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# Efficient asymmetrical silicon–metal dimer electrocatalysts for the nitrogen reduction reaction†

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The electrocatalytic nitrogen reduction reaction (ENRR) has been regarded as an eco-friendly and feasible substitute for the Haber–Bosch method. Identifying the effective catalysts for the ENRR is an extremely important prerequisite but challenging. Herein, asymmetrical silicon–metal dimer catalysts doped into g-C<sub>3</sub>N<sub>4</sub> nanosheets with nitrogen vacancies (SiM@C<sub>3</sub>N<sub>4</sub>) were designed to address nitrogen activation and reduction. The concept catalysts of SiM@C<sub>3</sub>N<sub>4</sub> can combine the advantages of silicon-based and metal-based catalysts during the ENRR. Among the catalysts investigated, SiMo@C<sub>3</sub>N<sub>4</sub> and SiRu@C<sub>3</sub>N<sub>4</sub> exhibited the highest activities towards the ENRR with ultra-low onset potentials of −0.20 and −0.39 V; meanwhile, they suppressed the competing hydrogen evolution reaction (HER) due to the relative difficulty in releasing hydrogen. Additionally, SiRu@C<sub>3</sub>N<sub>4</sub> is demonstrated to possess strong hydrophobicity, which is greatly beneficial to the production of ammonia. This research provides insights into asymmetrical silicon–metal dimer catalysts and reveals a new method for developing dual-atom electrocatalysts. This asymmetrical dimer strategy can be applied in other electrocatalytic reactions for energy conversion.

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## 1. Introduction

The electrocatalytic nitrogen reduction reaction (ENRR) has been considered to be the most promising route for artificial N<sub>2</sub> fixation under ambient conditions, as it can convert N<sub>2</sub> into NH<sub>3</sub> using renewable energy sources (wind and solar energies) on the surface of electrocatalysts.<sup>1–5</sup> Although tremendous efforts have been made, the performance of electrocatalysts as the core part of electrocatalytic systems is still far from that required for realizing a pragmatic application.<sup>6</sup> Now, our societies rely heavily on the century-old Haber–Bosch (HB) method for industrial NH<sub>3</sub> production, which consumes considerable energy and releases a tremendous amount of CO<sub>2</sub> annually.<sup>7</sup> To cope with the global energy crisis and climate change, high-performance ENRR catalysts are urgently needed to substitute for the HB route.

In recent years, metal-free ENRR catalysts have been attracting attention due to their application potential.<sup>3,5,8–14</sup> Unlike metal-based electrocatalysts, metal-free electrocatalysts can circumvent the intrinsic shortcoming of the strong \*H affinity on metal-based ones, which is conducive to increasing Faradaic efficiency (FE). Moreover, metal-free electrocatalysts possess the advantages of low cost and high modification versatility, which make them suitable for pragmatic applications. For example, Sun *et al.*<sup>15–18</sup> experimentally modified carbon-based materials *via* O, F, and S heteroatoms for N<sub>2</sub> electroreduction to NH<sub>3</sub> and achieved comparable performance with that of metal-based electrocatalysts. In addition, metal-free Si-based catalysts have begun to arouse research interests in relation to the ENRR. For instance, Li *et al.*<sup>19</sup> experimentally investigated atomically dispersed Si atoms on carbon nanolayers for N<sub>2</sub> fixation and found that isoelectric Si heteroatoms can function as metal-free single-atom-based catalysts to greatly improve the FE of the pristine carbon support, with comparable results to atomically dispersed metal-based catalysts. Our previous studies also investigated the potential of Si-based electrocatalysts for the ENRR from a theoretical viewpoint, of note,<sup>13,20,21</sup> finding the relatively lower affinity of N<sub>2</sub> on Si sites compared with that on transition metal sites, which could adversely affect the subsequent activation and hydrogenation of \*N<sub>2</sub>. However, low-coordination Si atoms can act as a Lewis acid to interact with

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$N_2$  as a Lewis base with under-occupied p-orbitals *via* an electron acceptance-donation process.<sup>22</sup> Compared with the carbon atom sites on the carbon-based catalysts mentioned above, the lower electronegativity of Si can contribute to more electron back-donation into the  $1\pi^*$  anti-bonding orbitals of  $*N_2$ .

The atomically dispersed dual-atom catalysts (DACs) have garnered extensive research interest in heterogeneous catalysis due to their unique electronic structures, maximum atom-utilization efficiencies, and flexible reaction sites.<sup>23–25</sup> Especially, the heteronuclear DACs with asymmetric active sites, as a new rising star, have opened a novel pathway in atomic catalysis, which will advance the material design to address critical challenges in energy conversion. For example, Wang *et al.* designed heteronuclear DACs to break through the restriction of scaling relations on  $CO_2$  catalytic activity by combining two kinds of metal atoms embedded in the 2D  $C_2N$  support.<sup>26</sup> Moreover, Du *et al.* proposed metal Cu and non-metal B atoms supported on  $g-C_3N_4$  (Cu-B@ $g-C_3N_4$ ) for CO dimerization, which effectively reduced the CO dimerization free energy barrier due to the asymmetric synergy of the Cu–B center and suppresses the parasitic hydrogen evolution reaction (HER) caused by the synergistic  $d_{Cu}$ – $p_B$  coupling.<sup>27</sup> Therefore, based on the aforementioned discussions, in this work, we hypothesized that the dual-atom silicon (Si)–metal (M) dimers on supports could be a viable way to increase the affinity of  $N_2$  on catalysts and achieve an excellent catalytic performance in the ENRR on an asymmetric active center. The chosen supporter was  $g-C_3N_4$  due to its facile synthesis methods, large surface, and porous structure.<sup>28</sup> And  $g-C_3N_4$  has been widely employed in photocatalysis and electrocatalysis.<sup>29–35</sup> More importantly, as for Si–M dimers, the comparably easily formed N vacancy sites ( $N_V$ ) during the synthesis of  $g-C_3N_4$  are suitable anchoring sites, and have been reported to facilitate electrocatalysis on doped  $g-C_3N_4$ .<sup>36–38</sup> Based on previous reports on efficient metal-based catalysts for the ENRR,<sup>39–46</sup> here we selected Fe, Co, Ni, Nb, Mo, Ru, Rh, W, and Re metal atoms for the design of the Si–M dimer on  $g-C_3N_4$ . The finally designed dimer catalysts were denoted as SiM@ $C_3N_4$ , and the corresponding single-atom Si/M-doped catalysts were denoted as Si@ $C_3N_4$  or M@ $C_3N_4$  (more information regarding the catalyst models is provided in the ESI†). After comprehensive calculations, it was found that the asymmetric dimer catalysts (SiM@ $C_3N_4$ ) can not only improve the capture of  $N_2$  in the horizontal mode but also boost the subsequent hydrogenation process. Among the concept catalyst models, SiMo@ $C_3N_4$  and SiRu@ $C_3N_4$  are demonstrated to have ultra-low onset potentials of  $-0.20$  and  $-0.39$  V, respectively, towards the ENRR. Meanwhile, the HER would be suppressed on these two dimer catalysts due to larger free-energy barriers for  $H_2$  release from active sites ( $*H + H^+ + e^- \rightarrow H_2$ ). This work for the first time explores asymmetrical dimer catalysts composed of metals and non-metals for the ENRR, which not only combine the advantages of two types of external atoms but also offer a novel avenue for designing high-performance artificial  $N_2$  fixation catalysts.

