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Rare-earth La-doped VS_{2-x} for electrochemical nitrate reduction to ammonia†

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We report rare-earth La-doped VS $_{2-x}$ enriched with S-vacancies (La-VS $_{2-x}$) towards the electrochemical nitrate reduction to ammonia (NO $_3$ RR), which shows a maximum NH $_3$ -faradaic efficiency of 96.6% with a corresponding NH $_3$ yield rate of 11.3 mg h $^{-1}$ cm $^{-2}$ at -0.6 V vs. RHE. Theoretical computations unveil that La-dopants and S-vacancies synergistically promote NO $_3$ $^-$ activation, suppress hydrogen evolution and lower the energetic barriers, leading to the enhanced NO $_3$ RR activity and selectivity of La-VS $_{2-x}$.

1. Introduction

 ${
m NH_3}$, a value-added chemical and also a renewable hydrogenrich carrier, is vital to modern agriculture and industry. ¹⁻³ Electrochemical nitrate reduction to ammonia (${
m NO_3RR}$) represents a fascinating approach to realising both green ${
m NH_3}$ generation and wastewater purification. ⁴⁻⁶ However, ${
m NO_3RR}$ effectiveness is still retarded by the complex multi-electron transfer process and easy occurrence of side reactions especially competing for the hydrogen evolution reaction (HER). ⁷⁻⁹ Therefore, it is urgently required to explore effective ${
m NO_3RR}$ electrocatalysts for active and selective ${
m NO_3}^-$ -to- ${
m NH_3}$ conversion. ¹⁰⁻¹⁴

To date, substantial efforts have been devoted to exploring many potential NO_3RR catalysts. $^{15-25}$ Metal chalcogenides have attracted wide attention in electrolysis due to their layered structure and high electrochemical stability. $^{26-28}$ Among them, VS_2 is most appealing due to its metallic nature with high conductivity, facilitating accelerated electron transfer for boosting the catalytic kinetics. 29,30 Nevertheless, investigations on VS_2 -based catalysts for the NO_3RR remain largely unexplored due presumably to the poor intrinsic activity of VS_2 for NO_3^- activation. Metal doping is a promis-

In this study, we report a rare-earth La-doped VS_{2-x} (La- VS_{2-x}) enriched with S-vacancies (V_S) towards the NO_3RR . La- VS_{2-x} delivers excellent NO_3RR performance with a highest NH_3 -faradaic efficiency (FE_{NH_3}) of 96.6% with the corresponding NH_3 yield of 11.3 mg h⁻¹ cm⁻² at -0.6 V νs . RHE. Detailed experiments combined with theoretical investigations are employed to unravel the catalytic NO_3RR mechanism of La- VS_{2-x} .

2. Results and discussion

La-VS $_{2-x}$ (4.8 wt% La) grown on carbon cloth (CC) was fabricated using a simple hydrothermal approach. The XRD pattern of La-VS $_{2-x}$ (Fig. 1a) shows major diffraction peaks assigned to the hexagonal VS $_2$ phase (JCPDS No. 89-1640). The SEM image of La-VS $_{2-x}$ (Fig. 1b) shows numerous nanosheets which grow perpendicularly on the CC substrate, and the nanosheet morphology of La-VS $_{2-x}$ is further verified by the TEM image (Fig. 1c). The elemental mapping images of La-VS $_{2-x}$ (Fig. 1d) reveal a uniform distribution of La elements. The HRTEM image of La-VS $_{2-x}$ (Fig. 1e) shows two d spacings of 0.25 and 0.60 nm, corresponding to the (011) and (001) facets of VS $_2$, respectively. The corresponding

ing approach to tuning the surface electronic structure of the catalysts to significantly enhance the catalytic activity. 31 By virtue of the unique 4f structure and rich redox capability, rare-earth lanthanides emerge as intriguing metal dopants to considerably improve the catalyst activities. $^{32-34}$ Nevertheless, the use of rare-earth metal dopants to tune the electronic structure and NO₃RR activity of the catalysts has not yet been explored.

