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# Electrocatalytic synthesis of methylamine from nitrate and carbon dioxide on a heterometallic polyphthalocyanine

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Electrocatalytic coreduction of nitrate and CO<sub>2</sub> provides an opportunity for the synthesis of organonitrogen chemicals. The major challenge is to realize the simultaneous reduction of nitrate and CO<sub>2</sub> into active intermediates for C–N bond formation. In this work, methylamine is synthesized from nitrate and CO<sub>2</sub> on a polyphthalocyanine electrocatalyst with heterometal centers (Co<sub>2</sub>Cu<sub>1</sub>PPc). Notably, it is found that the Co and Cu centers coordinated with the conjugated macrocyclic network of polyphthalocyanine can catalyze CO<sub>2</sub> reduction to formaldehyde and nitrate reduction to hydroxylamine, respectively. The nucleophilic attack of hydroxylamine on formaldehyde generates a formaldoxime intermediate, which is then further reduced to methylamine. The overreduction reactions of hydroxylamine and formaldehyde intermediates are suppressed by Co<sub>2</sub>Cu<sub>1</sub>PPc. This bifunctional catalyst with heteronuclear active centers simultaneously catalyzes nitrate and CO<sub>2</sub> reduction to key intermediates for C–N bond formation.

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## Introduction

The electrocatalytic coreduction reaction of nitrate (NO<sub>3</sub><sup>−</sup>) and CO<sub>2</sub> {denoted as (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR} offers an opportunity for the sustainable synthesis of valuable organonitrogen chemicals, such as urea and amines, under mild conditions, and is of significance from the perspective of alleviating energy and environmental issues.<sup>1–6</sup> Wang *et al.*<sup>7</sup> have demonstrated the feasibility of the (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR for forming methylamine, which is the simplest amine widely used in the pharmaceutical and agrochemical industries.<sup>8,9</sup> Yet, the electrocatalytic (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR usually generates multiple products, and the efficiency of the aimed organonitrogen product remains to be improved.<sup>10–14</sup> The formation of key intermediates is difficult and they tend to be reduced to inactive species, resulting in a low efficiency of C–N coupling. Therefore, the challenge is to generate active intermediates towards C–N bond formation in competition with other parallel processes during the NO<sub>3</sub><sup>−</sup> reduction reaction (NO<sub>3</sub><sup>−</sup>RR) and the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR).

Single atom electrocatalysts such as Cu and Co based metal phthalocyanines (MPcs) and metal doped carbon materials

have been reported to be active for nitrate or CO<sub>2</sub> reduction reactions.<sup>15–20</sup> Metal polyphthalocyanines (MPPcs) with atomically dispersed metal–N<sub>4</sub> sites have well-defined and adjustable structures, featuring a large conjugated structure and fully in-plane  $\pi$ -delocalization.<sup>21–23</sup> These characteristics enable more stable multi-phase interfaces compared with MPcs.<sup>24–26</sup> In addition, the electronic structure of MPPcs can be modulated *via* constructing a multinuclear structure and may be favorable for electrocatalysis.<sup>27–29</sup> These points motivated us to design MPPc catalysts with heterometal centers for the electrocatalytic (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR to selectively form C–N bonds and methylamine.

Herein, a series of MPPcs {CoPPc, Co<sub>*x*</sub>Cu<sub>1</sub>PPc (*x* = 1, 2, 3) and CuPPc} supported on carbon nanotubes (CNTs) were investigated for the synthesis of methylamine from NO<sub>3</sub><sup>−</sup> and CO<sub>2</sub>. The heterometallic Co<sub>2</sub>Cu<sub>1</sub>PPc catalyst gives a Faradaic efficiency (FE) of 11.3% for methylamine, much higher than those of its monometallic and non-polymeric counterparts (below 3.2%). Experiments and theoretical calculations show that the Co and Cu centers in the conjugated macrocyclic network of Co<sub>2</sub>Cu<sub>1</sub>PPc can catalyze the CO<sub>2</sub>RR to formaldehyde (HCHO) and the NO<sub>3</sub><sup>−</sup>RR to hydroxylamine (NH<sub>2</sub>OH), respectively. The C–N coupling between NH<sub>2</sub>OH and HCHO forms a formaldoxime (CH<sub>2</sub>=NOH) intermediate, which is further reduced to the desired methylamine on Co centers. In addition, the introduction of Cu centers can suppress the overreduction of hydroxylamine and formaldehyde and thus boost the C–N coupling process. Co<sub>2</sub>Cu<sub>1</sub>PPc works as a heteronuclear bifunctional catalyst for the (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR to active intermediates for C–N coupling and further production of methylamine.

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## Results and discussion

### Materials and characterization

MPPCs were synthesized by a modified solid-phase polymerization method (Fig. S1 and S2, SI) according to the literature.<sup>21,30</sup> Commercial CoPc and CuPc monomers were studied for comparison (Fig. S3). The elemental mapping images show the uniform distribution of different elements in Co<sub>2</sub>Cu<sub>1</sub>PPc (Fig. 1a). These MPPCs are amorphous as revealed by X-ray diffraction (XRD) patterns and the high-resolution TEM image (Fig. S4).<sup>31</sup> Further, these MPPCs were supported on CNTs (Fig. 1b) to prevent the stacking or aggregation of polymer molecules during electrocatalysis. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image displays atomically dispersed metal atoms (circled in yellow, Fig. 1c).

