INORGANIC CHEMISTRY
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RESEARCH ARTICLE

View Article Online
View Journal | View Issue

Cite this: *Inorg. Chem. Front.*, 2023, **10**, 2014

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

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Received 29th December 2022,
Accepted 13th February 2023

DOI: 10.1039/d2qi02757g

rsc.li/frontiers-inorganic

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_3RR), 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_3RR activity and selectivity of La-VS_{2-x}.

1. Introduction

NH_3, a value-added chemical and also a renewable hydrogen-rich carrier, is vital to modern agriculture and industry.[1–3] Electrochemical nitrate reduction to ammonia (NO_3RR) represents a fascinating approach to realising both green NH_3 generation and wastewater purification.[4–6] However, 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 NO_3RR electrocatalysts for active and selective NO_3^--to-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 promising 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 NO_3RR activity of the catalysts has not yet been explored.

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 *vs.* 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

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† Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d2qi02757g**

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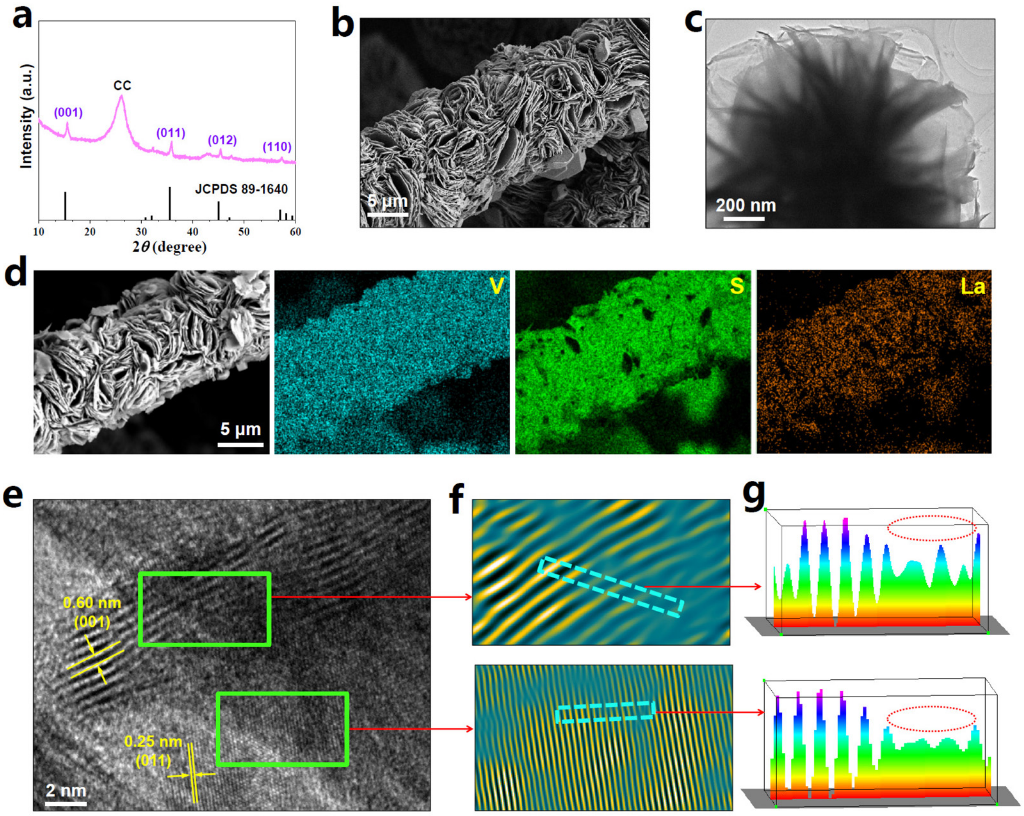

Fig. 1 (a) XRD pattern of La-VS_{2-x} on CC. (b) SEM image of La-VS_{2-x} on CC. (c) TEM image of La-VS_{2-x}. (d) Elemental mapping images of La-VS_{2-x} on CC. (e) HRTEM image of La-VS_{2-x} and (f) the corresponding IFFT pattern and (g) lattice line scanning analyses.

