the LSV curves of Au, Cu and Au<sub>3</sub>Cu between N<sub>2</sub> and CO<sub>2</sub>-saturated electrolytes. The total current densities (reaction activity) were significantly increased in the CO2-saturated electrolyte, showing an apparent contribution of CO<sub>2</sub> RR to the whole reaction. The activity of nanoporous Au<sub>3</sub>Cu is significantly higher than that of single nanoporous Cu. Although it is somewhat lower than that of nanoporous Au, HER gradually dictates the ability of nanoporous Au with the increase of potential. Thereafter, stepped-potential tests were conducted from -0.6 to -1.0 V (vs. RHE). As shown in Figure 4b, c, CO and H<sub>2</sub> are the major products, with the total FE approaching 100%. It is noticed that the selectivity of nanoporous Cu is poor, and the FE of CO is rather low, and does not increase with the change of potential. The nanoporous Au is affected by the potential significantly. As the potential increases, the HER becomes more serious. However, in the case of nanoporous Au<sub>3</sub>Cu, as the potential goes more negative, the FE of CO increases while the HER suppressed.



Figure 4. Electrocatalytic CO<sub>2</sub>RR performance of Au, Au<sub>3</sub>Cu and Cu. (a) LSV in N<sub>2</sub> and CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub>; (b, c) FE of CO and H<sub>2</sub> under different applied potentials; (d, e) partial current of CO and H<sub>2</sub> production at various potentials; (f) The CO<sub>2</sub>RR stability test of the current density on self-supported Au<sub>3</sub>Cu nanoporous electrode at -0.7V vs RHE for 80 h.

The CO<sub>2</sub>-to-CO conversion was initiated from -0.6 V vs RHE, rapidly increased to conversion ratio of 96.73%, and reached the highest FE of 98.12% at -0.7V vs RHE. The FE value is 1.47 times of that over pure nanoporous Au. The selectivity is also higher than reported data over AuCu alloys.<sup>[22]</sup> Moreover, a high FE of CO can be maintained at wide range of applied potentials. The

potential required at the highest FE is much lower than that of nanoporous Au. Figure 4d, e compares partial current density of CO and H<sub>2</sub>. It can be seen that the partial current density for CO production would be remarkably increased along with the raise of applied negative potential, indicating that the reaction rate of CO<sub>2</sub> RR is accelerated at high potentials.<sup>[23]</sup> Meanwhile, the partial current density of CO over nanoporous Au<sub>3</sub>Cu is much higher than Cu. Due to the high HER at high potentials, CO partial current density of nanoporous Au is lower than that of Au<sub>3</sub>Cu. As shown in Figure 4e, the sub-current density of H<sub>2</sub> of Au at the same overpotential is about 20 times higher than that over Au<sub>3</sub>Cu (approximate 0.44mA cm<sup>-2</sup> at -1 V vs. RHE), further demonstrating the high activity and selectivity of the Au<sub>3</sub>Cu towards CO<sub>2</sub> RR. Figure 4f shows that total current density over nanoporous Au<sub>3</sub>Cu still maintained ~10 mA cm<sup>-2</sup> after lasting electrolysis for more than 80 h at a potential of -0.7 V. XRD showed (Figure S5) that the pattern did not change and remained as Au<sub>3</sub>Cu. SEM image (Figure S6) shows nanoporous structures still retains. The mapping and XPS showed (Figure S7. 8) that the surface was still rich in Au structure, and no significant change was made, suggesting its good stability. For nanoporous Au, after testing at the same condition, the current density and the FE of CO over which were reduced after 50 h because of the vigorous surface HER (Figure S9, S10), although the porous structures have no change. The nanoporous Cu can only be maintained for about 7.5 h at -1.0 V vs. RHE, (Figure S11) which is significantly lower than that of the nanoporous Au<sub>3</sub>Cu, and the porous structure is completely collapsed (Figure S12).

