# Electrochemical Reduction of CO<sub>2</sub> Toward C<sub>2</sub> Valuables on Cu@Ag Core-Shell Tandem Catalyst with Tunable Shell Thickness

Shuaishuai Zhang, Shulin Zhao, Dongxue Qu, Xiaojing Liu, Yuping Wu,\* Yuhui Chen,\* and Wei Huang

Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is critical to converting CO<sub>2</sub> to high-value multicarbon chemicals. However, the Cu-based catalysts as the only option to reduce  $CO_2$  into  $C_{2+}$  products suffer from poor selectivity and low activity. Tandem catalysis for CO<sub>2</sub> reduction is an efficient strategy to overcome such problems. Here, Cu@Ag core-shell nanoparticles (NPs) with different silver layer thicknesses are fabricated to realize the tandem catalysis for CO<sub>2</sub> conversion by producing CO on Ag shell and further achieving C-C coupling on Cu core. It is found that Cu@Ag-2 NPs with the proper thickness of Ag shell exhibit the Faradaic efficiency (FE) of total C2 products and ethylene as high as 67.6% and 32.2% at -1.1 V (versus reversible hydrogen electrode, RHE), respectively. Moreover, it exhibits remarkably electrocatalytic stability after 14 h. Based on electrochemical tests and CO adsorption capacity analyses, the origin of the enhanced catalytic performance can be attributed to the synergistic effect between Ag shell and Cu core, which strengthens the bonding strength of CO on Cu/Ag interfaces, expedites the charge transfer, increases the electrochemical surface areas (ECSAs). This report provides a Cu-based catalyst to realize efficient C<sub>2</sub> generation via a rationally designed core-shell structured catalyst.

# **1. Introduction**

Electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is a highly promising strategy for valuable chemicals and fuels for realizing the carbon cycle.<sup>[1]</sup> Among different products of CO<sub>2</sub>RR, multicarbon compounds (C<sub>2+</sub>) such as ethylene and ethanol are very attractive for chemical raw materials and energy carriers.<sup>[2]</sup>

```
S. Zhang, Dr. S. Zhao, D. Qu, Dr. X. Liu, Prof. Y. Wu, Prof. Y. Chen
State Key Laboratory of Materials-Oriented Chemical Engineering
School of Energy Science and Engineering
Nanjing Tech University
Nanjing 211816, China
E-mail: wuyp@njtech.edu.cn; cheny@njtech.edu.cn
S. Zhang, Prof. Y. Wu, Prof. W. Huang
Key Laboratory of Flexible Electronics (KLOFE)
Institute of Advanced Materials (IAM)
Nanjing Tech University
Nanjing 210009, China
```

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/smll.202102293.

DOI: 10.1002/smll.202102293

After a great research on CO2 electroreduction catalysts, scientists found that copper (Cu) is the only metal that can reduce CO<sub>2</sub> into C<sub>2+</sub> products. However, Cu itself usually has poor selectivity due to the wide product distribution, which limits their potential application in CO<sub>2</sub>RR.<sup>[3]</sup> Extensive distinguished works have been devoted to regulating the selectivity of Cu catalysts, such as optimizing crystal facets,<sup>[4]</sup> alloying,<sup>[5]</sup> modifying oxidation state,<sup>[6]</sup> surface doping,<sup>[7]</sup> introducing defects,<sup>[8]</sup> and modifying ligand.<sup>[9]</sup> Even so, the reduction of CO<sub>2</sub> into C<sub>2+</sub> products with high selectivity is still a challenging work. Thus, the rational design and preparation of efficient catalysts hold great importance in their fundamental study as well as the technical advancement of CO<sub>2</sub>RR.

It is widely accepted that CO related intermediates are the key species to  $C_{2+}$  products in  $CO_2 RR^{[10]}$  Therefore, the designing of a two-step route (i.e.,  $CO_2$ 

to CO and CO to  $C_{2+}$  provides an appropriate pathway for the highly selective conversion of  $CO_2$  to  $C_{2+}$ , which can be achieved by the fabrication of tandem catalysts with multicomposite or hierarchical structure.<sup>[11]</sup> For multicomposite catalysts, a synergistic effect between different components can be used to achieve in situ CO generation, promoting the subsequently reduced to  $C_{2+}$ . Due to the excellent CO formation ability of Au and Ag,<sup>[12]</sup> many studies revealed that the combining Au or/and Ag with Cu could significantly improve the selectivity of  $C_{2+}$ products for CO<sub>2</sub>RR. Many composite catalysts, such as Au-bipy-and Cu-Au/Ag nanoframes,<sup>[20]</sup> have been developed. In addition to the composition control, the finely engineered structure of the catalysts can also improve their performance. Among them, the fabrication of core-shell structure has been verified to be an effective strategy to boost the performance of nanomaterials through the short diffusion path, high active surface area, low internal resistance, and excellent stability.<sup>[21]</sup> Therefore, core-shell nanomaterials are appealing as electrocatalysts since the core materials are the main active component with specific functions, while the shell materials act as protective layers to







