

## RESEARCH ARTICLE

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# Rare-earth La-doped VS<sub>2-x</sub> for electrochemical nitrate reduction to ammonia†

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We report rare-earth La-doped VS<sub>2-x</sub> enriched with S-vacancies (La-VS<sub>2-x</sub>) towards the electrochemical nitrate reduction to ammonia (NO<sub>3</sub>RR), which shows a maximum NH<sub>3</sub>-faradaic efficiency of 96.6% with a corresponding NH<sub>3</sub> yield rate of 11.3 mg h<sup>-1</sup> cm<sup>-2</sup> at -0.6 V vs. RHE. Theoretical computations unveil that La-dopants and S-vacancies synergistically promote NO<sub>3</sub><sup>-</sup> activation, suppress hydrogen evolution and lower the energetic barriers, leading to the enhanced NO<sub>3</sub>RR activity and selectivity of La-VS<sub>2-x</sub>.

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## 1. Introduction

NH<sub>3</sub>, a value-added chemical and also a renewable hydrogen-rich carrier, is vital to modern agriculture and industry.<sup>1-3</sup> Electrochemical nitrate reduction to ammonia (NO<sub>3</sub>RR) represents a fascinating approach to realising both green NH<sub>3</sub> generation and wastewater purification.<sup>4-6</sup> However, NO<sub>3</sub>RR 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).<sup>7-9</sup> Therefore, it is urgently required to explore effective NO<sub>3</sub>RR electrocatalysts for active and selective NO<sub>3</sub><sup>-</sup>-to-NH<sub>3</sub> conversion.<sup>10-14</sup>

To date, substantial efforts have been devoted to exploring many potential NO<sub>3</sub>RR catalysts.<sup>15-25</sup> Metal chalcogenides have attracted wide attention in electrolysis due to their layered structure and high electrochemical stability.<sup>26-28</sup> Among them, VS<sub>2</sub> is most appealing due to its metallic nature with high conductivity, facilitating accelerated electron transfer for boosting the catalytic kinetics.<sup>29,30</sup> Nevertheless, investigations on VS<sub>2</sub>-based catalysts for the NO<sub>3</sub>RR remain largely unexplored due presumably to the poor intrinsic activity of VS<sub>2</sub> for NO<sub>3</sub><sup>-</sup> activation. Metal doping is a promis-

ing approach to tuning the surface electronic structure of the catalysts to significantly enhance the catalytic activity.<sup>31</sup> 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.<sup>32-34</sup> Nevertheless, the use of rare-earth metal dopants to tune the electronic structure and NO<sub>3</sub>RR activity of the catalysts has not yet been explored.

In this study, we report a rare-earth La-doped VS<sub>2-x</sub> (La-VS<sub>2-x</sub>) enriched with S-vacancies (V<sub>s</sub>) towards the NO<sub>3</sub>RR. La-VS<sub>2-x</sub> delivers excellent NO<sub>3</sub>RR performance with a highest NH<sub>3</sub>-faradaic efficiency (FE<sub>NH<sub>3</sub></sub>) of 96.6% with the corresponding NH<sub>3</sub> yield of 11.3 mg h<sup>-1</sup> cm<sup>-2</sup> at -0.6 V vs. RHE. Detailed experiments combined with theoretical investigations are employed to unravel the catalytic NO<sub>3</sub>RR mechanism of La-VS<sub>2-x</sub>.

