Strained Lattice Gold-Copper Alloy Nanoparticles for Efficient Carbon Dioxide Electroreduction

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Abstract: Electrocatalytic conversion of carbon dioxide (CO$_2$) into specific renewable fuels is an attractive way to mitigate the greenhouse effect and solve the energy crisis. Au$_n$Cu$_{100-n}$/C alloy nanoparticles (Au$_n$Cu$_{100-n}$/C NPs) with tunable compositions, a highly active crystal plane and a strained lattice were synthesized by the thermal solvent co-reduction method. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) results show that Au$_n$Cu$_{100-n}$/C catalysts display a subtle lattice strain and dominant (111) crystal plane, which can be adjusted by the alloy composition. Electrochemical results show that Au$_n$Cu$_{100-n}$/C alloy catalysts for CO$_2$ reduction display high catalytic activity; in particular, the Faradaic efficiency of Au$_{75}$Cu$_{25}$/C is up to 92.6% for CO at $-0.7$ V (vs. the reversible hydrogen electrode), which is related to lattice shrinkage and the active facet. This research provides a new strategy with which to design strong and active nanoalloy catalysts with lattice mismatch and main active surfaces for CO$_2$ reduction reaction.

Keywords: lattice strain; crystal plane; Faradaic efficiency; CO$_2$ reduction reaction

1. Introduction

Converting CO$_2$ into useful chemicals can reduce the concentration of CO$_2$ in the atmosphere and realize the recycling of CO$_2$, which has attracted extensive attention of researchers. Electrocatalytic reduction reaction of CO$_2$ (CO$_2$RR) can be performed using electricity produced by renewable energy sources, such as wind energy and hydropower [1–3]. There have been a number of reports on catalysts for the electroreduction of carbon dioxide [4]. In this regard, noble metals have proved to be promising catalysts for the electroreduction of CO$_2$ to CO [5–9]. A large number of studies have shown that metal nanostructured catalysts with more active sites, such as Au, Ag and Pd, can greatly improve the catalytic activity of CO$_2$ reduction [5,10–15]. However, the multiple electron transfer in the CO$_2$RR process, the reaction pathway, the hydrogen evolution reaction (HER) and the high price and low reserves of noble metals hinder the wide application of precious metals [16–18]. Therefore, reducing catalyst costs and improving activity and selectivity are challenges [19]. Many studies have shown that the incorporation of cheap metals into noble metal nanocrystals can also improve their catalytic performances and efficiency. The formation of the alloy changes the lattice of the metal catalyst, resulting in lattice strain [20,21]. The lattice strain generated by the catalyst can change the electronic properties of the metal and improve the electrocatalytic activity [22]. Previous studies have shown that Au-based catalysts have high activity and selectivity for CO$_2$ reduction to CO [23]. Introducing cheap metals with Au to form alloy catalysts is necessary to improving the catalytic activity for CO$_2$ reduction and decreasing the price of catalyst [24,25]. The composition of the alloy catalyst can be adjusted to regulate the electronic structure and enhance the catalytic activity and stability [26]. Gold and copper form nano-alloys in different proportions, and lattice strains are controlled by changing the proportions of gold...
and copper in the material [27]. Previous studies have found that the lattice spacing of the alloy expands and contracts to varying degrees with the changes in the atomic proportions of the two metals [28,29]. The expansion and contraction of lattice spacing are the key factors affecting the electrochemical properties of the alloy [30,31].

In this work, the thermal solvent co-reduction method was used to synthesize Au\textsubscript{n}Cu\textsubscript{100−n}/C NPs with tunable compositions, a highly active crystal plane and a strained lattice. TEM results show that Au\textsubscript{n}Cu\textsubscript{100−n}/C catalysts display a dominant (111) crystal plane. XRD results show that the lattice constant shrinks and expands through tuning the compositions of catalysts. Electrochemical results show that Au\textsubscript{n}Cu\textsubscript{100−n}/C alloy catalysts for CO\textsubscript{2} reduction display highly catalytic activity; in particular, the Faradaic efficiency of Au\textsubscript{75}Cu\textsubscript{25}/C is up to 92.6% for CO at −0.7 V vs. RHE, which is related to lattice shrinkage and bimetallic compositions.

