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## Enhancing CO<sub>2</sub> electroreduction to CH<sub>4</sub> over Cu nanoparticles supported on N-doped carbon†

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The electroreduction of CO<sub>2</sub> to CH<sub>4</sub> has attracted extensive attention. However, it is still a challenge to achieve high current density and faradaic efficiency (FE) for producing CH<sub>4</sub> because the reaction involves eight electrons and four protons. In this work, we designed Cu nanoparticles supported on N-doped carbon (Cu-np/NC). It was found that the catalyst exhibited outstanding performance for the electroreduction of CO<sub>2</sub> to CH<sub>4</sub>. The FE toward CH<sub>4</sub> could be as high as 73.4% with a high current density of 320 mA cm<sup>-2</sup>. In addition, the mass activity could reach up to 6.4 A mg<sub>Cu</sub><sup>-1</sup>. Both experimental and theoretical calculations illustrated that the pyrrolic N in NC could accelerate the hydrogenation of \*CO to the \*CHO intermediate, resulting in high current density and excellent selectivity for CH<sub>4</sub>. This work conducted the first exploration of the effect of N-doped species in composites on the electrocatalytic performance of CO<sub>2</sub> reduction.

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### Introduction

The electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) is a promising approach to achieve carbon neutrality,<sup>1–6</sup> which can convert CO<sub>2</sub> into valuable chemicals and fuels using renewable energy.<sup>7–11</sup> Among all these products, CH<sub>4</sub> is a highly desired product because it holds the highest heating value of 55.5 MJ kg<sup>-1</sup>.<sup>12</sup> However, CO<sub>2</sub> electroreduction to CH<sub>4</sub> still suffers from high overpotential and low activity and selectivity.<sup>13–16</sup> Designing highly efficient and robust electrocatalysts is crucial to solve this problem.

Cu-based catalysts have been proven to be the most promising electrocatalysts for producing hydrocarbon products from the CO<sub>2</sub>RR. In recent years, many methods have been applied to enhance the activity of the CO<sub>2</sub>RR over Cu-based catalysts, including alloying,<sup>17</sup> doping,<sup>18,19</sup> modifying with other

compounds,<sup>20,21</sup> changing the shape and size,<sup>22–24</sup> and building an interface and defects.<sup>25–27</sup> However, it is still challenging to achieve high selectivity for CH<sub>4</sub> at a high current density.<sup>28–33</sup> This is because the generation of CH<sub>4</sub> involves eight electrons and four protons, which easily bifurcates to give broad product distributions.<sup>34–36</sup> According to a previous report,<sup>37</sup> the co-adsorption of \*CO and \*H played an important role in the production of CH<sub>4</sub>, and the selectivity of CH<sub>4</sub> can be enhanced by a high surface \*H coverage, due to sufficient \*H supply for the hydrogenation of intermediates.<sup>37</sup> However, the high surface \*H coverage could result in the undesired hydrogen evolution reaction (HER) and hinder the adsorption of intermediates. Thus, it is necessary to find a method to break the linear scale relationship of the single catalyst sites, which will enhance the selectivity of CH<sub>4</sub> and decrease the yield of H<sub>2</sub> simultaneously.

To solve the above problem, here we proposed the idea to introduce additional catalytic sites, which can enhance the activation of H<sub>2</sub>O and hydrogenation of intermediates but not cause excessive production of H<sub>2</sub>. According to a previous report, N-doped carbon (NC) catalysts could promote the activation of H<sub>2</sub>O.<sup>38–40</sup> In addition, the adsorption of \*H can be regulated by changing the type of N-doped species.<sup>41–43</sup> Thus we can assume that NC would be a potential platform for tuning the activity and selectivity of Cu-based catalysts. Although NC has been used to modify Cu-based catalysts, the products were ethanol and ethylene.<sup>41</sup> In addition, the role of the N-doped species in the composites is not clear.

Herein, we used NC with different contents of N-doped species as another component to modify Cu nanoparticles

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(Cu-np/NC). In this strategy, the selectivity of CH<sub>4</sub> over Cu-np could be enhanced by introducing NC with rich pyrrolic N species, and the faradaic efficiency (FE) of CH<sub>4</sub> could reach up to 73.4% with a current density of 320 mA cm<sup>-2</sup>. Especially, the mass activity reached up to 6.4 A mg<sub>Cu</sub><sup>-1</sup>. An *in situ* surface enhanced Raman spectroscopy (SERS) study demonstrated that the formation of the \*CHO intermediate could be promoted over Cu-np/NC, which is an important intermediate for producing CH<sub>4</sub>. Experimental and DFT studies indicated that the pyrrolic N in NC could accelerate the hydrogenation of intermediates, resulting in excellent selectivity for CH<sub>4</sub>.