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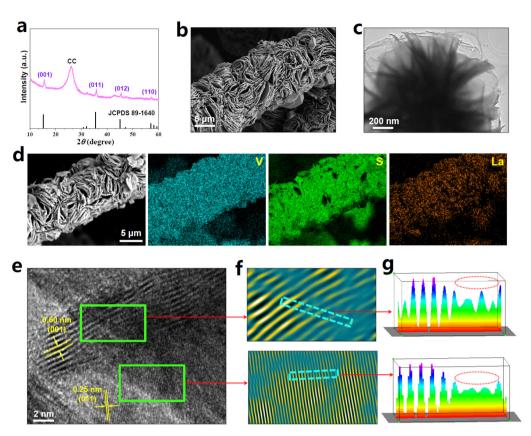


Fig. 1 (a) XRD pattern of La-VS_{2-x} on CC. (b) SEM image of La-VS_{2-x} on CC. (c) TEM image of La-VS_{2-x}. (d) Elemental mapping images of La-VS_{2-x} on CC. (e) HRTEM image of La-VS_{2-x} and (f) the corresponding IFFT pattern and (g) lattice line scanning analyses.

inverse fast Fourier transform (IFFT) pattern (Fig. 1f) and lattice line scanning analysis (Fig. 1g) signify the loss of some lattice atoms (dotted circles), indicating the presence of abundant defects/vacancies on La-VS_{2-x}. The elemental analysis further reveals a much reduced S/V molar ratio of 1.85 compared to the nominal ratio of VS₂ (2), demonstrating the V_S -rich nature of La- VS_{2-x} .

As shown in the electron paramagnetic resonance (EPR) spectrum (Fig. 2a), La-VS_{2-x} displays a much enhanced EPR signal compared to pristine VS2, further attesting to the existence of abundant V_S on La- VS_{2-x} . The X-ray absorption near-edge structure (XANES) spectra (Fig. 2b) show that the white line intensity of La-VS_{2-x} is lower than that of the La₂O₃ reference, suggesting that La-dopants carry a partially positive charge. 40 The extended X-ray absorption fine structure (EXAFS) spectra (Fig. 2c) show that La- VS_{2-x} presents a dominant peak at 2.16 Å, assigned to the La-S scattering path. Besides, no La-La (3.96 Å) scattering paths can be detected, confirming that La-dopants are atomically dispersed in La- VS_{2-x} . The evidence for the presence of atomically dispersed La-dopants in La- VS_{2-x} can be further proved by the wavelet transform (WT) plots (Fig. 2d), showing the absence of a La-La signal in La-VS_{2-x}. 41-43 The EXAFS fitting results (Fig. 2e, Table S1†) reveal that the La-S coordination is around 5, implying that Ladopants mainly substitute the five-fold coordinated V atoms of VS_{2-x} (Fig. 2f).

Theoretical calculations are carried out to examine the electronic structure of La-VS_{2-x}. The calculated La-dopant formation energy (E_{La} , Fig. S1†) reveals a much reduced E_{La} of $La-VS_{2-x}$ (1.94 eV) compared to V_S -free $La-VS_2$ (3.61 eV), suggesting that V_S plays a critical role in making the incorporation of La-dopants into VS_{2-x} lattices more thermodynamically feasible. 43,44 Electron contour maps reveal abundant electrons accumulated in the V_S region (Fig. S2 and S3†), while La-dopant affects little the electron accumulation nature of V_S in La-VS_{2-x} (Fig. 2g). These accumulated electrons are apt to be transferred to the antibonding orbital of NO₃ for the activation and dissociation of the N=O bond, 5,45 facilitating the boosted NO₃RR process. The partial densities of states (PDOS) plot of La-VS_{2-x} (Fig. S4†) reveals a significant La/S orbital hybridization, suggesting the strong La-S electronic interactions which allow La-dopants to be atomically dispersed and firmly stabilized in VS_{2-x}, resulting in the high thermodynamic stability of La-VS_{2-x} (Fig. S5 \dagger).⁴⁶ Furthermore, compared to VS2 and VS2-x, La-dopant incorporation makes La-VS_{2-x} exhibit the occupied electron states across the Fermi level (Fig. 2h) and reduced work function (Fig. S6†), thus endowing La- VS_{2-x} with enhanced conduc-

