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# ${\rm SiFeN_6}\text{-}{\rm graphene}$ : A promising dual-atom catalyst for enhanced ${\rm CO_2}\text{-}{\rm to}\text{-}{\rm CH_4}$ conversion

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# ABSTRACT

The synergistic effects in heteronuclear dual-atom catalysts create opportunities for designing highly efficient catalysts. In this work, we theoretically designed a stable SiFeN<sub>6</sub>-graphene with excellent  $CO_2$  electroreduction performance. The complementary properties of Si and Fe in the Si-Fe dual-atom center result in enhanced  $CO_2$  adsorption and activation, as well as weakened binding strength of the critical intermediate \*OH, compared to SiN<sub>3</sub>- and FeN<sub>3</sub>-graphene. A low onset potential of -0.60 V is predicted for selective conversion of  $CO_2$  to  $CH_4$ , with moderate kinetic barriers (less than 0.66 eV) during the whole reaction, readily surmountable under experimental conditions. This study provides vital insights into the rational design of dual-atom electrocatalysts by exploiting synergistic interactions between strategically paired atoms.

# 1. Introduction

Excessive carbon dioxide emission (CO<sub>2</sub>) is the primary cause of global warming and presents a significant challenge to sustainable economic and social advancement. Therefore, there is an urgent need to develop new technologies for carbon dioxide capture and utilization to reduce its emissions [1,2]. By now, various methods have been proposed, including direct capture, mineral carbonation, and electrocatalytic reduction of CO<sub>2</sub> [3]. Among these, CO<sub>2</sub> electrocatalytic reduction reaction (CO<sub>2</sub>RR) has been regarded as a profitable avenue to convert CO<sub>2</sub> into valuable and renewable chemicals such as carbon monoxide (CO), formic acid (HCOOH), formaldehyde (CH<sub>2</sub>O), methanol (CH<sub>3</sub>OH), methane (CH<sub>4</sub>) and ethylene (C<sub>2</sub>H<sub>4</sub>) [4,5]. Although mainstream CO<sub>2</sub>RR electrocatalysts, such as transition metals (Au, Ag, Zn, Cu, Ni, Pt, Fe), can catalyze CO<sub>2</sub> into various products, including CO, HCOOH,  $CH_4$ , and  $C_2H_4$  [6-8], their reaction kinetics are generally sluggish. The product selectivity is relatively poor, and they also inevitably face the competing hydrogen evolution reaction (HER). For instance, the widely used Cu-based electrocatalysts for  $CH_4$ and C<sub>2</sub>H<sub>4</sub> production, its applied overpotential is as high as -1.0 V versus the reversible hydrogen electrode (RHE) and multiple undesirable products are also generated simultaneously [9]. Therefore, it is essential to develop highly active and selective CO<sub>2</sub>RR electrocatalysts.

Researchers are actively engaged in the quest for novel catalysts, including metal alloys and bimetallic catalysts, non-metal catalysts, biologically inspired catalysts, single-atom catalysts (SACs), and dualatom catalysts (DACs). Among them, SACs have emerged as promising catalysts due to their 100% active atom utilization, the relatively high activity and selectivity, as well as the tunability of active center microenvironment [10,11]. The N-doped graphene supported single transition metal (TM) atom [12], namely TMN<sub>x</sub>-graphene (TM=Mn [13], Fe [14–17], Co [18–20], Ni [21], Cu [22], Zn [22], x=3, 4), have been widely investigated in CO<sub>2</sub>RR, both theoretically and experimentally. However, most of these reported TMN<sub>x</sub>-graphene possess poor CO<sub>2</sub> capture capabilities, and the linear CO<sub>2</sub> molecule can only be physisorbed on these active sites. Such insufficient activation of CO<sub>2</sub> makes the generation of bent \*CO<sub>2</sub> still face a thermodynamic barrier.

Compared with SACs, DACs generally show better electrocatalytic performance due to the synergistic effects of the introduced TM atom pairs [23–25], and they also provide more flexibility in regulating coordination environments. As a result, DACs possess stronger  $CO_2$  capture abilities, higher selectivity towards multi-electron reduction products, and lower overpotential [26–36].

At present, three typical types of  $TM1TM2N_6$ -graphene structures have been investigated (see Figure S1): the embedded TM atoms bond with two N atoms (Model 1), three N atoms (Model 2), or four N atoms (Model 3), respectively. DACs with Model 2 coordination have been successfully synthesized and characterized experimentally [34, 37]. Furthermore, He et al. conducted Density Function Theory (DFT)

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calculations on N-doped graphene DACs with various combinations of transition metal atoms, and they observed the TM1TM2N<sub>6</sub>-graphene takes the Model 2 coordination exhibited moderate CO adsorption strength and superior structural stability [38]. Zhao et al. successfully synthesized the Fe<sub>2</sub>N<sub>6</sub>-graphene catalyst and demonstrated its enhanced catalytic performance in CO<sub>2</sub> reduction towards CO due to the presence of two active centers, which facilitates the capture and activation of CO<sub>2</sub> molecule [33].

For heteronuclear DACs, such as NiFeN<sub>6</sub>-graphene [34], CoFeN<sub>6</sub>-graphene [35], and CuFeN<sub>6</sub>-graphene [36], have also been investigated. Enabled by incorporating other TM atoms, the heteronuclear DACs combine the advantages of two different TM atoms and exhibit superior catalytic performance than that of homonuclear DACs. Consequently, the multi-electron transfer processes become more feasible. As reported, Ni–Fe centers could decrease the reaction barriers for forming \*COOH and the desorption of CO [34]. CoFeN<sub>6</sub>-graphene assisted with pre-adsorbed CO exhibits low limiting potentials of -0.64 V for CH<sub>3</sub>OH and CH<sub>4</sub> generation [35].

