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Tuning nanocavities of Au@Cu₂O yolk–shell nanoparticles for highly selective electroreduction of CO₂ to ethanol at low potential†

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The electroreduction of high-value ethanol from carbon dioxide and carbon monoxide addresses the need for the large-scale storage of renewable electricity and reduction of carbon emissions. However, the electroreduction of ethanol by the CO₂ reduction reaction (CO₂RR) has suffered from low selectivity and energy efficiency. Here, we report a catalyst composed of Au nanoparticles in Cu₂O nanocavities (Au@Cu₂O) that is very active for CO₂ reduction to ethanol through the confinement of the CO intermediate. The architecture shows tandem catalysis mechanisms in which CO₂ reduction on Au yolks produces CO filling Cu nanocavities, where a sufficiently high CO concentration due to the confinement effect promotes ethanol formation and then results in an ethanol faradaic efficiency of 52.3% at –0.30 V *versus* the reversible hydrogen electrode (vs. RHE) *via* regulating the hollow size of the Cu₂O nanocavities. Such a strategy provides a new way of fabricating various tandem catalysts with high selectivity and efficiency for the CO₂RR.

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Introduction

The electrocatalytic reduction of CO₂ to valuable carbon-based fuels and chemicals offers a route to reduce CO₂ emissions and facilitate the long-term storage of renewable electricity.^{1–6} In particular, C₂ and C₂₊ products from the CO₂ reduction reaction (CO₂RR) have attracted considerable attention due to their relatively high energy density, added-value and widespread use as feedstocks in polymer synthesis, *etc.*^{7–9} Excellent electrocatalysts have been developed to boost the activity and selectivity of the CO₂RR towards C₂ and C₂₊ productions.^{10–14} Among currently available materials, Cu-based catalysts have been reported as the most promising electrodes for producing C₂ and C₂₊ compounds under aqueous conditions in CO₂RR, and have been extensively studied.^{8,12,15–21} However, there still present some scientific challenges, such as poor selectivity, low faradaic efficiency and durability, which need to be managed primarily in further work.

To date, several avenues have been employed to improve the selectivity of Cu-based catalysts for CO₂RR to specific products, including altering size, structure, composition, surface state, and so on.^{17–20} Hori *et al.* declared that the product selectivity of CO₂RR shifted greatly with the crystal orientation, where Cu(100) yielded mainly C₂H₄ and Cu(111) benefited CH₄

production.²² Sargent's group constructed a core–shell vacancy engineering catalyst (Cu₂S–Cu–V) to steer products beyond alkenes and toward ethanol at certain potentials.²³ More recently, theoretical and experimental investigations demonstrate that the activity and selectivity for C₂ and C₂₊ of Cu-based catalysts can be greatly advanced by bimetallic strategy or constraining the local CO concentration at the catalyst–electrolyte interface.^{24,25} Au/Cu bimetallic electrocatalyst was obtained with improved activity and selectivity for electrochemical transformation of CO₂ to alcohols over hydrocarbons at low overpotentials, and a tandem catalysis mechanism has been proposed where Au nanoparticles (Au NPs) reduce CO₂ to CO near the copper surface, driving a high CO coverage.²⁵ When supplied directly with CO instead of CO₂ as a feedstock, oxide-derived nanocrystalline copper electrodes produce ethanol with up to 30% faradaic efficiency at modest overpotentials under alkaline conditions.²⁶ In addition, the confinement effect is known to alter thermodynamic and transport properties of fluids.^{27–30} Prior studies of porous catalysts exploited confinement effect to implement a selectivity shift by extending the retention of C₁ or C₂ species, and then boost C₂ or C₃ production,^{16,24} which lack in-depth exploration. As such, developing a new strategy of combining bimetallic strategy and confinement effect is highly imperative for boosting the selectivity to ethanol in CO₂ electroreduction and its practical application.

