Selective electroreduction of CO$_2$ to acetone by single copper atoms anchored on N-doped porous carbon

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Efficient electroreduction of CO$_2$ to multi-carbon products is a challenging reaction because of the high energy barriers for CO$_2$ activation and C-C coupling, which can be tuned by designing the metal centers and coordination environments of catalysts. Here, we design single atom copper encapsulated on N-doped porous carbon (Cu-SA/NPC) catalysts for reducing CO$_2$ to multi-carbon products. Acetone is identified as the major product with a Faradaic efficiency of 36.7% and a production rate of 336.1 $\mu$g h$^{-1}$. Density functional theory (DFT) calculations reveal that the coordination of Cu with four pyrrole-N atoms is the main active site and reduces the reaction free energies required for CO$_2$ activation and C-C coupling. The energetically favorable pathways for CH$_3$COCH$_3$ production from CO$_2$ reduction are proposed and the origin of selective acetone formation on Cu-SA/NPC is clarified. This work provides insight into the rational design of efficient electrocatalysts for reducing CO$_2$ to multi-carbon products.
Electrochemical reduction of CO$_2$ to value-added chemicals and fuels offers a promising approach for solving issues related to energy crisis and global warming\textsuperscript{1–3}. CO$_2$ can be converted to C$_1$, C$_2$, or C$_2^+$/C$_2^+$ products via different proton- and electron-transfer steps and different CO$_2$ reduction pathways. Converting CO$_2$ to multi-carbon (C$_2$ and C$_2^+$/C$_2^+$) products is more desirable due to their higher value and higher energy density\textsuperscript{6–9}.

Recently, numerous electrocatalysts have been designed for CO$_2$ reduction, such as metals, metal oxides, and carbon-based materials\textsuperscript{10–14}. Among these catalysts, copper (Cu) owns the ability to generate multi-carbon products from CO$_2$ reduction. This may be related to the optimal binding energy of CO intermediate on Cu, leading to the further reduction of CO intermediate and achieving the C–C coupling\textsuperscript{12,13–17}. Although Cu-based catalysts can reduce CO$_2$ to C$_2$ products, it still suffers from high barriers for CO$_2$ activation and C–C coupling, resulting in large overpotentials for C$_2$ product formation\textsuperscript{18–21}. Moreover, efficient reduction of CO$_2$ to C$_2$ or C$_2^+$ products, such as C$_3$ oxygenates, on Cu-based electrocatalysts are rarely reported.

Single atom catalysts (SAC) with atomically distributed active metal centers have been demonstrated to possess enhanced activity and tunable selectivity toward CO$_2$ reduction due to its maximum atom utilization efficiency, unique electronic structure, and unsaturated coordination environment of metal centers\textsuperscript{22–24}. As reported previously, partially oxidized single atom cobalt can electrochemically reduce CO$_2$ to HCOOH with a Faradaic efficiency of ~90%\textsuperscript{25}. Isolated Ni centers in N- and S-doped graphene exhibit high activity toward CO production with a TOF value of 14,800 h$^{-1}$ and a maximum Faradaic efficiency of 97% at −0.5 V\textsuperscript{26}. Single Fe(II) sites on N-doped carbon are active for reducing CO$_2$ to CH$_3$COOH\textsuperscript{27}. These results have clearly demonstrated the potential in using single atom materials as active and selective electrocatalysts for CO$_2$ reduction.

In this work, the atomically distributed Cu is anchored on N-doped porous carbon (Cu-SA/NPC) and is evaluated for CO$_2$ electrochemical reduction. The Cu-SA/NPC reduces CO$_2$ to acetic acid, ethanol, and acetone products at a low overpotential, with acetone being the major product. The effects of Cu distribution and local coordination environment of SAC on CO$_2$ reduction are investigated. The active sites of Cu-SA/NPC and mechanisms of CO$_2$ activation, C–C coupling, and CH$_3$COCH$_3$ formation from CO$_2$ reduction are elucidated by combined experimental and density functional theory (DFT) studies.

