Theoretical Study on P-coordinated Metal Atoms Embedded in Arsenene for the Conversion of Nitrogen to Ammonia

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ABSTRACT: The conversion of gaseous N₂ to ammonia under mild conditions by artificial methods has become one of the hot topics and challenges in the field of energy research today. Accordingly, based on density function theory calculations, we comprehensively explored the d-block of metal atoms (Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, W, and Pt) embedded in arsenene (Ars) for different transition systems of phosphorus (P) coordination as potential electrocatalysts for N₂ reduction reaction (NRR). By adopting a “two-step” strategy with stringent NRR catalyst screening criteria, we eventually selected Nb@P₃-Ars as a research object for a further in-depth NRR mechanism study. Our results show that Nb@P₃-Ars not only maintains the thermodynamic stability at mild temperatures but also dominates the competition with the hydrogen evolution reaction when used as the electrochemical NRR (e-NRR) catalyst. In particular, while the NRR process occurs by the distal mechanism, Nb@P₃-Ars has a low overpotential (0.36 V), which facilitates the efficient reduction of N₂. Therefore, this work predicts the possibility of Nb@P₃-Ars as an e-NRR catalyst for reducing N₂ from a theoretical perspective and provides significant insights and theoretical guidance for future experimental research.

1. INTRODUCTION

The development and utilization of the energy field is one of the research hotspots that academia is concerned about today.¹⁻⁴ Ammonia (NH₃) is one of the important raw materials produced in the chemical industry, for example, synthetic fiber, nitric acid, and fertilizers.⁵,⁶ Its demand and significance are naturally self-evident. Besides, ammonia is gradually recognized as a clean energy medium.⁷ The mechanism of ammonia synthesis is based on the combination of gaseous N₂ and H₂. However, how to make good use of N₂, which occupies approximately three quarters of the atmosphere, is a matter of utmost importance in ammonia synthesis.⁸⁻¹² Currently, industrial ammonia synthesis still relies on the Haber−Bosch (H−B) method,¹³,¹⁴ but the disadvantages of high energy consumption and low conversion efficiency are obvious. Especially, the raw material of industrial production of H₂, which is obtained by decomposing water with fossil fuels, is contrary to the concept of environmental friendliness.¹⁵⁻¹⁷ Therefore, there is an urgent need to find less energy consuming, high-efficiency, and good stability methods to achieve the fixation of gaseous N₂.

Recently, photocatalytic synthesis,¹⁸,¹⁹ electrocatalytic synthesis,²⁰⁻²² and photo-electrocatalytic synthesis²³,²⁴ have become the mainstream methods for studying N₂ reduction today. However, compared with the electrocatalytic synthesis method, due to the conversion efficiency and controllability, the photocatalytic synthesis method shows certain disadvantages.¹,²,²¹ Hence, electrocatalytic ammonia synthesis is considered as the best alternative for the H−B method at mild conditions.

As an important part of the catalytic reaction, the performance of the catalyst directly affects the entire catalytic reduction process. The current challenges of electrocatalytic reduction catalysts are (1) extremely high applied potential, (2) competition with the hydrogen evolution reaction (HER), and (3) excessive consumption of precious metals.²⁵⁻²⁸ These challenges restrict the in-depth study of electrocatalytic N₂ reduction catalysts. In recent years, some scholars have begun to search for bulk materials of non-precious metals and have obtained more suitable N₂ reduction catalysts, which have been realized successively by Ti, Fe, Cu, Ni, and so forth.²⁵,²⁹

