Highly Efficient Photo-/Electrocatalytic Reduction of Nitrogen into Ammonia by Dual-Metal Sites

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ABSTRACT: The photo-/electrocatalytic nitrogen reduction reaction (NRR) is an up and coming method for sustainable NH₃ production; however, its practical application is impeded by poor Faradaic efficiency originating from the competing hydrogen evolution reaction (HER) and the inert N≡N triple bond activation. In this work, we put forth a method to boost NRR through construction of donor–acceptor couples of dual-metal sites. The synergistic effect of dual active sites can potentially break the metal-based activity benchmark toward efficient NRR. By systematically evaluating the stability, activity, and selectivity of 28 heteronuclear dual-atom catalysts (DACs) of M₁M₂/g-C₃N₄ candidates, FeMo/g-C₃N₄ is screened out as an effective electrocatalyst for NRR with a particularly low limiting potential of −0.23 V for NRR and a rather high potential of −0.79 V for HER. Meanwhile, TiMo/g-C₃N₄, NiMo/g-C₃N₄, and MoW/g-C₃N₄ with suitable band edge positions and visible light absorption can be applied to NRR as photocatalysts. The excellent catalytic activity is attributed to the tunable composition of metal dimers, which play an important role in modulating the binding strength of the target intermediates. This work may pave a new way for the rational design of heteronuclear DACs with high activity and stability for NRR, which may also apply to other reactions.

1. INTRODUCTION

An essential chemical in contemporary life is ammonia (NH₃), which has widely been used in agriculture, industry, and as a household chemical.¹⁻³ While the Haber–Bosch process is the primary source for the nitrogen (N₂) reduction reaction (NRR) on the industrial scale, a photo-/electrochemical method to bring the conversion of N₂ into NH₃ under milder conditions represents an attractive alternative. By using water as a proton donor in the photo-/electrocatalytic NRR, reliance on natural gas in conventional NH₃ synthesis can be reduced, resulting in reduced carbon dioxide (CO₂) emission.⁴⁻⁹ However, the high activation energy that is required to break the strong N≡N bond as well as the weak adsorption of nonpolarized N₂ onto catalysts are two major challenges in the NRR.¹⁰⁻¹¹ The ideal solution for this process requires a suitable catalyst to ensure a high reaction rate and selectivity, which remains a salivating goal.

Transition metal single-atom catalysts (SACs), a new class of catalysts, have recently been demonstrated to exhibit superior catalytic performances for NRR.¹²⁻¹⁶ However, it is still rather challenging for SACs to simultaneously improve the Faradaic efficiency and the yield rate. A promising strategy to address this issue is to introduce dual-metal sites to tune the adsorption property of the targeted intermediates. Double-atom catalysts (DACs), especially heteronuclear DACs, with synergetic interatomic interactions and flexible active sites, can maximize the potentials of SACs for multistep reactions, which makes the optimization of activity and selectivity feasible. For example, NiMn and NiCu anchored on g-C₃N₄ were found to suppress the competing HER more efficiently than their monometallic counterparts and therefore delivered high Faradaic efficiency and selectivity for the CO₂ reduction reaction (CO₂RR) into CO.¹⁷ The CuAu/g-C₃N₄ bimetallic photocatalyst could efficiently catalyze the hydroxylation of benzene via C–H activation under visible light irradiation.¹⁸ Heteronuclear dual metals (CoPt, FeCo, ZnCo) embedded on N-doped carbon enhanced the binding ability of oxygen (O₂) and facilitated the activation of O=O bond, which were served as efficient O₂ reduction reaction (ORR) catalysts with outstanding activity.¹⁹⁻²⁴ In particular, NiCo heteronuclear dimer anchored on g-C₃N₄ exhibited higher catalytic activity toward CO₂RR into CH₄ than CoCo and NiNi homonuclear dimers.²⁵ For NRR, several heteronuclear metal-dimers anchored on N-doped graphene and phthalocyanine were proposed to have an...
improved catalytic activity than the corresponding homonuclear DACs.\textsuperscript{26,27} Very recently, Chen et al.\textsuperscript{28} obtained a NRR Faradaic efficiency up to 67.8\% by constructing donor–acceptor couples of Au and Ni nanoparticles on N-doped carbon. The donor–acceptor couples can enhance the preadsorption of N\textsubscript{2} and decrease the energy of desorption of NH\textsubscript{3} on electron-rich surface of Au simultaneously. Therefore, design of heteronuclear DACs by constructing multiple active centers with correlative interactions is a potential strategy for improving the activity of many chemical reactions.