## 2. Calculation details

Spin-polarized density functional theory (DFT) calculations were performed using the DMol<sup>3</sup> code to study the structure properties of Si–M dimers on  $g-C_3N_4$  and their corresponding ENRR activity. The revised Perdew–Burk–Ernzerhof (RPBE) generalized gradient approximation (GGA) was used to describe the electron exchange–correlation. The DFT semi-core pseudopotentials (dspp) pseudopotentials and double numerical basis sets with polarization functions (DNP) were adopted in all calculations. The Tkatchenko–Scheffler (TS) scheme was employed to illustrate the van der Waals (VDW) interactions between catalysts and adsorbates.<sup>47</sup> The real-space global cutoff radius was set to be 5.2 Å. A  $(3 \times 3 \times 1)$   $k$ -point set within the Monkhorst–Pack scheme was used to sample the Brillouin zone. Moreover, the solvation effect was also considered using the COSMO scheme with an  $H_2O$  dielectric constant of 78.54 for the ENRR. All structural optimizations were performed until the energy tolerance and residual force were smaller than  $10^{-5}$  Ha and  $0.002$  Ha Å<sup>-1</sup>, respectively, and SCF tolerance was set as  $10^{-6}$  Ha. On the basis of the computational hydrogen electrode (CHE) model developed by Nørskov *et al.*,<sup>48,49</sup> the free energy of each elementary reaction at 298.15 K and pH = 0 without the extra potential was calculated as follows:

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

where  $\Delta E_{DFT}$ ,  $\Delta E_{ZPE}$ , and  $\Delta S$  are the differences in the total electronic energy ( $E_{DFT}$ ), zero-point vibration energy ( $E_{ZPE}$ ), and entropy ( $S$ ), respectively. The  $E_{ZPE}$  value can be obtained from the harmonic frequency analyses, where only the reaction intermediates ( $N_xH_y$ ) were taken into account for the calculation of partial Hessian. The entropy of the adsorbed intermediates was negligible in comparison with that of the free gas molecules ( $H_2$ ,  $N_2$  and  $NH_3$ ). From the free energy evolution of the ENRR, one can evaluate the activity of catalysts. The limiting potential ( $U_L$ ) of the ENRR was calculated as  $U_L = -\Delta G_{max}/e$ , which represents the potential required to eliminate the potential-determining step (PDS). Then overpotential ( $\eta$ ) can be calculated from  $\eta = U_e - U_L$ , where  $U_e$  is the equilibrium potential of the NRR ( $U_e = -0.16$  V vs. standard hydrogen electrode). Of note, here  $\Delta G_{max}$  comes from the hydrogenation or the proton-coupled electron transfer step, and not the release step of  $NH_3$ , because the formed  $NH_3$  could be easily converted into  $NH_4^+$  in acidic electrolytes and desorbed from active sites smoothly according to relevant reports.<sup>50</sup> The charge density difference of the system (AB) was calculated from  $\Delta\rho = \rho_{AB} - \rho_A - \rho_B$ , where  $\rho_{AB}$ ,  $\rho_A$ , and  $\rho_B$  are three different charge density quantities and the atomic positions were fixed as those in the AB system when calculating the latter two quantities. The complete LST/QST protocol and CI-NEB method were used to locate the transition state (TS) for the reaction barrier analysis.<sup>51</sup> When calculating the density of states (DOS) and the crystal orbital Hamiltonian population (COHP), the  $(6 \times 6 \times 1)$   $k$ -point set was used to sample the Brillouin zone.



### 3. Results and discussion

#### 3.1 N<sub>2</sub> adsorption and reduction on Si@C<sub>3</sub>N<sub>4</sub>

Before examining the ENRR performance of SiM@C<sub>3</sub>N<sub>4</sub>, we started with investigating the N<sub>2</sub> adsorption and reduction on single-atom Si-doped g-C<sub>3</sub>N<sub>4</sub> (Si@C<sub>3</sub>N<sub>4</sub>) for comparison purposes with the subsequent studies on SiM@C<sub>3</sub>N<sub>4</sub>. In g-C<sub>3</sub>N<sub>4</sub>, there are three types of N sites, as shown in Fig. 1a. According to the relevant report on defective g-C<sub>3</sub>N<sub>4</sub>,<sup>31,52</sup> N<sub>v1</sub> is the common and easily formed defective site on the plane of g-C<sub>3</sub>N<sub>4</sub>, which is an ideal anchoring site for heteroatom doping. Therefore, a single-atom Si heteroatom is embedded into this defect and then the designed Si@C<sub>3</sub>N<sub>4</sub> is optimized, as shown in Fig. 1a for the subsequent calculations and comparative analysis. According to the binding energy ( $E_b$ ) equation:  $E_b = E_{\text{cat.}} - E_{\text{Si}} - E_r$ , where  $E_{\text{cat.}}$ ,  $E_{\text{Si}}$ , and  $E_r$  represent the total electronic energies of the catalyst designed, atomic Si in the gas phase, and the remaining part of the catalyst with atoms constrained in the lattice position, we obtained  $E_{b,\text{Si}} = -6.51$  eV on g-C<sub>3</sub>N<sub>4</sub>, suggesting the strong binding strength of Si on the defective g-C<sub>3</sub>N<sub>4</sub> catalyst. Then compared with the cohesive

energy of Si ( $E_{\text{co,Si}} = -4.55$  eV), one can see the excellent stability of single-atom Si@C<sub>3</sub>N<sub>4</sub> catalysts under ambient conditions. Moreover, the formation energy ( $E_f$ ) of Si@C<sub>3</sub>N<sub>4</sub> was calculated as  $E_f = \frac{1}{2}E_{\text{N}_2} + E_{\text{Si@C}_3\text{N}_4} - \mu_{\text{Si}} - E_{\text{g-C}_3\text{N}_4} = -0.08$  eV, where  $E_{\text{N}_2}$ ,  $E_{\text{Si@C}_3\text{N}_4}$ , and  $E_{\text{g-C}_3\text{N}_4}$  represent the total electronic energies of the N<sub>2</sub> molecule, the Si@C<sub>3</sub>N<sub>4</sub> catalyst, and the pristine g-C<sub>3</sub>N<sub>4</sub> nanosheet, respectively.  $\mu_{\text{Si}}$  refers to the chemical potential of Si, obtained from  $1/n * E_{\text{Si-cell}}$ , suggesting the easy in-laboratory synthesis. Also, the interstitial Si-doping configuration, as shown in Fig. S2 (ESI<sup>†</sup>), was considered. A comparison between the two formation energies indicated that Si@C<sub>3</sub>N<sub>4</sub> is more energetically favorable. Therefore, the subsequent concept catalysts of Si–M dimers were built on two N<sub>v1</sub> sites, named SiM@C<sub>3</sub>N<sub>4</sub>.

