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The β -PdBi₂ monolayer for efficient electro-catalytic NO reduction to NH₃: a computational study†

Yuting Sun,^a Zhongxu Wang,^a Yuejie Liu,^{*b} Qinghai Cai ^{a,c} and Jingxiang Zhao ^{*a}

Electrocatalytic NO reduction to NH₃ (NORR) is regarded as an appealing strategy for both sustainable NH₃ production and harmful NO abatement, but the development of highly active and selective electro-catalysts to boost such a complex multiple proton-coupled electron-transferred process still remains a challenge. Here, by means of density functional theory (DFT) computations, we proposed the synthesized β -PdBi₂ monolayer as a highly efficient NORR catalyst. Our results revealed that the β -PdBi₂ monolayer possesses outstanding thermodynamic, dynamic, and electrochemical stabilities, as well as intrinsic metallicity. In particular, this catalyst exhibits excellent catalytic activity towards NORR with a low limiting potential of -0.35 V, which can be further enhanced by applying a suitable tensile strain. In addition, we also explored the effects of pH and applied potential on NORR over the β -PdBi₂ monolayer, among which an alkaline environment of pH = 7.92 facilitates the effective NO-to-NH₃ conversion. Thus, the β -PdBi₂ monolayer can be utilized as a promising catalyst with high efficiency for NORR, which offers cost-effective opportunities for advancing sustainable NH₃ production and eliminating nitric oxide pollutants.

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1. Introduction

As one of the most significant synthetic chemicals in industry, ammonia (NH₃) is not only a vital ingredient and building block of many nitrogenous compounds for the manufacture of plastics, explosives, fibers, dyes, and pharmaceuticals, but also is responsible for the production of 85% of fertilizers to boost sustainable food for meeting the ever-growing global population.^{1–4} In addition, NH₃ is an ideal carbon-free H₂ fuel for energy storage and transportation due to its high hydrogen content of 17.5%.^{5,6} At present, the large-scale NH₃ synthesis mainly depends on the traditional Haber–Bosch process, which has been regarded as the most impactful invention of the 20th century.^{7,8} However, such a process is energy intensive in that it requires harsh conditions (*e.g.*, 400–500 °C and 150 bar) to break the highly inert N≡N triple bond, leading to mass CO₂ emissions and extensive energy consumption.^{9,10}

Recently, the electrocatalytic N₂-to-NH₃ conversion (NRR) under ambient conditions has emerged as a green and energy-saving alternative to the Haber–Bosch technology.^{11–14} Nevertheless, the high energy (941 kJ mol⁻¹) required for N₂ dissociation, low water solubility, and a severe competing hydrogen evolution reaction (HER) make the NRR process suffer from serious activity and selectivity problems.^{15–18} Thus, the electrochemical NH₃ synthesis from N₂ fixation still remains a huge challenge.

Compared with the N₂ reactant, nitric oxide (NO) is more reactive and possesses a lower dissociation energy of the N=O bond, rendering the NO reduction reaction (NORR) more feasible than NRR for NH₃ electrosynthesis thermodynamically.^{19–21} Particularly, NO is one of the notorious air pollutants and poses a great threat to the ecological environment and human health.^{22–24} Thus, NORR represents an appealing strategy to produce valuable NH₃ and to remedy NO pollution simultaneously.^{25–32} Yet, the competitive HER still greatly limits the NORR, leading to low faradaic efficiencies (FE).^{33–36} Thus, it is of great significance to explore stable and highly efficient catalysts made from Earth-abundant elements to impede the unwanted HER and to promote the NORR process simultaneously.

As a low-toxic, highly-stable, environmentally-friendly group-VA metal, bismuth (Bi) has received extensive attention in electrocatalysis such as N₂ fixation and CO₂ reduction.^{37–45} More importantly, Bi has been revealed to exhibit a superior

^aCollege of Chemistry and Chemical Engineering, Key Laboratory of Photonic and Electronic Bandgap Materials, Ministry of Education, Harbin Normal University, Harbin 150025, Heilongjiang, China. E-mail: zhaojingxiang@hrbnu.edu.cn

^bModern Experiment Center, Harbin Normal University, Harbin, 150025, China. E-mail: liuyuejie@hrbnu.edu.cn

^cHeilongjiang Province Collaborative Innovation Center of Cold Region Ecological Safety, Harbin 150025, China

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suppressing effect on the competitive HER due to its rather weak binding strength with H species,⁴⁶ which normally helps improve the selectivity towards the NO electrocatalytic reduction. However, bulk Bi materials exhibit low efficiency due to the absence of accessible active sites.^{47,48} In this regard, the two-dimensional (2D) counterparts hold great promise for electrocatalytic application due to their large specific surface area to facilitate the diffusion of reactants and more exposed active sites to boost rapid charge transfer.^{49,50} For example, Zhang *et al.* prepared ultrathin 2D Bi nanosheets towards efficient electrocatalytic CO₂ conversion with a FE of 86.0% for formic acid production.⁵¹ Qiao's group reported that their synthesized Bi nanosheets can be used as a promising catalyst for NRR, which can be attributed to the sufficient exposure of edge sites.⁴⁵ However, the catalytic activity of these reported 2D Bi electrocatalysts is still unsatisfactory due to their low current density.^{39,52} Thus, the further development of 2D Bi-based electrocatalysts with high selectivity and high efficiency for NH₃ synthesis from NORR is of great significance.

