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# Evoking C<sub>2+</sub> production from electrochemical CO<sub>2</sub> reduction by the steric confinement effect of ordered porous Cu<sub>2</sub>O†

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Selective conversion of carbon dioxide (CO<sub>2</sub>) to multi-carbon products (CO<sub>2</sub>-to-C<sub>2+</sub>) at high current densities is in essential demand for the practical application of the resultant valuable products, yet it remains challenging to conduct due to the lack of efficient electrocatalysts. Herein, three-dimensional ordered porous cuprous oxide cuboctahedra (3DOP Cu<sub>2</sub>O–CO) were designed and synthesized by a molecular fence-assisted hard templating approach. Capitalizing on the merits of interconnected and uniformly distributed pore channels, 3DOP Cu<sub>2</sub>O–CO exhibited outstanding electrochemical CO<sub>2</sub>-to-C<sub>2+</sub> conversion, achieving faradaic efficiency and partial current density for C<sub>2+</sub> products of up to 81.7% and –0.89 A cm<sup>–2</sup>, respectively, with an optimal formation rate of 2.92 mmol h<sup>–1</sup> cm<sup>–2</sup> under an applied current density of –1.2 A cm<sup>–2</sup>. *In situ* spectroscopy and simulation results demonstrated that the ordered pores of 3DOP Cu<sub>2</sub>O–CO can effectively confine and accumulate sufficient \*CO adsorption during electrochemical CO<sub>2</sub> reduction, which facilitates efficient dimerization for the formation of C<sub>2+</sub> products. Furthermore, the 3DOP structure induces a higher local pH value, which not only enhances the C–C coupling reaction, but also suppresses competing H<sub>2</sub> evolution.

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## Introduction

The electrochemical conversion of carbon dioxide (CO<sub>2</sub>) to value-added multi-carbon (C<sub>2+</sub>) products with higher energy

density and market value provides a promising avenue to mitigate or solve the energy and environmental crisis that currently exists due to the excessive emission of CO<sub>2</sub> wastes.<sup>1–3</sup> However, the one-carbon (C<sub>1</sub>) nature and chemical stability of CO<sub>2</sub> molecules impose a great obstacle for the imperative carbon–carbon (C–C) bond-coupling reaction, which limits the efficiency of CO<sub>2</sub>-to-C<sub>2+</sub> conversion.<sup>4–7</sup> It has been demonstrated that adequate coverage of adsorbed CO intermediates (\*CO) on catalyst surfaces is essential for dimerization and protonation to form C<sub>2+</sub> products.<sup>4,8–10</sup> Thus far, catalyst design strategies that can promote \*CO coverage and/or suppress CO escape are promising for enabling deep CO<sub>2</sub> reduction to valuable C<sub>2+</sub> products with high selectivity and efficiency.

Among all the strategies, catalysts with concavities have demonstrated extraordinary confinement of reaction intermediates.<sup>4,11,12</sup> For instance, Cu<sub>2</sub>O cavities enabled a C<sub>2+</sub> faradaic efficiency (FE) of 75.2 ± 2.7% by spatial confinement for carbon intermediates,<sup>4</sup> and a maximum C<sub>2+</sub> FE of 77.0 ± 0.3% was realized by optimizing the confinement effect of Cu<sub>2</sub>O hollow multishell structures.<sup>11</sup> Unfortunately, the confinement effect reported in these studies is insufficient for high C<sub>2+</sub> selectivity to occur at ampere-level current densities, thus retarding their practical applications. Additionally, understanding of the structure–performance relationship is lacking, which hinders the production of elaborate designs for electrocatalysts with greater efficiency. To address these issues, ordered porous Cu<sub>2</sub>O

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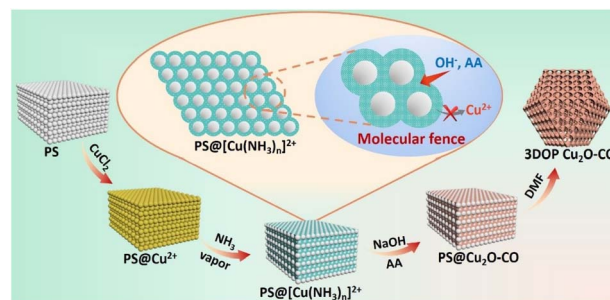
has been proposed to advance the production and selectivity of  $C_{2+}$  products by imparting a well-organized spatial confinement effect with its unique electrocatalytic  $CO_2$  performance.

Three-dimensional ordered porous (3DOP) materials, characterized by their well-defined pore arrangements, tunable pore sizes, and smooth mass transfer of the 3D interconnected pore channels, have demonstrated remarkable catalytic performance.<sup>13–19</sup> Employing hard templates, including mesoporous materials (*e.g.*, mesoporous silica and carbon)<sup>13,19–22</sup> and colloidal crystals (*e.g.*, polystyrene and silica spheres),<sup>20,23–29</sup> has been the most extensively explored method for fabricating 3DOP materials. Despite significant efforts in this area, it remains a substantial challenge to achieve precise control over the nanoarchitectures within the templates to create 3DOP materials, especially for those beyond the well-studied silica-, carbon- and metal-organic framework (MOF)-based materials.<sup>30–33</sup>

The main challenge for the nanospace-confined synthesis of 3DOP metal oxides lies in how to introduce metal precursors into the confined spaces and suppress the migration of metal species out of the confined spaces during the reaction processes. The notorious migration of metal species leads to fluctuations in the pore ordering and the overall morphologies, and even results in nonporous products.<sup>13,31,34,35</sup> Therefore, irregular porous metal oxides with particle sizes ranging from tens of nanometers to several micrometers have been created by different researchers.<sup>13,31</sup> It is crucial to develop a comprehensive understanding and precise control over the growth mechanism of metal oxides inside confined template spaces. By achieving simultaneous regulation of overall morphologies and structural ordering, we can anticipate significant advancements and superior applications of porous metal oxides.

To actualize this concept into practice, we proposed the synthesis of 3DOP  $Cu_2O$  crystals using a hard-templating strategy. The synthesis of  $Cu_2O$  is a multistep reaction involving different reagents and, therefore, conferring its confined growth inside hard templates requires several cycles of infiltration reaction procedures.<sup>36,37</sup> The processes that fulfill the voids of hard templates with reagents and prevent their leaching during the subsequent wet chemical reaction processes are crucial for preparing ordered porous  $Cu_2O$  crystals with satisfactory repeatability.