**Results**

**Characterization of Cu-SA/NPC.** The Cu-SA/NPC was synthesized by a continuous process including hydrothermal synthesis of Cu-doped ZIF-8 and subsequent carbonization of the precursor at 1000 °C under N$_2$ atmosphere. The elemental composition of obtained catalysts was characterized by XPS measurement. The NPC only showed the signal of C, N, and O elements (Supplementary Fig. 1), while the Cu-SA/NPC exhibited a small peak of Cu, indicating that Cu was successfully incorporated in the prepared material. The Cu content was determined to be about 0.59 wt% by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Supplementary Table 1). The XRD patterns of Cu-SA/NPC showed two broad diffraction peaks located at 23° and 44°, corresponding to the (002) and (101) plane of carbon, respectively (Supplementary Fig. 2). No Cu-related crystal phases were observed, which might be caused by the low loading amount of Cu species.

As shown in the scanning electron microscope (SEM) and transmission electron microscope (TEM) images, Cu-SA/NPC retained the rhombic dodecahedral morphology of the pristine ZIF precursor (Fig. 1 and Supplementary Fig. 3), while exhibiting...
Fig. 2 Structural characterization of Cu-SA/NPC. a Normalized XANES spectra at Cu K-edge of Cu-SA/NPC, Cu2O, cupric acetylacetonate (Cu(acac)2), copper meso-tetraphenylporphine (CuTPP), and Cu foil. b Fourier transforms (FT) magnitude of the experimental EXAFS spectra of Cu-SA/NPC, Cu (acac)2, CuTPP, and Cu foil. c EXAFS R space fitting curves of Cu-SA/NPC.

Electrochemical reduction of CO2 on Cu-SA/NPC. The CO2 reduction activity of Cu-SA/NPC was investigated by linear sweep voltammetry (LSV) measurements. The LSV tests were performed in a phosphate buffer (0.2 M, pH 6.8) saturated with CO2 or Ar. As shown in Fig. 3a, the current density in CO2-saturated solution was greater than that in Ar-saturated solution for both NPC and Cu-SA/NPC, demonstrating that NPC and Cu-SA/NPC were active for CO2 electrochemical reduction. The current density for CO2 reduction on Cu-SA/NPC was much higher than that on NPC. Moreover, the onset potential (CO2 reduction current density achieved 1.0 mA cm−2) for CO2 reduction on Cu-SA/NPC was −0.25 V, which was more positive than that on NPC (−0.62 V). These results suggested that the incorporation of single atom Cu into NPC material could significantly enhance its catalytic activity toward CO2 reduction.