Then, we examined the adsorption of N<sub>2</sub> on Si@C<sub>3</sub>N<sub>4</sub>. Fig. 1b exhibits two adsorption configurations of N<sub>2</sub>, *i.e.*, end-on and side-on modes, and their corresponding N<sub>2</sub>-induced charge density difference (CDD). The CDD shows that there exists noticeable electron transfer, *i.e.*, electron acceptance–backdonation, between the Si site and N<sub>2</sub>, and the Hirshfeld charge analysis shows that N<sub>2</sub> obtains more electrons from the catalyst

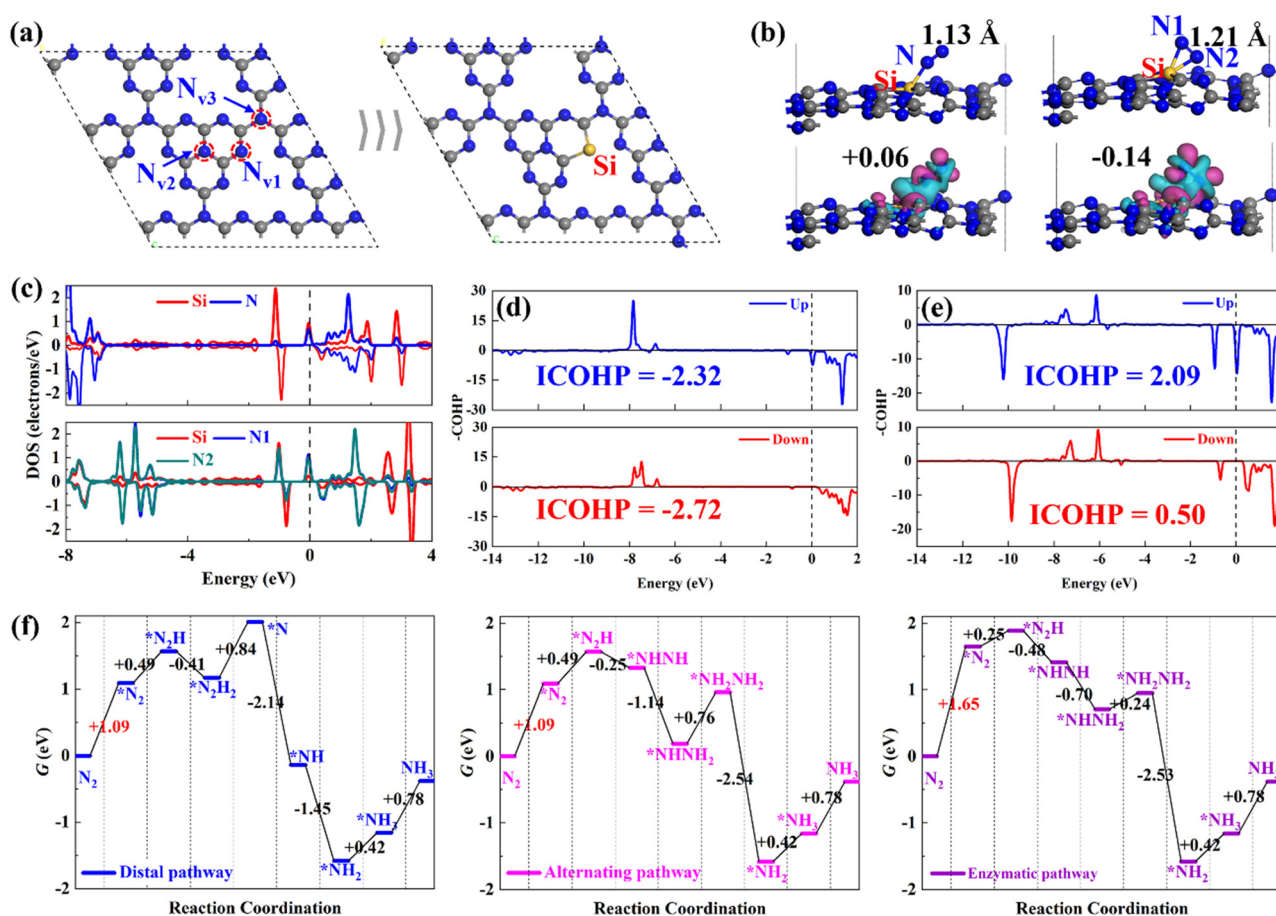


Fig. 1 Single Si doped in g-C<sub>3</sub>N<sub>4</sub> and the corresponding electronic structure and energy analyses: (a) schematic diagram of Si@C<sub>3</sub>N<sub>4</sub> formation through N<sub>v1</sub>; (b) two adsorption configurations and their corresponding electronic charge density difference induced by N<sub>2</sub> adsorption with the red and cyan color representing the electron accumulation and loss, respectively (isosurface = 0.01 a.u.). Black values show the Hirshfeld charges of adsorbed N<sub>2</sub>; (c) the Si–N electron interaction by DOS analysis; the –COHP and integrated –COHP analyses of the N–N bond from the end-on (d) and (e) side-on N<sub>2</sub> adsorption configurations; and (f) free energy evolutions through different reaction pathways. Color scheme: Si (yellow), N (blue), and C (grey).



in the side-on mode. The DOS results, shown in Fig. 1c, explain the electron interaction between Si and N: (1)  $N_2$  is polarized after adsorption and (2) the electron interaction is stronger in the side-on mode. To obtain an intuitive comparison on the degree of activation of  $N\equiv N$ , the –COHP calculations were conducted for the end-on and side-on models, as shown in Fig. 1d and 1e. The –COHP analysis shows that there are more electrons occupied in the  $1\pi^*$  anti-bonding orbitals below the Fermi level in the side-on configuration, leading to the activation of  $N_2$ . The analysis of the N–N bond length, as displayed in Fig. 1b, describes the  $N\equiv N$  triple bond elongation to 1.13 and 1.21 Å, also in agreement with the –COHP results. However, the polarized  $*N_2$  with more electrons occupying the  $1\pi^*$  orbital will increase the electronic energy. Fig. 1f shows the free energy evolutions of the ENRR starting from free  $N_2$  to the  $NH_3$  product (reaction mechanisms<sup>53,54</sup> refer to Fig. S1, ESI<sup>†</sup>), from which we can see that the adsorption of  $N_2$  presents a significant barrier to the reaction, with relatively large free energy changes of +1.09 and +1.65 eV. Such significant free energy changes are difficult to overcome under ambient conditions, indicating that the ENRR will not occur on  $Si@C_3N_4$ . Enhancing the  $N_2$  adsorption will boost the ENRR performance.

### 3.2 $N_2$ adsorption on $SiM@C_3N_4$

Here, asymmetric dimer electrocatalysts ( $SiM@C_3N_4$ ) were designed to address the low affinity of  $N_2$  on active sites. We chose some high-performance ENRR transition metals (TMs) to cooperate with Si to capture  $N_2$ , and the metal elements selected are shown in Fig. 2a. Fig. 2b displays the design scheme of concept- $SiM@C_3N_4$  which involves using two  $N_{V1}$  vacancies on  $g-C_3N_4$ . The optimized  $SiM@C_3N_4$  catalysts are shown in Fig. S3 (ESI<sup>†</sup>). According to  $E_b$  and ( $E_{co,Si} + E_{co,M}$ ) analyses of dimers (see Table S1, ESI<sup>†</sup>), it is anticipated that these  $SiM@C_3N_4$  concept models all exhibit strong stability under ambient conditions.