Herein, we further apply the confinement effect with a bimetallic yolk–shell structure of Au nanoparticle in Cu₂O nanocavity (Au@Cu₂O), whereas Au shows high catalytic activity for converting CO₂ to CO at low potentials,^{31,32} and Cu is able to

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catalyze the second step of the tandem reaction, the reduction of CO to C₂ products at low potentials.^{33–35} The Au@Cu₂O catalyst has higher selectivity for ethanol compared with hydrocarbons at lower overpotentials. We propose that the selectivity shifting from C₁ to C₂ originates from a tandem catalysis mechanism, where Au NPs reduce CO₂ to CO in the Cu nanocavities, producing a high CO concentration, thus boosts the ethanol production due to the confinement of CO intermediate. Meanwhile, we adjust the CO concentration in the nanocavities by regulating the hollow size of the Cu₂O nanocavities, and then achieve an ethanol faradaic efficiency of 52.3% at –0.30 V vs. RHE.

Experimental

Chemicals

Hydrogen tetrachloroaurate(III) trihydrate (HAuCl₄·3H₂O, 99.99%), citric acid, trisodium salt (98%), copper(II) nitrate trihydrate (99%), hydrazine hydrate (hydrazine, 64%), polyvinylpyrrolidone (PVP, average M.W 58000), 2-propanol (99.7+%), Nafion (5%). All chemicals were obtained directly without further purification.

Preparation of Au NPs

The Au NPs with a diameter of about 22 ± 2 nm were synthesized and used as the core materials for the Au@Cu₂O yolk-shell particle fabrication.^{36,37} Au NPs were prepared by a standard citrate reduction procedure. Typically, 150 mL of 0.025 M HAuCl₄ solution was added into a three-necked round bottom flask and heated to boiling under continuously magnetic stir with condensing and refluxing conditions. Then 7.5 mL of 0.02 M sodium citrate solution was added. After reaction for 30 min, heating resource was removed and the solution was allowed to cooled down naturally to room temperature. Finally, the Au NPs were collected from the solution by centrifugation (10 000 rpm), washed with deionized water several times and redispersed in 10 mL of deionized water.

Preparation of Au@Cu₂O yolk-shell NPs with different hollow sizes

Au@Cu₂O yolk-shell NPs was prepared by hydrazine hydration reduction method.^{36,38} Typically, 1 g of PVP powders was added into 10 mL of 0.01 M Cu(NO₃)₂ solution under constant stirring until the PVP powders dissolved completely. Then a certain amount of as-obtained Au NPs solution was added, followed by immediate introduction of trace hydrazine hydrate. After reaction, the Au@Cu₂O yolk-shell NPs were synthesized and centrifuged (10 000 rpm), washed three times with water and isopropyl alcohol, and then dried in an oven at 60 °C for later use. Au@Cu₂O NPs with different hollow sizes can be controlled through adjusting the amount of reducing agent and the reaction time (Fig. 1a).

Preparation of Cu₂O NPs

Cu₂O NPs was prepared in parallel by the same method as Au@Cu₂O yolk-shell NPs except for no addition of Au NPs and PVP powders.

Preparation of working electrode

To prepare the catalyst inks, 3 mg of catalyst powder, 10 μL of Nafion solution (5%) and 1200 μL of isopropyl alcohol were mixed and treated under sonication for 30 min. Then, 600 μL of the as-prepared ink was pipetted onto the two sides of a carbon cloth with area of 1 × 1.5 cm² giving a catalyst loading of 1 mg cm⁻².

Characterizations

X-ray diffraction (XRD) pattern was carried out on a Rigaku D/Max-2500 diffractometer equipped with a Cu Kα1 radiation (λ = 1.54 Å). Scanning electron microscopic images (SEM) were collected on a JEOL scanning electron microscope (S-4800, Japan). Transmission electron microscopic images (TEM) were obtained by a JEM-2100F microscope (JEOL, Japan) equipped with an EDS detector (Oxford Instrument, UK). X-ray photoelectron spectroscopy (XPS) was performed on an ESCALab220i-XL electron spectrometer (VG Scientific, UK) with a monochromatic Al Kα source. The gas products for CO₂ reduction were measured on a gas chromatography (GC, Agilent Technologies 7890B). The liquid products were analyzed with a Bruker AVANCE 600 using dimethyl sulphoxide (DMSO) as an internal standard.

