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Electrochemical synthesis of urea at cooperative active sites on Mo_2C grain boundary

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ABSTRACT

The design of multiple types of active sites with cooperative functions on catalyst surface holds great promise for urea synthesis, yet forming these specific sites and ensuring their functionality remain a prominent challenge. Here, we propose two types of Mo₂C grain boundaries (GBs) that feature intrinsic cooperative active sites, facilitating the coupling of C and N species and achieving efficient urea synthesis. By density-functional theory (DFT) calculations, we verify that positively charged Mo atoms on the GBs exhibit high adsorption and reduction activity for CO₂, whereas adjacent Mo atoms contribute to the activation of N₂ or NO. The cooperative effects of these active sites enables C-N coupling to proceed spontaneously on the GBs with ultralow limiting potentials ($-0.24 \sim -0.42$ V). Furthermore, analysis of the competing hydrogen evolution reaction and nitrogen reduction reaction confirms the high selectivity to generate urea on Mo₂C GBs. Our work demonstrates GB engineering as a promising strategy for urea generation through the synergistic cooperation between multiple active sites, thus paving the way towards the rational design of effective catalysts for urea electrosynthesis.

1. Introduction

Urea is not only an essential nitrogen-based fertilizer used in modern agriculture but a key raw material for chemical products such as urea-formaldehyde esters, uracil, urethanes, and barbiturates [1,2]. Ensuring sustainable and efficient production of urea is of paramount significance for the progress and well-being of human society. Currently, the predominant industrial synthesis of urea severely depends on the two-step Bosch-Meiser process to couple ammonia (NH₃) and carbon dioxide (CO₂) under harsh conditions [3–6]. However, industrial production of NH₃ is highly energy-intensive, with a significant portion of global NH₃ supply dedicated to urea synthesis, bringing about substantial carbon emissions and huge energy consumption during manufacturing, storage, and transportation processes [7]. Therefore, it is crucial to explore green and sustainable alternatives to this energyintensive urea production, particularly those driven by renewable energy sources. Electrocatalysis, which can utilize clean energy and feedstock into high-value-added chemical products, offers an eco-friendly solution for urea synthesis under mild conditions [8-10].

Utilizing greenhouse gas CO2 as a carbon source, along with abundant nitrogen (N₂) in air or nitric oxide (NO) from combustion exhaust as a nitrogen source, the electrochemical synthesis of urea represents an environmentally friendly and sustainable waste-to-energy technology. Unfortunately, it is extremely challenging to achieve both high activity and selectivity to generate urea in electrocatalysis due to the chemical inertness of feedstock gas (e.g., CO2 and N2) and the existing competition with hydrogen evolution reaction (HER) in solution [11-13]. Furthermore, the distinct nature of reactant gases requires different active sites, posing additional hurdles in catalyst design. Given the high-efficiency CO2, N2, and NO reduction achieved on various single active sites [14-16], there is potential to combine these active sites for electrocatalytic synthesis of urea [13,17–21]. Therefore, constructing multiple types of active sites with different functions on the catalyst surface is an attractive strategy to co-activate reactants, optimize intermediates adsorption, and ultimately enhance urea yield. Recently, a remarkable milestone was achieved in electrochemically synthesizing urea from N₂ and CO2, with a Faraday efficiency of 8.92 % on PdCu alloy, demonstrating the synergistic effect of bimetals [17]. Density functional theory

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Received 8 January 2025; Received in revised form 25 March 2025; Accepted 8 April 2025 Available online 11 April 2025 0021-9517/© 2025 Elsevier Inc. All rights are reserved, including those for text and data mining, AI training, and similar technologies. (DFT) calculations further unveiled that the activity of PdCu alloy originates from the positively charged Pd atoms, which promote the adsorption and activation of N₂, while the negatively charged Cu atoms facilitate CO₂ capture and conversion to CO [18]. However, identifying specific active sites and ensuring their synergistic cooperation for high-efficiency urea electrosynthesis remains a prominent challenge [22–24].

