ABSTRACT: Excessive accumulation of carbon dioxide in the atmosphere has become a serious environmental problem due to the increasing consumption of fossil fuels in modern society. Reasonably reducing CO₂ in the atmosphere has become a new research hotspot. Electrocatalytic CO₂ reduction reaction (CO₂RR) offers an appealing strategy to reduce the atmospheric CO₂ concentration and to produce value-added chemicals simultaneously. In this paper, two-dimensional (2D) N-decorated graphene (NG)-supported bimetallic trimers (Fe₂M@NG) were designed as triple-atom catalysts (TACs). Theoretical calculations showed that Fe₂M@NG can effectively activate CO₂, and among the 23 TACs examined, Fe₂Ir@NG not only has a good catalytic activity for CO₂RR (limiting potential is 0.49 V for CH₄ formation) but also limits the competing side reaction of the hydrogen evolution reaction (HER). Our theoretical study not only further extends the triple-atom catalysts, but also opens a new door to boost the sustainable CO₂ conversion.

1. INTRODUCTION

For centuries, the utilization of fossil fuels, coal, oil, and natural gas has led to the rapid development of human society.¹⁻³ However, the ever-increasing energy demands and serious environmental problems require the “optimization” of these traditional energy sources.⁴ The massive consumption of these carbonaceous substances results in the continuous increase and accumulation of carbon dioxide (CO₂) in the atmosphere.⁵ There are mainly three strategies to prevent increasing atmospheric CO₂ concentration: prohibition of CO₂ release, CO₂ storage, and CO₂ conversion.⁶ Among them, the CO₂ conversion technology has attracted the attention as the most promising approach to slow down or even reverse the rising trend of atmospheric carbon dioxide concentration.⁷⁻⁸ The electrochemical CO₂ reduction reaction (CO₂RR) can directly convert CO₂ into high value-added chemicals and fuels,⁹⁻¹¹ and renewable electricity can be used for this electrocatalytic process, resulting in a “net-zero emission” sustainable development.¹² As early as the 1990s, Hori et al. demonstrated the ability of different pure metal catalysts for the electrochemical reduction of CO₂, providing a solid foundation for subsequent CO₂RR.¹³ However, CO₂ molecules are chemically inert and the hydrogen evolution reaction (HER) competes fiercely with CO₂RR, and it is challenging to design suitable CO₂RR electrocatalysts with low limiting potential, high current density, high selectivity, and low cost.¹⁴ N-C-based materials have attracted attention because of their high-temperature resistance, acid and alkali resistance, poison resistance, and environmental protection.¹⁵ Compared to the low activity of pure carbon materials,¹⁶ on the one hand, the N-doped carbon materials as a support can provide stable anchoring sites for the metal atoms and thus endow the system with the characteristics of high stability, selectivity, and low coordination state;¹⁷ on the other hand, its strong interactions with the supported metal atoms can regulate the electronic structure of the catalyst¹⁸ and thus enhance the adsorption of CO₂ and facilitate CO₂RR.¹⁹ The single-atom catalysts (SACs) were considered as the minimum use of metal,²⁰⁻²³ and expansively, double-atom catalysts (DACs)²⁴⁻²⁷ and triple-atom catalysts (TACs)²⁸⁻³³ have gained enormous attention from both theoretical and experimental aspects owing to their synergistic effect and tunable composites in the metal dimers or trimers. For example, the experimentally obtained uniform Ru₃ clusters stabilized by nitrogen species (Ru₃/CN) were found to exhibit excellent catalytic activity for the oxidation of alcohols.²² Ma and collaborators fabricated Pt₃ clusters on a core-shell nanodiamond@graphene (ND@G) hybrid support.
which inhibits the side reactions and enhances catalytic performance in the direct dehydrogenation of n-butane at a low temperature (450 °C) toward olefin products with a selectivity >98%.33

