Urea is an important raw material in the chemical industry and is widely used as a nitrogen source in chemical fertilizers. The current industrial urea synthesis not only requires harsh reaction conditions, but also consumes most of the NH3 obtained through artificial synthesis. The conversion of N2 and CO2 into urea through electrochemical reactions under ambient conditions represents a novel green urea synthesis method. However, the large-scale promotion of this method is limited by the lack of suitable electrocatalysts. Here, by means of density functional theory computations, we systematically study the catalytic activity of three experimentally available two-dimensional metal borides (MBenes), Mo2B2, Ti2B2, and Cr2B2 toward simultaneous electrocatalytic coupling of N2 and CO2 to produce urea under ambient conditions. According to our results, these three MBenes not only have superior intrinsic basal activity for urea formation, with limiting potentials ranging from −0.49 to −0.65 eV, but also can significantly suppress the competitive reaction of N2 reduction to NH3. In particular, 2D Mo2B2 and Cr2B2 possess superior capacity to suppress surface oxidation and self-corrosion under electrochemical reaction conditions, rendering them relatively promising electrocatalysts for urea production. Our work paves the way for the electrochemical synthesis of urea.
Urea, also known as carbamide \((\text{CO(NH}_2)_2\)) or urea, is the first organic compound produced from inorganic raw materials. Because its nitrogen content is high (46%) and is readily converted to ammonia \((\text{NH}_3)\) in the soil, urea is now the most commonly used nitrogen fertilizer in the world, and more urea is manufactured by mass than any other organic chemical. While over 90% of produced urea is used as fertilizer, it also has important applications in other fields. For example, urea is a raw material for the manufacture of urea-formaldehyde and urea-melamine-formaldehyde resins. Urea-containing creams are used as topical dermatological products to promote skin hydration, and large amounts of urea are used for the synthesis of barbiturates. Since \(\text{NH}_3\) produced by the hydrolysis of urea can react with nitrogen oxides \((\text{NO}_x)\) to produce nitrogen, an increasingly important application of urea is to reduce \(\text{NO}_x\) impurities in exhaust gases from diesel and lean-burn natural gas engines. Therefore, maintaining a sustainable and efficient urea industry is of great importance for the development of human society.

At present, the production of urea in the industry is accomplished mainly through the reaction of \(\text{NH}_3\) and \(\text{CO}_2\) under high temperature and high pressure. However, this method is not only relatively energy-consuming but also relies on some complex types of equipment and multicycle processes to improve the conversion efficiency. Remarkably, urea production consumes ~80% of the global \(\text{NH}_3\), which is mainly derived from the artificial nitrogen reduction reaction \((\text{NRR})\). Nevertheless, \(\text{N}_2\) is a stable molecule, and substantial input energy is required for dissociation of the strong \(\text{N}≡\text{N}\) triple bond, making \(\text{N}_2\) reduction thermodynamically and kinetically very difficult. The industrial NRR is still dominated by the traditional Haber–Bosch process, which converts \(\text{N}_2\) and \(\text{H}_2\) into \(\text{NH}_3\) with the assistance of iron-based catalysts under harsh conditions. However, the very large energy consumption and the large amount of the greenhouse gas \(\text{CO}_2\) emitted by the Haber–Bosch process have aggravated the energy and environmental problems. Therefore, people have been striving for green ammonia synthetic techniques that can be carried out under mild conditions.