Electrochemical performance test

Electrochemical measurements were performed on a CHI 660E electrochemical workstation in a typical H-type electrolysis cell under ambient pressure and room temperature using platinum mesh (1 × 1 cm²) and Ag/AgCl electrode (saturated KCl) as counter and reference electrodes, respectively. The cathode and anode compartments were separated by a proton-exchange membrane (Nafion 117). The 0.1 M KHCO₃ aqueous solution was used as electrolyte directly without any purification. The electrode potentials were converted to the reversible hydrogen electrode reference (RHE) scale using the following Nernst equation:

$$E(\text{RHE}) = E(\text{Ag}/\text{AgCl}) + 0.197 \text{ V} + 0.0591 \times \text{pH}.$$

Before test, the catalyst was measured at –0.2 V vs. RHE for 30 min in Ar-saturated 0.1 M KHCO₃ solution to ensure all Cu₂O-shells had been reduced to Cu-shells. Then, the catalyst was immediately transfer into CO₂-saturated 0.1 M KHCO₃ solution to perform linear scanning voltammetry (LSV) test from 0.2 to –1.1 V vs. RHE until the performance of the electrode became stable. Finally, CO₂RR experiment at a constant applied voltage spanned over 3600 seconds. The electrochemically surface area (ECSA) was determined by measuring the double layer capacitance (C_{dl}), which was derived from the CV curves at various scan rates.

Analysis of CO₂ reduction products

We measure the reduction performance of the catalyst by calculating the faradaic efficiency (FE) of the CO₂ reduction