Due to its rich bonding features and well-matched energy levels with the adsorbates, the isolated nonmetal Si atom has recently been recognized as an active site and employed as metal-free SACs in specific catalytic reactions. Taking CO<sub>2</sub>RR for instances, Si-doped graphene edges [39] and SiN<sub>3</sub>-graphene [40] have shown remarkable CO<sub>2</sub> capture capabilities and can selectively reduce CO<sub>2</sub> to CH<sub>3</sub>OH at theoretical potentials of -0.49 V and -0.54 V, respectively. Additionally, HSi@g-C<sub>3</sub>N<sub>4</sub> [41] can further reduce CO<sub>2</sub> to CH<sub>4</sub> at a theoretical potential of -0.65 V. Inspired by these remarkable performances, it is intriguing to explore whether isolated diatomic Si-Fe sites could also efficiently capture CO<sub>2</sub> molecule and beneficial for the following reduction reaction.

Currently, Cao et al. strategically incorporated Si dopants near FeN<sub>4</sub> sites and synthesized Si-doped Fe-N-C catalyst (Fe-N-C-Si), realizing the precise modulation of the electronic structure of the Fe sites [42]. In comparison to FeN<sub>4</sub>-graphene, the Fe-N-C-Si catalyst improved CO<sub>2</sub>RR catalytic performance, and their theoretical results demonstrated that the overpotential could be reduced from -0.71 V to -0.64 V, which was attributed to decreased free energy changes during CO<sub>2</sub> conversion to \*COOH and CO desorption process [42]. Additionally, Kim et al. found that incorporating Si moieties into FeN<sub>4</sub>-graphene can enhance its catalytic performance in the oxygen reduction reaction (ORR), and the atomically distributed FeSi<sub>x</sub>N<sub>4-x</sub> sites formed by the substitution of Si for N atom and the C sites adjacent to the Si dopant are both active site during the ORR [43]. Given these exciting advancements, it is worth exploring the untapped potential of Si-Fe dual sites incorporated into N-doped graphene towards CO<sub>2</sub>RR and revealing its corresponding catalytic reaction mechanism.

In this work, SiFeN<sub>6</sub>-graphene was used as a catalyst for the electrochemical conversion of CO<sub>2</sub> to potential C<sub>1</sub> products. We comprehensively investigated the CO2 reduction performance based on DFT calculations. Our computational results demonstrated that the mutual effects of Si-Fe dual sites effectively regulate the electronic structure of the heteronuclear Si-Fe DAC, altering the binding strength of \*CO<sub>2</sub> and the critical species of \*OH simultaneously, giving rise to improved CO<sub>2</sub>RR catalytic performance towards CH<sub>4</sub>. In the potential range of -0.77 to 0.23 V, SiFeN<sub>6</sub>-graphene displays a higher affinity for CO<sub>2</sub> adsorption when compared to other species in the solution. This observation ensures uninterrupted CO<sub>2</sub>RR while simultaneously suppressing HER. The hydrogenation of  $^{*}OH \rightarrow ^{*}H_{2}O$  is the potential-determining step (PDS) of CO<sub>2</sub>RR on SiFeN<sub>6</sub>-graphene. The corresponding  $\Delta G_{max}$  is calculated as 0.44 eV under the applied potential of 0 V. Considering the significant influence of charge distribution and the applied potential on the substrate during electrochemical reactions, an overpotential of -0.60 V vs. RHE is actually required for the conversion of CO<sub>2</sub> to CH<sub>4</sub> catalyzed by SiFeN<sub>6</sub>-graphene. These findings provide valuable insights into the development of DACs for CO<sub>2</sub>RR.

#### 2. Computational details

All calculations were carried out in this work using the Vienna Ab initio Simulation Package (VASP) based on spin-polarized density functional theory [44,45]. The projector augmented-wave (PAW) method was used to describe the ion-electron interaction [46]. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) was used to describe exchange-correlation [47]. The DFT-D3 method was used to evaluate van der Waals interactions between the substrates and adsorbates [48,49]. The plane wave energy cutoff was set as 500 eV. The Brillouin-zone integration was performed using a  $3 \times 3 \times 1$  kpoint mesh for geometric optimization and a  $9 \times 9 \times 1$  k-point mesh for electronic property calculations. The electronic energy and forces were converged to within  $1.0 \times 10^{-5}$  eV/Å and 0.02 eV/Å, respectively. A  $6 \times 6$  graphene supercell with six doped N atoms and four carbon vacant sites (V<sub>4</sub>N<sub>6</sub>-graphene; V: vacancy, and N: nitrogen; Model 2 coordination) was selected to model N-doped graphene by taking into account the balance between efficiency and accuracy. Si and Fe atoms were incorporated into the vacant sites. A vacuum slab of 20 Å was set in the *z*-axis direction to minimize the interaction of periodic structure. The VASPKIT code [50] was used to post-process the VASP calculated data.

The formation energy  $(E_f)$  of Si-Fe dimer embedded N-doped graphene is calculated as,

$$E_f = \frac{1}{2} (E_{\rm SiFeN_6-graphene} - E_{\rm V_4N_6-graphene} - E_{\rm Si} - E_{\rm Fe})$$
(1)

The meaning of 1/2 represents the average formation energy of Si and Fe atoms embedded in V<sub>4</sub>N<sub>6</sub>-graphene.  $E_{\rm Si}$  and  $E_{\rm Fe}$  are the DFT energy of Si and Fe atoms in their most stable bulk structures, respectively.  $E_{\rm V_4N_6-graphene}$  is the DFT energy of N-doped graphene framework with four vacant sites.  $E_{\rm SiFeN_6-graphene}$  is the DFT energy of SiFeN<sub>6</sub>-graphene.