Compared to the Haber–Bosch process, the production of \(\text{NH}_3\) through the electrochemical NRR represents a more efficient and green strategy as it can utilize electricity generated from renewable energy sources and protons directly from water. However, separating and purifying \(\text{NH}_3\) from an aqueous electrolyte is very difficult, which is detrimental to its further application. Furthermore, most current studies mainly focus on \(\text{N}_2\) electrochemical reduction to \(\text{NH}_3\), while further processing of the product is rarely considered. Recently, Jouy et al. realized \(\text{C}−\text{N}\) coupling and the production of acetonitriles with a high rate and selectivity by using \(\text{NH}_3\) as a nitrogen source. More interestingly, Comer et al. demonstrated that during photocatalytic fixation on the surface of \(\text{TiO}_2\), \(\text{N}_2\) can have a strong interaction with carbon substitution sites that present as surface-bound radicals, implying the feasibility of direct formation of \(\text{C}−\text{N}\) bonds from the coupling of \(\text{N}_2\) and carbon-based reagents. Inspired by these pioneering works, Chen et al. recently successfully coupled \(\text{N}_2\) and \(\text{CO}_2\) in \(\text{H}_2\text{O}\) to produce urea using an electrocatalyst consisting of \(\text{Pd-Cu}\) alloy nanoparticles on \(\text{TiO}_2\) nanosheets, which opens a new avenue for urea production under mild conditions. However, in addition to the high price, precious metal-based alloy catalysts usually suffer from ambiguous active sites and easy corrosion. Therefore, for the development of emerging electrochemical urea synthesis, inexpensive and efficient electrocatalysts that can fix \(\text{N}_2\) and \(\text{CO}_2\) together are highly desirable.

In the past decade, the application of two-dimensional (2D) materials in the field of electrocatalysis have received much attention due to their large specific surface area and more exposed active sites. For example, Li et al. theoretically demonstrated that 2D transition metal carbides, namely MXenes, are capable of catalyzing the conversion of \(\text{CO}_2\) into hydrocarbons. However, the surface metal atoms of MXenes are easily passivated by some functional species (e.g., OH, F, O), thereby degrading the catalytic activity. Recently, several 2D transition metal borides (MBenes), which are boron analogs of MXenes, have also been realized experimentally. In contrast to MXenes, MBenes can be stabilized without the presence of surface passivation groups. Therefore, MBenes provide an ideal platform for the exploration of the catalytic behavior of boron-containing surfaces. Some recent theoretical studies have demonstrated that several types of MBenes could present good activity and selectivity for the NRR. Motivated by the regulated layered configuration and excellent electrical conductivity of MBenes, we explored whether the direct coupling of \(\text{N}_2\) and \(\text{CO}_2\) to produce urea could be realized on some specific MBenes. In this work, by means of density functional theory (DFT) computations, we show that the electrochemical synthesis of urea on the basal planes of three experimentally realized MBenes, including 2D \(\text{Mo}_2\text{B}_2\), \(\text{Ti}_2\text{B}_2\), and \(\text{Cr}_2\text{B}_2\) is thermodynamically and kinetically favorable. Remarkably, the competitive NRR can be significantly overwhelmed on these three MBenes, suggesting good selectivity. Especially, the surface oxidation/degradation problem can be avoided on the surfaces of \(\text{Mo}_2\text{B}_2\) and \(\text{Cr}_2\text{B}_2\), endowing these two MBenes with intrinsic activity, selectivity, and a large reaction region toward electrochemical urea synthesis.

**Results**

**Structural properties and stability of MBenes.** Figure 1 shows the schematic structure of a 2D \(\text{M}_2\text{B}_2\)-type MBene. Unlike many ordinary 2D materials (e.g., graphene, \(\text{MoS}_2\), MXenes) that possess a hexagonal lattice, our three studied 2D MBenes all present a rectangular lattice with the space group \(\text{Pmma}\) (No. 51), resulting in an in-plane structural anisotropy. The unit cell of a 2D \(\text{M}_2\text{B}_2\)-type MBene consists of two metal atoms and two B atoms, and each metal atom or B atom is connected to six neighboring atoms.
forming a buckled bilayer structure with metal atoms on the uppermost surface. Compared to MXenes, in which the surface metal atoms bind to three carbon or nitrogen atoms, the higher coordination number of surface metal atoms in M₂B₂-type MBenes endow them with distinct stability and properties. The optimized lattice parameters and representative bond lengths of Mo₂B₂, Ti₂B₂, and Cr₂B₂ MBenes are summarized in Supplementary Table 1. Moreover, the electronic band structure computations demonstrated that these three MBenes are all metallic (Supplementary Fig. 1), which is beneficial for their electrocatalytic activity. The above results achieved good agreement with previous studies.

