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View Article Online **PAPER**



Cite this: Phys. Chem. Chem. Phys., 2023, 25, 13126

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-C₃N₄ nanosheets with nitrogen vacancies (SiM@C₃N₄) were designed to address nitrogen activation and reduction. The concept catalysts of SiM@C₃N₄ can combine the advantages of siliconbased and metal-based catalysts during the ENRR. Among the catalysts investigated, SiMo@C3N4 and SiRu@ C_3N_4 exhibited the highest activities towards the ENRR with ultra-low onset potentials of -0.20and -0.39 V; meanwhile, they suppressed the competing hydrogen evolution reaction (HER) due to the relative difficulty in releasing hydrogen. Additionally, SiRu@C₃N₄ 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.

Received 21st December 2022, Accepted 13th April 2023

DOI: 10.1039/d2cp05959b

rsc.li/pccp

1. Introduction

The electrocatalytic nitrogen reduction reaction (ENRR) has been considered to be the most promising route for artificial N₂ fixation under ambient conditions, as it can convert N₂ into NH₃ using renewable energy sources (wind and solar energies) on the surface of electrocatalysts. 1-5 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.⁶ Now, our societies rely heavily on the century-old Haber-Bosch (HB) method for industrial NH₃ production, which consumes considerable energy and releases a tremendous amount of CO2 annually.7 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.3,5,8-14 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. 15-18 experimentally modified carbon-based materials via O, F, and S heteroatoms for N₂ electroreduction to NH₃ and achieved comparable performance with that of metalbased electrocatalysts. In addition, metal-free Si-based catalysts have begun to arouse research interests in relation to the ENRR. For instance, Li et al. 19 experimentally investigated atomically dispersed Si atoms on carbon nanolayers for N2 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, 13,20,21 finding the relatively lower affinity of N₂ on Si sites compared with that on transition metal sites, which could adversely affect the subsequent activation and hydrogenation of *N2. However, lowcoordination Si atoms can act as a Lewis acid to interact with

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[†] Electronic supplementary information (ESI) available. See DOI: https://doi.org/ 10.1039/d2cp05959b

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N₂ as a Lewis base with under-occupied p-orbitals via an electron acceptance-donation process.²² 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 atomutilization efficiencies, and flexible reaction sites. 23-25 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 CO2 catalytic activity by combining two kinds of metal atoms embedded in the 2D C2N support.²⁶ Moreover, Du et al. proposed metal Cu and nonmetal B atoms supported on g-C₃N₄ (Cu-B@g-C₃N₄) 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.²⁷ 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 N₂ on catalysts and achieve an excellent catalytic performance in the ENRR on an asymmetric active center. The chosen supporter was g-C₃N₄ due to its facile synthesis methods, large surface, and porous structure.28 And g-C3N4 has been widely employed in photocatalysis and electrocatalysis. ^{29–35} More importantly, as for Si-M dimers, the comparably easily formed N vacancy sites (N_V) during the synthesis of g-C₃N₄ are suitable anchoring sites, and have been reported to facilitate electrocatalysis on doped g-C₃N₄. ³⁶⁻³⁸ Based on previous reports on efficient metal-based catalysts for the ENRR, 39-46 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-C₃N₄. The finally designed dimer catalysts were denoted as SiM@C₃N₄, and the corresponding single-atom Si/M-doped catalysts were denoted as Si@C₃N₄ or M@C₃N₄ (more information regarding the catalyst models is provided in the ESI†). After comprehensive calculations, it was found that the asymmetric dimer catalysts (SiM@C₃N₄) can not only improve the capture of N₂ in the horizontal mode but also boost the subsequent hydrogenation process. Among the concept catalyst models, SiMo@C₃N₄ and SiRu@C₃N₄ are demonstrated to have ultra-low onset potentials of -0.20and -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 H2 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 N₂ fixation catalysts.