## Results and discussion

Cu-np and NC were prepared respectively according to previous reports.<sup>44,45</sup> The size of the obtained Cu-np was about 40 nm (Fig. S1†). NC(*x*:*y*) was prepared using arginine and melamine,<sup>45</sup> and *x*:*y* represents the ratio of arginine and melamine in the preparation process. All of the NC(*x*:*y*) exhibited a nanosheet morphology (Fig. S2†). Cu-np/NC(*x*:*y*) was prepared by blending Cu-np and NC(*x*:*y*) (see the Methods for experimental details).

The electrocatalytic performance of Cu-np/NC(1:4) was first studied, and the other Cu-np/NC(*x*:*y*) catalysts will be studied in the following section. The electrocatalytic performance of the CO<sub>2</sub>RR was evaluated in a flow cell, as reported in our previous report.<sup>34,41</sup> The catalysts were sprayed on hydrophobic carbon paper as the cathode, and Ni foam was used as the anode.<sup>34,41,46,47</sup> 1 M KOH solution was used as the electrolyte. The gaseous and liquid products were analyzed by gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy, respectively.

Over Cu-np, CO<sub>2</sub> could be reduced to various products, such as CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH (Fig. 1A and S3†). However, the selectivity of a single product is low (less than 45%). It is noted that the selectivity of CH<sub>4</sub> was significantly enhanced by adding NC(1:4) and increased with the content of NC(1:4) (Fig. 1A and S4†). The selectivity of CH<sub>4</sub> reached the highest when the content of NC(1:4) was 99 wt% (Cu-np/NC(1:4, 99 wt%)). The FE of CH<sub>4</sub> could reach up to 73.4%, which is much higher than that of Cu-np. When the content of NC(1:4) was 99.5 wt%, the selectivity of CH<sub>4</sub> decreased with increasing yield of H<sub>2</sub>, which may have originated from the insufficient Cu sites. For NC(1:4), only small amounts of CO were detected (Fig. S5†). Consequently, it can be assumed that the Cu sites were the active sites and the selectivity of CH<sub>4</sub> was enhanced by the addition of NC(1:4). The partial current density of CH<sub>4</sub> over Cu-np/NC(1:4, 99 wt%) was 234 mA cm<sup>-2</sup> at -1.1 V vs. RHE, which is about 4.1 times higher than that over Cu-np (Fig. S6†). In the meantime, the CH<sub>4</sub>-to-other ratio was enhanced from 0.25 on Cu-np to 20.2 on Cu-np/NC(1:4, 99 wt%) (Fig. S7†), indicating that the selectivity of CH<sub>4</sub> was enhanced and the other products were suppressed. Compared with the state-of-the-art catalysts, Cu-np/NC(1:4, 99 wt%) performed as one of the best catalysts in FE, current density and overpotential for CH<sub>4</sub> (Fig. 1B and Table S1†). In addition, based on such a low content (1 wt%) of Cu-np in Cu-np/NC(1:4, 99 wt%), the mass activity could be as high as 6.4 A mg<sub>Cu</sub><sup>-1</sup>. In the following discussion, the content of NC was fixed at 99 wt% in Cu-np/NC(*x*:*y*).

The electrolysis of the CO<sub>2</sub>RR was also carried out using membrane electrode assembly-based reactors (Fig. S8†). Cu-np/NC(1:4) was used as the cathode catalyst for the CO<sub>2</sub>RR and an iridium oxide-based catalyst as the anode for the oxygen evolution reaction. The selectivity of CH<sub>4</sub> was 60% with