Then  $N_2$  adsorption on  $SiM@C_3N_4$  was examined. Fig. 2c and 2d display two dimer models, *i.e.*,  $SiMo@C_3N_4$  and

$SiRu@C_3N_4$ . They all have strong  $N_2$  adsorption ability with the adsorption free energy ( $\Delta G_{*N_2}$ ) less than 0.50 eV (see Fig. 3), indicating the occurrence possibility of  $N_2$  adsorption under ambient conditions.<sup>55,56</sup> Fig. 3 displays the side-on adsorption configurations of  $N_2$  on  $SiM@C_3N_4$  except for  $SiRe@C_3N_4$ , because  $N_2$  can only be captured in the end-on model at the Re site after geometry optimization as shown in Fig. S4 (ESI<sup>†</sup>). Among nine dimer concept-electrocatalysts, based on  $E_{ads}$  and adsorption-free energies ( $\Delta G_{*N_2}$ ), only two dimer catalysts were shown to have good  $N_2$  adsorption ability, *i.e.*,  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$ , with  $\Delta G_{*N_2}$  of 0.17 and 0.28 eV, respectively. Moreover, the side-on adsorption modes on  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$  well-activated the adsorbed  $*N_2$  with the extended  $N\equiv N$  lengths of 1.21 and 1.20 Å, respectively. However, other dimers showed  $\Delta G_{*N_2} > 0.50$  eV, indicating that  $N_2$  adsorption under ambient conditions is challenging to overcome, although they all exhibited the activated characteristics due to the elongated N–N bond. To further analyze the adsorption process of  $N_2$  on  $SiM@C_3N_4$ , the kinetic barriers were analyzed as shown in Fig. S5 (ESI<sup>†</sup>), from which it was noticed that  $N_2$  adsorption barriers were all less than 0.50 eV except for  $SiNi@C_3N_4$ .  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$  with the most energetically favorable  $*N_2$  configurations demonstrated quite small reaction barriers of 0.23 and 0.24 eV, respectively. Therefore, from the perspective of adsorption thermodynamics and kinetics,  $N_2$  can be readily activated on  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$  under ambient conditions.

### 3.3 ENRR on $SiMo@C_3N_4$ and $SiRu@C_3N_4$

Following the discussion on  $N_2$  adsorption above, we examined the ENRR performance on  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$ . According to relevant reports,<sup>57,58</sup> when  $N_2$  is captured on dimer catalysts in a side-on mode, the ENRR generally can occur through two mechanisms, *i.e.*, enzymatic and consecutive ones, which is schematically depicted in Fig. S6 (ESI<sup>†</sup>). Therefore, the ENRR on  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$  was investigated according to the proposed mechanisms computationally.

Fig. 4 and Fig. S7 (ESI<sup>†</sup>) show the enzymatic and consecutive pathways on  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$ , respectively. For the first hydrogenation reduction step of  $*N_2 + H^+ + e^- \rightarrow *N_2H$ , there are two possible hydrogenation ways through the attack of the  $H^+/e^-$  pair (shown in Fig. S8, ESI<sup>†</sup>): one is to attack the N adatom bonded to Si and another is to attack the N adatom connected to the metal site. Based on free-energy analyses, the  $H^+/e^-$  pair energetically first tends to attack the N adatom bonded to the metal site. Likewise, on  $SiMo@C_3N_4$ ,  $*NH_3$  species also tend to form on the metal site; however, for  $SiRu@C_3N_4$ ,  $*NH_2$  and  $*NH_3$  species can only form on the Si site. Fig. 5 demonstrates their corresponding free energy evolutions along enzymatic and consecutive pathways, from which we can notice that the PDS is the first hydrogenation step. Due to the well-activated N–N bond of  $*N_2$ , free-energy changes during the first hydrogenation steps on these two asymmetrical dimer centers, *i.e.*,  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$ , are pretty low. The limiting potentials ( $U_L$ ) on  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$  are merely –0.20 and –0.39 V, respectively, for the ENRR, with the

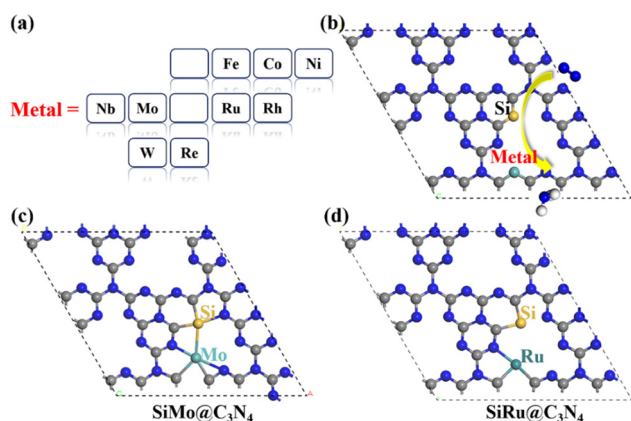


Fig. 2 (a) Chosen metal elements for the concept models of  $SiM@C_3N_4$ ; (b) the design strategy of  $SiM@C_3N_4$  for ENRR; (c and d) potential high-performance catalysts:  $SiMo@C_3N_4$  and  $SiRu@C_3N_4$ . Color scheme: Si (yellow), H (white), N (blue), and C (grey).



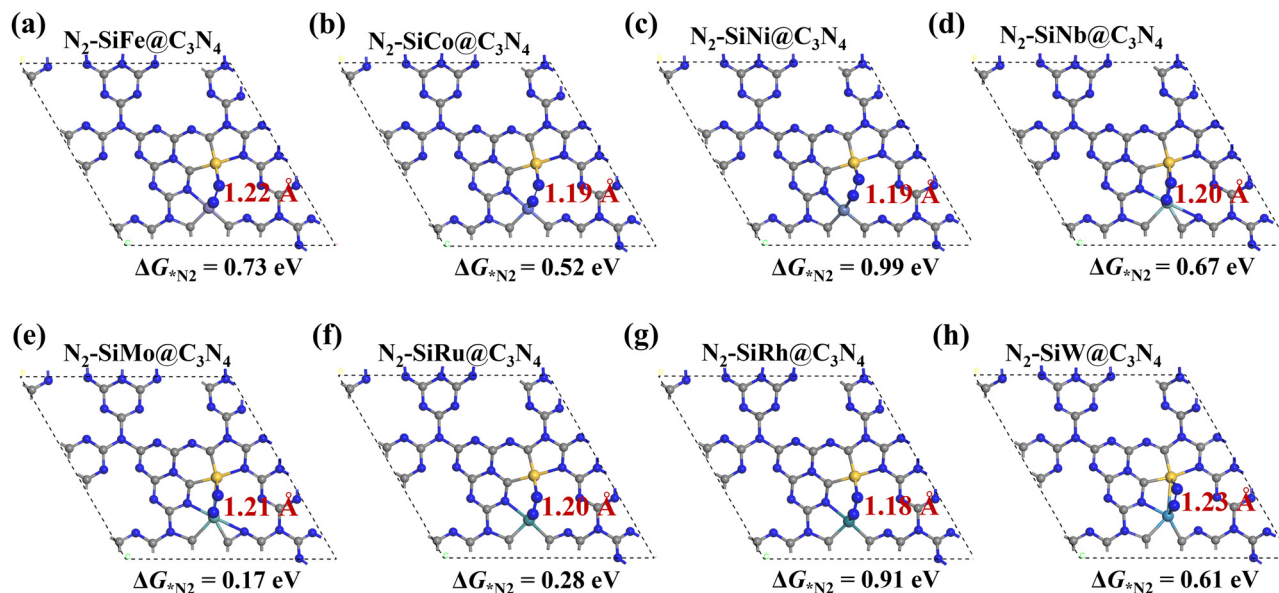


Fig. 3 (a–h) Side-on adsorption configurations of  $*N_2$  on  $SiM@C_3N_4$  with adsorption-free energies ( $\Delta G_{*N_2}$ ) and N–N bond lengths.  $N_2$  adsorption configuration on  $SiRe@C_3N_4$  is shown in Fig. S4 (ESI†).