## 2. Results and discussion

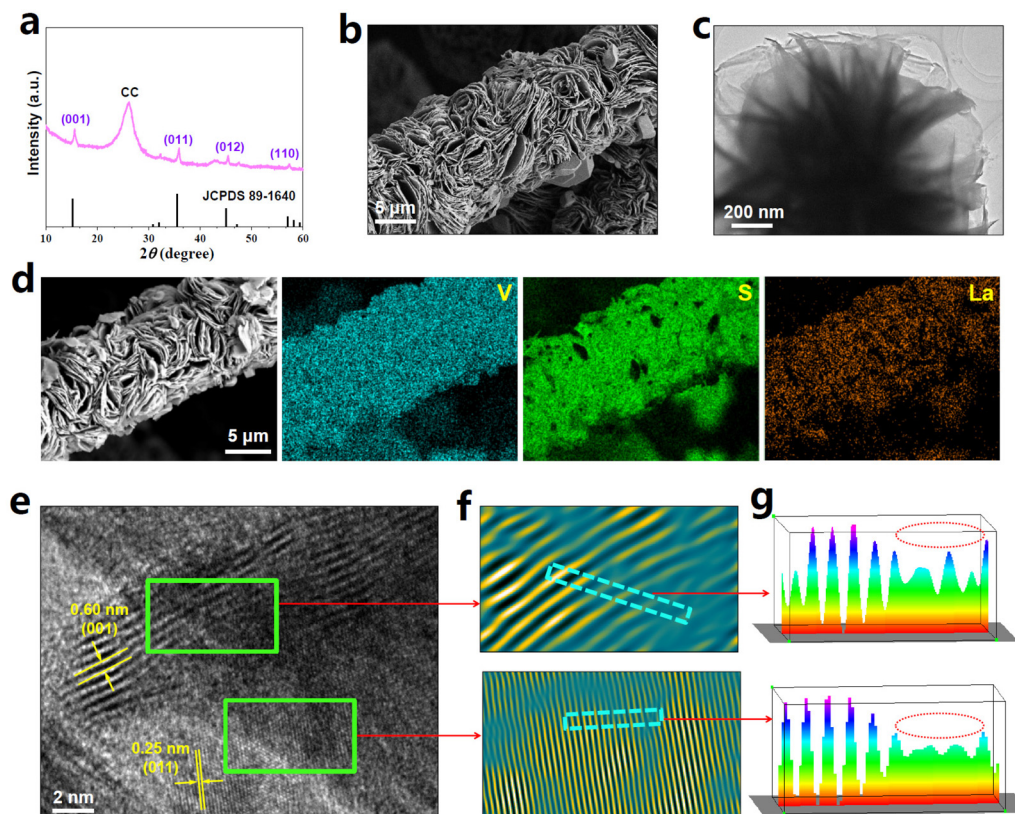
La-VS<sub>2-x</sub> (4.8 wt% La) grown on carbon cloth (CC) was fabricated using a simple hydrothermal approach. The XRD pattern of La-VS<sub>2-x</sub> (Fig. 1a) shows major diffraction peaks assigned to the hexagonal VS<sub>2</sub> phase (JCPDS No. 89-1640). The SEM image of La-VS<sub>2-x</sub> (Fig.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

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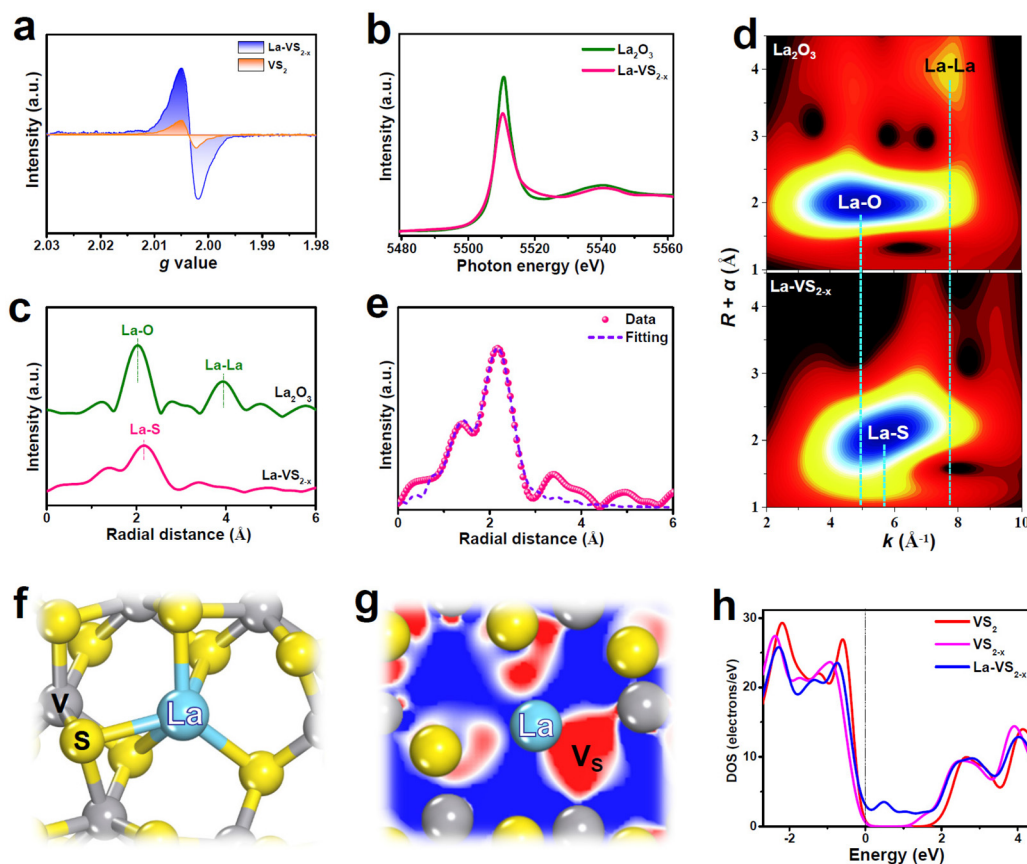
**Fig. 1** (a) XRD pattern of La- $\text{VS}_{2-x}$  on CC. (b) SEM image of La- $\text{VS}_{2-x}$  on CC. (c) TEM image of La- $\text{VS}_{2-x}$ . (d) Elemental mapping images of La- $\text{VS}_{2-x}$  on CC. (e) HRTEM image of La- $\text{VS}_{2-x}$  and (f) the corresponding IFFT pattern and (g) lattice 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- $\text{VS}_{2-x}$ .<sup>35</sup> The elemental analysis further reveals a much reduced S/V molar ratio of 1.85 compared to the nominal ratio of  $\text{VS}_2$  (2), demonstrating the  $\text{V}_\text{S}$ -rich nature of La- $\text{VS}_{2-x}$ .<sup>36</sup>