This work depicts that heteronuclear metal dimers embedded in g-C\textsubscript{3}N\textsubscript{4} as a dual metal active center can generate donor–acceptor couples and significantly boost the activity and selectivity for NRR. By comparing the thermodynamic and electrochemical stabilities of 28 candidates of M1M2/g-C\textsubscript{3}N\textsubscript{4}, we first screen out 16 heteronuclear DACs that meet the stability criteria for further investigation. Subsequently, we systematically evaluate the catalytic activity by studying the scaling relations of E\textsubscript{b}(N) vs E\textsubscript{b}(N\textsubscript{2}H) and E\textsubscript{b}(N) vs E\textsubscript{b}(NH\textsubscript{2}), FeMo, TiMo, MoW, and NiMo dimers are selected out as promising DACs for NRR. Finally, by comparing the potential determining step and limiting potential of above DACs, FeMo/g-C\textsubscript{3}N\textsubscript{4} is highlighted for NRR with a relatively low negative limiting potential of ~0.23 V through the enzymatic mechanism. Meanwhile, TiMo/g-C\textsubscript{3}N\textsubscript{4}, MoW/g-C\textsubscript{3}N\textsubscript{4}, and NiMo/g-C\textsubscript{3}N\textsubscript{4} possess suitable band gaps and band edge positions, allowing the reduction reaction to occur under visible light. The high activity stems from heteronuclear metal dimers and g-C\textsubscript{3}N\textsubscript{4} acting synergistically, which not only serves as a coordination skeleton but also provides a favorable local environment for NRR. Furthermore, the proposed model of donor–acceptor couples of heteronuclear dual-metals for N\textsubscript{2} activation can be extended to other systems such as FeMo-doped graphene for achieving high-efficiency NRR.

2. RESULTS AND DISCUSSION

The graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4}) monolayer possesses evenly distributed holes,\textsuperscript{29} which provide uniform and abundant nitrogen coordination sites with electron-rich lone pairs for capturing metals.\textsuperscript{13,30} In fact, the ultrathin material offers other inherent advantages as a substrate to attach metal catalysts such as keeping metal atoms in their neutral state, effective accumulation of surface polarization charges on metal atoms, and providing reliable and useful information in terms of identification of catalytically active sites. In addition, the layered g-C\textsubscript{3}N\textsubscript{4} is proven to be a potential photocatalytic material with a suitable band gap and has been extensively used in energy conversions with visible light.\textsuperscript{31,32} Meanwhile, the large periodic holes of s-heptazine can provide sufficient space for supporting heteronuclear metal dimers tightly by sp\textsuperscript{2}-bonded N atoms,\textsuperscript{33,34} thus, the s-heptazine g-C\textsubscript{3}N\textsubscript{4} is used as the substrate in this work.

According to the “acceptance-donation” mechanism,\textsuperscript{5,27} single metal atom and dual-metal sites with empty d-orbitals can accept lone-pair electrons of N\textsubscript{2} and the partially filled d-electrons donate electrons back to the antibonding orbitals of the adsorbed molecule; thus, the N≡N triple bonds are weaken and activated (Figure 1a,b). However, the empty d-orbital of a single-metal site can trap one lone pair electron of one side of the N\textsubscript{2} molecule (Figure 1c). To maximize the activation process, the empty d-orbitals of the dual-metal sites can pull two lone pair electrons at both ends of N\textsubscript{2} (Figure 1d). As discussed above, the incorporation of heteronuclear dual-metals provides an alternative strategy to get adjacent active sites and thus increase the binding strength of the targeted intermediates. In addition, the donor–acceptor couples of heteronuclear dual-metals (i.e., the synergistic effect from M1 and M2) lead to a polarized surface with multielectron sites and thus increase the binding strength of the targeted intermediates. In addition, the donor–acceptor couples of heteronuclear dual-metals (i.e., the synergistic effect from M1 and M2) lead to a polarized surface with multielectron sites and promote the activation of the nonpolarized N\textsubscript{2} molecule (Figure 1d). With the help of the dual-metal sites, it can also be expected that the inherent linear scaling relations limited by
a single metal site can be broken. As shown in Figure 1e, the large changes in Gibbs free energy can be attributed to the linear scaling relations between the binding energies of $^{*}$N versus $^{*}$N$_2$H, $^{*}$N versus $^{*}$NH$_2$ on the single-metal site. Additional N-binding sites are needed for the stabilization of N-containing intermediates in order to reduce the large changes in Gibbs free energy of the potential determining step (PDS). We expect that constructing the donor–acceptor couples of dual-metal sites will break the inherent linear scaling relations, thus causing the PDS to decrease dramatically (Figure 1f).