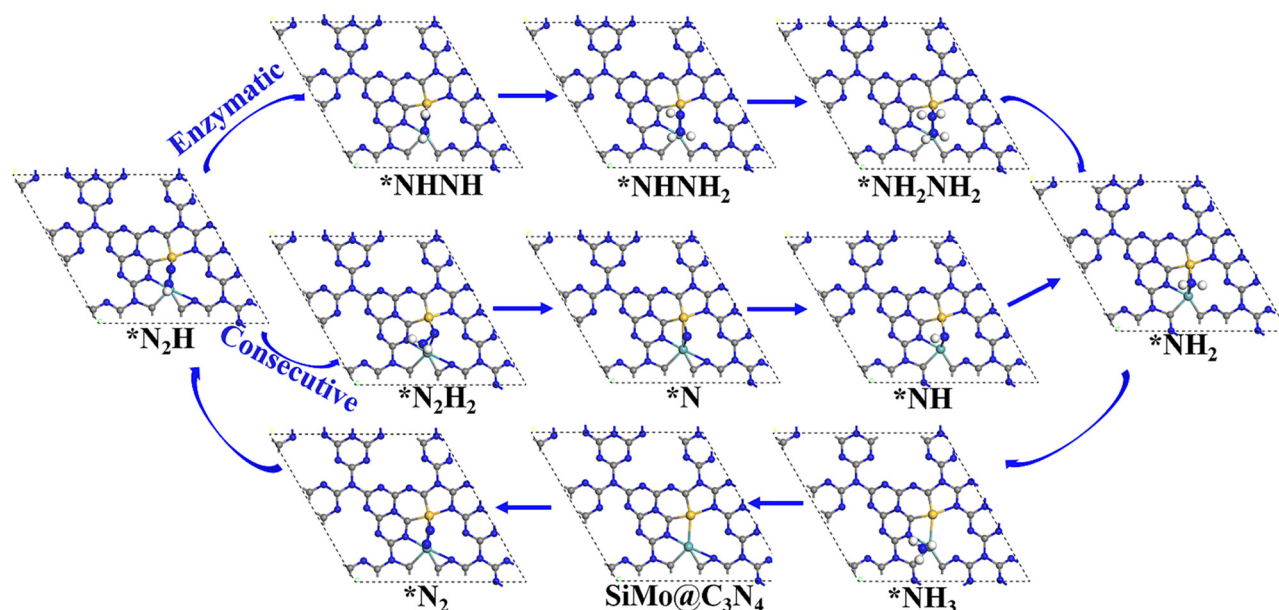


Fig. 4 The enzymatic and consecutive pathways of the ENRR on  $SiMo@C_3N_4$ , and the ENRR on  $SiRu@C_3N_4$  is shown in Fig. S7 (ESI†).

responding overpotentials ( $\eta$ ) of 0.04 and 0.23 V, respectively. Such low overpotentials indicate that the ENRR can be boosted under an ultra-low external potential. Moreover, these two dimers show comparable and even better performance than the reported metal-based electrocatalysts (FeV@ $C_2N$ :<sup>59</sup>  $U_L = -0.17$  V; NbB:<sup>60</sup>  $U_L = -0.40$  V; MnB:<sup>60</sup>  $U_L = -0.33$  V; Mo and W-doped Au-based single-atom alloys:<sup>61</sup>  $U_L = -0.30$  V; Mo@BM- $\beta_{12}$ :<sup>62</sup>  $U_L = -0.26$  V; and Mn@BM- $\beta_{12}$ :<sup>62</sup>  $U_L = -0.32$  V), even outperform some 2D Mxenes<sup>63</sup> ( $Mo_2C(OH)_2$ :  $U_L = -0.62$  V;  $V_2C(OH)_2$ :  $U_L = -0.71$  V; and  $Cr_2C(OH)_2$ :  $U_L = -0.78$  V) and TM

single-atom catalysts<sup>45,64</sup> ( $Mo_1$ /pyrrolic- $N_3$ -G:  $U_L = -0.49$  V,  $Re_1$ /pyrrolic- $N_3$ -G:  $U_L = -0.51$  V; and  $Nb@P_3$ -Ars:  $U_L = -0.52$  V), exhibiting a great promising prospect towards electrocatalytic nitrogen fixation.

#### ENRR on $Mo@C_3N_4$ and $Ru@C_3N_4$

Single-atom catalysts (SACs) have been the front line for upgrading ENRR electrocatalysts due to their peculiar properties, such as high-atom utilization, low-coordination sites, and tunable electronic properties. However, sometimes SACs suffer



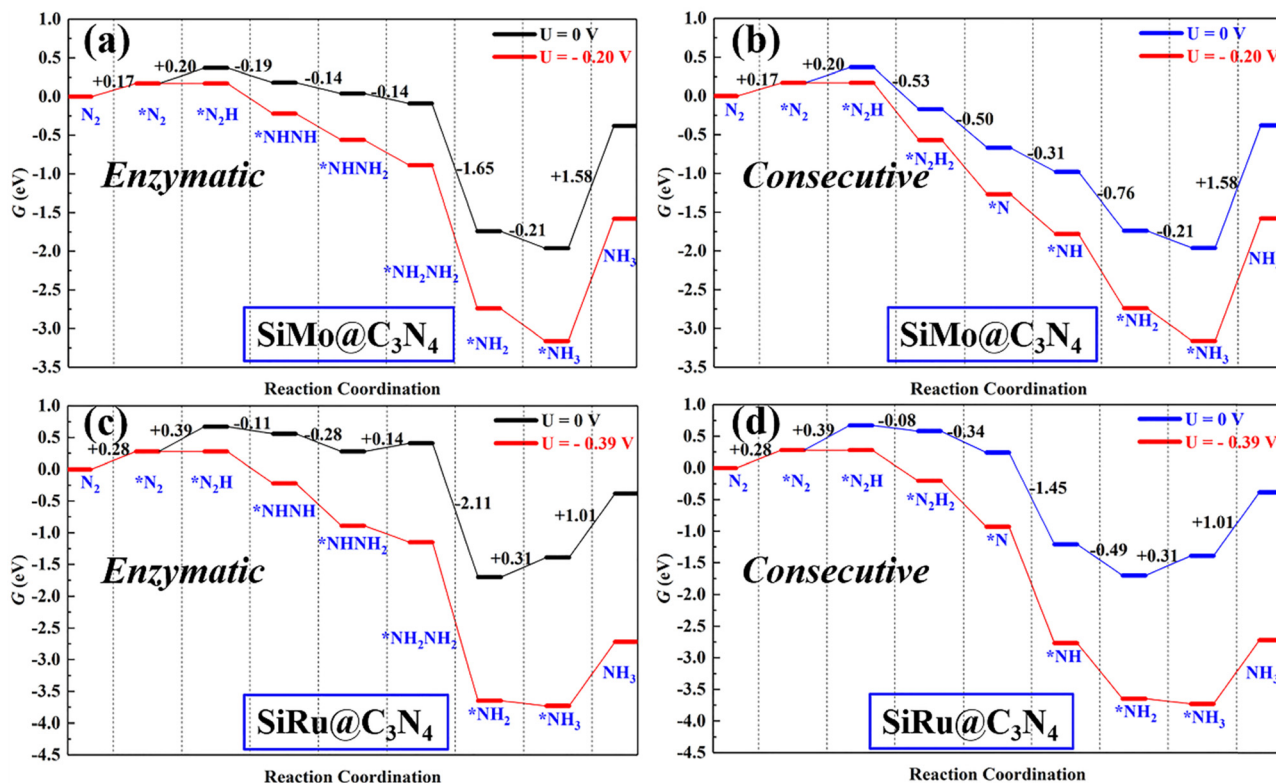


Fig. 5 The free energy evolutions of enzymatic and consecutive pathways on (a and b)  $\text{SiMo@C}_3\text{N}_4$  and (c and d)  $\text{SiRu@C}_3\text{N}_4$  with and without the applied potential ( $U$ ).

