Electroreduction of CO₂ into value-added products is an effective approach to remit the environmental and energy issues. In this study, a hierarchical, self-supported, and atomistic catalyst was successfully synthesized based on the solid-state diffusion strategy. This catalyst can be directly used as a binder-free electrode and exhibits superb catalytic CO₂ electroreduction performance. Directly synthesized by bulk metal foil, this catalyst is scalable to meet the industrial demand.
Solid-Diffusion Synthesis of Single-Atom Catalysts Directly from Bulk Metal for Efficient CO₂ Reduction

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SUMMARY
Electroreduction of CO₂ into value-added products is an effective approach to remit the environmental and energy issues. However, the development of an effective, accessible, and simple method for mass production of electrocatalyst is challenging. Herein, we demonstrate the solid-state diffusion between the N-doped carbon phase and bulk Ni metal can be utilized to synthesize hierarchical, self-supported, and atomistic catalyst. Strikingly, this hierarchical catalyst is programmable and scalable to meet the industrial demand and can be directly used as a binder-free electrode toward the CO₂ electroreduction, delivering a state-of-the-art current density of 48.66 mA cm⁻² at −1.0 V versus reversible hydrogen electrode (RHE) and high faradic efficiency of 97% to CO. The selectivity can be retained over 90% in a wide range of working potential of −0.7 to −1.2 V versus RHE. This solid-state diffusion strategy presents great potential to produce hierarchical and atomistic catalysts at industrial levels.

INTRODUCTION
In the aim of achieving the desired chemical and physical properties, solid-state diffusion has been widely used to engineer microstructures of functional intermetallics and alloys such as composition, crystal phase, and grain boundary for more than half a century.1–3 Notable examples have been reported in a diverse range of areas including catalytic performance,4,5 ferromagnetism,6 conductivity,7 shape-memory effects, and so on.8 The directional material and interface flows are affected by differential solid-state diffusion rates of the diffusion couple at high temperature, i.e., copper and zinc in brass.9 For the solid-state materials such as heterogeneous catalysts, the microstructures which determine their size- and shape-dependent properties in advanced applications are very sensitive to the synthetic conditions.10,11 Moreover, the ability to manipulate the structure of solid materials at nano even atomic levels would greatly modulate the local chemical environment and enhance the corresponding properties.12,13 However, this old method is not generally considered as an effective method of preparing solid materials with sophisticated atomistic structures due to poor control over the drastic reaction at high temperature.

The excessive emission of greenhouse gas CO₂ through massive fossil fuel consumption results in serious environmental issues.14 There is an urgent need to convert CO₂ into chemical fuels to mitigate atmospheric CO₂ level and alleviate the energy crisis.15,16 An ideal catalyst for CO₂ electroreduction should comprise...
sufficient accessible surface, highly reactive sites, and reliable steadiness to meet industrial demand, including high working overpotential, high current density to target products, and easy development to large production. Moreover, to reach industrial-scale electrodes, most of the previously reported catalysts for CO₂ electroreduction have to be fixed on a conductive substrate with the help of insulating polymer binders, such as Nafion or PVDF, which largely increases the synthetic complexity and cost. To satisfy the industrial requirements mentioned above, developing a scalable approach that can transform the inexpensive raw materials such as bulk metal into efficient and stable catalysts is highly needed.

RESULTS AND DISCUSSION
Synthesis and Characterization

Herein, we describe an effective approach to construct a hierarchical and atomistic catalyst by the solid-state diffusion between the bulk Ni and N-doped carbon (N-C) layer. Especially, this carbon paper is self-supported and can be directly used as a binder-free electrode for CO₂ reduction. In line with other reported rough surfaces in MoS₂, Ni₂Co₆@Ni₂Co₄Oₓ, and Cu films, the as-prepared carbon paper possesses a large surface with both superhydrophilic and superaerophobic properties, which is a benefit for the contact of dissolved CO₂ and the desorption of generated CO. In addition, the abundant single-Ni sites distributing on the catalyst’s surface also play a dominant impact on the activation of CO₂.