The phthalocyanine framework of these MPPCs can be proved by the Fourier transform infrared spectra (Fig. S5)<sup>21,27</sup> and the Raman spectra (Fig. S6).<sup>29</sup> As shown in Fig. 1d, there is a shift in the B<sub>1g</sub> Raman signal related to the stretching of C–N–C bonds

between CoPPc and CuPPc due to the different electron delocalization in the phthalocyanine macrocycle.<sup>29,31</sup> Notably, Co<sub>2</sub>Cu<sub>1</sub>PPc shows two B<sub>1g</sub> peaks of CoPPc and CuPPc, resulting from the two kinds of local metal–N<sub>4</sub> coordination centers. The UV-visible absorption spectra of MPPCs show two typical absorbance bands of phthalocyanine, which reflects the  $\pi \rightarrow \pi^*$  transition of the macrocyclic ligand (Fig. 1e).<sup>21,25</sup> Compared with CoPPc, the Q band of Co<sub>2</sub>Cu<sub>1</sub>PPc shifts to a longer wavelength, suggesting that the  $\pi$ -conjugation structure is modified due to the incorporation of Cu.

In addition, the X-ray photoelectron spectroscopy (XPS) results of Co<sub>2</sub>Cu<sub>1</sub>PPc show typical signals of the polymer skeleton (Fig. S7). And the metal centers exist as Co<sup>2+/3+</sup> and Cu<sup>1+/2+</sup> species, as shown in Fig. 1f and g. The Co 2p<sub>3/2</sub> peaks of Co<sub>2</sub>Cu<sub>1</sub>PPc shift to lower binding energy compared with those of CoPPc, while the Cu 2p<sub>3/2</sub> peaks shift oppositely compared with CuPPc. This suggests that the electronic properties of metal centers are modified *via* hybridizing CoPPc and CuPPc together. Moreover, compared with the mixture of CoPc and CuPc monomers (named CoPc–CuPc), the bonding and electron delocalization in the polyphthalocyanine macrocycles of