2. Materials and Methods

2.1. Chemicals

Hydrogen tetrachloroaurate (III) hydrate (HAuCl\textsubscript{4}·xH\textsubscript{2}O, 49%−51% Au basis), copper dinitrate (Cu(NO\textsubscript{3})\textsubscript{2}, AR), sodium hydroxide (NaOH, AR), ethylenediamine, hydrazine (80%), sodium thiosulphate (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, AR), deionized water, Nafion (5 wt%) and ethanol (99.7%) were obtained from Deen reagent. Carbon black (Vulcan XC-72) was purchased from Cabot. All gases were obtained from Airgas. All chemicals were used without further purification.

2.2. Preparation Cu NPs

The Cu NPs were prepared by a simple method. Cu(NO\textsubscript{3})\textsubscript{2} (376.0 mg) and NaOH (8.0 g) were dissolved in 20 mL deionized water to form a uniform solution. Then, 4 mL ethylenediamine and 1 mL hydrazine were added to the above solution. After all the reactants were thoroughly mixed and transferred to a flask, it was placed in a water bath at 80 °C for 1 h. Finally, the product was washed four times with deionized water and ethanol to obtain Cu NPs [32].

2.3. Preparation Au\textsubscript{n}Cu\textsubscript{100−n} NPs

Cu NPs (64.0 mg) and Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (79.0 mg) were dissolved in 100 mL deionized water saturated with N\textsubscript{2} and dispersed by ultrasonication. When Cu NPs were completely dispersed, 340.0 mg HAuCl\textsubscript{4}·xH\textsubscript{2}O was added, and the reaction was carried out under magnetic stirring for 30 min. Finally, the product was collected by centrifugation, washed four times with ethanol and dried under vacuum to obtain Au\textsubscript{25}Cu\textsubscript{75} NPs. Au\textsubscript{25}Cu\textsubscript{75} NPs and Au\textsubscript{75}Cu\textsubscript{25} NPs catalysts were prepared under similar conditions where n(HAuCl\textsubscript{4}·xH\textsubscript{2}O):n(Cu(NO\textsubscript{3})\textsubscript{2}) was 1:3 or 3:1, respectively. All the catalysts were loaded onto the carbon black to obtain Au\textsubscript{25}Cu\textsubscript{75}/C, Au\textsubscript{50}Cu\textsubscript{50}/C and Au\textsubscript{75}Cu\textsubscript{25}/C.

2.4. Characterizations

Transmission electron microscopy (TEM) and high-resolution TEM (HR-TEM) were used to characterize the morphology and size of Au\textsubscript{n}Cu\textsubscript{100−n}/C catalysts performed on JEM-2100F TEM working at 200 kV [33]. The structures of Au\textsubscript{n}Cu\textsubscript{100−n}/C were measured on a Shimadzu X-ray diffractometer (XRD) instrument operating with Cu K\textalpha\ (λ = 0.154 nm) radiation [34]. X-ray photoelectron spectroscopy (XPS) can determine the content and chemical states of the elements contained on the surface of a sample [35,36].

2.5. Electrochemical Measurements

To prepare a working electrode for electrochemical activity test, 2 mL of a mixture containing deionized water, isopropanol and Nafion (5% wt) (9:1:15, V/V/V) was ultrasonic dispersed on a 4 mg Au\textsubscript{n}Cu\textsubscript{100−n}/C powder catalyst for 60 min to form a homogeneous catalyst ink (2 mg/mL). The prepared catalyst suspension (300 μL) was coated on the surface of carbon paper with an area of 1 cm × 1 cm [37]. Electrocatalytic reduction of
CO\textsubscript{2} was performed on a computer-controlled electrochemical analyzer (CHI760e, CH Instruments). All the experiments were conducted in a gas-tight H-type cell with cathode and anode compartments separated by a Nafion® NRE-212 proton exchange membrane. The H-type cell was filled with a 0.1 M KHCO\textsubscript{3} solution (pH = 6.8, 45 mL) as the electrolyte in each chamber with 15 mL headspace. Platinum foil and Ag/AgCl (saturated KCl) were used as a counter electrode and reference electrode. The pH of the electrolyte was measured by the Thermo Scientific Orion Versa Star pH Benchtop Tester (INESA). In the process of electrochemical reduction of CO\textsubscript{2}, the mass flow controller (Sevenstar, Beijing) was used to purge CO\textsubscript{2} at the flow rate of 20 mL/min. Before each electrochemical experiment, CO\textsubscript{2} was purged into the cathodic compartment for at least 40 min until the solution pH reached 6.8 (CO\textsubscript{2}-saturated 0.1 M KHCO\textsubscript{3}). The working electrode was activated by cyclic voltammetry (CV) until a stable curve at room temperature and ambient pressure. The gas products in the cathode chamber were quantitatively analyzed by an online gas chromatograph (GC2030, Shimadzu) equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID) [38]. The Faraday efficiency (FE) was calculated by dividing the amount of charge transferred to the gas product by the total amount of charge transferred in a specific time or the entire reduction reaction (for gas products). In this work, the potentials were adjusted to reversible hydrogen electrode (RHE) potentials. The electrochemical active area (ECSA) was obtained from a cyclic voltammogram in 50 mM H\textsubscript{2}SO\textsubscript{4} [39].