The dissolution potential  $U_{diss}$ ,  $U_{diss}$ (Si) and  $U_{diss}$ (Fe) are defined as,

$$U_{diss} = U^o_{diss}(\text{Si, bulk}) + U^o_{diss}(\text{Fe, bulk}) - \frac{E_f}{n_{\text{Si}}e + n_{\text{Fe}}e}$$
(2)

$$U_{diss}(\text{Si}) = U_{diss}^{o}(\text{Si}, \text{bulk}) - \frac{1}{n_{\text{Si}}e} (E_{\text{SiFeN}_6-\text{graphene}} - E_{\text{FeN}_6-\text{graphene}} - E_{\text{Si}})$$
(3)

$$U_{diss}(\text{Fe}) = U_{diss}^{o}(\text{Fe}, \text{bulk}) - \frac{1}{n_{\text{Fe}}e} (E_{\text{SiFeN}_6-\text{graphene}} - E_{\text{SiN}_6-\text{graphene}} - E_{\text{Fe}})$$
(4)

where  $U_{diss}^{o}$ (Si, bulk) and  $U_{diss}^{o}$ (Fe, bulk) are the standard dissolution potential of Si and Fe bulk, respectively. And  $n_{Si}$  and  $n_{Fe}$  are the number of electrons involved in the Si and Fe bulk dissolution process, respectively.  $E_{SiN_6-graphene}$  and  $E_{FeN_6-graphene}$  are the DFT energy of Ndoped graphene framework without Fe and Si atoms, respectively.  $E_{Si}$ and  $E_{Fe}$  is the DFT energy of Si and Fe atom in its most stable bulk structure, respectively [51].

The adsorption energy  $(E_{ads})$  of adsorbates on the SiFeN<sub>6</sub>-graphene is defined as,

$$E_{ads} = E_{support+adsorbate} - E_{support} - E_{adsorbate}$$
<sup>(5)</sup>

 $E_{support}$  and  $E_{adsorbate}$  represent the energy of the adsorbed system and its separated parts. A negative value means the adsorbate could be adsorbed.

The adsorption free energy  $(G_{ads})$  of adsorbates on the SiFeN<sub>6</sub>-graphene is defined as,

$$G_{ads} = G_{support+adsorbate} - G_{support} - G_{adsorbate}$$
(6)

 $G_{support}$  and  $G_{adsorbate}$  represent the Gibbs free energy of the adsorbed system and its separated parts. The Gibbs free energy is calculated using JDFTx. A negative value means the adsorbate could be adsorbed.

The *ab-initio* molecular dynamics (AIMD) simulation [52] was performed to assess the thermodynamic stability of the targeted system, in which the time step was set at 2.0 fs for a total period of 14 ps and the temperature was set at 300 K. The transition states for the  $CO_2$  adsorption and the following reduction processes were implemented by the climbing image nudged elastic band (CI-NEB) method [53], in which the convergence criterion of force was 0.05 eV/Å. The dynamic energy barriers were evaluated using the constant potential method (CPM) implemented in the JDFTx code, and all the corresponding structures were obtained from VASP results.

The Si( $3p_z$ ) and Fe(3d) centers may be used as a descriptor of CO<sub>2</sub> adsorption strength, and it is estimated by the following equation,

$$\varepsilon = \frac{\int_{-\infty}^{+\infty} n(\varepsilon)\varepsilon d\varepsilon}{\int_{-\infty}^{+\infty} n(\varepsilon)d\varepsilon}$$
(7)

where  $n(\varepsilon)$  is the density of states (DOS) of the Si( $3p_z$ ) or Fe(3*d*) band at a given energy *E*. The integration interval is  $(-\infty, +\infty)$ , where the energy E = 0 has been calibrated to the Fermi energy level ( $E_{\text{Fermi}}$ ).

During the electrochemical reactions, the free energy profiles for  $CO_2RR$  were evaluated using the constant potential method (CPM) implemented in the JDFTx code [54], and all the corresponding intermediates were obtained from VASP results. The PBE-D3 functional was used to treat the core-valence interactions, and the kinetics cutoff was set to 20 Hartree [48,49]. The convergence criteria of electronic energies were set to  $10^{-8}$  Hartree. Meanwhile, the charge-asymmetric, local response, and nonlocal-cavity (CANDEL) model was utilized to depict the aqueous solution [55]. The free energy change of each fundamental step was calculated by [56],

$$\Delta G_{\rm CPM} = G(I_2) - G(I_1) - G({\rm H}_2({\rm g}))/2 + |e|U - (q_1 - q_2)\mu_e \tag{8}$$

where the  $G(I_1)$  and  $G(I_2)$  donated the free energies of the reactants and products at corresponding potentials, and the  $G(H_2(g))/2$  was the free energy of the hydrogen. The *U* was the applied potential versus reversible hydrogen electrode (RHE). Also,  $q_1$  and  $q_2$  represented the total net charges of reactants and products, respectively. And the  $\mu_e$ was the electron energy determined by the electrode potential.

## 3. Results and discussion

#### 3.1. Structure, electronic properties and stability of SiFeN<sub>6</sub>-graphene

Firstly, we optimized the structure of SiFeN<sub>6</sub>-graphene (Model 2 coordination) as depicted in Fig. 1(a), and we also give the optimized geometries of SiN<sub>3</sub>-, FeN<sub>3</sub>-, Si<sub>2</sub>N<sub>6</sub>- and Fe<sub>2</sub>N<sub>6</sub>-graphene for comparison (see Figure S2). From them, one can see that three N atoms surround each Si and Fe atom, and the Si atom directly bonds with the Fe atom at a bond length of 2.27 Å. The obtained Si-N bond lengths are 1.87, 1.89, and 1.98 Å, while the Fe-N bond lengths are found to be 1.86, 1.94, and 1.95 Å. For homonuclear Si<sub>2</sub>N<sub>6</sub>- and Fe<sub>2</sub>N<sub>6</sub>-graphene, the bond lengths of Si-N and Fe-N fall within the range of 1.86 to 1.91 and 1.91 to 2.01 Å, respectively. The bond lengths of Si-N and FeN in DACs are slightly larger than those in SiN<sub>3</sub>-graphene (1.85 Å) and FeN<sub>3</sub>-graphene (1.87 Å), respectively.