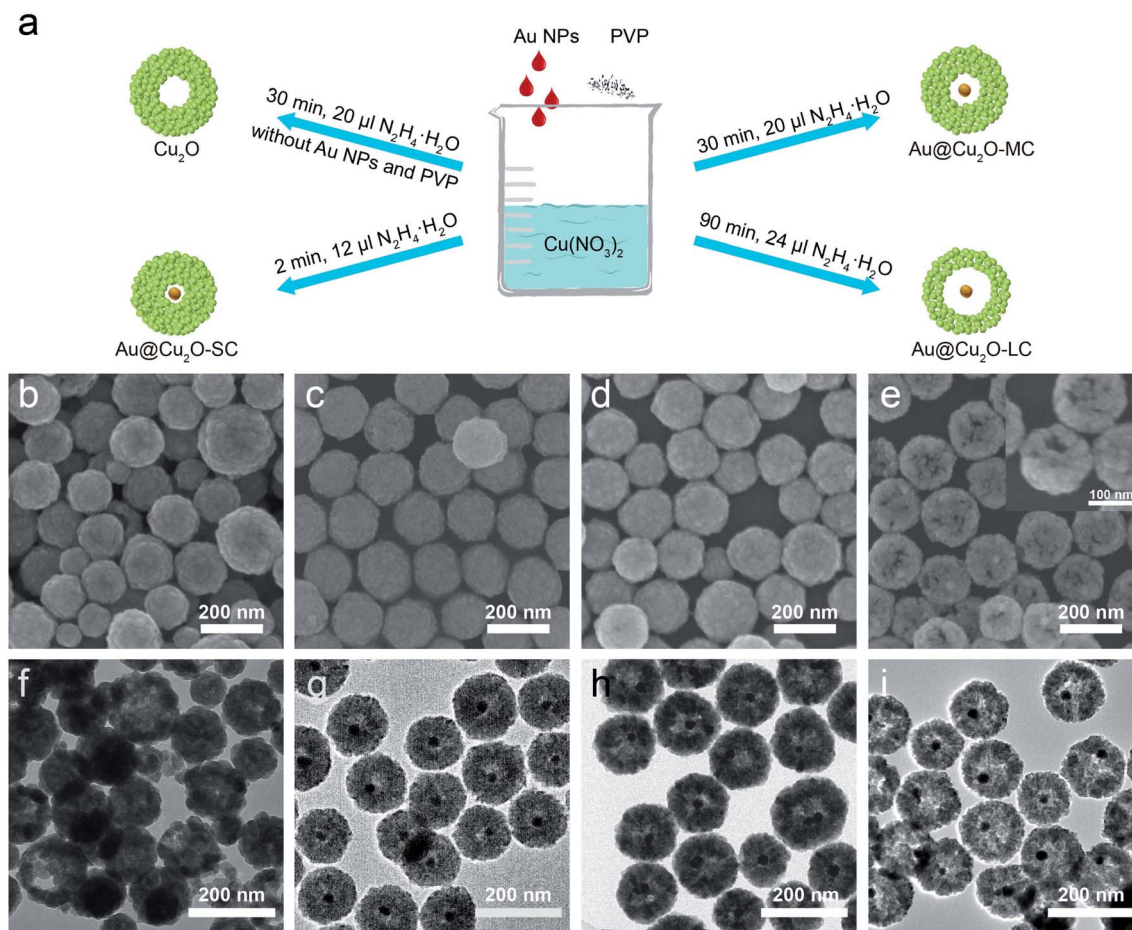


Fig. 1 (a) Schematic illustration of the synthetic process of different samples. (b–e) SEM, (f–i) TEM images of Cu_2O , $\text{Au@Cu}_2\text{O-SC}$, $\text{Au@Cu}_2\text{O-MC}$, $\text{Au@Cu}_2\text{O-LC}$, respectively.

product. The FE of products can be calculated using the following formula:³⁹

$$\text{FE}_i = \frac{Q_i}{Q_{\text{total}}} = \frac{N_i \times n \times F}{Q_{\text{total}}}$$

i : the specific reduction product, CO , HCOO^- , $\text{C}_2\text{H}_5\text{OH}$ or H_2 ; Q_{total} : the total charge of CO_2RR , C; Q_i : charge used for the reduction of certain product, C; N_i : number of moles for certain product, mol; n : number of electrons transferred for the CO_2 -to- CO , HCOO^- and $\text{C}_2\text{H}_5\text{OH}$ conversion or water-to- H_2 reduction, which is 2, 2, 12, 2 for CO , HCOO^- , $\text{C}_2\text{H}_5\text{OH}$ and H_2 , respectively; F : faradaic constant, which is $96\,485\text{ C mol}^{-1}$.

Results and discussion

The Au NPs with uniform size and morphology were obtained according to previous literature (Fig. S1†).^{36,37} Subsequently, the Au nanoparticle was encapsulated within a porous Cu_2O shell with an average size of 140 nm and the hollow size was precisely controlled by regulating the reaction time and the amount of reducing agents, as depicted in Fig. 1a. Meanwhile, Fig. S2† shows the geometry of the multilayer particle we simulated, in which the radius of the Cu_2O NPs is donated as R

and the radius of the hollow size is donated as R1. In the structure, C_2 chemical selectivity can be tuned by systematically altering the R1 of 14, 35, 48 nm, which are named small cavity $\text{Au@Cu}_2\text{O}$ ($\text{Au@Cu}_2\text{O-SC}$), middle cavity $\text{Au@Cu}_2\text{O}$ ($\text{Au@Cu}_2\text{O-MC}$) and large cavity $\text{Au@Cu}_2\text{O}$ ($\text{Au@Cu}_2\text{O-LC}$), respectively. Scanning electron microscopy (SEM) images in Fig. 1b–e reveal that the surfaces of all obtained samples are uneven, and as reaction time went on, a clear porous structure was seen on the surface of $\text{Au@Cu}_2\text{O-LC}$. Corresponding to SEM images, transmission electron microscopy (TEM) images in Fig. 1f–i show all the samples have a porous Cu_2O shell. And the inner hollow size became larger along with the increased reaction time and the shell structure gradually grew looser. In addition, the samples except porous Cu_2O NPs belong to yolk-shell structure and exhibit an average diameter of 140 ± 10 nm with an average Au-cores diameter of 22 ± 2 nm. Moreover, the statistical analysis based on over 100 nanoparticles indicates that they are in narrow size distribution (Fig. S3†), agreeing well with SEM and TEM results. Take $\text{Au@Cu}_2\text{O-MC}$ catalyst for example, more detailed structural information was characterized in Fig. 2. High-resolution TEM image (HRTEM) clearly shows the lattice fringes in spacings of 0.30 and 0.25 nm corresponding to (110) and (111) planes of cubic Cu_2O