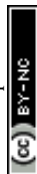
from the limitation of scaling relationship during the ENRR, *i.e.*, less flexibility to meet all energetic requirements of multiple proton-coupled electron-transfer steps by tuning the electronic structures. Therefore, dual active sites may provide a solution to this issue.

For comparison with dimer catalysts, here ENRR performance on TM single-atom  $\text{Mo@C}_3\text{N}_4$  and  $\text{Ru@C}_3\text{N}_4$  (see Fig. S9–S11, ESI<sup>†</sup>) catalysts was also investigated. First,  $\text{N}_2$  adsorption on  $\text{Mo@C}_3\text{N}_4$  and  $\text{Ru@C}_3\text{N}_4$  was also studied and is shown in Fig. S10 (ESI<sup>†</sup>). One can find that, on  $\text{Mo@C}_3\text{N}_4$ , the end-on adsorption configuration with  $\Delta G_{\text{N}_2} = -0.20$  eV is more favorable energetically than the side-on mode with  $\Delta G_{\text{N}_2} = 0.56$  eV, while as for  $\text{Ru@C}_3\text{N}_4$ ,  $\text{N}_2$  can be chemically adsorbed on the Ru site only in the end-on mode with  $\Delta G_{\text{N}_2} = 0.33$  eV. Therefore, tasking the  $\text{N}_2$  end-on adsorption modes on both SACs as starting points, the ENRR along the distal and alternating pathway was investigated as shown in Fig. S11 (ESI<sup>†</sup>). Their corresponding free-energy evolutions are presented in Fig. 6, from which again we noticed that the first hydrogenation step ( $^*\text{N}_2 + \text{H}^+ + e^- \rightarrow ^*\text{N}_2\text{H}$ ) is the PDS, with  $\Delta G$  of 0.78 and 0.89 eV, for  $\text{Mo@C}_3\text{N}_4$  and  $\text{Ru@C}_3\text{N}_4$ , respectively. As a result, the limiting potentials on  $\text{Mo@C}_3\text{N}_4$  and  $\text{Ru@C}_3\text{N}_4$  are  $-0.78$  and  $-0.89$  V, respectively, which are distinctly greater than those on  $\text{SiMo@C}_3\text{N}_4$  and  $\text{SiRu@C}_3\text{N}_4$  dimer catalysts. Generally, the first hydrogenation step is determined from the activation degree of  $^*\text{N}_2$  on electrocatalysts. This suggests that dimer catalysts possess a superb activity in the ENRR than

SACs, demonstrating the synergistic advantage of the combination of Si and metal sites (Mo/Ru) in  $\text{N}_2$  adsorption and activation.

### 3.5 Origin of high-performance dimers

For studying the high-performance origin of  $\text{SiMo@C}_3\text{N}_4$  and  $\text{SiRu@C}_3\text{N}_4$ , we investigated their electronic structures, as shown in Fig. 7. First, the calculated charge density difference (Fig. 7a) suggests that  $\text{N}_2$  has a stronger electron exchange on  $\text{SiM@C}_3\text{N}_4$  than on  $\text{M@C}_3\text{N}_4$ , and the Hirshfeld charge analysis (Table S2, ESI<sup>†</sup>) proved it quantitatively. The DOS data demonstrate the electron interaction around the Fermi level, and the strong electron exchange between  $\text{N}_2$  and  $\text{SiM@C}_3\text{N}_4$  resulted in splitting of the  $1\pi$  molecular-orbital (MO). As for the  $\text{N}_2$  adsorption on  $\text{Mo@C}_3\text{N}_4$  and  $\text{Ru@C}_3\text{N}_4$ , the DOS overlap between the metal site and  $\text{N}_2$  below the Fermi level was very small, suggesting a weaker electron interaction. This is also in accordance with the N–N bond length and electron density analyses (Fig. 7a). The COHP, offering an atom pair's chemical bonding and anti-bonding information, is a visual bonding indicator. Thus, the COHP analysis was performed for  $^*\text{N}_2$ , as shown in Fig. 7c. Indeed, a larger electron occupation in the  $1\pi^*$  orbital for side-on adsorption configurations on  $\text{SiM@C}_3\text{N}_4$  was observed, and ICOHP results are on the order of  $-11.72$  ( $^*\text{N}_2$  on  $\text{SiRu@C}_3\text{N}_4$ )  $< -10.32$  ( $^*\text{N}_2$  on  $\text{SiMo@C}_3\text{N}_4$ ),  $-4.37$  ( $^*\text{N}_2$  on  $\text{Ru@C}_3\text{N}_4$ )  $< -4.08$  ( $^*\text{N}_2$  on  $\text{Mo@C}_3\text{N}_4$ ), quantitatively explaining the activation degree. The larger activation degree of  $\text{N}_2$  is