Herein, by means of density functional theory (DFT) computations, we proposed a novel 2D material, namely the β -PdBi₂ monolayer, as a promising NORR catalyst. Notably, using a Bi(111) film on Si(111) as a substrate, β -PdBi₂ films with various layers have been successfully synthesized in experiments.⁵³ Our results revealed that β -PdBi₂ indeed exhibits good catalytic performance toward NO electroreduction to the NH₃ product with high efficiency and high selectivity, which can be further enhanced by applying a 7% tensile strain. In addition, the alkaline conditions are also conducive to boost the NORR catalytic activity of the β -PdBi₂ monolayer. Thus, the β -PdBi₂ monolayer can be utilized as an eligible NORR catalyst for NH₃ synthesis.

2. Computational models and methods

All spin-polarized density functional theory (DFT) computations were carried out by using the Vienna *Ab Initio* Simulation Package (VASP)^{54,55} with the projector-augmented-wave (PAW) method,^{56,57} and a cutoff energy of 550 eV was adopted. The exchange–correlation interactions were described by the Perdew–Burke–Ernzerhof (PBE) functional⁵⁸ within the generalized gradient approximation (GGA). The convergence thresholds for energy and force were set to 10^{−5} eV and 0.01 eV Å^{−1}, respectively. The DFT + D3 method within the Grimme scheme⁵⁹ was used to account for the van der Waals (vdW) interactions of the reaction intermediates with the catalysts.

A 4 × 4 × 1 supercell was constructed to explore the catalytic activity of the β -PdBi₂ monolayer, in which a vacuum space of 20 Å in the z-direction was adopted to avoid the interactions between periodic images. The Brillouin zone was sampled with a Monkhorst–Pack grid of 3 × 3 × 1 for geometry optimization, while a denser *k*-mesh of 15 × 15 × 1 was used for computations of electronic properties. The hybrid functional based on the Heyd–Scuseria–Ernzerhof (HSE06) method^{60,61} was

adopted to compute the band structure. The *ab initio* molecular dynamics (AIMD) simulations were carried out by the NVT ensemble with the Nose–Hoover thermostat.⁶² To evaluate the electrocatalytic performance of the NO-to-NH₃ process, the Gibbs free energy changes (ΔG) of all elementary steps along all possible reaction pathways were computed by the computational hydrogen electrode (CHE) model^{63,64} and further computational details are presented in the ESI.†

3. Results and discussion

3.1. Structure, stability, and electronic property of the β -PdBi₂ monolayer

It has been experimentally reported that 2D β -PdBi₂ films can be synthesized from a single layer up to dozens of triple layers using a Bi(111) film on Si(111) as the substrate based on the molecular beam epitaxy method.⁵³ In Fig. 1a, we have presented the structure of the optimized β -PdBi₂ monolayer. Obviously, the primitive cell of the β -PdBi₂ monolayer is square with two Bi and one Pd atoms in one unit, in which each Pd atom is located at the center of a square prism of eight Bi atoms, resulting in the formation of a layered body-centred unit cell. Furthermore, the optimized lattice constant of β -PdBi₂ is computed to be 3.27 Å with the length of the Pd–Bi bond being 2.98 Å. Notably, the obtained structure and the corresponding lattice parameters of the β -PdBi₂ monolayer were well consistent with previous theoretical studies,^{65–67} indicating the accuracy of the employed methods and models in this work. Furthermore, according to the Bader charge analysis, each Bi atom with smaller electronegativity denotes 0.22 e[−] to each Pd atom, accumulating positive charges on the Bi atoms (Fig. 1b), which may be conducive not only to activate the NO reactant, but also to hinder the H⁺ approaching Bi active site and the *H formation due to the electrostatic repulsion between positively charged Bi and H⁺. To deeply understand the bonding feature, we computed the electron localization function (ELF) of the β -PdBi₂ monolayer, where a large ELF (>0.5) represents the covalent bond or core electrons, whereas a smaller ELF (<0.5) corresponds to the ionic bonds, and an ELF value of 0.5 suggests the metallic nature. It can be seen from Fig. 1c that there are obvious electron delocalizations in the whole β -PdBi₂ monolayer, implying strong interactions between Pd and Bi atoms in the whole framework and belonging to the robust ionic bonds, which may be beneficial for the excellent stability of the β -PdBi₂ monolayer.