The Charge Density Difference (CDD) of SiFeN<sub>6</sub>-, SiN<sub>3</sub>-, FeN<sub>3</sub>-, Si<sub>2</sub>N<sub>6</sub>- and Fe<sub>2</sub>N<sub>6</sub>-graphene are illustrated in Figure S3(a-e), and the substantial charge transfer indicates the strong interactions between the embedded Si or Fe atoms and the N-doped graphene. Compared with homonuclear dual-atom centers and the isolated single-atom sites, the charge density on the heteronuclear SiFeN<sub>6</sub>-graphene center significantly increases. Moreover, the Bader charge analysis indicates that the Fe atom in SiFeN<sub>6</sub>-graphene loses fewer electrons (0.78|*e*|) than that in FeN<sub>3</sub>-graphene (0.97|*e*|) and Fe<sub>2</sub>N<sub>6</sub>-graphene (0.82|*e*|) due to the introduction of Si, which is a more electronegativity element. The calculated total magnetic moments for SiFeN<sub>6</sub>-, SiN<sub>3</sub>-, FeN<sub>3</sub>-, Si<sub>2</sub>N<sub>6</sub>-, and Fe<sub>2</sub>N<sub>6</sub>-graphene are 2.00, 0.00, 3.11, 0.00 and 4.22  $\mu_{\rm B}$ , respectively. For the heteronuclear SiFeN<sub>6</sub>-graphene, the spin densities are predominantly located on the Fe and Si atoms as plotted in Fig. 1(b). The induced spin polarization on the Si atom could be understood from the charge

transfer between Si and Fe atoms. Such locally induced spin polarization would be beneficial for enhancing the catalytic performance of a catalyst. In addition, we present the band structure, as well as the DOS of SiFeN<sub>6</sub>-graphene in Fig. 1(c). From it, one can see that the SiFeN<sub>6</sub>graphene is a magnetic semiconductor with a small indirect gap of 63.8 meV, and a flat band can be found near the Fermi level, primarily due to the contributions of C(2*p*) and Fe(3*d*) orbitals.

Next, we evaluated the stability of SiFeN<sub>6</sub>-graphene based on its formation energy  $(E_f)$ , dissolution potential  $(U_{diss})$ , and the AIMD simulation at 300K. The calculated  $E_f$  of SiFeN<sub>6</sub>-graphene is -1.15 eV, and the values of  $U_{diss}$ ,  $U_{diss}$  (Si) and  $U_{diss}$  (Fe) in SiFeN<sub>6</sub>-graphene are -0.02, 0.11 and 0.15 V, respectively. According to the definition of  $E_f$ , a negative value of  $E_f$  means the Si and Fe codoping process is exothermic, and the heteronuclear SiFeN<sub>6</sub>-graphene could be expected to be synthesized experimentally. Meanwhile, all calculated values of  $U_{diss}$  are more positive than the experimental applied potential for  $CO_2 RR$  (ranging from -0.20 to -1.20 V). The thermodynamic stability of the SiFeN<sub>6</sub>-graphene at 300 K is verified by the AIMD result, as shown in Fig. 1(d). The total energy converges, and the structure of SiFeN<sub>6</sub>-graphene keeps very well after 14 ps AIMD simulation, demonstrating that such configuration possesses good thermal stability at 300 K. These findings suggest that the SiFeN<sub>6</sub>-graphene is a structurally and energetically stable material, and it also exhibits electrochemical stability during the CO<sub>2</sub>RR process.

#### 3.2. Adsorption and activation of $CO_2$

As a fundamental prerequisite for the CO<sub>2</sub>RR process, the adsorption of CO<sub>2</sub> on the catalyst surface plays a crucial role in the subsequent reaction. All possible initial configurations for CO<sub>2</sub> adsorption are considered here, and we finally obtained one physical adsorption and three representative chemical adsorption configurations, as illustrated in Figure S4(a-d). According to the obtained adsorption free energies, the most stable chemisorption of CO<sub>2</sub> takes bidentate mode, in which one O atom of the CO<sub>2</sub> molecule adsorbed on the Si site while the C atom of CO<sub>2</sub> molecule interacts with the Fe site, and the two C-O bonds are stretched from 1.18 to 1.22/1.37 Å along with the reduced  $\angle_{O-C-O}$ of 125.3°, indicating that the adsorbed CO<sub>2</sub> is fully activated. Moreover, we also evaluated the transition of physisorbed CO<sub>2</sub> to its most stable chemisorbed state on SiFeN6-graphene using the CI-NEB method, as depicted in Fig. 2(a). Such a kinetic process only needs a tiny energy barrier of 0.04 eV, revealing that SiFeN<sub>6</sub>-graphene could easily capture the inert CO<sub>2</sub> molecule. Fig. 2(b) presents the CDD of CO<sub>2</sub>-adsorbed SiFeN<sub>6</sub>-graphene taking the bidentate configuration (see Figure S4(d)). There is a noticeable bidirectional charge transfer between CO<sub>2</sub> and SiFeN<sub>6</sub>-graphene, and the Bader charge analysis showed that substrate donates 1.10 |e| to the adsorbed CO<sub>2</sub>. Specifically, the occupied CO<sub>2</sub>- $1\pi_{q}$  orbitals donate electrons to Si- $3p_{z}$  and Fe-3*d* orbitals. At the same time, Si- $3p_z$  and Fe-3d orbitals back-donate electrons to the antibonding  $2\pi_{\mu}$  orbitals of the CO<sub>2</sub> molecule. Such donate/back-donate activation mechanism is consistent with previous research [35,39].

By considering the most favorable adsorption patterns, the structures, adsorption free energies and CDD of CO<sub>2</sub>-adsorbed SiN<sub>3</sub>-, FeN<sub>3</sub>-, Si<sub>2</sub>N<sub>6</sub>- and Fe<sub>2</sub>N<sub>6</sub>-graphene are also plotted in Figure S5–S6. All the calculated adsorption free energies of CO<sub>2</sub> ( $G_{ads}$ ) at 0 V and the corresponding charge transfer (CT) values obtained from Bader charge analysis are tabulated in Table S1. The obtained  $G_{ads}$  on these substrates are all negative (from -0.12 to -1.34 eV), and the adsorbed CO<sub>2</sub> gains electrons (0.60 to 1.39 |e|) from the substrates above. Our results suggest that these SACs and DACs can effectively capture and activate the inert CO<sub>2</sub> molecule through an electron donation-back-donation interaction mechanism.