As shown in the electron paramagnetic resonance (EPR) spectrum (Fig. 2a), La- $\text{VS}_{2-x}$  displays a much enhanced EPR signal compared to pristine  $\text{VS}_2$ , further attesting to the existence of abundant  $\text{V}_\text{S}$  on La- $\text{VS}_{2-x}$ .<sup>36–39</sup> The X-ray absorption near-edge structure (XANES) spectra (Fig. 2b) show that the white line intensity of La- $\text{VS}_{2-x}$  is lower than that of the  $\text{La}_2\text{O}_3$  reference, suggesting that La-dopants carry a partially positive charge.<sup>40</sup> The extended X-ray absorption fine structure (EXAFS) spectra (Fig. 2c) show that La- $\text{VS}_{2-x}$  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- $\text{VS}_{2-x}$ . The evidence for the presence of atomically dispersed La-dopants in La- $\text{VS}_{2-x}$  can be further proved by the wavelet transform (WT) plots (Fig. 2d), showing the absence of a La-La signal in La- $\text{VS}_{2-x}$ .<sup>41–43</sup> 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  $\text{VS}_{2-x}$  (Fig. 2f).

Theoretical calculations are carried out to examine the electronic structure of La- $\text{VS}_{2-x}$ . The calculated La-dopant formation energy ( $E_{\text{La}}$ , Fig. S1†) reveals a much reduced  $E_{\text{La}}$  of La- $\text{VS}_{2-x}$  (1.94 eV) compared to  $\text{V}_\text{S}$ -free La- $\text{VS}_2$  (3.61 eV), suggesting that  $\text{V}_\text{S}$  plays a critical role in making the incorporation of La-dopants into  $\text{VS}_{2-x}$  lattices more thermodynamically feasible.<sup>43,44</sup> Electron contour maps reveal abundant electrons accumulated in the  $\text{V}_\text{S}$  region (Fig. S2 and S3†), while La-dopant affects little the electron accumulation nature of  $\text{V}_\text{S}$  in La- $\text{VS}_{2-x}$  (Fig. 2g). These accumulated electrons are apt to be transferred to the antibonding orbital of  $\text{NO}_3^-$  for the activation and dissociation of the N=O bond,<sup>5,45</sup> facilitating the boosted  $\text{NO}_3\text{RR}$  process. The partial densities of states (PDOS) plot of La- $\text{VS}_{2-x}$  (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  $\text{VS}_{2-x}$ , resulting in the high thermodynamic stability of La- $\text{VS}_{2-x}$  (Fig. S5†).<sup>46</sup> Furthermore, compared to  $\text{VS}_2$  and  $\text{VS}_{2-x}$ , La-dopant incorporation makes La- $\text{VS}_{2-x}$  exhibit the occupied electron states across the Fermi level (Fig. 2h) and reduced work function (Fig. S6†), thus endowing La- $\text{VS}_{2-x}$  with enhanced conduc-