Calculation details

Spin-polarized density functional theory (DFT) calculations were performed using the DMol³ code to study the structure properties of Si-M dimers on g-C₃N₄ 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 pseudopots (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. 47 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 H₂O 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^{-1} , 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., 48,49 the free energy of each elementary reaction at 298.15 K and pH = 0 without the extra potential was calculated as follows:

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

where ΔE_{DFT} , ΔE_{ZPE} , and ΔS 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_v) 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 (H₂, N₂ and NH₃). 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 $U_L = -\Delta G_{\text{max}}/e$, which represents the potential required to eliminate the potential-determining step (PDS). Then overpotential (η) can be calculated from $\eta = U_e - U_L$, where U_e is the equilibrium potential of the NRR ($U_e = -0.16 \text{ V } \nu s.$ standard hydrogen electrode). Of note, here ΔG_{max} comes from the hydrogenation or the proton-coupled electron transfer step, and not the release step of NH₃, because the formed NH₃ could be easily converted into NH4+ in acidic electrolytes and desorbed from active sites smoothly according to relevant reports.⁵⁰ The charge density difference of the system (AB) was calculated from $\Delta \rho = \rho_{AB} - \rho_{A} - \rho_{B}$, where ρ_{AB} , ρ_{A} , and ρ_{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.51 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.

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3. Results and discussion

N₂ adsorption and reduction on Si@C₃N₄

Before examining the ENRR performance of SiM@C₃N₄, we started with investigating the N2 adsorption and reduction on single-atom Si-doped g-C₃N₄ (Si@C₃N₄) for comparison purposes with the subsequent studies on SiM@C₃N₄. In g-C₃N₄, there are three types of N sites, as shown in Fig. 1a. According to the relevant report on defective g-C₃N₄, 31,52 N_{v1} is the common and easily formed defective site on the plane of g-C₃N₄, 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@C₃N₄ is optimized, as shown in Fig. 1a for the subsequent calculations and comparative analysis. According to the binding energy (E_b) equation: $E_b =$ $E_{\rm cat.}-E_{\rm Si}-E_{\rm r}$, where $E_{\rm cat.}$, $E_{\rm Si}$, and $E_{\rm r}$ represent the total electronic energies of the catalyst designed, atomic Si in the gas phrase, and the remaining part of the catalyst with atoms constrained in the lattice position, we obtained $E_{\rm b,Si} = -6.51$ eV on g-C₃N₄, suggesting the strong binding strength of Si on the defective g-C₃N₄ catalyst. Then compared with the cohesive

energy of Si ($E_{\text{co,Si}} = -4.55 \text{ eV}$), one can see the excellent stability of single-atom Si@C₃N₄ catalysts under ambient conditions. Moreover, the formation energy (E_f) of Si@C₃N₄ was calculated as $E_f = \frac{1}{2}E_{N_2} + E_{Si@C_2N_4} - \mu_{Si} - E_{g-C_2N_4} = -0.08 \text{ eV}$, where E_{N_2} , $E_{Si@C_3N_4}$, and $E_{g\cdot C_3N_4}$ represent the total electronic energies of the N2 molecule, the Si@C3N4 catalyst, and the pristine g-C₃N₄ nanosheet, respectively. μ_{Si} refers to the chemical potential of Si, obtained from $1/n*E_{Si-cell}$, suggesting the easy in-laboratory synthesis. Also, the interstitial Si-doping configuration, as shown in Fig. S2 (ESI†), was considered. A comparison between the two formation energies indicated that Si@C₃N₄ is more energetically favorable. Therefore, the subsequent concept catalysts of Si-M dimers were built on two Nv1 sites, named SiM@C2N4.

Then, we examined the adsorption of N₂ on Si@C₃N₄. Fig. 1b exhibits two adsorption configurations of N2, i.e., end-on and side-on modes, and their corresponding N2-induced charge density difference (CDD). The CDD shows that there exists noticeable electron transfer, i.e., electron acceptance-backdonation, between the Si site and N2, and the Hirshfeld charge analysis shows that N2 obtains more electrons from the catalyst