Good stability is a prerequisite for the wide utilization of a catalyst. We thus first assessed the stability of 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ MBenes before revealing their catalytic activity toward urea formation. As shown in Supplementary Fig. 2, no imaginary modes are found in the phonon spectra of the three MBenes, which is indicative of good kinetic stability. The elastic constants of the three monolayers presented in Supplementary Table 2 all meet the criteria for a rectangular 2D structure (Cubic >0, C₆₆ >0) indicating that they are mechanically stable. Moreover, we also performed first-principles molecular dynamics (FPMD) simulations to examine the thermal stability. According to the diagrams presented in Supplementary Fig. 3, no obvious structural deformation can be observed in the structures of the three MBenes after 10 ps FPMD simulations at 300 K, suggesting good thermal stability.

**Mechanism of electrochemical urea synthesis.** To date, the reaction mechanism for electrochemical N₂ and CO₂ coupling to produce urea has only been proposed by Chen et al. As shown in Fig. 2, the entire reaction can be divided into four stages, namely, the adsorption of N₂ and CO₂, the reduction of *N₂ to *CO, the coupling of *N₂ and *CO into *NCON, and the hydrogenation of *NCON to urea. Specifically, effective adsorption of N₂ and CO₂ on the surface of the catalyst is the primary condition for electrochemical urea production. Moreover, the adsorbed N₂ should not be reduced to NH₃, or at least the limiting potential for urea formation (U²⁰⁰⁺) should be lower than that of NH₃ formation (U²⁺) to guarantee a high selectivity. Once N₂ is adsorbed, the coadsorbed CO₂ should be effectively and selectively reduced to *CO. Then, instead of being released or further reduced, the generated *CO should move to the top of the three M₂B₂-type MBenes, we followed the above-discussed reaction mechanism. The free-energies of reaction intermediates of electrochemical urea production on Mo₂B₂, Ti₂B₂, and Cr₂B₂ were then computed. The optimized atomic configurations of various intermediates along the reaction pathway are displayed in Supplementary Fig. 4, and the corresponding free energy profiles are summarized in Fig. 3.

**Electrochemical reactivity of MBenes toward urea production.** We first investigated the adsorption of N₂ and CO₂ on the
surfaces of the three MBenes. For the adsorption of N₂, both side-on and end-on configurations were considered. According to our computations, the side-on adsorption of N₂ on the bridge site of two metal atoms is preferred for all three MBenes (Supplementary Fig. 4). This is because the back-donation of electrons from the d-orbitals of metal atoms to the π* orbitals of N₂ could be facilitated by side-on adsorption. The adsorption energies of N₂ ($\Delta E_{ads}$) on 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ are $-0.93$, $-1.27$, and $-0.85$ eV, respectively. Due to the strong interaction between N₂ and the three MBenes, the bond length of N₂ is enlarged from 1.10 Å to 1.21, 1.22, and 1.20 Å on 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. Once N₂ is adsorbed, the accommodation of a CO₂ molecule on its neighboring bridge site is also feasible, with adsorption energies ($\Delta E_{CO}$) of $-1.04$, $-1.65$, and $-1.07$ eV for 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. Remarkably, the adsorbed CO₂ is pronouncedly bent due to the formation of chemical bonds between C and metal atoms. Overall, the above results vividly reveal that both N₂ and CO₂ can be strongly adsorbed and effectively activated on the surface of our three chosen MBenes.

After disclosing the adsorption behavior of N₂ and CO₂, we next assessed the feasibility of *CO₂ reduction to *CO on the surface of the three MBenes in the presence of adsorbed N₂. Generally, the electoreduction of *CO₂ to *CO initiates with the hydrogenation of one O atom through a PCET step, resulting in the formation of a *COOH species. According to our computations, this step is endothermic with a $\Delta G$ of 0.24, 0.22, and 0.21 eV for 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. Upon the second PCET, the *COOH species can be transformed to a *CO species by releasing a H₂O molecule, which is endothermic by 0.10 eV for 2D Mo₂B₂ but exothermic by $-0.11$ and $-0.08$ eV for 2D Ti₂B₂ and Cr₂B₂, respectively. Therefore, the key intermediate *CO can be feasibly generated on the surfaces of the three MBenes. The adsorption energies of *CO species on 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ are $-0.69$, $-1.53$, and $-0.94$ eV, respectively, which are all higher than that of Pd-Cu catalyst ($-0.62$ eV)23. Due to the low CO yield of Pd-Cu catalyst, we can expect that the *CO desorption can be significantly suppressed for three 2D MBenes, which could facilitate the following coupling process.