The detected liquid products on Cu-SA/NPC were formic acid (HCOOH), acetic acid (CH3COOH), methanol (CH3OH), ethanol (C2H5OH), and acetone (CH3COCH3), while the gaseous products were H2 and CO. Fig. 3b showed the product distribution on Cu-SA/NPC, which was found to be dependent on the applied potential (its current−time curves were presented in Supplementary Fig. 5). It is worthy to note that oxygenate products were generated at a low potential of −0.16 V versus RHE, revealing that the overpotential for CH3OH, C2H5OH, and CH3COCH3 production on Cu-SA/NPC was about 180, 250, and 250 mV, respectively. Among these reduction products, the CH3COCH3 was the major reduced product of CO2 reduction on the Cu-SA/NPC catalyst at low potential. Moreover, the production rate of CH3COCH3 increased at potentials between −0.16 and −0.76 V, and then decreased with the applied potential further negatively shifted to −1.0 V, likely due to the competing reaction of H2 evolution. The maximum CH3COCH3 production rate reached 336.1 μg h−1 (−0.76 V), which was 4.3, 2.8, 16.9, and 12.8 times larger than that of HCOOH, CH3COOH, CH3OH, and CH2OH, respectively. No liquid products were detected during the electrolysis in Ar-saturated solution on Cu-SA/NPC catalysts, confirming that the oxygenates were generated from CO2 electrochemical reduction (Supplementary Fig. 7). As shown in Supplementary Fig. 8, no peak associated with acetone was detected from 1H NMR spectra after reducing HCOOH or CH3COOH in 0.1 M KHCO3 electrolyte, suggesting that the formed HCOOH and CH3COOH products could not be further reduced to acetone on Cu-SA/NPC. The isotope experiment using 13CO2 gas as carbon source was conducted and products were analyzed by GC-MS (Supplementary Fig. 9). The peaks at m/z = 59 and m/z = 60 were characteristic peak of 13C-labeled CH2COCH3, which confirmed that the gas 13CO2 was reduced on Cu-SA/NPC catalyst. The peak at m/z = 61 was not observed, which may be caused by the participation of HCO3− electrolyte in
CO2 reduction and it was evidenced by the isotope experiment using H13CO3− (Supplementary Fig. 10). As shown in Supplementary Fig. 11, the characteristic peaks of CH3OH (m/z = 31 and m/z = 32), and C2H5OH (m/z = 27, m/z = 28, and m/z = 29) were detected in 13CO2 and H13CO3. These results were consistent with those reported in the literature30,31. According to the previous studies, there should be a dynamic equilibrium between CO2 partial pressure and HCO3− concentration and the CO2 in equilibrium with HCO3− was the source for CO2 reduction reaction30,31.

Energy efficiency was a major consideration for converting CO2 into chemicals by the electrochemical method, and thus the Faradaic efficiency for CO2 reduction on Cu-SA/NPC was investigated. As shown in Fig. 3c, the Faradaic efficiency of CH3COCH3 generation was 15.6−36.7% at the applied potential range of −0.16 to −0.96 V, which was much higher than those of other oxygenate products at tested potentials. With the applied potential negatively shifted, the Faradaic efficiency of CH3COCH3 generation increased and reached to a maximum value of 36.7% at −0.36 V, which was 11.2 and 12.7 times as great as those for CH3OH and C2H5OH, respectively. Both the production rate and Faradaic efficiency of acetone generation on Cu-SA/NPC were significantly enhanced as compared with other electrocatalysts reported in the literature32,33 (Supplementary Table 3). The stability of the Cu-SA/NPC catalyst was measured by five sequential CO2 electroreduction experiments at −0.36 V (Fig. 3d). The Faradaic efficiency for CH3COCH3 generation remained at −36.7% for each cycle. Furthermore, the catalysts were characterized by SEM and HAADF-STEM (Supplementary Fig. 12) after five sequential CO2 reduction. The rhombic dodecahedral morphology of the post-reaction catalysts was intact. The HAADF-STEM results showed that Cu remained atomically distributed in porous carbon. These results indicated that the Cu-SA/NPC catalyst showed good stability in CO2 electrochemical reduction.