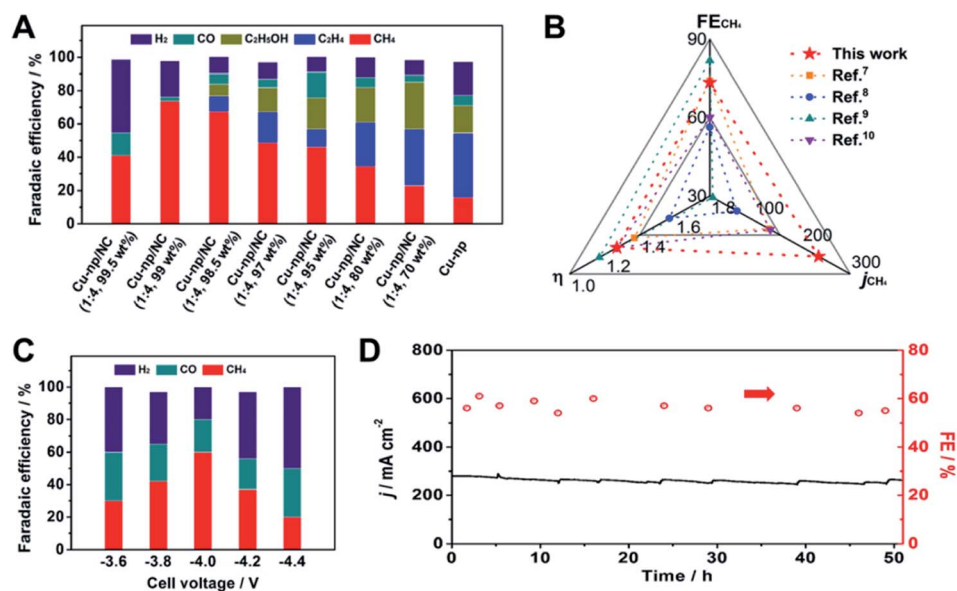


Fig. 1 (A) The distribution of products at -1.1 V vs. RHE over Cu-np and Cu-np/NC(1:4). (B) Comparison of the overpotential ( $\eta$ ), FE and CH<sub>4</sub> partial current density of Cu-np/NC(1:4, 99 wt%) with those of state-of-the-art Cu-based catalysts. (C) The distribution of products over Cu-np/NC(1:4, 99 wt%) at different cell voltages in a MEA system. (D) The current density and FE of CH<sub>4</sub> on Cu-np/NC(1:4, 99 wt%) at -4 V in 50 hour potentiostatic electrolysis tests.



a current density of  $230 \text{ mA cm}^{-2}$  at a cell voltage of  $-4 \text{ V}$  (Fig. 1C and S9<sup>†</sup>). Furthermore, the stability of Cu-np/NC(1 : 4) was investigated at a cell voltage of  $-4 \text{ V}$ .  $\text{H}_2\text{O}$  was injected into the cathode flow channel to prevent salt accumulation in the gas diffusion layer (GDL) micropores. The selectivity of  $\text{CH}_4$  and the current density had no obvious change for 50 h (Fig. 1D), indicating that Cu-np/NC(1 : 4) exhibited excellent stability.

The electrocatalytic performance of the  $\text{CO}_2\text{RR}$  over other Cu-np/NC( $x : y$ ) was also evaluated in a flow cell. As shown in Fig. S10,<sup>†</sup> the selectivity of  $\text{CH}_4$  over Cu-np/NC( $x : y$ ) varied with the  $x : y$  value. The highest FEs of  $\text{CH}_4$  over Cu-np/NC(1 : 2) and Cu-np/NC(1 : 8) were 65.8% and 59.6% respectively. Thus, we can deduce that NC( $x : y$ ) played an important role in the selectivity of  $\text{CH}_4$ . According to a previous report,<sup>45</sup> the intrinsic properties of NC were mainly attributed to the N-doped species. The correlation between  $\text{CH}_4$  selectivity and the type of N-doped species was investigated (Fig. S11, S12 and Table S2<sup>†</sup>). The FE of  $\text{CH}_4$  increased with increasing pyrrolic N content, whereas no regularity can be found for pyridinic N and graphitic N. These results indicated that the pyrrolic N in the NC( $x : y$ ) may play a crucial role in the enhancement of selectivity of  $\text{CH}_4$ .

In addition, the electrochemically active surface areas (ECSAs) and Nyquist plots of Cu-np/NC( $x : y$ ) were measured. The charge transfer resistance ( $R_{\text{ct}}$ ) for the different Cu-np/NC( $x : y$ ) was similar (Fig. S13<sup>†</sup>). Although the ECSAs of Cu-np/NC( $x : y$ ) varied slightly with the different NC( $x : y$ ) (Fig. S14<sup>†</sup>),

the normalized partial current densities for  $\text{CH}_4$  by ECSAs were similar to the geometric partial current density (Fig. S15<sup>†</sup>). These results indicated that different  $\text{CO}_2\text{RR}$  performances of Cu-np/NC( $x : y$ ) with different  $x : y$  values were not originated from the slight change of the  $R_{\text{ct}}$  and ECSAs.