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However, the utilization efficiency of metal atoms has not been efficiently used, resulting in potential waste of metal catalysts and low ammonia yield. To improve the utilization efficiency of metal atoms, Zhang et al. proposed to disperse bulk metals to the atomic scale and use single atoms as catalytically active sites, which will greatly improve the utilization of metal atoms; that is, single-atom catalysts (SACs). SACs have been implemented as a new type of catalytically active sites, which will greatly improve the performance but also the stability should be concerned. It has been shown that when metallic SACs are anchored to a suitable substrate material with intermediate interactions, both activity and stability issues are well resolved. In recent years, two-dimensional (2D) materials have been widely used as excellent substrates for anchoring metal atoms due to their unique physical and chemical properties, such as high specific surface area, abundant active sites, and thermodynamic stability. Graphene (Gr), a widely recognized 2D group IVA materials, exhibits excellent performance as single-atom anchored graphene for N₂ reduction processes. Yang et al. designed a series of metal atoms anchored on the surface of N-doped graphene, among which Mo₆(Cr₇)/Nₓ-Gr showed good electroreduction performance for nitrogen. Also, MoSe/Gr, S/Gr, Fe/Mn-N-Gr, and P/Gr have been theoretically predicted or experimentally synthesized. Graphene analogues, h-BN, g-C₃N₄, borophene, and stanene, have been extensively explored in the field of nitrogen reduction. Chen et al. constructed a W atom-anchored g-C₃N₄ model to achieve nitrogen reduction at room temperature due to the excellent intrinsic properties of the W atom. In addition, Nb@g-C₃N₄, Pt@g-C₃N₄, C-BN, V@borophene, and Mo/stanene have also been reported in the process of ammonia synthesis. Phosphorene, the first 2D material of the VA group, has been predicted theoretically and synthesized in experiments. Black phosphorene (BP), the most stable phase of phosphorene, also shows potential advantages in the field of catalytic nitrogen reduction. With the help of theoretical calculations, Ou et al. designed an NₓP₃−x (x = 0, 1, 2, and 3)-coordinated Mo atom doped with BP to catalytically reduce nitrogen. Moreover, Ru@phosphor-ene, W@BP, and W-BP have been successively predicted and experimentally demonstrated by recent nitrogen reduction studies. Encouraged by the excellent properties of phosphorene, arsenene (Ars), a novel fifth main family 2D material, has been predicted by theoretical calculations and subsequently synthesized experimentally. From theoretical predictions to experimental synthesis, and then to extensive research in different fields, arsenene gradually becomes an emerging object of research in low-dimensional materials. In the catalysis field, the transition metal (TM) atom-doped arsenene is quite favorable for CO oxidation. Besides, arsenene is also considered as a good catalyst in water splitting. Until now, however, few studies have been carried out on N₂ reduction. Thus, further exploration is needed in such a significant field.

Phosphorus (P) atoms, metal-free catalytic sites, and ligands have been widely used in various catalytic reactions. Particularly, As is a homologous group element. Accordingly, we may ask the following questions: (1) can a P atom act as a metal-free active site for doping arsenene to fix N₂? (2) Can P-coordinated metal atoms embedded in arsenene still show stable or different N₂ reduction reaction (NRR) properties? To answer these questions, this work, using the first-principles calculations, searches electrochemical NRR (e-NRR) properties for Pₓ-doped defective arsenene and metal atoms in the different TM element regions (i.e., 3d, 4d, and 5d periods) embedded in the Pₓ-doped monolayer arsenene. Our study shows that the N₂ molecule is quite sensitive to the P site due to the elongation of the N–N bond once adsorbed on (Figure S1). However, the weak physical adsorption energy (∼0.85 eV) and the difficulty of final N₂ dissociation require further modification. After modification with TM atoms, molybdenum (Mo) and niobium (Nb) atoms exhibit excellent nitrogen reduction properties based on the “two-step” strategy. However, further study has shown that Mo@Pₓ-Ars is more selective for hydrogen than for nitrogen. Therefore, Nb@Pₓ-Ars has the potential to be an e-NRR catalyst. Next, a systematic study of Nb@Pₓ-Ars is carried out, showing excellent thermodynamic stability [such as binding energy and molecular dynamics (MD)], adsorption energy, and overpotential (0.36 V) and occupying a dominant position in the competition with HER. Consequently, this work provides a new idea for the design of electrocatalytic nitrogen reduction, which will hopefully be experimentally realized in the near future.

Figure 1. Diagram of the top and side view of the optimized Pₓ-Ars structure and the catalytic site where a single metal atom is embedded in Pₓ-Ars.
2. RESULTS AND DISCUSSION

In order to screen out the e-NRR catalysts with the best performance as much as possible, we have conducted five follow-up studies: (1) the binding ability of metal atoms with the P3-Ars substrate, (2) the selectivity of e-NRR catalysts based on the “two-step” strategy, (3) the systematic NRR process of Nb@P3-Ars, and (4) the electronic and (5) thermodynamic properties of the selected structure.