with a characteristic interplanar angle of 90° on the shell (Fig. 2a).⁴⁰ Dark-field scanning transmission electron microscopy (DF-STEM) image (Fig. 2b) exhibits the loose and porous structure of the shell material, which will promise efficient mass transport for potential electrochemical applications. Meanwhile, the corresponding energy dispersive X-ray spectroscopic (EDS) elemental mapping images (Fig. 2c–f) clearly display that Au distributes homogeneous on the core part while Cu and O are distributed mainly across the nanoparticle shell section, confirming the yolk-shell structure of Au@Cu₂O.

The composition and crystalline structure of these samples were investigated by X-ray diffraction (XRD) technique. All of the recorded diffraction peaks in the typical XRD patterns (Fig. 3a) can be well indexed to cubic Au (JCPDS no. 89-3697) and cubic Cu₂O (JCPDS no. 78-2076), corresponding to the HRTEM results. Further clues can be seen in X-ray photoelectron spectroscopic spectra (XPS) (Fig. 3b and c). By comparing the Cu 2p and Cu-LMM XPS peaks of Cu₂O and Au@Cu₂O-MC, it could be clearly seen that the Cu atom in Au@Cu₂O-MC is Cu⁺, which is beneficial for CO₂RR according to previous reports.^{15,16,26,41} In addition, since XPS is a surface analysis technique with investigation depth of 2–5 nm and the Au-core is coated by Cu₂O, the signal of Au element is not detected.⁴² Based on these results, it can be concluded that Au-core encapsulates in porous Cu₂O-shell particle, which constitute the tandem catalyst.

Consequently, it is suggested that the active Cu sites of the catalyst during CO₂RR are derived from Cu₂O.

The CO₂RR performances were evaluated over the as-obtained samples supported on the carbon cloth in 0.1 M KHCO₃ solution saturated with CO₂ using H-cell set-up. The products of CO₂RR were analyzed and quantified by online gas chromatography (GC) for the gas products and ¹H nuclear magnetic resonance spectroscopy (¹H NMR) for the liquid-phase products. We can determine the electrochemical activity by linear sweep voltammetry (LSV) towards CO₂RR, initially. Compared with the current density under Ar-saturated 0.1 M KHCO₃, it has a significant increase under CO₂-saturated electrolyte, indicating that Au@Cu₂O-MC has superior CO₂RR performance (Fig. S4a†). From Fig. S4b,† it can be seen the difference of current density between these samples, and Au@Cu₂O-MC has the maximum current density at the same potential, showing the excellent CO₂RR performance. For porous Cu₂O NPs, at low applied cathodic potential of -0.3 and -0.35 V vs. RHE, the only detectable product is ethanol and the faradaic efficiency (FE_{C₂H₅OH}) reaches 16% at -0.3 V vs. RHE (Fig. 4a), demonstrating the Cu₂O NPs has intrinsic C–C coupling potential. At more cathodic potentials, a substantial difference in the product distribution is found with the products of C₂ and significant increases in the CO, HCOO[−] production rates. After introducing Au NPs in the cavities (Fig. 4b), the selectivity shifts clearly and CO, HCOO[−], C₂H₅OH products are generated at -0.3 and -0.35 V vs. RHE. The