A mechanism illustrating the programmable formation process of the catalyst is summarized in Figure 1A. Firstly, the melamine was deposited onto the Ni foil surface by spray painting equipment to form a thin film. By precisely controlling the heating rate from room temperature to 1,000 °C, the melamine film was gradually converted to a C₃N₄ structure, covering over the Ni foil. The C₃N₄ can be converted to N-C at high temperature catalyzed by Ni source. Driven by a strong Lewis acid-base interaction between Ni-N coordination, the abundant unsaturated carbon vacancies formed at high temperature allowed the surface Ni atoms to diffuse into the covered N-C soil and occupy the carbon vacancies. Meanwhile, this directional material flow of Ni from Ni foil into the N-C layer was balanced by an opposite flow of C into the Ni foil. The Ni NPs acted as seeds to germinate nitrogen-doped carbon nanotubes (N-CNT) by a vapor-liquid-solid mechanism, when the C was supersaturated in the metal particles, C precipitation at the rear of the metal droplet occurred and the droplet was located on the top of growing nanotube. The C₃N₄ would vaporize at a continuous high temperature to give C and N sources for the growth of carbon tubes. Catalyzed by the Ni “seeds” derived from the bulk Ni, N-CNTs were cultivated on the surface of N-C layer to obtain a hierarchical structure (Figures 1B, 1C, and S1), in which the as-grown one-dimensional nanotube are perpendicular to the two-dimensional N-C layer. The cross-sectional scanning electron microscope (SEM) images (Figure 1B) and the corresponding energy-dispersive X-ray spectroscopy (EDS) mapping images (Figure 1D) both confirm the hierarchical structure and the diffusion of Ni NPs into the N-C soil from the bulk Ni foil. These flexible and freestanding carbon papers can be easily peeled off from the Ni foil surface to form freshly prepared carbon papers (F-CPs). Finally, after an acid-leaching step to dissolve a majority of Ni seeds within the N-C soil, hierarchical carbon papers (H-CPs) with abundant N-CNT on both sides were obtained (Figures 1E and S2).

As revealed by Figure S3, the rigorous encapsulation within a few layer of graphene would result in some residual Ni crystals by cutting off the interaction between Ni and proton. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Figures 1F and 1G) of
Figure 1. Schematic Illustration and Characterization of H-CPs

(A) Scheme of the formation of H-CPs. 
(B and C) Cross-sectional (B) and top view (C) SEM images of H-CPs. 
(D) Corresponding EDS mapping images of cross-sectional SEM images of H-CPs. 
(E–G) TEM (E) and magnified HAADF-STEM (F and G) images of H-CPs. The Ni single atoms are marked with red circles. 
(H) Corresponding EDS mapping images of N-CNTs of H-CPs. 
(I) Different shapes of the carbon papers was programmable and controllable by selecting different shapes of Ni foil. More importantly, this approach is feasible for scale-up. 
(J) An example showing the flexibility of the H-CPs. 
(K) Stress-strain curves of H-CPs and F-CPs.
H-CPs show that the Ni atoms dominantly presented an atomic dispersion over the surface of nanotube, demonstrating their robust resistance to acid leaching.\textsuperscript{29–31} The isolated heavier Ni single atoms (SAs) could be discerned in the carbon support because of the different $Z$ contrasts among Ni, N, and C.\textsuperscript{32} The Ni and N were homogeneously dispersed on the N-CNTs, as demonstrated by EDS analysis (Figure 1 H). Importantly, the whole synthetic procedure is programmable so that the areas and shape of the H-CPs is strictly determined by the bulk Ni foil substrate (Figure 1 I). To fulfill the industrial production requirements, this flexible and self-supported H-CPs is easy to be massively manufactured according to the standard steps, and the Ni foil can be reused after removing the surface carbide by a simple polishing treatment, which is shown in Video S1. As shown in Figure 1 J and Video S1, the H-CP is as robust and flexible as the commercial carbon cloth, since it can retain the paper structure under bending stress to some extent. It also can tolerate more than 6 MPa tensile strength, as revealed by the stress-strain curves in Figure 1 K. Due to the excellent mechanical properties, the H-CPs can be directly assembled as an electrode for CO$_2$ electrochemical reduction, without the addition of binder and support.

As shown by X-ray powder diffraction (XRD) patterns in Figure 2 A, the F-CPs showed typical mixed crystal patterns including Ni nanoparticles (NPs) and graphene. After acid treatment, the peak intensity assigned to the crystalline Ni clearly decreased, in line with transmission electron microscopy (TEM) observations. To investigate the electronic structure of the catalysts, near-edge X-ray absorption fine structure (NEXAFS) measurements were performed. For the N K-edge spectrum (Figure 2 B), peak A (399.5 eV) and peak C (402.4 eV) can be assigned to pyridinic $\pi^*$ and...