2.1. Metal Atoms Embedded in the P3-Ars Substrate. Based on previous studies, \(^8,^{64,65}\) the “acceptance and back-donation” mechanism has been commonly recognized for the NRR process. This indicates that not only the unoccupied d orbital of the TM atom accepts the lone pair of electrons from the \(\text{N}_2\) molecule but also the occupied d electrons donate back to the anti-bonding orbital of the \(\text{N}_2\) molecule. Considering this, we performed a screening for TM atoms (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, W, Pt, etc.) with unfilled d electrons. Such atoms are designed as SACs embedded in the P3-Ars substrate serving as e-NRR catalytic candidates (Figure 1).

The stability of the structure, as the basic condition for the electrocatalyst, is the primary concern. Therefore, we investigated the binding capacity and electronic properties of single metal atoms embedded in the P3-Ars substrate. It is clear from our binding energy calculations (Figure 2a) that, in the range of \(-5.24\) to \(-8.71\) eV, all of the TM atoms considered exhibit good binding abilities associated with P3-Ars. However, particle aggregation is another problem reducing the catalytic performance. The cohesive energy is hence calculated to evaluate the aggregation ability of these particles and to see whether these particles can be dispersed at the atomic level and be embedded stably in the substrate. As shown in Figure 2a, the cohesive energy of the W particle is larger than its binding energy, which indicates the smaller dispersivity in the designed substrate. Next, we performed the calculation of charge transfer of TM@P3-Ars based on the Bader charge analysis (Figure 2b). From the calculated results, the majority of metal atoms exhibit a significant loss of charge, except for Rh (near \(-0.00\) eV). In general, as the number of electron transfers increases, it facilitates the effective combination of the two species. However, the electronegativity also affects the electron transfer and binding energy of the TMs embedded in substrates.\(^{66}\) For instance, Ti, the smallest electronegativity (1.54 e) among all the candidates, has a strong ability to bind to substrates, accompanying large amounts of electron transfer. However, for Rh (2.28 e for electronegativity), the contrary is observed. This is why, the electron transfer is not promising despite the excellent bonding performance of Rh. Overall, after the initial screening, the W atom is theoretically excluded since it could not be stably embedded in the P3-Ars substrate. However, if the negative effects of binding energy can be overcome experimentally, then using the W atom as a central catalytic site in association with P3-Ars is still to be considered as a good choice for e-NRR catalysts.

2.2. “Two-step” Strategy Screening for e-NRR Catalysts. Regarding the current state of theoretical studies on NRR catalysts,\(^69,70\) the vast majority of them are still focused on the most basic large-scale search, which leads to problems such as high computational workload and low screening efficiency. Therefore, there is an urgent need for an efficient method to screen NRR catalysts.

In recent years, high-throughput computing has gradually emerged in the field of computational chemistry based on the fundamentals of density functional theory (DFT) and machine learning.\(^{57,68}\) On this basis, the “two-step” strategy for screening NRR catalysts was proposed by Wang et al., which relied on several key parameters to screen efficiently. In this section, we employed the following key steps as criteria for measuring e-NRR catalysts: (1) the adsorption energy of N\(_2\) on TM@P3-Ars (\(\Delta E_{N_2} < -0.55\) eV), (2) the free energy of \(\text{N}_2\text{H}\) species formation (\(\Delta G_{\text{N}_2\text{H} \rightarrow \text{N}_2\text{H}_2} < 0.55\) eV), and (3) the hydrogenation free energy of \(\text{NH}_2\) to \(\text{NH}_3\) (\(\Delta G_{\text{NH}_2 \rightarrow \text{NH}_3} < 0.55\) eV). As shown in Figure 3a, although the \(\text{N}_2\) molecule can be adsorbed on the most candidates of TM@ P3-Ars, only Ti, V, Fe, Nb, Mo, and Ru satisfy criterion 1. To illustrate this phenomenon, we further explored the electron transfer, which is displayed in Figure 3b. The calculated results show that the adsorption energy of \(\text{N}_2\) is to some extent linearly related to the obtaining of electrons from the metal atom, indicating the activation of the inert N–N bond. As shown in Table S1, the results reveal the changes of the N–N bond adsorbed on TM@P3-Ars, most of which are stretched more or less except that on Pt@P3-Ars. This is consistent with our previous Bader charge analysis. The hydrogenation process of \(\text{N}_2\text{H} \rightarrow \text{N}_2\text{H}_2\) is a state change from stable to unstable, and the energy goes up the hill as usual, while the \(\text{N}_2\text{H}_2\) species is stable due to the half-filled hybrid orbital of sp\(^3\) of N.\(^{69}\) Accordingly, we evaluated the free energies of two steps mentioned above. As can be seen, Figure 3c is divided into three different color areas, where red indicates that two criteria are not met, ocher indicates that only one criterion is met, and light green indicates that both criteria are met. Thus, Nb@P3-Ars and Mo@P3-Ars essentially meet all the prerequisites to be NRR catalysts. However, HER is often accompanied by \(\text{N}_2\) reduction, and thus, the dominance of the
catalytic process needs to be thoroughly considered. Hence, we performed the comparison of the selectivity of TM@P3-Ars for N₂ and H. As shown in Figure 3d, while the catalyst in the grass green region dominates the NRR process, the opposite is not the case in the pink region. Especially, there is a certain probability of HER or NRR occurring near the diagonal region. 