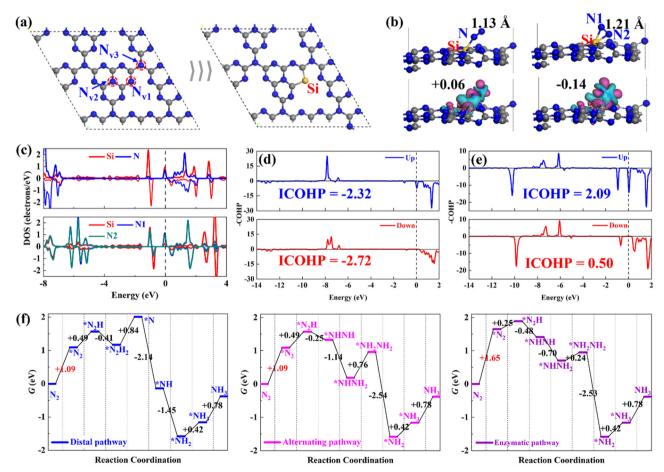


Fig. 1 Single Si dopped in $g-C_3N_4$ and the corresponding electronic structure and energy analyses: (a) schematic diagram of Si@ C_3N_4 formation through N_{vl} ; (b) two adsorption configurations and their corresponding charge density difference induced by N_2 adsorption with the red and cyan color representing the electron accumulation and loss, respectively (isosurface = 0.01 a.u.). Black values show the Hirshfeld charges of adsorbed N₂; (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 N₂ adsorption configurations; and (f) free energy evolutions through different reaction pathways. Color scheme: Si (yellow), N (blue), and C (grey).

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in the side-on mode. The DOS results, shown in Fig. 1c, explain the electron interaction between Si and N: (1) N₂ 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=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 N₂. 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 *N₂ 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 N2 to the NH3 product (reaction mechanisms^{53,54} refer to Fig. S1, ESI†), from which we can see that the adsorption of N2 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@C₃N₄. Enhancing the N₂ adsorption will boost the ENRR performance.

3.2 N₂ adsorption on SiM@C₃N₄

Here, asymmetric dimer electrocatalysts (SiM@C₃N₄) were designed to address the low affinity of N₂ on active sites. We chose some high-performance ENRR transition metals (TMs) to cooperate with Si to capture N2, and the metal elements selected are shown in Fig. 2a. Fig. 2b displays the design scheme of concept-SiM@C3N4 which involves using two NV1 vacancies on g-C₃N₄. The optimized SiM@C₃N₄ catalysts are shown in Fig. S3 (ESI†). According to E_b and $(E_{co.Si} + E_{co.M.})$ analyses of dimers (see Table S1, ESI†), it is anticipated that these SiM@C₃N₄ concept models all exhibit strong stability under ambient conditions.

Then N₂ adsorption on SiM@C₃N₄ was examined. Fig. 2c and 2d display two dimer models, i.e., SiMo@C₃N₄ and

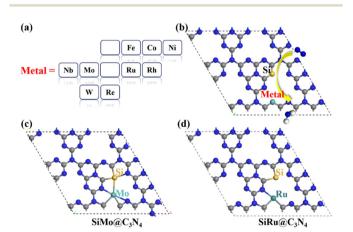


Fig. 2 (a) Chosen metal elements for the concept models of SiM@C₃N₄; (b) the design strategy of SiM@C₃N₄ for ENRR; (c and d) potential highperformance catalysts: SiMo@C₃N₄ and SiRu@C₃N₄. Color scheme: Si (yellow), H (white), N (blue), and C (grey)

SiRu@C₃N₄. They all have strong N₂ adsorption ability with the adsorption free energy (ΔG_{*N_2}) less than 0.50 eV (see Fig. 3), indicating the occurrence possibility of N2 adsorption under ambient conditions. 55,56 Fig. 3 displays the side-on adsorption configurations of N2 on SiM@C3N4 except for SiRe@C3N4, because N₂ can only be captured in the end-on model at the Re site after geometry optimization as shown in Fig. S4 (ESI†). Among nine dimer concept-electrocatalysts, based on E_{ads} and adsorption-free energies (ΔG_{*N_2}), only two dimer catalysts were shown to have good N2 adsorption ability, i.e., SiMo@C3N4 and SiRu@C₃N₄, with ΔG_{*N_3} of 0.17 and 0.28 eV, respectively. Moreover, the side-on adsorption modes on SiMo@C₃N₄ and SiRu@C₃N₄ well-activated the adsorbed *N₂ with the extended N≡N lengths of 1.21 and 1.20 Å, respectively. However, other dimers showed $\Delta G_{*N_2} > 0.50$ eV, indicating that N₂ 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 N₂ on SiM@C₃N₄, the kinetic barriers were analyzed as shown in Fig. S5 (ESI†), from which it was noticed that N2 adsorption barriers were all less than 0.50 eV except for SiNi@C₃N₄. SiMo@C₃N₄ and SiRu@C₃N₄ with the most energetically favorable *N2 configurations demonstrated quite small reaction barriers of 0.23 and 0.24 eV, respectively. Therefore, from the perspective of adsorption thermodynamics and kinetics, N2 can be readily activated on SiMo@C3N4 and SiRu@C₃N₄ under ambient conditions.