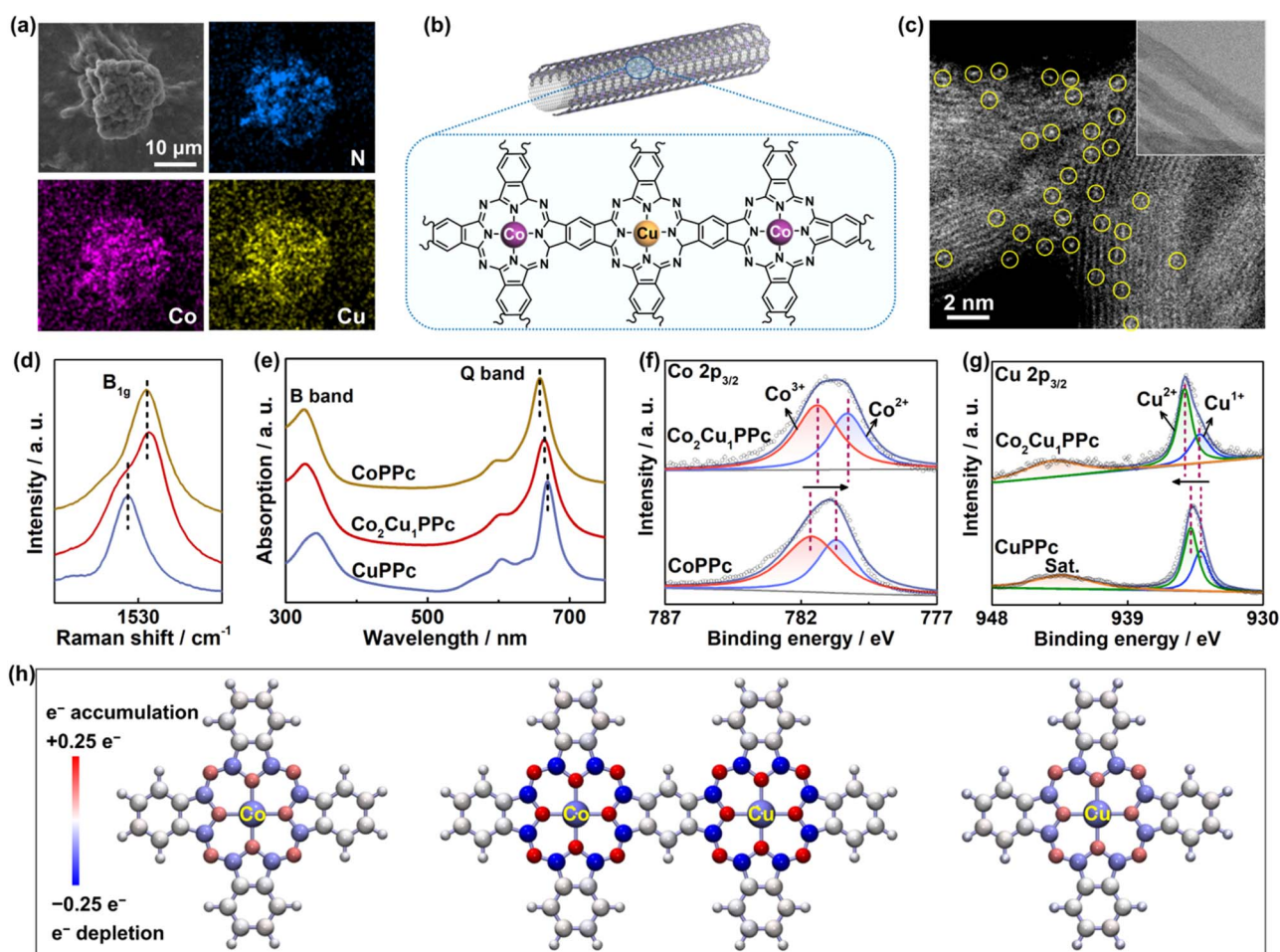


Fig. 1 Material characterization. (a) SEM and EDS mapping of unsupported Co<sub>2</sub>Cu<sub>1</sub>PPc. (b) Schematic diagram of Co<sub>2</sub>Cu<sub>1</sub>PPc supported on CNTs. (c) Atomic-resolution HAADF-STEM images of Co<sub>2</sub>Cu<sub>1</sub>PPc supported on CNTs (circled bright spots represent the metal atoms; inset: HRTEM). (d) Raman and (e) UV-Vis spectra of unsupported CoPPc, Co<sub>2</sub>Cu<sub>1</sub>PPc and CuPPc. High-resolution XPS spectra of (f) Co 2p<sub>3/2</sub> and (g) Cu 2p<sub>3/2</sub> of CoPPc, Co<sub>2</sub>Cu<sub>1</sub>PPc and CuPPc. (h) Bader charge analysis of CoPc, CuPc and simplified heteronuclear Co<sub>2</sub>Cu<sub>1</sub>PPc (the red and blue colors represent accepting and losing electrons, respectively).



Co<sub>2</sub>Cu<sub>1</sub>PPc are enhanced, judging from the shift in N 1s spectra and higher  $\pi$ - $\pi^*$  satellite in C 1s spectra (Fig. S7a–c).<sup>21</sup> And the average valence states of both Co and Cu in Co<sub>2</sub>Cu<sub>1</sub>PPc are higher than those in CoPc–CuPc (Fig. S7d and e). Further, we did Bader charge calculations on CoPc, CuPc and the simplified model of heteronuclear Co<sub>2</sub>Cu<sub>1</sub>PPc. Fig. 1h shows that there is more electron transfer from the metal center to the polyphthalocyanine ligand in heterometallic Co<sub>2</sub>Cu<sub>1</sub>PPc, and the polyphthalocyanine macrocycle may serve as an electron reservoir during electrocatalysis. Briefly, the characterizations above verify that the electronic structures of metal centers and the macrocycle network are both modified *via* constructing the heterometallic polyphthalocyanine.

### Electrocatalytic performance for methylamine synthesis and mechanism analysis

We then evaluated the performance of various catalysts for methylamine synthesis *via* the (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR in an H-type cell

with 0.1 M KHCO<sub>3</sub> and 0.8 M KNO<sub>3</sub> saturated with CO<sub>2</sub>. For all electrochemical measurements, the MPc and MPPc catalysts were supported on CNTs, and all potentials were reported after 80% *i*R-correction unless otherwise noted. Reaction products were determined by nuclear magnetic resonance (<sup>1</sup>H NMR), UV-visible spectrophotometry and gas chromatography (Fig. S8 and S9).

Fig. 2a shows the FE(CH<sub>3</sub>NH<sub>2</sub>) of Co<sub>x</sub>Cu<sub>1</sub>PPc (*x* = 1, 2, 3) as a function of potential, in comparison with CoPPc, CoPc, and the CoPc–CuPc mixture for methylamine production. All catalysts exhibit similar potential-dependent performance, and the optimized FEs are summarized in Fig. S10. CoPPc displays a FE(CH<sub>3</sub>NH<sub>2</sub>) of 3.2% at −0.84 V vs. RHE (denoted as *V*<sub>RHE</sub>), higher than that of CoPc (2.1%). CuPPc and CuPc show no activity for methylamine production (Fig. S11). In contrast, Co<sub>2</sub>Cu<sub>1</sub>PPc exhibits the highest FE(CH<sub>3</sub>NH<sub>2</sub>) of 11.3% at −0.76 *V*<sub>RHE</sub> among these catalysts. The FE(CH<sub>3</sub>NH<sub>2</sub>) values of both Co<sub>3</sub>Cu<sub>1</sub>PPc and Co<sub>1</sub>Cu<sub>1</sub>PPc are lower than that of Co<sub>2</sub>Cu<sub>1</sub>PPc, but are obviously higher than those of CoPPc and CuPPc.