Figure 3. (a) Adsorption energies for N₂ on TMs@P₃-Ars with the optimal adsorption configuration where the value of the critical adsorption energy (−0.55 eV) is indicated by the orange dashed line and (b) the corresponding charge accumulation of N₂ from TMs@P₃-Ars. (c) The free energy barrier of *N₂ to *N₂H vs the free energy barrier of *NH₂ to *NH₃ for the N₂ reduction process. (d) Free energy distribution of HER or NRR domination of TMs@P₃-Ars.

Figure 4. (a) Schematic depiction of the four mechanisms for N₂ reduction to NH₃: distal, alternating, enzymatic, and mixed. Optimized structures of N₂ adsorption on Nb@P₃-Ars: (b) end-on and (c) side-on configurations. The N–N bond lengths in Å are also provided.
phenomenon indicates that the two N atoms with side-on configurations are elongated by 2.70 and 8.11%, respectively. Obviously, the side-on configuration is more than the end-on configuration for inert N2 activation. However, the adsorption energy of the end-on configuration is more that of the side-on configuration, about ~0.30 eV. This phenomenon indicates that the two N atoms with side-on configuration can obtain more electrons from Nb@P3-Ars. At the same time, the filling of the electrons makes them relatively active, resulting in the reduction of the partial adsorption energy. For end-on configuration, only the proximal N atom has gained electrons.

Once the Nb@P3-Ars electrocatalyst satisfies the requirement for N2 molecule adsorption, we further explored the three mechanisms of NRR. Free energy profile diagrams are depicted in Figure 5a−c, via distal, alternating, and enzymatic mechanisms, while the corresponding structures of intermediate reactants are shown in Figures S2−S4. For the distal mechanism, the proton−electron pair attacked the remote N to form the *N2H2 species. The free energy is decreased to ~0.75 eV, which is an exothermic process. In the following step, the first NH3 is released with a slight endothermic process (~0.17 eV). It will be followed by another similar hydrogenation process of the proximal N atom until the second ammonia escapes, with the corresponding species (i.e., *NH, *NH2, and *NH3) and the free energies of ~1.75, ~0.10, and 0.41 eV, respectively. According to previous studies,69,70 electrocatalysts can only be recycled efficiently by continuously exposing catalytically active sites, accompanying the desorption of *NH3 species. However, the desorption process is influenced by the chemical reaction environment, and relevant experiments as well as theoretical calculations show that the high acid environment will further hydrogenate and form NH* near the electrode. As a result, we are not overly concerned with the desorption of NH3 despite the existence of a relatively large energy barrier (about 1.67 eV). In addition, Figure S5 shows that the N−N bond increased continuously from 1.11 to 1.14, 1.24, and 1.34 Å until it breaks at the first NH3 formation. Therefore, the PDS in the distal mechanism for Nb@P3-Ars is *N−N + H2 + e− → *N2H due to the maximum ΔG (0.52 eV), and thus, the corresponding onset potential is ~0.52 V in the whole NRR process. The alternating mechanism is shown in Figure 5b in the same way as the distal mechanism for N2 adsorption; however, the electron−proton pair will consecutively attack both N atoms alternately. Once the proton−electron pair completes the first step of the attack on the remote N, hydrogenation occurs at the proximal N atom. The free energy is uphill to 0.44 eV, and further hydrogenation process occurs again on the remote N atom, where the corresponding free energy is reduced by 0.89 eV. Subsequently, reducing *NH−NH2 to *NH2−NH and *NH3 is a small endothermic process, except the step of first NH3 released, where the free energy changes are 0.37 eV (*NH−NH2 to *NH2−NH3), −2.35 eV (*NH2−NH to *NH3), and 0.41 eV (*NH3 to *NH4). Notably, it can be seen that the hydrogenation process of *N−NH + H2 + e− → *NH−NH limits the overall reduction process via an
alternating mechanism. In other words, the PDS is the second protonation step with an onset potential of $-0.53$ V. Interestingly, the computational result is extremely close to the applied potential required by the distal mechanism. The enzymatic mechanism is similar to biological N$_2$ fixation, with six proton–electron transfer alternately occurring at the two N atoms bound to the catalytic active site. Along the enzymatic mechanism (Figure 5c), the N$_2$ molecule is adsorbed approximately parallel to Nb@P$_3$-Ars, and the corresponding free energy is $-0.27$ eV. In the following successive hydrogenation process, there is a significant uphill climb at the elemental step of $^{*}$NH$_2$+$^{*}$NH + H$^+$ + e$^-$ $\rightarrow$ $^{*}$NH$_2$+$^{*}$NH$_2$. Simultaneously, an applied potential of 0.73 V is required to overcome this energy barrier and thus complete the entire N$_2$ reduction process. Remarkably, the fourth protonation step ($^{*}$NH$_2$+$^{*}$NH + H$^+$ + e$^-$ $\rightarrow$ $^{*}$NH$_2$+$^{*}$NH$_2$) is the PDS for NRR processes via the enzymatic mechanism.

