RETRACTED ARTICLE: Preparation of hollow Au$_x$-Cu$_2$O nanospheres by galvanic replacement to enhance the selective electrocatalytic CO$_2$ reduction to ethanol

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ABSTRACT
Electrocatalytic CO$_2$ reduction to fuel is one of the important ways to solve energy and environmental problems. In this work, the preparation of hollow Au$_x$-Cu$_2$O electrocatalyst and the performance of electrocatalytic CO$_2$ reduction to ethanol were studied. Hollow Cu$_2$O nanospheres were prepared by a soft template method, and Au$_x$-Cu$_2$O composites were prepared by galvanic replacement. The characterization results of XRD and XPS reveal that Cu$^+$ is the main chemical state of Cu in the catalysts. The results of electroactive surface area demonstrate that the electroactive surface area of Au$_{0.51}$-Cu$_2$O is the largest. The performance evaluation of electrocatalytic CO$_2$ reduction shows that the Faraday efficiency of H$_2$ on Au$_{0.51}$-Cu$_2$O is the lowest ($\sim$19.5%) and the Faraday efficiency of ethanol can reach $\sim$18.8% at $\sim$1.2 V vs. RHE. Compared with hollow Cu$_2$O nanospheres, Au$_x$-Cu$_2$O catalysts have an earlier onset for ethanol production and promote the CO$_2$ reduction to ethanol with high efficiency, while the hydrogen evolution reaction is significantly inhibited. Our study demonstrates an effective approach to develop Cu-based electrocatalysts favourable toward ethanol in electrocatalytic CO$_2$ reduction.

1. Introduction
Electrocatalytic CO$_2$ reduction (ECR) to C$_2$+ products with high energy density is a current research hotspot. At present, the main challenge is that it is difficult to effectively realize C–C bond coupling reaction [1]. The results show that copper-based materials are the only catalysts that can reduce CO$_2$ to hydrocarbons and oxygen-containing compounds, but the catalytic activity and selectivity need to be improved to meet the requirements of industrial application [2–7].

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Many studies have shown that the copper-based catalysts designed based on the double active sites or tandem catalysis mechanism can significantly improve the selectivity of C\textsubscript{2}+ products [8–10]. For example, Ag, Au and Zn all have high activity and selectivity for electrocatalytic CO\textsubscript{2} reduction to CO. Cu-M and other copper-based catalysts exhibit the performance of promoting the formation of C–C bond coupling reaction to C\textsubscript{2}+ products [11–19]. Therefore, the introduction of active sites to promote the formation of CO on Cu-based catalysts can effectively improve the CO\textsubscript{2} reduction to C\textsubscript{2}+ products.

Recent studies have shown that Cu(I) species on copper-based catalysts can remain relatively stable in the process of electrocatalytic CO\textsubscript{2} reduction and play an important role in promoting CO\textsubscript{2} activation and *CO intermediate dimerization or protonation, and then the production of C\textsubscript{2} products increases [20–26]. In addition, it has also been found that the catalyst with a hollow structure has the advantages of large specific surface area and low density compared with single-component solid nanoparticles [27,28]. Especially as an electrocatalyst the hollow structure provides a larger electrolyte-electrode contact area and abundant electrochemical active sites for rapid diffusion and reaction [29–31].

In our study, hollow Au\textsubscript{x}–Cu\textsubscript{2}O electrocatalysts were designed based on the tandem catalysis mechanism. The role of Au is to promote the conversion of CO\textsubscript{2} to CO, which is beneficial to increase the local concentration of the key intermediate *CO in order to promote the C–C bond coupling reaction, and then enhance the formation of multi-carbon products. Firstly, hollow Cu\textsubscript{2}O nanospheres were prepared with CTAB (Hexadecyl trimethyl ammonium Bromide) as a soft template, and hollow Au\textsubscript{x}–Cu\textsubscript{2}O electrocatalysts were prepared by galvanic replacement. The physical and chemical properties and electrochemical properties of the prepared electrocatalysts were characterized, and the performance of CO\textsubscript{2} reduction to ethanol was evaluated.