Fig. 2 Electrocatalytic performance of the (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR and reaction mechanism. (a) FE(CH<sub>3</sub>NH<sub>2</sub>) and (b) *J*(CH<sub>3</sub>NH<sub>2</sub>) for the (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR with CoPPc, Co<sub>x</sub>Cu<sub>1</sub>PPc (*x* = 1, 2, 3), CoPc and CoPc–CuPc (mixture of CoPc and CuPc) as a function of potential. (c) FEs of all products of the (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR with Co<sub>2</sub>Cu<sub>1</sub>PPc at different potentials. (d) <sup>1</sup>H NMR spectra of the formaldoxime formed from the mixture of NH<sub>2</sub>OH and HCHO (black trace), and the solution after the (NO<sub>3</sub><sup>−</sup> + CO<sub>2</sub>)RR (green trace) and the isotopic-labelling (<sup>15</sup>NO<sub>3</sub><sup>−</sup> + <sup>13</sup>CO<sub>2</sub>)RR (pink trace). (e) Control experiments of different nitrogen and carbon sources. (f) Proposed reaction pathway for methylamine synthesis from NO<sub>3</sub><sup>−</sup> and CO<sub>2</sub>.

Accordingly, Fig. 2b shows that  $\text{Co}_2\text{Cu}_1\text{PPc}$  gives the highest partial current density of methylamine production ( $3 \text{ mA cm}^{-2}$ ), and the overpotential corresponding to the optimized activity shifts positively with the increase of Cu content. In addition, the  $\text{CoPc-CuPc}$  mixture delivers a  $\text{FE}(\text{CH}_3\text{NH}_2)$  of only 1.6% (Fig. S12), lower than that of  $\text{Co}_2\text{Cu}_1\text{PPc}$  by one order of magnitude. In  $\text{Co}_2\text{Cu}_1\text{PPc}$ , the two kinds of metal centers are uniformly dispersed and hybridized together in the same conjugated macrocyclic network, and their electronic structures are modified, different from the physically mixed  $\text{CoPc}$  and  $\text{CuPc}$  monomers. Briefly, heterometallic polyphthalocyanines show higher performance for methylamine synthesis than the monometallic and non-polymeric counterparts. Moreover, the reaction current is steady as a function of reaction time and there is negligible change in XPS spectra before and after the reaction (Fig. S13), suggesting  $\text{Co}_2\text{Cu}_1\text{PPc}$  remains stable during the electrolysis.

To understand the reaction mechanism of methylamine formation, we first evaluated the pH effect on the  $(\text{NO}_3^- + \text{CO}_2)$  RR. An optimal  $\text{FE}(\text{CH}_3\text{NH}_2)$  is achieved at a neutral pH ( $\sim 6.8$ ), which balances the competing pathways during the  $(\text{NO}_3^- + \text{CO}_2)$  RR (Fig. S14). At this pH condition,  $\text{NH}_2\text{OH}$  ( $\text{p}K_a = 5.96$ ) exists predominantly in its neutral form. Fig. 2c illustrates the FEs of all products which are close to 100%.  $\text{CO}$  is the main side product, and there is a small quantity of  $\text{CH}_3\text{OH}$ .  $\text{NH}_4^+$  is the main inorganic side-product with higher FE at more negative potentials, and some  $\text{NO}_2^-$  and  $\text{NH}_2\text{OH}$  are also detected. The hydrogen evolution reaction (HER) is only observed at potentials more negative than  $-0.80 \text{ V}_{\text{RHE}}$ . Formaldoxime and methylamine display similar volcanic curves as a function of the applied potential. Importantly, the detection of formaldoxime indicates the formation of  $\text{NH}_2\text{OH}$  and  $\text{HCHO}$  during the  $(\text{NO}_3^- + \text{CO}_2)$  RR (Fig. 2d). In the isotope-labelling experiment of  $(^{15}\text{NO}_3^- + ^{13}\text{CO}_2)$  RR, typical signals of  $^{13}\text{CH}_3\text{OH}$  and  $^{13}\text{CH}_3^{15}\text{NH}_2$  are observed in the  $^1\text{H}$  NMR spectra, and a minor signal of  $^{12}\text{CH}_3^{15}\text{NH}_2$  is also detected at 2.47 ppm. These results confirm that the produced methylamine indeed originates from  $\text{NO}_3^-$  and  $\text{CO}_2$ .

Then, other N-sources and C-sources were examined to confirm the active species for methylamine formation. Fig. 2e shows that  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  and  $\text{NH}_2\text{OH}$  can all serve as N-sources to form methylamine over  $\text{Co}_2\text{Cu}_1\text{PPc}$ . However, no methylamine is detected with  $\text{NH}_3 \cdot \text{H}_2\text{O}$  as the N-source, which excludes the direct involvement of  $\text{NH}_3 \cdot \text{H}_2\text{O}$  in C–N bond formation and indicates that  $\text{NH}_2\text{OH}$  is the active N-species for C–N coupling. As for the C-sources, we found that  $\text{HCHO}$  is active in generating methylamine in the presence of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$  or  $\text{NH}_2\text{OH}$ , but  $\text{CH}_3\text{OH}$  cannot. This suggests that  $\text{HCHO}$  from  $\text{CO}_2$  RR is the key intermediate for C–N bond formation.