Inspired by the theoretical finding that the stable Fe₃@NG (iron trimer-embedded N-decorated graphene) exhibits high catalytic activity to convert CO₂ through the C₂ and C₃ pathways and considering the large space of mediating the combination and electronic coupling of the bimetallic trimers, we explored the stability and catalytic performance of 23 Fe-based bimetallic TACs (Fe₂M@NG) for CO₂ reduction to C₂ products by means of first-principles calculations and elucidated that the Fe₃Ir@NG has excellent catalytic activity for the electroreduction of CO₂ to CH₄ with a small limiting potential of 0.49 V and can also inhibit the competing hydrogen evolution reaction (HER). Our theoretical explorations provide an effective approach for designing bimetallic trimers of high-performance for electrocatalyzing CO₂ reduction.

2. COMPUTATIONAL METHODS

All of the spin-polarized density functional theory (DFT) calculations were carried out using the Vienna Ab initio Simulation Package (VASP).34 The exchange−correlation functional was described by the Perdew−Burke−Ernzerhof (PBE) parameterization of the generalized gradient approximation (GGA).35 The cutoff energy of 500 eV was adopted. The van der Waals interactions were described using the empirical correction in the Grimme scheme (DFT + D3).36 The convergence parameters of geometric optimization of the maximum force and energy were designated as 0.01 eV/Å and 10⁻⁴ eV, respectively. The Brillouin k-point grid was sampled using a 2 × 2 × 1 γ centered Monkhorst−Pack scheme.37 To weaken the interaction between the layers, a 20 Å vacuum layer was applied. The binding energy (Eₜ) of Fe₂M@NG based on Fe₂@NG was determined by the following equation

\[ E_b = E_{Fe_2@NG} + E_M - E_{Fe_2M@NG} \]

where \( E_M \) represents the energy of a single metal atom, \( E_{Fe_2M@NG} \) and \( E_{Fe_2@NG} \) are the energies of Fe₂M@NG and Fe₂@NG, respectively. The free energy \( G \) was calculated based on the hydrogen electrode (CHE) model proposed by Nørskov and colleagues38,39

\[ G = E + G(T) \]

where \( E \) is the reaction energy, which can be directly obtained from the DFT calculation, \( G(T) = E_{ZPE} - TS \), where \( E_{ZPE} \) and \( S \) are the zero-point energy and entropy, respectively, which can be obtained by calculating the vibration frequencies.39 \( T \) is 298.15 K.40 The calculated values of gas molecules and intermediates are presented in Tables S1 and S2, respectively. Free energy change (\( \Delta G \)) of the elementary reaction represents the free energy difference between the product and the reactant (\( \Delta G = G_{product} - G_{reactant} \)).41 The limiting potential (\( \eta \)) of the entire reduction process is determined by the potential limiting step, which has the most positive (\( \Delta G_{TS} \)), as computed by \( \eta = \Delta G_{TS}/F \).42

3. RESULTS AND DISCUSSION

3.1. Structure and Stability of Fe₂M@NG. A 7 × 7 graphene supercell doped with six N atoms, forming a hole structure similar to that of a pyridine hole, as shown in Figure 1a, was taken as the support for bimetallic trimers.17 The optimized configurations of the 23 TACs examined are displayed in Figure S1, and the geometric parameters are given in Table S3. The binding energies were in the range of 1.25–7.70 eV (Figure 1b). With similar treatment in ref17, we performed a first-principles molecular dynamics (FPMD) simulation for Fe₂Zn@NG, whose binding energy is the smallest among the 23 Fe-based TACS, in the NVT ensemble with a temperature of 500 K, a time step of 0.5 fs, and the total time scale of 10 ps. The Fe₂Zn@NG can maintain its original structure through the 10 ps’ FPMD simulation at 500 K (Figure S2), indicating the high thermal stability in Fe₂Zn@NG and other bimetallic TACs.