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}.[35] The elemental analysis further reveals a much reduced S/V molar ratio of 1.85 compared to the nominal ratio of VS_2 (2), demonstrating the V_S-rich nature of La-VS_{2-x}.[36]

As shown in the electron paramagnetic resonance (EPR) spectrum (Fig. 2a), La-VS_{2-x} displays a much enhanced EPR signal compared to pristine VS_2, further attesting to the existence of abundant V_S on La-VS_{2-x}.[36–39] 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 La_2O_3 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 La-dopants 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 NO_3^- for the activation and dissociation of the N=O bond,[5,45] facilitating the boosted NO_3RR 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†).[46] Furthermore, compared to VS_2 and VS_{2-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-

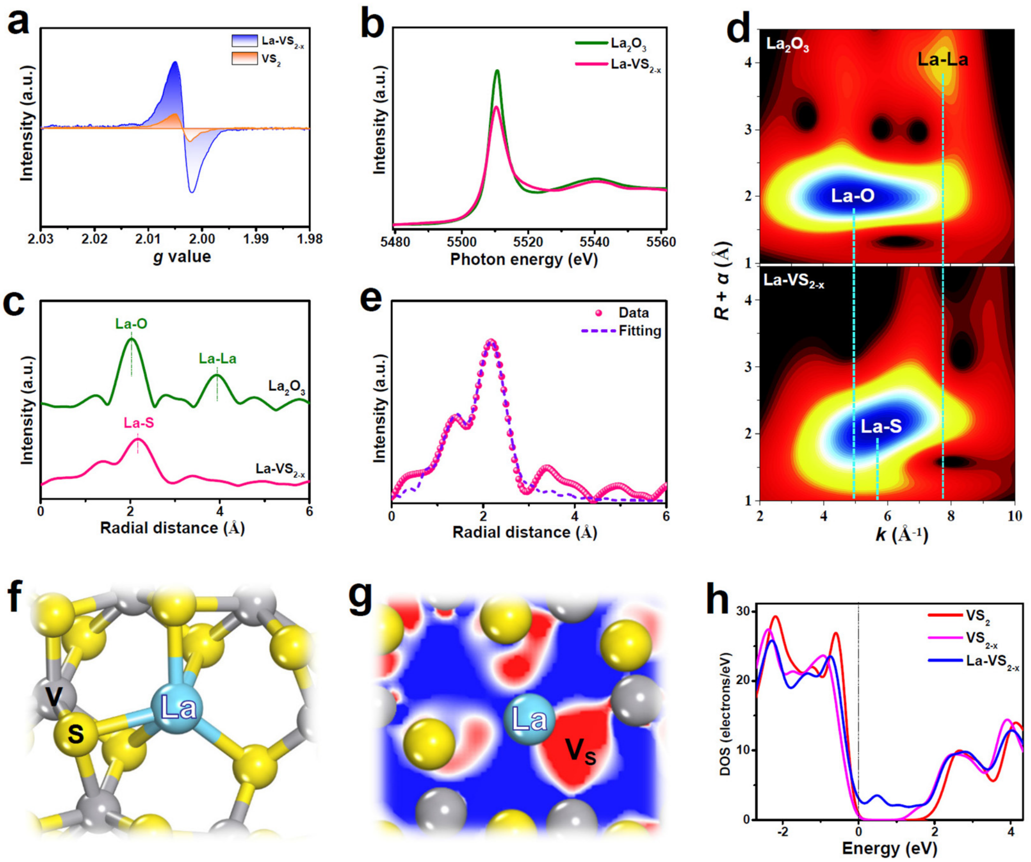

Fig. 2 (a) EPR spectra of VS_2 and La-VS_{2-x}. (b) La L_3-edge XANES, (c) EXAFS spectra and (d) WT profiles of La-VS_{2-x} and reference La_2O_3. (e) EXAFS fitting curve of La-VS_{2-x} and (f) the corresponding fitting model. (g) Electron contour map of La-VS_{2-x} (red: charge accumulation, blue: charge 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 NO_3RR 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 Na_2SO_4 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 NO_3^-, indicating that La-VS_{2-x} is catalytically effective towards the NO_3RR. The NH_3 yield rates and FE_{NH_3} of La-VS_{2-x} are then quantitatively estimated by the combination of chronoamperometric (Fig. S10†) and colorimetric approaches (Fig. S11–S13†).