High stability is a prerequisite for the long-term application of any catalysts. We first computed the cohesive energy (E_{coh}) of the β -PdBi₂ monolayer using the following equation: $E_{\text{coh}} = (E_{\beta\text{-PdBi}_2} - E_{\text{Pd}} - 2E_{\text{Bi}})/3$, where $E_{\beta\text{-PdBi}_2}$, E_{Pd} , and E_{Bi} represent the total energies of the β -PdBi₂ monolayer, Pd, and Bi atoms. According to this definition, the computed E_{coh} of the β -PdBi₂ monolayer is −3.44 eV, which is comparable to those of some synthesized 2D nanomaterials, such as Cu₂Si (−3.46 eV)⁶⁸ and germanene (−3.26 eV),⁶⁸ well consistent with previous results on its experimental synthesis.⁵³ To assess the thermodynamic

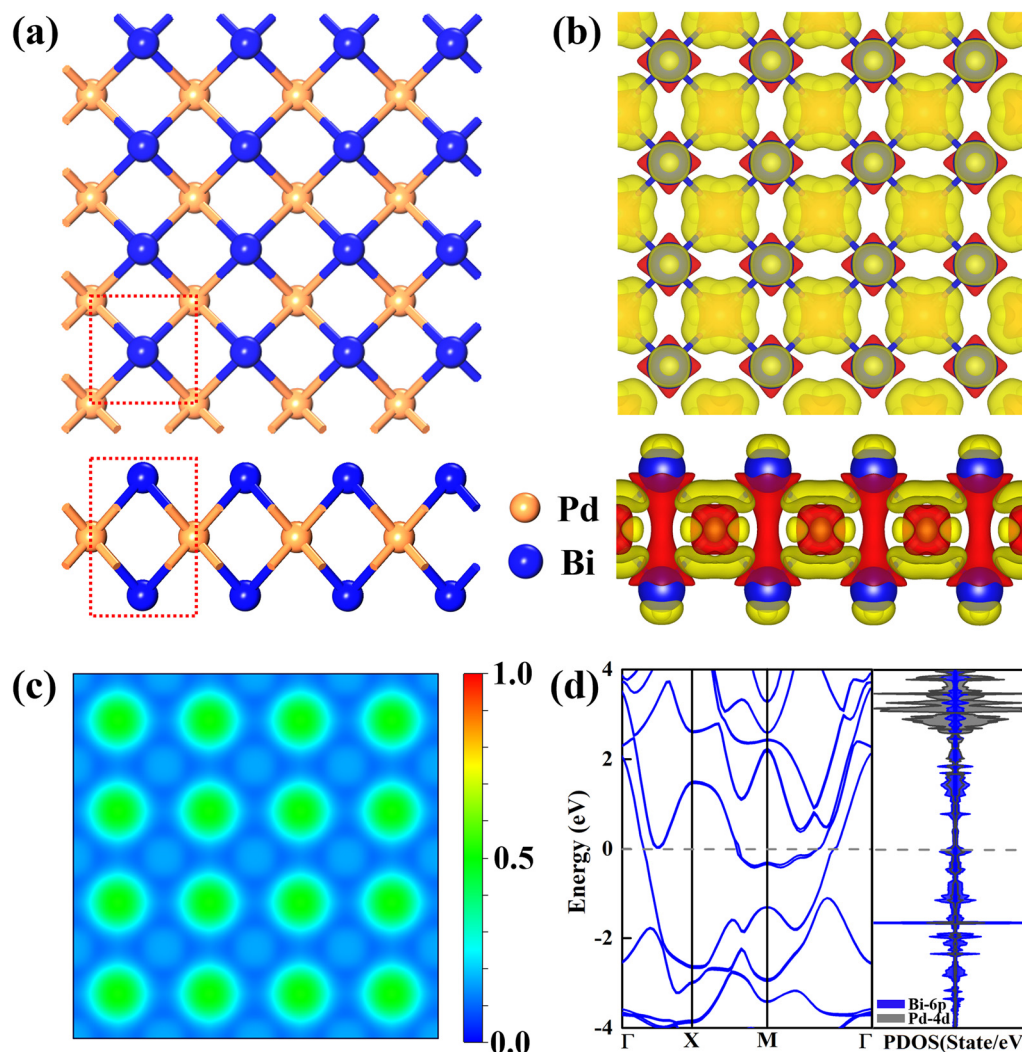


Fig. 1 (a) Top and side view of the optimized β -PdBi₂ monolayer. The red dashed lines represent a unit cell of the β -PdBi₂ monolayer. (b) The charge difference density of the β -PdBi₂ monolayer with an isovalue of $0.003 \text{ e} \text{ \AA}^{-3}$, and yellow and red bubbles represent positive and negative charges, respectively. (c) ELF analysis of β -PdBi₂ monolayer along the (001) plane. (d) Band structure with the spin-orbit coupling (SOC)-corrected and projected density of states (PDOS) of the β -PdBi₂ monolayer.

stability of the β -PdBi₂ monolayer, *ab initio* molecular dynamics (AIMD) simulations were further performed at 500 K. It can be observed that the β -PdBi₂ monolayer well maintains its pristine structure without obvious deformation throughout a 10 ps (Fig. S1 in the ESI[†]), indicative of its outstanding thermal stability. In addition, a good electrochemical stability is also vital to guarantee its practical application under realistic aqueous conditions. To this end, we computed the dissolution potential (U_{diss} , ESI[†]), which is a well-accepted descriptor to assess the electrochemical stability of a catalyst.^{69,70} Fortunately, our results showed that the β -PdBi₂ monolayer has a positive U_{diss} of 0.75 V, suggesting that this material is electrochemically stable under realistic conditions. Another important question is whether the bare surfaces of the β -PdBi₂ monolayer could be covered by *O/*OH species in an aqueous solution under working conditions. To address this question, the surface Pourbaix diagram⁷¹ of the β -PdBi₂

monolayer was constructed to reveal its most stable surface configurations under different equilibrium potentials and pH values. The results showed that the redox potential (U_{R}) of the β -PdBi₂ monolayer is much less negative than the corresponding U_{L} of NORR, indicating that this catalyst exhibits outstanding electrochemical stability against surface oxidation under working conditions (Fig. S2[†]).