In this work, we developed a molecular fence-assisted hard-templating strategy, in which  $Cu^{2+}$  ions are converted to  $[Cu(NH_3)_n]^{2+}$  complexes for the synthesis of 3DOP  $Cu_2O$  crystals (Scheme 1). The loose and less soluble  $[Cu(NH_3)_n]^{2+}$  (Fig. S1†) allowed reagents to infiltrate into the inner region of the well-patterned polystyrene (PS) monolith by capillary effect. Once the aqueous reagents entered the voids of the PS monoliths, the pre-adsorbed  $Cu^{2+}$  ions were dissolved and reacted to form  $Cu(OH)_2$ , thereby inhibiting the migration of  $Cu^{2+}$  ions to the outside of the template. Taking advantage of the capsulating effect of the molecular fence and the shaping effect of the assembled PS template, 3DOP  $Cu_2O$  cuboctahedra (abbreviated as 3DOP  $Cu_2O$ -CO) were successfully synthesized. The spatial confinement effect of 3DOP  $Cu_2O$ -CO was clarified in the electrocatalyzing  $CO_2$  reduction reaction ( $CO_2RR$ ), with FEs for



**Scheme 1** Schematic diagram illustrating the procedure for synthesis of 3DOP  $Cu_2O$ -CO using a molecular fence-assisted hard templating strategy.

$C_{2+}$  products up to 73.4% and 81.7% that were attained due to the 3DOP  $Cu_2O$ -CO in an H-type reactor and flow cell, respectively. More impressively, 3DOP  $Cu_2O$ -CO provides a maximum partial current density of  $C_{2+}$  products up to  $-0.89\text{ A cm}^{-2}$  at an applied current density of  $-1.2\text{ A cm}^{-2}$  in a flow cell.

## Results and discussion

### Synthesis and characterization of 3DOP $Cu_2O$ -CO

The molecular fence strategy for synthesizing 3DOP  $Cu_2O$ -CO is schematically illustrated in Scheme 1. As the essence of this approach, ammonia vapor was utilized to stabilize  $Cu^{2+}$  and prevent its dissolution from the template. In the synthetic procedure, the 3D-ordered PS template pre-adsorbed with  $Cu^{2+}$  (denoted as  $PS@Cu^{2+}$ ) was treated in an airtight container saturated with ammonia vapor. During this process, the color of the PS cake changed from light yellow to bright cyan (Fig. S2†), indicating that  $Cu^{2+}$  was converted to other forms. The cyan color began to form at the outmost layer and then gradually expanded from the exterior to the interior of the  $PS@Cu^{2+}$  monoliths, depending on the treatment time (Fig. S3†). To reveal the exact change, the products formed at this stage were collected and characterized by powder X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectrometry.

The XRD results revealed that after ammonia treatment, the cyan-colored complex is a mixture of  $[Cu(NH_3)_2]^{2+}$  and  $[Cu(NH_3)_4]^{2+}$  complexes (Fig. S4†). For simplicity, we denote the copper-ammonia complex formed after ammonia treatment as  $[Cu(NH_3)_n]^{2+}$ . Distinctly different from the FTIR profile of the  $CuCl_2$  precursor, several new peaks appeared in the FTIR spectra for the sample after ammonia vapor treatment. Typically, the sharp maximum peaks at approximately  $3350\text{ cm}^{-1}$  and  $3130\text{ cm}^{-1}$  were ascribed to the N-H stretching vibrations of  $NH_3$ . Additionally, the antisymmetric bending fundamental mode of  $NH_4^+$  occurred as an intense absorption at approximately  $1406\text{ cm}^{-1}$ , and the  $NH_3$  wagging of  $NH_3$  in  $[Cu(NH_3)_n]^{2+}$  appeared at approximately  $1254\text{ cm}^{-1}$  (Fig. S5†).<sup>38,39</sup> Based on the above results and the influence of synthetic conditions on the complexation of Cu, the  $[Cu(NH_3)_n]^{2+}$  compound was formed under exposure to ammonia vapor. In the successive wet-chemical reactions, the preformed  $[Cu(NH_3)_n]^{2+}$  compound ensured the infiltration of reagents to the PS voids yet inhibited



the dissolution of the adsorbed  $\text{Cu}^{2+}$  into the solutions (Fig. S6†), thus dictating that the reactions occur in the confined space of the templates.

After completion of the reaction and removal of the PS template by dimethylformamide (DMF), the products obtained under typical conditions were collected. The XRD diffraction patterns were consistent with the standard patterns of  $\text{Cu}_2\text{O}$  nanocrystals (JCPDS no. 05-0667) (Fig. S7†), demonstrating the formation of  $\text{Cu}_2\text{O}$  in the synthesis. No other diffraction peaks were observed, excluding the formation of undesired impurities. The results showed that the  $[\text{Cu}(\text{NH}_3)_n]^{2+}$  compound formed during the ammonia treatment only serves as a unidirectional encapsulating agent without influencing the formation of  $\text{Cu}_2\text{O}$ .<sup>40</sup>

Low-magnification scanning electron microscopy (SEM) images showed that cuboctahedra with uniform and well-patterned pores were obtained (Fig. 1a). Although the crystal size slightly deviated, there are sharp edges on the cuboctahedra, and a dominant edge length of 1.5  $\mu\text{m}$  was confirmed by statistical analysis (Fig. S8a†). As is known, a cuboctahedron possesses eight triangular facets and six square facets. To more closely examine the pore organization inside the polyhedron, individual particles projected in the directions of the [110] and [100] zone axes were selected and characterized by SEM, transition electron microscopy (TEM), and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) (Fig. 1e–g and i–k). The corresponding schematic models are also displayed for comparison (Fig. 1d and h).

All the results indicate that ordered macropores (approximately 215 nm) interconnected by mesopore channels with an

average length of 50 nm were evenly arranged inside the  $\text{Cu}_2\text{O}$  cuboctahedra (Fig. 1b, d–k, S8b and S9†). Thus, the resultant porous  $\text{Cu}_2\text{O}$  cuboctahedra were characterized by the close-packed order of monodisperse PS templates without any decrease in ordering (Fig. S10†). Thus, the aforementioned results indicated that the 3DOP  $\text{Cu}_2\text{O}$  cuboctahedra were successfully synthesized. The selected-area electron diffraction (SAED) pattern of one individual 3DOP  $\text{Cu}_2\text{O}$ -CO crystal demonstrated its polycrystalline nature by showing diffraction rings (Fig. S11†). This was consistent with the small grain size (23.6 nm) of 3DOP  $\text{Cu}_2\text{O}$ -CO, as calculated by the Scherrer equation based on the most intense (111) diffraction peak (Table S1†).