3. Results and Discussion

3.1. Morphology

Au\textsubscript{n}Cu\textsubscript{100−n} NPs was prepared by galvanic replacement reaction assisted by Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} in an aqueous solution composed of HAuCl\textsubscript{4} and copper NPs, where Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} acted as an inhibitor of CuCl disproportionation caused by Cu/HAuCl\textsubscript{4} substitution. The compositions of Au\textsubscript{n}Cu\textsubscript{100−n} NPs were controlled by adjusting the ratios of Cu NPs and HAuCl\textsubscript{4}. The morphology and alloy structure of the Au\textsubscript{n}Cu\textsubscript{100−n} NPs were obtained by TEM and HR-TEM. The compositions of the Au\textsubscript{n}Cu\textsubscript{100−n} NPs were controlled by the metal precursor ratios and analyzed by ICP-MS, indicating that the compositions of the Au\textsubscript{n}Cu\textsubscript{100−n} NPs can be controlled well by tuning the feeding ratio during the synthesis. It can be seen in Figure 1 that the diameter of Au\textsubscript{25}Cu\textsubscript{75} NPs was 10–16 nm (Figure 1a), that of Au\textsubscript{50}Cu\textsubscript{50} NPs was 8–12 nm (Figure 1b) and that of Au\textsubscript{75}Cu\textsubscript{25} NPs was 6–10 nm, via TEM (Figure 1c). It can be concluded from the TEM images that with the increase in Au content in Au\textsubscript{n}Cu\textsubscript{100−n} alloy NPs, the diameter of Au\textsubscript{n}Cu\textsubscript{100−n} alloy NPs gradually decreased. HR-TEM images revealed that Au\textsubscript{n}Cu\textsubscript{100−n} NPs are a dominant (111) facet and the continuous lattice fringes of Au\textsubscript{n}Cu\textsubscript{100−n} NPs were controlled by the metal precursor ratios and analyzed by XPS spectra, indicating that Au successfully replaced Cu to form AuCu alloy catalysts, as shown in Figure 1d–f. The Au\textsubscript{n}Cu\textsubscript{100−n} alloyed structure was also achieved by the elemental mapping technique (Figure 1g–i) [32], which showed that Au and Cu were evenly distributed in the Au\textsubscript{n}Cu\textsubscript{100−n} NPs.

3.2. Structures

The differences in crystalline structures between Au\textsubscript{n}Cu\textsubscript{100−n}/C NPs were determined from X-ray diffraction (XRD). As shown in Figure 2a, the peak positions located at 38.2°, 44.4° and 64.9° diffractions further confirmed the formation of an alloy system, as they are located between those of pure Au and pure Cu. Figure 2b shows that the lattice spacing was basically linear in accordance with Vegard’s law, but there was a slight deviation, which mainly depended on the compositions of Au\textsubscript{n}Cu\textsubscript{100−n}/C. The lattice constant shrunk when the Au% was more than 50%, but when the Au% was less than 50%, the lattice spacing showed lattice expansion. The compositions, structures and valence states on the surface of catalysts were further analyzed by XPS spectra. Figure 2c–d show the Au 4f region (Au 4f\textsubscript{5/2} and Au 4f\textsubscript{7/2}) and Cu 2p region (Cu 2p\textsubscript{1/2} and Cu 2p\textsubscript{3/2}), corresponding to Au\textsuperscript{0} and Cu\textsuperscript{0} chemical states, respectively. However, the positive shift of the Au 4f spectrum...
occurred with the increase in Au%, especially for the Au_{75}Cu_{25}/C composition, indicating that the catalyst had a partial positive charge, and the transition of the d-band center, which is usually regarded as an effective descriptor for evaluating the catalytic activity and is beneficial for electrochemical catalysis. The adsorption and desorption capacity of the reaction product on the catalyst surface is closely related to the binding energy, which indicates that the center of the d band moves downward in the Au_{n}Cu_{100-n}/C catalyst compared with pure Au. The electrons from Cu to Au in the Au_{n}Cu_{100-n} NPs catalyst doubled the local electron density around the Au sites, which has been shown to reduce the intermediate CO generated during the catalytic process and the adsorption of catalyst poisons to prevent catalytically active sites’ formation.