3.2. CO₂ Adsorption. The capture of CO₂ molecules on the catalyst is the first step in the CO₂RR process.43 Due to the strong interaction between CO₂ and the catalyst, the C–O–C angle of the adsorbed CO₂ in the most stable configuration on these TACs is reduced to 121.36°–139.78° compared to 180° of the isolated CO₂ molecule. We denoted the O of CO₂ closer to the TAC as O₂, and the other as O₁. The lengths of the C–O₁ and C–O₂ bonds were elongated to 1.20–1.26 and 1.29–1.45 Å, respectively, compared with 1.18 Å of free CO₂. For comparison, C–O₁ and C–O₂ bonds are 1.21 and 1.33 Å for the adsorbed CO₂ on Fe₃@NG. The adsorption energy (\( E_{ads} \)) of CO₂ was estimated by the following formula

\[ E_{ads} = E_{*CO_2} - E_* - E_{CO_2} \]
where $E_{\text{CO}_2}$, $E_\text{ads}$, and $E_{\text{CO}_2}$ represent the energies of CO$_2$-adsorbed Fe$_2$M@NG, clean Fe$_2$M@NG, and a free CO$_2$ molecule, respectively. The $E_{\text{ads}}$ values on these stable TACs ranged from $\sim$3.21 to $\sim$0.86 eV, and the adsorption energy of CO$_2$ on Fe$_3$@NG was calculated to be $\sim$1.57 eV, the same as the value reported in ref 17. The charge density difference of the CO$_2$-adsorbed Fe$_2$M@NG (Figure 2) showed that the electron depletion (cyan) is around bimetallic trimers, suggesting that the metal trimers donate electrons to the CO$_2$, and Bader charge analysis confirmed that the electrons are transferred from Fe$_2$M@NG to CO$_2$ by 0.57–0.98 e$^-$. The DOS (density of states, Figure S3) clearly shows the couplings between the $d$ orbitals of the transition metal and the molecular orbitals of CO$_2$ near the Fermi level. The above results indicate that the TACs well activate the adsorbed CO$_2$, which is beneficial to facilitate CO$_2$ activation and reduction.

### 3.3. CO$_2$ Reduction Pathways

To find the optimal CO$_2$RR pathway, the free energies of the reaction over these TACs were calculated. The reaction pathways of all catalysts are given in Table S3, and the $\Delta G$ of each elementary step is illustrated in free energy diagrams (Figures 3 and S4–S8). The CO$_2$ electroreduction reaction involves multiple electron transfers.
transfer paths, and the general form is $\text{CO}_2 + n\text{H}^+ + ne^- \rightarrow \text{products} + \text{H}_2\text{O}$. In the formula, $n$ is usually equal to 2, 4, and 8, and the corresponding products are $\text{CO}/\text{HCOOH}$, methanol, and methane. The $\text{C}_1$ products and pathways are discussed in the following subsections, and the potential limiting steps (PLSs) and limiting potentials ($\eta$) of our examined TACs are illustrated in Table S4.

### 3.3.1. First Proton-Coupled Electron Transfer (PCET) Process

For $n = 1$, the first proton-coupled electron transfer (PCET) process involves the hydrogenation of the C or O atom. We calculated the free energies of the first hydrogenation of $\text{CO}_2$ in Figure S4. Therefore, the reaction pathway in this study was along $\text{*CO} \rightarrow \text{M} + \text{H} + \text{(O1/C2/O2)}$, i.e., hydrogenation occurs at different positions (O1, C, O2 atoms). After structural optimization, we noticed that it is easier to form $\text{OCOH}$ on the five Fe$_2$M@NG (M = Co, Ni, Rh, Pd, Re), whose free energy changes are 0.16, 0.16, 0.44, −0.16, and 0.24 eV, respectively. $\text{OCHO}$ is favored to be generated over two Fe$_2$M@NG (M = Cr, Mn) with $\Delta G$ values of −0.44 and −0.34 eV, respectively. In addition, on the other 16 Fe$_2$M@NG (M = Sc, Ti, V, Cu, Zn, Zr, Nb, Mo, Ru, Hf, Ta, W, Os, Ir, Pt), protons preferentially react with O2 atom, thereby promoting breaking of the O1C–O2 bond. Therefore, compared with other products, the free energy for forming $\text{*CO} + \text{*OH}$ on these TACs exhibits a downhill trend ($-0.42, -1.15, -0.45, -1.12, -0.67, -0.55, -0.64, -0.85, -1.42, -0.90, -0.69, -0.81, -0.71, -0.72, -0.74, and -0.61$ eV, respectively).