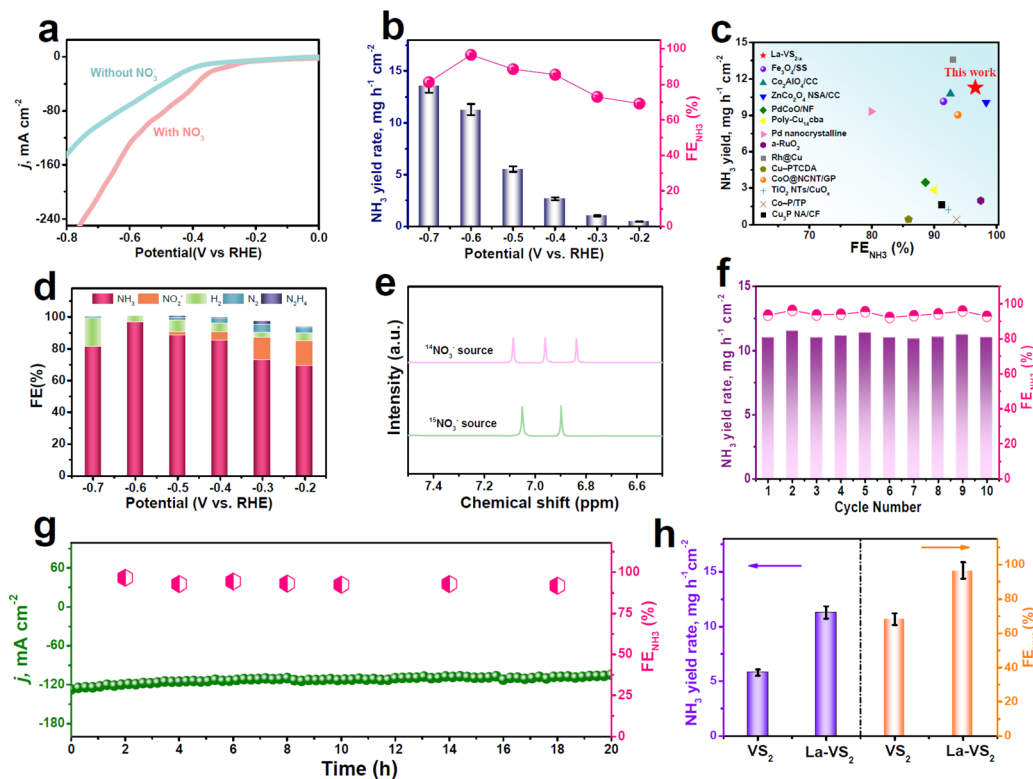
**Fig. 2** (a) EPR spectra of  $\text{VS}_2$  and  $\text{La-VS}_{2-x}$ . (b)  $\text{La L}_3$ -edge XANES, (c) EXAFS spectra and (d) WT profiles of  $\text{La-VS}_{2-x}$  and reference  $\text{La}_2\text{O}_3$ . (e) EXAFS fitting curve of  $\text{La-VS}_{2-x}$  and (f) the corresponding fitting model. (g) Electron contour map of  $\text{La-VS}_{2-x}$  (red: charge accumulation, blue: charge depletion). (h) DOS plots of  $\text{VS}_2$ ,  $\text{VS}_{2-x}$  and  $\text{La-VS}_{2-x}$ .

tivity to accelerate electron transfer and catalytic kinetics (Fig. S7†).<sup>47–51</sup>

The electrochemical  $\text{NO}_3\text{RR}$  activity of  $\text{La-VS}_{2-x}$  directly used as the working electrode is evaluated in an H-type cell on the basis of a standard procedure flow chart (Fig. S8†).<sup>52–55</sup> The electrolyte used is 0.5 M  $\text{Na}_2\text{SO}_4$  with 0.1 M  $\text{NaNO}_3$  (Fig. S9†). As displayed in Fig. 3a,  $\text{La-VS}_{2-x}$  exhibits a much higher current density in the presence of  $\text{NO}_3^-$ , indicating that  $\text{La-VS}_{2-x}$  is catalytically effective towards the  $\text{NO}_3\text{RR}$ . The  $\text{NH}_3$  yield rates and  $\text{FE}_{\text{NH}_3}$  of  $\text{La-VS}_{2-x}$  are then quantitatively estimated by the combination of chronoamperometric (Fig. S10†) and colorimetric approaches (Fig. S11–S13†).<sup>56–59</sup> As shown in Fig. 3b,  $\text{La-VS}_{2-x}$  exhibits the highest  $\text{FE}_{\text{NH}_3}$  of 96.6% at  $-0.6$  V. The corresponding  $\text{NH}_3$  yield rate and partial current density at  $-0.6$  V are  $11.3 \text{ mg h}^{-1} \text{ cm}^{-2}$  and  $121.2 \text{ mA cm}^{-2}$  (Fig. S14†), respectively. Such  $\text{NO}_3\text{RR}$  performance of  $\text{La-VS}_{2-x}$  exceeds that of most reported  $\text{NO}_3\text{RR}$  catalysts (Fig. 3c, Table S2†). We also investigate the effect of the La-dopant content on the  $\text{NO}_3\text{RR}$  performance of  $\text{La-VS}_{2-x}$  and determine that 4.8 wt% is the optimum La-dopant content (Fig. S15†). Meanwhile,  $\text{FE}_{\text{NH}_3}$  is dramatically higher than the FEs of other byproducts shown in Fig. 3d,