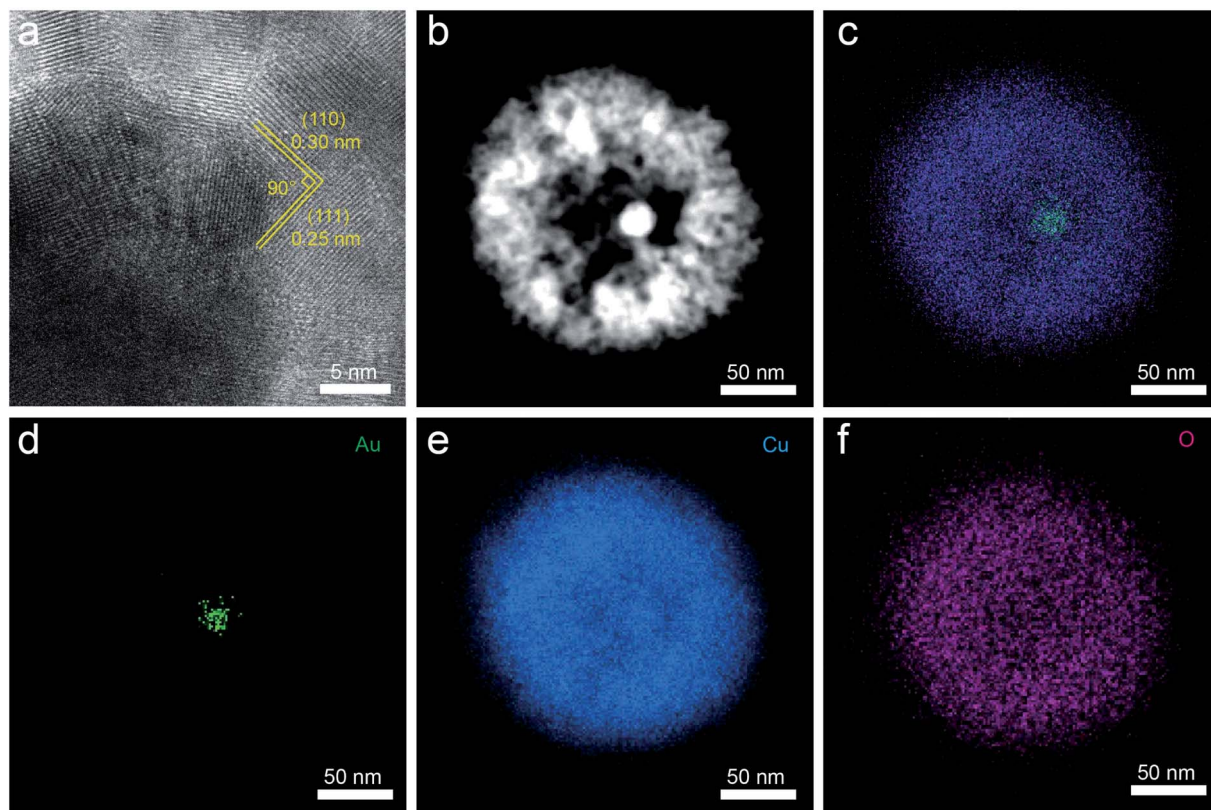


Fig. 2 (a) HRTEM, (b) DF-STEM and (c–f) EDS elemental mapping images of Au@Cu₂O-MC.



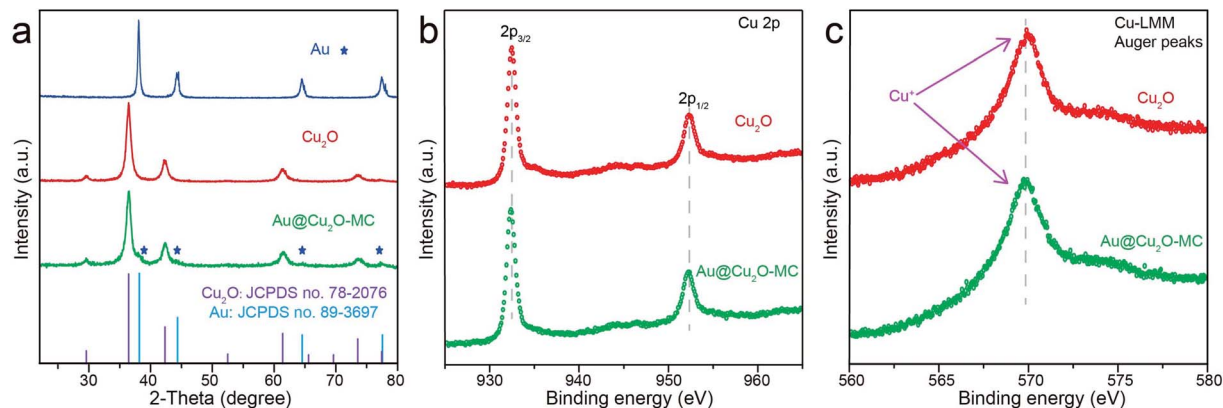


Fig. 3 (a) XRD patterns of different samples, (b) high-resolution Cu 2p and (c) Cu-LMM XPS spectra for Cu₂O and Au@Cu₂O-MC.