**Figure 1.** Transmission electron microscopy (TEM) images of a) Cu@Ag-1, b) Cu@Ag-2, c) Cu@Ag-3, and d) Cu@Ag-4. e,f) High-resolution TEM (HRTEM) images of Cu@Ag-2. g–j) Energy-dispersive spectroscopy (EDS) elemental mappings images for Cu@Ag-2.

enhance the core materials' performance or to produce new properties.

In this work, we report the synthesis of Cu@Ag core-shell NPs with tunable shell thickness for C<sub>2</sub> products during the CO<sub>2</sub>RR process. A series of Cu@Ag core-shell NPs with average sizes of 10.7, 11.2, 11.8, and 12.2 nm (denoted as Cu@Ag-1, Cu@ Ag-2, Cu@Ag-3, and Cu@Ag-4) were prepared. The Cu@Ag-2 catalyst with optimal thickness of Ag shell exhibited the highest catalytic activity and selectivity toward C<sub>2</sub>, with a Faradaic efficiency (FE) of 67.6% and a current density of -22.7 mA cm<sup>-2</sup> at -1.1 V (versus RHE). Based on experimental results, the excellent performance of Cu@Ag-2 catalysts can be attributed to the strong bonding strength to CO on Cu/Ag interfaces, large electrochemical surface areas (ECSAs), and fast interfacial charge transfer.

# 2. Results and Discussion

#### 2.1. Component and Microstructure Characterization

The Cu@Ag core-shell NPs were prepared via a two-step reduction process. The Cu NPs were firstly prepared by the reduction of copper (II) acetylacetonate (Cu(acac)<sub>2</sub>) in an inert atmosphere. These obtained Cu NPs exhibited spherical shapes with an average size of about 9.7 nm (Figure S1, Supporting Information). After that, AgNO3 was added into the above system to form the shell of Ag on the surface of Cu NPs. By changing the amount of silver precursor, four kinds of Cu@Ag NPs with different thicknesses of Ag shell were prepared. Transmission electron microscopy (TEM) images of all these Cu@Ag NPs are shown in Figure 1a-d, which took spherical morphologies. The sizes of Cu@Ag NPs increased consistently to 10.7, 11.2, 11.8, and 12.2 nm (denoted as Cu@Ag-1, Cu@Ag-2, Cu@Ag-3, and Cu@Ag-4) (Figure S2, Supporting Information). Represented by Cu@Ag-2 NPs, the high-resolution TEM (HRTEM) images are shown in Figure 1e,f, from which we can see the clear lattice fringes, and the lattice spacing is measured to be 0.21 nm for the core, assigned to the (111) plane of metallic Cu. In the shell region, the lattice fringe spacing of 0.23 nm is indexed to the (111) plane of pure cubic-phase Ag. Energy-dispersive spectroscopy (EDS) mapping of Cu and Ag clearly shows the Cu (red) core was entirely covered by Ag (green) shell (Figure 1g–j), which further confirmed the core-shell structure of Cu@Ag-2.