The surface structure around the nanopores of the 3DOP  $\text{Cu}_2\text{O}$ -CO was further investigated using aberration-corrected atomic-resolution HAADF-STEM (Fig. S12†). The lattice fringes with distances of 0.21 nm and 0.25 nm were attributed to the (200) and (111) planes of  $\text{Cu}_2\text{O}$  (Fig. S12a†). The magnified HAADF-STEM image illustrated in Fig. 1c shows that the concave surface possesses a large number of atomic defect sites, which usually enable the adsorption of intermediates in electrocatalysis.<sup>41,42</sup> The HAADF-STEM and corresponding elemental mapping images (Fig. 1l) show the uniform distribution of Cu and O over the entire particle, and the Cu/O atomic ratio was determined to be 2/1 (Fig. S13†). All these results consistently demonstrate the formation of high-quality ordered porous  $\text{Cu}_2\text{O}$  cuboctahedra without impurities.

To the best of our knowledge, this study presents the first synthesis of 3DOP  $\text{Cu}_2\text{O}$  cuboctahedra. Elucidating the mechanism behind the simultaneous regulation of porous structure and morphology holds paramount significance in the development of a diverse range of innovative porous materials. Considering the synthetic conditions in the present study, the surfactant (polyvinylpyrrolidone (PVP)) and assembled PS template may be the two factors responsible for morphology control. Therefore, we conducted control experiments to reveal the reasons for the formation of 3DOP  $\text{Cu}_2\text{O}$ -CO. Although PVP is effective in regulating the geometry of  $\text{Cu}_2\text{O}$  in wet-chemical synthesis,<sup>36,37</sup> irregularly shaped products were obtained under the same synthetic procedure to synthesize 3DOP  $\text{Cu}_2\text{O}$ -CO using PVP as an additive but without the PS template (Fig. S14†).

When the well-assembled  $\text{PS} @ [\text{Cu}(\text{NH}_3)_n]^{2+}$  monolith was ground to very small pieces for the subsequent synthesis, the ordered porous structure and cuboctahedral morphology remained in the obtained products (Fig. S15†). All of these results indicate that the 3D-ordered assembly of the PS template, and not the PVP surfactant, shaped the morphology of the porous  $\text{Cu}_2\text{O}$ . Therefore, an inspection of the PS assembly was carried out by SEM, which revealed that PS spheres assumed a face-centered cubic (*fcc*) structure to form a closely packed PS template (Fig. S16†). In a basic *fcc* unit, each PS sphere is surrounded by 12 other spheres (Fig. S17a†) that are located at the vertexes of a cuboctahedron (Fig. S17b†). Consequently, the space around each sphere in the assembled template is divided into 14 parts, with different orientations by the 12 adjacent spheres.<sup>34</sup> When  $\text{Cu}_2\text{O}$  crystals grow inside the closely packed PS template, the crystals can move in only 14 directions (6 in the [100] direction and 8 in the [111] direction)

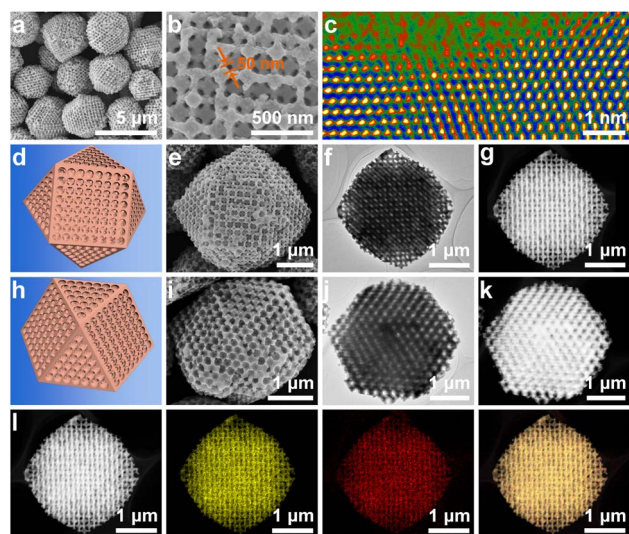


Fig. 1 Morphological characterization of 3DOP  $\text{Cu}_2\text{O}$ -CO. (a and b) Representative low- and high-magnification SEM images, respectively. (c) Atomic resolution aberration-corrected HAADF-STEM image of the concave surface of the 3DOP  $\text{Cu}_2\text{O}$ -CO. False color is applied to enhance the contrast. (d–g) Structural characterization of an individual 3DOP  $\text{Cu}_2\text{O}$ -CO in the (d–g) [100] and (h–k) [110] zone axes: (d and h) schematic illustration, (e and i) SEM, (f and j) TEM, and (g and k) HAADF-STEM images. (l) HAADF-STEM image and corresponding elemental maps of Cu (yellow), O (red), and their overlap (orange).





under the confinement effect imposed by the adjacent 12 spheres. The consecutive growth of  $\text{Cu}_2\text{O}$  by the same limitations of each PS sphere template will exclusively result in the formation of cuboctahedral morphology (Fig. 2a).

To validate the nanospace-confined growth model, control experiments were carried out by changing the assembly ordering of the PS template. It was found that only the closely packed PS template produced porous cuboctahedra, which were gradually transformed to porous spheres after increasing the chaos of the assembled PS template (Fig. S18†). The HAADF-STEM image consistently revealed that the formed pores were randomly distributed inside the spheres (Fig. 2c–e). Except for the above-mentioned shaping and pore-directing effect of the assembled PS template, fulfilling the template voids by reagents is critical for producing high-quality 3DOP  $\text{Cu}_2\text{O}$ -CO because the severe and distinct volume shrinkage occurring during the conversion of copper precursors to  $\text{Cu}_2\text{O}$  can easily deform the porous structures and aggravate the irregular morphologies.<sup>13,31</sup> In a typical synthesis without ammonia treatment of the  $\text{PS@Cu}^{2+}$ , the pre-adsorbed Cu precursors will be dissolved and migrate out of the PS template, resulting in irregular products containing porous and nonporous particles (Fig. S19†). Therefore, the success of 3DOP  $\text{Cu}_2\text{O}$ -CO production in the present study relies on the shape and templating effect of the 3DOP PS template and the subtle utilization of a molecular fence, which guarantees the fulfillment of  $\text{Cu}^{2+}$ .