[56–59] As shown in Fig. 3b, La-VS_{2-x} exhibits the highest FE_{NH_3} of 96.6% at −0.6 V. The corresponding NH_3 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 NO_3RR performance of La-VS_{2-x} exceeds that of most reported NO_3RR catalysts (Fig. 3c, Table S2†). We also investigate the effect of the La-dopant content on the NO_3RR performance of La-VS_{2-x} and determine that 4.8 wt% is the optimum La-dopant content (Fig. S15†). Meanwhile, FE_{NH_3} is dramatically higher than the FEs of other byproducts shown in Fig. 3d, demonstrating the exceptional selectivity of La-VS_{2-x} for electrocatalytic NO_3^--to-NH_3 conversion.

Several control tests are carried out to validate the NH_3 origin. It is shown in Fig. S16† that NH_3 is barely detected both in the NO_3^--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 $^{14}NO_3^-$ and $^{15}NO_3^-$ tracing agents, the resulting NMR spectra show three characteristic signals of $^{14}NH_4^+$ and two signals of $^{15}NH_4^+$, respectively, proving that the detected NH_3 originates from the NO_3RR.[60–62] We further tested the catalytic stability of La-VS_{2-x} for the NO_3RR. Fig. 3f depicts no obvious decay in NH_3 yield rates and FE_{NH_3} during ten consecutive NO_3RR cycles, indicating the good cycling durability of La-VS_{2-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}.