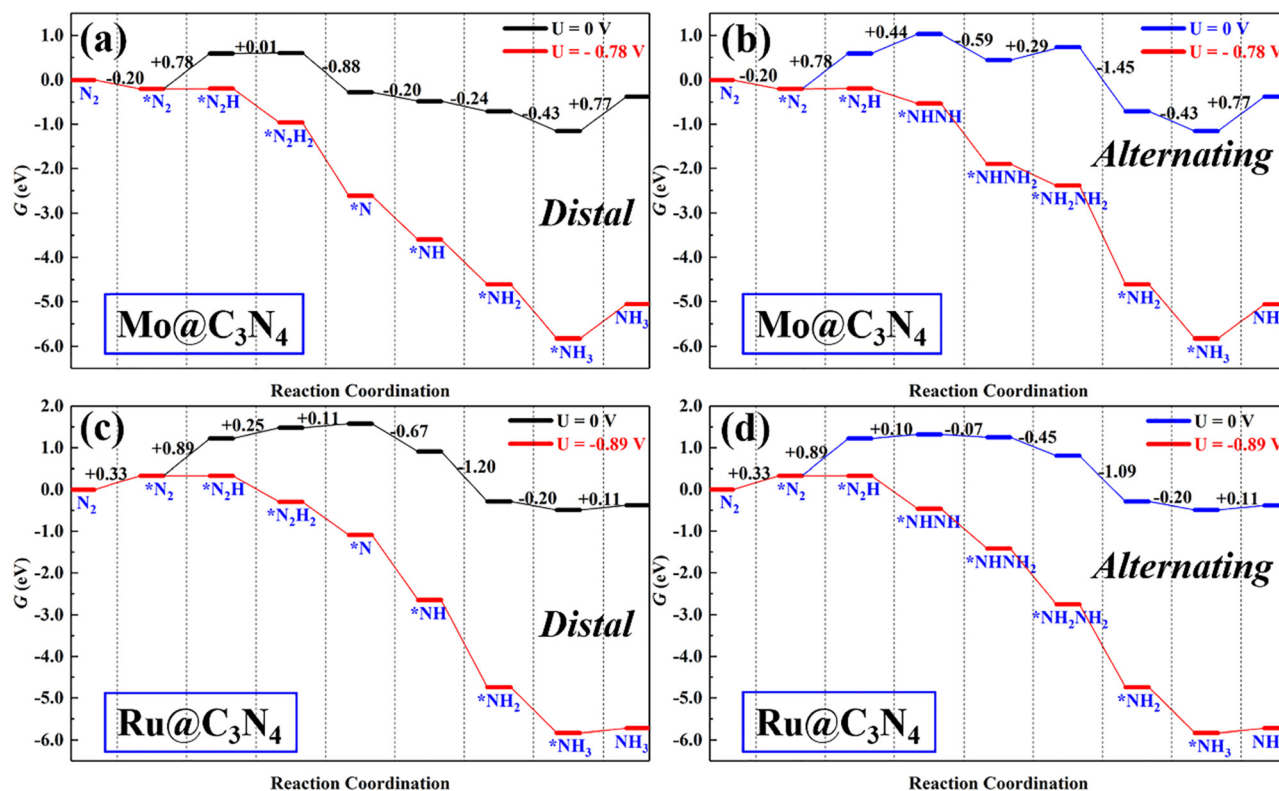


Fig. 6 The free energy evolution of the ENRR on (a and b)  $\text{Mo@C}_3\text{N}_4$  and (c and d)  $\text{Ru@C}_3\text{N}_4$ .

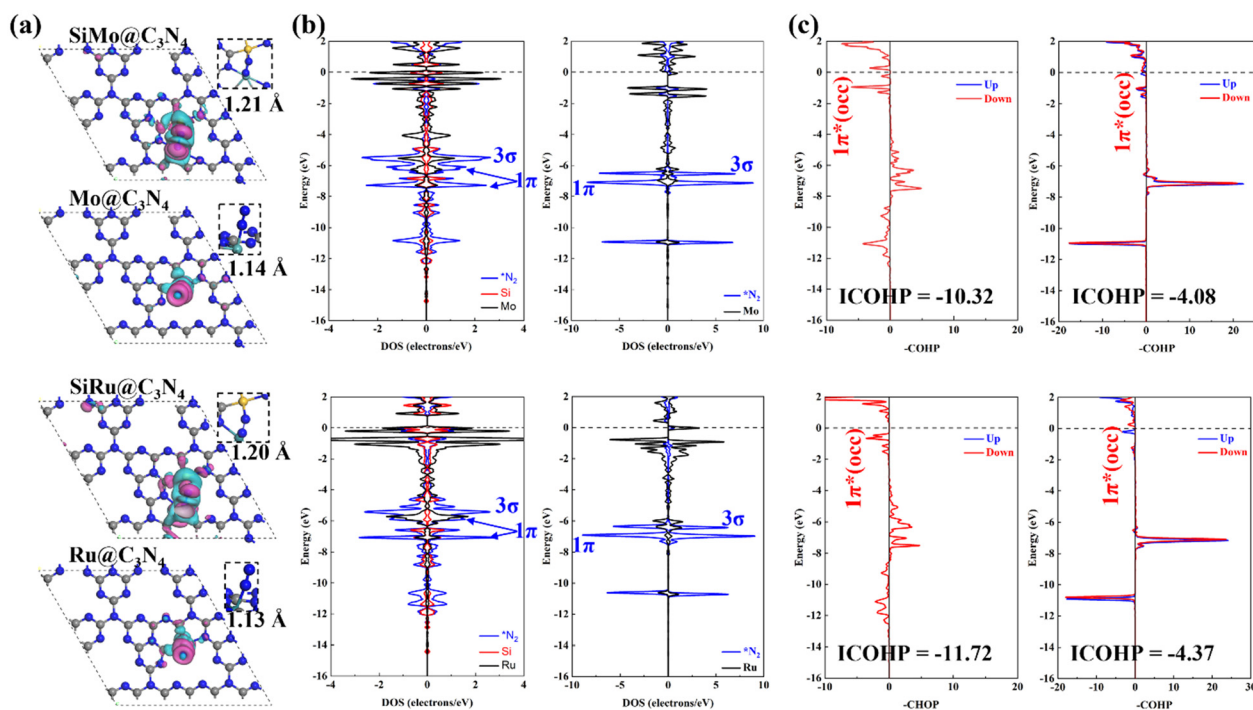


Fig. 7 Analyses of the electronic structure: (a) the DFT-calculated charge density difference induced by  $\text{N}_2$  adsorption with the N–N bond length, and the red and cyan represent the electron accumulation and loss, respectively (isosurface = 0.01 a.u.); (b) DOS analyses for  $^*\text{N}_2$ , Si, Mo, and Ru of four concept-models; and (c) the  $-\text{COHP}$  analyses for  $^*\text{N}_2$ , where “ $1\pi^*$  (occ)” refers to the occupation of  $1\pi^*$  anti-bonding orbitals.



conductive to decreasing the free energy of the first hydrogenation step.

Besides, the electron transfer between reaction intermediates and active sites also plays a crucial role during the hydrogenation process. Thus, we analyzed the Hirshfeld charge evolution of the ENRR on SiM@C<sub>3</sub>N<sub>4</sub> and M@C<sub>3</sub>N<sub>4</sub> (M = Mo and Ru) as shown in Fig. S13 (ESI<sup>†</sup>). Here, we analyzed Hirshfeld charges of four moieties on SiM@C<sub>3</sub>N<sub>4</sub> (M = Mo and Ru) and three moieties on M@C<sub>3</sub>N<sub>4</sub> (M = Mo and Ru): N<sub>x</sub>H<sub>y</sub>, (the reaction intermediates), Si (the non-metal site), Mo/Ru (the metal site) and defective g-C<sub>3</sub>N<sub>4</sub> (the supporter structure). First, on SiMo@C<sub>3</sub>N<sub>4</sub> (see Fig. S13a, ESI<sup>†</sup>), the charge evolution of N<sub>x</sub>H<sub>y</sub> was different from that of g-C<sub>3</sub>N<sub>4</sub>, and obvious charge oscillation for both N<sub>x</sub>H<sub>y</sub> and g-C<sub>3</sub>N<sub>4</sub> could be observed. However, the charges on active sites (Si and Mo) oscillate slightly, and even the charge on Mo remains almost unchanged along the reaction coordinate. These findings suggest that g-C<sub>3</sub>N<sub>4</sub> serves as the electron reservoir, and the active sites (Si and Mo) act as the electron adaptors. Similar results can also be obtained on SiRu@C<sub>3</sub>N<sub>4</sub> (see Fig. S13c, ESI<sup>†</sup>). Additionally, these two active sites of SiM@C<sub>3</sub>N<sub>4</sub> (M = Mo and Ru) could slightly regulate the charges on N<sub>x</sub>H<sub>y</sub> as a mediator during the synthesis of second ammonia. But, as for single-atom Mo@C<sub>3</sub>N<sub>4</sub> and Ru@C<sub>3</sub>N<sub>4</sub> (see Fig. S13b and d, ESI<sup>†</sup>), only the metal site can transfer electrons back and forth between g-C<sub>3</sub>N<sub>4</sub> and N<sub>x</sub>H<sub>y</sub> intermediates. And the active site (Mo/Ru) mainly acts as an electron adaptor during the ENRR process because of almost unchanged Hirshfeld charges on them.