For contrast, solid Au<sub>3</sub>Cu was also obtained by annealing nanoporous Au<sub>3</sub>Cu alloys at 500 ° C. XRD pattern in Figure S13 indicate the constituents of the obtained solid Au<sub>3</sub>Cu is basically the same as that of porous sample. The pores disappeared after annealing, and the selectivity over which towards CO<sub>2</sub> RR is apparently decreased (Figure S14, S15). Therefore, the nanoporous Au<sub>3</sub>Cu with unsaturated coordination Au atoms, and curved interfaces plays essential role on the enhancement of CO<sub>2</sub> RR performance.



Figure 5. Fitting graph of linear relation between formation free energy of \*COOH and adsorption free energy of \*CO. (a) average distance between \*CO

and the catalyst surface; (b) Hirshfeld charge distribution of Au\_3Cu {311} and Au {311} and \*COOH adsorption structure on Au\_3Cu {311} and Au {311} (c, d).

The most important elementary process in the preparation of CO through CO<sub>2</sub> RR is the formation of \*COOH intermediates and the following dissociation of \*CO. Figure 5a plotted the formation energy of \*COOH and adsorption energy of \*CO. The lower the ordinates, the smaller free energy change needed to be overcome for the generation of \*COOH intermediates on the catalyst surface. Meanwhile, the more positive adsorption free energy of \*CO adsorption on the catalyst, the easier the \*CO is dissociated from the surface, which is beneficial for the completion of the entire reaction. Among all the catalysts examined, the nanoporous Au<sub>3</sub>Cu {311} has the lowest free energy change of \*COOH formation, while the energy required for \*CO desorption is relatively low. Therefore, Au<sub>3</sub>Cu {311} has the best catalytic activity. The average distance between \*CO and surface in Figure 5b also indicates that there is a relatively long distance between \*CO and Au<sub>3</sub>Cu {311} in the adsorption structure, making \*CO desorb easily. Therefore, the catalyst is not prone to be positioned by CO. The Hirshfeld charge distribution of Au<sub>3</sub>Cu {311} and Au {311} in Figure 5c,d show that the surface of pure Au is negatively charged, making it prefer interacting with positively charged C atoms in \*COOH intermediate, meanwhile the surface Au<sup>5-</sup> has a repulsion effect to the negatively charged O atom in the \*COOH. Thus, the \*COOH intermediate tends to be a monodentate form on single Au (Figure 5c). The introduction of Cu to Au significantly changes the surface charge distribution of the catalyst. Electronic charge redistributed from Cu to Au creates regions of localized positive charge on the Cu sites. While the Au atoms around the Cu atoms are obviously more negatively charged. This positive and negative charge center can be simultaneously bonded with the C, O atoms in the \*COOH, forming a more stable (lower energy) bidentate adsorption structure (Figure 5d). Therefore, the formation of \*COOH becomes easier on the surface of Au<sub>3</sub>Cu, and boost the CO production.

### Conclusions

In summary, we have developed a mild oxidative etching route for the synthesis of three-dimensional nanoporous Au<sub>3</sub>Cu with enriched gold on the surface. The as-obtained nanoporous Au<sub>3</sub>Cu can be directly applied as self-supported electrode for conversion from CO<sub>2</sub> to CO with high efficiency, which is superior to single porous Au and Cu. The nanoporous Au<sub>3</sub>Cu realized FE<sub>CO</sub> of 98.12 % with a stable current density of 12.77 mA cm<sup>-2</sup> at a voltage of -0.7 V. The increased catalytic activity is attributed to the presence of great amount of unsaturated coordination active sites on the nanoporous surface, which also promotes transport of the reactants as well as the products. Theroetical simulation reveals that the nanoporous Au<sub>3</sub>Cu catalyst has the lowest \*COOH intermediate adsorption energy, because the introduction of Cu causes more negative charge on the surface of the Au atom, thereby forming stable double-dentate adsorption mode. Meanwhile \*CO has a relatively long distance on the surface of nanoporous Au<sub>3</sub>Cu, making CO easier to desorb from the surface and avoids CO poisoning. In short, the present work provides a

pathway to engineer the phases and surfaces of the nanoporous catalysts.