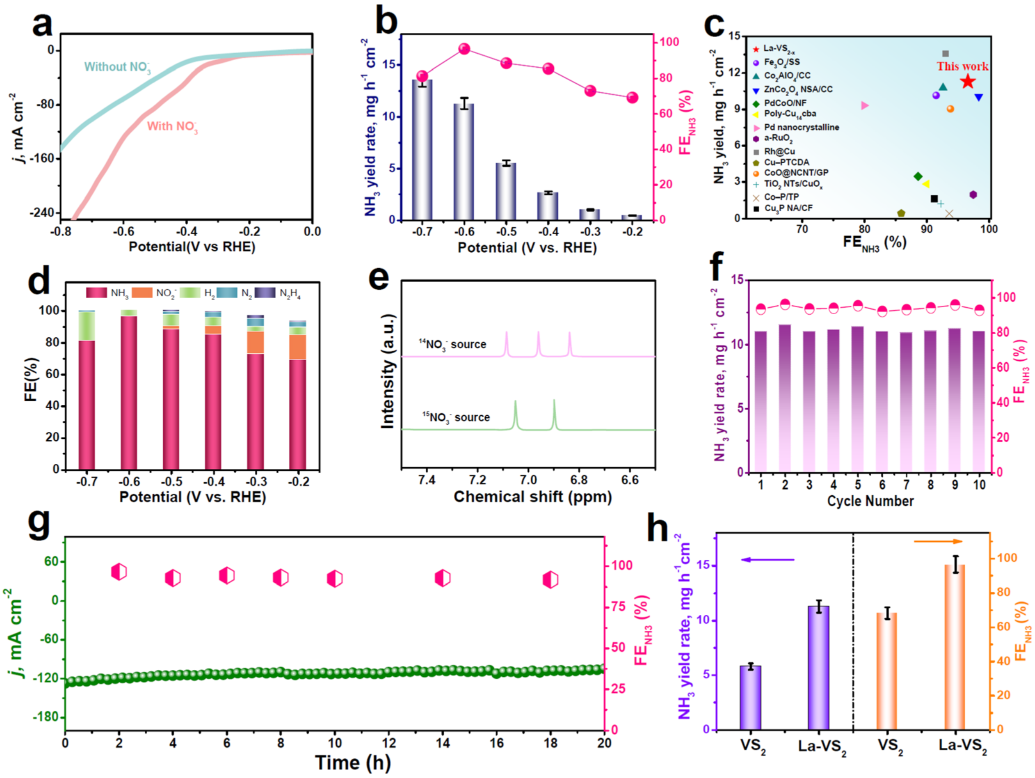

Fig. 3 (a) LSV curves of La-VS_{2-x} with and without the addition of 0.1 M NO_3^-. (b) NH_3 yield rates and FE_{NH_3} of La-VS_{2-x} at various potentials. (c) NO_3RR performance comparison between La-VS_{2-x} and reported catalysts. (d) FEs of different products after NO_3RR electrolysis at various potentials. (e) ^{1}H NMR measurements fed by $^{14}NO_3^-/^{15}NO_3^-$ after NO_3RR 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 NO_3RR activity of pristine VS_2 under the same conditions at −0.6 V (Fig. 3h). Obviously, the NO_3RR performance of VS_{2-x} is considerably lower than that of La-VS_{2-x}, with FE_{NH_3} and the corresponding NH_3 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 NO_3RR 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 VS_2 (Fig. S18†), indicating the superior intrinsic NO_3RR activity of La-VS_{2-x}. The in-depth mechanistic understanding of the enhanced NO_3RR of La-VS_{2-x} is elucidated by theoretical investigations.

Since NO_3^- adsorption is a critical prerequisite for the NO_3RR,[63] we first examined NO_3^- adsorption on various catalysts. As shown in Fig. S19,† in contrast to the negligible N═O bond elongation on pristine VS_2, 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 NO_3^- 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 NO_3^- (Fig. 4a). The corresponding electron location function maps (Fig. 4b) reveal that both the V_S-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^- activation on La-VS_{2-x}. Benefitting from the enhanced NO_3^- activation on the La-V_S 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 NO_3RR 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 NO_3RR selectivity.[56]

The free energy changes of NO_3RR 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 NO_3RR process for NH_3 formation comprises the initial deoxidation steps of $^*NO_3 \rightarrow {}^*NO_2 \rightarrow {}^*NO$ and the following hydrogenation steps of $^*NOH \rightarrow {}^*N \rightarrow {}^*NH \rightarrow {}^*NH_2 \rightarrow {}^*NH_3$.[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 NO_3RR process. Therefore, the co-introduction of V_S and La-dopants can synergistically promote NO_3^- activation, retard the HER and lower the reaction energetic barriers, thereby greatly promoting the NO_3RR activity and selectivity of La-VS_{2-x} for NO_3^--to-NH_3 conversion.