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**Figure 2.** Characterizations of H-CPs

(A) XRD patterns of H-CPs and F-CPs.
(B and C) N K-edge (B) and C K-edge (C) NEXAFS spectra of H-CPs and F-CPs.
(D and E) Ni K-edge XANES spectra (D) and $k^3$-weighted $\chi(k)$ function of the EXAFS spectra (E).
(F) CV curves in 0.1 M KOH electrolyte at a scan rate of 5 mV s$^{-1}$.  

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graphitic π* transitions in H-CPs and F-CPs, respectively. Peak D (408.5 eV) suggests the formation of C—N—C or C—N α* bond. For the C K-edge spectrum (Figure 2C), peak A (285.6 eV) derived from C=C π* (ring) excitations, and peak D (293.2 eV) originated from C—C α* (ring) transitions. These results strongly support the idea that acid treatment does not damage the skeleton structure of the N-C support but instead dissolves most of the Ni crystals, which can also be confirmed by the unchanged I_D/I_G value at Raman spectra (Figure S4). More detailed structural information was obtained from X-ray absorption fine structure (XAFS). As shown in the X-ray absorption near-edge structure (XANES) spectra of H-CPs (Figure 2D), the intensity of the line located between those of the Ni foil and NiO clearly display the unique electronic structure of Ni^{3+} (0 < δ < 2). Compared with the F-CPs, the Fourier transform k^3-weighted χ(k) function of the EXAFS spectra for H-CPs indicated the dominating Ni—Ni bonding (at 2.15 Å) significantly decreased and a new Ni—N coordination at 1.42 Å appeared (Figure 2E). Combined with XRD and TEM findings, these results suggest that the majority of Ni NPs could be removed after a chemical etching process in diluted HCl, leaving a small amount of Ni NPs encapsulated within the multiwall carbon nanotube. Reinforced by the cyclic voltammetry (CV) curves measurements in N_2-saturated alkaline media (Figure 2F), the disappeared Ni reduction/oxidation redox peaks corroborate that the exposed Ni crystals were largely leached, mainly leaving the single coordinated Ni species. As shown by the Brunauer-Emmett-Teller measurements in Figure S7, the H-CPs inherited a higher surface area of 143.97 m^2 g^-1 than that of F-CPs (113.21 m^2 g^-1) because of the dissolution Ni NPs. This enhancement in specific surface area could result in an increased CO_2 adsorption capacity from 3.85 to 7.64 cm^3 g^-1 at 100 kPa, as verified by the CO_2 adsorption isotherms.