Although N-doped graphene supported single Si atom or Si dimer exhibits superior capabilities in capturing and activating  $CO_2$ , their strong adsorption ability of intermediate \*OH may decrease their



Fig. 1. (a) The top- and side-view of optimized SiFeN<sub>6</sub>-graphene. Bonds are in Å; (b) The calculated spin density of SiFeN<sub>6</sub>-graphene. Yellow and cyan indicate positive and negative densities, respectively. The isosurface value was set to be 0.001  $e^{\text{Å}-3}$ ; (c) The band structure, density of states of SiFeN6-graphene and spin down projected density of states of C(2p), N(2p), Si(3p), Fe(3d); (d) Diagrams of the temperature and total energy changing with time at 300 K obtained by AIMD simulation.

electrocatalytic activity to some extent as reported by previous research [57]. Table S1 shows that the adsorption free energy of \*OH on SiN<sub>3</sub>- and Si<sub>2</sub>N<sub>6</sub>-graphene at 0 V is -1.73 and -1.23 eV, respectively. Furthermore, it increases to -0.03 and -0.77 eV for that on FeN<sub>3</sub>and Fe<sub>2</sub>N<sub>6</sub>-graphene, respectively. Such adsorption free energy on the heteronuclear SiFeN<sub>6</sub>-graphene is -1.02 and 0.05 eV for Si and Fe sites. Clearly, the presence of Fe effectively addresses the issue of strong adsorption of \*OH on the Si site, improving its electrocatalytic activity during the CO<sub>2</sub> reduction reaction.

Since most of the reported adsorption energy of CO<sub>2</sub> on DACs is obtained using VASPSol, we further calculated it using the same method, and the value is -1.05 eV on SiFeN<sub>6</sub>-graphene, which is much negative than CoFeN<sub>6</sub>-graphene (-0.64 eV, VASPSol) [35] and FeFeN<sub>6</sub>-graphene (-0.10 eV, VASPSol) [33]. While for NiFeN<sub>6</sub>-graphene [34] and CuFeN<sub>6</sub>-graphene [36], the effective capture of CO<sub>2</sub> is still challenging. Thus, the Si-Fe dual site ensures the strong adsorption of CO<sub>2</sub> and the relatively weak binding of \*OH simultaneously, facilitating the CO<sub>2</sub> reduction reaction and improving the catalytic efficiency.

To better understand the strong adsorption of CO2 on SiFeN6graphene and the synergistic effect of Si-Fe dual site, we also plot the projected density of states (PDOS) of  $CO_2(2p)$ ,  $Si(3p_z)$ , and Fe(3d)before and after the adsorption of CO2 on SiFeN6-, SiN3-, FeN3-, Si2N6and Fe<sub>2</sub>N<sub>6</sub>-graphene in Fig. 2(c) and Figure S7–S8, respectively. Among the considered five cases, the energy level of the isolated CO<sub>2</sub> molecule matches better with the heteronuclear SiFeN<sub>6</sub>-graphene, and the  $p_z$ band center of Si atom (Si- $\epsilon(p_z)$ ) or the spin up *d*-band center of Fe atom (Fe- $\epsilon(d)$ ) of the dual-atom centers are higher than that of the singleatom sites. Notably, for heteronuclear SiFeN<sub>6</sub>-graphene, the calculated spin up Si- $\epsilon(p_z)$  and Fe- $\epsilon(d)$  are both higher than their homonuclear counterparts. And the calculated spin down Si- $\epsilon(p_z)$  and Fe- $\epsilon(d)$  are close to their homonuclear counterparts. It is known that the upshift of  $\epsilon(p_z)$  and  $\epsilon(d)$  generally correspond to higher reactivity. Therefore, the synergistic effects originating from heteronuclear Si-Fe dual sites could better modulate the catalytic performance of active sites.

#### 3.3. Competitive adsorption with \*O, \*H, and \*OH

Noted that, the active sites of DACs may be potentially blocked by the pre-adsorption of some electrochemically-driven molecules under natural electrocatalytic reaction environment [58]. Therefore, evaluating the adsorption of some common functional groups or molecules generated from the liquid phase is essential to analyze a catalyst's electrocatalytic activity better. Here, we utilized the JDFTx code to investigate the competitive relationship between  $CO_2$  and functional groups such as O, H, and OH under varying applied potentials. We first calculate the adsorption free energy of various molecules at different electrode potentials, including -0.80, -0.60, -0.40, -0.20, and 0.00 V. During our calculations, we observed a noteworthy linear relationship between the adsorption free energy of the same molecule at different electrode potentials. Subsequently, we employed linear fitting techniques, as shown in Fig. 3.

According to the definition of adsorption free energy, a more negative value means a stronger binding strength. Four linear scaling relations are obtained, suggesting that the binding strengths of these adsorbates are all potential-dependent. More specifically, as the applied potential decreases, the adsorption strength of \*H and \*CO<sub>2</sub> increases, and the former displays a more pronounced increase. On the contrary, the adsorption strength of \*O and \*OH decreases with the increased applied potential. Within a wide range of -0.77 to 0.23 V, the adsorption of \*CO<sub>2</sub> prevails over \*O, \*H, and \*OH, ensuring its priority adsorption, making CO<sub>2</sub>RR more favorable.

# 3.4. Entire pathways of $CO_2RR$ at 0 V

Subsequently, based on the most stable  $CO_2$  adsorption configuration on SiFeN<sub>6</sub>-graphene, we evaluated the free energy landscapes of  $C_1$ products on SiFeN<sub>6</sub>-graphene, including CO, HCOOH, CH<sub>2</sub>O, CH<sub>3</sub>OH, and CH<sub>4</sub>. In Fig. 4, we summarize the favorable free energy diagram for CO<sub>2</sub>RR on SiFeN<sub>6</sub>-graphene, and detailed structural diagrams of the reaction intermediates are shown in Figure S9–S10. As we know, the kinetic barrier plays a crucial role in fundamental reactions. For the electrochemical reduction of CO<sub>2</sub>RR, hydrogenation occurs by adding



**Fig. 2.** (a) Relative energies profile for the CO<sub>2</sub> adsorption process on SiFeN<sub>6</sub>-graphene. Bonds are in Å; (b) The Charge Density Difference of CO<sub>2</sub>-adsorbed SiFeN<sub>6</sub>-graphene. Yellow and cyan indicate positive and negative densities, respectively. The isosurface value was set to be 0.003 eÅ<sup>-3</sup>; (c) The projected density of states of CO<sub>2</sub>(2*p*), Si(3*p*<sub>z</sub>) and Fe(3*d*) on SiFeN<sub>6</sub>-graphene before and after the adsorption process.