Cu-np/NC(1 : 4) was characterized by transmission electron microscopy (TEM), and we can observe that Cu-np was dispersed on NC(1 : 4), as shown in Fig. 2A and B. In addition, the lattice distance of Cu(111) was observed by high-resolution transmission electron microscopy (HR-TEM) (Fig. 2C), which is consistent with that in Cu-np. However, the characteristic peaks of Cu cannot be observed on Cu-np/NC(1 : 4) in XRD patterns, and this is because the content of Cu is too low (Fig. S16<sup>†</sup>).

X-ray photoelectron spectroscopy (XPS) and operando X-ray absorption spectroscopy (XAS) were carried out to monitor the valence state and coordinate environment of Cu during the  $\text{CO}_2\text{RR}$  by the method used in our previous study.<sup>34,41,48</sup> From XPS, we can observe that the Cu valence state in Cu-np and Cu-np/NC(1 : 4) was similar, which is attributed to  $\text{Cu}^0$  (Fig. S17<sup>†</sup>). As shown in X-ray absorption near edge structure (XANES) spectroscopy (Fig. 2D), the pre-edge peaks of Cu-np and Cu-np/NC(1 : 4) were close to Cu foil before reaction. When the potential ( $-0.7 \text{ V vs. RHE}$ ) was applied, the spectra of Cu-np and Cu-np/NC(1 : 4) were still similar to that of metallic Cu. According to extended X-ray absorption fine structure (EXAFS) spectroscopy (Fig. 2E and S18<sup>†</sup>), only a peak corresponding to