Figure 1. TEM and HR-TEM images of the Au_{n}Cu_{100-n} NPs samples. Au_{25}Cu_{75} (a,d), Au_{50}Cu_{50} (b,e) and Au_{75}Cu_{25} (c,f) with lattice fringes and corresponding facets indicated. EDS element mappings of Au_{25}Cu_{75} (g), Au_{50}Cu_{50} (h) and Au_{75}Cu_{25} (i).
was the most active catalyst for CO$_2$ reduction. Moreover, the cathodic current densities of the three catalysts in CO$_2$-saturated electrolyte were all higher than in the Ar-saturated electrolyte, indicating that CO$_2$RR occurred. Furthermore, the electrochemically active surface area (ECSA) of the Au$\textsubscript{n}$Cu$_{100-n}$/C catalyst doubled the local electron density around the Au sites, which has been shown to reduce the intermediate CO generated during the catalytic process suggesting that Au$_{75}$Cu$_{25}$/C was the most active catalyst for CO$_2$ reduction. Additionally, the electrochemically active surface area was increased with Au content, which is related to the facet and lattice strain of catalysts. In the process of CO$_2$ reduction, the gas products produced in the electrolytic cell were analyzed every 30 min by the GC sampling system at each given potential. Figure 6b shows the FE of CO for different component catalysts in CO$_2$-saturated 0.1 M KHCO$_3$ electrolyte are given in Figure 6a. Apparently, Au$_{75}$Cu$_{25}$/C exhibited higher total current density than the other catalysts, suggesting that Au$_{75}$Cu$_{25}$/C was the most active catalyst for CO$_2$ reduction. Moreover, the electrochemically active surface area (ECSA) of the Au$_{n}$/Cu$_{100-n}$/C alloy was tested to verify the catalytic activity. The results are shown in Figure 7. Au$_{75}$Cu$_{25}$/C had the largest electrochemically active surface area. The electrochemically active surface area of Au$_{75}$Cu$_{25}$/C was 25.2 m$^2$ g$^{-1}$, greater than those of Au$_{25}$Cu$_{75}$/C (6.38 m$^2$ g$^{-1}$) and Au$_{50}$Cu$_{50}$/C (17.6 m$^2$ g$^{-1}$). The value of the electrochemically active surface area was increased with Au content, which is related to the facet and lattice strain of catalysts. In the process of CO$_2$ reduction, the gas products produced in the electrolytic cell were analyzed every 30 min by the GC sampling system at each given potential. Figure 6b shows the FE of CO for different component catalysts in CO$_2$-saturated 0.1 M KHCO$_3$ electrolyte, respectively (Figures 3–5). The LSV of three different composition catalysts in CO$_2$-saturated 0.1 M KHCO$_3$ electrolyte are given in Figure 6a. Appar-
the CO\textsubscript{2}RR process. It can be seen in Figures 6b and 8 that the gas products only included CO and H\textsubscript{2}. The FE\textsubscript{CO} of Au\textsubscript{75}Cu\textsubscript{25}/C was the highest at −0.7 V vs. RHE, achieving 92.6%. As shown in Figure 6c, the current density of Au\textsubscript{75}Cu\textsubscript{25}/C for CO was 28.5 mA cm\textsuperscript{−2} at −0.7 V vs. RHE, which is several times the values of other catalysts.