Fig. 3. Calculated adsorption free energies for the  $^{*}CO_{2}$ ,  $^{*}O$ ,  $^{*}H$  and  $^{*}OH$  adsorbed on SiFeN<sub>6</sub>-graphene under various applied potentials.

protons and electrons. In this study, electrochemical hydrogenation was modeled by a dissociated neutral H atom adsorbed near the SiFeN<sub>6</sub>-graphene center using the CI-NEB method, as illustrated in Figure S11.

Starting from the bidentate configuration, the adsorbed \*CO<sub>2</sub> could be first reduced to \*OCHO, \*COOH, and dissociated \*CO+\*OH. The \*OCHO formation requires a tiny energy rise of 0.15 eV, while the latter two are downhill, with the free energy decreasing by 0.22 and 1.32 eV, respectively. Especially, when a proton attacks the adsorbed O atom in \*CO<sub>2</sub>, the weakened C–O bond breaks and produces \*CO+\*OH by overcoming an energy barrier of 0.31 eV (Figure S11(a)). Compared with the direct C-O bond cleavage barrier without the participation of proton (0.59 eV, see Figure S12), the C-O bond dissociation becomes more kinetically feasible. Considering the large energy release and the low kinetic barrier, \*CO+\*OH is chosen as the most possible reduction product for the first hydrogenation reaction. The further reduction of \*CO+\*OH may lead to \*COH+\*OH, \*CHO+\*OH, or \*CO+\*H<sub>2</sub>O. All of them are endothermic steps, and the corresponding  $\Delta G$  are 1.06, 0.64, and 0.41 eV, respectively. Based on the energy point of view, the second hydrogenation reaction tends to generate \*CO+\*H<sub>2</sub>O, and such a step possesses a moderate barrier of 0.57 eV (Figure S11(b)). Then, due to the accumulation of a large number of positive charges around the C atom in \*CO (see Figure S13), it is impossible to hydrogenate C further to form \*CHO+\*H<sub>2</sub>O. The subsequent hydrogenation reaction exhibits a relatively high  $\Delta G$  for \*COH+\*H<sub>2</sub>O formation (1.25 eV) compared with the H<sub>2</sub>O desorption (0.48 eV), suggesting the aforementioned hydrogenation process is unlikely to occur. Although H<sub>2</sub>O desorption is endothermic, it could be compensated by the previous electrochemical processes. When the generated H<sub>2</sub>O desorbs from the substrate, the CO desorption needs to overcome a quite high free energy of 2.37 eV while the following hydrogenated  $\Delta G$  for \*CO to produce \*CHO and \*COH is



Fig. 4. The relative Gibbs free energies for the possible intermediates generated in CO<sub>2</sub>RR on SiFeN<sub>6</sub>-graphene under the applied potential of 0 V.

0.02 and 1.15 eV, respectively. Thus, the third hydrogenation product is more likely to be \*CHO, displaying a small energy barrier of 0.39 eV (Figure S11(c)). The further hydrogenation free energy of \*CH<sub>2</sub>O is much lower than that of \*CHOH (-2.58 vs. -1.39 eV), indicating its high selectivity to generate \*CH<sub>2</sub>O. As shown in Figure S11(d), a low energy barrier of 0.22 eV is observed to reduce \*CHO to \*CH<sub>2</sub>O. Since the  $CH_2O$  desorption is endothermic by a large energy of 2.17 eV, the further reduction should be more facile, which may lead to  $^{*}OCH_{3}$  ( $\Delta G$ = -0.32 eV) or dissociated \*CH<sub>2</sub>+\*OH ( $\Delta G$  = -0.63 eV), depending on the proton attacks the C or O atom in \*CH<sub>2</sub>O. Since the coadsorption of \*CH<sub>2</sub>+\*OH is 0.31 eV lower than \*OCH<sub>3</sub>, the reduction of \*CH<sub>2</sub>O to \*CH2+\*OH is more energy favored, and such reduction process exhibits a mild barrier of 0.48 eV (Figure S11(e)). By comparing the obtained free energies, the sixth and seventh hydrogenation processes tend to occur on the C atom of  $*CH_x$  (x=2 and 3) rather than the  $*OH_x$ both of them are exothermic and exhibit negligible kinetic barriers (less than 0.05 eV), as depicted in Figure S11(f-g). Note that the last hydrogenation step of  $^{*}OH \rightarrow ^{*}H_{2}O$  possesses the largest  $\Delta G$  of 0.44 eV, which is the potential-determining step (PDS) during the CO2RR, and the corresponding barrier is 0.52 eV (Figure S11(h)). Finally, the H<sub>2</sub>O desorption process is thermodynamically uphill by 0.57 eV. From the above results, the optimal reduction path for CO<sub>2</sub>RR to generate CH<sub>4</sub> at 0 V follows the pathway:  $CO_2 \rightarrow {}^*CO_2 \rightarrow {}^*CO+{}^*OH \rightarrow {}^*CO+{}^*H_2O$  $\rightarrow$  \*CO  $\rightarrow$  \*CHO  $\rightarrow$  \*CH<sub>2</sub>O  $\rightarrow$  \*CH<sub>2</sub>+\*OH  $\rightarrow$  \*CH<sub>3</sub>+\*OH  $\rightarrow$  \*OH+CH<sub>4</sub>  $\rightarrow$  $*OH \rightarrow *H_2O.$ 

The eight elemental proton-coupled electron transfers for the  $CO_2RR$  path are given as follows:

$$^{*}CO_{2} + (H^{+} + e^{-}) \rightarrow ^{*}CO + ^{*}OH$$
 (9)

$$^{*}CO + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}CO + ^{*}H_{2}O$$
 (10)

$$(CO + (H^+ + e^-)) \rightarrow (CHO)$$

\* 0110

. (11+

$$^{*}CHO + (H^{+} + e^{-}) \rightarrow ^{*}CH_{2}O$$
 (12)