3.3 ENRR on SiMo@C₃N₄ and SiRu@C₃N₄

Following the discussion on N2 adsorption above, we examined the ENRR performance on SiMo@C₃N₄ and SiRu@C₃N₄. According to relevant reports, 57,58 when N2 is captured on dimer catalyts 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†). Therefore, the ENRR on SiMo@C₃N₄ and SiRu@C₃N₄ was investigated according to the proposed mechanisms computationally.

Fig. 4 and Fig. S7 (ESI†) show the enzymatic and consecutive pathways on SiMo@C₃N₄ and SiRu@C₃N₄, respectively. For the first hydrogenation reduction step of *N₂ + H⁺ + $e^- \rightarrow *N_2H$, there are two possible hydrogenation ways through the attack of the H^+/e^- pair (shown in Fig. S8, ESI†): 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@C₃N₄, *NH₃ species also tend to form on the metal site; however, for SiRu@C₃N₄, *NH₂ and *NH₃ 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 *N2, free-energy changes during the first hydrogenation steps on these two asymmetrical dimer centers, i.e., SiMo@C₃N₄ and SiRu@C₃N₄, are pretty low. The limiting potentials (U_L) on SiMo@C₃N₄ and SiRu@C₃N₄ are merely -0.20 and -0.39 V, respectively, for the ENRR, with the

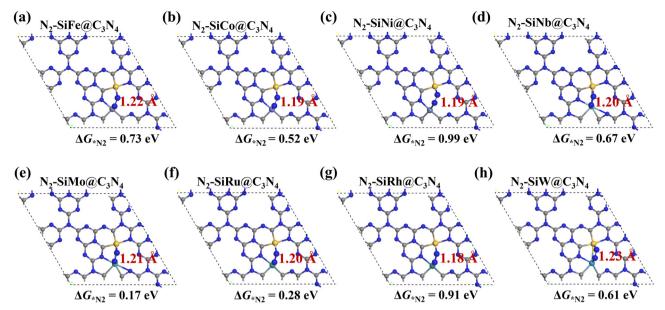


Fig. 3 (a-h) Side-on adsorption configurations of *N_2 on SiM@C₃N₄ with adsorption-free energies ($\Delta G_{{}^*N_2}$) and N-N bond lengths. N₂ adsorption configuration on SiRe@C₃N₄ is shown in Fig. S4 (ESI†).

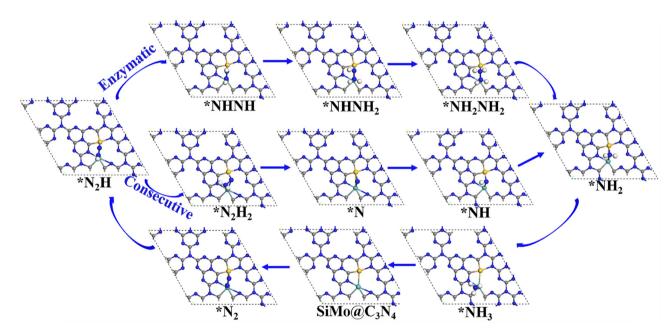


Fig. 4 The enzymatic and consecutive pathways of the ENRR on SiMo@ C_3N_4 , and the ENRR on SiRu@ C_3N_4 is shown in Fig. S7 (ESI†).

responding overpotentials (η) 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@C₂N:⁵⁹ $U_{\rm L} = -0.17 \text{ V}$; NbB:⁶⁰ $U_{\rm L} = -0.40 \text{ V}$; MnB:⁶⁰ $U_{\rm L} = -0.33 \text{ V}$; Mo and W-doped Au-based single-atom alloyes: 61 $U_{\rm L}$ = -0.30 V; Mo@BM- β_{12} :⁶² $U_L = -0.26 \text{ V}$; and Mn@BM- β_{12} :⁶² $U_L = -0.32 \text{ V}$;), even outperform some 2D Mxenes⁶³ (Mo₂C(OH)₂: $U_L = -0.62$ V; $V_2C(OH)_2$: $U_L = -0.71 \text{ V}$; and $Cr_2C(OH)_2$: $U_L = -0.78 \text{ V}$) and TM single-atom catalysts^{45,64} (Mo₁/pyrrolic-N₃-G: $U_L = -0.49$ V, Re₁/ pyrrolic-N₃-G: $U_L = -0.51$ V; and Nb@P₃-Ars: $U_L = -0.52$ V), exhibiting a great promising prospect towards electrocatalytic nitrogen fixation.