Nonprecious metals including Cr, Ti, Fe, Mn, Co, Mo, Ni, and W, which have been widely used as single-atom catalysts to catalyze NRR, are considered in this work. The feasibility of 28 types of dual-metals (two out of Cr, Ti, Fe, Mn, Co, Mo, Ni, and W are taken in combination to form heteronuclear dual-metals, i.e., TiCr, TiMn, TiFe, TiCo, TiNi, TiMo, TiW, CrMn, CrCo, CrFe, CrMo, CrNi, CrW, MnCo, MnFe, MnNi, MnMo, MnW, FeNi, FeCo, FeMo, FeW, CoMo, CoNi, CoW, NiMo, NiW, and MoW dimer) deposited on the g-C$_3$N$_4$ monolayer. Calculation of the dissolution potential ($E_{\text{diss}}$ versus SHE) was performed to further evaluate the electrochemical stabilities of heteronuclear DACs. According to the definition (see Supporting Information), a positive value ($E_{\text{diss}} > 0$ V vs SHE) indicates the strong binding of the dual metals with the substrate. As shown in Table S1, TiCr, TiMn, TiMo, TiW, MnFe, CrMn, CrFe, CrCo, CrW, MnFe, MnCo, MnNi, MnMo, MnW, FeCo, FeNi, FeMo, CoMo, CoNi, NiMo, and MoW anchored in g-C$_3$N$_4$ possess positive $E_{\text{diss}}$ values, implying that they are energetically stable. Finally, 16 DACs are screened out that meet the stability criteria for further investigation.

Generally, the potential-limiting step of NRR is either N$_2$ $\rightarrow$ N$_2$H or NH$_2$ $\rightarrow$ NH$_3$, thus the binding energies of $^{*}$N [$E_b(N)$], $^{*}$N$_2$H [$E_b(NH_2)$] and $^{*}$NH$_2$ [$E_b(NH_2)$] determine the overall reaction rate in most cases. Earlier DFT studies have revealed that the poor activity with high NRR limiting potential originates from the inherent linear scaling relations of $E_b(N)$ vs $E_b(N_2H)$ and $E_b(NH_2)$ on the pure transition metal (TM) based catalysts surfaces and single-atom metal catalysts, averting them to approach optimal NRR activity region. Therefore, a successful catalyst design must circumvent or even break this limitation to achieve high NRR activity. Several strategies have been proposed to circumvent the linear scaling relations of the adsorbed surface intermediates. Typically, Wang et al. showed that by intervening in the TM-mediated catalysis with a second catalytic site, the scaling relations could be broken. On the basis of this, we further calculated the adsorption of $^{*}$N, $^{*}$N$_2$H, and $^{*}$NH$_2$ on g-C$_3$N$_4$ supported metal dimers. As shown in Figure 1g,h, four heteronuclear DACs of TiMo/g-C$_3$N$_4$, NiMo/g-C$_3$N$_4$, FeMo/g-C$_3$N$_4$, and MoW/g-C$_3$N$_4$ can break the scaling relation of the transition metal surface and effectively optimize the adsorption properties of NRR intermediates, which are expected to achieve improved NRR activity.