The reduced products for the electrochemical reduction of CO2 on NPC were measured for comparison. As shown in Supplementary Fig. 13, the products on NPC were detected to be HCOOH and CH3COOH at tested potentials. The trace amount of Zn impurity should have a negligible effect on acetone production from CO2 reduction on Cu-SA/NPC, as discussed in the Supplementary Note 1. Such comparison suggested that the production of CH3OH, CH3HCOH, and CH3COCH3 on Cu-SA/NPC was attributed to the presence of single atom Cu. The Cu-SA/NPC catalysts with different Cu content were prepared. The Cu-SA/NPC catalyst was synthesized with the Zn/Cu ratio of 10/1. The catalysts with Zn/Cu ratios of 20/1, 5/1, 10/3, and 5/3 were also synthesized and denoted as Cu-SA/NPC0.5, Cu-SA/NPC2, Cu-SA/NPC3, and Cu-SA/NPC6, respectively. As shown in Supplementary Fig. 14, the Cu-SA/NPC0.5, Cu-SA/NPC2, and Cu-SA/NPC3 retained the rhombic dodecahedral morphology of pristine ZIF-8, and the size of prepared catalysts increased with increasing Cu content. The pristine rhombic dodecahedral morphology was destroyed when further increased the Cu content to a Zn/Cu ratio of 5/3 (Cu-SA/NPC6). Therefore, the CO2 electroreduction was conducted on Cu-SA/NPC0.5, Cu-SA/NPC, Cu-SA/NPC2, and Cu-SA/NPC at −0.76 V (Supplementary Fig. 15), with a acetone production rate of 108.6, 336.1, 194.7, and 129.3 µg h−1, respectively. The Faradaic efficiency of acetone generation followed the same trend as Cu-SA/NPC > Cu-SA/NPC0.5 > Cu-SA/NPC2 > Cu-SA/NPC6. According to the XPS results, the Cu content of Cu-SA/NPC0.5, Cu-SA/NPC, Cu-SA/NPC2, and Cu-SA/NPC6 catalysts increased from 0.1 to 0.3% (Supplementary Table 4). However, the N content also increased slightly from 8.3 to 8.4% as the Zn/Cu ratio increased to 10/1, and the N content decreased to 6.4% with further increasing the Zn/Cu ratio to 10/3.
atmosphere and denoted as Cu-SA/NPCAr. According to the LSV conditions of MOFs, the Cu catalyst was prepared under Ar comparison (Fig. 4a, b). At the applied potential of \(0.76 \text{ V} \), the acetone production rate on Cu-SA/NPC was about 336.1 \(\mu\text{g h}^{-1}\), NPCAr showed a similar total N content, while the distribution of methods. Based on the XPS results, the Cu-SA/NPC and Cu-SA/NPCAr showed a similar total N content, while the distribution of N species was different (Supplementary Table 4). As shown in Supplementary Table 4, the NPC possessed the oxidized N content of 1.1%, similar to that of Cu-SA/NPC (1.2%). However, there was no acetone production from CO2 reduction on NPC without Cu (Supplementary Fig. 13), suggesting the oxidized N alone might not play an important role in acetone production. As shown in Supplementary Table 4, the content of pyridinic N on Cu-SA/NPC was 2.2% and 1.8%, respectively, while that on Cu-SA/NPCAr was 2.7% and 1.4%, respectively. This comparison indicated that the Cu-SA/NPC had a higher content of pyrrolic N than that of Cu-SA/NPCAr, which might play an important role for acetone production on Cu-SA/NPC. In view of CO2 reduction measurements and XPS results, the CH\(_3\)COOH production from CO2 reduction might be determined by the single atom Cu and the content of pyrrolic N. However, how these two species combined with each other was not confirmed based on experimental results and DFT calculations were conducted to identify the active sites of Cu-SA/NPC and to uncover the mechanisms for acetone production from CO2 reduction.

### Active sites identification and mechanisms

As the electrocatalytic activity of SAC could be affected by the coordination environment of isolated metal atoms\(^{37}\), different types of coordinated N species were first examined. According to the combined HAADF-STEM and EXAFS results, the Cu species should be atomically dispersed and was fourfold coordinated with N atoms in the Cu-SA/NPC\(^{39}\) catalyst. Herein, two catalyst models were constructed, in which single atom Cu was doped into a graphitic sheet with coordination environments with four pyridine N atoms (Cu-pyridinic-N\(_4\) site) and four pyrrole N atoms (Cu-pyrrolic-N\(_4\) site) (inside the Fig. 5a). The Gibbs free energy diagrams of CO2 reduction and \(\Delta G\) values of elementary steps.
involved were calculated based on the computational hydrogen electrode model. Fig. 5a illustrated the lowest energy pathways of CH₃COCH₃ formation from CO₂ reduction on Cu-pyridinic-N₄ and Cu-pyrrolic-N₄ sites of Cu-SA/NPC at a potential of −0.36 V versus RHE. The free energy diagrams at 0 V on the two sites were provided in Supplementary Fig. 21. Fig. 5b showed the optimized structures of all reaction intermediates involved in the pathways of CO₂ reduction on the Cu-pyrrolic-N₄ site (gray: C of catalyst; black: C of adsorbate; red: O; orange: Cu; blue: N; white: H).