2. Experiment

2.1. Materials and method

Copper(II) sulphate pentahydrate (CuSO\textsubscript{4}·5H\textsubscript{2}O, AR, J&K Scientific LTD), Sodium citrate (Na\textsubscript{3}C\textsubscript{6}H\textsubscript{5}O\textsubscript{7}·2H\textsubscript{2}O, AR, J&K Scientific LTD), Sodium borohydride (NaBH\textsubscript{4}, 98%, J&K Scientific LTD), Ascorbic acid (AA, 98%, HEOWNS), Hexadecyl trimethyl ammonium Bromide (CTAB, 97.0%, HEOWNS), isopropanol ((CH\textsubscript{3})\textsubscript{2}CHOH, AR, HEOWNS), Chlorauric Acid (HAuCl\textsubscript{4}, 99.0%, HEOWNS), Deuterium Oxide (D\textsubscript{2}O, 99.79%, HEOWNS), Potassium bicarbonate (KHCO\textsubscript{3}, 99%, HEOWNS), Sodium hydroxide (NaOH, AR, Aladdin), Ethanol absolute (C\textsubscript{2}H\textsubscript{5}OH, AR, Tianjin Yuanli Chemical Co., Ltd.), Deionized water. All reagents were used directly without further purification and deionized water was used in our experiments.

2.2. Synthesis of hollow Cu\textsubscript{2}O

Hollow Cu\textsubscript{2}O nanospheres were prepared by a soft template method using Hexadecyl trimethyl ammonium Bromide (CTAB) as soft template [32]. In a typical synthesis procedure, 50 mg CuSO\textsubscript{4}·5H\textsubscript{2}O was added to the 0.13 M CTAB aqueous solution (100 mL), then 0.18 g ascorbic acid (AA) was added to the above solution and heated to 60 °C. After stirring for 20 min at 60 °C, 0.2 M NaOH (10 mL) aqueous solution was added to the above solution. After 10 min, the mixture was cooled to room temperature, and the yellow Cu\textsubscript{2}O precipitate was separated and washed sequentially using deionized water and ethanol five times by centrifuging at 9000 rpm. The obtained Cu\textsubscript{2}O was dried at 60 °C for 12 h under vacuum.
2.3. Synthesis of hollow Au-Cu$_2$O

Hollow Cu$_2$O nanospheres were prepared following the procedure in the 2.2. section. The schematic diagram of the formation process of Au-Cu$_2$O composites is illustrated in Figure 1. 10 mg Cu$_2$O nanospheres was dispersed into the mixed solution of 20 mL water and ethanol (volume ratio 1:1). After ultrasonic for 10 min, 0.05 M sodium citrate aqueous solution (1.5 mL) was added to the above solution drop by drop. After ultrasonic for 10 min, 0.25 mL HAuCl$_4$ (20 mg mL$^{-1}$) aqueous solution was added to the mixed solution drop by drop. After 20 min, the precipitate was separated and washed sequentially using deionized water and ethanol five times by centrifuging at 9000 rpm. The obtained Au-Cu$_2$O was dried at 60 °C for 12 h under vacuum. The sample was named Au$_{0.17}$-Cu$_2$O. By changing the addition amount of HAuCl$_4$ (0.50 mL, 0.75 mL), the samples were named Au$_{0.34}$-Cu$_2$O and Au$_{0.51}$-Cu$_2$O, respectively. 0.17, 0.34 and 0.51 represents the molar ratio of Au to Cu$_2$O, respectively.

2.4. Characterization

X-ray diffraction (XRD, Rigaku D/MAX-2500 diffractometer, Japan, 2θ = 20°~85°, scanning rate 8°/min) with Cu Kα radiation was recorded to determine the phase composition of the tested sample. The microscopic morphologies of the prepared catalysts were observed by scanning electron microscope (SEM, Hitachi, S-4800, Japan) and Transmission electron microscopy (TEM, Japan, JEOLJ, EM-2100F). Analysis of element composition and chemical environment of sample surface by X-ray photoelectron spectroscopy (XPS, Britain, Thermo Fisher Scientific, K-Alpha) and all the XPS spectra were calibrated by the binding energy with contaminated carbon C1s (284.8 eV as the correction value).