demonstrating the exceptional selectivity of  $\text{La-VS}_{2-x}$  for electrocatalytic  $\text{NO}_3^-$ -to- $\text{NH}_3$  conversion.

Several control tests are carried out to validate the  $\text{NH}_3$  origin. It is shown in Fig. S16† that  $\text{NH}_3$  is barely detected both in the  $\text{NO}_3^-$ -free electrolyte and at the open circuit potential (OCP). The N source is further confirmed by isotopic labeling  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy (Fig. 3e). Visibly, upon using  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  tracing agents, the resulting NMR spectra show three characteristic signals of  $^{14}\text{NH}_4^+$  and two signals of  $^{15}\text{NH}_4^+$ , respectively, proving that the detected  $\text{NH}_3$  originates from the  $\text{NO}_3\text{RR}$ .<sup>60–62</sup> We further tested the catalytic stability of  $\text{La-VS}_{2-x}$  for the  $\text{NO}_3\text{RR}$ . Fig. 3f depicts no obvious decay in  $\text{NH}_3$  yield rates and  $\text{FE}_{\text{NH}_3}$  during ten consecutive  $\text{NO}_3\text{RR}$  cycles, indicating the good cycling durability of  $\text{La-VS}_{2-x}$ . During the chronopotentiometric test for 20 h of continuous electrolysis (Fig. 3g), negligible variations in current density and corresponding  $\text{FE}_{\text{NH}_3}$  can be observed, suggesting the outstanding long-term stability of  $\text{La-VS}_{2-x}$ . After the stability tests,  $\text{La-VS}_{2-x}$  reveals no obvious changes in the morphology, crystal phase and La content (Fig. S17†), confirming the robust structural and compositional stability of  $\text{La-VS}_{2-x}$ .



**Fig. 3** (a) LSV curves of La- $\text{VS}_{2-x}$  with and without the addition of 0.1 M  $\text{NO}_3^-$ . (b)  $\text{NH}_3$  yield rates and  $\text{FE}_{\text{NH}_3}$  of La- $\text{VS}_{2-x}$  at various potentials. (c)  $\text{NO}_3\text{RR}$  performance comparison between La- $\text{VS}_{2-x}$  and reported catalysts. (d) FEs of different products after  $\text{NO}_3\text{RR}$  electrolysis at various potentials. (e)  $^1\text{H}$  NMR measurements fed by  $^{14}\text{NO}_3^-/^{15}\text{NO}_3^-$  after  $\text{NO}_3\text{RR}$  electrolysis. (f) Cycling and (g) long-term chronoamperometry tests at  $-0.6$  V. (h) Comparison of the  $\text{NO}_3\text{RR}$  performance between  $\text{VS}_2$  and La- $\text{VS}_{2-x}$  at  $-0.6$  V.

We also evaluate the  $\text{NO}_3\text{RR}$  activity of pristine  $\text{VS}_2$  under the same conditions at  $-0.6$  V (Fig. 3h). Obviously, the  $\text{NO}_3\text{RR}$  performance of  $\text{VS}_{2-x}$  is considerably lower than that of La- $\text{VS}_{2-x}$ , with  $\text{FE}_{\text{NH}_3}$  and the corresponding  $\text{NH}_3$  yield rate being 1.4 and 1.9 times poorer than those of La- $\text{VS}_{2-x}$ , respectively, suggesting that La-dopants have a significant contribution to the  $\text{NO}_3\text{RR}$  activity of La- $\text{VS}_{2-x}$ . We measured the electrochemical surface areas (ECSAs) of the two catalysts and found that the ECSA-normalized performance of La- $\text{VS}_{2-x}$  is still considerably better than that of  $\text{VS}_2$  (Fig. S18<sup>†</sup>), indicating the superior intrinsic  $\text{NO}_3\text{RR}$  activity of La- $\text{VS}_{2-x}$ . The in-depth mechanistic understanding of the enhanced  $\text{NO}_3\text{RR}$  of La- $\text{VS}_{2-x}$  is elucidated by theoretical investigations.