Fig. 5 DFT calculations of reaction pathways on different Cu-N sites of Cu-SA/NPC. a Free energy diagrams calculated at a potential of −0.36 V for CO₂ reduction to CH₃COCH₃ on Cu-pyridinic-N₄ and Cu-pyrrolic-N₄ sites of Cu-SA/NPC (the computational models were included in the figure). b Optimized structures of all reaction intermediates involved in the pathways of CO₂ reduction on the Cu-pyrrolic-N₄ site.
with a ΔG value of −0.05 eV and −0.53 eV on Cu-pyridinic-N₄ and Cu-pyrrolic-N₄, respectively. The formation of COCOH⁺ species was also reported by Goddard III et al., which was considered as a key intermediate for C₂ or C₃ product formation from CO₂ reduction³. The COCOH⁺ was converted into the COC⁺ species by breaking the C–O(H) bond, and the formed COC⁺ was further reduced to the COCH₃⁺ intermediate via sequential hydrogenation steps. These steps were all downhill in free energies on the both sites at −0.36 V, as shown in Fig. 5a. The subsequent C–C bond formed by coupling of the COCH₃⁺ intermediate with another adsorbed CO⁺ led to the formation of COOCCH₃⁺ with a ΔG value of −0.18 eV on Cu-pyridinic-N₄ and −0.92 eV on Cu-pyrrolic-N₄, showing a more favorable formation of C₃ species from C₂ intermediates on the Cu-pyrrolic-N₄ site. Subsequent conversions of COOCCH₃⁺ to acetone were all downhill in free energy change on Cu-pyrrolic-N₄ whereas the elementary step of COOCCH₃⁺ reduction to COHCOCH₃⁺ still had an endothermic ΔG of 0.70 eV on Cu-pyridinic-N₄. The free energy calculations revealed that CO₂ activation to COOH⁺ was the only slow step on Cu-pyrrolic-N₄ (Supplementary Table 6), determining the overall rate for CH₂OCH₃ production. The C–C coupling reactions were quite facile to occur, leading to a high selectivity to acetone formation on this site. Other possible C–C coupling pathways including CO*⁺–CHO* and COO*⁺–COH* were also considered on Cu-pyrrolic-N₄, but these routes were found to be energetically unfavorable as compared with the direct coupling of two CO* species (Supplementary Note 2 and Supplementary Fig. 23). In contrast, several steps proceeded slowly on Cu-pyridinic-N₄, including CO₂ reduction to COOH*, COO*⁺–CO* coupling and COCOCH₃* reduction to COHCOCH₃⁺ (Supplementary Table 6). The C–C coupling was non-electrochemical reaction and could not be facilitated by the applied potential, therefore, the significantly endothermic free energy change (ΔG of 1.67 eV) in the coupling of two CO* species hindered acetone formation from CO₂ reduction on the Cu-pyridinic-N₄ site. These calculation results revealed that Cu coordinated with pyrrolic N species (Cu-pyrrolic-N₄) was active for acetone production rather than pyridinic N species.