#### **Experimental Section**

#### Materials synthesis

Au<sub>20</sub>Cu<sub>80</sub> alloy was prepared by an arc melting furnace (WK type, Physcience Opto-electronics Co., Ltd., Beijing). In a typical procedure, pure metals of Cu (99.99 wt.%), and Au (99.99 wt.%) were melted 3 times on a water-cooled copper hearth under a Ti-gettered argon atmosphere. With a melt spinning equipment (WK-IIB type, Physcience Opto-electronics Co., Ltd., Beijing), the pre-alloyed ingot was remelted in a quartz tube by high-frequency induction heating. Then its melt was injected onto a copper roller of 25 cm in diameter, which was rotated at a speed of ~3000 rpm in a controlled argon atmosphere. The as-spun ribbons were ~25  $\mu$ m in thickness, 2.0 mm in width and 10 cm in length (Illustrated in Figure S1), respectively.

#### Preparation of nanoporous Au<sub>3</sub>Cu alloy

40 mg of the as-prepared  $Au_{20}Cu_{80}$  was immersed into 0.08 M of FeCl<sub>3</sub> solution at room temperature under stirring for 30 min. Then the obtained sample was rinsed with deionized water several times, and dried in a vacuum oven at 60 ° C for 12 h.

When the FeCl<sub>3</sub> concentration was increased to 0.5 M, the nanoporous Au was obtained and the other conditions were kept constant. For comparison, nanoporous Cu was prepared by chemical corrosion of  $Cu_{17}Al_{83}$  ribbons (1.48 g) in alkaline (2 M NaOH) solution for 4 h at 298 K.

#### Characterizations

X-ray diffraction (XRD, Rigaku UltimalV) was performed to analyze the crystal structure. The microstructures were observed on an FEI Verios 460L field emission scanning electron microscopy (SEM), high-resolution transmission electronic microscopy (HRTEM) with FEG (Talos F200X), and the high-angle annular dark field scanning transmission electronic microscopy (Titan Themis Cubed G2 60-300) equipped with an Oxford SDD X-Max energy dispersive X-ray spectrometer (EDS). The chemical valences and surface composition were analyzed with a THERMO SCIENTIFIC ESCALAB 250xi X-ray photoelectronic spectrometer (XPS), using monochromatized AI Kα X-ray as the excitation source, and C 1s (284.80 eV) as the reference line.

The XAFS spectra at Au  $L_3$  ( $E_0 = 11919.0$  eV) edge was performed at BL14W1 beamline of Shanghai Synchrotron Radiation Facility (SSRF) operated at 3.5 GeV under "top-up" mode with a constant current of 260 mA. The XAFS data were recorded under transmission mode with two Oxford ion chambers. The energy was calibrated according to the absorption edge of pure Au foil. Athena and Artemis codes were used to extract the data and fit the profiles. For the X-ray absorption near edge structure (XANES) part, the experimental absorption coefficients as function of energies  $\mu(E)$  were processed by background subtraction and normalization procedures, and reported as "normalized absorption" with  $E_0$ = 11919.0 eV for the measured sample and Au foil standard. For the extended X-ray absorption fine structure (EXAFS) part, the Fourier transformed (FT) data in R space were analyzed by applying first-shell approximate model for Au-Cu contributions, and metallic Au model for Au-Au contribution. The passive electron factors, S<sub>0</sub><sup>2</sup>, were determined by fitting the experimental data on Au foils and fixing the coordination number

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(*CN*) of Au-Au to be 12, and then fixed for further analysis of the tested samples. The parameters describing the electronic properties (e.g., correction to the photoelectron energy origin,  $E_0$ ) and local structure environment including *CN*, bond distance (*R*) and Debye-Waller factor around the absorbing atoms were allowed to vary during the fit process. The fitted ranges for *k* and *R* spaces were selected to be k = 3-12 Å<sup>-1</sup> with R = 1.0-3.5 Å ( $k^3$  weighted).