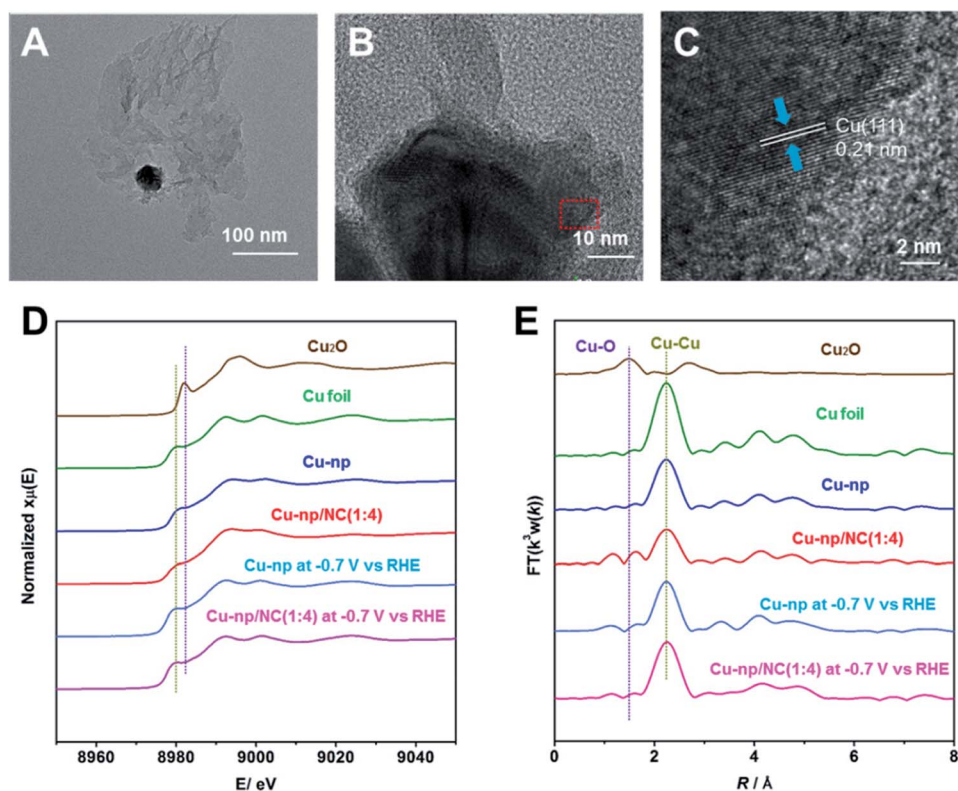


Fig. 2 (A and B) The TEM images of Cu-np/NC(1 : 4). (C) The HR-TEM image of Cu-np/NC(1 : 4). (D) The operando XANES spectra at the Cu K-edge for Cu-np and Cu-np/NC(1 : 4) at  $-0.7 \text{ V vs. RHE}$  during the  $\text{CO}_2\text{RR}$ . (E) The corresponding Fourier transform  $\text{FT}(k^3w(k))$  for Cu-np and Cu-np/NC(1 : 4) at  $-0.7 \text{ V vs. RHE}$  during the  $\text{CO}_2\text{RR}$ .



the Cu–Cu bond was observed, indicating that the metallic Cu was the active site for Cu-np and Cu-np/NC(1 : 4) during the CO<sub>2</sub>RR. Furthermore, the Cu–Cu coordination number of Cu-np and Cu-np/NC(1 : 4) during the CO<sub>2</sub>RR were quantified by using the ARTEMIS programs of IFEFFIT (Fig. S19, S20 and Table S3†). The Cu–Cu coordination number and bond distance in Cu-np/NC(1 : 4) were close to that in Cu-np during the CO<sub>2</sub>RR. These results indicate that the addition of NC did not change the coordination properties of Cu during the CO<sub>2</sub>RR.

DFT calculations were then carried out to gain insights into the effect of the N-doped species in Cu-np/NC on the selectivity of CH<sub>4</sub>. Cu(111) was used to represent Cu-np (Fig. S21†), which is in accordance with the results of HR-TEM. Cu(111) was located on a layer of N-doped graphene (NG) to represent the model of Cu-np/NC (Fig. S22†). From the results above, the pyrrolic N species played a crucial role in the selectivity of CH<sub>4</sub>. Then, the reaction energy diagrams of CO<sub>2</sub> reduction to CH<sub>4</sub> were first characterized over Cu(111) and Cu(111) on pyrrolic N-doped graphene (Cu(111)/pyrrolic N).

As shown in Fig. 4A, S23 and S24,† CO<sub>2</sub> was first reduced to \*CO through the \*COOH intermediate, and then \*CO was further reduced to CH<sub>4</sub> through the \*CHO intermediate. On Cu(111), the hydrogenation of \*CO to \*CHO shows the highest

energy barrier (0.71 eV), which is considered as the rate-limiting step for producing CH<sub>4</sub>. The hydrogenation of CO<sub>2</sub> to \*COOH and hydrogenation of \*CO to \*CHO were promoted over Cu(111)/pyrrolic N. Although the hydrogenation of \*CO to \*CHO still shows the highest energy barrier over Cu(111)/pyrrolic N, it was only 0.30 eV, which was much lower than that over Cu(111). These results suggested that the reduction of CO<sub>2</sub> to CH<sub>4</sub> over Cu(111) can be significantly enhanced by combining with pyrrolic N doped NC. Furthermore, the reaction energy diagrams were characterized at –0.5 V applied potential (Fig. S25†), and Cu(111)/pyrrolic N also is more favorable for producing CH<sub>4</sub> than Cu(111).

In addition, the hydrogenation of \*CO to \*CHO was also studied over Cu(111)/NC with different N-doped species (Fig. 3B and S26–S29†), and H<sub>2</sub>O was used as the donor of hydrogen, because 1 M KOH solution was used as the electrolyte in the CO<sub>2</sub>RR. Compared with Cu(111), the formation of \*CHO and \*OH from \*CO and \*H<sub>2</sub>O can be enhanced over Cu(111)/graphitic N, Cu(111)/pyrrolic N and Cu(111)/pyridinic N. It is noted that Cu(111)/pyrrolic N exhibited the lowest energy barrier (–0.16 eV), indicating that the pyrrolic N played the main role in the outstanding activity and selectivity of CH<sub>4</sub>, which was consistent with the experimental results.