Grain boundaries (GBs), as intrinsic defects in materials, typically feature various defects and unsaturated bonds, providing multiple types of active sites and holding great potential for urea electrosynthesis [25-28]. For example, a two-dimensional (2D) Bi nanosheet with highdensity GBs profoundly enhances C-N coupling efficiency, leading to urea yield rates that are 2 and 8.2 times higher than those observed with low-density GBs and bulk Bi, respectively [28]. Recently, 2D a-Mo₂C GBs have been confirmed to contain rich localized atomic structures [29,30]. Further, our DFT calculations demonstrated that these diverse localized structures as active sites break the symmetry of CO₂ adsorption on pristine Mo_2C , thereby enhancing the activation of CO_2 [31]. Importantly, the reduced potential barriers at the GBs facilitate the C–C coupling and broaden the range of CO₂RR products. These findings sparked our scientific curiosity regarding the roles that Mo₂C GBs might play in urea synthesis, as the cooperation of these active sites holds significant promise for promoting C-N reactions by coupling CO with related nitrogen-containing species, ultimately enabling efficient urea synthesis.

Here, we addressed two experimentally reported Mo₂C GBs (referred to as 5|7I and 5|7II GBs) for urea electrosynthesis by utilizing CO₂ as a carbon source and N2 / NO as a nitrogen source. By density-functional theory (DFT) calculations, the catalytic activity and mechanism of GBs were theoretically delved for urea electrosynthesis. Firstly, the geometric and electronic structures of Mo₂C GBs were examined. Subsequently, the co-adsorption and activation of CO_2 and N_2 / NO on pristine Mo₂C and GBs were investigated and compared. Further, the reaction process for urea synthesis was explored by analyzing the activation energy of C-N coupling and the thermodynamic step diagrams. Our results demonstrate that Mo active sites on the GBs are beneficial to the reduction of CO2 to CO, while adjacent active sites favor side-on adsorption of N2 or NO molecule. The high activity of both GBs for urea synthesis is attributed to the synergistic cooperation between these active sites, which markedly lowers the activation energy of C-N coupling reactions. Lastly, the competing reactions in urea electrosynthesis were assessed, and good selectivity to yield urea was confirmed on both GBs. To the best of our knowledge, this is the first theoretical evidence for efficient urea electrosynthesis through GB engineering.

2. Computational methodology

Spin-polarized density functional theory was employed using the Vienna Ab-initio Simulation Package (VASP) [32]. The exchange-correlation potential was described using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) [33]. The electron-ion interaction was represented using the project-augmented wave (PAW) method [34]. To address van der Waals interactions, a dispersion correction was incorporated through the DFT-D3 method [35]. The plane-wave cutoff energy was set to 450 eV, with an energy and force convergence criterion of 10^{-4} eV and -0.01eV/Å, respectively. A vacuum region of 20 Å was added to prevent interference arising from interactions between periodic images. The crystal orbital Hamilton population (COHP) analysis was conducted using the LOBSTER software [36,37]. Ab-initio molecular dynamics (AIMD) simulations were conducted within the canonical (NVT) ensemble using a Nosé-Hoover thermostat. Besides, constrained DFTmolecular dynamics (cDFT-MD) simulations with the slow-growth sampling approach [38,39], were employed to evaluate the kinetic barriers of C-N coupling. The free energy profiles were derived through the integration of the potential of mean force (PMF). A stepwise increment of 0.0005 Å was applied to collective variables to facilitate the

progression of reactions. The collective variables were selected according to the distance changes between atoms involved in elementary reactions. An explicit solvent model was employed, in which the density of H_2O molecules was set to be approximately 1 g/ml. More computational details can be referred to the Supporting Information.