As revealed by Chen et al.23 the most important intermediate for urea formation is the tower-like *NCON species, which can be directly produced from the coupling of *CO and *N₂. We thus explored the feasibility of forming the *NCON species on the surfaces of the three MBenes using the CI-NEB method. As shown in Supplementary Fig. 5, the coupling of *N₂ and *CO into *NCON is exothermic by $-0.10$ and $-0.18$ eV on 2D Mo₂B₂ and Cr₂B₂, respectively, indicating that the formation of the *NCON species on these two MBenes is energetically favorable. In contrast, due to the relatively strong binding strength of the *CO species, the formation of *NCON on Ti₂B₂ is slightly endothermic by 0.06 eV. Remarkably, the kinetic barriers for the formation of *NCON on 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ are 0.58, 0.81, and 0.71 eV respectively, which are comparable to or even lower than that of the Pd-Cu catalyst (0.79 eV)23, indicating that the coupling of *N₂ and *CO on these three MBenes is kinetically feasible.

Once the *NCON species is formed, the formation of urea becomes very straightforward, although there exist different sequences of hydrogenation on the two N atoms. Remarkably, the hydrogenation of *NCON to *NCONH via a PCET is exothermic for all three MBenes with a $\Delta G$ of $-0.09$, $-0.76$, and $-0.12$ eV for Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. Notably, we also considered the hydrogenation of the O atom but found that it is relatively endothermic. When the second H is added to *NCONH, two possible reaction pathways may occur. One is the distal pathway in which the second H is added to the hydrogenated N atom in the last step to form the *NCONH₂ species, and the other is the alternative path in which the second H is added to the bare N atom to form *NHCONH species. According to our computations, the formation of the distal product *NCONH₂ is endothermic by as high as 0.88, 0.93, and 1.02 eV for 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. In contrast, the formation of the alternative product *NHCONH is 0.68, 0.70, and 0.83 eV lower in energy than that of the distal product for 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. As a comparison, the distal product is preferred by the Pd-Cu catalyst23. Additionally, we noted that at this stage, the chemical bonding between metal atoms and N atoms is still robust, while the N–N length in *NHCONH is enlarged to 2.35, 2.34, and 2.33 Å for 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. Due to the breaking of one M–N bond, the third PCET step to form *NH₂CONH is considerably endothermic, with a $\Delta G$ of 0.49, 0.65, and 0.52 eV for 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. Since the fourth PCET step to form *NH₂CONH₂ is exothermic for all three M₂B₂ monolayers, the formation of the *NH₂CONH₂ species was identified as the potential-limiting step, and the corresponding $U_{urea}$ were computed to be $-0.49$, $-0.65$, and $-0.52$ V for Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. Remarkably, the $U_{urea}$ of three MBenes are comparable to or even lower than that of the Pd-Cu catalyst ($-0.64$ V), which is indicative of superior electrocatalytic reactivity toward urea formation. Moreover, the adsorption energies of *NH₂CONH₂ on 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ are $-1.28$, $-1.55$, and $-1.21$ eV, respectively, which are lower than that of the Pd-Cu catalyst ($-1.68$ eV)23, indicating that the formed urea molecule can be easily released, especially when electrochemical reactions are carried out in flow cells.

For computational simplicity, the above results on electrochemical steps were all obtained by assuming that the catalyst is charge neutral, and thus, the Fermi-level of the catalyst would change with the variation in adsorbed reaction species. However, in real electrochemical reactions, electron transfer between the catalyst and the electrode to match the Fermi-level of the catalyst with the applied electrode potential. In a recent theoretical study, Kim et al.40 revealed that the surface charge can have a substantial effect on the electrochemical activity of graphene-based materials. To this end, we also performed grand-canonical DFT computations to investigate the effect of surface charge on the electrocatalytic reactivity of the three MBenes toward urea formation. Supplementary Fig. 6 presents the free energy of all reaction intermediates of urea formation computed using the constant-potential method (CPM), and those computed from the constant-charge method (CCM) are also listed for comparison. Remarkably, the energy difference between the two methods is within the range of 0.1 eV for all three MBenes, which is similar to the values found in bulk materials but much lower than that of graphene. The less pronounced charge effect on MBenes in comparison to graphene should be attributed to greater thickness.