![Figure 3](image1.png)

**Figure 3.** Cyclic voltammograms (a) and linear scan voltammograms (b) of Au\textsubscript{75}Cu\textsubscript{25}/C in Ar saturated and CO\textsubscript{2}-satruated 0.1 M KH\textsubscript{CO3} solutions collected at a scan rate of 20 mV s\textsuperscript{−1}.

![Figure 4](image2.png)

**Figure 4.** Cyclic voltammograms (a) and linear scan voltammograms (b) of Au\textsubscript{50}Cu\textsubscript{50}/C in Ar saturated and CO\textsubscript{2}-satruated 0.1 M KH\textsubscript{CO3} solutions collected at a scan rate of 20 mV s\textsuperscript{−1}.

![Figure 5](image3.png)

**Figure 5.** Cyclic voltammograms (a) and linear scan voltammograms (b) of Au\textsubscript{25}Cu\textsubscript{75}/C in Ar saturated and CO\textsubscript{2}-satruated 0.1 M KH\textsubscript{CO3} solutions collected at a scan rate of 20 mV s\textsuperscript{−1}.
Figure 6. Performances of the Au$_{25}$Cu$_{75}$/C, Au$_{50}$Cu$_{50}$/C, Au$_{75}$Cu$_{25}$/C electrocatalysts for CO$_2$ reduction with Cu/C and Au/C as controls. (a) The LSV in 0.1 M KHCO$_3$ electrolyte saturated with CO$_2$. (b) Faradaic efficiencies (%) at applied potential ranging from $-0.5$ V to $-0.9$V vs. RHE. (c) CO$_2$ reduction current density ($j_{CO}$) with all the carbonaceous products taken into account. (d) Stability test and FE(%) of CO and H$_2$.

Figure 7. The ECSA of Au$_{25}$Cu$_{75}$/C, Au$_{50}$Cu$_{50}$/C and Au$_{75}$Cu$_{25}$/C. Cyclic voltammograms in 50 mM H$_2$SO$_4$, scan rate 50 mV s$^{-1}$. 
For comparisons with the pure metal catalysts, we used the same method to synthesize Au NPs and Cu NPs, and they were tested for CO₂RR, as shown in the Figures 6, 9 and 10, respectively. The results show that the activity and selectivities of the two catalysts are lower than those of the alloy catalysts.

**Figure 8.** The H₂ FE of Au₂₅Cu₇₅/C, Au₅₀Cu₅₀/C and Au₇₅Cu₂₅/C, Au/C and Cu/C.

**Figure 9.** Cyclic voltammograms (a) and linear scan voltammograms (b) of Au/C in CO₂-saturated 0.1 M KHCO₃ solution collected at a scan rate of 20 mV s⁻¹.

**Figure 10.** Cyclic voltammograms (a) and linear scan voltammograms (b) of Cu/C in CO₂-saturated 0.1 M KHCO₃ solution collected at a scan rate of 20 mV s⁻¹.
Stability is an important indicator with which to evaluate the performances of electrocatalysts. The stability of Au75Cu25/C was tested by the timing current method (i–t), and the gas products were detected with an online gas chromatograph every hour for 10 h (Figure 6d). In the reaction process for 10 h, the catalytic activity of Au75Cu25/C catalyst for CO had no obvious attenuation, and FE_{CO} remained above 90%. This indicates that Au75Cu25/C maintained good catalytic activity and selectivity for CO in the CO2RR process, and could keep stable. The results show that alloying caused changes in lattice parameters between catalysts which affected the performance of the catalysts for the CO2RR. In order to further prove that Au75Cu25/C catalyst has good stability, XPS was used to characterize the Au75Cu25/C catalyst after electrolysis. XPS results show that Au75Cu25/C retained its original composition after a long period of electrolysis (Figure 11).

In the process of electroreduction for CO2, Au and Cu cooperated with each other to form an alloy and showed high catalytic activity and selectivity for CO. Meanwhile, the unique nanostructure of Au_{n}Cu_{100−n} alloy could reduce the adsorption of CO on the surface and increase the yield of CO. The high selectivity of this gas product makes the separation process relatively simple, which is beneficial for practical applications.