ENRR on Mo@C₃N₄ and Ru@C₃N₄

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

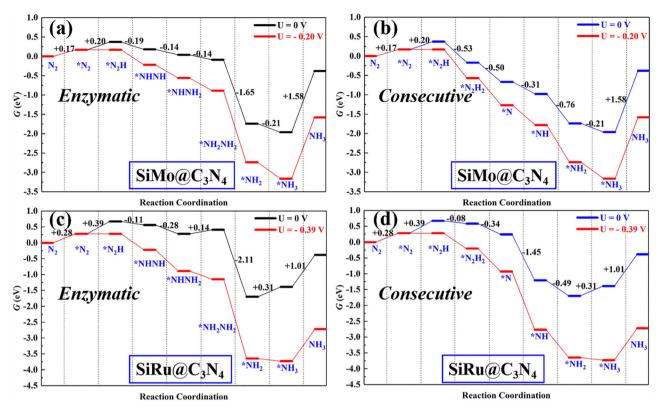


Fig. 5 The free energy evolutions of enzymatic and consecutive pathways on (a and b) $SiMo@C_3N_4$ and (c and d) $SiRu@C_3N_4$ with and without the applied potential (U_1)

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 Mo@C₃N₄ and Ru@C₃N₄ (see Fig. S9-S11, ESI†) catalysts was also investigated. First, N₂ adsorption on Mo@C₃N₄ and Ru@C₃N₄ was also studied and is shown in Fig. S10 (ESI†). One can find that, on Mo@C₃N₄, the end-on adsorption configuration with $\Delta G_{*N_2} = -0.20$ eV is more favorable energetically than the side-on mode with $\Delta G_{*N_a} = 0.56$ eV, while as for Ru@C₃N₄, N₂ can be chemically adsorbed on the Ru site only in the end-on mode with $\Delta G_{*N_2} = 0.33$ eV. Therefore, tasking the N₂ 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†). Their corresponding free-energy evolutions are presented in Fig. 6, from which again we noticed that the first hydrogenation step (*N₂ + H⁺ + $e^- \rightarrow *N_2H$) is the PDS, with ΔG of 0.78 and 0.89 eV, for Mo@C₃N₄ and Ru@C₃N₄, respectively. As a result, the limiting potentials on Mo@ C_3N_4 and Ru@ C_3N_4 are -0.78and -0.89 V, respectively, which are distinctly greater than those on SiMo@C₃N₄ and SiRu@C₃N₄ dimer catalysts. Generally, the first hydrogenation step is determined from the activation degree of *N2 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 N2 adsorption and activation.

Origin of high-performance dimers

For studying the high-performance origin of SiMo@C₃N₄ and SiRu@C₃N₄, we investigated their electronic structures, as shown in Fig. 7. First, the calculated charge density difference (Fig. 7a) suggests that N2 has a stronger electron exchange on SiM@C₃N₄ than on M@C₃N₄, and the Hirshfeld charge analysis (Table S2, ESI†) proved it quantitatively. The DOS data demonstrate the electron interaction around the Fermi level, and the strong electron exchange between N2 and SiM@C3N4 resulted in splitting of the 1π molecular-orbital (MO). As for the N_2 adsorption on Mo@C₃N₄ and Ru@C₃N₄, the DOS overlap between the metal site and N2 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 *N2, as shown in Fig. 7c. Indeed, a larger electron occupation in the $1\pi^*$ orbital for side-on adsorption configurations on SiM@C3N4 was observed, and ICOHP results are on the order of -11.72 (*N₂ on $SiRu@C_3N_4$) < -10.32 (*N₂ on $SiMo@C_3N_4$), -4.37 (*N₂ on $Ru@C_3N_4$ < -4.08 (*N₂ on Mo@C₃N₄), quantitatively explaining the activation degree. The larger activation degree of N2 is