2.5. Electrochemical measurements

All electrochemical measurements were controlled on an electrochemical station (Switzerland, Metrohm AutoLab 302 N) in an H-type two-chamber electrochemical cell.
separated by proton exchange Naion membrane (Tianjin Incole Union Technology Co., Ltd.). The catalyst Ink was prepared by ultrasonic dispersion of 5 mg catalyst and 50 μL Naion in isopropanol solution. 105 μL Ink was dripped on the glassy carbon electrode (1.0 cm × 1.0 cm), which was as the working electrode. The saturated calomel electrode (SCE) was used as the reference electrode, and the platinum plate (1.0 cm × 2.0 cm) was used as the counter electrode. Electrochemical tests were carried out in 0.1 M KHCO3 solution. The applied potential is converted to reversible hydrogen electrode potential (RHE) by using the formula: $E_{(RHE)} = E_{(SCE)} + 0.0591 \times \text{pH} + 0.24$. Before electrocatalytic CO2 reduction, N2 and CO2 were purged into the electrolyte for 50 min. The working electrode was scanned by LSV at N2 atmosphere for 2 h to achieve the purpose of pre-reduction and surface activation, and then the CO2 reduction performance of each electrode was tested at five potentials (−0.9 V, −1.1 V, −1.2 V, −1.3 V, −1.5 V vs. RHE). CO2 was continuously purged into the cathode chamber at a flow rate of 20 mL/min. The gas phase products were detected using the gas chromatography (GC, Agilent 7890B) with a TCD and the liquid phase products were detected by 400 MHz 1H 1D liquid NMR spectrometer (Bruker, AVANCE III). The Faraday efficiency of each product is calculated according to the formula (1)–(3).

$$j_{H_2\text{or}CO} = V_{H_2\text{or}CO} \times q \times \frac{zFP_0}{RT}$$

$$FE_{H_2\text{or}CO} = \frac{j_{H_2\text{or}CO}}{j_{total}} \times 100\%$$

$$FH_{HCOOH\text{or}C_2H_5OH} = \frac{znF}{Q} \times 100\%$$

where $q$ is the flow rate of CO2 during ECR, $F$ is the Faraday constant (96,485.3 C/mol), $P_0$ is pressure, $T$ is room temperature, $R$ is the ideal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $z$ is the number of electrons transferred during ECR, $n$ is the molar mass of the products, and $Q$ is the total electric quantity during ECR.

### 3. Results and discussion

#### 3.1. Structural characterisation

The X-ray diffraction (XRD) patterns of Cu2O and Au$\_x$-Cu2O composites are shown in Figure 2. For hollow Cu2O catalyst, the diffraction peaks at 29.55°, 36.41°, 42.30°, 61.34° and 73.53° correspond to the (110), (111), (200), (220) and (311) of Cu2O, respectively. For Au$\_x$-Cu2O composites, except for the typical peaks of Cu2O, the diffraction peaks observed at 38.18°, 44.39°, 64.58°, 77.55° and 81.72° correspond to the face-centred cubic crystal Au (PDF#04-0784), indicating that Au nanoparticles have been successfully supported on the hollow Cu2O nanospheres by galvanic replacement. In addition, with the increase of the amount of HAuCl4, the area of the diffraction peak of Au increases and the area of Cu2O diffraction peak decreases gradually, which is due to the increase of the number of Au nanoparticles formed by Cu2O replacement and the increase of Cu2O consumption as a sacrificial template in the galvanic replacement reaction [33]. No impurity peak was observed in the Cu2O and Au$\_x$-Cu2O composites, indicating that the purity of the prepared catalysts was high.

Figure 3 shows the SEM and TEM images of hollow Cu2O nanospheres. The size of hollow Cu2O nanospheres is about 150–180 nm, and the surface is uneven. Because the surface of the shell is composed of many Cu2O particles attached along the CTAB vesicles.
From the TEM Figure 3c, the single-shell and double-shell structure of nanospheres were observed clearly, the latter of which was dominated. From the HRTEM Figure 3d, the clear crystal plane spacing of 0.241 nm is consistent with the lattice spacing of Cu$_2$O (111) plane.

