Mechanism of C-N bonds formation in electrocatalytic urea production revealed by ab initio molecular dynamics simulation

Electrosynthesis of urea from CO2 and NOX provides an exceptional opportunity for human society, given the increasingly available renewable energy. Urea electrosynthesis is challenging. In order to raise the overall electrosynthesis efficiency, the most critical reaction step for such electrosynthesis, C-N coupling, needs to be significantly improved. The C-N coupling can only happen at a narrow potential window, generally in the low overpotential region, and a fundamental understanding of the C-N coupling is needed for further development of this strategy. In this regard, we perform ab initio Molecular Dynamics simulations to reveal the origin of C-N coupling under a small electrode potential window with both the dynamic nature of water as a solvent, and the electrode potentials considered. We explore the key reaction networks for urea formation on Cu(100) surface in neutral electrolytes. Our work shows excellent agreement with experimentally observed selectivity under different potentials on the Cu electrode. We discover that the *NH and *CO are the key precursors for C-N bonds formation at low overpotential, while at high overpotential the C-N coupling occurs between adsorbed *NH and solvated CO. These insights provide vital information for future spectroscopic measurements and enable us to design new electrochemical systems for more value-added chemicals.

The importance of artificial nitrogen fertilizer, i.e. urea, production is underpinned by the fact that these fertilizers led to about 30-50% of the crop yield increase assured food for almost half of humanity1. However, the associated processes – feedstock ammonia synthesis through Haber-Bosch, and urea synthesis – greatly rely on fossil fuel resources, both as raw materials and energy sources, which is highly unsustainable with heavy CO2 emission2. Another critical problem associated with artificial nitrogen fertilizer is the accumulation of reactive nitrogen, which accounts for algal blooms and leads to a decline in the quality of surface and ground waters3. Using renewable electricity to electrochemically convert CO2 and reactive nitrogen to urea could solve the two issues at the same time, enabling decarbonization of the nitrogen fertilizers production industry and assuring better sustainability as well as on-the-site and on-demand production of nitrogen fertilizers4-7. The most investigated nitrogen source for electrochemical urea production was ammonia and di-nitrogen; however, this incurs additional process and cost for ammonia collection and purification8-15, and shows low Faradic efficiency (FE)16. An alternative nitrogen source is nitrate/nitrite ions (NO3-/NO2-), which could improve the FE for urea production (35% on copper; over 40% on TiO2-based catalysts)17-21. An additional benefit of using nitrate/nitrite ions as the nitrogen source

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for urea production is their sourcing from wastewater, which contributes to reducing the excess of reactive nitrogen in the ecosystem.

To further improve the efficiency of urea synthesis using nitrate/nitrite ions as feedstock, the reaction mechanism for direct electrocatalytic urea production needs a better understanding, especially the C-N coupling step. C-N coupling can only happen at a narrow potential window, generally in the low overpotential region\(^{16,19,24}\). So far, the exact reaction pathways for urea formation at this narrow potential window remain an open question\(^{16,19,24}\).

Therefore, the mechanisms for C-N formation from NO\(_X\) and CO\(_2\) at earlier attempts usually adopted vacuum models; the effect of solvent and applied potentials are ignored during the calculation and were considered at a later stage by mathematical methods\(^{32,29}\). Several recent efforts involved implicit or hybrid implicit/explicit models with a few water molecules; however, these calculations might lead to inconsistent kinetic barrier values\(^{16,19,24}\).

Such C-N coupling mechanism can be investigated by first-principle-based molecular modelling because this methodology provides atomic-level insights into electrocatalytic reactions\(^{29}\). However, earlier attempts usually adopted vacuum models; the effect of solvent and applied potentials are ignored during the calculation and were considered at a later stage by mathematical methods\(^{32,29}\). Several recent efforts involved implicit or hybrid implicit/explicit models with a few water molecules; however, these calculations might lead to inconsistent kinetic barrier values\(^{16,19,24}\).

To better consider the dynamic nature of water and thermodynamics ensemble effect, as well as the impact from hydrogen bonds and electrode potentials, ab Initio Molecular Dynamics (AIMD) simulations should be adopted and give more reliable results\(^{16,19,24}\).