3. Results and discussion

Structural stability and electronic properties of Mo₂C GBs

Experimentally, 2D Mo₂C GBs have been successfully synthesized through chemical vapor deposition (CVD) [29,30]. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) observations have demonstrated that low-angle (LA) Mo₂C GBs are composed of dislocation arrays distributed in a straight line, while high-angle (HA) Mo₂C GBs exhibit dislocation cores connected end-to-end [30]. Based on these observations, we addressed two types of Mo₂C GBs in this work: One containing a dislocation structure and the other having an end-toend connection structure with pentagonal-heptagonal rings, respectively denoted as 5|7I and 5|7II GBs. Both GBs were constructed by splicing the edges of two Mo₂C nanosheets with misorientation angles of 21.8° and 32.2° [31], as shown in Fig. 1a and 1b. According to our prior DFT calculations [31], the formation energies of 5|7I and 5|7II GBs are respectively 0.52 and 0.73 eV, which fall within the formation energy region of 0.34 to 1.0 eV for common 2D MoS₂ GBs [40]. To estimate the thermodynamic stability of both GBs, they were relaxed for 10 ps at 300 K by AIMD simulations. The results show that their total energy fluctuations are minor, and the structures remain well without deformation (see Fig. S1). To further investigate the electrochemical stability, they were put in an explicit solvent at the potential of -0.7 V to hold for 10 ps at 300 K by AIMD simulations. The simulated results indicate that their structures remain undeformed and the surface is not oxidized (see Fig. S2), suggesting their good stability in the electrochemical environment.

Further, the charge distributions of both GBs were investigated using the charge density difference (CDD), as depicted in Fig. 1c and 1d. The results show that an amount of charge is transferred from Mo atoms to C atoms, and the Mo atoms adjacent to the GB lose more charges than those of the GB. According to the available literature [18], the different charge distributions of Pd and Cu atoms serve as a bifunctional role in the co-activation of CO₂ and N₂, thereby promoting C-N coupling reactions on PdCu alloys during urea synthesis. Therefore, it is expected that the diversity of charge distributions of Mo atoms on Mo₂C GBs are beneficial to the co-adsorption of CO₂ and N₂ / NO, hence providing the possibility of cooperation for the C-N coupling reaction.

Adsorption and activation of reactant gas molecules

The greenhouse gas (CO₂) and the earth-abundant or harmful gas (N₂ or NO) were considered as C and N sources for urea synthesis. The effective adsorption and activation of these gas molecules are crucial for the subsequent electrocatalytic reaction process. Therefore, the coadsorption of CO2 and N2, as well as CO2 and NO, on MO2C with and without GBs, were first addressed. Since these gas molecules should be adsorbed successively on the catalyst surface, it is essential to determine the adsorption sites for the gas molecules on these GBs. The possible active sites of the first gas molecule adsorbed on 5|7I and 5|7II GBs are marked in Figs. S3a and S4a, respectively, and the adsorption energies of CO₂ on different active sites were referred to our prior work [31]. On 5 7I GB, CO₂ is primarily physically absorbed, while N₂ and NO are expected to be adsorbed first due to chemical adsorption. From the comparison of the adsorption energy on different active sites in Fig. S3d, the most stable adsorption site for N_2 / NO is ascertained to be site "15", with the maximum adsorption energy of -1.01 and -2.65 eV, respectively. Following this, six possible adsorption sites around the pre-adsorbed N2 / NO were tested for secondary gas molecule adsorption (as shown in Fig. S3b and S3c), and CO2 displays the strongest adsorption at site "1". A similar analysis was performed for 5|7II GB, and the corresponding results are illustrated in Fig. S4. On 5|7II GB, CO₂ exhibits the stronger



Fig. 1. Atomic structures of Mo_2C GBs: (a) 5|7I GB and (b) 5|7II GB. Charge density difference (CDD) of Mo_2C GBs: (c) 5|7I GB and (d) 5|7II GB. Note that purple and brown spheres respectively denote Mo and C atoms, and the blue and red regions in (c-d) respectively represent charge accumulation and depletion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