Taken together, we propose the reaction pathway of methylamine synthesis from  $\text{NO}_3^-$  and  $\text{CO}_2$  (Fig. 2f). First,  $\text{NH}_2\text{OH}$  and  $\text{HCHO}$  intermediates are formed from the independent  $\text{NO}_3^-$  RR and  $\text{CO}_2$  RR through multi-proton and multi-electron transfer processes. Then, the  $\text{NH}_2\text{OH}$  intermediate attacks the  $\alpha$ -carbon of  $\text{HCHO}$  to form formaldoxime. This C–N coupling process is a spontaneous condensation reaction, as evidenced by the rapid and high-yield formation of oximes *via*

the reaction between  $\text{NH}_2\text{OH}$  and aldehydes such as  $\text{HCHO}$  or  $\text{CH}_3\text{CHO}$  (Fig. S15). The further reduction of formaldoxime through the transfer of four protons and four electrons generates the desired methylamine. This nucleophilic coupling route may also be applied for the formation of other amines from  $\text{NO}_x$  and  $\text{CO}/\text{CO}_2$ .

### Active sites for the conversion of C-species and N-species

We further tried to unveil the roles of different metal centers in heterometallic polyphthalocyanines during the  $(\text{NO}_3^- + \text{CO}_2)$  RR by studying the  $\text{NO}_3^-$  RR and  $\text{CO}_2$  RR separately. Fig. 3a shows that the current densities for  $\text{NO}_3^-$  RR follow the trend  $\text{CuPPc} > \text{Co}_2\text{Cu}_1\text{PPc} > \text{CoPPc} \approx \text{metal-free polyphthalocyanine (PPc)}$ , and the onset potential of  $\text{CuPPc}$  for  $\text{NO}_3^-$  RR is most positive. The current density of  $\text{Co}_x\text{Cu}_1\text{PPc}$  for the  $\text{NO}_3^-$  RR increases with the content of Cu (Fig. S16a).

Moreover, by density functional theory (DFT) calculations, we found that the Cu center in  $\text{Co}_2\text{Cu}_1\text{PPc}$  shows strong affinity for  $\text{NO}_3^-$ , and thus  $^*\text{NO}_3^-$  (\* represents surface adsorbed species) tends to be adsorbed on the Cu site rather than the Co site (Fig. 3b, S17). Accordingly,  $\text{CuPPc}$  exhibits the highest performance for the  $\text{NO}_3^-$  RR to  $\text{NO}_2^-$  (Fig. 3c), which may be the rate-determining step for the  $\text{NO}_3^-$  RR on  $\text{Co}_2\text{Cu}_1\text{PPc}$  as the current density of  $\text{NO}_2^-$  reduction is much higher than that of the  $\text{NO}_3^-$  RR (Fig. S16b).<sup>32,33</sup> In addition, Fig. 3d shows that the Cu site in  $\text{Co}_2\text{Cu}_1\text{PPc}$  adsorbs  $^*\text{NO}_2$  much more strongly than the Co site. Therefore, we deduce that the  $\text{NO}_3^-$  RR mainly occurs on the Cu centers of  $\text{Co}_2\text{Cu}_1\text{PPc}$ .

Interestingly, Fig. 3e shows that  $\text{Co}_2\text{Cu}_1\text{PPc}$  displays a superior performance for the  $\text{NO}_3^-$  RR to  $\text{NH}_2\text{OH}$ , with an optimized  $\text{FE}(\text{NH}_2\text{OH})$  of 25.2% (detailed data in Fig. S18), about 2.5 times those of  $\text{CoPPc}$ ,  $\text{CoPc}$  and the  $\text{CoPc-CuPc}$  mixture. The  $\text{FE}(\text{NH}_2\text{OH})$  values of  $\text{CuPPc}$  and  $\text{CuPc}$  are the lowest. That's to say, although  $\text{CuPPc}$  is very active for the  $\text{NO}_3^-$  RR, its performance for  $\text{NH}_2\text{OH}$  formation is low. Metal-free PPc does not show activity for  $\text{NH}_2\text{OH}$  production (Fig. S19a). So, the Cu centers play a crucial role in catalyzing the  $\text{NO}_3^-$  RR, and the process of  $\text{NH}_2\text{OH}$  formation is obviously enhanced *via* the construction of heterometallic polyphthalocyanines.