Discussion

Electrocatalytic selectivity of CO₂ reduction on MBenes. The above results demonstrated that the electrochemical production of urea could be feasible on the surfaces of 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂. However, at present we still cannot claim that these three 2D MBenes are qualified catalysts for urea production as some important issues concerning the selectivity are still pending. First, as we discussed above, the *CO species is the key intermediate for the entire reaction. Although we demonstrated that the formation of *CO on the surfaces of the three studied MBenes is feasible via the intermediate *COOH, the transfer of a first proton/electron pair to CO₂ could also lead to the formation of *CHO, which is
a key intermediate of formate. Therefore, knowing whether CO₂ can be selectively reduced to *CO is very important. To address this concern, we first computed the binding energy of the *OCHO species on three MBenes, and found that the binding energy of *OCHO is generally higher than the binding energy of *COOH. However, this does not mean that the formation of *OCHO is preferred. As revealed by previous studies⁴¹,⁴², many transition metal catalysts bind the *OCHO species more strongly than the *COOH species, but they all have CO rather than formate, as the major product. Therefore, predicting the selectivity of *CO formation solely based on thermodynamics computations is actually not reliable.

As revealed by Cheng et al.⁴³, the selectivity of CO₂ reduction is essentially controlled kinetically, and the formation of *COOH and *OCHO can be achieved via either the Eley–Rideal (ER) mechanism by accepting a H atom from water or via the Langmuir-Hinshelwood (LH) mechanism by accepting a surface-bound H atom (Fig. 4A). To obtain some deep insight into the selectivity, we also constructed explicit liquid/solid interfaces for all three MBenes by adding a water layer on their surfaces (Supplementary Fig. 7), and both the ER and LH mechanisms were considered for the formation of *COOH and *OCHO. As shown in Fig. 4b–d, for the formation of the *COOH species, the ER mechanism is preferred with kinetic barriers of 0.38, 0.31, and 0.32 eV for the 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂, respectively. In contrast, the formation of the *OCHO species entails much large kinetic barrier via either the ER mechanism or the LH mechanism. Therefore, on the surfaces of our three chosen 2D MBenes, CO₂ would be dominantly reduced to *CO rather than formate.

The second concern regarding the *CO species is whether it could be further reduced to *CHO or *COH under the working conditions of urea production. To address this question, we also computed the free energy of *CO reduction to *CHO and *COH for 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ (Supplementary Table 4). The limiting potential for the formation of *CHO or *COH on the three MBenes is at least −1.22 V, which is much higher than the Uₚرأٜa. Therefore, the formation of *CHO or *COH would be significantly suppressed under the working potential of urea production.

Moreover, we are also aware of that there would be competition between *CO adsorption and adsorption/dissociation of H₂O molecule in the realistic aqueous environment. According to our results, the kinetic barrier for the direct dissociation of one H₂O molecule on 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ is 0.63, 0.53, and 0.72 eV, respectively (Supplementary Fig. 8), indicating the formation of surface bounded *H and *OH is also feasible for three MBenes. While the *H species can serve as the proton source to react with the reaction intermediates via the LH mechanism, there could exist the adsorption competition between *CO and *OH species on three MBenes. Therefore, we then plotted the curves of equilibrium surface coverages of these two species as a function of electrode potential by performing microkinetic simulations. As shown in Supplementary Fig. 9, the population of *OH and *CO is potential dependent. Specifically, the surfaces of three MBenes would be predominately covered by OH* species under low electrode potential. When the electrode potential is higher than −0.31, −0.64, and −0.22 V, respectively, the coverage of CO* on 2D Mo₂B₂, Ti₂B₂ and Cr₂B₂ begins to increase, while the coverage of OH* begins to decrease. Since the critical potential of *CO/*OH adsorption for each MBene is lower than the respective Uₚرأٜا, it can be expected that surface active sites of 2D MBenes, especially Mo₂B₂ and Cr₂B₂, would be mainly covered by *CO rather than *OH under working potentials.