### Electrochemical $\text{CO}_2\text{RR}$ performance in an H-type cell

As a proof-of-concept, the confined enhancement of the 3DOP  $\text{Cu}_2\text{O}$ -CO for the electrochemical  $\text{CO}_2$  reduction reaction

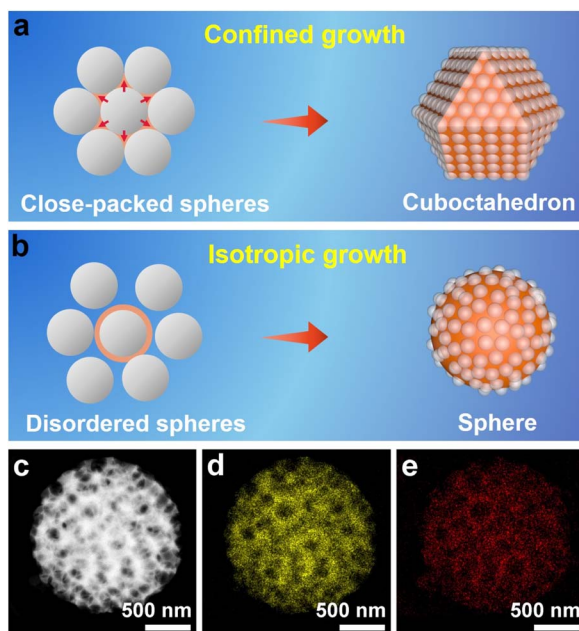


Fig. 2 Effect of the assembled PS template on crystal morphology. Schematic illustration of the crystal growth manner and the resultant products using (a) a closely packed and (b) a disordered PS template. (c) HAADF-STEM image and corresponding elemental maps of (d) Cu and (e) O of one individual porous  $\text{Cu}_2\text{O}$  sphere.

( $\text{CO}_2\text{RR}$ ) was conducted using a three-electrode H-type cell in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  electrolyte. For comparison, nonporous  $\text{Cu}_2\text{O}$  cuboctahedra (abbreviated as  $\text{Cu}_2\text{O}$ -CO) (Fig. S20†) were synthesized and examined under the same conditions. The linear sweep voltammetry (LSV) plots obtained in  $\text{CO}_2$ -saturated electrolyte catalyzed by the two different catalysts are displayed in Fig. 3a. The 3DOP  $\text{Cu}_2\text{O}$ -CO exhibited a higher current response over the entire potential range, indicating that  $\text{CO}_2\text{RR}$  is kinetically favored on the 3DOP  $\text{Cu}_2\text{O}$ -CO in comparison to the nonporous catalyst.

To investigate the number of active sites and their accessibility, the electrochemically active surface areas (ECSA) of different catalysts were then estimated by the electrochemical double-layer capacitance ( $C_{\text{dl}}$ ) method after electrode activation treatment. The 3DOP  $\text{Cu}_2\text{O}$ -CO produced a larger  $C_{\text{dl}}$  value of  $2.9 \text{ mF cm}^{-2}$  as compared to that of  $\text{Cu}_2\text{O}$ -CO ( $1.6 \text{ mF cm}^{-2}$ ) (Fig. 3b and S21†), indicating the high exposure and accessibility of the active sites in 3DOP  $\text{Cu}_2\text{O}$ -CO. The sequence of the ECSA value was in agreement with that of the Brunauer–Emmett–Teller (BET) surface area calculated from  $\text{N}_2$  sorption isotherms (Fig. S22†), in which 3DOP  $\text{Cu}_2\text{O}$ -CO possessed a higher surface area of  $66.0 \text{ m}^2 \text{ g}^{-1}$  in comparison to  $\text{Cu}_2\text{O}$ -CO ( $5.0 \text{ m}^2 \text{ g}^{-1}$ ). More importantly, the capacity of 3DOP  $\text{Cu}_2\text{O}$ -CO to adsorb  $\text{CO}_2$  molecules ( $4.96 \text{ m}^3 \text{ g}^{-1}$ ) was much larger than that of  $\text{Cu}_2\text{O}$ -CO ( $2.79 \text{ m}^3 \text{ g}^{-1}$ ), suggesting the promising

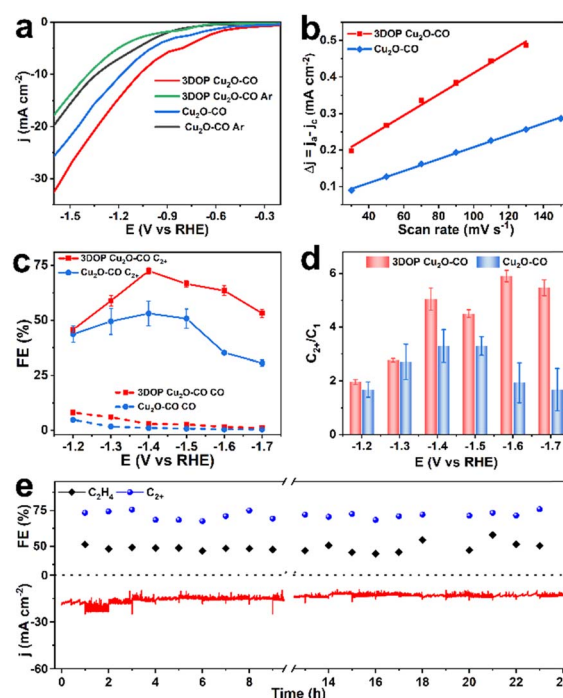


Fig. 3 Electrochemical  $\text{CO}_2\text{RR}$  performance measured in an H-type cell. (a) Current–voltage curves obtained in 0.1 M  $\text{KHCO}_3$  electrolyte saturated with  $\text{CO}_2$  or Ar. (b) Half of the capacitive current density at 0.28–0.4 V vs. RHE as a function of the scan rate for 3DOP  $\text{Cu}_2\text{O}$ -CO and  $\text{Cu}_2\text{O}$ -CO. (c)  $\text{C}_2\text{H}_4$  and  $\text{C}_2^+$  FEs and (d)  $\text{C}_2^+$ -to- $\text{C}_1$  product selectivity at different applied potentials for different catalysts. (e) Stability test over a span of 24 h for  $\text{CO}_2\text{RR}$  catalyzed by 3DOP  $\text{Cu}_2\text{O}$ -CO in 0.1 M  $\text{KHCO}_3$  at  $-1.4 \text{ V}$  vs. RHE.

advantages of using 3DOP Cu<sub>2</sub>O–CO for CO<sub>2</sub> electrolysis (Fig. S23†).