Once  $\text{NH}_2\text{OH}$  is generated, it may participate in the C–N coupling process, or be further reduced to inactive  $\text{NH}_3$ . Fig. 3f shows that the overreduction of  $\text{NH}_2\text{OH}$  with the  $\text{CoPPc}$  catalyst is serious, which mainly occurs on Co centers as the PPc shows low activity for this reaction. Interestingly,  $\text{CuPPc}$  shows very low activity for the  $\text{NH}_2\text{OH}$  reduction reaction. The  $^*\text{NH}_2\text{OH}$  adsorption energy on the Co site in  $\text{Co}_2\text{Cu}_1\text{PPc}$  changes little compared with that on  $\text{CoPPc}$  (Fig. S19b). The absolute number of Co sites available for  $^*\text{NH}_2\text{OH}$  reduction is obviously decreased in  $\text{Co}_2\text{Cu}_1\text{PPc}$ . Therefore, the overreduction of  $\text{NH}_2\text{OH}$  is obviously reduced on  $\text{Co}_2\text{Cu}_1\text{PPc}$ . In other words, the Cu centers in  $\text{Co}_x\text{Cu}_1\text{PPc}$  not only serve as active sites for  $\text{NO}_3^-$  reduction to  $\text{NH}_2\text{OH}$ , but also keep the active  $\text{NH}_2\text{OH}$  intermediate from overreduction, thus enhancing the efficiency for C–N bond formation.

Then, what is the active site for  $\text{CO}_2$  reduction? From the LSV curves,  $\text{CoPPc}$  and  $\text{Co}_2\text{Cu}_1\text{PPc}$  display large current densities for





Fig. 3 Electrocatalytic performance for the  $\text{NO}_3^-$ RR. (a) LSV curves of PPc, CoPPc,  $\text{Co}_2\text{Cu}_1\text{PPc}$  and CuPPc in Ar-saturated  $0.1 \text{ M KHCO}_3$  containing  $0.8 \text{ M KNO}_3$ . (b) Adsorption energy of  $^*\text{NO}_3$  on the Co or Cu sites of  $\text{Co}_2\text{Cu}_1\text{PPc}$  (inset: the most stable adsorption configurations of  $^*\text{NO}_3$ ). (c) FEs of  $\text{NO}_2^-$  formation after the  $\text{NO}_3^-$ RR with CoPPc, CuPPc, and  $\text{Co}_2\text{Cu}_1\text{PPc}$ . (d) Adsorption energy of  $^*\text{NO}_2$  on the Co or Cu sites of  $\text{Co}_2\text{Cu}_1\text{PPc}$  (inset: the most stable adsorption configurations of  $^*\text{NO}_2$ ). (e)  $\text{FE}(\text{NH}_2\text{OH})$  for the  $\text{NO}_3^-$ RR with CoPPc, CuPPc,  $\text{Co}_2\text{Cu}_1\text{PPc}$ , CoPc, CuPc, and CoPc-CuPc as a function of potential. (f) Current densities for the side-reaction of  $\text{NH}_2\text{OH}$  reduction at  $-0.76 \text{ V}_{\text{RHE}}$  in  $0.1 \text{ M KHCO}_3$  containing  $30 \text{ mM NH}_2\text{OH}$ .

the  $\text{CO}_2\text{RR}$ , whereas CuPPc and metal-free PPc exhibit negligible activity (Fig. 4a). The activity of the  $\text{CO}_2\text{RR}$  is enhanced when increasing the Co content in  $\text{Co}_x\text{Cu}_1\text{PPc}$  (Fig. S20). Based on the above results, HCHO is the active intermediate for C–N coupling, yet HCHO is not detected in the electrolyte after the  $\text{CO}_2\text{RR}$  or  $(\text{NO}_3^- + \text{CO}_2)\text{RR}$  (Fig. S21), possibly as adsorbed  $^*\text{HCHO}$  can be easily reduced to  $\text{CH}_3\text{OH}$  or consumed by C–N coupling with  $\text{NH}_2\text{OH}$  before its desorption into the solution. So, we used the amount of  $\text{CH}_3\text{OH}$  derived from HCHO reduction to assess the performance of forming active C-species from the  $\text{CO}_2\text{RR}$ . Notably, Fig. 4b shows that  $\text{Co}_2\text{Cu}_1\text{PPc}$  gives the highest  $\text{FE}(\text{CH}_3\text{OH})$  of 20.7%, about 5 times that of CoPc-CuPc and 3 times that of CoPPc (details in Fig. S22). And  $\text{CH}_3\text{OH}$  is not detected with CuPPc and CuPc. These results reveal that the Co atoms in  $\text{Co}_x\text{Cu}_1\text{PPc}$  are the active sites for the  $\text{CO}_2\text{RR}$  to form the  $^*\text{HCHO}$  intermediate, and the introduction of the Cu component boosts HCHO formation possibly through modifying the electronic structure of Co atoms. Furthermore, Fig. 4c shows that CoPPc is very active for HCHO reduction, which is unfavorable for methylamine synthesis. In contrast, it is suppressed with  $\text{Co}_2\text{Cu}_1\text{PPc}$ , and is negligible with CuPPc. Theoretical calculation shows that the adsorption of HCHO on the Co site in  $\text{Co}_2\text{Cu}_1\text{PPc}$  is weakened (Fig. S23), and thus its subsequent reduction to  $\text{CH}_3\text{OH}$  is inhibited.

The above results show that CuPPc presents high performance for the  $\text{NO}_3^-$ RR, but can hardly catalyze the  $\text{CO}_2\text{RR}$ . CoPPc is rather active for the  $\text{CO}_2\text{RR}$  but shows low activity for

the  $\text{NO}_3^-$ RR. However, the heterometallic polyphthalocyanines are active for both the  $\text{NO}_3^-$ RR to  $\text{NH}_2\text{OH}$  and  $\text{CO}_2\text{RR}$  to HCHO, and the overreduction of  $\text{NH}_2\text{OH}$  and HCHO intermediates is suppressed. These points promote the formation of key intermediates and are crucial for the high performance of methylamine production.