X-ray diffraction (XRD) was conducted to confirm the crystalline structure and composition of all these Cu@Ag catalysts. The characteristic peaks of Cu and Ag were observed in both the related XRD patterns of Cu@Ag NPs (Figure 2a). The diffraction peaks at 43.30°, 50.43°, and 74.13°, which were indexed to the (111), (200), and (220) planes of cubic Cu (JCPDS-04-0836), respectively. Besides, the diffraction peaks at 38.12°, 44.28°, 64.43°, and 77.47° were assigned to the (111), (200), (220), and (311) planes of cubic Ag (JCPDS-04-0783), respectively. It is found that the intensities of silver diffraction peaks increase from Cu@Ag-1 to Cu@Ag-4, indicating the increase of the amount of Ag shell. In addition, the diffraction peaks of Ag (111) in Cu@Ag NPs shifted to higher diffraction angles (Figure S3, Supporting Information), which could be due to the compression of the lattice of Ag shell.<sup>[22]</sup> In order to further prove the thicknesses of Ag shell are increased with the increasing amount of silver precursor, Cu LMM Auger spectra for all Cu@Ag NPs were measured (Figure 2b). Cu LMM peaks (564-570 eV) and Ag 3p<sub>3/2</sub> peaks (573 eV) can be observed in all the spectra, while the ratios of intensity for Ag to Cu are increased with the increasing amount of silver precursor, which is strong evidence that the thicknesses of Ag layer are increased from Cu@Ag-1 to Cu@Ag-4. The accurate molar percentages of Ag of these catalysts identified by ICP-OES are 11.2%, 15%, 18.3%, and 24.7%, respectively. The above characterizations suggest that the Cu@ Ag core-shell NPs with different thicknesses of Ag shell have been synthesized successfully.

The surface electronic structures and chemical states of elements of Cu@Ag NPs were further characterized by X-ray photoelectron spectroscopy (XPS). The survey XPS spectra (Figure S4, Supporting Information) indicate the presence of Cu, Ag, O, and C elements in the Cu@Ag NPs catalysts. The intensities of Cu 2p XPS spectra decrease with the increase of the thickness of the Ag shell. The high-resolution Cu 2p XPS spectra of the



**Figure 2.** a) X-ray diffraction (XRD) patterns of Cu NPs, Cu@Ag NPs, and Ag nanoparticles (NPs). b) Cu LMM X-ray photoelectron spectroscopy (XPS) spectra of Cu@Ag catalysts. High-resolution XPS spectra of c) Cu 2p region and d) Ag 3d region for Cu NPs, Cu@Ag NPs, and Ag NPs.

Cu@Ag NPs in Figure S5 (Supporting Information) indicates that both Cu(II) and Cu(I)/Cu(0) species exist on the Cu surface, suggesting that these Cu@Ag catalysts contained a very small amount of oxidized copper. Meanwhile, the content of the Cu(II) is decreased with the increase of the silver laver thickness, indicating that the Ag shell could protect the Cu core from oxidation. Furthermore, a small amount of oxidized copper can effectively reduce the overpotential, increase the activity, and facilitate the production of C<sub>2</sub> products for CO<sub>2</sub>RR.<sup>[23]</sup> To show the evolution trends of the electronic structures for Cu and Ag, the higher resolution scans of the Cu 2p region and Ag 3d region for Cu NPs, Ag NPs, and all Cu@Ag NPs are placed together for comparison, as shown in Figure 2c,d. The highresolution Cu 2p XPS spectra show that the band positions of Cu  $2p_{1/2}$  and Cu  $2p_{3/2}$  shifted to the lower binding energy with thicker Ag shell. On the contrary, the trends of Ag  $3d_{5/2}$ and Ag 3d<sub>3/2</sub> shifted to the opposite direction, which indicated that the existence of electrons transfer between the Cu core and Ag shell. As we know, in comparison with Cu, Ag is richer in electrons and can transfer electrons to Cu. Meanwhile, Cu acts as the electron acceptor, which leads to the shift of binding energy.<sup>[17]</sup> Moreover, the core-shell structure is beneficial for the charge transfer between Cu and Ag.

#### 2.2. Electrochemical Properties of Cu@Ag Catalysts

The  $CO_2RR$  performance over the Cu@Ag catalysts was tested in a flow cell system. The electrocatalysts were spray-coated on a carbon gas diffusion electrode (GDE) and subsequently tested in Ar- and CO2-saturated 1.0 м KOH solutions. Linear sweep voltammetry (LSV) curves of Cu@Ag core-shell catalysts are depicted in Figure 3a. The current density of all catalysts in CO<sub>2</sub>saturated solution shows a dramatic increase and onset potential shifted to the positive direction compared with that in the Ar-saturated solution, suggesting the CO<sub>2</sub>RR occurs readily on the Cu@Ag catalysts. A series of chronoamperometry measurements were performed to investigate the potential dependence of the electrode on the FEs of the reduction products. The gaseous and liquid products were analyzed by gas chromatography (GC) and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) (Figure S6, Supporting Information) measurements, respectively. In addition, Cu NPs without coating with Ag shell were studied as controls. Figure 3b shows the FEs of all products for Cu@Ag-2 at the different applied potentials. Specifically, the FEs of total C<sub>2</sub> products for Cu@Ag-2 reached a maximum of 67.6% at -1.1 V (versus RHE), in which acetate, ethanol, and C<sub>2</sub>H<sub>4</sub> accounted for 5%, 30.4%, and 32.2%, respectively. Moreover, the FEs of total C2 products of Cu@Ag-2 are 16.1, 1.3, 1.6, and 2.0 times higher than those of Cu NPs (4.2%), Cu@Ag-1 NPs (53.9%), Cu@Ag-3 NPs (41.7%), and Cu@Ag-4 NPs (34.0%), respectively, as shown in Figure S7 (Supporting Information) and Figure 3c. In order to demonstrate the core-shell structure of the catalyst is beneficial for the electrochemical reaction, the Cu and Ag NPs were mixed together (mass fraction of Ag is 15%) for CO<sub>2</sub>RR. In comparison with the mixture of Cu-Ag catalyst, the core-shell Cu@Ag catalyst can inhibit the production of hydrogen, while the yields of CO and C<sub>2</sub> products were