To ensure rapid charge transfer in electrocatalysis, an excellent electrical conductivity is also indispensable. Therefore, we computed the band structure through the hybrid HSE06 functional, in which the spin-orbit coupling (SOC) effect was considered, as Bi is a heavy element. As shown in Fig. 1d, we found that there are some energy bands crossing the Fermi level, suggesting that the β -PdBi₂ monolayer exhibits a metallic feature. Moreover, its projected density of states (PDOSs) was computed, from which the high peaks around the Fermi level could be observed (Fig. 1d). In general, the high DOS at the

Fermi level indicates a high density of carriers, promoting good electron transfer and boosting the chemical reactivity towards the adsorbates. Thus, the β -PdBi₂ monolayer exhibits outstanding electrical conductivity, which may be constructive to its electrocatalytic performance. In addition, there is strong hybridization between the Bi-6p and the Pd-4d in the whole PDOSs, again verifying the strong interaction between each other.

3.2. NORR catalytic performance of the β -PdBi₂ monolayer

Prior to the exploration of the NORR catalytic activity, we first examined the adsorption of the NO reactant on the β -PdBi₂ monolayer, which is a pivotal step for affecting or determining the subsequent reduction pathways. To this end, three typical adsorption configurations were considered, namely, N-end, O-end, and side-on patterns (Fig. S3[†]), on different sites of β -PdBi₂, including the top site of Bi, the bridge site of two Bi atoms, and the hollow site of a Bi-based square.

After the fully structural relaxation, we found that NO is the most energetically favorable to be adsorbed on the hollow site of β -PdBi₂ *via* the N-end pattern, leading to the formation of four Bi–N bonds with a length of 2.36 Å (Fig. 2a). Moreover, the corresponding adsorption energy (E_{ads}) was determined by: $E_{\text{ads}} = E_{*NO} - E_* - E_{\text{NO(g)}}$, where E_{*NO} and E_* represent the DFT energies of β -PdBi₂ with and without adsorbed NO molecules, respectively, while $E_{\text{NO(g)}}$ is the energy of the isolated NO

molecule. According to this definition, the computed E_{ads} value for NO adsorption on β -PdBi₂ is -0.92 eV, corresponding to a ΔG of -0.24 eV after taking the contributions of the zero-point and entropy into account (Fig. 2b) and thus suggesting a strong NO chemisorption on β -PdBi₂. The chemisorption also elongates the N–O bond length from 1.15 Å in free NO to 1.17 Å in β -PdBi₂, indicating that the NO reactant is activated on the β -PdBi₂ catalyst surface. Furthermore, the computed PDOSs in Fig. 2c showed that the electronic coupling mainly exists between Bi-6p and NO-2p orbitals. Importantly, β -PdBi₂ donates about 0.51 electrons to the adsorbed NO, resulting in the significant accumulation of negative charges (yellow regions in Fig. 2d) on the *NO species, which may promote the subsequent reduction reaction.

In addition to the most stable NO adsorption configuration, we also obtained other several meta-stable configurations: NO is adsorbed on the Bi-atop site *via* the N-end pattern or two possible Bi–Bi bridge sites of β -PdBi₂ *via* the side mode (Fig. S4[†]). The computed E_{ads} values are -0.57 , -0.44 , and -0.57 eV, respectively, which are less negative than that of on the hollow site of -0.92 eV. Furthermore, as for the O-end pattern, the obtained NO adsorption is even weaker with a considerable small E_{ads} value of -0.27 and -0.04 eV, and the distance between NO and β -PdBi₂ is larger than 3.30 Å. As a result, the ΔG values for these meta-stable species are generally positive ranging from 0.11 to 0.64 eV (Fig. 2b), which are