Figure 4 shows the SEM and TEM images of Au$_{0.17}$-Cu$_2$O composite. The sample basically maintains the hollow shell structure of Cu$_2$O. The surface of the sample with an average particle size of about 150–200 nm, and small particles can be observed on the surface. The relatively brighter particles in Figure 4c are Au nanoparticles produced by galvanic replacement reaction, which are dispersed on the surface of Cu$_2$O. From the HRTEM Figure 4e, it can be seen that the particle size of Au nanoparticles is about 5–7 nm. In addition, 0.241 nm crystal plane spacing corresponding to Cu$_2$O planes and 0.235 nm crystal plane spacing corresponding to Au planes can be observed. From the TEM-mapping, it can see that Au nanoparticles are almost uniformly dispersed on the surface of Cu$_2$O. Figure S1 shows the SEM and TEM images of Au$_{0.34}$-Cu$_2$O composite. The sample basically maintains the hollow shell structure of Cu$_2$O, and the average particle size is about 140–180 nm. In addition, small particles and more uniform dispersion can be observed on the sample surface. Although the variable controlled in our study is the amount of HAuCl$_4$, the pH of the whole system is changed by adding more HAuCl$_4$. It is speculated that the environment of the system may be more suitable for galvanic replacement reaction at this time [35]. It can be also seen from the TEM-mapping that Au nanoparticles are basically uniformly dispersed on the surface of Cu$_2$O. Figure S2 shows the SEM and TEM images of Au$_{0.51}$-Cu$_2$O composite. The average particle size is about 180–200 nm and the surface of the sample has some pores and more small particles, indicating that under the condition of a certain amount of carriers, the increase of HAuCl$_4$ addition leads to the overreaction of the shell and the exposure of pores. On the one hand, the increase of carrier consumption is due to the fact that the increase of AuCl$_4^-$ aggravates the galvanic replacement reaction, and the other is that the increase of H$^+$ accelerates the consumption of Cu$_2$O. From the HRTEM Figures S2c and 2d, it can be seen that the number of Au nanoparticles loaded on Cu$_2$O surface increases and the particle size of Au nanoparticles is larger (about 10–20 nm), which may be due to the
increase of Au nanoparticles generated by galvanic replacement reaction with the increase of HAuCl₄ addition and partial aggregation on the surface of Cu₂O.

Furthermore, the surface compositions and chemical states of the catalysts were determined by XPS characterization. The XPS characterization results of Auₓ·Cu₂O and Cu₂O catalysts are shown in Figures 5 and S3–S5. Take Au₀.₁₇·Cu₂O as an example, from the spectrum of Figure 5a, there are three elements Cu, Au and O, indicating that Au₀.₁₇·Cu₂O electrocatalyst was successfully prepared by galvanic replacement reaction. From Figure 5c, there are four typical peaks of Cu in the Cu 2p spectrum, indicating that there is a mixed oxidation state of copper [36,37]. The peaks at the binding energies of 952.3 eV and 932.5 eV correspond to Cu 2p₃/₂ and Cu 2p₁/₂, respectively [38]. Combined with the Auger spectrum of Cu in Figure 5b, it indicates that Cu⁺ is the main chemical state of Au₀.₁₇·Cu₂O. In addition, the peak at 933.8 eV belongs to CuO.

Figure 3. (a) and (b) SEM images of hollow Cu₂O nanospheres; (c) and (d) HRTEM images of hollow Cu₂O nanospheres.
which is due to the galvanic replacement reaction of $\text{AuCl}_4^-$ with $\text{Cu}^+$ and the formation of trace $\text{CuO}$ on the surface. The Au 4f spectrum of $\text{Au}_{0.17}\text{-Cu}_2\text{O}$ is shown in Figure 5d. There are two peaks at Au 4f$_{7/2}$ and Au 4f$_{5/2}$, which are located at 84.1 eV and 87.7 eV, respectively, indicating the existence of Au$^0$ [40,41]. According to the XPS results, the atomic composition of $\text{Cu}_2\text{O}$ and $\text{Au}_{x}\text{-Cu}_2\text{O}$ catalysts is summarized in Table S1. The change trend of the surface atomic composition of the catalysts is consistent with that of the theoretical Au/Cu atomic ratio.

### 3.2. Electrochemical measurements

After the galvanic replacement of hollow $\text{Cu}_2\text{O}$ nanospheres with $\text{AuCl}_4^-$, part of the surface of $\text{Cu}_2\text{O}$ will be covered by Au, which leads to the change of electrochemical reaction
The redox behaviour of the Aux-Cu2O nanospheres was investigated by cyclic voltammetry (CV). The prepared Cu2O and Aux-Cu2O electrodes were scanned by CVs in the potential range of −0.75 to +1.25 V vs. RHE, respectively. Then, the same CV tests were carried out on the electrode after surface activation treatment. By comparing the CVs obtained twice, the effect of different loading amount of Au nanoparticles on the redox properties of copper on the surface of Aux-Cu2O can be investigated (there is no redox reaction in the test potential range of Au nanoparticles).