Figure 2. Optimized structure of (a) M1M2/g-C$_3$N$_4$ and (b) adsorption of N$_2$ on M1M2/g-C$_3$N$_4$. (c) Charge density difference for N$_2$ adsorption on M1M2/g-C$_3$N$_4$ where yellow and cyan show the positive and negative charges, respectively. The isosurface value is 0.001 e/Å$^3$. (d) Adsorption energies of N$_2$ on M1M2/g-C$_3$N$_4$ with the end-on and side-on pattern. Green circles mark the cases with mild adsorption strengths and small differences of adsorption energies via both side-on and end-on pattern adsorption of N$_2$, blue squares have much low adsorption energies and pink squares have very large adsorption energies. Optimized structures of adsorption of $^{*}$N$_2$H intermediates on (e) MoMo/g-C$_3$N$_4$ and (f) M1M2/g-C$_3$N$_4$. The C, N, and H atoms are labeled as gray, blue, and white balls, respectively.
Figure 2a shows the optimized structures of M1M2/g-C3N4, the metal dimers are anchored on porous g-C3N4, in which there is strong coordination of each dispersed metal atom with the other metal atom as well as three N atoms, forming N-coordinated N3M1-M2N3 configuration. Figure 2b presents the structures of N2 adsorbed on M1M2/g-C3N4, the dual-metal sites act as *N binding. To gain a deep insight into the interaction between the N2 and M1M2, the charge density difference is further calculated. As evident from Figure 2c, the charge transfer process between the anchored M1M2 and the adsorbed N2 is bidirectional, and the charge accumulation and depletion can be found on both sides. These characteristics are in good agreement with the donation/back-donation picture (Figure 1b); i.e., dual-metal catalysts can “push” electrons into the N2 antibonding orbitals and “pull” the N2 lone-electrons pair, which can activate N2, leading to the significant increase in elongation of N≡N bond (1.20−1.24 Å, vs 1.12 Å in the free gas phase).

In the following, the adsorption energies of N2 on M1M2/g-C3N4 (Figure 2d) are calculated via both the end-on and side-on patterns. Our results show that the N2 prefers to attach the dual-metals with an end-on configuration, and the adsorption energies range from −1.01 to −2.09 eV. Notably, the moderate adsorption energies via both side-on and end-on adsorption of N2 on FeMo, MoW, NiMo, and TiMo (green circles) suggest that these four catalysts can be good NRR catalysts (Figure S2). On the contrary, the adsorption energies of N2 on CrCo, FeCo, and MnMo (blue squares) are very low (∼−0.50 eV), implying that they are not suitable for N2 adsorption. In other words, the activity of Mo-based catalysts is enhanced by introducing a second metal (i.e., the synergistic effect of dual-metal sites).

In general, three typical mechanisms have been proposed for the NRR process, which are known as distal, alternating, and enzymatic mechanisms (Figure 3a), and all the possible intermediates and reaction processes are included. For end-on adsorption, the conversion of N2 to NH3 follows either an alternating or distal mechanism, while the enzymatic pathway exhibits a different feature starting from N2 adsorption with a side-on pattern. Figure 3b summarizes the PDS and limiting potential of NRR on M1M2/g-C3N4. Among all the 11 DACs, the PDS of 4 DACs (MnCo/g-C3N4, MnFe/g-C3N4, CoNi/g-C3N4, and FeNi/g-C3N4) is the first protonation step of *NH3H + (H+ + e−) → *NH3 (Figure S3), and the PDS of other 6 DACs (TiMo/g-C3N4, TiCr/g-C3N4, NiMo/g-C3N4, MoW/g-C3N4, TiMn/g-C3N4 and CrW/g-C3N4) is the final protonation step of *NH3H2 + (H+ + e−) → *NH3 (Figure S4). In contrast, FeMo/g-C3N4 shows a different PDS of *NNHH + (H+ + e−)
protonation step of that for most studied transition metal based catalysts, the *FeFe/g-C₃N₄ are calculated to be 0.47 and 1.01 eV, which are intermediates for NRR. The PDS of MoMo/g-C₃N₄ and thermodynamically uphill step,⁴⁰ while the process for the C₃N₄, the sixth protonation step of C₃N₄ exhibit superior catalytic activity of NRR with relatively small negative limiting potentials, which are much lower than FeMo/g-C₃N₄ (targeted systems in this work can be exothermic in cases of C₃N₄, and NiMo/g-C₃N₄, indicating that multiple active centers of heteronuclear DACs can reduce the PDS of NRR efficiently. Note that the above conclusions have been drawn based on a computational hydrogen electrode model, in which the hydrogen bonding between the water and reaction intermediates and the net surface charge is not explicitly considered. These effects may affect the chemical reactivity and product selectivity as found in CO₂RR.⁵⁰,⁵¹ Note that the hydrogen bonding between the water and reaction intermediates in NRR can greatly improve the yield rate of NH₃, and the Faradaic efficiency and suppress the HER performance.¹²