adsorption (-1.12 eV) than N₂ (-1.02 eV), indicating that CO₂ molecule has priority to occupy the active site over N₂ molecule, and site "3" is found as the most stable site for the adsorption of secondary gas molecule (N₂) (see Fig. S4b and S4d). In contrast, the maximum adsorption energy for NO (-2.55 eV) is markedly stronger than that for CO₂. Therefore, after pre-adsorption of NO, the subsequent adsorption of NO and CO₂ were tested, and site "1" is found to be the most stable adsorption site for CO₂, as indicated by Fig. S4c and S4d. For pristine Mo₂C, CO₂ adsorption is preferential over N₂ with corresponding adsorption energies of -1.02 eV for CO₂ and -0.38 eV for N₂. Notably, the adsorption energy for NO (-2.35 eV) is stronger than that for CO₂. The co-adsorption configurations of CO₂ and N₂ as well as CO₂ and NO on both pristine Mo₂C and Mo₂C GBs are respectively illustrated in Fig. 2 and Fig. S5. Furthermore, the electrode potential may influence the adsorption behavior of the reactant gas molecules. Fig. S6 illustrates the changes in adsorption free energy for CO₂ + N₂ and CO₂ + NO on Mo₂C GBs at electrode potentials. It can be observed that the adsorption free energy slightly decreases (negative) with increasing electrode potential



Fig. 2. Adsorption structures of CO₂ and N₂ on (a) pristine Mo₂C, (b) 5/7I GB, and (c) 5/7II GB. Charge density difference (CDD) of CO₂ and N₂ adsorbed on (d) pristine, (e) 5/7I GB, and (f) 5/7II GB. (g) Partial density of states (PDOS) of CO₂ and N₂ as well as pristine Mo₂C and GBs. (h) Crystal orbital Hamilton population (COHP) of CO₂ and N₂ adsorbed on pristine Mo₂C and 5/7I and 5/7II GBs. The charge depletion and accumulation are indicated by cyan and yellow in (d-f), respectively, and the insert values represent the calculated Bader charge transferred to CO₂ and N₂. All *iso*-surfaces are set at 0.005 e/Å³. The blue, orange, and gray cures represent the *p*-orbitals of N₂, the *p*-orbitals of CO₂, and the *d*-orbitals of Mo atoms at active sites in (g), respectively. The orange and blue curves represent the COHP values for C-O and N-N bonds in (h), respectively, and the orange and blue regions represent the anti-bonding and bonding states, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(negative), indicating that high electrode potential could be beneficial to the adsorption of the reactants.

By determining the active sites and adsorption configurations of gas molecules on Mo₂C GBs, one can find that CO₂ molecule is more prone to be captured by Mo atoms at the GBs, whereas those adjacent to GBs exhibit a higher affinity for N₂ and NO adsorption, as shown in Figs. 2 and S5. It can be observed that the multiple active sites on Mo₂C GBs can separately adsorb CO₂ and N₂ / NO, making their synergistic cooperation in the C-N coupling reactions possible during urea synthesis. Additionally, the N₂ molecule is adsorbed on pristine Mo₂C through the end-on configuration, while on Mo₂C GBs, it adopts a side-on configuration. The latter typically promotes the coupling of N2 with the C source at a lower energy barrier [12,41]. Given that N₂ is more inert than NO (with the bonding energies of 941 kJ/mol for $N\equiv N$ and 639 kJ/mol for N=O), the activation of N₂ poses a greater challenge. However, once N₂ achieves a high level of activation, it is reasonable to assume that NO could also be effectively activated. Consequently, our work focuses on the co-adsorption and activation of N2 and CO2 rather than CO2 and NO on the surface of Mo₂C GBs.