The gaseous and liquid products derived from electrocatalyzing CO<sub>2</sub>RR at different potentials were quantitatively analyzed by online gas chromatography and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopy, respectively. Based on the number of carbon atoms in the products, there were three categories of products: C<sub>2+</sub> products (C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH, and *n*-C<sub>3</sub>H<sub>7</sub>OH), C<sub>1</sub> products (CO, CH<sub>4</sub>, and HCOOH), and H<sub>2</sub> (Fig. S24†). 3DOP Cu<sub>2</sub>O–CO showed superior selectivity for C<sub>2+</sub> products in comparison to that of the nonporous Cu<sub>2</sub>O–CO sample (Fig. 3c, S24, and Table S2†). 3DOP Cu<sub>2</sub>O–CO provided a maximum C<sub>2+</sub> FE of 73.4% at −1.4 V *versus* a reversible hydrogen electrode (*vs.* RHE), exceeding that of Cu<sub>2</sub>O–CO (56.2%) (Fig. 3c and Table S2†). The 3DOP Cu<sub>2</sub>O sample promoted the conversion of CO<sub>2</sub> to C<sub>2+</sub> products other than the C<sub>1</sub> products, with relatively high C<sub>2+</sub>-to-C<sub>1</sub> ratios at all the examined potentials, suggesting that the ordered porous structures evoke additional C–C coupling during the CO<sub>2</sub>RR (Fig. 3d).

Even when compared with the reported results, the 3DOP Cu<sub>2</sub>O–CO provided top-level FE for the valuable C<sub>2+</sub> products (Table S3†). To assess the catalytic stability and selectivity of the catalysts, the electrochemical CO<sub>2</sub>RR was carried out under steady-state conditions at −1.4 V *vs.* RHE. It is worth noting that 3DOP Cu<sub>2</sub>O–CO possessed robust long-term stability in current response and product selectivity for C<sub>2</sub>H<sub>4</sub> and C<sub>2+</sub> during a 24 hour CO<sub>2</sub>RR electrolysis test (Fig. 3e). Structural degradation and composition regression are the two key factors that decrease the catalytic activity in the CO<sub>2</sub>RR catalyzed by Cu<sub>2</sub>O.<sup>43,44</sup> By imparting porosity to Cu<sub>2</sub>O crystals to generate interconnected ordered porous structures, superior structural integrity prevented the 3DOP Cu<sub>2</sub>O–CO from undergoing such degradation (Fig. S25 and S26†). All the above results demonstrate that the as-prepared 3DOP Cu<sub>2</sub>O–CO promotes the conversion of CO<sub>2</sub> into C<sub>2+</sub> products with a high catalytic durability.

## Mechanism investigation

To explore the origins of the superior C<sub>2+</sub> selectivity of 3DOP Cu<sub>2</sub>O–CO, finite-element method (FEM) simulations were implemented to track the key reaction species of CO<sub>2</sub>RR in the confined space of 3DOP architectures. In the simulations, CO<sub>2</sub> molecules diffused into the nanopores of the 3DOP architecture, where the CO<sub>2</sub> molecules were adsorbed onto the pore walls and reduced to C<sub>1</sub> intermediates (Fig. 4a and S27†). The local concentration of C<sub>1</sub> intermediates will accumulate and then dimerize to C<sub>2</sub> species by increasing likelihood of C–C coupling (Fig. 4b). All the results validate the concentration of C<sub>1</sub> species by nanopores *via* the steric confinement effect, and significantly enhanced accumulation was achieved in the internal pores of the 3DOP architecture, indicating the coherent effect of the ordered porous structure in confining C<sub>1</sub> intermediates for C–C coupling reactions. However, in the case of nonporous Cu<sub>2</sub>O–CO, the CO<sub>2</sub> molecules can only be adsorbed on the external surfaces, and the formed C<sub>1</sub> intermediates are

easily released as C<sub>1</sub> products (CO, CH<sub>4</sub>, and HCOOH) (Fig. S28†).

To provide mechanistic insights into the enhanced C<sub>2+</sub> production, we performed *in situ* attenuated total reflectance-surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) under CO<sub>2</sub>RR conditions to identify the key intermediates and their evolution as the applied potentials were varied. As displayed in the ATR-SEIRAS spectra of 3DOP Cu<sub>2</sub>O–CO, the vibrational band centered at approximately 2100 cm<sup>−1</sup>, which corresponds to the atop configuration of \*CO adsorption, appeared at 0.2 V *vs.* RHE and gradually increased to the maximum at −0.2 V *vs.* RHE (Fig. 4c). As the applied potential bias increased further, the peaks assigned to \*CO adsorption disappeared, and new peaks ascribed to \*CHO (1490 cm<sup>−1</sup>), \*OCCOH (1593 cm<sup>−1</sup>), and \*OCCO (1548 cm<sup>−1</sup>),<sup>45</sup> which are the key reaction intermediates for forming C<sub>2</sub> products, appeared in the ATR-SEIRAS spectra (Fig. 4c).

The \*CO is widely used to evaluate the \*CO coverage on a catalyst,<sup>9,46</sup> and, therefore, it can be concluded that the \*CO first accumulates on 3DOP Cu<sub>2</sub>O–CO, and then is consumed by the C–C coupling reaction to form multi-carbon products. As two-factor authentication, the peaks corresponding to the Cu–CO stretching (369 cm<sup>−1</sup>) and C≡O stretching (2090 cm<sup>−1</sup>) of adsorbed \*CO were also observed in the *in situ* Raman spectra for 3DOP Cu<sub>2</sub>O–CO (Fig. 4d).<sup>47</sup> In great contrast to 3DOP Cu<sub>2</sub>O–CO, no obvious adsorption peaks related to the above-mentioned intermediates were detected for the nonporous Cu<sub>2</sub>O–CO sample (Fig. 4e and S29†). All the above results supply evidence that the 3DOP nanoarchitectures can entrap CO intermediates to form an adequate amount of \*CO ready for C–C coupling, thus evoking the formation of C<sub>2+</sub> products.