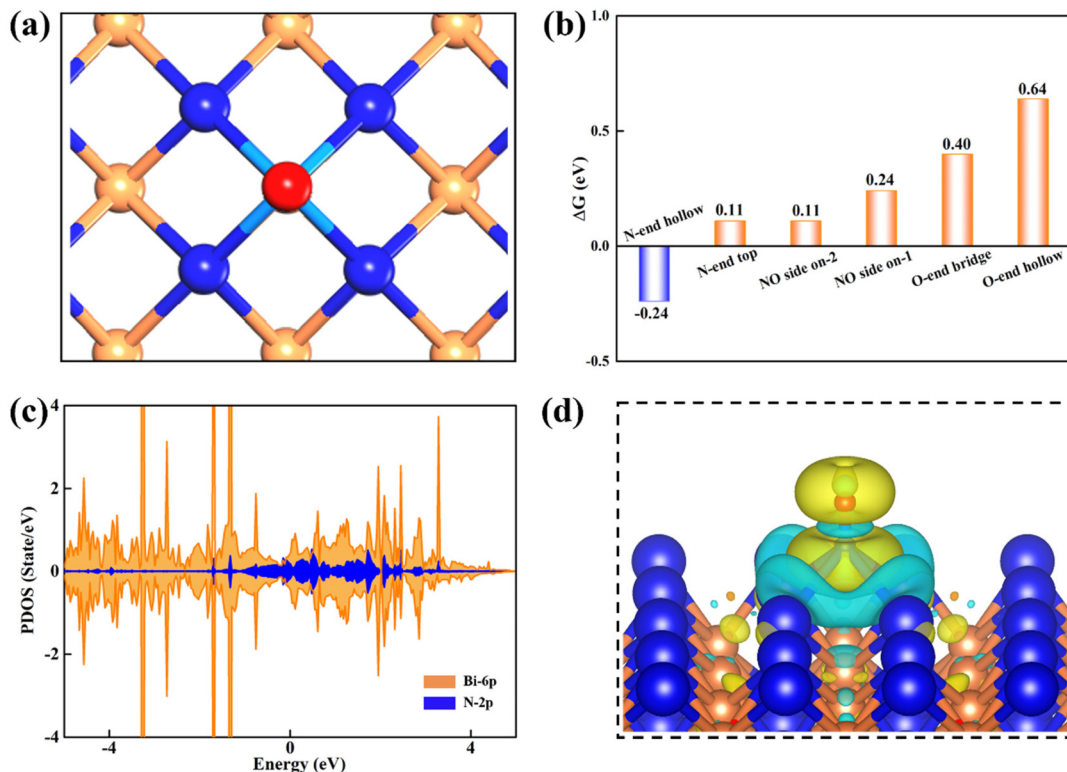


Fig. 2 (a) The optimized configuration, (b) the adsorption free energies (ΔG) for NO adsorption on the β -PdBi₂ monolayer in various possible adsorption patterns, (c) the projected density of states (PDOS) and (d) the charge difference density of the β -PdBi₂ monolayer with an iso-value of $0.003 \text{ e} \text{ \AA}^{-3}$ (before and after NO adsorption). Cyan and yellow bubbles represent positive and negative charges, respectively.

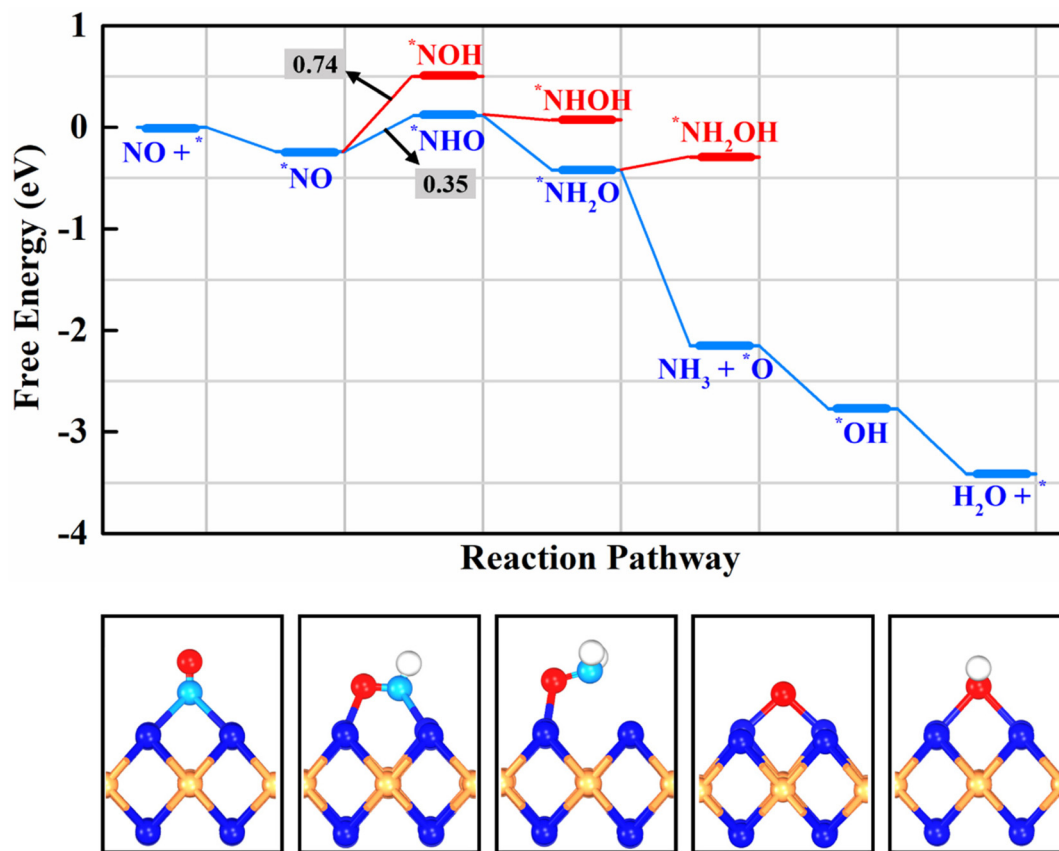


Fig. 4 The energetically most favorable free energy profile for the electroreduction of NO molecules to NH₃ product on the β -PdBi₂ monolayer and the involved reaction intermediates. The blue, orange, red, light blue, and white spheres represent the Bi, Pd, O, N, and H atoms, respectively.

formance of the proposed β -PdBi₂ for NH₃ synthesis from NORR.