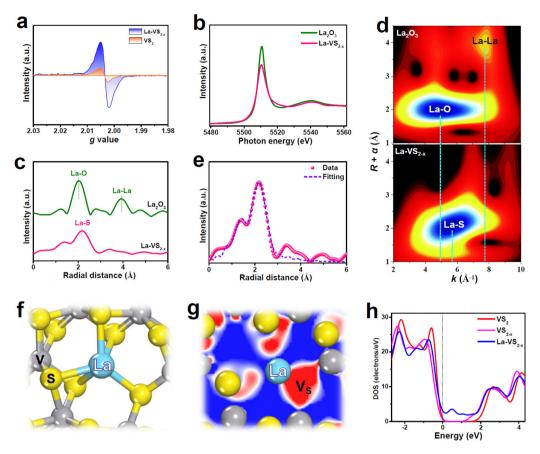


Fig. 2 (a) EPR spectra of VS₂ and La-VS_{2-x}. (b) La L₃-edge XANES, (c) EXAFS spectra and (d) WT profiles of La-VS_{2-x} and reference La₂O₃. (e) EXAFS fitting curve of La-VS_{2-x} and (f) the corresponding fitting model. (g) Electron contour map of La-VS_{2-x} (red: charge accumulation, blue: charge depletion). (h) DOS plots of VS_2 , VS_{2-x} and $La-VS_{2-x}$.

tivity to accelerate electron transfer and catalytic kinetics (Fig. S7†).47-51

The electrochemical NO₃RR activity of La-VS_{2-x} directly used as the working electrode is evaluated in an H-type cell on the basis of a standard procedure flow chart (Fig. S8†). 52-55 The electrolyte used is 0.5 M Na₂SO₄ with 0.1 M NaNO $_3$ (Fig. S9†). As displayed in Fig. 3a, La-VS $_{2-x}$ exhibits a much higher current density in the presence of NO₃, indicating that La- VS_{2-x} is catalytically effective towards the NO₃RR. The NH₃ yield rates and FE_{NH₂} of La-VS_{2-x} are then quantitatively estimated by the combination of chronoamperometric (Fig. S10†) and colorimetric approaches (Fig. S11-S13†). S13+). As shown in Fig. 3b, La-VS_{2-x} exhibits the highest FE_{NH}, of 96.6% at -0.6 V. The corresponding NH₃ yield rate and partial current density at -0.6 V are 11.3 mg h⁻¹ cm⁻² and 121.2 mA cm⁻² (Fig. S14†), respectively. Such NO₃RR performance of La-VS2-x exceeds that of most reported NO₃RR catalysts (Fig. 3c, Table S2†). We also investigate the effect of the La-dopant content on the NO₃RR performance of La-VS_{2-x} and determine that 4.8 wt% is the optimum Ladopant content (Fig. S15†). Meanwhile, FE_{NH}, is dramatically higher than the FEs of other byproducts shown in Fig. 3d,

demonstrating the exceptional selectivity of La-VS2-x for electrocatalytic NO₃-to-NH₃ conversion.