In this work, we performed AIMD simulations to explore the reaction mechanisms of the key steps for simultaneous electrochemical reduction of CO\(_2\) and NO\(_X\)/NO\(_2\) towards urea formation on the Cu(100) surface as a model catalyst. With the solvent and applied potential effects taken into considerations, a potential-dependent mechanism was found to account for the selective formation of urea at the appropriate potential window. A two-step coupling between 'NH' and 'CO' constitutes the C-N bond formation at low overpotential region as evidenced by careful examining different coupling intermediates and competing protonation reactions. At higher overpotential, the selectivity toward urea formation is reduced due to the enhancement of competing reactions; also, this process proceeds via different C-N coupling reaction mechanism involving desorbed CO.

Our work provides atomic mechanism of urea formation and shows excellent agreement with key experimental observation on the Cu electrode\(^{18}\). This work will stimulate the development of electrochemical methods utilizing CO\(_2\) and NO\(_3^-\)/NO\(_2^-\) to synthesize urea or more value-added compounds with C-N bond formation at ambient conditions, as well as the future design of relevant catalyst materials.

Results

Pathways toward ammonia at low overpotential

As a representative simultaneous electroreduction of CO\(_2\) and nitrite ions, the current efficiency of main products as a function of potential measured by Shibata et al. with a Cu gas-diffusion electrode, is reproduced and shown in Fig. 1\(^\text{a}\). Ammonia (NH\(_3\)) and urea (CO(NH\(_2\))\(_2\)) are the dominant products at -0.75 V vs SHE (standard hydrogen electrode), which are produced by nitrite reduction and electrochemical C-N coupling, respectively. At more negative potentials, the formation of carbon monoxide (CO) and formic acid (HCOOH) via CO\(_2\) reduction increases monotonically while production of NH\(_3\) and CO(NH\(_2\))\(_2\) continuously decreases.

We first constructed and equilibrated the electrochemical Cu (100)/water interface with various reaction intermediates. The performed AIMD simulations of the as-constructed interface were used to obtain the temperature and potential energy profiles shown in Supplementary Fig. S1. Information on the calculation of the electrode potential at these interfaces, and detailed workflow are provided in the section devoted to the Determination of Electrode Potential and Supplementary Fig. S2. The work functions used to calculate electrode potential are summarized in Supplementary Tables S1-S2. We found that our calculated electrode potential values (-0.85 - -0.59 V vs SHE) are in accordance with the experimental value (-0.73 V vs SHE) for the potential of zero charge of single crystal Cu(100) under neutral environment by Łukomska and Sobkowski\(^{35}\).

Figure 2a depicts the most relevant reaction pathways starting from NO, as well as the reaction barrier values for each step using the AIMD-derived thermodynamic integration method (as shown in Supplementary Table S3). A detailed discussion on the accuracy of the estimation of barriers could be found in Supplementary Figs. S3-S5. NO could be reduced to either NH\(_3\) or HNO; in the meantime, it also could dissociate into atomic nitrogen and oxygen\(^{36}\). We found that the formation of HNO is via a chemical step (i.e., without the direct involvement of proton and electron transfer) preceded by surface hydrogenation. Whereas NH\(_3\) is formed through an electrochemical reduction step (i.e., with the involvement of proton and electron transfer) with water molecule as the proton source; this is similar to the case of CO in CO\(_2\)/CO reduction at a small overpotential\(^{42,44}\). Dissociation of 'NO' to 'N' and 'O' with free energy barrier 0.81 eV is kinetically less favorable than protonation to HNO (0.51 eV) or to HNO\(_2\) (0.56 eV).