As shown in Fig. 2d-2f, *N₂ (* denotes the active site) gains more charges from Mo₂C GBs (1.08 e⁻ for 5|7I GBs and 1.22 e⁻ for 5|7II GBs) than from pristine Mo₂C (0.26 e^{-}). Similarly, *CO₂ acquires more charges from Mo₂C GBs (1.11 *e*⁻ for 5|7I GBs and 1.25 *e*⁻ and 5|7II GBs) than from pristine Mo_2C (0.90 e^-). Moreover, the partial density of states (PDOS) of N₂ and CO₂, along with pristine Mo₂C and GBs (see Fig. 2g), indicate that the hybridization of the *p*-orbitals of *N₂ and *CO₂ and the d-orbitals of Mo atoms on Mo₂C GBs is greater than on pristine Mo₂C, confirming their stronger interactions. Furthermore, the increased charge transfer to *N2 and *CO2 from the substrate corresponds to weaker intra-molecular bonding, as illustrated in Fig. 2h through the crystal orbital Hamilton population (COHP) analysis. The integrated COHP (ICOHP) values further facilitate comparison, revealing that the ICOHP values for C-O bonds of *CO2 and N-N bonds of *N2 are respectively -14.54 and -21.96 eV on the pristine Mo₂C, -13.34 and -15.04eV on 5|7I GB, and -11.84 and -14.24 eV on 5|7II GB. Evidently, the C-O bonds of $*CO_2$ and the N-N bonds of $*N_2$ on Mo_2C GBs are weaker than those on pristine Mo₂C, resulting in lower activation energy for these reactants on the GBs. Therefore, the activated $*CO_2$ and $*N_2$ could facilitate their subsequent hydrogenation and urea synthesis on the GBs.

Reactivity for urea electrosynthesis on Mo₂C GBs

To explore the reaction activity for urea synthesis on Mo₂C GBs by using CO₂ and N₂, we investigated the free energy changes of each reaction step based on possible reaction pathways (see Fig. S7 for details). The electro-reaction begins with the hydrogenation of either CO₂ or N₂. As shown in Fig. 3a, the free energy change (ΔG) for CO₂ hydrogenation (0.19 eV for 5|7I GB and 0.18 eV for 5|7II GB) is lower than that for N_2 hydrogenation (0.36 eV for 5|7I GB and 0.29 eV for 5|7II GB), making the formation of *COOH more favorable. During the second protoncoupled electron transfer (PCET) step, *COOH continues to be transformed into *CO by releasing an H_2O molecule with ΔG of -0.10 eV for 5|7I GB and 0.21 eV for 5|7II GB, whereas the Δ G for hydrogenation of N₂ is higher, hindering the formation of *NNH species. This signifies that the key intermediate *CO can be readily generated on the GBs. Subsequently, *CO can undergo a C-N coupling reaction with N2 or its hydrogenated species. As depicted in Fig. 3a, the ΔG for *CO coupling with N₂ to form *NCON is less than that for N₂ hydrogenation, manifesting that the *NCON formation is thermodynamically favorable. Meanwhile, the DFT-MD calculations with slow-growth sampling were performed to evaluate the reaction kinetics of *CO and *N₂ coupling, and the related results are shown in Fig. 3b. The free energy profiles of C-N coupling are obtained by thermodynamic integration over force profiles. The activation energies for *CO and *N2 coupling to form *NCON species are 2.35, 0.56, and 0.74 eV on pristine Mo₂C, 5|7I GB, and 5|7II GB, respectively. Therefore, the C-N coupling of *CO and *N2 as precursors is thermodynamically and kinetically feasible on Mo₂G GBs. Evidently, the activation energies on Mo₂C GBs are significantly lower than those on pristine Mo₂C. This reduced activation energy for C-N coupling on Mo₂C GBs can primarily be attributed to the side-on adsorption configuration of *N₂, which exhibits a weaker N-N bond compared to pristine Mo₂C. Specifically, the N-N bond lengths are measured at 1.131, 1.305, and 1.311 Å for *N₂ on pristine Mo₂C, 5|7I GB, and 5|7II GB, respectively. Due to the considerably high activation energy required to form *NCON species on pristine Mo₂C, the subsequent PCET process will not be considered in the following discussion.



Fig. 3. Free energy change diagram of urea synthesis from (a) CO_2 and N_2 , (c) CO_2 and NO. Free energy profiles and representative structures at the initial state, transition state, and final state for the reaction of (b) $*N_2 + *CO \rightarrow *NCON$, (d) $*NH_2 + *CO \rightarrow *NH_2CO$.