### 3.6 Hydrogen evolution reaction

The HER is parasitic in electrocatalysis, which can primarily consume electrons and reduce the selectivity of ammonia during the ENRR. The HER is a common issue in electrocatalysis, and many electro-chemical reduction reactions, including but not limited to carbon dioxide reduction,<sup>65,66</sup> nitrate reduction,<sup>67</sup> and nitrogen reduction. A suitable catalyst should not only have high activity but also possess decent selectivity. Here, adsorption of \*H on two potential active sites of dimer catalysts, *i.e.*, Si and M (M = Mo/Ru), was examined as shown in Fig. 8a and 8b. We can find that  $\Delta G_{\max}^{\text{HER}}$  on SiMo@C<sub>3</sub>N<sub>4</sub> is larger than  $\Delta G_{\max}^{\text{NRR}}$  (0.20 eV), and  $\Delta G_{\max}^{\text{HER}}$  on SiRu@C<sub>3</sub>N<sub>4</sub> is also larger than  $\Delta G_{\max}^{\text{NRR}}$  (0.39 eV), which suggests that the HER will be suppressed due to the hindered Heyrovsky step (\*H + H<sup>+</sup> + e<sup>-</sup> → H<sub>2</sub>). Therefore, the ENRR is energetically more favorable compared to the HER. Therefore, SiMo@C<sub>3</sub>N<sub>4</sub> and SiRu@C<sub>3</sub>N<sub>4</sub> would have high ammonia selectivity.

In addition, the water molecules in electrolytes may affect the N<sub>2</sub> adsorption. Therefore, water adsorption was also studied, as shown in Fig. 8c and d. In comparison with the N<sub>2</sub> adsorption, we can notice that the Mo site on SiMo@C<sub>3</sub>N<sub>4</sub> will be occupied by H<sub>2</sub>O due to a lower adsorption free energy of -0.45 eV, which will adversely influence the nitrogen activation and reduction; while SiRu@C<sub>3</sub>N<sub>4</sub> tends to adsorb N<sub>2</sub> rather than H<sub>2</sub>O due to the lower adsorption free energy (0.35 eV) than that (0.72 and 0.72 eV) of H<sub>2</sub>O. This indicates that SiRu@C<sub>3</sub>N<sub>4</sub> will exhibit high activity and selectivity towards the ENRR, while SiMo@C<sub>3</sub>N<sub>4</sub> will favor the ENRR in electrolytes

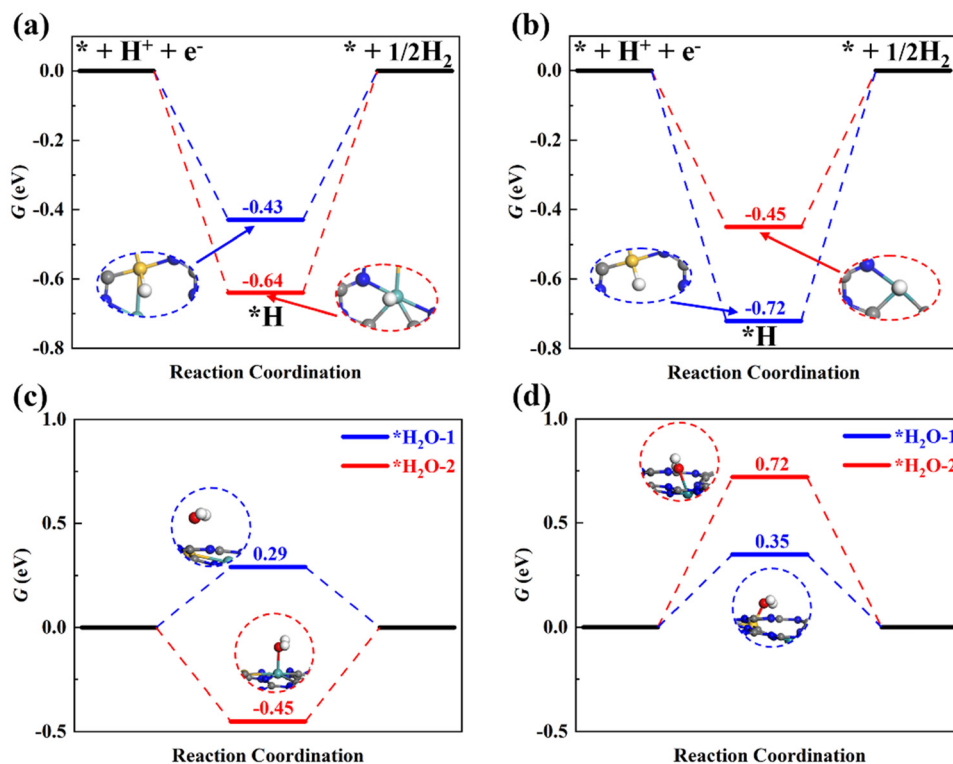


Fig. 8 Hydrogen evolution reaction on (a) SiMo@C<sub>3</sub>N<sub>4</sub> and (b) SiRu@C<sub>3</sub>N<sub>4</sub>; the adsorption free energies of H<sub>2</sub>O on (c) SiMo@C<sub>3</sub>N<sub>4</sub> and (d) SiRu@C<sub>3</sub>N<sub>4</sub>. Note that there are two potential active sites on dimer catalysts for hydrogen and water adsorption.





with a low concentration of H<sub>2</sub>O, for example, ionic liquids.<sup>68</sup> To evaluate the synthetic availability of SiMo@C<sub>3</sub>N<sub>4</sub> and SiRu@C<sub>3</sub>N<sub>4</sub> with high activity in the laboratory, their formation energy was analyzed, which was found to be 2.19 and 1.36 eV, respectively, which means that both of them can be synthesized using some precursors and SiRu@C<sub>3</sub>N<sub>4</sub> is easier to synthesize. Meanwhile, we designed another two models, SiMo-C<sub>3</sub>N<sub>4</sub> and SiRu-C<sub>3</sub>N<sub>4</sub> (see Fig. S14, ESI<sup>†</sup>), which are derived by directly doping two atoms into the holes of g-C<sub>3</sub>N<sub>4</sub> nanosheets. By comparing their formation energies (Table S3, ESI<sup>†</sup>), we can see that the concept models of SiMo@C<sub>3</sub>N<sub>4</sub> and SiRu@C<sub>3</sub>N<sub>4</sub> are easier to synthesize. Therefore, again it is shown that the N<sub>v</sub> site is a perfect anchoring site for atomic catalysts.

## Conclusion

To sum up, asymmetrical dimer electrocatalysts were designed to realize the ENRR efficiently. Among the investigated SiM@C<sub>3</sub>N<sub>4</sub> catalyst models, SiMo@C<sub>3</sub>N<sub>4</sub> and SiRu@C<sub>3</sub>N<sub>4</sub> exhibited the highest activity towards the ENRR with strong N<sub>2</sub> adsorption abilities and ultra-low onset potentials of -0.20 and -0.39 V, respectively. Moreover, these catalysts are capable of suppressing the competitive HER. Especially, SiRu@C<sub>3</sub>N<sub>4</sub> exhibiting strong hydrophobicity possesses high NH<sub>3</sub> selectivity. This design strategy not only addresses the issue of low adsorption and activation ability towards N<sub>2</sub> on Si but also opens up a new avenue for designing asymmetrical dimer electrocatalysts for the ENRR, with the advantage of metal-based and non-metal-based catalysts.

## Conflicts of interest

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

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