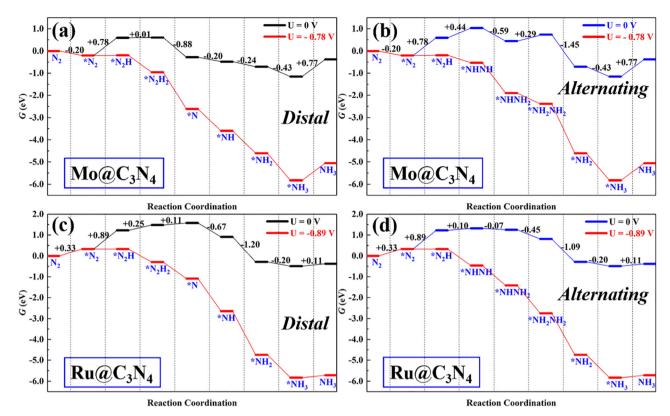
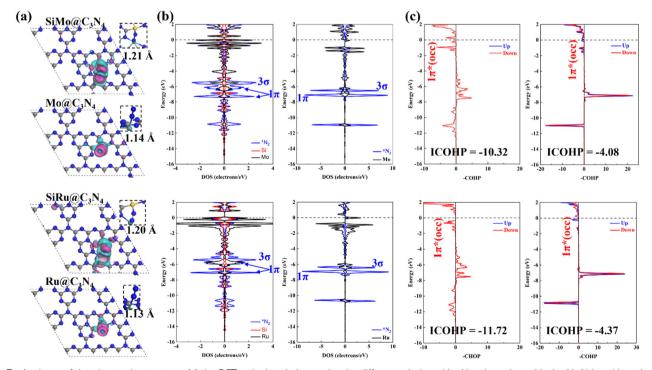


Fig. 6 The free energy evolution of the ENRR on (a and b) $Mo@C_3N_4$ and (c and d) $Ru@C_3N_4$.



 $\textbf{Fig. 7} \quad \text{Analyses of the electronic structure: (a) the DFT-calculated charge density difference induced by N_2 adsorption with the $N-N$ bond length, and N_2 and N_2 are consistent of the electronic structure. The same of the electronic structure is a supplied to the electronic structure of the electronic structure. The electronic structure is a supplied to the electronic structure is a supplied to the electronic structure. The electronic structure is a supplied to the electronic structure in the electronic structure is a supplied to the electronic structure. The electronic structure is a supplied to the electronic structure is a supplied to the electronic structure. The electronic structure is a supplied to the electronic structure in the electronic structure is a supplied to the electronic structure i$ the red and cyan represent the electron accumulation and loss, respectively (isosurface = 0.01 a.u.); (b) DOS analyses for *N2, Si, Mo, and Ru of four concept-models; and (c) the -COHP analyses for *N₂, where " $1\pi^*$ (occ)" refers to the occupation of $1\pi^*$ anti-bonding orbitals.

conducive 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@C₃N₄ and M@C₃N₄ (M = Mo and Ru) as shown in Fig. S13 (ESI†). Here, we analyzed Hirshfeld charges of four moieties on SiM@C3N4 (M = Mo and Ru) and three moieties on M@C₃N₄ (M = Mo and Ru): N_xH_v , (the reaction intermediates), Si (the non-metal site), Mo/ Ru (the metal site) and defective g-C₃N₄ (the supporter structure). First, on SiMo@C₃N₄ (see Fig. S13a, ESI†), the charge evolution of N_xH_y was different from that of g-C₃N₄, and obvious charge oscillation for both N_xH_y and g-C₃N₄ 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-C₃N₄ 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@C₃N₄ (see Fig. S13c, ESI†). Additionally, these two active sites of $SiM@C_3N_4$ (M = Mo and Ru) could slightly regulate the charges on N_xH_v as a mediator during the synthesis of second ammonia. But, as for singleatom Mo@C₃N₄ and Ru@C₃N₄ (see Fig. S13b and d, ESI†), only the metal site can transfer electrons back and forth between g-C₃N₄ and N_rH_v 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, 65,66 nitrate reduction, 67 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 $\Delta G_{\rm max}^{\rm HER}$ on SiMo@C₃N₄ is larger than $\Delta G_{\rm max}^{\rm NRR}$ (0.20 eV), and $\Delta G_{\rm max}^{\rm HER}$ on SiRu@C₃N₄ is also larger than $\Delta G_{\text{max}}^{\text{NRR}}$ (0.39 eV), which suggests that the HER will be suppressed due to the hindered Heyrovskey step (*H + H⁺ + $e^- \rightarrow H_2$). Therefore, the ENRR is energetically more favorable compared to the HER. Therefore, SiMo@C3N4 and SiRu@C₃N₄ would have high ammonia selectivity.