### Evaluation of Activity for Electrochemical Reduction of CO_2

The CO_2 electroreduction was performed in a two-compartment gas-tight cell, which was separated by a Nafion-115 proton exchange membrane to prevent the oxidation of as-generated products. The cathodic compartment was continuously purged with CO_2 (20 mL min^-1) and vented directly into the gas-sampling loop (0.5 mL) for the periodic quantification of the gas-phase products by gas chromatography (GC). Liquid products were analyzed by 1H NMR spectroscopy after electrochemical CO_2 reduction processes. The comparison of the CO_2 reduction activity for F-CPs and H-CPs is summarized in Figure 3. Linear sweep voltammetry measurements (Figure 3A) for F-CPs and H-CPs were conducted in N_2-saturated 0.5 M NaClO_4 solution and CO_2-saturated 0.5 M KHCO_3 solution to exclude the influence of HCO_3^- and CO_3^{2-}. The H-CPs showed a much higher activity in CO_2-saturated KHCO_3 solution with a low onset potential of ~0.32 V versus a reversible hydrogen electrode (RHE) (all potentials are with reference to the RHE). In addition, the specific CO current density catalyzed by H-CPs reached a high value of 60.11 mA cm^-2 at ~1.2 V, almost seven times higher than that for F-CPs (Figure S8). The H-CPs maintain excellent faradic efficiency (FE) in a wide range of working potentials from ~0.7 to ~1.2 V (the FE of CO is over 90.8%), which indicates that the competitive hydrogen evolution reaction (HER) is largely prohibited over the single Ni sites. The primary products catalyzed by the H-CPs and F-CPs are CO and H_2 (Figure S9), and no liquid product is detected by 1H NMR (Figure S10). As revealed by Figure 3C, the Tafel slope of H-CPs is 105 mV/decade, much smaller than that of F-CPs (136 mV/decade),
indicating more favorable kinetics for the formation of CO.\textsuperscript{35} Accounting for the reduction of CO\textsubscript{2} to CO, this catalytic behavior outperforms most of the previously reported catalysts to the best of our knowledge (Figure 3D; Table S1), especially at high current density. Nyquist plots reveals that H-CPs have a lower interfacial charge-transfer resistance (RCT) than F-CPs (Figure 3E), hence ensuring faster electron transfer from the electrodes to CO\textsubscript{2} and favorable formation of the CO\textsubscript{2}/C\textsubscript{0} radical anion intermediate. Strikingly, the H-CPs also exhibited a long-term stability over 40-hr operations at 1.0 V, without obvious decay in both FE and current density (Figure 3F). As revealed in Figure S11, a plot of log\textsuperscript[1]{j\textsubscript{CO}} versus log\textsuperscript[1]{[HCO\textsubscript{3}/C\textsubscript{0}]} shows a slope of 0.96, demonstrating that the HCO\textsubscript{3}/C\textsubscript{0} concentration greatly influences the efficiency of electrochemical CO\textsubscript{2} reduction. The HCO\textsubscript{3} may not only simply act as a pH buffer and proton donor in the reaction, but also increase the concentration of CO\textsubscript{2} near the electrode surface via rapid equilibrium with bicarbonate.\textsuperscript{36,37} Interestingly, the current density of Ni foil and Ni NPs/C was even lower in the CO\textsubscript{2}-saturated electrolyte than in the N\textsubscript{2}-saturated electrolyte (Figure S12). This confirmed that the surface of the Ni bulk may be poisoned by the generated CO to further restrict the HER.\textsuperscript{38} The CV measurements (Figure 2F) further confirmed that the Ni NPs in H-CPs was protected by the graphene shell and cannot directly contact with the solution.\textsuperscript{33} There is no evidence to demonstrate the Ni NPs be directly in contact with the electrolyte to be involved in the gas reduction reactions.\textsuperscript{21} It has documented that the SCN\textsuperscript{−} ion has a high affinity to nickel and thus can poison the isolated Ni single-atom sites.\textsuperscript{31} As shown in Figure S13, a significant depression of catalytic activity for H-CPs is observed, which could be attributed to

![Figure 3. Performance of CO\textsubscript{2} Electroreduction](image)

(A) Linear sweep voltammetry curves in N\textsubscript{2}-saturated (dotted line) 0.5 M KClO\textsubscript{4} or CO\textsubscript{2}-saturated (solid line) 0.5 M KHCO\textsubscript{3} electrolyte at a scan rate of 10 mV s\textsuperscript{-1}.
(B and C) FE of CO and (C) Tafel plot of the partial CO current density for H-CPs (red) and F-CPs (black) at different applied potentials.
(D) Specific current density of H-CPs compared with those of other state-of-the-art catalysts for CO\textsubscript{2} to CO reduction (highlighted in the high potential region).
(E) Nyquist plots for H-CPs and F-CPs.
(F) Stability test of H-CPs at a potential of −1.0 V versus RHE during 40 hr.
the blocking effect of SCN⁻ on single Ni sites. Hence, it is reasonable to attribute the dominant impact on the high activity and selectivity to the exposed isolated Ni sites. To further demonstrate that Ni SAs were active sites, Ni NPs encapsulated by the graphitic carbons (Ni NPs@GC) were prepared. The results show these Ni NPs encapsulated by the multilayered graphene (Figure S14) present nearly no activity toward CO formation (Figure S15). In addition, the CO₂ electroreduction activity of H-CPs was evaluated onto a gas diffusion layer electrode in a flow cell configuration (Figures S16 and S17) using 1.0 M KOH and CO₂-saturated 1.0 M KHCO₃ electrolyte (Figures S18–S20), where a CO partial current of 91.1 mA cm⁻² was obtained at 3.0 V cell voltage.