For further reduction steps of HNO or NO\(_2\), various intermediates were involved in different pathways. We identified three kinetic favorable pathways for NO\(_2\) reduction toward ammonia: i) 'NO' + HNO + N + NH\(_2\) + NH\(_3\) (red); ii) 'NO' + HNO + NH\(_2\) + NH\(_3\) (blue); iii) 'NO' + HNO + OH\(_2\) + NH\(_2\) + NH\(_3\) (green). Both i) and ii) pathways end with the formation of NH\(_3\), which is gradually protonated to NH\(_4\). For pathway i) the reduction starts with NO\(_2\) with the formation of N + H\(_2\)O (red in Fig. 2a). For pathway ii), the NH\(_3\) formation occurs through HNO and NH\(_2\)OH (blue). Pathway iii) shares the same precursor as ii) – HNO and bases on the formation of NH\(_2\)OH (green).

There are many possible rate-limiting steps for these three pathways. For pathways i) and ii), as shown in Fig. 2b, protonation of NH\(_2\) to NH\(_3\) via an electrochemical step is the rate-determining step with a barrier value of 0.85 eV. The dehydroxylation of NH\(_2\)OH as displayed in Fig. 2c could also be considered as the rate-determining step for
pathway i), because of a relatively high barrier value of 0.74 eV, which is comparable with that of NH protonation to NH2 considering the estimated errors.

For pathway ii), protonation of HNO and dehydroxylation of HNOH via electrochemical mechanism are facile with barriers of 0.84 eV and 0.50 eV, respectively. While for pathway iii), the successive formation of ONH2 and NH2OH through an electrochemical step is facile as indicated by barrier values of 0.47 eV and 0.41 eV, respectively. Thus, the dehydroxylation of NH2OH to NH2 has a free energy change of 0.67 eV (Fig. 2d) and is regarded as the rate-determining step. In summary, although three different pathways possess various intermediates, the kinetic barriers toward common product ammonia are very close (0.67-0.85 eV).

Since Cu(100) surface has been identified as the major active facet under similar reduction reaction conditions, we compare our results from AIMD simulations with experiments conducted on copper-based catalysts. The most significant agreement between previous experiments and our theoretical prediction is that ammonia is the major product but not N2O or N2 in neutral electrolyte. This can be explained by the ultra-low barrier of NH protonation to NH2 (0.21 eV), and such a low barrier inhibits N coupling with another N or NO to form N2 or N2O, respectively. We found that in pathway iii), NH2OH is a key intermediate toward the formation of ammonia. These results are in accordance with the recent report that NH2OH was detected as an intermediate during nitrate reduction to ammonia on copper-based materials by online differential electrochemical mass spectrometry. However, Pèrez-Gallent et al. found that hydroxylamine (NH2OH) is the final product for nitrate reduction on Cu(100) in alkaline media. One possible explanation is that this pathway is sensitive to pH as well as the applied electrode potential. To validate pathways i) and ii), determination of intermediates like NH or NH2OH via spectroscopy-based characterization is still challenging, and we believe that a combination of electrochemical measurements coupled with in situ characterization techniques as well as advanced atomic simulation methods would benefit determination of the complex reaction mechanisms.

The first C-N bond formation at low overpotential

The previous section proved that reduction of NO toward ammonia is facile at about -0.75 V vs SHE, indicating that there should be considerate amounts of various related intermediates on the catalyst surface. At the same time, if CO2 is also involved, it has been reported that ethylene starts to form on Cu(100) surface from -0.81 V vs SHE in neutral solutions. In view of these two points, there could be a potential window, within which dimerization of CO is not dominant (or even does not begin) whereas nitrogen-containing intermediates are accumulated on the surface because of the rapid reduction of NO. Keeping this in mind, we hypothesize that within this potential window, CO could couple with nitrogen intermediates and C-N bond would be formed. This hypothesis is in accordance with the previous experimental reports on the production of urea (two amide bonds) by simultaneous reduction of carbon dioxide and nitrite or nitrate ions. However, the detailed reaction mechanisms of urea formation are still absent.