In addition, the water molecules in electrolytes may affect the N2 adsorption. Therefore, water adsorption was also studied, as shown in Fig. 8c and d. In comparison with the N₂ adsorption, we can notice that the Mo site on SiMo@C₃N₄ will be occupied by H₂O due to a lower adsorption free-energy of -0.45 eV, which will adversely influence the nitrogen activation and reduction; while SiRu@C3N4 tends to adsorb N2 rather than H₂O due to the lower adsorption free energy (0.33 eV) than that (0.35 and 0.72 eV) of H2O. This indicates that SiRu@ C₃N₄ will exhibit high activity and selectivity towards the ENRR, while SiMo@C₃N₄ will favor the ENRR in electrolytes

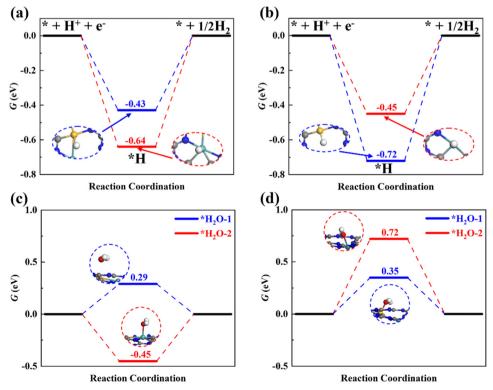


Fig. 8 Hydrogen evolution reaction on (a) SiMo@ C_3N_4 and (b) SiRu@ C_3N_4 ; the adsorption free energies of H_2O on (c) SiMo@ C_3N_4 and (d) SiRu@ C_3N_4 . Note that there are two potential active sites on dimer catalysts for hydrogen and water adsorption.

with a low concentration of H₂O, for example, ionic liquids.⁶⁸ To evaluate the synthetic availability of SiMo@C₃N₄ and SiRu@C₃N₄ 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@C₃N₄ is easier to synthesize. Meanwhile, we designed another two models, SiMo-C₃N₄ and SiRu-C₃N₄ (see Fig. S14, ESI†), which are derived by directly doping two atoms into the holes of g-C₃N₄ nanosheets. By comparing their formation energies (Table S3, ESI†), we can see that the concept models of SiMo@C₃N₄ and SiRu@C₃N₄ are easier to synthesize. Therefore, again it is shown that the N_v 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@C₃N₄ catalyst models, SiMo@C₃N₄ and SiRu@C₃N₄ exhibited the highest activity towards the ENRR with strong N2 adsorption abilities and ultra-low onset potentials of -0.20and -0.39 V, respectively. Moreover, these catalysts are capable of suppressing the competitive HER. Especially, SiRu@C₃N₄ exhibiting strong hydrophobicity possesses high NH3 selectivity. This design strategy not only addresses the issue of low adsorption and activation ability towards N2 on Si but also opens up a new avenue for designing asymmetrical dimer electrocatalysts for the ENRR, with the advantage of metalbased 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.

Acknowledgements

The authors acknowledge the Center for Computational Materials Science, Institute for Materials Research, Tohoku University, for the use of MASAMUNE-IMR (project no. 202212-SCKXX-0204) and the Institute for Solid State Physics (ISSP) at the University of Tokyo for the use of their supercomputers. This work was supported by the China BaoWu Low Carbon Metallurgical Innovation Foundation (no. BWLCF202113), the Fundamental Research Funds for the Central Universities (no. N2202012), JSPS KAKENHI (No. JP23K13703), and the Iwatani Naoji Foundation. The authors also thank Beijing PARATERA Tech Co., Ltd., for providing HPC resources.

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