It was demonstrated that the product selectivity of the electrochemical CO<sub>2</sub>RR was pH sensitive. A great pH gradient always occurs at the electrode surfaces with large roughness factors,<sup>48</sup> and, therefore, monitoring the local pH near the electrode surface is critical to elucidating the correlation between the local pH environment and the catalytic activity and selectivity. In the CO<sub>2</sub>/bicarbonate system, the *in situ* Raman measurement, which displays the adsorbed HCO<sub>3</sub><sup>−</sup> (1015 cm<sup>−1</sup>) and CO<sub>3</sub><sup>2−</sup> (1078 cm<sup>−1</sup>) signals, is an effective method for providing the local pH values.<sup>45,49</sup> The local pH value of 3DOP Cu<sub>2</sub>O–CO increased from 10.8 to 11.2 when the potential bias changed from 0 to −0.5 V *vs.* RHE, whereas the pH value remained lower than 10.8 for Cu<sub>2</sub>O–CO (Fig. 4f and Table S4†), suggesting the steric confinement of the OH<sup>−</sup> of the ordered porous structures. The high local alkalinity triggered by the 3DOP nanoarchitecture not only suppresses the competing reaction of the hydrogen evolution reaction (HER), but also greatly benefits the C–C coupling reaction of \*CO in the formation of C<sub>2+</sub> products.<sup>48</sup>

The chemical states of Cu<sub>2</sub>O during the electrocatalysis of CO<sub>2</sub> were investigated using X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The deconvolution of the Cu 2p spectra and the related analysis of the component fitting for different samples (Fig. S30 and Table S5†) were carried out according to previous studies.<sup>50</sup> The Cu 2p and Auger Cu LMM XPS spectra revealed that the surface



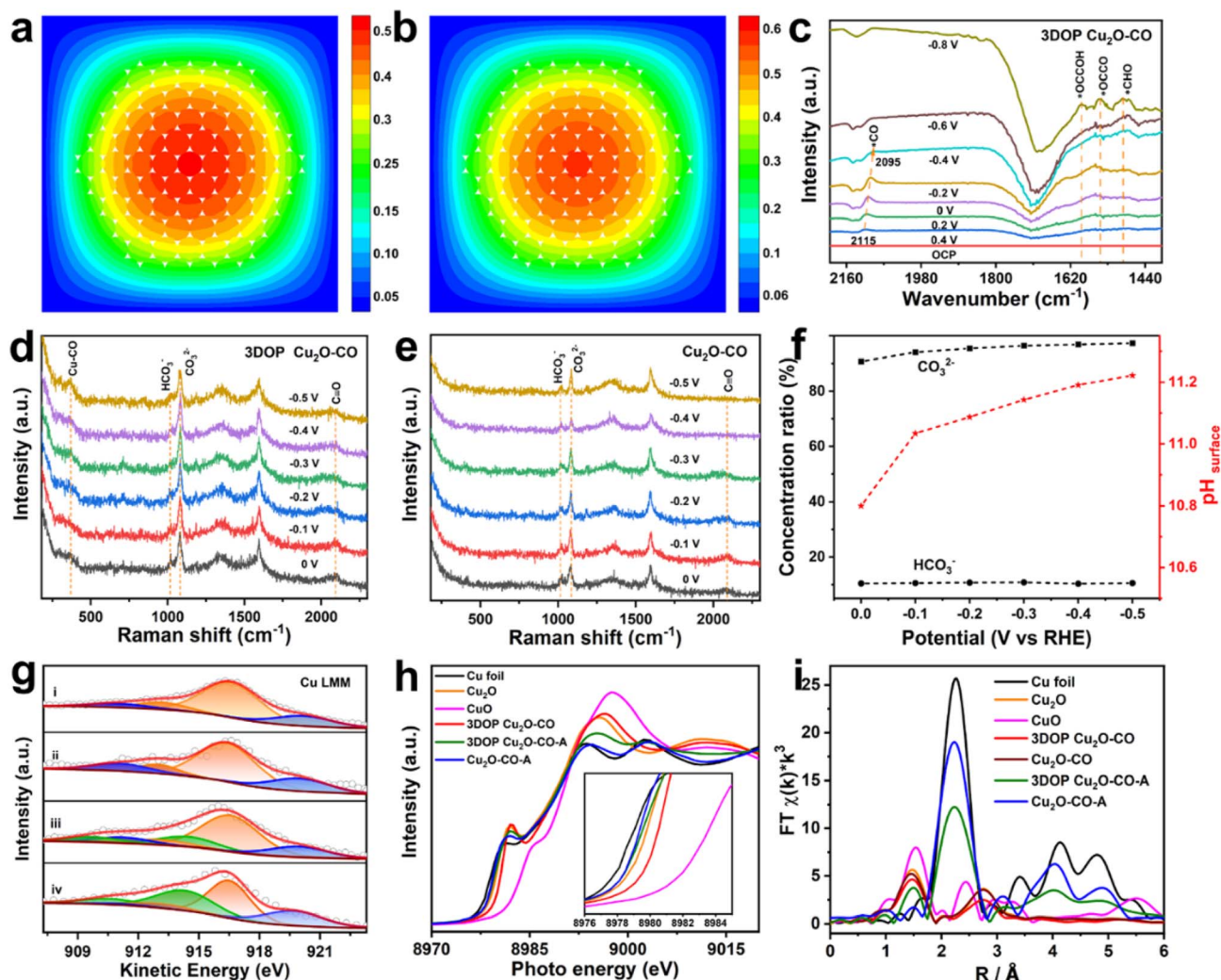


Fig. 4 FEM simulations and *in situ* spectroscopy characterizations. The FEM simulated distributions of (a)  $C_1$  and (b)  $C_2$  over 3DOP  $\text{Cu}_2\text{O-CO}$ . (c) *In situ* ATR-SEIRAS spectra of 3DOP  $\text{Cu}_2\text{O-CO}$  in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  aqueous solution. *In situ* Raman spectra of (d) 3DOP  $\text{Cu}_2\text{O-CO}$  and (e)  $\text{Cu}_2\text{O-CO}$  in  $\text{CO}_2$ -saturated 0.1 M  $\text{KHCO}_3$  aqueous solution. (f) Ratios of  $[\text{HCO}_3^-]/[\text{C}_{\text{total}}]$  and  $[\text{CO}_3^{2-}]/[\text{C}_{\text{total}}]$  and corresponding calculated  $\text{pH}_{\text{surface}}$ . (g) Cu LMM, (h) Cu K-edge XANES and (i) Fourier transform (FT) Cu K-edge EXAFS data for the indicated samples. The compositions of the fitted plots in panel (g) are  $\text{Cu}_2\text{O}$  (orange plot),  $\text{CuO}$  (blue plot and satellite peak), and  $\text{Cu}$  (green plot). Representative example of catalyst XANES data fitting with a linear combination of reference spectra. 3DOP  $\text{Cu}_2\text{O-CO-A}$  and  $\text{Cu}_2\text{O-CO-A}$  represent the corresponding samples after electrolyzing  $\text{CO}_2$  for 5 h.

compositions of both samples transformed from  $\text{Cu}_2\text{O}$  to a  $\text{Cu}_2\text{O}$  and  $\text{Cu}$  mixture, indicating that  $\text{Cu}_2\text{O}$  is partially reduced to  $\text{Cu}$  after electrolyzing  $\text{CO}_2$  (Fig. 4g, S30, and Table S6†).<sup>51</sup> The existence of  $\text{CuO}$  for all the samples may be associated with the exposure of the samples to air before injection into the vacuum chamber of the XPS apparatus.