Several control tests are carried out to validate the NH3 origin. It is shown in Fig. S16† that NH3 is barely detected both in the NO₃-free electrolyte and at the open circuit potential (OCP). The N source is further confirmed by isotopic labeling ¹H nuclear magnetic resonance (NMR) spectroscopy (Fig. 3e). Visibly, upon using ¹⁴NO₃⁻ and ¹⁵NO₃⁻ tracing agents, the resulting NMR spectra show three characteristic signals of 14NH4+ and two signals of 15NH4+, respectively, proving that the detected NH₃ originates from the NO₃RR.⁶⁰⁻⁶² We further tested the catalytic stability of La- VS_{2-x} for the NO₃RR. Fig. 3f depicts no obvious decay in NH₃ yield rates and FE_{NH}, during ten consecutive NO₃RR cycles, indicating the good cycling durability of La-VS2-x. During the chronopotentiometric test for 20 h of continuous electrolysis (Fig. 3g), negligible variations in current density and corresponding FE_{HN3} can be observed, suggesting the outstanding long-term stability of La-VS_{2-x}. After the stability tests, La-VS_{2-x} reveals no obvious changes in the morphology, crystal phase and La content (Fig. S17†), confirming the robust structural and compositional stability of La-VS_{2-x}.

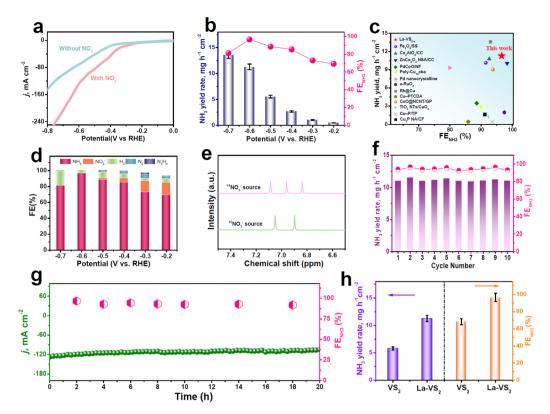


Fig. 3 (a) LSV curves of La-VS_{2-x} with and without the addition of 0.1 M NO₃⁻. (b) NH₃ yield rates and FE_{NH₂} of La-VS_{2-x} at various potentials. (c) NO₃RR performance comparison between La-VS_{2-x} and reported catalysts. (d) FEs of different products after NO₃RR electrolysis at various potentials. (e) 1 H NMR measurements fed by 14 NO $_{3}^{-}$ / 15 NO $_{3}^{-}$ after NO $_{3}$ RR electrolysis. (f) Cycling and (g) long-term chronoamperometry tests at -0.6 V. (h) Comparison of the NO_3RR performance between VS_2 and La- VS_{2-x} at -0.6 V.

We also evaluate the NO₃RR activity of pristine VS₂ under the same conditions at -0.6 V (Fig. 3h). Obviously, the NO₃RR performance of VS_{2-x} is considerably lower than that of La-VS_{2-x}, with FE_{NH}, and the corresponding NH₃ yield rate being 1.4 and 1.9 times poorer than those of La- VS_{2-x} , respectively, suggesting that La-dopants have a significant contribution to the NO₃RR activity of La-VS_{2-x}. We measured the electrochemical surface areas (ECSAs) of the two catalysts and found that the ECSA-normalized performance of La-VS_{2-x} is still considerably better than that of VS₂ (Fig. S18†), indicating the superior intrinsic NO₃RR activity of La-VS_{2-x}. The in-depth mechanistic understanding of the enhanced NO₃RR of La- VS_{2-x} is elucidated by theoretical investigations.

Since NO₃⁻ adsorption is a critical prerequisite for the NO₃RR,⁶³ we first examined NO₃ adsorption on various catalysts. As shown in Fig. S19,† in contrast to the negligible N=O bond elongation on pristine VS2, the N=O bond of the absorbed NO_3^- on the V_S site of VS_{2-x} is stretched to 1.305 Å, and it is further stretched to 1.365 Å on La-dopant-adjacent V_S site of La-VS_{2-x}, indicating that NO₃ can be significantly activated on La- VS_{2-x} . This is further corroborated by the differential charge density maps, showing that compared to the cases of VS_2 and VS_{2-x} (Fig. S20†), La- VS_{2-x} exhibits a more intense charge transfer with the adsorbed NO₃⁻ (Fig. 4a). The corresponding electron location function maps (Fig. 4b) reveal that both the Vs-induced unsaturated V atom and the La-dopant (or La-V_S site) synergistically donate electrons to the absorbed NO_3^{-35} resulting in effective NO_3^{-35} activation on La- VS_{2-x} . Benefitting from the enhanced NO3- activation on the La-VS site, La-VS_{2-x} shows a largely reduced binding free energy of NO_3 relative to VS_2 and VS_{2-x} (Fig. 4c), thus facilitating the subsequent NO₃RR process. Meanwhile, compared to the V_S site of VS_{2-x}, the La-V_S site of La-VS_{2-x} exhibits a more energy requirement for H_2 evolution (Fig. 4d), and thus La-VS_{2-x} can effectively impede the HER to benefit NO₃RR selectivity.⁵⁶