Further, theoretical calculations for the  $\text{CO}_2\text{RR}$  on the heterometallic catalyst were conducted to verify the proposed mechanism (Fig. 4d). It is found that  $^*\text{CO}_2$  on the Co center is reduced to  $^*\text{CO}$ , which is subsequently reduced to  $^*\text{CHO}$  rather than  $^*\text{COH}$ . The next proton-electron transfer process yields  $^*\text{HCHO}$  with an energy barrier of  $0.52 \text{ eV}$ , lower than that of  $^*\text{CHOH}$  formation. Further,  $\text{CH}_3\text{OH}$  is formed by exothermic processes. Additionally, the desorption of  $^*\text{HCHO}$  shows a high energy barrier of  $2.2 \text{ eV}$ , so it tends to exist as a surface-bound intermediate for further formation of  $\text{CH}_3\text{OH}$  or C–N coupling with  $\text{NH}_2\text{OH}$ . Consistently, free HCHO is not detected in the electrolyte (Fig. S21). These theoretical and experimental results strongly support the participation of  $^*\text{HCHO}$  in the  $(\text{NO}_3^- + \text{CO}_2)\text{RR}$ .

As for the formaldoxime reduction process, theoretical calculations reveal that the  $^*\text{formaldoxime}$  molecule tends to be adsorbed on the Co site of  $\text{Co}_2\text{Cu}_1\text{PPc}$  (Fig. 4e). CoPPc and  $\text{Co}_2\text{Cu}_1\text{PPc}$  show similar current densities for the reduction of formaldoxime, and both are more active than CuPPc (Fig. 4f). Therefore, the Co centers in  $\text{Co}_2\text{Cu}_1\text{PPc}$  are also the active sites for the reduction of formaldoxime to methylamine. In addition,





Fig. 4 Electrocatalytic performance for the CO<sub>2</sub>RR and oxime reduction reaction. (a) LSV curves of PPc, CoPPc, Co<sub>2</sub>Cu<sub>1</sub>PPc and CuPPc for the CO<sub>2</sub>RR. (b) FE(CH<sub>3</sub>OH) for the CO<sub>2</sub>RR with CoPPc, Co<sub>2</sub>Cu<sub>1</sub>PPc, CoPPc, and CoPPc-CuPPc as a function of potential. (c) Current densities for the side-reaction of HCHO reduction at -0.55 V<sub>RHE</sub> in Ar-saturated 0.1 M KHCO<sub>3</sub> containing 30 mM HCHO. (d) Free-energy diagram and adsorption configurations for the CO<sub>2</sub>RR to CH<sub>3</sub>OH on Co<sub>2</sub>Cu<sub>1</sub>PPc. (e) Adsorption energy of \*formaldoxime on the Co and Cu sites of Co<sub>2</sub>Cu<sub>1</sub>PPc (inset: the most stable adsorption configurations of \*formaldoxime). (f) LSV curves of PPc, CoPPc, Co<sub>2</sub>Cu<sub>1</sub>PPc and CuPPc for formaldoxime reduction. (g) Maximum FE(CH<sub>3</sub>NH<sub>2</sub>) with Co<sub>2</sub>Cu<sub>1</sub>PPc for the (NO<sub>3</sub><sup>-</sup> + CO<sub>2</sub>)RR and oxime reduction. Conditions: CO<sub>2</sub>RR in CO<sub>2</sub>-saturated 0.1 M KHCO<sub>3</sub>; oxime reduction in Ar-saturated 0.1 M KHCO<sub>3</sub> containing 30 mM NH<sub>2</sub>OH and 30 mM HCHO.

as shown in Fig. 4g, the formaldoxime reduction with Co<sub>2</sub>Cu<sub>1</sub>-PPc shows an optimized FE(CH<sub>3</sub>NH<sub>2</sub>) as high as 80% (details in Fig. S24a), which is about 7.1 times that of the (NO<sub>3</sub><sup>-</sup> + CO<sub>2</sub>)RR. And the current density of formaldoxime reduction is higher than that of the CO<sub>2</sub>RR and NO<sub>3</sub><sup>-</sup>RR (Fig. S24b). All of this indicates the formaldoxime reduction process is relatively easier than the NO<sub>3</sub><sup>-</sup>RR and CO<sub>2</sub>RR.