Computational Studies and Further Research
The vertically aligned structure of N-CNTs provided not only excellent conductivity but also large contact area for ion diffusion due to the superhydrophilic and superaerophobic surface. The superhydrophilic structure is benefited for mass transfer by electrolyte-wetting on the catalyst’s surface, and the superaerophobic surface can facilitate the removal of an as-formed gas product within the bubbles, especially at high reaction rates.¹⁸,²⁰ As shown in Figure 4A, the water contact angle (CA) of H-CPs was nearly 0°, showing the outstanding wetting property of the surface constituting vertically aligned carbon nanotubes. The rough nanostructured surface could significantly reduce the adhesion force between electrode surface and gas bubbles. Meanwhile, the CA of the gas bubble on this surface in aqueous solution was...
measured to be 148.3° ± 2.6°, implying the excellent superaerophobic property. As shown in Video S1, the generated bubbles quickly disappear before they grew larger without stirring, which is conductive to the real industrial operation. To better evaluate the impact of superhydrophilic and superaerophobic surface on the catalytic performance, we directly load the N-doped carbon decorated by Ni SAs on commercial carbon fiber papers (Ni SAs/CFPs) as a control sample. Without the vertically aligned array structure (Figure S21), the water and gas CA of Ni SAs/CFPs are 142.0° ± 2.1° and 116.1° ± 3.8°, respectively, which is detrimental to the desorption of the gas product. In spite of the same catalyst loading, the current density delivered by Ni-N-C/CFPs is significantly inferior to that of H-CPs under the same potential (Figure S22).

The differences in activity between Ni in single-atom and non-single-atom states toward CO₂RR were further understood using spin-polarized density functional theory (DFT) calculations. Here, the activity center of Ni SAs was modeled as various Niₙₙ moieties (x = 1–4) embedded in a graphene nanosheet while the Ni NPs were represented by a Ni₃₀₉ cluster (see computational details and Figure 4E). We first studied the O* formation and OH* removal on the Ni systems, since these intermediates (occupation of active sites) are required to be cleared before CO₂RR. Compared with the Ni₃₀₉ cluster that is prone to oxidation with an O* formation free energy (∆G₀*) of −0.16 eV, the Ni sites of NiN₄, NiN₃, NiN₂, and NiN are more oxidation resistant (∆G₀* = 4.35, 1.90, 1.80, and 0.62 eV, respectively). Besides, in sharp contrast to Ni₃₀₉ cluster which requires a potential of −0.31 V to remove the adsorbed OH, the four Ni SAs do not need an additional potential to remove OH* because these processes are considerably exothermic (∆G: −1.66 eV for NiN₄, −1.35 eV for NiN₃, −1.47 eV for NiN₂, and −1.19 eV for NiN).

The adsorption free-energies of CO₂RR intermediates (Table S2) and the reaction free-energies (∆G) of elementary steps for all studied systems were then calculated employing the computational hydrogen electrode model. The corresponding free energy profiles of all five systems are summarized in Figure 4F, and the proposed reaction paths of CO₂RR on NiN₄ are also displayed. According to our calculations, the reduction of CO₂ to COOH* on the surfaces of all five systems are uphill in the free energy profiles, revealing that the first electronic step (CO₂ activation) is the potential-limiting step for both Ni SAs and Ni NPs. Especially, the Ni₃₀₉ cluster has the most favorable ∆G (0.1 eV) for this step, followed by NiN (0.59 eV), NiN₂ (1.10 eV), NiN₃ (1.11 eV), and NiN₄ (1.64 eV). The formed COOH* species can be easily reduced to a CO* species for both NiN₄ and Ni₃₀₉ clusters with the help of a proton coupled with an electron transfer. For four kinds of NiNₙ, the steps of CO* desorption all have a negative ∆G, indicating that the formed CO* species can be effectively removed from the surface of the catalyst to complete the reduction. In sharp contrast, the CO* desorption from the Ni₃₀₉ cluster is rather difficult (∆G = 1.13 eV) due to the rather strong binding strength of CO*, which is rather unfavorable for an efficient catalyst. Therefore, our calculations revealed that Ni NPs would show a much poorer catalytic performance than Ni SAs toward CO₂ reduction to CO. Considering that several Ni atoms of H-CPs may feature dimer or trimer states, we then studied the CO₂ reduction over the Ni dimer and trimer sites, and five types of activity center are accordingly constructed (Figure S23). After exploring the free energy changes along the reaction path, it is found that, although Ni dimer and trimer can well fulfill the conversion of CO₂ to COOH*, their subsequent CO desorption steps generally are energetically unfavorable. Hence, the Ni dimer and trimer should not contribute to CO formation.
The HCOO* pathway on the NiN₄ was further simulated. As shown in Figure S24, NiN₄, NiN₂, and NiN prefer the COOH* pathway, whereas NiN₃ is slightly prone to HCOO* formation. Another pathway, direct dissociation of CO₂, was not explored in this work because it is generally difficult under the mild electrochemical environment, and there is no available active site near the single-atom Ni to accommodate the dissociated CO* or O*. We also performed DFT calculations to access the HER activity of NiN₄ via calculating their adsorption free energy of *H species (ΔGₙ₇°). According to our calculations, NiN₄ has an impressive positive ΔGₙ₇° of 1.52 eV, whereas the chemical adsorption of H* is not stable on the single-atom Ni sites of the rest of NiNx. Therefore, competitive H₂ production would be significantly suppressed over all four single-atom Ni sites, which confirms the experimentally observed preferential CO₂RR over HER (Figure 3). Moreover, we find that the ΔGₙ₇° of the Ni₃09 cluster is −0.37 eV, implying that Ni would be more prone to H₂ formation if it is not in the single-atom state (Figure S15).