Most recently, considering the randomness of the experimental hydrogenation operation, a new hybrid reaction mechanism has been proposed, called the mixed mechanism. The mixed mechanism is essentially a fusion of distal and alternating mechanisms, with the key step being the transformation of the third hydrogenation step of the distal mechanism into an alternating mechanism (i.e., $^{*}$N$-$NH$_2$ + H$^+$ + e$^-$ $\rightarrow$ $^{*}$NH$-$NH$_2$). We also evaluated the performance of the mixed mechanism to implement the NRR process on Nb@P$_3$-Ars, and the corresponding free energy profiles are depicted in Figure 5d. Based on our computational result, the PDS is still dominated by the fourth protonation step, which is equivalent to the alternating mechanism concerning the performance of N$_2$ reduction.

According to the specific details of the above discussions about NRR mechanisms, it is easy to see that varying reaction mechanisms (i.e., distal, alternating, enzymatic, and mixed) are constrained by different PDSs with onset potentials of 0.52, 0.53, 0.73, and 0.53 V, relying on the magnitude of the overcoming energy barrier. In addition, we also calculated the overpotential for distal, alternating, enzymatic, and mixed mechanisms, and the corresponding value is 0.36, 0.37, 0.57, and 0.37 V, respectively. Overall, the NRR process prefers to take place through the distal mechanism on the Nb@P$_3$-Ars sheet with the ultralow onset potential. As we know, such an onset potential is quite small in many theoretical predictions, for example, TiN$_4$@Gra (0.69 V),$^{71}$ MoBC$_2$@BP (0.60 V),$^{72}$ Re@MoS$_2$ (0.43 V),$^{69}$ and B@C$_2$N (0.45 V).$^{25}$ Moreover, considering the effect of solvents on the catalyst in the actual catalytic environment, we introduced an implicit solvation model with the VASPsol code.$^{73,74}$ The free energy profiles of the difference in the effect of the solvent model and the vacuum model on the NRR via distal mechanism is shown in Figure S6. As a result, the free energy barrier is slightly reduced by 0.07 eV in the H$_2$O$^-$ solvent model, which drives the e-NRR in a favorable tendency. Owing to the heavy computational workload and the slight influence of the solvent, the systematic study on the reduction of N$_2$ under the H$_2$O$^-$ solvent model is beyond the scope of this research and will not be discussed here. Overall, investigation of the systematic NRR mechanism shows that Nb@P$_3$-Ars is a promising e-NRR catalyst.