**Electrocatalytic selectivity of N₂ reduction on MBenes.** As reported by previous studies³⁷,³⁸, many 2D MBenes have basal
plane activity for N₂ electroreduction to NH₃. Would the adsorbed N₂ molecule also be reduced to NH₃ on our three chosen M₂B₂-type MBenes? To address this question, we investigated the thermodynamics of the electrochemical NRR on 2D Mo₂B₂, Ti₂B₂, Cr₂B₂ to get some deep insight. As shown in Supplementary Fig. 10, the electrochemical NRR on all three M₂B₂ monolayers is feasible, with \( U_{\text{L}}^{\text{NH}_3} \) values of \(-0.79, -0.71, \) and \(-0.65 \) V, respectively. Encouragingly, for all three MBenes, \( U_{\text{L}}^{\text{NH}_3} \) is higher than \( U_{\text{L}}^{\text{NH}_2} \), suggesting that the formation of the NH₃ can be greatly suppressed on these three MBenes.

Since kinetic factors play an important role in determining the selectivity, we further computed the kinetic barriers of elementary steps of N₂ reduction to urea for three 2D MBenes and compared with those of N₂ reduction NH₃. Especially, both ER and LH mechanisms were considered for the electrochemical steps. As presented in Supplementary Figs. 11–13, for all three 2D MBenes, the non-electrochemical step of *NCON formation has the biggest kinetic barrier, which is 0.53, 0.77, and 0.70 eV for Mo₂B₂, Ti₂B₂, Cr₂B₂, respectively. Note that the kinetic barriers of *NCON formation predicted from explicit solvent model are quite close to those predicted from implicit solvent model. As a comparison, the first electrochemical step of N₂ reduction to NH₃, namely N₂ reduction to NNH, already has a relatively big kinetic barrier, which is 0.78, 0.80, and 0.76 for 2D Mo₂B₂, Ti₂B₂, Cr₂B₂, respectively (Supplementary Fig. 14). Therefore, the urea synthesis is also kinetically favorable on these three 2D MBenes.

**Pourbaix diagrams of MBenes.** Finally, another concern that also needs to be addressed is the electrochemical stability of the three MBenes. Although no evidence yet confirm the existence of functional groups on experimentally realized MBenes, we wondered whether the bare surfaces of MBenes could be covered by *OH groups in aqueous solution under working conditions. To answer this question, we constructed surface Pourbaix diagrams of the three MBenes to reveal the most stable surface configurations under different equilibrium potentials and pH values (the computational details are given in Supplementary Methods). As shown in Fig. 5, when the electrode potential is 0 V vs SHE, the basal plane of the 2D Mo₂B₂ is fully covered by *O species independent of the pH value, whereas the basal planes of the 2D Ti₂B₂ and Cr₂B₂ are covered by *O and *OH groups in a strong acid environment. When an electrode potential is applied, the hydrogenation of *O and *OH becomes energetically favorable on the surfaces of all three MBenes. In particular, the minimum potentials required to remove the surface *O/*OH species at pH = 0 (\( U_R \)) are \(-0.37, -1.04, \) and \(-0.31 \) V for the 2D Mo₂B₂, Ti₂B₂, and Cr₂B₂ monolayers, respectively. It is worth noting that the \( U_R \) of 2D Mo₂B₂ and Cr₂B₂ is less negative than the respective \( U_{\text{L}}^{\text{NH}_2} \), indicating that these two MBenes could possess superior electrochemical stability against surface oxidation under working conditions. In sharp contrast, the \( U_R \) of 2D Ti₂B₂ is far more negative than its \( U_{\text{L}}^{\text{NH}_2} \) and even \( U_{\text{L}}^{\text{NH}_3} \). As the electrode potential of urea production on the 2D Ti₂B₂ should not exceed the \( U_{\text{L}}^{\text{NH}_3} \) to guarantee a high selectivity, the surface of the...
2D Ti$_2$B$_2$ would inevitably be occupied by $^\ast$OH/$^\ast$O species under working conditions, resulting in decreased reactive sites on the basal plane.