### 3.3.2. $\text{CO}_2$ Reduction to $\text{CO}$

After the first hydrogenation of $\text{*CO}_2$, the intermediates ($\text{*CO} + \text{*OH}, \text{*OCHO}$, and $\text{*OCOH}$) became the targets of the next proton–electron pair attack. Based on our computations, the following intermediates may be formed in the subsequent hydrogenation process: $\text{*COH} + \text{*OH}$ (M = Sc), $\text{*CHO} + \text{*OH}$ (M = Cr, Cu, W), $\text{*CO}$ (after releasing a water molecule, M = Ti, V, Co, Ni, Zn, Y, Zr, Nb, Mo, Ru, Hf, Ta, Os, Ir, Pt), and $\text{*OCHOH}$ (M = Mn, Rh, Re). The free energies of releasing the adsorbed CO were in the range of 0.92–2.62 eV; thus, the strong interaction between CO(g) and the TACs (Ti, V, Co, Ni, Zn, Y, Zr, Nb, Mo, Ru, Pd, Hf, Ta, Os, Ir, Pt) makes these TACs suffer CO poisoning; however, strong adsorption is beneficial to further hydrogenation of *CO on the other hand.

### 3.3.3. $\text{CO}_2$ Reduction to $\text{CH}_3\text{OH}(g)$

Regarding the reduction of $\text{CO}_2$ to $\text{CH}_3\text{OH}(g)$, we will continue the discussion based on the above results. For the third hydrogenation, the $\text{*COH} + \text{*OH}$ intermediate on the Fe$_3$Sc@NG released a water molecule to form the $\text{*COH}$ intermediate. The $\text{*CO}$ species on the TACs may further form $\text{*CHO}$ (M = Ti, V, Zn, Y, Nb, Mo, Ru, Pd, Hf, Ta) or $\text{*CHO}$ (M = Zr, Os, Ir, Pt). The $\text{*OCHOH}$ on Fe$_2$M@NG (M = Mn, Rh, Re) may also be converted into $\text{*COH}$ (M = Re) or $\text{*CHO}$ species (M = Mn, Rh) by releasing an H$_2$O molecule. The $\text{*CHO} + \text{*OH}$ species on Fe$_2$M@NG (M = Cr, Cu, W) were further reduced to $\text{*CHOH} + \text{*OH}$ (M = Cu, W) and $\text{*CH}_2\text{O} + \text{*OH}$ (M = Cr). From the point of energy calculations, these hydroxyl intermediates will remain until the final hydrogenation into $\text{H}_2\text{O}$. For the fourth hydrogenation, $\text{*CHOH}$ (M = Sc, Ti, V, Zn, Y, Zr, Nb, Mo, Ru, Hf, Ta, Os, Ir, Pt), $\text{*CH}_2\text{O} + \text{*OH}$ (M = Cr), $\text{*CH}_3\text{OH} + \text{*OH}$ (M = Cu, W), and $\text{*CH}_2\text{O} + \text{*OH}$ (M = Mn, Zr, Rh, Re) will be formed on the Fe$_2$M@NG. Subsequently, these intermediates will be further reduced to $\text{*CH}_3\text{OH}$ (M = Sc, Ti, V, Zn, Y, Zr, Nb, Mo, Ru, Hf, Ta, Os, Ir, Pt) and $\text{*OH}$ (M = Cu, W, Cr) on Fe$_2$M@NG. For the final hydrogenation, $\text{*CH}_3\text{OH}(g)$ (M = Sc, Ti, V, Zn, Y, Zr, Nb, Mo, Ru, Pd, Hf, Ta, Re, Os, Ir, Pt) and $\text{H}_2\text{O}$ (M = Cu, W, Cr) will be formed. Moreover, the Fe$_2$M@NG (M = Cr, Cu, Rh, Pd, Ir) have small limiting potentials (0.76, 0.75, 0.55, 0.76, 0.60 V, respectively) in the pathway for $\text{CH}_3\text{OH}$ formation. Their PLSs in the generation of $\text{CH}_3\text{OH}(g)$ are $\text{*OH} + (\text{H}^+ + e^-) \rightarrow \text{H}_2\text{O}$ ({$\text{*CO} + \text{*OH}$ + (H$^+$ + e$^-$)} → $\text{CHO} + \text{*OH}$, $\text{*CHOH} + (\text{H}^+ + e^-)$ → $\text{CH}_2\text{OH}$, $\text{*COH} + (\text{H}^+ + e^-)$ → $\text{CHOH}$, and $\text{*CHOH} + (\text{H}^+ + e^-)$ → $\text{CH}_3\text{OH}$, respectively. In comparison, the $\eta$ to form $\text{CH}_3\text{OH}(g)$ over the Fe$_2$M@NG is 1.09 eV (PLS: $\text{CHOH} + \text{*CHOH}$, see Table S4 and Figure S8), largely because $\text{COH}$ is adsorbed on the hollow position of the Fe$_3$ cluster, making it unsuitable to attach H to C of $\text{COH}$.