The first step is to investigate the mechanisms of the coupling intermediates to form C-N bond. For carbonaceous (C-) intermediates, CO was chosen because it is a key intermediate for CO2/CO reduction, as well as it’s abundant on the Cu(100) surface at this potential due to a sluggish protonation of CO to COH. For the nitrogenous intermediates (N-), a number of candidate intermediates relevant to the NO-to-NH pathway need to be considered. Also, the protonation of N- intermediates via Eley-Rideal (ER; proton from solution) or Langmuir-Hinshelwood (LH; proton from surface adsorption) mechanism could compete with coupling reactions with CO. After considering all possible reaction pathways, including C-N coupling and protonation, the
reaction barrier values are summarized in Fig. 3a (details are given in Supplementary Table S3 and S4). These two panels indicate that for *NO and *NH, the C-N coupling is more facile than the alternative protonation via LH or ER mechanism (Fig. 3a). The snapshots of reactive trajectories for these two coupling steps are displayed in Fig. 3b-c. The calculated reaction barriers are both 0.66 eV, demonstrating relatively fast kinetics. In comparison, the coupling of *CO with *HNO, *N and *NH2 is kinetically precluded (blocked) at room temperature and protonation reactions are favored. We noticed that although the coupling of *CO and *NH was previously claimed as the rate-determining step of ammonia formation, our calculated reaction barrier is 1.15 eV, which is less favorable than protonation to ammonia via ER mechanism and could be regarded as blocked at 300 K [7,8,23].

For *NO, considering the relatively close value of protonation (0.56 eV for ER to *NOH and 0.51 eV for LH to HNO) and C-N coupling barrier (0.64 eV) and the estimated error of the adopted methodology as shown in Table S4, we investigated three possible C-N intermediates, namely, *NO-CO, *NOH-CO, and *NH-CO for the following steps towards urea formation. Similar to previous considerations, we shall compare the kinetic barrier of protonation as well as further coupling with the second *CO of these C-N intermediates. Starting from *NO-CO, it needs four successive reduction steps towards NH2-CO, as evidenced by the detailed results provided in Table S5. As shown in Fig. 3d, protonation of *NO-CO and *NOH-CO is very facile with reaction barriers of 0.12 and 0.36 eV, respectively. However, both *N-CO (to NH2-CO) and the following *NH-CO (to NH2-CO) are hard to be reduced at this potential due to the large reaction barrier. Furthermore, *NH2-CO could not be formed under this scenario since the direct coupling of NH2-CO is excluded as discussed previously. In conclusion, only *N-CO and *NH2-CO could be considered for further coupling at this stage.

The second C-N bond formation at low overpotential

To form urea, another C-N bond needs to be formed, and further couplings of the previously identified *N-CO and *NH-CO with various N-intermediates (*NO, *NH, and *NH2) to form the second C-N bond should be explored. We excluded *N and *HNO because previous discussions have demonstrated that the relatively low barrier of protonation to form NH and ONH2, respectively. As such, *N/*HNO couplings with *CO or *NH-CO are difficult to proceed with, similar to in the case of the first C-N bond formation. As for *N-CO intermediate, as shown in Supplementary Fig. S6, the coupling with N-intermediates to form the second C-N bond is less favorable (all kinetic barrier values are higher than 0.93 eV) than protonation for all of the possible precursors (*NO, *NOH, *NH, and *NH2). Therefore, *N-CO is not reactive towards urea production. For *NH-CO, the coupling barriers to form the second C-N bond are summarized in Fig. 4a, and *NH is the only intermediate that could be coupled with *CO-NH (more details could be found in Supplementary Table S5). The associated barrier value is 0.51 eV for coupling *NH with *NH-CO to form *NH-CO-NH (Supplementary Table S6), which is also lower than *NH protonation (0.85 eV), and favors coupling instead of protonation. While for *NO, *NOH, and *NH2, the barriers are relatively large and less facile than the corresponding protonation of these N-intermediates as shown in Fig.4a. Once *NH-CO-NH is formed as displayed in Fig. 4b after two consecutive coupling steps between *CO and *NH, the key intermediate experiences further protonation to urea ((NH2)2CO). Protonation of *NH-CO-NH is predicted to be facile with two barriers of 0.52 eV and 0.50 eV via the ER mechanism (Supplementary Table S7), and the step is shown in Fig. 4c.