**Figure 3.** a) Linear sweep voltammetry (LSV) curves for Cu@Ag NPs in Ar- and CO<sub>2</sub>-saturated 1.0  $\mu$  KOH. b) Faradaic efficiency (FE) values of all products at various applied potentials for Cu@Ag-2 NPs. c) FEs, d) Current density of C<sub>2</sub> products for CO<sub>2</sub>RR over all Cu@Ag NPs. e) FEs of C<sub>2</sub>H<sub>4</sub> over all Cu@Ag NPs. f) Stability test of Cu@Ag-2 NPs at -1.1 V (versus RHE).

increased (Figure 3b and Figure S8, Supporting Information). Furthermore, the C<sub>2</sub> partial current densities  $(j_{C2})$  of all Cu@ Ag samples increased gradually with the negative variation of potentials (Figure 3d). Notably, Cu@Ag-2 presented the highest  $j_{C2}$  of -22.7 mA cm<sup>-2</sup> at -1.1 V (versus RHE), which is superior to the other Cu@Ag samples in this work. The CO<sub>2</sub>RR performance parameters of Cu@Ag-2 and some reported Cu-based catalysts are summarized in Table S1 (Supporting Information). The above findings demonstrate the great effect of the thickness of Ag shell on selectivity and activity for CO2RR. Among all products, C<sub>2</sub>H<sub>4</sub> has been regarded as one of the important chemical materials. Figure 3e and Figure S9 (Supporting Information) show the FEs and current densities for C2H4 of Cu@ Ag catalysts at different applied potentials. The  $FE_{C2H4}$  and  $j_{C2H4}$ achieved on the Cu@Ag-2 catalyst are 32.2% and 9.0 mA cm<sup>-2</sup> at -1.1 V (versus RHE), respectively. Besides the catalytic selectivity and activity, the excellent durability of the CO<sub>2</sub>RR catalysts is another crucial condition for practical applications. Furthermore, long-term operation was conducted at the potential of -1.1V versus RHE on Cu@Ag-2 catalyst. There was no significant decay in both current density and FE of C<sub>2</sub>H<sub>4</sub> during 14 h (Figure 3f). The morphology and XRD pattern (Figure S10,

Supporting Information) of Cu@Ag-2 catalyst indicate that there was no change in both composition and structure of the sample. All these results proved that Cu@Ag-2 catalyst can operate stably for a long time under this condition.

From the analysis of the results given above, it is worthy to understand the relationship between the activity and selectivity and structure for the series of Cu@Ag. Figure 4a summarizes the FEs of CO and C<sub>2</sub> products at -1.1 V (versus RHE) for various Cu@Ag NPs. An obvious volcano-type curve for C2 was observed for four Cu@Ag electrocatalysts. While the FEs for CO presented the opposite trend. From the FEs of products for Cu@Ag-1 and Cu@Ag-2, it can be seen that the increase of Ag layer thickness promotes the generation of C2. However, when the Ag layer thickness keeps growing, such as Cu@Ag-3 and Cu@Ag-4, FEs of C2 decrease sharply, and CO increases correspondingly. The results demonstrate that there is a delicate balance between the Cu core and Ag shell for the CO<sub>2</sub>RR performance. Therefore, we can infer that a two-step process of CO2 electroreduction was achieved through the Cu@Ag core-shell structure that acted as a tandem catalyst, that is, CO2 was firstly adsorbed, activated and reduced to CO on the Ag shell, and subsequently converted to  $C_{2+}$  products on Cu