#### **Electrochemical measurements**

A three-electrode system was used with the self-supported nanoporous Au<sub>3</sub>Cu alloy as the working electrode, Pt as the counter electrode on an electrochemical station (CHI 760E). All the potentials were measured against an Ag/AgCl reference electrode (3.0 M KCl), and converted to the RHE reference scale using the equation *E* (vs RHE) = *E* (vs Ag/AgCl) + 0.1989 V + 0.0591 V × pH. The CO<sub>2</sub> RR was used to probe their electrocatalytic performance over nanoporous electrodes (Figure S1). Nanoporous Cu is evaluated on carbon paper because of its powder form. The tests were performed in a two-compartment electrochemical cell with a piece of anion exchange membrane (Nafion®117) as the separator. The electrolyte was 0.1 M KHCO<sub>3</sub> saturated with CO<sub>2</sub> at pH value of 6.8. Each compartment contained 40 mL of electrolyte. Before the reaction was initiated, the electrolyte in the cathodic compartment was bubbling CO<sub>2</sub> gas for at least 30 min. Magnetic stirring was applied at a rate of 500 rpm throughout the whole tests.

#### CO<sub>2</sub> RR product analysis

CO<sub>2</sub> gas was bubbled into the cathodic compartment at an average rate of 10 sccm (at room temperature and ambient pressure), which was vented directly into the gas sampling loop of a gas chromatograph (GC9790II, Zhejiang Fuli Analyzing Instruments Co. Ltd.). The GC was initiated every 25 min, and nitrogen (99.999%) was used as the carrier gas. The separated gas mixtures were passed through a thermal conductivity detector (TCD), where the concentration of hydrogen was analyzed. The concentration of CO was analyzed by a flame ionization detector (FID) with a methanizer.

#### **Theoretical calculations**

All the calculations in this work were performed using the Generalized gradient approximation (GGA)-perdew, Burke and ernzerhof (PBE) [24] in the full-electron DMol<sup>3</sup> program.<sup>[25]</sup> The normal metal surface are simulated using (111) surface of Cu. Au and Au<sub>3</sub>Cu allov with a five-lavered slab of (4x4) surface unit cell. The (311) surface was simulated over porous Au\_3Cu and Au with a five-layered slab of (3x3) surface unit cell. A vacuum region was 30 Å between repeated slabs. In our calculations, the atoms in the bottom two layers were fixed at their bulk position and those in the top three layers together with the adsorbates are allowed to relax. Double numerical plus polarization (DNP) basis set was used throughout the calculation. The convergence criteria were set to be 1x10<sup>-5</sup> Ha. 0.001 HaÅ<sup>-</sup> <sup>1</sup>, and 0.005 Å for energy, force, and displacement convergence, respectively. A self-consistent field (SCF) density convergence with a threshold value of 1x10<sup>-6</sup> Ha was specified. K-points were sampled using the 3x3x1 Monkhorst-Pack mesh. The Gibbs free energy diagrams for CO2 reduction are calculated with reference to the computational hydrogen electrode (CHE) proposed by Nørskov et al. [26] A vibrational analysis was used to calculate the thermodynamic properties of all related molecules in the gas phase and stable adsorption state involved in the reaction.

Formation free energy for \*COOH and adsorption free energy for \*CO are calculated through the following equations.

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 $\Delta G_{COOH} = G_{COOH^*} - (G_* + G_{CO_2} + \frac{1}{2G_{H_2}})$ 

 $\Delta G_{CO} = G_{CO^*} - (G_* + G_{CO})$ 

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**Keywords:** Nanoporous alloy • self-supported • AuCu • carbon dioxide reduction

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