As shown in Figure 6, there are two oxidation peaks (A1 and A2) and three reduction peaks (C1, C2 and C3) before and after activation of Cu2O and Aux-Cu2O electrodes. The two anodic peaks at 0.45 V (A1) and 0.69 V (A2) correspond to the oxidation of Cu0 to Cu+ and Cu+ to Cu2+, respectively. The three reduction peaks at 0.22 V, −0.19 V and −0.41 V are attributed to the reduction of CuO to Cu2O (C1) and further to Cu (C2) and HCuO2− (C3) [42,43]. Among them, the C3 peaks of Au0.34-Cu2O and Au0.51-Cu2O electrodes are weak and not prominent. As shown in Figure 6a, the Cu2O electrode has two typical reduction peaks at 0.22 V and −0.19 V. Comparing the CVs before and after activation, the current densities of both oxidation and reduction reactions on the activated electrode increase, indicating that clear Cu2O reduction occurs on the surface of the electrode during activation, resulting in a significant change in the redox properties of the surface. In contrast, as shown in Figure 6b–d, the corresponding reduction peak changes little in the CV curve measured by Aux-Cu2O electrode before and after activation, which may be due to the fact that after the galvanic replacement of Cu2O and AuCl4−, part of the Cu on the surface of the sample is covered, the Cu2O reduction reaction is weakened.
to a certain extent in the process of electrode activation, and the redox reaction on the surface is relatively stable. Because of the high loading of Au, the CV curve of Au0.51-Cu2O electrode is close to coincidence before and after activation. The results show that a small amount of Cu0 can be formed after electrode activation, but most of the Cu2O is still remained. In addition, with the increase of the amount of HAuCl4, the exposed copper on the surface of the sample decreased, and the loading of Au nanoparticles improved the stability of the electrode to some extent.

The electrochemical active surface area (EASA) of Cu2O and Au-x-Cu2O composites was measured by double layer capacitance method. The CV test results of different scanning speeds are shown in Figure 7, and a straight line is obtained by analysing and fitting the current density and scanning rate of the midpoint of the curve (−0.33 V). The slope of the fitting line in Figure 8 is the double layer capacitance of each electrode. Among these catalysts, Au0.51-Cu2O has the largest double-layer capacitance of 0.66 mF. Because the double-layer capacitance is proportional to the electroactive surface area, Au0.51-Cu2O has the largest electroactive surface area. It may be due to the severe galvanic replacement reaction on the surface of Au0.51-Cu2O sample, which provides more active sites for electrocatalytic CO2 reduction, therefore the Au0.51-Cu2O catalyst has better electrocatalytic performance.

### 3.3. Electrocatalytic CO2 reduction

After Cu2O and Au-x-Cu2O electrodes were activated, electrocatalytic CO2 reduction was conducted at five potentials (−0.9 V, −1.1 V, −1.2 V, −1.3 V, −1.5 V vs. RHE, respectively). The electrolysis time was 4 h. The ECR catalytic performance of each catalyst was
investigated by H₂, CO, HCOOH and C₂H₅OH products, as shown in Figure 9. Figure 9a shows the distribution of ECR products of Cu₂O electrode. The hydrogen evolution reaction of Cu₂O electrode is serious (~40%). At the potential of −0.9 V, CO was detected but no liquid product was detected in the ECR product of the Cu₂O electrode. At the relatively negative reduction potential of −1.1 V and above, the Faraday efficiency of HCOOH and C₂H₅OH increased to about 15% and 6%, respectively. At the same time, as the Faraday efficiency of CO decreased from about 41.5% to 28.9%, the production of HCOOH and C₂H₅OH increased. These results show that the prepared hollow Cu₂O nanospheres have active sites for further reduction of CO molecules to ethanol, but the selectivity is low and requires a higher reduction potential [44]. The distribution of ECR products of Aux-Cu₂O electrodes is shown in Figure 9b–d. Compared with Cu₂O, the hydrogen evolution reaction of the three Aux-Cu₂O electrodes are weakened, indicating that the existence of Au helps to reduce the coverage of *H [45], so that intermediates (such as *CO, *CHO or *CH₂O) have more adsorption sites on the surface of the catalyst, thus promoting the formation of C₂ products. In addition, the three Aux-Cu₂O catalysts all have an earlier onset for ethanol production than Cu₂O. Among them, the Faraday efficiency of H₂ on Au₀.₃₄-Cu₂O electrode (Figure 9c) is the lowest (~17.1%) at −1.1 V, and the Faraday efficiency of ethanol is ~16.5%. The Faraday efficiency of H₂ on Au₀.₅₁-Cu₂O electrode (Figure 9d) is the lowest (~19.5%) at −1.2 V, and the Faraday efficiency of ethanol is ~18.8%. It is speculated that while the loading of Au nanoparticles increases, the Au₀.₅₁-Cu₂O catalyst may also have some pores on the surface due to the over-intense galvanic replacement reaction, which is beneficial to the electrocatalytic CO₂ reduction. All the Aux-Cu₂O catalysts can promote the CO₂ reduction to ethanol with high efficiency.
In addition, the Faraday efficiency and current density of CO$_2$ reduction products of Cu$_2$O and Au$_x$-Cu$_2$O catalysts at different potentials (−0.9 V, −1.1 V, −1.2 V, −1.3 V, −1.5 V vs. RHE) were compared and analysed. As shown in Figures S6–S9, it can be seen that for each electrode, the Faraday efficiency of each product was kept at a stable level.