To examine whether the uncoordinated pyrrolic N species was active toward acetone formation, DFT calculations were performed on two types of uncoordinated pyrrolic N models without Cu, as shown in Supplementary Figs. 24 and 25, and Supplementary Table 7. The free energy diagrams for acetone production form CO₂ reduction on uncoordinated pyrrolic-N₁, uncoordinated pyrrolic-N₃ and Cu-pyrrolic-N₄ at 0 V potential were compared in Supplementary Fig. 24. Clearly, the uncoordinated pyrrolic-N₄ was not active toward acetone formation due to several uphill elementary steps other than CO₂ reduction to COOH* (ΔG of 1.35 eV), such as COCOH⁺ reduction to COC⁺ (ΔG of 1.17 eV), COCH₃* reduction to COCH₂⁺ (ΔG of 1.07 eV), and COCH₂* coupling with CO* to form COCOCH₂⁺ (ΔG of 1.05 eV). For the uncoordinated pyrrolic-N₁, although the first step of CO₂ reduction to COOH* had a smaller ΔG value (0.75 eV) than that (1.42 eV) obtained on Cu-pyrrolic-N₄, subsequent CO₂ formation from COOH⁺ reduction had a larger ΔG of 1.24 eV. In addition, steps such as COCO* reduction to COCH₂⁺ and COCOCH₂⁺ reduction to COCOCH₃⁺ were energetically endothermic with ΔG values of 0.70 and 0.97 eV, respectively, indicating that the uncoordinated pyrrolic-N₁ did not have an advantage for acetone production. The comparison results in Supplementary Fig. 24 revealed that Cu single atom coordinated with pyrrolic N species (Cu-pyrrolic-N₄) was catalytically more active than the uncoordinated pyrrolic N species, and should be responsible for the acetone production from CO₂ reduction on Cu-SA/NPC, as shown in Supplementary Table 4, other than the difference in the content of pyridinic N and pyrrolic N, the content of oxidized N was also different on Cu-SA/NPC and Cu-SA/NPAr. The experimental results on the NPC catalyst without adding Cu showed no acetone formation from CO₂ reduction, which suggested that the oxidized N should not be the active site for acetone production on Cu-SA/NPC. To further confirm this, DFT calculations of energetic pathways for CO₂ reduction to acetone on pyridinic- and pyrrolic-N=O sites were performed (Supplementary Figs. 26–28), and detailed results were provided in the Supplementary Note 3 and Supplementary Table 8. Since several elementary steps involved in the paths were highly uphill in ΔG (Supplementary Fig. 26), the oxidized N sites were not active for acetone formation. Furthermore, the influence of Zn impurity on acetone production from CO₂ reduction on the Cu-SA/NPC catalyst was also investigated by DFT calculations (Supplementary Figs. 29, 30) which revealed that Zn was not responsible for acetone production from CO₂ reduction (Supplementary Note 4).

These DFT results revealed that the active sites for acetone synthesis from CO₂ reduction on Cu-SA/NPC were Cu-pyridinic-N₄, consistent with the structural prediction of Cu/N coordination environment from EXAFS characterization and the N species identified from XPS. From CO₂ reduction to acetone, the formation of reaction intermediates required the synergy between Cu and coordinated pyrrolic N species (Fig. 5b), leading to a facile C–C coupling toward C₂ and C₃ species formation (Fig. 5a). The ICP results provided in Supplementary Table 1 revealed that the content of Cu dispersed into the Cu-SA/NPC catalyst was relatively small, and the EXAFS results (Fig. 2b) confirmed that the Cu coordinated with N atom. The combined experimental and DFT studies confirmed that the Cu single atom coordinated with four pyrrolic N (Cu-pyrrolic-N₄) should be responsible for the acetone production from CO₂ reduction on Cu-SA/NPC, and therefore were proposed as the active sites.