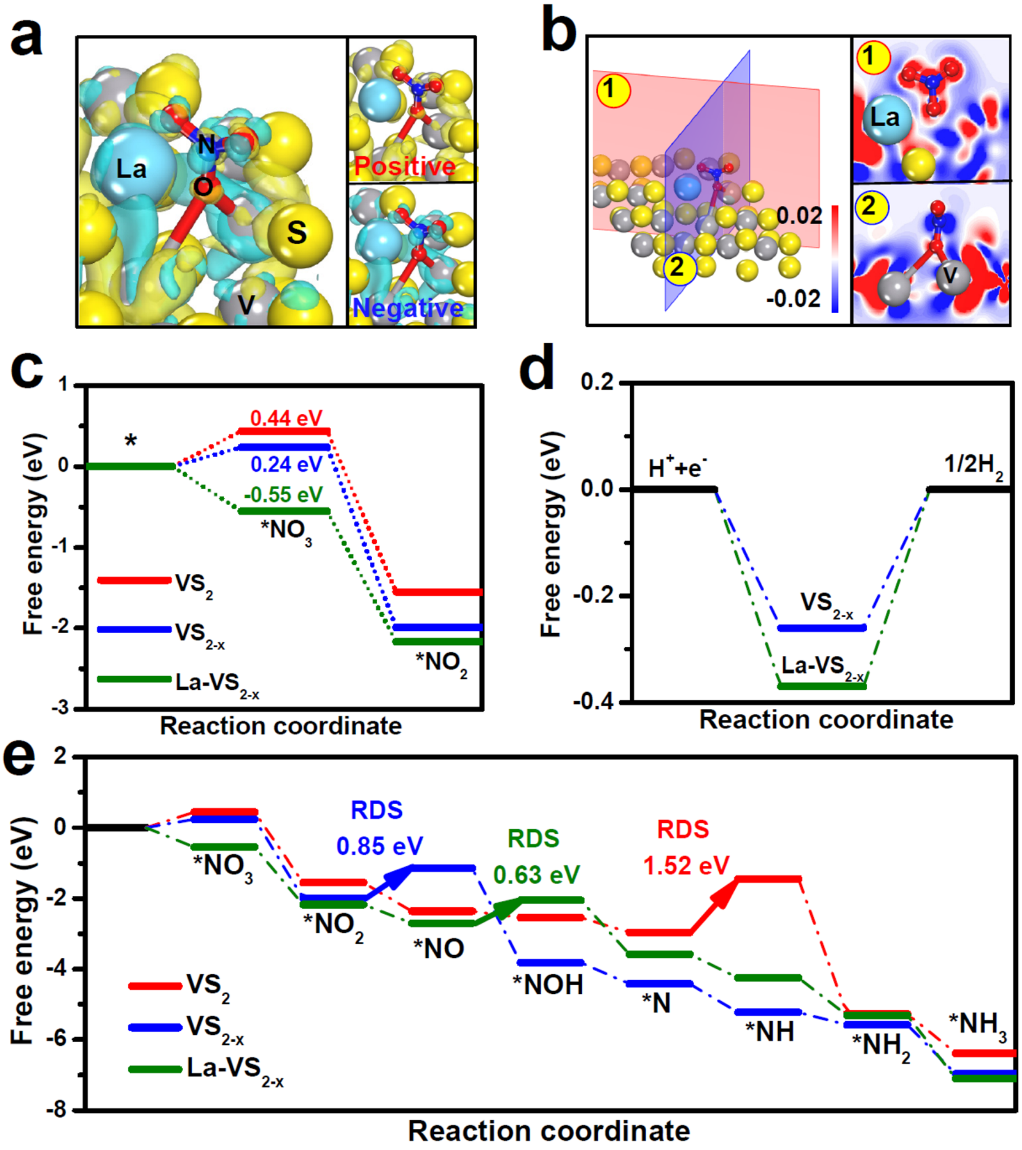

Fig. 4 (a) Differential charge density maps of NO_3^- adsorption on La-VS_{2-x} (yellow: accumulation, cyan: depletion) and (b) the corresponding electron location function maps (red: accumulation, blue: depletion). (c and d) Binding free energies of (c) NO_3^- and (d) H on different catalysts. (e) Gibbs free energy diagrams of the NO_3RR pathway of VS_2, VS_{2-x} and La-VS_{2-x}, respectively.

3. Conclusion

In summary, La-VS_{2-x} is verified to be a highly active and selective NO_3RR catalyst. Theoretical computations reveal that the excellent NO_3RR performance of La-VS_{2-x} originates from the synergy of La-dopants and V_S to promote NO_3^- activation, suppress the HER and lower the energetic barriers. This work demonstrates the great potential of rare earth catalysts toward the efficient NO_3RR for NH_3 electrosynthesis.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

This work was supported by the Central Government Guides Local Science and Technology Development Project (206Z1003G) and the Longyuan Youth Innovative and Entrepreneurial Talents Project ([2021]17).

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