After the formation of *NCON species on 5|7I and 5|7II GBs, urea synthesis proceeds with a four-step hydrogenation process. As depicted in Fig. 3a, the hydrogenation of *NCON to form *NCONH is exothermic, with ΔG of -0.78 for 5|7I GB and -0.55 eV for 5|7II GB. Upon hydrogenation of the *NCONH species, two possible reaction pathways may occur. (1) Distal pathway: the H atom connected to the N atom is hydrogenated to form *NCONH2 species, with endothermic accompanied by ΔG of 0.23 and 0.42 eV on 5|7I and 5|7II GBs, respectively. (2) Alternating pathway (more favorable): the H atom is added to the bare N atom to form *NHCONH, with ΔG values of -0.06 and 0.03 eV for 5|7I and 5|7II GBs, respectively. In the more favorable pathway, the chemical bond between Mo atoms and N atoms in the *NHCONH species remains robust, with Mo-N bond lengths measuring 1.60 Å for 5/7I and 1.66 Å for 5 7II GBs, as presented in Figs. S8 and S9. Therefore, breaking one side of the Mo-N bond to form the *NHCONH2 species is endothermic, and this process occurs as the potential-determining step (PDS), with ΔG values of 0.42 eV for 5|7I GB and 0.37 eV for 5|7II GB. Finally, urea (*NH₂CONH₂) is produced by the hydrogenation of *NHCONH₂, which entails increasing ΔG values of 0.03 and 0.10 eV for 5|7I and 5|7II GBs, respectively. Notably, the limiting potentials (U_{I}) for urea synthesis are -0.42 V on 5|7I GB and -0.37 V on 5|7II GB, both of which are less negative than those for Pd-Cu (-0.64 V) [17] and MBenes (Mo_2B_2) : -0.49 V, Ti₂B₂: -0.65 V, Cr₂B₂: -0.52 V) [42], indicating the superior electrocatalytic reactivity of Mo₂C GBs.

Based on the above discussion, we further explored the co-reduction of NO and CO₂ into urea on Mo₂C GBs along with possible reaction pathways (see Fig. S10 for details). This investigation significantly broadens the potential applications of these GBs in urea synthesis. The initial PCET process selectively hydrogenates *NO instead of hydrogenating *CO₂, as indicated by Δ G for forming *NOH species (0.03 eV on 5|7I GB and -0.19 eV on 5|7II GB). For the following PCET steps on 5|7I GB, they are all exothermic, and the continuous hydrogenation of *NOH to form *N + H₂O is energetically most advantageous, as indicated by Fig. 3c. Similarly, for 5|7II GB, the dehydration of *NOH to form *N is also most favorable. Afterwards, hydrogenation of *NH to form *NH₂ is hindered due to high Δ G (0.46 eV for 5|7I GB and 0.63 eV for 5|7II GB). By contrast, the hydrogenation of CO₂ is easier (corresponding to Δ G of 0.01 eV for 5|7I GB and 0.09 eV for 5|7II GB), leading to the formation of *COOH. In comparison with the formation of *COOH + *NH₂ via alternating hydrogenation, the hydrogenation of *COOH to form *CO is more feasible, corresponding to Δ G of -0.02 and 0.31 eV for 5|7II and 5|7II GBs, respectively. The following PCET step via the pathway of *CO + *NH + H⁺ + e⁻ → *CO + *NH₂ requires relatively high Δ G values of 0.24 and 0.40 eV for 5|7I and 5|7II GBs, respectively. This increased energy can be attributed to the shorter distance of *NH from the GB surface (1.33 Å for 5|7I GB and 1.31 Å for 5|7II GB), which necessitates more energy to achieve a larger distance required for *NH₂ formation, measured at 1.56 Å for 5|7I GB and 1.77 Å for 5|7II GB. Notably, the PDS for co-reduction of CO₂ and NO to *CO and *NH₂ occurs here, with *U*_L of -0.24 (5|7I GB) and -0.40 V (5|7II GB).