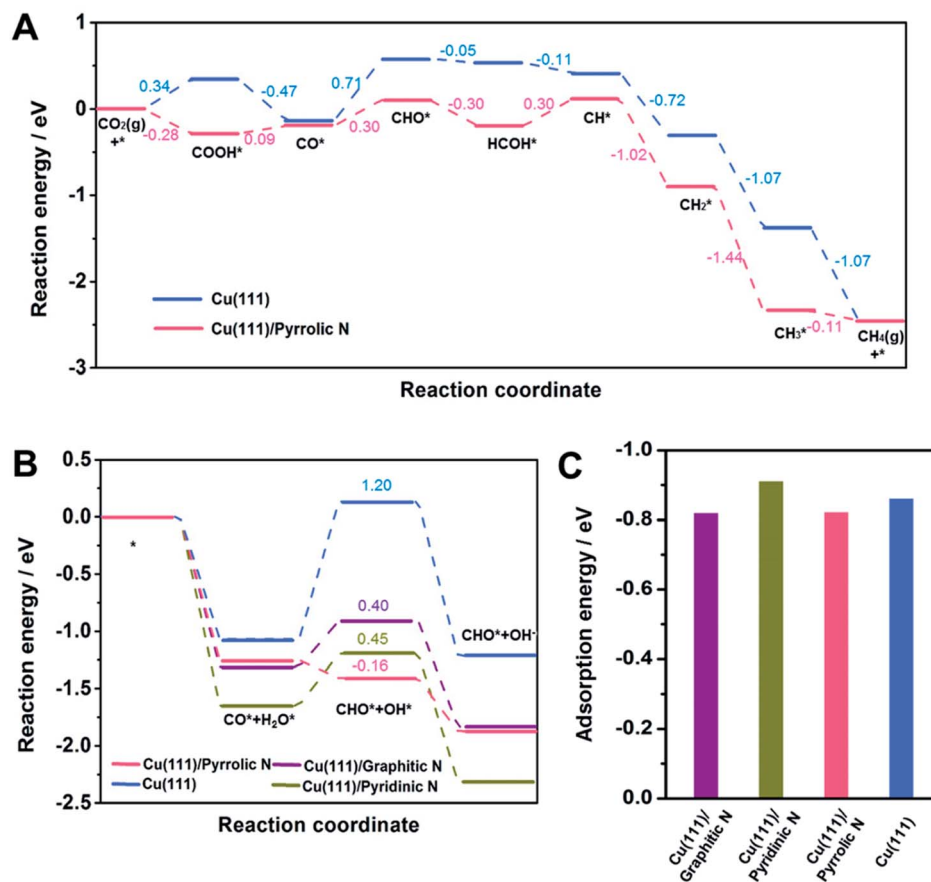


Fig. 3 (A) A reaction energy diagram for the CO<sub>2</sub>RR to CH<sub>4</sub> over Cu(111) and Cu(111)/pyrrolic N. (B) A reaction energy diagram for \*CO hydrogenation to \*CHO on Cu(111), Cu(111)/graphitic N, Cu(111)/pyridinic N and Cu(111)/pyrrolic N. (C) The adsorption energy of \*CO on different models.



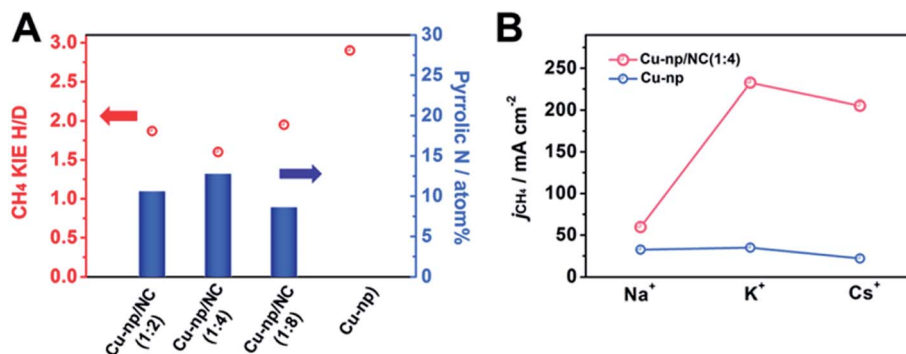


Fig. 4 (A) Kinetic isotopic effect (KIE) of H/D on the CO<sub>2</sub>RR to CH<sub>4</sub> at -1.1 V versus RHE. (B) Effect of alkali metal cations in the MOH (M = Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>) electrolyte on the CO<sub>2</sub>RR to CH<sub>4</sub> at -1.1 V versus RHE over Cu-np and Cu-np/NC(1 : 4) catalysts.