Figure 8. The linear relationship between current density and scan rate.

Figure 9. The FEs of H$_2$, CO, HCOOH and C$_3$H$_6$OH at different potentials on (a) Cu$_2$O, (b) Au$_{0.17}$-Cu$_2$O, (c) Au$_{0.34}$-Cu$_2$O, (d) Au$_{0.51}$-Cu$_2$O.
during the whole electrolysis process and the current density was stable within 4 h, indicating that the prepared catalysts had a good electrocatalytic stability.

4. Conclusions

In summary, hollow Cu$_2$O nanospheres with particle size of about 150–180 nm were synthesized by a soft template method, and hollow Au$_x$-Cu$_2$O electrocatalysts were successfully prepared by galvanic replacement reaction. The characterization results of SEM and TEM show that Au$_x$-Cu$_2$O basically maintained the hollow shell structure of Cu$_2$O, and Au nanoparticles were uniformly dispersed on the surface of Cu$_2$O nanospheres. Besides, the density of Au nanoparticles on the Cu$_2$O surface increases clearly with the increase of HAuCl$_4$ addition, and some pores appear on the surface of Au$_{0.51}$-Cu$_2$O samples due to the intense galvanic replacement reaction. The characterization results of XRD and XPS reveal that Cu$^{+}$ is the main chemical state of Cu of the prepared catalysts. The effect of Au nanoparticles loading on surface Cu$_2$O was investigated by cyclic voltammetry. The results show that with the increase of HAuCl$_4$ addition, the coverage of Au nanoparticles on Cu$_2$O surface is higher, the reduction degree of Cu$_2$O was weaker and the stability is better. The results of electroactive surface area demonstrate that the electroactive surface area of Au$_{0.51}$-Cu$_2$O was the largest. The performance evaluation of ECR shows that Au$_x$-Cu$_2$O catalysts promote the high efficiency of CO$_2$ reduction to ethanol, while the hydrogen evolution reaction is significantly inhibited. Among them, the Faraday efficiency of ethanol on Au$_{0.51}$-Cu$_2$O can reach ~18.8% at −1.2 V vs. RHE. Our study shows that Au$_x$-Cu$_2$O composites prepared by galvanic replacement reaction is beneficial to the electrocatalytic CO$_2$ reduction to ethanol.

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Disclosure statement

No potential conflict of interest was reported by the authors.

Supplementary materials

The following are available online at www.mdpi.com/xxx/s1, Figure S1: SEM and TEM images of Au$_{0.34}$-Cu$_2$O composite, Figure S2: SEM and TEM images of Au$_{0.51}$-Cu$_2$O composite, Figure S3: XPS results of Au$_{0.34}$-Cu$_2$O, Figure S4: XPS results of Au$_{0.51}$-Cu$_2$O, Figure S5: XPS results of Cu$_2$O, Figure S6: Current density and Faraday efficiency of each product of Cu$_2$O, Figure S7: Current density and Faraday efficiency of each product of Au$_{0.17}$-Cu$_2$O, Figure S8: Current density and Faraday efficiency of each product of Au$_{0.34}$-Cu$_2$O, Figure S9: Current density and Faraday efficiency of each product of Au$_{0.51}$-Cu$_2$O, Table S1: The XPS semiquantitative analysis of Cu$_2$O and Au$_x$-Cu$_2$O.
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References