In the co-reduction of CO₂ and NO, the C-N coupling reaction occurs in the reaction process of *NO + *CO, *N + *CO, *NH + *CO, or *NH₂ + *CO [43]. Among these C-N coupling reactions, using *CO and *NH₂ as precursor exhibits the lowest activation energy (see Figs. S11 and 3d), mainly due to the weakest adsorption energy compared to others (the adsorption energy for *NO + *CO, *N + *CO, *NH + *CO, and $*NH_2$ + *CO is -2.04, -2.96, -2.43, and -1.23 eV on 5|7I GB, and -2.05, -2.66, -2.40, and -1.28 eV on 5|7II GB, respectively). As shown in Fig. 3d, the activation energy for the reaction $*NH_2 + *CO \rightarrow *NH_2CO$ is 0.89, 0.12, and 0.21 eV on pristine Mo₂C, 5|7I GB, and 5|7II GB, respectively. This implies that the first C-N coupling reaction (*NH₂ + $*CO \rightarrow *NH_2CO$) is more favorable on Mo₂C GBs compared to pristine Mo₂C. Urea is synthesized through the coupling of *NH₂CO with second *NH₂ species (see Fig. 4). The activation energy for the second C-N coupling (*NH₂ + *NH₂CO \rightarrow *NH₂CONH₂) is 0.13 eV on 5|7IGB and 0.40 eV for 5/7II GB. Overall, urea synthesis via CO₂ and NO on Mo₂C GBs is feasible, and the adsorption structures of the intermediates along the most favorable pathway are presented in Figs. S12 and S13.

In addition, the free energy profile for urea synthesis was evaluated using the implicit solvation model integrated in VASPsol. The free energy change diagram exhibits a similar trend regardless of whether implicit solvation is considered, indicating that the solvent effect is negligible (see Fig. S14). Finally, since the computational hydrogen electrode (CHE) model with the constant-charge method used above does not accurately describe variations in electrode potential, which may result in inaccuracies in simulating electrocatalytic reactions, we re-examined the free energy profile of urea synthesis along the most



Fig. 4. Free energy profiles and representative structures at the initial state, transition state, and final state of the reaction for $*NH_2 + *NH_2CO \rightarrow *NH_2CONH_2$ on (a) 5/71 and (b) 5/71I GBs.

favorable pathway using the constant-potential method. As shown in Fig. S15, at the potential of 0 V, the ΔG values for each elementary step in urea synthesis are slightly lower compared to those predicted by the CHE model (see Fig. 3a and 3c). However, no significant difference can be found in the overall results, demonstrating that it should be reliable to employ the CHE model to investigate the electrocatalytic urea synthesis on Mo₂C GBs.

Mechanism of urea electrosynthesis on Mo₂C GBs

Based on the aforementioned analysis, the electrochemical synthesis mechanism of urea on Mo₂C GBs is summarized in Fig. 5. For urea synthesis from N₂ and CO₂, the process be divided into four stages (see: Fig. 5a): (i) Co-adsorption and activation of N₂ and CO₂; (ii) Reduction of $*CO_2$ to *CO through two PCET steps; (iii) Coupling of *CO and $*N_2$ to form *NCON species; (iv) Four PCET steps for *NCON species, including distal and alternating pathways, which is similar to available research [9,17,43]. As shown in Fig. 5b, for urea synthesis by NO and CO₂, the initial step also involves co-adsorption onto the catalyst surface. The following process is deemed to be the co-reduction of *NO and *CO₂, starting with the conversion of *NO into *NH, followed by the transformation of *CO₂ into *CO, and concluding with the hydrogenation of *NH to *NH₂. Afterward, the third process involves the first C-N coupling reaction to form *CONH₂. In the same way, another *NH₂ may be generated through the similar reduction reaction, followed by the second C-N coupling with *CONH₂, ultimately resulting in urea production.