According to a previous report,<sup>49</sup> the adsorption of \*CO played an important role in the selectivity of products. Thus, the adsorption of \*CO on different models was studied. The adsorption of \*CO on Cu(111), Cu(111)/graphitic N, Cu(111)/pyrrolic N and Cu(111)/pyridinic N was comparable (Fig. 3C), indicating that the adsorption of \*CO was not changed by adding NC. Thus we can assume that the outstanding performance for CH<sub>4</sub> over Cu-np/NC was attributed to the activation of H<sub>2</sub>O by pyrrolic N.

From the results of DFT calculations above, we can know that the pyrrolic N in NC can enhance the activation of H<sub>2</sub>O and accelerate the hydrogenation of intermediates. To explore the effect of H<sub>2</sub>O activation on the generation of CH<sub>4</sub>, the kinetic isotopic effect (KIE) of H/D over Cu-np/NC(x : y) catalysts was measured (Fig. 4A and S30<sup>†</sup>). The KIEs of H/D are defined as the ratio of CH<sub>4</sub> formation rates in H<sub>2</sub>O and D<sub>2</sub>O. It has been reported that the reaction is considered to be controlled by the primary isotope effect when the KIE value is greater than 2.<sup>49,50</sup>

The KIE value was 2.9 over Cu-np, suggesting that the activation of H<sub>2</sub>O was involved in the rate-determining step. The KIE value over Cu-np/NC(x : y) decreased with the increase of the content of pyrrolic N in NC, suggesting that the dissociation of H<sub>2</sub>O can be enhanced by the pyrrolic N. For Cu-np/NC(1 : 4), the content of pyrrolic N reached the highest, and the KIE value was about 1.6, indicating that the dissociation of H<sub>2</sub>O was no longer involved in the rate-determining step, which is consistent with the results of DFT. Thus it can be deduced that the pyrrolic N in NC can accelerate H<sub>2</sub>O activation.

The role of H<sub>2</sub>O activation in the generation of CH<sub>4</sub> was further studied by investigating the effect of alkali metal (M) cations in a MOH electrolyte. It is known that the cation can combine with H<sub>2</sub>O to form a hydrated cation of M<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub>, and the value of *n* was 13, 7 and 6 for Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>, respectively.<sup>49</sup> The radii of M<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> decrease in the order of Na<sup>+</sup> > K<sup>+</sup> > Cs<sup>+</sup>.<sup>51</sup> The smaller *n* and radii of M<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub> enable a greater ability to dissociate H<sub>2</sub>O.<sup>49,51</sup> It can be known that the formation rate of

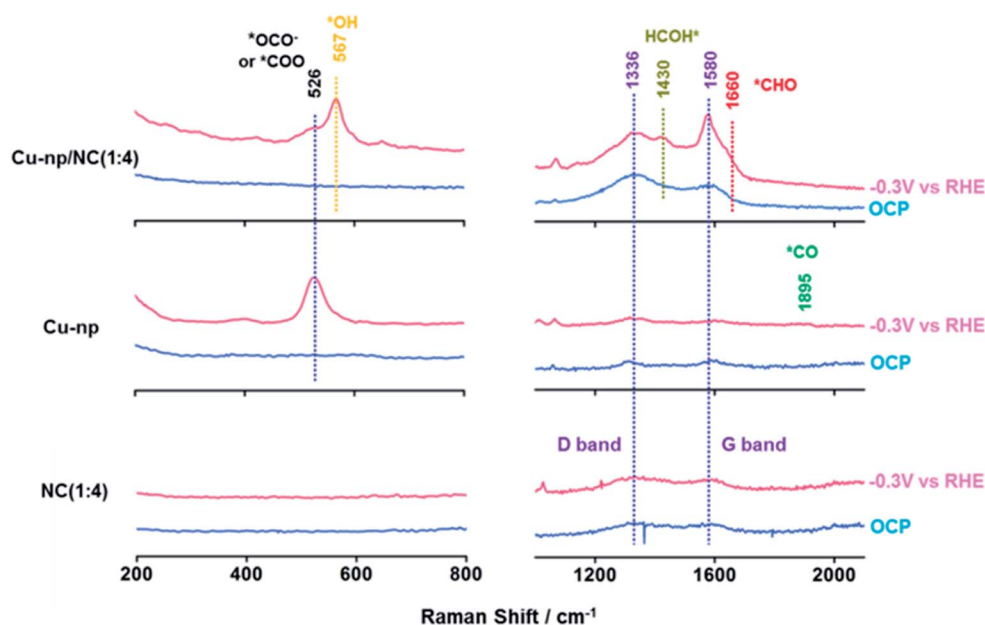


Fig. 5 The *in situ* surface-enhanced Raman spectra over Cu-np, Cu-np/NC(1 : 4) and NC(1 : 4) at -0.3 V vs. RHE during the CO<sub>2</sub>RR.