The generality of this method was validated by construction of a cobalt single-atom catalyst supported on H-CPs under identical conditions. Similar H-CPs, with carbon nanotubes perpendicular to the N-C layer, were manifested by cross-section SEM (Figure S25) and EDS mapping (Figures S26 and S27). The aberration-corrected HAADF-STEM (Figure S28) and EXAFS spectra (Figure S29) both demonstrated the atomically dispersed cobalt atoms stabilized on H-CPs.

In summary, we prepared a self-supported, flexible, and programmable H-CPs catalyst containing abundant single Ni sites by a solid-state diffusion between the loose N-doped carbon phase and a compact bulk Ni metal. This catalyst can be directly used in CO₂ electroreduction without the use of conductive substrate and insulating polymer binders. The FE of CO maintained over 90% in a wide range of working potentials (−0.7 to −1.2 V). Together, this approach shed light to the construction of efficient and stable catalyst directly from the non-precious bulk materials and show great promise for industrial-scale production.

**EXPERIMENTAL PROCEDURES**

**Synthesis of F-CPs**

In a typical procedure, 2.0 g melamine was mixed with 4 mL deionized (DI) water under ultrasonic dispersing to get a homogeneous ink. A total of 200 mg cm⁻² melamine was evenly sprayed on a Ni foil substrate using an air brush. After being dried in a vacuum chamber, the sample was placed in a porcelain boat (as shown in Video S1) and placed in a tube furnace and heated at 1,000 °C for 2 hr (heating rate 10°C/min) in a stream of Ar (10 mL/min). After the temperature was naturally cooled down to room temperature, the black carbon paper peeled off automatically from the Ni foil surface. The shape of the carbon paper can be controlled by the shape of the Ni foil, which can be reused for several times after polishing.

**Synthesis of H-CPs**

The as-prepared F-CPs was treated in 3.0 mol/L HCl solution for 4 hr, then sample rinsed with 0.5 M KHCO₃ solution and DI water three times to remove residual HCl. Finally, the sample was dried and can be directly used for further tests.

All other experimental and setup details, as well the DFT calculations, are provided in the Supplemental Experimental Procedures.
SUPPLEMENTAL INFORMATION
Supplemental Information includes Supplemental Experimental Procedures, 30 figures, 2 tables, and 1 video and can be found with this article online at https://doi.org/10.1016/j.joule.2018.11.008.

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AUTHOR CONTRIBUTIONS
Y. Wu. conceived the idea and co-wrote the paper. C.Z. and Y. Wang. contributed equally to this work. C.Z. and F.Z. carried out the sample synthesis, characterization, and CO2 electroreduction measurement. Y. Wang. and Y.L. carried out the theoretical calculations. Z.L., Y.Q., J.Y., Z.Y., X.W., H.D., and Y.L. helped with the modification of the paper. Q.X. performed the NEXAFS experiments. D.X. and J.L. performed the SEM experiments. W.C. helped with the XAFS measurements and discussion. Q.Z. helped with the spherical aberration electron microscopy tests. All authors participated in the discussion of the results, commented on the implications, and fully approved the content of the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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