Additionally, HER, the major competing reaction in NRR, which normally affects the Faradaic efficiency for NRR largely, should also be considered. We thus carried out investigation on the free energy of HER on these four selected catalysts. The H⁺ structures of adsorption site and corresponding free energy HER diagrams are depicted in Figure S9 and Figure 4a, respectively. The free energy barriers (0.49, 0.68, 0.79, and 1.12 eV) are considerable larger than PDS barriers for NRR (0.35, 0.34, 0.23, and 0.32 eV) on heteronuclear DACs of TiMo/g-C₃N₄, NiMo/g-C₃N₄, FeMo/g-C₃N₄ and MoW/g-C₃N₄. Thus, all these four selected catalysts exhibit an excellent suppression effect on HER during NRR. A comparison of the relative limiting potentials (U₁) for each reaction can provide a qualitative estimation for the competition between them. The difference U₁(NH₃)−U₁(H₂) between NRR and HER in terms of their limiting potentials has been used to estimate the selectivity of NRR. A more positive value indicates a higher selectivity toward NRR over HER.⁵³ As shown in Figure 4b, all of these four catalysts have positive U₁(NH₃)−U₁(H₂) values, demonstrating their high selectivity toward NRR.

Another side effect of H adsorption on the catalytic surface would be H-poisoning, which would thus block the active sites for NRR. To determine whether the NRR is preferred on these four catalysts, the adsorption energies of *H [E_ads(*H)] and *N₂ [E_ads(*N₂)] were compared as seen in Figure S10. Obviously, heteronuclear DACs of FeMo/g-C₃N₄, TiMo/g-C₃N₄ and NiMo/g-C₃N₄ possess a stronger adsorption ability for *N₂ than *H, suggesting that the surface concentration of *N₂ is higher than *H. For MoW/g-C₃N₄, the small difference between E_ads(*H) and E_ads(*N₂) implies coadsorption of *N₂ and *H on the active sites. However, experimental strategies, such as enhancing the pH of the solution by diluting the water concentration and using nonaqueous electrolytes can effectively reduce the proton donor activity and suppress the HER on the heteronuclear DACs.

Figures 4. (a) Free energy diagrams of HER on FeMo/g-C₃N₄, NiMo/g-C₃N₄, TiMo/g-C₃N₄ and MoW/g-C₃N₄. (b) Limiting potentials for HER U₁(H₂), NRR U₁(NH₃), and the difference between them U₁(NH₃)−U₁(H₂) on these four catalysts.
The thermal stability of FeMo/g-C\textsubscript{3}N\textsubscript{4}, NiMo/g-C\textsubscript{3}N\textsubscript{4}, TiMo/g-C\textsubscript{3}N\textsubscript{4}, and MoW/g-C\textsubscript{3}N\textsubscript{4} was evaluated by AIMD (ab initio molecular dynamics) simulations. As evident in Figures S11 and S12, the energy fluctuation along with time evolution oscillates close to the equilibrium state, and the atomic configuration remains stable at 400 K, indicating the high structural stability of these catalysts. The high stability stems from the strong covalent bonds between the dual-metals and the g-C\textsubscript{3}N\textsubscript{4} substrate based on the hybridization of metal-3d and N-2p orbitals, and the metal dimers form strong covalent bonds with N atoms at the cavity edge (Figure S13).

To get more insights into the kinetic stability of M1M2/g-C\textsubscript{3}N\textsubscript{4}, we further investigated the minimum energy path for the dissociation of FeMo, MoW, NiMo, and TiMo dimers into two separated monomers. As shown in Figure S14, the calculated diffusion barriers of metal dimers segregated into two individual monomers at two pore sites of a g-C\textsubscript{3}N\textsubscript{4} monolayer are 3.14, 3.78, 2.63, and 2.97 eV, respectively, implying that these four DACs of FeMo/g-C\textsubscript{3}N\textsubscript{4}, MoW/g-C\textsubscript{3}N\textsubscript{4}, NiMo/g-C\textsubscript{3}N\textsubscript{4}, and TiMo/g-C\textsubscript{3}N\textsubscript{4} have high kinetic stability.