In addition to the NH₃ product at a low NO coverage, N₂ and N₂O are the possible products of NORR at high NO coverage, which can be modulated by controlling the partial pressure according to a recent experimental study reported by Jiao *et al.*⁸¹ To this end, we also examined the feasibility to produce N₂O and N₂ in the NORR process, in which the NO-

dimer, *i.e.*, *N₂O₂, is a key intermediate. On the β -PdBi₂ monolayer, two relatively stable *N₂O₂ configurations were obtained *via* the O- and N-end modes with ΔG values of -1.23 and -0.39 eV, respectively (Fig. S7[†]). Starting from the O-end adsorption configuration, the N₂O product can be generated after two hydrogenation steps, which are downhill in the free energy profile, indicative of the spontaneous N₂O formation (Fig. 5a). We have noted that N₂O adsorption on the β -PdBi₂

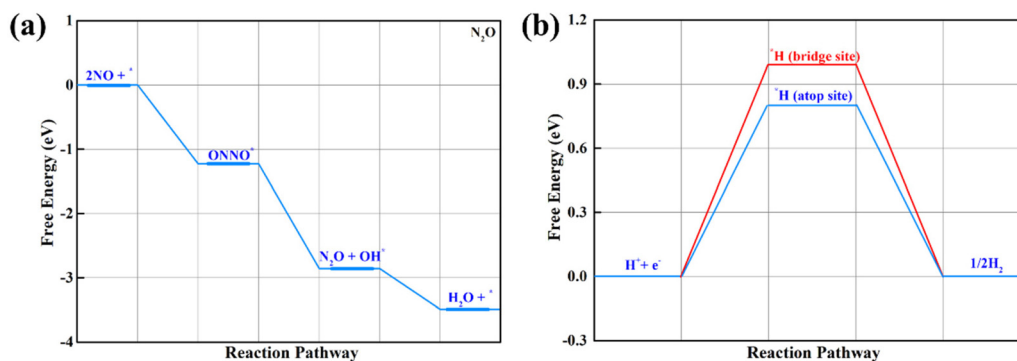


Fig. 5 (a) The energetically most favorable free energy profile for the electroreduction of 2NO molecules to the N₂O product on the β -PdBi₂ monolayer and (b) the calculated Gibbs free profile of HER on the β -PdBi₂ monolayer.

monolayer is rather weak, enabling its rapid release from the catalyst surface, rather than a further reduction to the N_2 product. Thus, at high NO coverage, N_2O is the main product of NORR on the β -PdBi₂ monolayer, which can thus be utilized as a promising catalyst to generate tunable multiproducts by control the NO coverage.⁸² Another important question is the competition between NORR and the HER side reaction, which may greatly impact the faradaic efficiency toward NH_3 synthesis. After considering various initial adsorption sites, including atop, bridge, and hollow sites, we found that the *H adsorption on the Bi-Bi bridge site and Bi atop site is stable, and the computed ΔG values are 0.99 and 0.80 eV, respectively, as shown in Fig. 5b, which is much larger than that of the PDS in NORR (0.35 eV), implying its overwhelming suppressing effect on HER and thus guaranteeing the high NORR selectivity.

3.3. Effect of strain on the NO-to- NH_3 catalytic activity

Strain engineering has been widely reported to be a powerful strategy to tailor the reactivity of electrocatalysts for achieving outstanding performance.^{83–85} Thus, the external biaxial tensile strain was imposed on β -PdBi₂ (Fig. 6a), which can be realized by direct stretching or using a pre-stretched substrate in the experiment. Note that the strain range is from 1% to 7% with a step of 1%. Our AIMD simulations showed that the structural integrity of β -PdBi₂ can be well maintained under a 7% tensile strain (Fig. S8†), indicating its rather high thermo-

dynamic stability. Moreover, we re-computed the free energy diagrams of the NO-to- NH_3 process, which was plotted as a function of the external tensile strain (Fig. 6b). Our results showed that the binding strength of NO will be weakened with the increase of strain (E_{ads} for NO decreases from -0.92 eV to -0.61 eV at a 7% strain). Moreover, the PDS is unchanged with the variation of strain, which always occurs in the first hydrogenation step ($*NO + H^+ + e^- \rightarrow *NHO$). Interestingly, the computed ΔG value of this step decreases gradually, implying the decrease of the limiting potential with the enhancement of the tensile strain. As a result, the NO reduction on β -PdBi₂ exhibits the highest catalytic activity with a limiting potential of -0.09 V after applying 7% tensile strain (Fig. 6c), suggesting that the strain engineering can greatly enhance the NORR catalytic activity of β -PdBi₂ for NH_3 synthesis. Notably, under the tensile strain of 7%, the competing HER reaction is still greatly suppressed due to its larger energy input (0.64 eV, Fig. S9†), suggesting that the high NORR selectivity is unchanged by the tensile strain.