production of CO and HCOOH on the Au@Cu₂O-SC as well as its absence on the pure porous Cu₂O NPs, together with the promoted FE_{C₂H₅OH} (36%) at low potentials, prove the effect of the suggested tandem reaction mechanism within the nano-confined space with both catalytic sites located in cavities. The Au-core is active for electroreduction of CO₂ to CO, yet the Cu-shell is able to reduce the retention of CO in the cavities to improve ethanol production (Fig. 4e). When the hollow size of the catalyst was increased to 35 nm, the largest FE_{C₂H₅OH} was improved to 52.3% at -0.3 V vs. RHE (Fig. 4c). The reduction of

the FE_{C₂H₅OH} at higher cathodic potentials from -0.45 to -0.6 V vs. RHE indicates that the previously described tandem mechanism is almost inactive in this potential window for Au@Cu₂O-MC due to the overwhelmingly competitive HER from the exposed metal species (Fig. S5†). Further increasing the hollow size to 48 nm, the largest FE_{C₂H₅OH} is 38% at -0.35 V vs. RHE (Fig. 4d), which is slightly less than that of Au@Cu₂O-MC. However, the active potential window of tandem reaction mechanism for Au@Cu₂O-LC is broader than that of Au@Cu₂O-MC, and all of the FE_{C₂H₅OH} at whole potentials from -0.27 to