To summarize, we found that at about -0.75 vs SHE, the kinetically favorable pathway from *NH and *CO to urea is *CO + 2*NH → *NH + CO(NH)2 → NH2CO-NH → (NH2)2CO. Each step of the C-N bond formation process has a lower kinetic barrier than protonation of NH to NH2 (0.85 eV), indicating the selectivity to urea formation is higher than, or at least comparable to, ammonia formation at such a potential. This prediction is in accordance with experimental reports by Shibata et al. that the current efficiency for urea and ammonia is 37% and 35%, respectively as shown in Fig. 1. However, it is hard to determine, which is the rate determining step and several steps might be regarded as the rate destemming steps on the pathway to urea due to the comparable values of kinetic barriers, which are actually within the range of intrinsic DFT (Density functional theory) calculation errors as well as the error range of our computations [10]. To validate the
C-N bond formation mechanism we proposed, based on the AIMD simulations, that the key intermediates like *CO-NH and *CO(NH)_2 are subject to future experimental measurements by advanced characterization techniques on well-defined systems.

**Decreased urea and ammonia production at high overpotential**

As shown in Fig. 1, the selectivity toward ammonia and urea is highly potential dependent. From -0.75 V to -1.5 V vs SHE, the current efficiency toward ammonia and urea formation continues to decrease, while CO(g) and HCOOH production are accelerated. To reveal the origins of this behavior, we introduced one lithium atom into the system and thus adjusted the potential to about -1.5 V vs SHE and employed AIMD simulations to explore the kinetics of related reaction pathways (results are summarized in Supplementary Table S8). We then explored the C-N coupling reaction via *NH and surface adsorbed *CO at the same potential because this is the key step for ammonia formation at -0.75 V vs SHE. However, the calculated reaction barrier for this surface coupling reaction step is 1.25 eV, indicating that this pathway is blocked due to a large reaction barrier at room temperature. Hence, there should be a different pathway for the C-N bond formation and urea production at such high overpotential. According to Fig. 1, as the applied electrode potential decreases, the release of gaseous hydrogen and carbon monoxide increase, which indicate the enhancement of competing hydrogen evolution and CO desorption. This could be attributed to the fact that more negative potential benefits hydrogen adsorption as Cheng et al claimed. We found that the surface adsorbed *NH is capable of coupling with non-adsorbed CO to form CO-NH with a barrier of 0.62 eV. A similar mechanism was previously proposed for CO-CHO coupling at large overpotential in CO_2 reduction. These two mechanisms are shown in Fig. 3c; namely, adsorbed *CO participates in coupling with the surface adsorbed *NH at a relatively positive potential, while at a very negative potential CO molecule in solution originating from CO desorption could directly react with *NH. Hence there is still urea production at -1.5 V vs SHE as shown in Fig. 1.

Besides NO reduction and C-N coupling, CO_2 reduction and hydrogen evolution reactions also occur at the same time under the high overpotential window, leading to a wide spectrum of products including CO(g), HCOOH and H_2 other than ammonia and urea. It is believed that these competing reactions are indispensable for explaining the experimental observation of decreased current efficiency toward urea and ammonia formation. Since the production of carbon monoxide significantly increases, it is rational to infer that reduction of CO_2 to CO/HCOOH is accelerated and these reactions
would compete with NO reduction for proton source from water molecule at the interface. Therefore, we inferred that production of ammonia slows down due to the less favorable kinetics than CO2 reduction. The surface coverage of associated NH would decrease and affect both ammonia and urea formation because of its crucial role in the reaction network. If the potential continues to become more cathodic, hydrogen evolution reaction would dominate due to a dramatically boosted the Volmer step (H+ + e− → *H)19,35. Therefore, H2(g) eventually becomes the only final product, similarly as in the case of sole CO2 reduction50.