Competing reactions with urea electrosynthesis on Mo₂C GBs

Lastly, we examined the possible competing reactions during the electrochemical synthesis of urea. As discussed previously, the high activation of *N₂ on Mo₂C GBs may favor the nitrogen reduction reaction (NRR), which could compete with urea synthesis. Besides, hydrogen evolution reaction (HER) would also compete with urea synthesis under aqueous solution conditions. Therefore, these competing reactions are our primary concern in the electrochemical synthesis of urea. Fig. 6a compares the first hydrogenation step of urea synthesis with NRR. It is evident that the ΔG for urea synthesis is lower than that for the NRR, indicating that the urea synthesis is more favorable than the NRR at the initial stage. Additionally, the potential impacts of NRR and HER are also evaluated on the urea synthesis *via* CO₂ and N₂ / NO remarkably exceed those for NRR and HER on 5|7I and 5|7II GBs. This signifies that

the urea synthesis reaction is predominant, while the competing reactions are effectively suppressed during the electrochemical synthesis of urea. Moreover, the same verification was performed using the constpotential method, as shown in Fig. S16. It can be seen that at the potential of 0 V, the free energy changes of the relevant reactions decrease, but the trend remains unchanged, with urea synthesis still being the dominant process.

4. Conclusions

In summary, we performed comprehensive DFT calculations to systematically investigate the two types of Mo₂C GBs (i.e., 5|7I and 5|7II GBs) for the urea electrosynthesis from CO $_2$ and N $_2$ / NO. The geometric and electronic structures show that positively charged Mo atoms on the GBs exhibit strong adsorption capability for CO₂ molecule, while adjacent active sites are prone to capturing N₂ / NO molecule. For the coreduction of CO2 and N2 to yield urea, the reactant gas molecules exhibit higher activation on Mo₂C GBs compared to pristine Mo₂C. This corresponds to a significant decrease in the activation energy for the C-N coupling reaction, which falls from 2.35 eV on pristine Mo₂C to 0.56 eV on 5|7I GB and 0.74 eV on 5|7II GB. Furthermore, considerably low limiting potentials were disclosed for urea synthesis on 5|7I GB (-0.42) V) and 5|7II GB (-0.37 V). In the urea generation via the co-reduction of CO2 and NO, *NO can initially be reduced to *NH2 and then coupled with *CO to form *NH2CO, followed by the second coupling of *NH2 and *NH₂CO to form urea with the limiting potentials -0.24 V on 5|7I GB and -0.40 V on 5|7II GB. Correspondingly, the activation energies for the first C-N coupling on 5|7I and 5|7II GBs are respectively 0.12 and 0.13 eV, while the second C-N coupling requires 0.21 and 0.40 eV. Finally, a comparison of the competing reactions, including both NRR and HER during the electrochemical process, demonstrated good selectivity to generate urea on the GBs. Therefore, Mo₂C GBs hold great potential for urea generation, harnessing the synergistic cooperation of distinct active sites. Our work not only highlights the importance of GB engineering in achieving efficient C-N coupling reactions but also opens a new avenue towards designing and developing high-performance electrocatalysts for urea synthesis.

Fig. 5. Reaction mechanism of urea synthesis by co-reduction of (a) N₂ and CO₂, (b) NO and CO₂.

Fig. 6. (a) Free energy change of the first hydrogenation step in urea synthesis and NRR. (b) Comparison of the limiting potentials for the syntheses of urea, ammonia, and hydrogen on Mo₂C GBs.

CRediT authorship contribution statement

Yuxing Lin: Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. Weihua Yang: Validation, Software, Methodology, Formal analysis. Meijie Wang: Validation, Investigation, Data curation. Lei Li: Writing – review & editing, Software, Formal analysis, Data curation. Yameng Li: Validation, Investigation, Formal analysis, Data curation. Xing Chen: Software, Data curation. Rao Huang: Writing – review & editing, Investigation, Data curation. Yuhua Wen: Writing – review & editing, Visualization, Supervision, Resources, Project administration, Methodology, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2025.116139.

Data availability

Data will be made available on request.

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