### 2.4. Electronic Properties for N$_2$ on Nb@P$_3$-Ars.

Employing electronic structure calculations, we further explored the origin of N$_2$ reduction by Nb@P$_3$-Ars. Precisely, changes in electronic structure are described by partial density of states (PDOS). (Figure 6a) PDOS of N$_2$-$p$, P$_3$-$p$, and Nb-$d$ orbitals before and (b) after adsorption on Nb@P$_3$-Ars with end-on configuration and (c) the corresponding CDD after N$_2$ adsorption from side and top views. The isosurface level is 0.008 e/Å$^3$. Cyan and yellow represent charge accumulation and depletion, respectively.
of states (PDOS) and charge density differences (CDDs). As shown in Figure 6a, before N₂ molecule adsorption, the Nb atom and the three associated P atoms form a significant orbital hybridization near the Fermi level (energies in the range of ~4 to 4 eV). Such results show that the Nb atom can form strong bonds with the surrounding P atoms. This agrees with the strong binding energy of Nb@P₃-Ars that we obtained previously.

In addition, the phase-gaseous N₂ molecule near the Fermi level provides π*(σ anti-bonding orbital) and σ (σ bonding orbital) orbitals. Upon capture by Nb@P₃-Ars (Figure 6b), the π* orbital-splitting appears and it strongly interacts with the d orbital of Nb, resulting in d-π* orbital hybridization. This result reveals that partial occupation of the d orbitals can provide electrons to the N₂ anti-bonding orbitals, which in turn weakens the N=N bonding effect and provides some activation of the inert N₂ molecule. This is consistent with the “acceptance and backdonation” mechanism proposed in previous studies. Especially, partial hybridization of the P₁-P₃ orbital with Nb-d, N₂-p orbitals in the vicinity of the near Fermi level (about ~1 to 3 eV) contributes to the bonding, indicating that Nb-P₁ cooperatively activates N₂. Meanwhile, with CDD analysis, as shown in Figure 6c, the electron transfer in the adsorption process is demonstrated. Obviously, the charge accumulation and depletion can occur both in the absorbed N₂ and the Nb@P₃-Ars. It is easy to see that for end-on configuration, the charge accumulation formed near the proximal N is much better than that formed near the remote N. While near the Nb atoms, there is some degree of charge depletion. Such a phenomenon would equally explain the “acceptance and backdonation” mechanism. Besides, from PDOS and CDD, the accumulation and depletion of charge around the Nb atom and its associated P atoms occurred. This indicates that Nb remains strongly associated with the substrate material (P₁-Ars) even after N₂ adsorption, which may be due to the greater electronegativity of the P element. Moreover, although the electrons lost by the Nb atom are not fully used for the activation of inert N₂, the stability of the catalyst is guaranteed to some extent, which is a new strategy for catalyst design. Continuous Bader charge analysis shows that the N₂ molecule obtained 0.36 e from the Nb@P₃-Ars via end-on configuration. Consequently, through the comprehensive analysis of electronic properties, it is clear that Nb@P₃-Ars can catalyze the reduction of N₂. The orbital hybridization ensures the stability of the catalyst and the occurrence of chemical reactions, and the electron transfer promotes the activation of the N=N bond. Therefore, when N₂ is captured by Nb@P₃-Ars in the end-on configuration, the e-NRR process will be efficiently achieved.

2.5. Thermal Stability of Nb@P₃-Ars. The catalytic performance can be influenced more or less by the substrate except for the central catalytic site. Processes in catalytic reactions are dynamic and the catalytic efficiency can change as a consequence of changes in the ligand environment, even for the same SAC. Therefore, the combination of DFT and molecular dynamics (DFT-MD) provides options for obtaining basic information on the reaction kinetics and exploring the dynamics of the active sites of SAC.84,85 For example, the e-NRR model designed by Ren et al.,75 Nb/CN, can maintain good thermal stability and catalytic activity at 500 K. Furthermore, it is worth exploring whether changes in the ligand environment and substrate can still maintain excellent performance for Nb@P₃-Ars. For this reason, we performed the DFT-MD simulation at different temperatures to examine the thermal stability of Nb@P₃-Ars. Figure S7a-f shows the MD trajectories of Nb@P₃-Ars at a temperature of 300 K. The simulated results reveal that the structure is robust at room temperature. When the temperature is increased to 400 K, the structure remains quite stable (Figure S8). After 500 K, the structure starts to reconstruct slightly with apparent displacement of the central catalytic site (Nb) observed. At 800 K, the structure is significantly damaged. Therefore, Nb@P₃-Ars has excellent thermal stability under ~400 K and can be synthesized experimentally at room conditions.