 $^{*}CH_{2}O + (H^{+} + e^{-}) \rightarrow ^{*}CH_{2} + ^{*}OH$  (13)

$$^{*}CH_{2} + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}CH_{3} + ^{*}OH$$
 (14)

$$^{*}CH_{3} + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}OH + CH_{4}$$
 (15)

$$^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}H_{2}O$$
 (16)

Figure S14 depicts the maximum Gibbs free energy ( $\Delta G_{max}$ ) for various potential pathways leading to possible reduction products. Due to the strong adsorption capability of SiFeN<sub>6</sub>-graphene, the desorption process of byproducts such as CO, HCOOH, and CH<sub>2</sub>O are challenging, and they are more prone to undergo further hydrogenation, resulting in the production of CH<sub>4</sub>, as shown in Fig. 4 and Figure S15(a).

Additionally, the CH<sub>4</sub> formation is more energy favorable compared to the production of CH<sub>3</sub>OH, as shown in Figure S15(b). These results reveal that SiFeN<sub>6</sub>-graphene exhibits a high selectivity for reducing  $CO_2$  to CH<sub>4</sub>.

We have also investigated the performance of SiN<sub>3</sub>-, FeN<sub>3</sub>-, Si<sub>2</sub>N<sub>6</sub>and Fe<sub>2</sub>N<sub>6</sub>-graphene for CO<sub>2</sub> to CH<sub>4</sub> conversion, as shown in Figure S16(a-b) and S17(a-b), and the predicted  $\Delta G_{max}$  is 1.63, 0.86, 0.80 and 0.68 eV. The PDS of CO2RR towards the production of CH4 catalyzed by SiN<sub>3</sub>-, FeN<sub>3</sub>-, Si<sub>2</sub>N<sub>6</sub>- and Fe<sub>2</sub>N<sub>6</sub>-graphene is \*OH  $\rightarrow$  \*H<sub>2</sub>O, \*OCHO  $\rightarrow$  \*OCH<sub>2</sub>O, \*OH  $\rightarrow$  \*H<sub>2</sub>O and \*CO  $\rightarrow$  \*CHO, respectively. And FeN<sub>4</sub>-graphene has been demonstrated to be capable of reducing  $CO_2$  to CO [16]. However, its reduction of  $CO_2$  to  $CH_4$  requires an overpotential of -0.95 V and is accompanied by relatively weak CO<sub>2</sub> adsorption [17]. Similarly, The overpotential for  $SiN_4$ -graphene in reducing CO<sub>2</sub> to CH<sub>4</sub> is -1.15 V [40]. Obviously, SiFeN<sub>6</sub>-graphene shows superior catalytic performance than N-doped graphene supported single or dual Si and Fe atoms in CO2 to CH4 conversion, which can be attributed to the synergistic effects of Si and Fe, leading to the enhanced CO<sub>2</sub> capture ability and the relatively weakened adsorption capability of \*OH.

# 3.5. Influence of applied potential on $CO_2RR$

As reported by previous literature, the applied potential generally significantly impacts the two dimensional system during an electrochemical reaction [59,60]. Therefore, it is necessary to evaluate its influence.

Since the conversion of  $*CO+*OH+(H^++e^-) \rightarrow *CO+*H_2O$  and  $*OH+(H^++e^-) \rightarrow *H_2O$  are the two most significant steps of free energy rise in the obtained free energy profile of  $CO_2RR$  at 0 V, we calculate the  $\Delta G$  for them at different electrode potentials, including -0.80, -0.60, -0.40, -0.20, and 0.00 V. In our calculations, we identified a remarkable linear correlation between the  $\Delta G$  values at various electrode potentials. Subsequently, we applied linear regression techniques, as illustrated in Fig. 5(a).

According to the fitted results, the  $\Delta G$  will become negative or close to zero at approximately -0.66 V for the two steps above. Then, we proceeded to investigate the CO<sub>2</sub>RR pathways on SiFeN<sub>6</sub>-graphene at an applied potential of -0.66 V, and the results are summarized in Figure S18. Notably, the reduction of CO<sub>2</sub> is downhill along the entire reaction pathway at -0.66 V.

Additionally, we calculated the total net charge of \*CO+\*OH and \*OH at different potentials, as plotted in Figure S19. From it, one can see that the net charge and the applied potential exhibit an exponential behavior, and the distribution of charges can significantly influence

(11)



**Fig. 5.** (a) The  $\Delta G$  of  $^{*}CO+^{*}OH+(H^{+}+e^{-}) \rightarrow ^{*}CO+^{*}H_{2}O$ ,  $^{*}OH+(H^{+}+e^{-}) \rightarrow ^{*}H_{2}O$  and  $^{*}CO+^{*}OH+(H^{+}+e^{-}) \rightarrow ^{*}CHO+^{*}OH$  under various applied potentials; (b) The relative Gibbs free energies in CO<sub>2</sub>RR on SiFeN<sub>6</sub>-graphene under the applied potential of -0.60 V; (c) Possible reaction cycle for CO<sub>2</sub>-to-CH<sub>4</sub> conversion at -0.60 V, and the corresponding free energy changes are presented.

the progress of electrochemical reactions, consistent with previous studies [61].

Intriguingly, we observed that the free energy of the reaction intermediate of \*CHO+\*OH is more negative than \*CO+\*H<sub>2</sub>O at -0.66 V due to the charge effect, resulting in a change in the optimal reaction pathway. In the new pathway, the third protonation of \*CO+\*OH  $\rightarrow$  \*CO+\*H<sub>2</sub>O transforms into \*CO+\*OH  $\rightarrow$  \*CHO+\*OH, followed by \*CHO+\*OH  $\rightarrow$  \*CHOH+\*OH  $\rightarrow$  \*CH<sub>2</sub>OH+\*OH  $\rightarrow$  \*CH<sub>2</sub>OH+\*H<sub>2</sub>O, and ultimately returning to \*CH<sub>2</sub>+\*OH. Moreover, detailed structural diagrams of the new reaction intermediates are shown in Figure S20.