Besides the stability of active surfaces, whether the catalyst itself would corrode under electrochemical conditions also needs to be addressed$^{46,47}$. Taking advantage of the fact that the formation energies are transferable between energy reference systems, we further plotted the whole Pourbaix diagram of the three 2D MBenes as a function of pH and potential at standard conditions to identify their stability window in aqueous solutions by directly combining Gibbs free energies from DFT computations with experimental arbitrary aqueous states. As shown in Fig. 6, a wide passivation region can be identified for Mo$_2$B$_2$ ($pH < 7.08$) and Cr$_2$B$_2$ ($pH < 7.22$) at the potential of $–0.49$ V and $–0.52$ V, respectively. Using the electrolyte of Pd–Cu catalyst ($pH = 6.8$)$^{33}$ as a reference, both 2D Mo$_2$B$_2$ and Cr$_2$B$_2$ can maintain structure integrity under working conditions due to high barriers for solid–liquid phase transformations. In sharp contrast to 2D Mo$_2$B$_2$ and Cr$_2$B$_2$, 2D Ti$_2$B$_2$ has a narrow passivation region ($pH < 2.26$) when subjected to an external potential of $–0.65$ V. At high $pH$ region, Ti$_2$B$_2$ would be transformed into Ti(OH)$_3$, indicating that Ti$_2$B$_2$ would be easily corroded under working conditions of urea synthesis. Therefore, 2D Ti$_2$B$_2$ is not a qualified electrocatalyst for urea formation due to its low electrochemical stability.

Activity origin of MBenes toward urea production. Due to the good reactivity, selectivity, and stability, 2D Mo$_2$B$_2$ and Cr$_2$B$_2$ have been identified as promising electrocatalysts for urea synthesis. However, at present, the activity origin of these two MBenes is not yet clear. It is known that the activity of an electrocatalyst is essentially governed by its electronic structure. Therefore, in order to get some deeper insights into the specialty of MBenes for urea synthesis, we further computed their electronic density of states (DOS) at the Fermi level and compared with those of some other experimentally realized 2D metallic materials, including four bare MXenes (Ti$_3$C$_2$, Mo$_2$C, Ti$_2$C$_2$, Mo$_2$C$_2$) and two transition metal chalcogenides (1T-MoS$_2$, VS$_2$). As shown in Supplementary Fig. 15, the DOS per atom of MXenes are generally much higher than those of 2D Mo$_2$B$_2$ and Cr$_2$B$_2$, implying stronger metallicity and more active surfaces of MXenes. However, this does not mean that MXenes have better electrochemical activity than MBenes, because the active surfaces of MXenes are known to be easily passivated in solvents$^{27–29}$. Interestingly, the DOS of Ti$_2$B$_2$ are quite close to those of Mo$_2$C and Mo$_2$C$_2$, which could explain the instability of Ti$_2$B$_2$ in aqueous solution. Remarkably, the DOS of Mo$_2$B$_2$ and Cr$_2$B$_2$ are significantly higher than those of 1T-MoS$_2$ and VS$_2$ that are actually inert to urea production according to our test computations. Therefore, the good activity and stability of 2D Mo$_2$B$_2$ and Cr$_2$B$_2$ should be attributed to their moderate metallicity.

To summarize, on the basis of comprehensive DFT computations, we have systematically explored the potential of utilizing the three experimentally realized MBenes, Mo$_2$B$_2$, Ti$_2$B$_2$, and Cr$_2$B$_2$, as electrocatalysts for urea synthesis. The activity, selectivity, and stability of the three MBenes under aqueous conditions were carefully studied. Our computations demonstrated that all three MBenes can adsorb N$_2$ and CO$_2$ on their basal planes, and the adsorbed CO$_2$ can be easily reduced to $^\ast$CO. Afterwards, the key intermediate $^\ast$NCON can be formed via the coupling of $^\ast$N$_2$ and $^\ast$CO, which can be further reduced to urea via four PCET steps. The limiting potentials of urea formation for our three studied MBenes are in the range of $–0.49$ to $–0.65$ eV, which are comparable to that of the Pd–Cu alloy catalyst. In particular, it is found that 2D Mo$_2$B$_2$ and Cr$_2$B$_2$ can prevent the problems of active sites blockage and self-corrosion, while 2D Ti$_2$B$_2$ not only has its surface active sites occupied by $^\ast$OH and $^\ast$O groups, but also could be easily corroded under reaction conditions. Therefore, 2D Mo$_2$B$_2$ and Cr$_2$B$_2$ can serve as promising catalysts for urea production, which can be attributed to their moderate metallicity. Our work provides a clear roadmap for the design of electrocatalysts for simultaneously fixing N$_2$ and CO$_2$ to produce urea, which could promote more experimental and theoretical efforts on developing 2D electrocatalysts for this challenging reaction.