As discussed above, the NORR activity of β -PdBi₂ at different tensile strains is highly dependent on the binding strength of *NO: the adsorption strength of *NO should be as small as possible, but large enough to prevent NO desorption, which is well consistent with the famous Sabatier principle. Thus, to gain a vivid insight into the strain effect on the NORR activity of the β -PdBi₂ monolayer, it is essential to analyze the bonding nature of the adsorbed *NO species. Hence, we com-

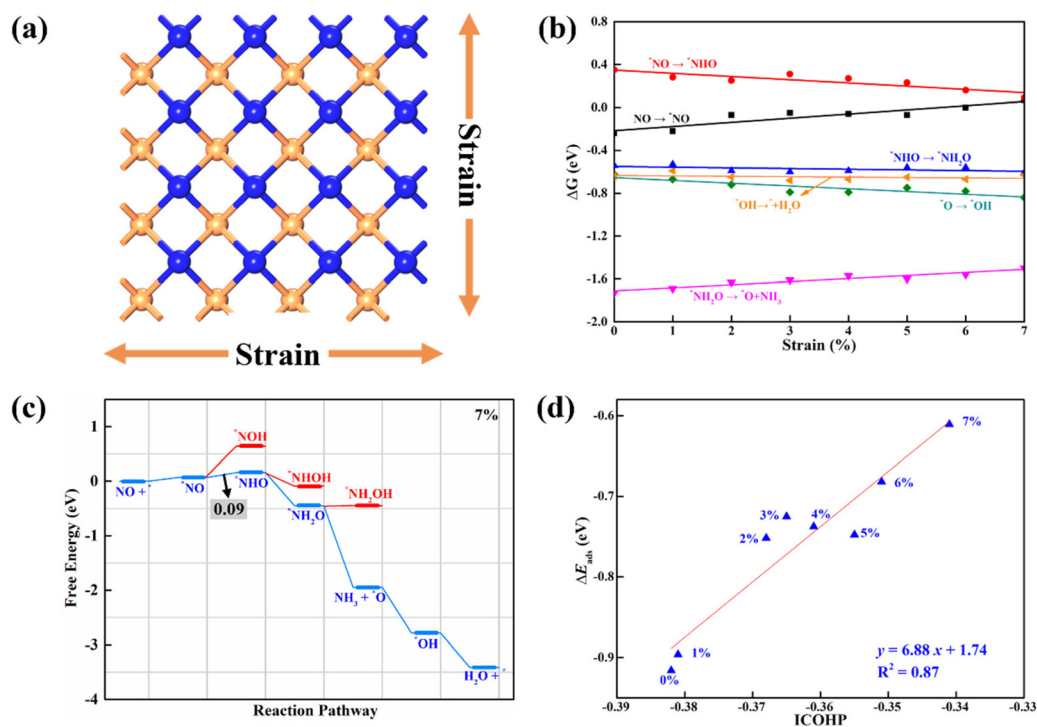


Fig. 6 (a) Schematic of the β -PdBi₂ monolayer under biaxial tensile strain; (b) the relationship of ΔG with the strain; (c) the energetically most favorable free energy profile for the electroreduction of NO molecules to the NH_3 product on the β -PdBi₂ monolayer after applying 7% tensile strain and (d) the correlation of the adsorption energy (ΔE_{ads}) of *NO species with the integrated crystal orbital Hamilton population (ICOHP).

puted the projected crystal orbital Hamilton population (pCOHP) of the formed Bi–N bonds between *NO and the β -PdBi₂ monolayer. As shown in Fig. S10,[†] the regions in the Bi–N antibonding states around the Fermi level increase with the increase of tensile strain, indicative of a weakened binding strength of the *NO species on the strained β -PdBi₂ monolayer. The weakened Bi–N bond was further testified using a less negative integrated crystal orbital Hamilton population (ICOHP). More importantly, there is a good linear relationship between ICOHP and E_{ads} of *NO (Fig. 6d), which well accounts for the role of the external tensile strain in determining the occupancy of the Bi–N bonding/antibonding orbital populations.

3.4. pH-Dependent NORR activity

Although the CHE model has been successfully employed to rapidly screen out promising electrocatalysts and to well explain the underlying reaction mechanism, the pH-dependent activity of a given electrocatalyst can not be accurately reflected due to the limitations of a simple metal/vacuum model at zero charge to represent a charged electrochemical interface normally operating at constant potential conditions. Thus, we employed the constant-potential method (CPM)^{86–90} to examine the effects of pH values on the NORR catalytic activity of a 2D β -PdBi₂ monolayer. The computed total energies of