Generally speaking, as a consequence of a relatively large band gap, the g-C\textsubscript{3}N\textsubscript{4} monolayer shows weak visible-light absorption.\textsuperscript{31,32} The deposition of FeMo, TiMo, MoW, and NiMo dimers on g-C\textsubscript{3}N\textsubscript{4} can possibly modify its electronic structure and boost the infrared (IR) and visible (VI) light response. Figure S15 shows the electronic band structures of the deposited catalysts.
FeMo/g-C\textsubscript{3}N\textsubscript{4}, TiMo/g-C\textsubscript{3}N\textsubscript{4}, MoW/g-C\textsubscript{3}N\textsubscript{4}, and NiMo/g-C\textsubscript{3}N\textsubscript{4} at the Heyd–Scuseria–Ernzerhof (HSE06) level. The bandgap of the pristine g-C\textsubscript{3}N\textsubscript{4} monolayer is 2.7 eV, which agrees with experimental\textsuperscript{31} and other theoretical\textsuperscript{32} studies. Therefore, it can only absorb the ultraviolet (UV) light. With the deposition of metal dimers, the TiMo/g-C\textsubscript{3}N\textsubscript{4}, MoW/g-C\textsubscript{3}N\textsubscript{4}, and NiMo/g-C\textsubscript{3}N\textsubscript{4} exhibit semiconducting properties, while FeMo/g-C\textsubscript{3}N\textsubscript{4} shows metallic properties (Figure S15). The bandgap of NiMo/g-C\textsubscript{3}N\textsubscript{4}, TiMo/g-C\textsubscript{3}N\textsubscript{4}, and MoW/g-C\textsubscript{3}N\textsubscript{4} are reduced to 0.8, 0.9, and 1.2 eV, respectively, endowing these catalysts with the ability to capture the VI and IR light. Figure 5a shows that light absorption peak of pristine g-C\textsubscript{3}N\textsubscript{4} lies around 4.50 eV, indicating its strong UV light absorbance and very limited VI light absorbance, consistent with previous studies.\textsuperscript{31,32,56} With NiMo, TiMo, and MoW dimers deposited on g-C\textsubscript{3}N\textsubscript{4}, although the UV light absorbance will be decreased more or less, the VI and IR light absorbances are greatly enhanced due to the decrease of the bandgap value. Therefore, comparing with the pristine g-C\textsubscript{3}N\textsubscript{4} monolayer, the selected catalysts are able to harvest VI and IR light with a higher solar conversion efficiency.

To be a good photocatalyst for NRR, besides the satisfactory absorption to sunlight, the semiconductor should have suitable band edge positions that match the N\textsubscript{2}/NH\textsubscript{3} potentials.\textsuperscript{57−59} As clearly displayed in Figure 5b, the conduction band minimum (CBM) of TiMo/g-C\textsubscript{3}N\textsubscript{4}, MoW/g-C\textsubscript{3}N\textsubscript{4}, and NiMo/g-C\textsubscript{3}N\textsubscript{4} is higher than the N\textsubscript{2}/NH\textsubscript{3} potential, and their valence band maximum (VBM) locate below the N\textsubscript{2}/NH\textsubscript{3} potential. The band edge positions indicate that the injected photogenerated electrons on CBM can transfer to adsorbed N\textsubscript{2} for proton coupled electron process effectively, rather than recombine with the holes on VBM. Therefore, comparing with the pure g-C\textsubscript{3}N\textsubscript{4} these three DACs are expected to obtain a higher photoconversion efficiency, which ensures photocatalytic performance by the efficient separation of the photoexcited electrons and holes. Hence, we conclude that the above three DACs have the merits of suitable visible light absorption, highly active surface, and suitable band edge positions and may be efficient photocatalysts for NRR.

Above, we have demonstrated that constructing donor–acceptor couples of dual-metal sites is a powerful method to boost NRR. In fact, the generality of this proposed strategy for N\textsubscript{2} activation, i.e., the pull–pull effect based on dual-metal sites to activate the N≡N bond, can also be extended to other 2D porous materials such as g-C\textsubscript{3}N\textsubscript{4},\textsuperscript{25,56} phthalocyanine,\textsuperscript{26} N-doped graphene,\textsuperscript{19−24} and so on. As shown in Figure 6a, the optimized structures of FeMo dual-metal were anchored on N-doped graphene by forming N-coordinated N\textsubscript{2}Fe-MoN\textsubscript{3} with an average absorption energy of ~6.0 eV per metal atom. The robust thermodynamic stability of FeMo/graphene was further confirmed (see Figures 6b and S16). Charge density difference demonstrates the accumulation and depletion of charge can occur on both sides of N\textsubscript{2} and FeMo (Figure 6c). More importantly, NRR can be achieved for FeMo/graphene through the enzymatic mechanism with a relatively low limiting potential value of ~0.24 V (Figure 6d). The first hydrogenation site of N\textsubscript{2} occurs on the Fe site of FeMo metal dimer (Figure 6e), in line with the donor–acceptor couples on M1M2/g-C\textsubscript{3}N\textsubscript{4} (Figure 2f). In addition, the free energy for \textsuperscript{4}H\textsuperscript{ad} absorption is ~0.37 eV (Figure S17), suggesting that the HER can be suppressed by the FeMo bimetallic catalyst.