The pre-edge features of Cu K-edge X-ray absorption near-edge spectra (XANES) further verified the composition regression of both  $\text{Cu}_2\text{O}$  samples during electrolysis of  $\text{CO}_2$  by showing a less intense profile shifting to a lower energy for the spectrum of a metallic Cu foil (Fig. 4h). The Cu local structure was probed by extended X-ray absorption fine structure spectroscopy (EXAFS), and showed the typical Cu-Cu bond (2.3 Å) for Cu foil, and Cu-Cu (2.8 Å) and Cu-O (1.5 Å) bonds for the  $\text{Cu}_2\text{O}$  reference sample (Fig. 4h). Transformation of the  $\text{Cu}_2\text{O}$ -related peaks to the Cu-Cu bond in Cu foil was clearly

recognized for both samples after electrocatalysis of the  $\text{CO}_2\text{RR}$ , and additional Cu-O bonds were retained in the 3DOP  $\text{Cu}_2\text{O-CO}$  sample, suggesting that less conversion occurs in 3DOP  $\text{Cu}_2\text{O-CO}$  (Fig. 4i).

To quantitatively analyze the coordination number (CN) of the Cu-O and Cu-Cu bonds in each sample, an EXAFS curve-fitting analysis was carried out for the samples before and after electrolysis of  $\text{CO}_2$ . The smaller CN value for the 3DOP  $\text{Cu}_2\text{O-CO}$  sample suggests a larger number of unsaturated sites (Fig. S31 and Table S7†), which was in agreement with the abundant atomic defects recognized on the concave surface of 3DOP  $\text{Cu}_2\text{O-CO}$  and the grain boundaries in the  $\text{Cu}_2\text{O}$  skeletons (Fig. 1c and S12†). Such unsaturated atomic sites have been proven to be favorable for the adsorption of reaction intermediates.<sup>8,52</sup> The abundant adsorption of  $^*\text{CO}$ ,  $^*\text{OCCOH}$ , and  $^*\text{OCCO}$  intermediates is capable of preventing the reduction of