### 3.3.4. $\text{CO}_2$ Reduction to $\text{CH}_4(g)$

The first few elementary steps are the same for the formation of $\text{CH}_4(g)$ and $\text{CH}_3\text{OH}(g)$; we thus mainly discuss the variant hydrogenating steps. For these Fe$_2$M@NG (M = Sc, Ti, V, Co, Ni, Zn, Y, Nb, Mo, Ru, Pd, Hf, Ta), the hydrogenation of $\text{*COH}$ follows the pathway of $\text{*C} \rightarrow \text{*CH} \rightarrow \text{*CH}_2 \rightarrow \text{*CH}_3 \rightarrow \text{*CH}_4(g)$ to generate $\text{CH}_4(g)$; the $\text{*COH}$ intermediates on the three Fe$_2$M@NG (M = Os, Ir, Pt) will be converted into $\text{CH}_4(g)$ as follows, which is further hydrogenated to form $\text{CH}_3(g)$ and then follows the pathway: $\text{*CO} \rightarrow \text{*CHOH} \rightarrow \text{*CH} \rightarrow \text{*CH}_2 \rightarrow \text{*CH}_3 \rightarrow \text{*CH}_4(g)$. On the Fe$_3$Cr@NG and Fe$_2$W@NG, the pathways are $\text{*CH}_3\text{O} + \text{*OH} \rightarrow \text{*OH} + \text{*CHO} \rightarrow \text{*OH} + \text{*OH} \rightarrow \text{H}_2\text{O}$ and $\text{*CHOH} + \text{*OH} \rightarrow \text{*CH}_3\text{OH}$. 

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**Figure 4.** (a) Variation of limiting potentials of Fe$_2$M@NG catalysts for $\text{CO}_2$ reduction to $\text{C}_1$ products with respect to the $\text{CO}_2$ adsorption strength, and (b) comparison of the adsorption energies of *CO$_2$ and *H on Fe$_2$M@NG.
→ *CH₂*OH → *CH₂* + *OH → *OH → *H₂O*, respectively. The three Fe₂M@NG (M = Sc, Ni, Ir) have small limiting potentials (0.71, 0.77, 0.49 V) in producing CH₄(g), and the PLSSs are *CH₂* + (H⁺ + e⁻) → CH₄(g), *CO* + (H⁺ + e⁻) → *COH* and *CHO* + (H⁺ + e⁻) → *CHOH*, respectively. Overall, for CO₂RR on the 23 bimetallic Fe₂M@NG catalysts, the Fe₂Ir@NG has the smallest limiting potential (η = 0.49 V) on the path toward CH₄ generation (*→*CO₂ → CO + *OH → *CO → *CHO → *CHOH → *CH₂ → *CH₂ → CH₄(g)) among the three C1 conversion routes (Figure 3), lower than the η value of the Fe₂@NG at the same level of theory (Figure S8, η = 0.79 V).