3. CONCLUSION

In summary, several monolayer g-C\textsubscript{3}N\textsubscript{4} supported heteronuclear metal dimers have been designed with excellent activity for NRR. The high activity stems from dual active sites acting synergistically that can potentially break the transition metal-based activity benchmark toward efficient NRR. By evaluating the stability, activity, and selectivity, FeMo/g-C\textsubscript{3}N\textsubscript{4}, TiMo/g-C\textsubscript{3}N\textsubscript{4}, MoW/g-C\textsubscript{3}N\textsubscript{4}, and NiMo/g-C\textsubscript{3}N\textsubscript{4} are selected out from 28 candidates as promising catalysts for NRR. Among them, FeMo/g-C\textsubscript{3}N\textsubscript{4} exposes a particularly low limiting potential of ~0.23 V for NRR and a rather high potential of ~0.79 V for HER. Meanwhile, TiMo/g-C\textsubscript{3}N\textsubscript{4}, MoW/g-C\textsubscript{3}N\textsubscript{4}, and NiMo/g-C\textsubscript{3}N\textsubscript{4} show suitable band edge positions and visible light absorption, which can act as promising photocatalysts for NRR. The design concept of donor–acceptor couples of dual-metal sites is also applicable to other multielectron reactions such as ORR and CO\textsubscript{2}RR, which will inspire intensive experiments and computations to further explore other chemical reactions.

4. COMPUTATIONAL DETAILS

Plane-wave density functional theory as implemented in the Vienna Ab Initio Simulation Package (VASP)\textsuperscript{60} was used to do all the first-principles spin-polarized calculations with the ion cores described by the projector augmented wave potentials.\textsuperscript{61} The Perdew–Burke–Ernzerhof (PBE) functional was used to calculate the electronic exchange-correlation energy within the generalized gradient approximation,\textsuperscript{62} and 500 eV was set as the kinetic energy cutoff for the plane-wave basis. 10\textsuperscript{−5} eV was set as the convergence criteria for the energy, and ~0.02 eV/Å was set as the convergence criteria for the forces on each atom. A vacuum space of 20 Å was applied in the perpendicular z direction in order to avoid the interaction between two periodic units. The Grimme’s semiempirical DFT-D3\textsuperscript{63} scheme of dispersion correction was employed to account for the weak interactions. Bader charge analysis was used to evaluate the atomic charge transfer.\textsuperscript{64} AIMD simulations were carried out under the canonical ensemble lasted for 10 ps. Using the N\textsuperscript{o}se–Hoover method, the temperature was set to 400 K.\textsuperscript{65} Accurate calculations of the electronic band structures and the optical absorption spectra were performed by using the HSE06\textsuperscript{66} hybrid functional. The most positive \Delta G value (\Delta G\textsubscript{max}) of the whole process was used to obtain the limiting potential \textit{U}_\textsubscript{lim} by using the equation \textit{U}_\textsubscript{lim} = \Delta G\textsubscript{max}/e. Further details of the calculation are provided in the Supporting Information.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscentsci.0c00552.

Details of the calculations of energy difference between adsorption energy (\textit{E}_\textsubscript{ad}) of metal dimers anchored on g-C\textsubscript{3}N\textsubscript{4} and the cohesive energy (\textit{E}_\textsubscript{coh}) of metal atoms in their crystals; computed the dissolution potential (\textit{U}_\textsubscript{lim,ad}) of metal-dimers for 28 heteronuclear M1M2/g-C\textsubscript{3}N\textsubscript{4}; calculated free energy diagrams, the structures of different intermediates; optimized geometries of H\textsuperscript{ad} adsorbed; temperature variations and energy fluctuations versus the AIMD simulation time; calculated diffusion energy barriers of metal dimers segregated into two individual monomers at two pore sites of g-C\textsubscript{3}N\textsubscript{4};
electronic band structures of pure g-C_3N_4 and M1M2/g-C_3N_4 (PDF) CIF files of 16 heteronuclear M1M2/g-C_3N_4 (ZIP)

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