Moreover, we also investigated the Nb-doped arsenene (Nb@Ar₃) for comparison. The results show that the binding energy of Nb@Ar₃ (~6.56 eV) is weaker than the cohesive energy (~7.03 eV), indicating the easy aggregation of the doped Nb atoms. As for the hydrogenation process, the energy barrier of the PDS in NRR for Nb@Ar₃ is ~0.18 eV higher, compared with the favorable mechanism of Nb@P₃-Ars. Owning to these disadvantages, the coordination of P₁ is further confirmed in the improvement on the NRR catalytic performance.

3. CONCLUSIONS

In summary, utilizing DFT calculations, we designed an extensive range of electrocatalysts of P-coordinated metal atoms (i.e., Ti, V, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ru, Rh, W, and Pt) embedded into arsenene for reducing N₂ by the electrochemical method. On screening of NRR catalysts based on the “two-step” strategy, our computational results reveal that Nb@P₃-Ars exhibits the performance of best N₂ reduction among all candidates. Moreover, the activity of HER is greatly suppressed. Further studies show that when NRR occurs by the distal mechanism, the gaseous N₂ molecule exhibits adsorption stability when captured by Nb@P₃-Ars with end-on configuration while requiring an overpotential (0.36 V) less than the alternating, enzymatic and mixed mechanisms. Through the analysis of electronic properties, we further elucidate the physical mechanism of Nb@P₃-Ars capture and activation of N₂; in particular, we find that the coordination element P, due to its strong electronegativity, also forms charge aggregation and consumption, and Nb, although losing some electrons for N₂ activation, ensures the most basic stability of the catalyst. Subsequent DFT-MD simulations prove the thermal stability of Nb@P₃-Ars at temperatures below 400 K. This theoretical study paves a way for designing a novel e-NRR catalyst with low cost and high efficiency.

4. COMPUTATIONAL DETAILS

All theoretical calculations were described through the Vienna Ab Initio Simulation Package (VASP) software based on DFT.76,77 The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation mimicked the exchange–correlation energy,78 and the corresponding cut-off energy for the plane-wave basis was set as 500 eV. The projector augmented wave method was adapted for electron–electron interactions.76 The convergence criteria for self-consistent electronic energy and residual force were, respectively, assumed to be 10⁻⁶ eV/atom and 0.01 eV/Å, which could ensure sufficient accuracy. Considering the van der Waals interaction, we employed the DFT-D3 methods with Becke–Johnson damping in the whole process.79 In addition, the MD based on the first-principles calculations was
used to investigate the thermodynamic stability of the structure at different temperatures taking advantage of the NVT ensemble,\(^8^0\) and the total simulation time was 10 ps with a time step of 1 fs. Charges transfer was described in terms of the Bader charge analysis.\(^8^1,^8^2\)

In order to visually describe the P-coordinated metal atoms embedded in the defective arsenene, we established a 2D defective arsenene nanosheet (5 × 5 supercell) with 49 atoms, in which the three As atoms around a point defect were replaced by P atoms. Particularly, we set a vacuum layer of ~20 Å to eliminate the interaction of periodically repeated units along the z axis. For full relaxation of the structure, a 3 × 3 × 1 \(k\)-point mesh for a supercell based on the Gamma centered Brillouin zone and 5 × 5 × 1 for the calculations of electron properties with the DFT–PBE level. More computational details are described in the Supporting Information.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00581.

Relevant formulas needed for theoretical calculation; \(\text{N}_2\) adsorption at \(\text{P}_3\)-Ars; structures of the reaction intermediates for \(\text{N}_2\) reduction on \(\text{Nb@P}_3\)-Ars via the distal, alternating, and enzymatic mechanisms; bond length variations of the N–N bond and the N–Nb bond through the distal mechanism; difference in free energy between vacuum and solvent models in the NRR process; DFT–MD calculation results; \(\text{N}_2\) and TM-N bond changes; and all the corrections for zero-point energy and TS for our systems (PDF)

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Z.X., G.L., and R.S. conceived the research. R.S. carried out the theoretic simulations. Z.X. and R.S. wrote the initial manuscript. All authors discussed the results and revised the manuscript.

### Notes

The authors declare no competing financial interest.

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