We also calculated the  $\Delta G$  of \*CO+\*OH+(H<sup>+</sup>+e<sup>-</sup>)  $\rightarrow$  \*CHO+\*OH at different potentials and observed a linear relationship between  $\Delta G$ and applied potential, as shown in Fig. 5(a). According to the fitted equation, the  $\Delta G$  for \*CO+\*OH+(H<sup>+</sup>+e<sup>-</sup>)  $\rightarrow$  \*CHO+\*OH will decrease to zero at approximately 0.60 V. Then, we further investigated the new pathway of CO<sub>2</sub>RR on SiFeN<sub>6</sub>-graphene at an applied potential of -0.60 V, and the corresponding results are summarized in Fig. 5(b). Clearly, -0.60 V is the least potential requirement to make the whole CO<sub>2</sub>RR route exergonic, that is, the limiting potential for CO<sub>2</sub>RR over SiFeN<sub>6</sub>-graphene. In Fig. 5(c), we gave the possible reaction cycle for CO<sub>2</sub>-to-CH<sub>4</sub> conversion at -0.60 V.

Moreover, the new CO<sub>2</sub>RR path is given as follows:

$$^{*}CO_{2} + (H^{+} + e^{-}) \rightarrow ^{*}CO + ^{*}OH$$
 (17)

 $*CO + *OH + (H^{+} + e^{-}) \rightarrow *CHO + *OH$  (18)

- $^{*}CHO + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}CHOH + ^{*}OH$  (19)
- $^{*}CHOH + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}CH_{2}OH + ^{*}OH$  (20)
- $^{*}CH_{2}OH + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}CH_{2}OH + ^{*}H_{2}O$  (21)
- $^{*}CH_{2} + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}CH_{3} + ^{*}OH$  (22)

$$^{*}CH_{2} + ^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}OH + CH_{4}$$
(23)

$$^{*}OH + (H^{+} + e^{-}) \rightarrow ^{*}H_{2}O$$
 (24)

The kinetic barriers for new pathways and other kinetic processes (Non-proton-coupled electron transfers) are illustrated in S21 and S22, respectively. Furthermore, the highest energy barrier is 0.75 eV (see Figure S21(d)), which occurs during the process of \*CHOH+\*OH  $\rightarrow$  \*CH<sub>2</sub>OH+\*OH.

After obtaining the optimized configurations through CI-NEB, we employ the JDFTx program to calculate the free energies of each structure at -0.60 V to consider the influence of potential and solvation effect. As shown in Table S2, for the original pathway, the fourth hydrogenation process(\*CO+\*OH $\rightarrow$  \*CO+\*H<sub>2</sub>O) exhibits the highest kinetic barrier (0.48 eV). As shown in Table S3, for the new pathway, the fourth hydrogenation process (\*CHOH+\*OH $\rightarrow$  \*CH<sub>2</sub>OH+\*OH) exhibits the highest kinetic barrier (0.66 eV). These are very easy to overcome under reaction conditions.

Although the absolute value of the onset potential (-0.60 V) is slightly higher than some recently reported catalysts, such as CoFeN<sub>6</sub>-graphene (-0.37 V), theoretical) [62], CuFeN<sub>6</sub>-graphene (-0.51 V), theoretical) [36] and AgCrN<sub>6</sub>-graphene (-0.55 V), theoretical) [63], it is still comparable and even lower than many well-established catalysts, such as HSi-C<sub>3</sub>N<sub>4</sub> (-0.65 V), theoretical) [41], Cu-Ag interfaces (-1.17 V), experimental) [64] and vacancy-metal-nitrogen sites (-1.50 V), experimental) [65].

As mentioned previously, the current results indicate that  $SiFeN_6$ graphene exhibits lower overpotential and higher selectivity than  $SiN_3$ graphene and  $FeN_3$ -graphene. Furthermore, the product is converted from CO to the more valuable  $CH_4$ , which positions  $SiFeN_6$ -graphene as a highly promising DAC for  $CO_2RR$ .

# 4. Conclusions

In summary, through first-principles calculations, we have demonstrated isolated Si-Fe dual-atom sites embedded in N-doped graphene as stable electrocatalysts for CO2-to-CH4 conversion with high activity and selectivity. The Si-Fe dual-atom centers are anchored in the N-doped graphene, forming stable covalent bonds with surrounding N atoms. Negative formation energies, positive dissolution potentials, and AIMD simulation demonstrate the feasibility and electrochemical stability of synthesizing SiFeN<sub>6</sub>-graphene. Thanks to synergistic effects between Si and Fe, SiFeN<sub>6</sub>-graphene can achieve strong CO<sub>2</sub> adsorption and activation while preventing overbinding of the critical intermediate \*OH on Si sites. Within a potential range of -0.77 to 0.23 V, SiFeN<sub>6</sub>graphene exhibits stronger adsorption of CO<sub>2</sub> compared to other species in solution, ensuring unimpeded CO2RR and suppressed HER. The unique synergistic mechanism of the Si-Fe pair enables selective reduction of CO<sub>2</sub> to CH<sub>4</sub> on SiFeN<sub>6</sub>-graphene at a low onset potential of -0.60 V with moderate kinetic energy barriers. Overall, this work provides valuable insights into the catalytic mechanism of heteronuclear DACs for CO<sub>2</sub>-to-CH<sub>4</sub> conversion and contributes design principles to guide the development of more efficient and sustainable CO<sub>2</sub> electrocatalysts.

#### CRediT authorship contribution statement

Meijie Wang: Investigation, Data curation, Writing – original draft, Visualization. Yaowei Xiang: Formal analysis. Wengeng Chen: Formal analysis. Shunqing Wu: Writing – review & editing. Zi-Zhong Zhu: Writing – review & editing. Xinrui Cao: Conceptualization, Writing – review & editing.

#### 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.

#### Data availability

Data will be made available on request.

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# Appendix A. Supplementary data

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.apsusc.2023.158724.

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