CH<sub>4</sub> was improved markedly over Cu-np/NC(1 : 4) by changing the cation from Na<sup>+</sup> to K<sup>+</sup> (Fig. 4B). The formation rate of CH<sub>4</sub> in CsOH was smaller than that in KOH. This may be because the generation of H<sub>2</sub> was also enhanced (Fig. S31†). For Cu-np, the formation rate of CH<sub>4</sub> increased slightly when changing the cation from Na<sup>+</sup> to K<sup>+</sup>. Thus we can assume that NC can enhance CH<sub>4</sub> formation by promoting H<sub>2</sub>O activation through interaction with hydrated cations.

Furthermore, the reaction intermediates during the CO<sub>2</sub>RR were traced by *in situ* surface-enhanced Raman spectroscopy (SERS).<sup>34,41</sup> At open-circuit potential (OCP), no Cu<sub>x</sub>O species were observed on Cu-np and Cu-np/NC(1 : 4), which was consistent with the results of XPS and XAS. The peaks located at 1336 cm<sup>-1</sup> and 1580 cm<sup>-1</sup> were observed on NC and Cu-np/NC(1 : 4), which were assigned to the D band and G band of graphene, respectively.<sup>52–54</sup> Weak peaks were also observed on Cu-np, which may be from the carbon paper. It is noted that a new Raman peak located at 526 cm<sup>-1</sup> appeared on Cu-np and Cu-np/NC(1 : 4) at -0.3 V vs. RHE, which was attributed to the adsorption of preliminary intermediates (such as \*CO<sub>2</sub> or \*OCO<sup>-</sup>) on the Cu surface.<sup>55</sup> These results indicated that the activation of CO<sub>2</sub> occurred on Cu sites. For Cu-np, a new Raman band located at 1895 cm<sup>-1</sup> appeared at -0.3 V vs. RHE, which corresponded to the C≡O stretching on Cu.<sup>41</sup> In contrast, no adsorption of \*CO was observed on Cu-np/NC(1 : 4). This may be because the obtained \*CO can be consumed quickly. Compared with Cu-np, Cu-np/NC(1 : 4) showed three other new peaks located at 567 cm<sup>-1</sup>, 1430 cm<sup>-1</sup> and 1660 cm<sup>-1</sup> at -0.3 V vs. RHE, which may be attributed to the adsorption of \*OH, \*HCOH and \*CHO on the Cu surface.<sup>50,54,55</sup> Thus we can deduce that the reaction \*CO + \*H<sub>2</sub>O → \*CHO + \*OH can be accelerated over Cu-np/NC and thus the selectivity of CH<sub>4</sub> can be enhanced, which was consistent with the experimental and calculation results (Fig. 5).

## Conclusions

In summary, Cu-np/NC composites were designed to enhance the electroreduction of CO<sub>2</sub> to CH<sub>4</sub>. The selectivity of CH<sub>4</sub> reached 73.4%, with a current density of 320 mA cm<sup>-2</sup>. Based on experimental and theoretical studies, the effect of the N-doped species on the electrocatalytic performance of CO<sub>2</sub> reduction was elucidated. The pyrrolic N in NC can enhance the activation of H<sub>2</sub>O, which could accelerate the hydrogenation of intermediates, resulting in excellent selectivity for CH<sub>4</sub> and high current density. We believe that this work opens a way for the design of efficient catalysts for the electroreduction of CO<sub>2</sub> to CH<sub>4</sub>.

## Data availability

The data that support the findings of this study are available within the article and its ESI.†

## Author contributions

Y. H. W., C. J. C., and B. X. H. proposed the project, designed the experiments, and wrote the manuscript; Y. H. W. performed the

whole experiments; X. P. Y., R. Z. W., S. J. L., J. M., J. L. Z., Z. M. L., X. Q. X., Z. H. W. performed the analysis of experimental data; C. J. C. and B. X. H. supervised the whole project.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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