**Figure 4.** a) Faradaic efficiencies (FEs) of CO and  $C_2$  for the Cu@Ag NPs at -1.1 V (versus RHE). b) Schematic illustration of tandem catalysis for CO<sub>2</sub>RR to C<sub>2</sub> over Cu/Ag core-shell NPs. c) Current density as a function of the scan rate for Cu@Ag NPs. d) Electrochemical impedance spectroscopy (EIS) spectrum for Cu@Ag NPs.

core, as shown in Figure 4b. Thus, the reason why C<sub>2</sub> products of Cu@Ag-1 are lower than that of Cu@Ag-2 may be due to the silver shell of the former is thinner than the latter, which cannot provide enough active sites to produce CO intermediate that could be converted to C<sub>2</sub> products by C-C coupling. However, as the thickness of silver shell continually grows to form the Cu@Ag-3 and Cu@Ag-4 NPs, the silver shell becomes the dominant phase to control the overall behavior of CO<sub>2</sub>RR. Such a thick silver shell prevents CO intermediates from reaching Cu core efficiently, resulting in the dramatically different product distribution from Cu@Ag-2 on Cu@Ag-3 and Cu@ Ag-4 NPs for C<sub>2</sub> products. In addition, the adsorption capacity of CO on Cu@Ag-2 NPs was investigated by CO temperature programmed desorption (CO-TPD), and Cu@Ag-4 was taken as the contrast sample. As shown in Figure S11 (Supporting Information), compared with Cu@Ag-4, in addition to the CO desorption peak at 295 °C, the peak of Cu@Ag-2 at 341 °C is attributed to the chemical adsorption of CO on Cu/Ag interface, which was similar to the reported phenomena.<sup>[21a]</sup> This result indicates that the Cu@Ag-2 has stronger bonding strength to CO, which is beneficial to the further C-C coupling to form  $C_2$  products during  $CO_2RR$ .

In order to investigate the essential reason why the  $CO_2$  reduction performance of Cu@Ag-2 is optimal, ECSA and electrochemical impedance spectroscopy (EIS) measurements were conducted. ECSA was examined through the method of double layer capacitance ( $C_{dl}$ ), which was obtained from the cyclic voltammograms (CVs) under different scan rates (Figure S12, Supporting Information). Figure 4c shows the differences of

charging current density against scan rates on series of Cu@Ag catalysts. Obviously, the  $C_{dl}$  value for Cu@Ag-2 (9.9 mF cm<sup>-2</sup>) is larger than the others Cu@Ag catalysts in this work, which suggested that Cu@Ag-2 exposed more active sites to promote the CO<sub>2</sub>RR process. In addition, the Tafel plots (Figure S13, Supporting Information) of all catalysts were obtained to reveal the reaction kinetics. From the picture, we can intuitively see that the Tafel slope of Cu@Ag-2 was the smallest, indicating the Cu@Ag-2 possessed the most favorable kinetic rate for CO<sub>2</sub>RR. Moreover, EIS was further conducted to explore the charge transfer kinetics of Cu@Ag catalysts. The Nyquist plots (Figure 4d) and equivalent circuit (Figure S14, Supporting Information) show that Cu@Ag-2 with an interfacial charge transfer resistance ( $R_{ct}$ ) of 17.5  $\Omega$ , which was lower than those of Cu@Ag-1 (43.2 Ω), Cu@Ag-3 (79.8 Ω), and Cu@Ag-4 (33.5 Ω), confirming that Cu@Ag-2 processes the fastest interfacial electron-transfer dynamics. Therefore, the excellent CO2RR performance of the Cu@Ag-2 NPs might be attributed to the synergistic effect of components, the strong bonding strength to CO on the Cu/Ag interfaces, high availability of active sites, and fast electron transfer rate.

# 3. Conclusions

In summary, Cu@Ag core-shell NPs with tunable shell thickness were fabricated as efficient  $CO_2RR$  electrocatalysts. It was found that the thickness of Ag shell have an important impact on the selectivity of C<sub>2</sub> products. The optimized Cu@Ag-2 NPs

exhibited the total FE of C<sub>2</sub> products and ethylene are as high as 67.6% and 32.2% at –1.1 V (versus RHE), respectively. The Cu@ Ag-2 catalysts with proper Ag shell thickness could produce and boost the local CO concentration on the Cu core efficiently, which help to improve the selectivity for C<sub>2</sub> products. Electrochemical tests and CO adsorption capacity analyses confirmed that the Cu@Ag-2 catalysts process stronger bonding strength of CO on Cu/Ag interfaces, more active sites, and faster charge transfer. This report provides an efficient core-shell tandem catalyst and a rational design approach of electrocatalysts for boosting CO<sub>2</sub> conversion toward the C<sub>2</sub> and C<sub>2+</sub> products.