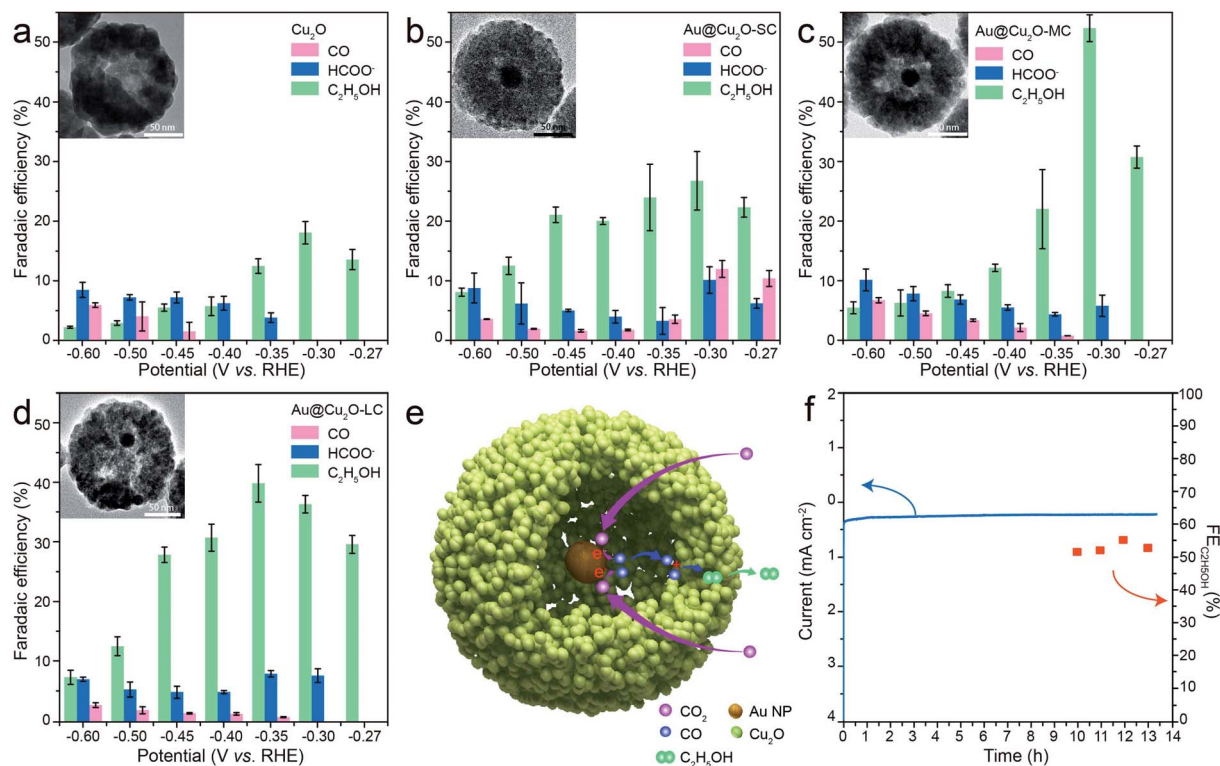


Fig. 4 (a–d) The faradaic efficiencies of carbon monoxide, formic acid, and ethanol from the CO₂RR products under a range of potentials of different samples. (e) Schematic illustration of tandem catalysis mechanism in the Au@Cu₂O cavity. (f) Time-dependent current density curve and FE_{C₂H₅OH} of Au@Cu₂O-MC in CO₂-saturated 0.1 M KHCO₃ solution at -0.3 V vs. RHE.



−0.45 V vs. RHE is higher than that of Au@Cu₂O-SC, as well as a reduction of the detected CO at −0.27 and −0.3 V vs. RHE for Au@Cu₂O-MC and Au@Cu₂O-LC, suggesting the reaction mechanism of CO₂RR can be monitored *via* regulating the concentration of CO intermediate by steering the hollow size of the Cu₂O cavity.⁴³ Therefore, advisable hollow size for tandem reaction drove by spatial confinement effect is very important. Moreover, the ECSA of all the samples have been determined from the CV curves at different scan rates from 10 to 50 mV s^{−1} (Fig. S6†) to estimate the effect from morphology. As shown in Fig. S7,† the Au@Cu₂O-SC shows a C_{d1} value of 2.71 μF cm^{−2}, similar to 2.08 and 2.23 μF cm^{−2} of Au@Cu₂O-MC and Au@Cu₂O-LC, further verify the reaction mechanism we have proposed previously.

The durability of each catalyst was further assessed by chronoamperometry (CA) measurement since it is another important performance parameter for estimating an electrocatalyst. Fig. 4f exhibits the consecutive over 13 h CA curves at a constant potential of −0.3 V vs. RHE for Au@Cu₂O-MC, and it outputs a steady current density for ethanol production with a nearly unchanged FE_{C₂H₅OH}. The FE_{C₂H₅OH} was retained >50% during the entire period, suggesting the excellent long-term durability of the catalyst, comparable with or outperforming most of other state-of-the-art Cu-based CO₂RR catalysts (Table S1†). In addition, the catalysts after CO₂RR tests were further characterized. TEM image (Fig. S8a†) and XRD pattern (Fig. S8b†) reveal that Au@Cu₂O was *in situ* electroreduction to Au@Cu, hinting that the actual active sites are from Au-core and Cu-shell, which is in agreement with previously reported results.^{16,25,26}

Conclusions

In summary, we have developed a bimetallic catalyst of Au@Cu₂O yolk-shell with improved activity and selectivity for the electrochemical reduction of CO₂ to ethanol at lower potential. It was demonstrated that the spatial confinement of different active sites with a tandem catalysis mechanism leads to the selectivity shift from C₁ to C₂. The Au-core can reduce CO₂ to CO in the copper nanocavity, producing a high CO concentration, thus the Cu-shell transforms CO to ethanol production. In addition, we confine the CO concentration in the nanocavity by optimizing the hollow size of the Cu₂O nanocavity, and then perform an ethanol faradaic efficiency of 52.3% at −0.30 V vs. RHE. These results suggest that the present strategy may shed light on the design and preparation of highly active tandem catalysts for other electrochemical reactions.

Conflicts of interest

There are no conflicts to declare.

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