Subsequently, the formation rates of NH<sub>2</sub>OH and HCHO intermediates are investigated. Fig. 5a and b show that the production rates of NH<sub>2</sub>OH and HCHO during the (NO<sub>3</sub><sup>-</sup> + CO<sub>2</sub>)RR with CoPPc are mismatched in a wide potential range. In contrast, with Co<sub>2</sub>Cu<sub>1</sub>PPc, the formation rates of NH<sub>2</sub>OH and HCHO are enhanced at low overpotentials (Fig. 5b), becoming comparable at -0.76 V<sub>RHE</sub>, which corresponds to the peak performance for methylamine production. Interestingly, the

formation rate of NH<sub>2</sub>OH during the (NO<sub>3</sub><sup>-</sup> + CO<sub>2</sub>)RR with Co<sub>2</sub>Cu<sub>1</sub>PPc is enhanced compared with that during individual NO<sub>3</sub><sup>-</sup>RR (Fig. 5c). This suggests a possible synergetic effect between CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup> conversion, which promotes C-N coupling during the (NO<sub>3</sub><sup>-</sup> + CO<sub>2</sub>)RR.

Taking all results together, we propose an electrocatalytic-chemical-electrocatalytic mechanism of the (NO<sub>3</sub><sup>-</sup> + CO<sub>2</sub>)RR to methylamine with the Co<sub>2</sub>Cu<sub>1</sub>PPc catalyst (Fig. 5d). The electrocatalytic reduction of CO<sub>2</sub> to \*HCHO mainly occurs on the Co centers of Co<sub>2</sub>Cu<sub>1</sub>PPc, while the process of NO<sub>3</sub><sup>-</sup> reduction to NH<sub>2</sub>OH is mainly catalyzed by the Cu centers. Then, the nucleophilic attack of NH<sub>2</sub>OH on the adsorbed \*HCHO forms a formaldoxime intermediate with a C-N bond *via* a chemical process. The formaldoxime intermediate is further electro-reduced on Co centers to produce methylamine.



Fig. 5 Calculated  $\text{NH}_2\text{OH}$  and  $\text{HCHO}$  species produced during the  $(\text{NO}_3^- + \text{CO}_2)$ RR on (a) CoPPc and (b) Co<sub>2</sub>Cu<sub>1</sub>PPc. (c) Optimized activity of  $\text{NH}_2\text{OH}$  formation from the  $\text{NO}_3^-$ -RR and  $(\text{NO}_3^- + \text{CO}_2)$ RR on Co<sub>2</sub>Cu<sub>1</sub>PPc. (d) Illustration of methylamine synthesis from the  $(\text{NO}_3^- + \text{CO}_2)$ RR catalyzed by the bifunctional metal polyphthalocyanine.

In the heterometallic polyphthalocyanines, the heteronuclear metal centers are atomically dispersed and hybridized together in the same conjugated macrocyclic network. Cu sites modulate the electronic structure of Co, thereby suppressing the over-reduction of  $\text{NH}_2\text{OH}$  and  $\text{HCHO}$ . Such a unique structure enables the heterometallic polyphthalocyanines to work as bifunctional catalysts for efficient reduction of nitrate and  $\text{CO}_2$  parallelly to key intermediates for C-N coupling to the formaldehyde intermediate and its further reduction to methylamine. In addition, no urea product is observed, possibly as the spatially separated metal centers enforced by the macrocyclic ligand make the proximity of surface-adsorbed species such as  $^*\text{NO}_x/^*\text{NH}_x$  and  $^*\text{CO}_2/^*\text{CO}$  on adjacent active sites more difficult. Briefly, the special structure of Co<sub>2</sub>Cu<sub>1</sub>PPc steers the reaction toward methylamine in the  $(\text{NO}_3^- + \text{CO}_2)$ RR.

## Conclusions

We developed a polyphthalocyanine electrocatalyst with heterometal centers (Co<sub>2</sub>Cu<sub>1</sub>PPc) for the synthesis of methylamine from  $\text{NO}_3^-$  and  $\text{CO}_2$ . It shows a much higher Faradaic efficiency for methylamine production than the monometallic and nonpolymeric counterparts. We found that the Co centers in Co<sub>2</sub>Cu<sub>1</sub>PPc are the active sites for  $\text{CO}_2$  reduction to formaldehyde, and Cu sites are active for the  $\text{NO}_3^-$  reduction to hydroxylamine. The nucleophilic attack of  $\text{NH}_2\text{OH}$  on  $\text{HCHO}$  forms a formaldoxime intermediate, which is further reduced to methylamine. The overreduction of  $\text{NH}_2\text{OH}$  and  $\text{HCHO}$

intermediates is suppressed with heterometallic Co<sub>2</sub>Cu<sub>1</sub>PPc. Overall, the heterometallic centers coordinated with the conjugated macrocyclic network of polyphthalocyanine enable the efficient reduction of  $\text{NO}_3^-$  and  $\text{CO}_2$  parallelly on different active sites to the key intermediates for C-N coupling. This work provides a new class of bifunctional electrocatalysts for the synthesis of organonitrogen chemicals from  $\text{CO}_2$  and  $\text{NO}_x$ .

## Author contributions

Y. Z. conducted the characterization and electrocatalytic measurements, performed data analysis, and drafted the manuscript. R. D. conducted DFT calculations. L. L. assisted in GC-based gas-phase product analysis. C. D. and C. L. conceived the idea, devised the project, revised the manuscript, and developed the conceptual ideas. All authors were involved in the discussion and analysis of this manuscript.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the SI. See DOI: <https://doi.org/10.1039/d5sc04641f>.



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