1. Yuan Q, Li Y, Yu P, et al. Reaction mechanism on Ni-C2-NS single-atom catalysis for the efficient CO2 reduction reaction. J Exp Nanosci. 2021;16(1):256–265.
2. Ledezma-Yanez I, Gallet EP, Koper MTM, et al. Structure-sensitive electroreduction of acetaldehyde to ethanol on copper and its mechanistic implications for CO and CO2 reduction. Catal. Today. 2016;262:90–94.
3. Lum Y, Ager JW. Stability of residual oxides in oxide-derived copper catalysts for electrochemical CO2 reduction investigated with 18O labeling. Angew Chem Int Ed. 2018;57(2):551–554.
4. Lum Y, Yue B, Lobaccaro P, et al. Optimizing C-C coupling on oxide-derived copper catalysts for electrochemical CO2 reduction. J Phys Chem C. 2017;121(26):14191–14203.
5. Zhang Y, Li Y, Tan Q, et al. Facile synthesis of two-dimensional copper terephthalate for efficient electrocatalytic CO2 reduction to ethylene. J Exp Nanosci. 2021;16(1):247–255.
6. Li M, Zhang S, Li L, et al. Construction of highly active and selective polydopamine modified hollow ZnO/Co3O4 pn heterojunction catalyst for photocatalytic CO2 reduction. ACS Sustain Chem Eng. 2020;8(30):11465–11476.
7. Zhang S, Li M, Qiu W, et al. Heterogeneous molecular rhenium catalyst for CO2 photoreduction with high activity and tailored selectivity in an aqueous solution. Appl Catal, B. 2019;259:118113.
8. Kuhl KP, Cave ER, Abram DN, et al. New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces. Energy Environ Sci. 2012;5(5):7050–7059.
9. Sandberg RB, Montoya JH, Chan K, et al. CO-CO coupling on Cu facets: coverage, strain and field effects. Surf. Sci. 2016;654:56–62.
10. Huang Y, Handoko A, Hirunsit P, et al. Electrochemical reduction of CO2 using copper single-crystal surfaces: effects of COx coverage on the selective formation of ethylene. ACS Catal. 2017;7(3):1749–1756.
11. Li YC, Wang Z, Yuan T, et al. Binding site diversity promotes CO2 electroreduction to ethanol. J Am Chem Soc. 2019;141(21):8584–8591.
12. Ren D, Ang BS, Yeo BS. Tuning the selectivity of carbon dioxide electroreduction toward ethanol on oxide-derived Cu2Zn catalysts. ACS Catal. 2016;6(12):8239–8247.
13. Morales-Guio CG, Cave ER, Nitopi SA, et al. Improved CO2 reduction activity towards C2+ alcohols on a tandem gold on copper electrocatalyst. Nat Catal. 2018;1(10):764–771.
14. Calle-Vallejo F, Koper MTM. Theoretical considerations on the electroreduction of CO to C2 species on Cu (100) electrodes. Angew Chem Int Ed Engl. 2013;52(28):7282–7285.
15. Ren D, Deng Y, Handoko AD, et al. Selective electrochemical reduction of carbon dioxide to ethylene and ethanol on copper (I) oxide catalysts. ACS Catal. 2015;5(5):2814–2821.
16. Senlin C, Xin L, Robertson Alex W. Electrocatalytic CO2 reduction to ethylene over CeO2-Supported Cu nanoparticles: Effect of exposed facets of CeO2. Acta Phys Chim Sin. 2021;37(5):2009023.
17. Fan Q, Zhang M, Jia M, et al. Electrochemical CO2 reduction to C2+ species: heterogeneous electrocatalysts, reaction pathways, and optimization strategies. Mater Today Energy. 2018;10:280–301.
18. Zhang L, Li M, Zhang S, et al. Promoting carbon dioxide electroreduction toward ethanol through loading Au nanoparticles on hollow Cu2O nanospheres. Catal Today. 2021;365:348–356.
19. Cao X, Cao G, Li M, et al. Enhanced ethylene formation from carbon dioxide reduction through sequential catalysis on Au decorated cubic Cu2O electrocatalyst. Eur J Inorg Chem. 2021;2021(24):2353–2364.
20. Dinh C, Burdyny T, Kibria G, et al. CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science. 2018;360(6390):783–787.
21. De Luna P, Quintero-Bermudez R, Dinh C-T, et al. Catalyst electro-redeposition controls morphology and oxidation state for selective carbon dioxide reduction. Nat Catal. 2018;1(2):103–110.
22. Nie X, Griffin GL, Janik MJ, et al. Surface phases of Cu2O(111) under CO2 electrochemical reduction conditions. Catal. Commun. 2014;52:88–91.