Methods

DFT computations. Our DFT computations based on first-principles were performed via the Vienna ab initio simulation package (VASP)$^{48}$. The ion-electron interactions were described with the projector-augmented plane-wave (PAW) method$^{49}$. Exchange-correlation potentials were expressed by Perdew–Burke–Ernzerhof (PBE) functional with the generalized gradient approximation (GGA)$^{49}$. A 460 eV cutoff energy for the plane wave expansion was adopted in all the computations. A Monkhorst-Pack k-points setting of $3 \times 3 \times 1$ and $15 \times 15 \times 1$ was used to sample the 2D Brillouin zone for geometry optimizations and electronic structure computations, respectively. We set the $x$ and $y$ directions parallel and the $z$ direction perpendicular to the layer plane, and adopted a vacuum layer length of 20 Å in the $z$ direction. The systems were relaxed until the energy and force reaching the convergence threshold of $10^{-3}$ eV and $0.01$ eV/Å.

The phonon spectra were computed using the density functional perturbation theory (DFPT), as implemented in the Phonon code$^{51}$. The ab initio molecular dynamic (AIMD) simulations were performed using the NVT ensemble. The Nosé–Hoover method simulations last 10 ps with a time step of 1.0 fs$^{51}$. The solvation effects in aqueous solution were considered with the Poisson–Boltzmann implicit solvation model solvation model as implemented in VASP (VASP-sol), where the dielectric constant of water was taken as 80$^{53}$. The climbing-image nudged elastic band (CI-NEB) method$^{54}$ as implemented in VASP was used to obtain the kinetic barriers.

The grand-canonical DFT computations, which allow the number of electrons to adjust automatically at a fixed electron chemical potential, were performed using the PBE functional as implemented in JDFTx code$^{55}$ with a cutoff energy of 20 Hartree. The JDFTx code combines electronic DFT with classical DFT and continuum models of liquids for first-principles computations of electrochemical systems. The charge-asymmetric nonlocal determined local electric (CANDLE)$^{56}$ solvation model as implemented in JDFTx was utilized for describing the electrolyte. Other numerical parameters, including k-point sampling, convergence criteria, etc. are similar to the VASP computations.

Free energy computations. To compute the free energy change ($\Delta G$) of each elementary step of electrochemical urea synthesis, we adopted the computational hydrogen electrode (CHE) model developed by Nørskov et al.$^{57–58}$ according to which the $\Delta G$ of an electrochemical reaction is computed as:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T S$$

(1)

where $\Delta E$ is the DFT computed reaction energy, $\Delta E_{ZPE}$ and $S$ are the zero-point energy difference and the entropy difference between the adsorbed state and the gas phase, respectively, and $T$ is the temperature (298.15 K, in our work). For adsorbed reaction intermediates, their $E_{ZPE}$ and $S$ are obtained via vibrational frequencies computations with harmonic approximation and neglecting contributions from the slab, while for molecules these are taken from the NIST database. Moreover, in accordance with the CHE model, the effects of electrode potential ($U$) and pH can be treated as an energy shift to free energy change in the electrochemical steps:

$$\Delta G_{U} = -UE$$

(2)

$$\Delta G_{pH} = -k_B T \ln 10 \times pH$$

(3)

where $k_B$ is Boltzmann constant. In this work, the value of pH was assumed to be zero in free energy computations.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files. All of the other data are available from the corresponding author upon reasonable request.

Code availability

The computational codes used in this work are available from the corresponding author on reasonable request.

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Author contributions
Y.L. designed the research, X.R.Z., X.C.Z., and Y.J. demonstrated the initial idea and collected all the data. X.R.Z. and Y.L. wrote the paper and all authors commented on it.

Competing interests
The authors declare no competing interests.

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Correspondence and requests for materials should be addressed to Y.L.

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