![Figure 11](image)

**Figure 11.** The XPS of Au75Cu25/C after the stability test. (a) Au and (b) for XPS data.

### 4. Conclusions

In summary, an Au_{n}Cu_{100−n} alloy dominant (111) facet was synthesized with a simple method. The composition of Au_{n}Cu_{100−n} alloy can be simply controlled by adjusting the Au/Cu atomic ratio of the precursor. Na2S2O3 and NaOH as inhibitors that also prevent NPs aggregation play important roles in the synthesis of Au_{n}Cu_{100−n}. Au75Cu25/C exhibits excellent catalytic activity and stability for CO2 electroreduction. The excellent catalytic performance of Au75Cu25/C mainly depends on the large specific surface area and inter-lattice shrinkage. Meanwhile, the coordination of Au and Cu in the catalyst is also a reason for its good stability and the good performance of the catalyst. Au75Cu25/C had the highest Faradaic efficiency and the highest CO selectivity compared with pure gold catalysts in the CO2 reduction process. Our study on Au_{n}Cu_{100−n} alloy catalysts demonstrated that the formation of alloys of noble metals with inexpensive metals can improve the activity and selectivity of the catalysts, which provides a new strategy for the design of catalysts for CO2RR.

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References

1. Li, M.; Wang, H.; Luo, W.; Sherrell, P.C.; Chen, J.; Yang, J. Heterogeneous single-atom catalysts for electrochemical CO₂ reduction reaction. *Adv. Mater.* 2020, 32, 2001848. [CrossRef] [PubMed]

2. Wu, Z.Z.; Gao, F.Y.; Gao, M.R. Regulating the oxidation state of nanomaterials for electrocatalytic CO₂ reduction. *Energy Environ. Sci.* 2021, 14, 1121–1139. [CrossRef]

3. Daiyan, R.; Saputra, W.H.; Masood, H.; Leverett, J.; Lu, X.; Amal, R. A disposition on the active sites of heterogeneous catalysts for electrochemical reduction of CO₂ to value-added chemicals and fuel. *Adv. Energy. Mater.* 2020, 10, 1902106. [CrossRef]

4. Cao, Z.; Zacate, S.B.; Sun, X.; Liu, J.; Hale, E.M.; Carson, W.P.; Liu, W. Tuning gold nanoparticles with chelating ligands for highly efficient electrocatalytic CO₂ reduction. *Angew. Chem. Int. Ed.* 2018, 130, 12857–12861. [CrossRef]

5. de Jesus Gálvez-Vázquez, M.; Moreno-García, P.; Xu, H.; Hou, Y.; Hu, H.; Montiel, I.Z.; Broekmann, P. Environment matters: CO₂RR electrocatalyst performance testing in a gas-fed zero-gap electrolyzer. *ACS Catal.* 2020, 10, 13096–13108. [CrossRef]

6. Shen, S.; Peng, X.; Song, L.; Qi, Y.; Li, C.; Zhuo, L.; Luo, J. AuCu alloy nanoparticle embedded Cu submicrocone arrays for selective conversion of CO₂ to ethanol. *Small* 2019, 15, 1902229. [CrossRef] [PubMed]

7. Back, S.; Yeom, M.S.; Jung, Y. Active sites of Au and Ag nanoparticle catalysts for CO₂ electroreduction to CO. *ACS Catal.* 2015, 5, 5089–5096. [CrossRef]

8. Kim, J.H.; Woo, H.; Choi, J.; Jung, H.W.; Kim, Y.T. CO₂ electroreduction on Au/TiC: Enhanced activity due to metal-support interaction. *ACS Catal.* 2017, 7, 2101–2106. [CrossRef]

9. Li, S.; Alfonso, D.; Nagarajan, A.V.; House, S.D.; Yang, J.C.; Kauffman, D.R.; Jin, R. Monopalladium substitution in gold nanoclusters enhances CO₂ electroreduction activity and selectivity. *ACS Catal.* 2020, 10, 12011–12016. [CrossRef]

10. Kim, C.; Eom, T.; Jee, M.S.; Jung, H.; Kim, H.; Min, B.K.; Hwang, Y.J. Insight into electrochemical CO₂ reduction on surface-molecule-mediated Ag nanoparticles. *Adv. Mater.* 2017, 7, 779–785. [CrossRef]

11. Bagger, A.; Ju, W.; Varela, A.S.; Strasser, P.; Rossmeisl, J. Electrochemical CO₂ reduction: Classifying Cu facets. *ACS Catal.* 2019, 9, 7894–7899. [CrossRef]