#### 4. Experimental Section

ADVANCED SCIENCE NEWS \_\_\_\_\_

Synthesis of Cu NPs and Cu@Ag NPs: Cu NPs were prepared based on the typical approach with modifications. In briefly, of Copper (II) acetylacetonate (Cu(acac)<sub>2</sub>) (1.0 mmol, 261.6 mg) and 10 mL of oleylamine (OAm) were added into a 50 mL three-necked flask with a condenser pipe, which was connected to a Schlenk line. First, the solution was heated to 80 °C at a rate of 5 °C min<sup>-1</sup> and maintained at 80 °C for 1 h. Then, the solution was gradually heated to 170 °C and 210 °C at a rate of 10 °C min<sup>-1</sup>, and each temperature section was maintained for 1 h to obtain Cu NPs. The obtained purple solution was cooled naturally to room temperature. For the preparation of Cu@Ag-2 NPs, the mixture of AgNO<sub>3</sub> (0.2 mmol, 33.9 mg) and 10 mL of OAm was poured dropwise into the above purple solution of Cu NPs at the rate of 30 mL  $h^{-1}$ . After vigorous stirring, the mixture solution was heated to 60 °C at 5 °C min<sup>-1</sup> for 3 h under Ar atmosphere. The products were washed with hexane and acetone, and centrifuged at 3000 rpm for 10 min. The Cu@Ag-2 NPs were dried under vacuum at room temperature overnight for further characterization. The entire experiment process was kept under strict anaerobic conditions to prevent the possibility of NPs being oxidized.

The synthetic procedures for other Cu@Ag catalysts were the same as that for Cu@Ag-2 NPs. The main difference lies on the amount of used AgNO<sub>3</sub> was adjusted. The amount of substance of AgNO<sub>3</sub> for Cu@ Ag-1, Cu@Ag-3, and Cu@Ag-4 were 0.1, 0.5, and 1.0 mmol, respectively.

*Characterization and Instruments*: The morphology of these materials was performed on TEM (JEOL JEM-2100F). The crystal structure and phase analysis of the material was carried out by XRD on a Rigaku SmartLab diffractometer equipped with a Cu K $\alpha$  radiation. Elemental analysis was tested by ICP-OES using a Perkin Elmer OPTIMA7000DV. XPS tests were conducted on a PHI 5000 Versa Probe spectrometer with Al K $\alpha$  radiation (1486.6 eV). The carbon peak at 284.6 eV was used as a reference to correct for charging effects.

Electrochemical Measurements: Electrocatalysis experiments of all the catalysts were measured on a Biologic VMP3 potentiostat controlled by EC-Lab. The flow cell configuration that consisted of GDE ( $1.8 \times 1.8$  cm) modified with catalysts as the working electrode, proton exchange membrane (Nafion 115, Dupont), and nickel foam  $(1.8 \times 1.8 \text{ cm})$  as the anode. GDEs were prepared using an air-brush method. Five milligrams of catalyst was dispersed in 500 µL water, 450 µL isopropyl alcohol, and 50  $\mu$ L Nafion solution (5 wt%) and sonicated for 30 min to form a uniform catalyst ink. Then, the ink was sprayed on the gas diffusion layer (GDL,  $1.8 \times 1.8$  cm) with catalyst loading was to be 1 mg cm<sup>-2</sup>. Here, the geometric area of the working electrode and the anode were designed to be 1.0 cm<sup>2</sup>. The electrolyte (1.0  $\mu$  KOH) with a flow rate of 2.5 mL min<sup>-1</sup> was circulated using a peristaltic pump. Before testing, high-purity  $CO_2$  was pumped into the cell for 20 min by a mass flow controller with the flow rate was 5 mL min<sup>-1</sup>. All potentials were converted to a RHE values by the following formula:  $E_{\rm RHE}$  (V) =  $E_{\rm Ag/AgCl(3.5~M)}$  (V) + 0.209 V + (0.0591 V  $\times$  pH). The LSV curves were measured in Ar- or  $\rm CO_2\mbox{-}saturated$  1.0  $\,\mbox{m}$  KOH solutions at a scan rate of 5 mV  $\rm s^{-1}$  . The chronoamperometry measurement was conducted under different potentials. The quantification of the gas phase products was conducted using a gas chromatograph (Nanjing Hope, GC-9860-5C) equipped with a Valcoplot HayeSep Q column and a Molsieve 5 A column. The liquid products were analyzed by <sup>1</sup>H NMR recorded on a Bruker AVANCE AV-300 spectrometer. The FE for a target product was calculated using the following formula:

$$FE(\%) = \frac{z \cdot n \cdot F}{Q} \tag{1}$$

Where z is the number of electrons required to produce a target molecule, *n* is the number of moles for a target product, *F* is the Faradaic constant of 96 485 C mol<sup>-1</sup>, Q is the total charge of the electrochemical reaction.

To estimate the ECSA,  $C_{dl}$  were conducted by measuring CVs with a potential range of 0.054–0.154 V (versus RHE) that non-Faradaic capacitive current. The scan rates were changed from 20 to140 mV s<sup>-1</sup>. The  $C_{dl}$  was estimated by plotting the capacitance current density  $(\Delta j = j_a - j_c$ , where  $j_a$  and  $j_c$  are the cathodic and anodic current densities, respectively) at the potential of 0.104 V (versus RHE) with respect to the CV scan rate of CV curves. The slope of the line was twice of the  $C_{dl}$ , and the value of ECSA was positively correlated with  $C_{dl}$ . EIS measurement was carried out by applying an AC voltage with 10 mV amplitude in a frequency range from 0.01 to 10<sup>6</sup> Hz at open-circuit voltage.

## **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

S.Z. and S.Z. contributed equally to this work. All authors have given approval to the final version of the manuscript. This work was supported by the financial support from the National Natural Science Foundation of China (51773092, 51425301, 21603209, and 21975124), the Research Foundation of State Key Lab (ZK201717), and the Natural Science Foundation of Jiangsu Province (BK20190685).

## **Conflict of Interest**

The authors declare no conflict of interest.

## Data Availability Statement

Research data are not shared.

## **Keywords**

CO2 reduction reaction, core-shell structure, Cu@Ag, synergy

Received: April 19, 2021 Revised: June 1, 2021 Published online:

a) D. Gao, R. M. Arán-Ais, H. S. Jeon, B. R. Cuenya, *Nat. Catal.* **2019**, *2*, 198; b) Y. Y. Birdja, E. Pérez-Gallent, M. C. Figueiredo, A. J. Göttle, F. Calle-Vallejo, M. T. M. Koper, *Nat. Energy* **2019**, *4*, 732;
 c) S. Zhao, S. Li, T. Guo, S. Zhang, J. Wang, Y. Wu, Y. Chen, *Nano-Micro Lett.* **2019**, *11*, 62.