The free energy changes of NO₃RR pathways of all considered VS_2 , VS_{2-x} and La- VS_{2-x} catalysts are further assessed, with their corresponding atom configurations being displayed in Fig. S21-S23.† It is known that the electrocatalytic NO₃RR process for NH3 formation comprises the initial deoxidation steps of *NO₃ → *NO₂ → *NO and the following hydrogenation steps of *NOH \rightarrow *N \rightarrow *NH \rightarrow *NH₂ \rightarrow *NH₃.⁶⁴⁻⁶⁶ As shown in Fig. 4e, in comparison with VS_2 and VS_{2-x} , La- VS_{2-x} shows the lowest energy barrier of -0.63 eV for its rate-determining step (RDS) of *NO \rightarrow *NOH, suggesting its favorable energetics to boost the NO₃RR process. Therefore, the co-introduction of V_S and La-dopants can synergistically promote NO₃⁻ activation, retard the HER and lower the reaction energetic barriers, thereby greatly promoting the NO₃RR activity and selectivity of La- VS_{2-x} for NO_3 -to- NH_3 conversion.

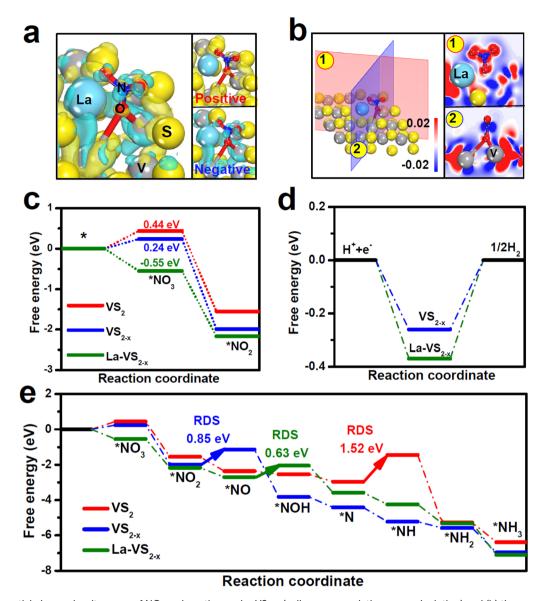


Fig. 4 (a) Differential charge density maps of NO₃⁻ adsorption on La-VS_{2-x} (yellow: accumulation, cyan: depletion) and (b) the corresponding electron location function maps (red: accumulation, blue: depletion). (c and d) Binding free energies of (c) NO₃⁻ and (d) H on different catalysts. (e) Gibbs free energy diagrams of the NO_3RR pathway of VS_2 , VS_{2-x} and $La-VS_{2-x}$, respectively.

3. Conclusion

Research Article

In summary, La- VS_{2-x} is verified to be a highly active and selective NO₃RR catalyst. Theoretical computations reveal that the excellent NO₃RR performance of La-VS_{2-x} originates from the synergy of La-dopants and V_S to promote NO₃⁻ activation, suppress the HER and lower the energetic barriers. This work demonstrates the great potential of rare earth catalysts toward the efficient NO₃RR for NH₃ electrosynthesis.

Conflicts of interest

There are no conflicts of interest to declare.

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