3.4. Essential Analysis of Catalytic Performance.

Previous studies reveal that an ideal catalyst should provide moderate adsorption strength for all reactants, intermediates, and products. Therefore, we evaluated the relationship between the limiting potential of the C1 pathways over Fe₂M@NG and the CO₂ adsorption energy (Figure 4a). The results revealed that there is a volcano relationship between the limiting potentials of the C1 pathways and the CO₂ adsorption energies. By comparison, we found that six Fe₂M@NG have moderate E_ad for CO₂ (ranging from −1.40 to −1.13 eV) and have smaller η (0.77, 0.75, 0.55, 0.76, 0.70, and 0.49 V for Ni, Cu, Rh, Pd, Re, and Ir, respectively) compared with the Fe₂@NG (η = 0.79 V, E_ad = −1.57 eV). As the main competitive reaction of CO₂RR, the hydrogen evolution reaction (HER) also consumes proton–electron pairs (H⁺ + e⁻), we considered the HER activity of the Fe₂M@NG. We first calculated the E_ad of *H* on Fe₂M@NG and compared with the E_ad of *CO₂* (Figure 4b) and found that on the Fe₂M@NG (M = Rh, Ni, Pd, Mn, Pt), whose η values are lower than 0.79 V of Fe₂@NG, the E_ad of *H* is more negative than that of CO₂, indicating that it is not conducive for the progress of CO₂RR on these TACs. However, the Fe₂Ir@NG has a stronger interaction with *CO₂* than *H*, and the ΔG (0.94 eV) for the HER (Figure S9) is much greater than the maximum ΔG for CO₂RR toward CH₄(g) (0.49 eV). Thus, the Fe₂Ir@NG has high selectivity for CO₂RR.

According to the density of states (Figure S3), compared to the case of Fe₂@NG, in bimetallic TACs, the coupling between M and Fe₂ weakens or strengthens the hybridization with CO₂ near the Fermi level and thereby modulates the catalytic capability of the TACs. Among the 23 bimetallic TACs, the Fe₂Ir@NG has a medium adsorption strength for CO₂ and a minimum limiting potential and can effectively suppress the HER. All in all, the Fe₂Ir@NG is a very promising catalyst for CO₂ reduction to CH₄.

4. CONCLUSIONS

In summary, by performing comprehensive first-principles calculations, we explored the stability and catalytic behavior of 23 bimetallic triple-atom catalysts (Fe₂M@NG) for CO₂ reduction to C1 products (including CO, CH₂OH, and CH₄). Our results showed that the supported bimetallic trimers provide sufficient adsorption sites to adsorb CO₂, thereby effectively activating the CO₂ and promoting the breaking of the C–O bond. The synergy between Ir and Fe atoms in the outstanding TAC of Fe₂Ir@NG improves the catalytic activity (low limiting potential 0.49 V for CH₂ formation) and selectivity (reducing the rate of the competing reaction HER) for CO₂RR. Our theoretical study offers guidance to design bimetallic TACs with high catalytic performance beyond CO₂RR.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01385.

The G(T) of the free gas molecules and adsorbed intermediates on Fe₂M@NG; the binding energy of M, bond lengths, and the adsorption energy of CO₂ for the Fe₂M@NG; the potential limiting steps of CO₂RR via C1 pathways and the limiting potentials on Fe₂M@NG; top and side views of optimized Fe₂M@NG structures; the energy profile and the final structure of FPMD simulation of Fe₂Zn@NG at 500 K; the density of states of the CO₂-adsorbed Fe₂M@NG; the free energy diagram of the first hydrogenation of *CO₂*; the free energy diagrams of different pathways on Fe₂M@NG and Fe₂@NG; the free energy diagram of the HER on Fe₂Ir@NG (PDF).

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Notes

The authors declare no competing financial interest.

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