#### **ADVANCED** SCIENCE NEWS

www.advancedsciencenews.com

- Sci Adv 2020 Lett 2018 3 193. b) M Ma
- [2] a) L. Fan, C. Xia, F. Yang, J. Wang, H. Wang, Y. Lu, *Sci. Adv.* 2020, 6, eaay3111; b) Y. Zheng, A. Vasileff, X. Zhou, Y. Jiao, M. Jaroniec, S. Z. Qiao, *J. Am. Chem. Soc.* 2019, 141, 7646.
- [3] A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl, J. K. Nørskov, *Energy Environ. Sci.* 2010, 3, 1311.
- [4] Z. Wang, G. Yang, Z. Zhang, M. Jin, Y. Yin, ACS Nano 2016, 10, 4559.
- [5] a) S. Ma, M. Sadakiyo, M. Heima, R. Luo, R. T. Haasch, J. I. Gold, M. Yamauchi, P. J. Kenis, *J. Am. Chem. Soc.* 2017, *139*, 47; b) C. W. Lee, K. D. Yang, D.-H. Nam, J. H. Jang, N. H. Cho, S. W. Im, K. T. Nam, *Adv. Mater.* 2018, *30*, 1704717.
- [6] a) W. Zhang, C. Huang, Q. Xiao, L. Yu, L. Shuai, P. An, J. Zhang, M. Qiu, Z. Ren, Y. Yu, J. Am. Chem. Soc. 2020, 142, 11417;
  b) A. D. Handoko, C. W. Ong, Y. Huang, Z. G. Lee, L. Lin, G. B. Panetti, B. S. Yeo, J. Phys. Chem. C 2016, 120, 20058.
- [7] W. Ma, S. Xie, T. Liu, Q. Fan, J. Ye, F. Sun, Z. Jiang, Q. Zhang, J. Cheng, Y. Wang, Nat. Catal. 2020, 3, 478.
- [8] B. Zhang, J. Zhang, M. Hua, Q. Wan, Z. Su, X. Tan, L. Liu, F. Zhang, G. Chen, D. Tan, X. Cheng, B. Han, L. Zheng, G. Mo, *J. Am. Chem. Soc.* 2020, *142*, 13606.
- [9] J. Liu, J. Fu, Y. Zhou, W. Zhu, L. P. Jiang, Y. Lin, Nano Lett. 2020, 20, 4823.
- [10] J. Gao, H. Zhang, X. Guo, J. Luo, S. M. Zakeeruddin, D. Ren, M. Gratzel, J. Am. Chem. Soc. 2019, 141, 18704.
- [11] a) S. Overa, T. G. Feric, A.-H. A. Park, F. Jiao, *Joule* 2021, *5*, 8;
   b) X. Fu, J. Zhang, Y. Kang, *React. Chem. Eng.* 2021, *6*, 612.
- [12] a) S. Verma, Y. Hamasaki, C. Kim, W. Huang, S. Lu, H.-R. M. Jhong, A. A. Gewirth, T. Fujigaya, N. Nakashima, P. J. A. Kenis, ACS Energy

Lett. 2018, 3, 193; b) M. Ma, B. J. Trzesniewski, J. Xie, W. A. Smith, Angew. Chem., Int. Ed. 2016, 55, 9748.

- [13] J. Fu, W. Zhu, Y. Chen, Z. Yin, Y. Li, J. Liu, H. Zhang, J. J. Zhu, S. Sun, Angew. Chem., Int. Ed. 2019, 58, 14100.
- [14] C. G. Morales-Guio, E. R. Cave, S. A. Nitopi, J. T. Feaster, L. Wang, K. P. Kuhl, A. Jackson, N. C. Johnson, D. N. Abram, T. Hatsukade, C. Hahn, T. F. Jaramillo, *Nat. Catal.* **2018**, *1*, 764.
- [15] L. R. L. Ting, O. Piqué, S. Y. Lim, M. Tanhaei, F. Calle-Vallejo, B. S. Yeo, ACS Catal. 2020, 10, 4059.
- [16] W. J. Dong, C. J. Yoo, J. W. Lim, J. Y. Park, K. Kim, S. Kim, D. Lee, J.-L. Lee, *Nano Energy* **2020**, *78*, 105168.
- [17] Z. Chang, S. Huo, W. Zhang, J. Fang, H. Wang, J. Phys. Chem. C 2017, 121, 11368.
- [18] C. Chen, Y. Li, S. Yu, S. Louisia, J. Jin, M. Li, M. B. Ross, P. Yang, *Joule* 2020, 4, 1688.
- [19] J. Huang, M. Mensi, E. Oveisi, V. Mantella, R. Buonsanti, J. Am. Chem. Soc. 2019, 141, 2490.
- [20] L. Xiong, X. Zhang, H. Yuan, J. Wang, X. Yuan, Y. Lian, H. Jin, H. Sun, Z. Deng, D. Wang, J. Hu, H. Hu, J. Choi, J. Li, Y. Chen, J. Zhong, J. Guo, M. H. Rummerli, L. Xu, Y. Peng, *Angew. Chem.*, *Int. Ed.* **2021**, *133*, 2538.
- [21] a) P. Wang, H. Yang, Y. Xu, X. Huang, J. Wang, M. Zhong, T. Cheng, Q. Shao, ACS Nano 2021, 15, 1039; b) W. Luc, C. Collins, S. Wang, H. Xin, K. He, Y. Kang, F. Jiao, J. Am. Chem. Soc. 2017, 139, 1885.
- [22] Y. Xing, X. Kong, X. Guo, Y. Liu, Q. Li, Y. Zhang, Y. Sheng, X. Yang, Z. Geng, J. Zeng, Adv. Sci. 2020, 7, 1902989.
- [23] C. J. Chang, S. C. Lin, H. C. Chen, J. Wang, K. J. Zheng, Y. Zhu, H. M. Chen, J. Am. Chem. Soc. 2020, 142, 12119.