12. Yang, D.R.; Liu, L.; Zhang, Q.; Shi, Y.; Zhou, Y.; Liu, C.; Xia, X.H. Importance of Au nanostructures in CO₂ electrochemical reduction reaction. *Sci. Bull.* 2020, 65, 796–802. [CrossRef]

13. Ma, M.; Liu, K.; Shen, J.; Kas, R.; Smith, W.A. In situ fabrication and reactivation of highly selective and stable Ag catalysts for electrochemical CO₂ conversion. *ACS Energy Lett.* 2018, 3, 1301–1306. [CrossRef] [PubMed]

14. He, Q.; Lee, J.H.; Liu, D.; Liu, Y.; Lin, Z.; Xie, Z.; Chen, J.G. Accelerating CO₂ electroreduction to CO over Pd single-atom catalyst. *Adv. Funct. Mater.* 2020, 30, 2000407. [CrossRef]

15. Zhu, W.; Zhang, L.; Yang, P.; Hu, C.; Dong, H.; Zhao, Z.J.; Gong, J. Formation of enriched vacancies for enhanced CO₂ electrocatalytic reduction over AuCu alloys. *ACS Energy Lett.* 2018, 3, 2144–2149. [CrossRef]

16. Zheng, T.; Jiang, K.; Wang, H. Recent advances in electrochemical CO₂-to-CO conversion on heterogeneous catalysts. *Adv. Mater.* 2018, 30, 1802066. [CrossRef]

17. Yin, Z.; Gao, D.; Yao, S.; Zhao, B.; Cai, F.; Lin, L.; Bao, X. Highly selective palladium-copper bimetallic electrocatalysts for the electrochemical reduction of CO₂ to CO. *Nano Energy* 2016, 27, 35–43. [CrossRef]

18. Geng, Z.; Kong, X.; Chen, W.; Su, H.; Liu, Y.; Cai, F.; Zeng, J. Oxygen vacancies in ZrO nanosheets enhance CO₂ electrochemical reduction to CO. *Angew. Chem. Int. Ed.* 2018, 130, 6162–6167. [CrossRef]

19. He, J.; Johnson, N.J.; Huang, A.; Berlinguette, C.P. Electrocatalytic alloys for CO₂ reduction. *ChemSusChem* 2018, 11, 48–57. [CrossRef]

20. Chang, F.; Liu, Y.; Zhang, Q.; Jia, Z.; Yang, L.; Wang, X.; Bai, Z. Regulating the lattice strain of platinum-copper catalysts for enhancing collaborative electrocatalysis. *Inorg. Chem. Front.* 2022, 9, 249–258. [CrossRef]

21. Miao, R.; Chang, F.; Ren, M.; He, X.; Yang, L.; Wang, X.; Bai, Z. Platinum-palladium alloy nanotetrahedra with tuneable lattice-strain for enhanced intrinsic activity. *Catal. Sci. Technol.* 2020, 10, 6173–6179. [CrossRef]

22. Ren, M.; Chang, F.; Miao, R.; He, X.; Yang, L.; Wang, X.; Bai, Z. Strained lattice platinum-palladium alloy nanowires for efficient electrocatalysis. *Inorg. Chem. Front.* 2020, 7, 1713–1718. [CrossRef]

23. Dong, C.; Fu, J.; Liu, H.; Ling, T.; Yang, J.; Qiao, S.Z.; Du, X.W. Tuning the selectivity and activity of Au catalysts for carbon dioxide electroreduction via grain boundary engineering: A DFT study. *J. Mater. Chem. A* 2017, 5, 7184–7190. [CrossRef]

24. Kim, D.; Xie, C.; Becknell, N.; Yu, Y.; Karamad, M.; Chan, K.; Yang, P. Electrochemical activation of CO₂ through atomic ordering transformations of AuCu nanoparticles. *J. Am. Chem. Soc.* 2017, 139, 8329–8336. [CrossRef]

25. Ismail, A.M.; Samu, G.F.; Balog, A.; Csapó, É.; Janáky, C. Composition-dependent electrocatalytic behavior of Au–Sn bimetallic nanoparticles in carbon dioxide reduction. *ACS Energy Lett.* 2018, 4, 48–53. [CrossRef]