As observed in Fig. 3b, other oxygenates such as HCOOH, CH₃COOH, CH₃OH, and C₂H₅OH were also detected at different potentials. The energetic pathways for the formation of these oxygenates on the Cu-pyrrolic-N₄ active site of Cu-SA/NPC were examined by DFT calculations and the results were illustrated in Fig. 6a–d. Optimized structures of all intermediates were provided in Supplementary Figs. 31–34, with the free energy change for each elementary step involved given in Supplementary Table 9. The relative selectivity to acetone versus these oxygenates was evaluated based on DFT results at 0 and −0.36 V. For acetone, the rate-determining step was CO₂ reduction to COOH*, which had a free energy change of 1.42 eV at 0 V potential. For HCOOH formation, the rate-limiting step was CO₂ reduction to HCOO* with a ΔG of 2.42 eV, determining the selectivity to formic acid and making it difficult to form at lower potentials. However, the formation of CH₃COOH, CH₃OH and C₂H₅OH all went through a CO* intermediate via CO₂ → COOH* → CO*, similar to that for acetone formation. Therefore, the selectivity determining step for acetone versus other oxygenates should appear after CO* formation, which was found to be the COCOCH₃* → COHCOCH₃* → COOH* reaction, similar to that for acetone formation. Therefore, the selectivity determining step for acetone versus other oxygenates should appear after CO* formation, which was found to be the COCOCH₃* → COHCOCH₃* → COOH* reaction, similar to that for acetone formation. Therefore, the selectivity determining step for acetone versus other oxygenates should appear after CO* formation, which was found to be the COCOCH₃* → COHCOCH₃* → COOH* reaction, similar to that for acetone formation. Therefore, the selectivity determining step for acetone versus other oxygenates should appear after CO* formation, which was found to be the COCOCH₃* → COHCOCH₃* → COOH* reaction, similar to that for acetone formation.
due to higher uphill $\Delta G$ values; the formation of CH$_3$COCH$_3$ and CH$_3$OH was relatively fast because the selectivity determining step became more energetically favorable with the applied potentials; the C$_2$H$_5$OH could be produced but the selectivity should be lower than that of CH$_3$COCH$_3$ and CH$_3$OH due to a moderate uphill free energy change of the selectivity determining step when the potential was applied. The higher selectivity toward acetone formation from CO$_2$ reduction on the Cu-SA/NPC catalyst should originate from the unique Cu-pyrrolic-N$_4$ active site in stabilizing the reaction intermediates involved in acetone production as well as facilitating the C–C coupling reactions involved in CO$_2$ reduction to acetone. As shown in Fig. 5a, the two C–C coupling steps were largely downhill in free energy change (−1.22 and −0.92 eV, respectively, for CO$^*$–CO$^*$ and CO$^*$–COCH$_3^*$ coupling) and the formation of reaction intermediates was energetically quite favorable (except for the first CO$_2$ reduction to COOH$^*$ step) due to the synergy of Cu–N coordination and interaction with intermediate species for acetone formation on the Cu-pyrrolic-N$_4$ site of Cu-SA/NPC.

**Discussion**

Efficient and selective electrochemical reduction of CO$_2$ to CH$_3$COCH$_3$ was achieved on Cu-SA/NPC. The maximum production rate of CH$_3$COCH$_3$ was 336.1 $\mu$g h$^{-1}$ and the highest Faradaic efficiency of CH$_3$COCH$_3$ production was 36.7%, significantly enhanced as compared with other electrocatalysts reported in the literature. Based on CO$_2$ reduction experiments and DFT calculations, the high activity and selectivity of Cu-SA/NPC for CH$_3$COCH$_3$ generation were mainly originated from single atom Cu coordinated to four pyrrolic N atoms, which lowered the reaction energies required for CO$_2$ activation and C–C bond coupling. The proposed energetically most favorable pathways for CH$_3$COCH$_3$ generation from CO$_2$ reduction went through CO$_2$ → COOH$^*$ → CO$^*$ → COOC$^*$ → COOH$^*$ → COCH$^*$ → COCH$_2^*$ → COCH$_3^*$ → COOCCH$_3^*$ → COOCCH$_2^*$ → COCCCH$_3^*$ → COCCCH$_2^*$ → CH$_3$COCH$_3$. The higher selectivity toward acetone formation from CO$_2$ reduction on the Cu-SA/NPC catalyst should originate from the unique Cu-pyrrolic-N$_4$ active sites in stabilizing the
reaction intermediates involved in acetone production as well as facilitating the C-C coupling reactions due to the Cu–N synergy. This work offers fundamental insight into the design of efficient electrocatalysts for reducing CO2 to multi-carbon products, which is valuable in the field of energy regeneration and electrochemical synthesis.