bare β -PdBi₂ and its surface with adsorbed NORR intermediates (*NO, *NHO, *NH₂O, *O, and *OH) as a function of the applied electrode potential (standard hydrogen electrode, SHE) are shown in Fig. 7a. Interestingly, we found that all energy-potential points well fit a quadratic relation, and the fitted data are summarized in Table S2.[†] The computed E_{ads} values of the five reaction intermediates with respect to the applied potential are presented in Fig. 7b. Clearly, the adsorption energy of *NO is highly dependent on the applied potential, which would affect the limiting potential under different applied potentials and pH values. Furthermore, we plotted the pH-dependent and potential-dependent contour of adsorption energies of *NO on β -PdBi₂ (Fig. 7c). The results indicated that the adsorption strength of *NO on β -PdBi₂ increases as the pH increases or the applied potential decreases. For example, the E_{ads} of *NO is -0.42 eV at pH = 1, while it can be increased to -0.83 eV at pH = 13. Thus, the acidic environment makes the *NO activation more difficult due to its weak capability to activate the NO reactant, which may explain the pH-dependent NORR activity of the β -PdBi₂ monolayer. More importantly, we found that this system will exhibit the highest catalytic activity at a pH of 7.92 with the limiting potential of -0.23 V vs. reverse hydrogen electrode (RHE) due to its optimal *NO adsorption energy of -0.68 eV. The corresponding free energy profile is presented in Fig. 7d.

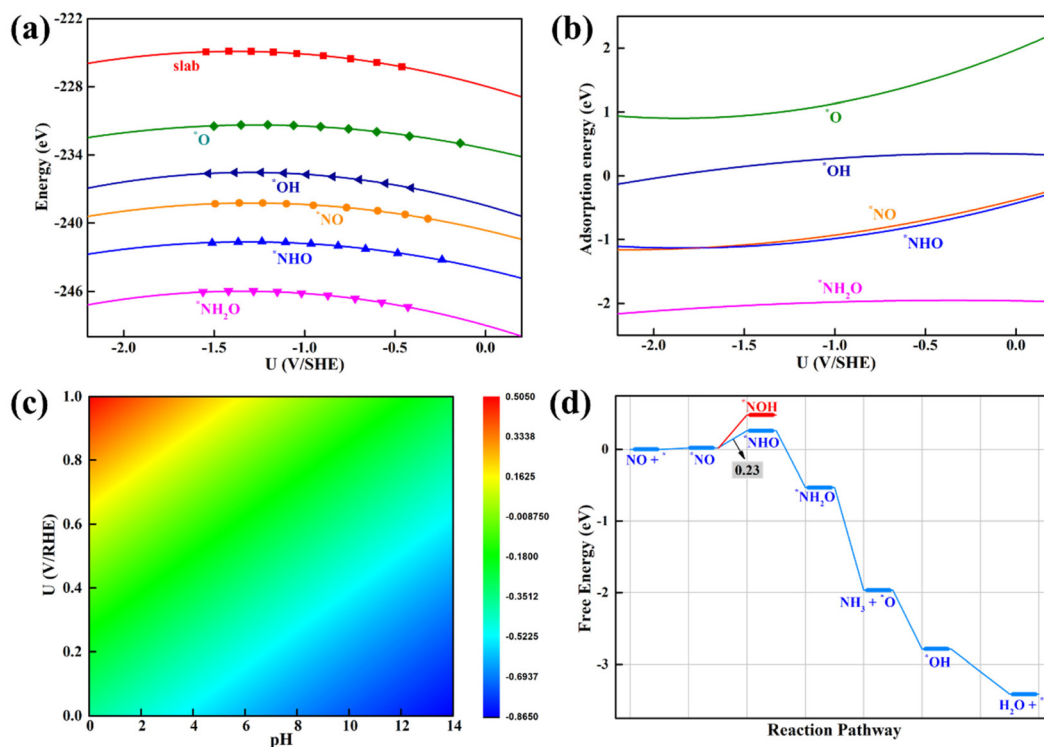


Fig. 7 (a) Computed energies of the β -PdBi₂ monolayer and the corresponding reaction intermediates as a function of the applied electrode potential. (b) Adsorption energies of *NO, *NHO, *NH₂O, *O, and *OH as a function of the applied electrode potential. (c) pH-Dependent and potential-dependent contour plot of adsorption energies of *NO on the β -PdBi₂ monolayer. (d) The free energy profile for NO-to-NH₃ electrocatalytic reduction on the β -PdBi₂ monolayer in pH = 7.92.

4. Conclusions

In summary, by performing comprehensive DFT computations, we explored the catalytic performance of the experimentally available β -PdBi₂ monolayer for the NO electrocatalytic reduction to NH₃. Interestingly, our results revealed that the β -PdBi₂ monolayer with high stability and inherent metallicity exhibits a superior NOER catalytic performance for NH₃ synthesis with a low limiting potential (−0.35 V) and the overwhelming suppressing effect on HER. Particularly, applying a 7% tensile strain can effectively optimize the NO adsorption strength to further enhance the NOER catalytic activity of the β -PdBi₂ monolayer. More importantly, based on the constant-potential method, we found that the alkaline conditions with a pH of 7.92 are also beneficial for boosting the effective NO conversion to NH₃. Our findings not only present an ideal candidate for NO-to-NH₃ electrolysis, but also offer promising strategies to enhance the NORR catalytic activity, which would inspire more experimental and theoretical studies to explore the potential of main-group metal materials in electrocatalysis.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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