Discussion
By adopting ab initio Molecular Dynamics simulation, which could describe the electrode potential and dynamic nature of water in the electrolyte, we identified the reaction pathways for urea and ammonia production on Cu (100) surface at the neutral solution. After exploring various combinations of coupling intermediates, we elucidated the role of NH and CO as the critical surface intermediates for C-N coupling along the urea pathway under low overpotentials. At higher overpotentials, C-N coupling proceeds with a different mechanism that is impacted by competitive CO(2) reduction, which leads to the narrow potential window for urea production. Our modelling results successfully explain the experimentally observed activity/selectivity for simultaneous reduction of CO2 and nitrogen source (nitrite/nitrate), and demonstrate that the knowledge of the electrode potential and the dynamic water structure at the same time is critical in modelling potential dependent electrocatalytic reactions. These insights in reaction mechanisms enable us to design new electrochemical systems, provide vital information for future spectroscopic measurements, and pave the way for catalyst materials to synthesize more value-added chemicals to meet future energy and environmental challenges. A new opportunity emerges: using electrolysis systems as a platform to produce a broader range of complex compounds other than simple carbon species or nitrogen-containing species to cover more aspects of the modern chemical production supply chain38,53.

Methods
Considerations of the catalyst, pH, electrode potential and starting reactants
Copper is selected as the model catalyst since it was found to display a high selectivity of urea19. Here, we simulate the Cu(100)/water interface using 32 explicit water molecules on 3×4×3 Cu(100) surface slab, because Cu(100) proved to be a dominant surface for polycrystalline copper when a considerate reductive potential is applied43. The size of chosen system was based on previous report on CO2 reduction, where also three layers of copper and around thirty water molecules were used33,34. For the selection of solution pH values, we only focus on the neutral condition. The reason is that in acidic solutions, NO3- or NO2- are involved in competing homogeneous side reactions. In alkaline solutions, surface CO2 reduction is suppressed due to the undesired carbonates generation54. At the same time, the available experimental data on the urea generation from CO2 and NO3-/NO2- were conducted.
in neutral solutions, which could serve as a key benchmark for our computation study52.

Two electrode potential windows were investigated according to Fig. 1. The first potential of interest is -0.75 V vs SHE where the current efficiency toward urea formation reached the maximum, which we refer to as the low overpotential. When electrode potential becomes more negative, the urea and ammonia production efficiency decreases monotonously which is accompanied with an increase in CO production. The high overpotential region around -1.5 V vs SHE is modelled by introducing one lithium atom into the Cu(100)/water interface.

Another consideration is the starting reactants that would simplify the problem allowing focus on the critical aspects of the reaction networks. The formation of urea needs both nitrogen and carbon source. In CO2 electrocatalysis, any deeply reduced product must be reduced to NO when the applied potential is relatively negative as the case in the current work53.4. Therefore, we adopt ‘NO and ‘CO as the starting reactants to investigate the crucial aspects of the reaction networks and explore the C-N bond formation mechanisms.

Density functional theory computations

DFT method was employed for all calculations using the Vienna ab initio Simulation Package (VASP)55–58. The projector-augmented wave pseudo-potential was utilized to treat the core electrons, while the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional of the generalized gradient approximation (GGA) was used for describing the electron interactions59. The van der Waals interactions were described using the empirical correction in the Grimme’s scheme60.61.

We carried out AIMD simulations to equilibrate the system at 300 K for over 30 ps, with a time step of 1 fs. Based on the well-equilibrated interface, the reaction barriers were estimated by thermodynamic integration based on Blue Moon ensemble method62. Both electrochemical (Eley-Rideal) and chemical (Langmuir-Hinshelwood) reaction mechanisms were considered for intermediate hydrogenation. A more detailed description of the setup of AIMD simulations and electrode potential calculations could be found in the Supporting Information section devoted to the computational method.

Data availability

Data supporting the reported findings are available in the article and Supplementary Information and Source Data file. All trajectories are deposited in the open database of Materials Cloud (https://doi.org/10.24435/materialscloud:8t-6e). Source data are provided with this paper.

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Author contributions

S.-Z.Q. and Y.J. conceived and supervised this research; X.L. designed and carried out the computations with the help of Y.J.; S.-Z.Q. and Y.J. acquired research and computational resources; Y.Z. assisted with the design of modelling system from experimental perspectives; S.-Z.Q., Y.J. and M.J. reviewed and revised the manuscript. All authors discussed results and commented on the manuscript.

Competing interests

The authors declare no competing interests.