26. Zhang, J.; Qu, X.; Han, Y.; Shen, L.; Yin, S.; Li, G.; Sun, S. Engineering PtRu bimetallic nanoparticles with adjustable alloying degree for methanol electrooxidation: Enhanced catalytic performance. *Appl. Catal. B Environ.* 2020, 263, 118345. [CrossRef]
27. Xia, Z.; Guo, S. Strain engineering of metal-based nanomaterials for energy electrocatalysis. Chem. Soc. Rev. 2019, 48, 3265–3278. [CrossRef]
28. Andersen, M.; Medford, A.J.; Nørskov, J.K.; Reuter, K. Scaling-relation-based analysis of bifunctional catalysis: The case for homogeneous bimetallic alloys. ACS Catal. 2017, 7, 3960–3967. [CrossRef]
29. Wu, Z.; Yang, B.; Miao, S.; Liu, W.; Xie, J.; Lee, S.; Ma, D. Lattice strained Ni-Co alloy as a high-performance catalyst for catalytic dry reforming of methane. ACS Catal. 2019, 9, 2693–2700. [CrossRef]
30. Que, L.; Yu, F.; Zheng, L.; Wang, Z.B.; Gu, D. Tuning lattice spacing in titanate nanowire arrays for enhanced sodium storage and long-term stability. Nano Energy 2018, 45, 337–345. [CrossRef]
31. Wu, Z.; Yang, B.; Miao, S.; Liu, W.; Xie, J.; Lee, S.; Ma, D. Lattice strained Ni-Co alloy as a high-performance catalyst for catalytic dry reforming of methane. ACS Catal. 2019, 9, 2693–2700. [CrossRef]
32. Zhao, Y.; Liu, J.; Liu, C.; Wang, F.; Song, Y. Amorphous CuPt alloy nanotubes induced by Na2S2O3 as efficient catalysts for the methanol oxidation reaction. ACS Catal. 2016, 6, 4127–4134. [CrossRef]
33. Chang, F.; Bai, Z.; Li, M.; Ren, M.; Liu, T.; Yang, L.; Lu, J. Strain-modulated platinum-palladium nanowires for oxygen reduction reaction. Nano Lett. 2020, 20, 2416–2422. [CrossRef] [PubMed]
34. Chang, F.; Shan, S.; Petkov, V.; Skeete, Z.; Lu, A.; Ravid, J.; Zhong, C.J. Composition tunability and (111)-dominant facets of ultrathin platinum-gold alloy nanowires toward enhanced electrocatalysis. J. Am. Chem. Soc. 2016, 138, 12166–12175. [CrossRef] [PubMed]
35. Chang, F.; Yu, G.; Shan, S.; Skeete, Z.; Wu, J.; Luo, J.; Zhong, C.J. Platinum–nickel nanowire catalysts with composition-tunable alloying and faceting for the oxygen reduction reaction. J. Mater. Chem. 2017, 5, 12557–12568. [CrossRef]
36. Chang, F.; Wei, J.; Zhang, Q.; Jia, Z.; Liu, Y.; Yang, L.; Bai, Z. Modulating the multiple intrinsic properties of platinum–iron alloy nanowires towards enhancing collaborative electrocatalysis. Mater. Chem. Front. 2021, 5, 8118–8126. [CrossRef]
37. Zhu, W.; Zhang, Y.J.; Zhang, H.; Lv, H.; Li, Q.; Michalsky, R.; Sun, S. Active and selective conversion of CO2 to CO on ultrathin Au nanowires. J. Am. Chem. Soc. 2014, 136, 16132–16135. [CrossRef]
38. Park, S.; Kim, Y.; Han, H.; Chung, Y.S.; Yoon, W.; Choi, J.; Kim, W.B. In situ exsolved Co nanoparticles on Ruddlesden-Popper material as highly active catalyst for CO2 electrolysis to CO. Appl. Catal. B Environ. 2019, 248, 147–156. [CrossRef]
39. Liu, M.; Pang, Y.; Zhang, B.; Luna, P.; Voznyy, O.; Xu, J.; Zheng, X.; Dinh, C.; Fan, F.; Cao, C.; et al. Enhanced electrocatalytic CO2 reduction via field-induced reagent concentration. Nature 2016, 537, 382–386. [CrossRef]