Methods

Synthesis. The catalyst was obtained by carbonization of Cu-doped ZIF-8 (Cu-ZIF-8) precursor. For synthesis of Cu-ZIF-8, 5.258 g of 2-methylimidazole was dissolved in 80 mL of methanol (solution A). 4.76 g of Zn(NO3)2·6H2O, and 0.31 g of Cu(CH3COO)2·H2O were dissolved in 120 mL of methanol (solution B). After ultrasound for 10 min, solution B was added into solution A and the mixed solution was stirred for 30 min at room temperature. Subsequently, the mixture was transferred into Teflon-lined autoclave and heated at 120 °C for 4 h. The products were washed with methanol and DMF several times, and dried at 80 °C under vacuum. The obtained Cu-ZIF-8 powder was carbonized at 1000 °C for 4 h under nitrogen (N2) or argon (Ar) atmosphere. The heating rate was set to 5 °C min⁻¹. The sample was denoted as Cu-SA/NPC or Cu-SA/NPCP, respectively. The catalysts with different content of Cu (0.16, 0.62, 0.93, and 1.86 g Cu with Zn/Cu ratios of 20/1, 5/1, 1/3, and 5/5) were synthesized and the obtained catalysts were denoted as Cu-SA/NPC20, Cu-SA/NPC50, Cu-SA/NPC100, and Cu-SA/NPC-P, respectively.

Characterization. X-ray diffraction (XRD) patterns were measured by a Shimadzu LabX XRD-6000 diffractometer with Cu ka radiation (λ = 0.15406 nm). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were performed on a Hitachi S-4800 microscope and an FEI Tecnai G2 20 microscope, respectively. XPS measurements were conducted by using a VG ESCALAB 250 instrument with a monochromatized Al Kα X-ray source (1486.6 eV). Nitrogen adsorption–desorption isotherms were obtained from a Quadrasorb instrument at 77 K. ICP-AES was detected by a PerkinElmer 8100 instrument. TEM, XRD, and XPS analyses were performed on a Hitachi S-4800 microscope and an FEI-Tecnai G2 20 microscope, respectively. XPS measurements were conducted by using the Vienna Ab-initio Simulation Package. The exchange-correlation energies were treated with the spin-polarized generalized gradient approximation and Perdew–Brake–Ernzerh of functional. Core electrons were represented by projector augmented-wave pseudopotentials. A 400 eV plane wave cutoff energy and a 2 × 2 × 1 k-point sampling were used for all calculations. The Cu single atom doped in graphene sheet with coordination environments of four pyridine nitrogen atoms and four pyrrole nitrogen atoms were constructed and denoted as Cu-pyridinic-N4 and Cu-pyrrolic-N4, respectively. The computational hydrogen electrode model was utilized to calculate the free energies of intermediates involved in CO2 reduction under experimental conditions.

Data availability

The authors declare that all data supporting the results of this study are available within the paper and its supplementary information files or from the corresponding authors upon reasonable request.

Code availability

All codes are available upon reasonable request.

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Author contributions

K.Z. and X.N. contributed equally to this work. K.Z. and X.Q. conceived the idea and designed the experiments. K.Z. synthesized the catalysts. K.Z., S.C., and H.Y. performed the catalytic performance evaluations. X.N. and H.W. conducted the DFT calculations. K.Z., X.N., and J.G.C. analyzed the data. W.C., G.Z., and B.K. performed the EXAFS test. K.Z., X.N., X.Q., and J.G.C. co-wrote the paper. X.Q. and J.G.C. supervised the whole project.

Competing interests

The authors declare no competing interests.

Additional information

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