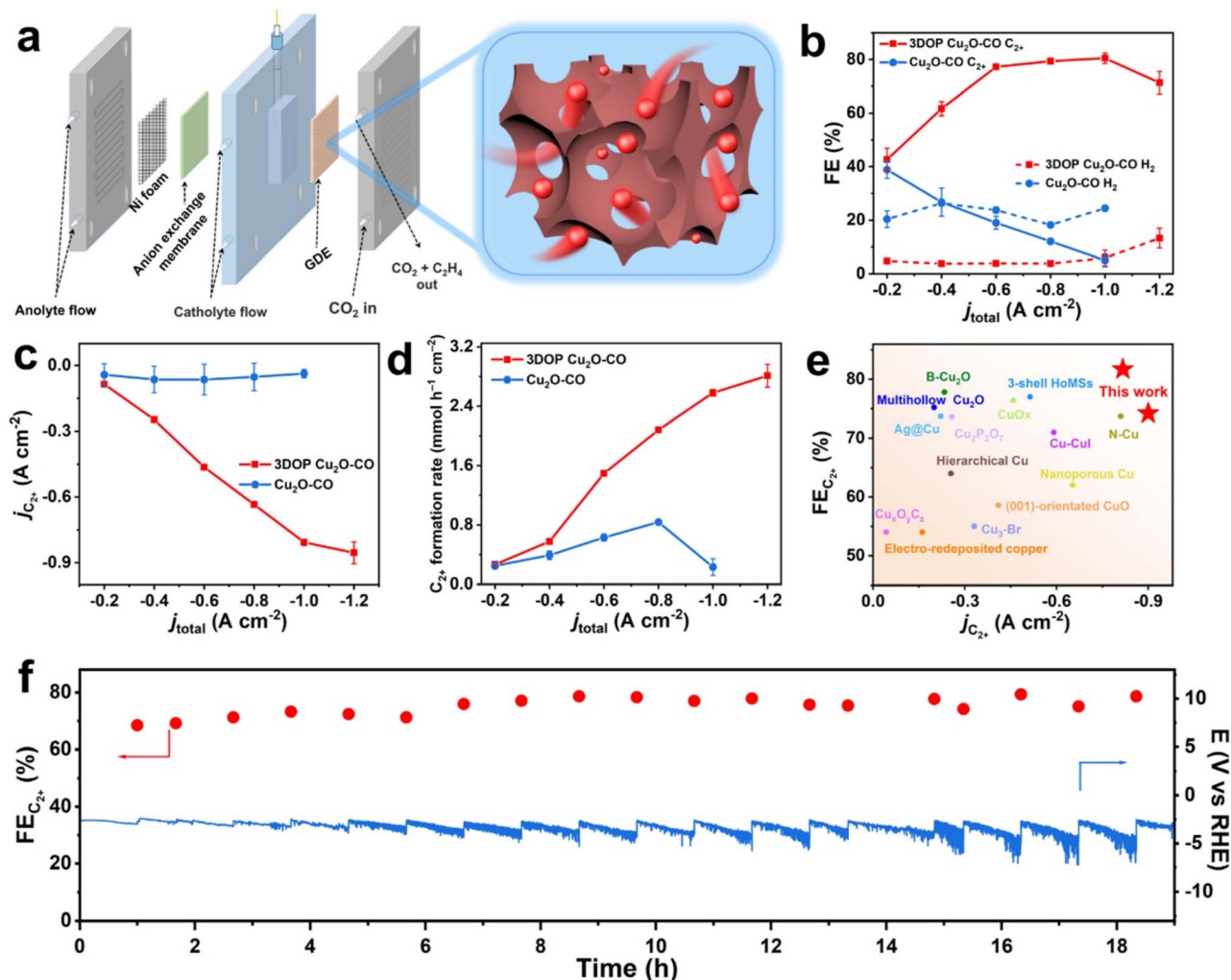


Fig. 5 Electrochemical CO<sub>2</sub>RR performance measured in a flow cell reactor. (a) Components of the flow cell reactor and the diffusion of 3DOP Cu<sub>2</sub>O–CO. (b) FEs for C<sub>2+</sub> and H<sub>2</sub> products over 3DOP Cu<sub>2</sub>O–CO and Cu<sub>2</sub>O–CO samples. (c) C<sub>2+</sub> partial current densities and (d) C<sub>2+</sub> formation rate under different applied current densities over 3DOP Cu<sub>2</sub>O–CO and Cu<sub>2</sub>O–CO samples. (e) Comparison of FEs and partial current densities for C<sub>2+</sub> products over 3DOP Cu<sub>2</sub>O–CO with the reported state-of-the-art electrocatalysts. (f) Long-term stability of 3DOP Cu<sub>2</sub>O–CO at a current density of  $-0.6 \text{ A cm}^{-2}$ . All measurements were performed in a flow cell reactor using 1.0 M KOH as the electrolyte.

Cu<sub>2</sub>O during electrocatalysis of the CO<sub>2</sub>RR and results in a stable catalytic performance with little decay in product selectivity.<sup>4,43</sup>

### Electrochemical CO<sub>2</sub>RR performance for practical applications

High C<sub>2+</sub> selectivity at industrial current density is critical to realize the potential utilization of valuable products, and remains challenging. Targeted to CO<sub>2</sub>-to-C<sub>2+</sub> conversion at ampere-level current density, the electrochemical CO<sub>2</sub>RR of the 3DOP Cu<sub>2</sub>O–CO was then performed in a flow cell reactor, which enabled gaseous CO<sub>2</sub> to diffuse to the catalyst layer directly from the gas-diffusion layer.<sup>53–55</sup> Catalyst ink consisting of 3DOP Cu<sub>2</sub>O–CO or Cu<sub>2</sub>O–CO was directly spray-coated on hydrophobic carbon paper to form a gas-diffusion electrode (GDE), which was then constructed as the cathode in the flow cell reactor (Fig. 5a).

The flow cell measurement revealed that 3DOP Cu<sub>2</sub>O–CO exhibited high C<sub>2+</sub> selectivity and largely depressed H<sub>2</sub> and CO production under the entire range of applied current densities (Fig. 5b and S32†). At a current density of  $-1.0 \text{ A cm}^{-2}$ , the 3DOP Cu<sub>2</sub>O–CO sample achieved the highest FE of 81.7% for C<sub>2+</sub> products. However, the FE for C<sub>2+</sub> sharply decreased from 41.2% to 6.7% over nonporous Cu<sub>2</sub>O–CO when the applied current density decreased from  $-0.2$  to  $-1.0 \text{ A cm}^{-2}$  (Fig. 5b). More impressively, the partial current density of C<sub>2+</sub> products over 3DOP Cu<sub>2</sub>O–CO continued to increase, and reached  $-0.89 \text{ A cm}^{-2}$  at an applied current density of  $-1.2 \text{ A cm}^{-2}$ , outperforming that of Cu<sub>2</sub>O–CO (no higher than  $-0.12 \text{ A cm}^{-2}$ ) (Fig. 5c). Additionally, the C<sub>2+</sub> formation rate consistently increased to  $2.92 \text{ mmol h}^{-1} \text{cm}^{-2}$  under a current density of  $-1.2 \text{ A cm}^{-2}$  (Fig. 5d).

A careful comparison of the CO<sub>2</sub>-to-C<sub>2+</sub> electrochemical catalytic performance revealed that 3DOP Cu<sub>2</sub>O–CO exhibited



superiority in the FE and partial current density of  $C_{2+}$  products as compared to the state-of-the-art samples (Fig. 5e and Table S3†). The durability of 3DOP  $Cu_2O$ -CO in the electrochemical  $CO_2$ RR was measured at a current density of  $-0.6\text{ A cm}^{-2}$ . The FE for  $C_{2+}$  products remained higher than 68.5%, with no obvious decay for the recorded potential during a time period of 19 h (Fig. 5f). The 3DOP  $Cu_2O$ -CO catalyst exhibited high and stable  $CO_2$ -to- $C_{2+}$  conversion at ampere-level current density.

## Conclusions

Ordered porous  $Cu_2O$  was designed to selectively convert  $CO_2$  to value-added  $C_{2+}$  products by imparting spatial confinement engineering to an effective  $Cu_2O$  catalyst. A molecular fence-assisted hard templating strategy was used to successfully synthesize 3DOP  $Cu_2O$ -CO in a confined space for the first time. The resultant 3DOP  $Cu_2O$ -CO exhibited a three-dimensional interconnected porous structure obtained from the well-patterned templates. The integrity of the 3DOP construction not only prevented structural deformation, but also entrapped additional CO intermediates to form an adequate amount of  $^*CO$ , which was ready for C-C coupling to form  $C_{2+}$  products under  $CO_2$  electrolysis.

Therefore, the as-designed 3DOP  $Cu_2O$ -CO exhibited excellent performance for  $CO_2$  electrolysis, with FEs for  $C_{2+}$  up to 73.4% in the H-type reactor, 81.7% in the flow cell reactor, and satisfactory retention of product selectivity. Importantly, 3DOP  $Cu_2O$ -CO achieved  $CO_2$ -to- $C_{2+}$  conversion with a partial current density of  $-0.89\text{ A cm}^{-2}$  at a formation rate of  $2.92\text{ mmol h}^{-1}\text{ cm}^{-2}$  under an applied current density of  $-1.2\text{ A cm}^{-2}$ . This work introduces novel insights into the design of highly active and selective electrocatalysts for  $CO_2$ RR, with great promise for practical applications.

## Data availability

All relevant data are presented in the main text and ESI.†

## Author contributions

L. F. designed and performed the experiments and analyzed the data. Q. G. drew the scheme and assisted with the electrochemical measurements in the flow cell reactor. R. S. performed the TEM characterization. L. M., C. W. and J. L. carried out the product analysis of  $CO_2$  electrolysis. W. Z. performed synthetic experiments. W. L. created sliced samples using the FIB technique. X. F. and Y. Y. revised the manuscript. C. L. wrote the manuscript. C. L. and L. J. supervised the project.

## Conflicts of interest

There are no conflicts to declare.

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