23. Shang L, Lv X, Shen H, et al. Selective carbon dioxide electroreduction to ethylene and ethanol by core-shell copper/copper oxide. J. Colloid. Interf. Sci. 2019;552:426–431.
24. Mistry H, Varela AS, Bonifacio CS, et al. Highly selective plasma-activated copper catalysts for carbon dioxide reduction to ethylene. Nat Commun. 2016;7:12123–12130.
25. Xiao H, Cheng T, Goddard WA, et al. Atomistic mechanisms underlying selectivities in C1 and C2 products from electrochemical reduction of CO on Cu(111). Nat. Commun. 2017;139:130–136.
26. Hao L, Sun Z. Metal oxide-based materials for electrochemical CO2 reduction. Acta Physico-Chimica Sinica. 2021;37(7):2009033.
27. Begum S, Jones IP, Lynch DE, et al. One-step deposition of Au nanoparticles onto chemically modified ceramic hollow spheres via self-assembly. J Exp Nanosci. 2012;7(1):1–16.
28. Fu S, Gao J, Wu Y, et al. Facile synthesis of hierarchically structured NiO flower-like hollow spheres. J Exp Nanosci. 2016;11(7):531–539.
29. Sun S, Zhang X, Yang Q, et al. Cuprous oxide (Cu2O) crystals with tailored architectures: a comprehensive review on synthesis, fundamental properties, functional modifications and applications. Prog. Mater. Sci. 2018;86:111–173.
30. Zhang S, Wu Y, Zhang YX, et al. Dual-atom catalysts: controllable synthesis and electrocatalytic applications. Sci China Chem. 2021;64(11):1908–1915.
31. Zhang S, Wu Q, Tang L, et al. Individual high-quality N-doped carbon nanotubes embedded with nonprecious metal nanoparticles toward electrochemical reaction. ACS Appl Mater Interf. 2018;10(46):39757–39767.
32. Xu H, Wang W. Template synthesis of multishelled Cu2O hollow spheres with a single-crystalline shell wall. Angew Chem Int Ed Engl. 2007;46(9):1489–1492.
33. Xu H, Wang W, Zhou L. A growth model of single crystalline hollow sphere: oriented attachment of Cu2O nanoparticles to the single crystalline shell wall. Cryst. Growth Des. 2008;8(10):3486–3489.
34. Papaderakis A, Mintsouli I, Georgieva J, et al. Electrocatalysts prepared by galvanic replacement. Catalysts. 2017;7:80–114.
35. Xiong L, Li S, Zhang B, et al. Galvanic replacement-mediated synthesis of hollow Cu2O-Au nanocomposites and Au nanocages for catalytic and SERS applications. RSC Adv. 2015;5(93):76101–76106.
36. Li Q, Fu J, Zhu W, et al. Tuning Sn-catalysis for electrochemical reduction of CO2 to CO via the core/shell Cu/SnO2 structure. J Am Chem Soc. 2017;139(12):4290–4293.
37. Sahai A, Goswami N, Kaushik SD, et al. Cu/Cu2O/CuO nanoparticles: novel synthesis by exploding wire technique and extensive characterization. Appl. Surf. Sci. 2016;390:974–983.
38. Li P, Lv W, Ai S. Green and gentle synthesis of Cu2O nanoparticles using lignin as reducing and capping reagent with antibacterial properties. J Exp Nanosci. 2016;11(1):18–27.
39. Zhu C, Osherov A, Panzer MJ. Surface chemistry of electrodeposited Cu2O films studied by XPS. Electrochim Acta. 2013;11:771–778.
40. Wang L, Li S, Zhang B, et al. Novel Au/Cu2O multi-shelled porous heterostructures for enhanced efficiency of photoelectrochemical water splitting. J Mater Chem A. 2017;5(27):14415–14421.
41. Xiong Z, Zhang L, Ma J, et al. Photocatalytic degradation of dyes over graphene-gold nanocomposites under visible light irradiation. Chem Commun (Camb). 2010;46(33):6099–6101.
42. Procaccini RA, Schreiner WH, Vázquez M, et al. Surface study of films formed on copper and brass at open circuit potential. Appl Surf Sci. 2013;268:171–178.
43. Li Q, Li M, Zhang S, et al. Tuning Sn-Cu catalysis for electrochemical reduction of CO2 on partially reduced oxides SnOx-CuOx-modified Cu electrodes. Catalysts. 2019;9(5):476–489.
44. Lee S, Park G, Lee J, et al. Importance of Ag-Cu biphasic boundaries for selective electrochemical reduction of CO2 to ethanol. ACS Catal. 2017;7(12):8594–8604.
45. Gao J, Ren D, Guo X, et al. Sequential catalysis enables enhanced C-C coupling towards multi-carbon alkenes and alcohols in carbon dioxide reduction: a study on bifunctional Cu/Au electrocatalysts. Faraday Discuss. 2019;215:282–296.