Since  $\text{NO}_3^-$  adsorption is a critical prerequisite for the  $\text{NO}_3\text{RR}$ ,<sup>63</sup> we first examined  $\text{NO}_3^-$  adsorption on various catalysts. As shown in Fig. S19,<sup>†</sup> in contrast to the negligible N=O bond elongation on pristine  $\text{VS}_2$ , the N=O bond of the adsorbed  $\text{NO}_3^-$  on the  $\text{V}_s$  site of  $\text{VS}_{2-x}$  is stretched to 1.305 Å, and it is further stretched to 1.365 Å on La-dopant-adjacent  $\text{V}_s$  site of La- $\text{VS}_{2-x}$ , indicating that  $\text{NO}_3^-$  can be significantly activated on La- $\text{VS}_{2-x}$ . This is further corroborated by the differential charge density maps, showing that compared to the cases of  $\text{VS}_2$  and  $\text{VS}_{2-x}$  (Fig. S20<sup>†</sup>), La- $\text{VS}_{2-x}$  exhibits a more intense charge transfer with the adsorbed  $\text{NO}_3^-$  (Fig. 4a). The corresponding electron location function maps (Fig. 4b) reveal that

both the  $\text{V}_s$ -induced unsaturated V atom and the La-dopant (or La- $\text{V}_s$  site) synergistically donate electrons to the adsorbed  $\text{NO}_3^-$ ,<sup>35</sup> resulting in effective  $\text{NO}_3^-$  activation on La- $\text{VS}_{2-x}$ . Benefitting from the enhanced  $\text{NO}_3^-$  activation on the La- $\text{V}_s$  site, La- $\text{VS}_{2-x}$  shows a largely reduced binding free energy of  $\text{NO}_3^-$  relative to  $\text{VS}_2$  and  $\text{VS}_{2-x}$  (Fig. 4c), thus facilitating the subsequent  $\text{NO}_3\text{RR}$  process. Meanwhile, compared to the  $\text{V}_s$  site of  $\text{VS}_{2-x}$ , the La- $\text{V}_s$  site of La- $\text{VS}_{2-x}$  exhibits a more energy requirement for  $\text{H}_2$  evolution (Fig. 4d), and thus La- $\text{VS}_{2-x}$  can effectively impede the HER to benefit  $\text{NO}_3\text{RR}$  selectivity.<sup>56</sup>

The free energy changes of  $\text{NO}_3\text{RR}$  pathways of all considered  $\text{VS}_2$ ,  $\text{VS}_{2-x}$  and La- $\text{VS}_{2-x}$  catalysts are further assessed, with their corresponding atom configurations being displayed in Fig. S21–S23.<sup>†</sup> It is known that the electrocatalytic  $\text{NO}_3\text{RR}$  process for  $\text{NH}_3$  formation comprises the initial deoxidation steps of  $^*\text{NO}_3 \rightarrow ^*\text{NO}_2 \rightarrow ^*\text{NO}$  and the following hydrogenation steps of  $^*\text{NOH} \rightarrow ^*\text{N} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$ .<sup>64–66</sup> As shown in Fig. 4e, in comparison with  $\text{VS}_2$  and  $\text{VS}_{2-x}$ , La- $\text{VS}_{2-x}$  shows the lowest energy barrier of  $-0.63$  eV for its rate-determining step (RDS) of  $^*\text{NO} \rightarrow ^*\text{NOH}$ , suggesting its favorable energetics to boost the  $\text{NO}_3\text{RR}$  process. Therefore, the co-introduction of  $\text{V}_s$  and La-dopants can synergistically promote  $\text{NO}_3^-$  activation, retard the HER and lower the reaction energetic barriers, thereby greatly promoting the  $\text{NO}_3\text{RR}$  activity and selectivity of La- $\text{VS}_{2-x}$  for  $\text{NO}_3^-$ -to- $\text{NH}_3$  conversion.



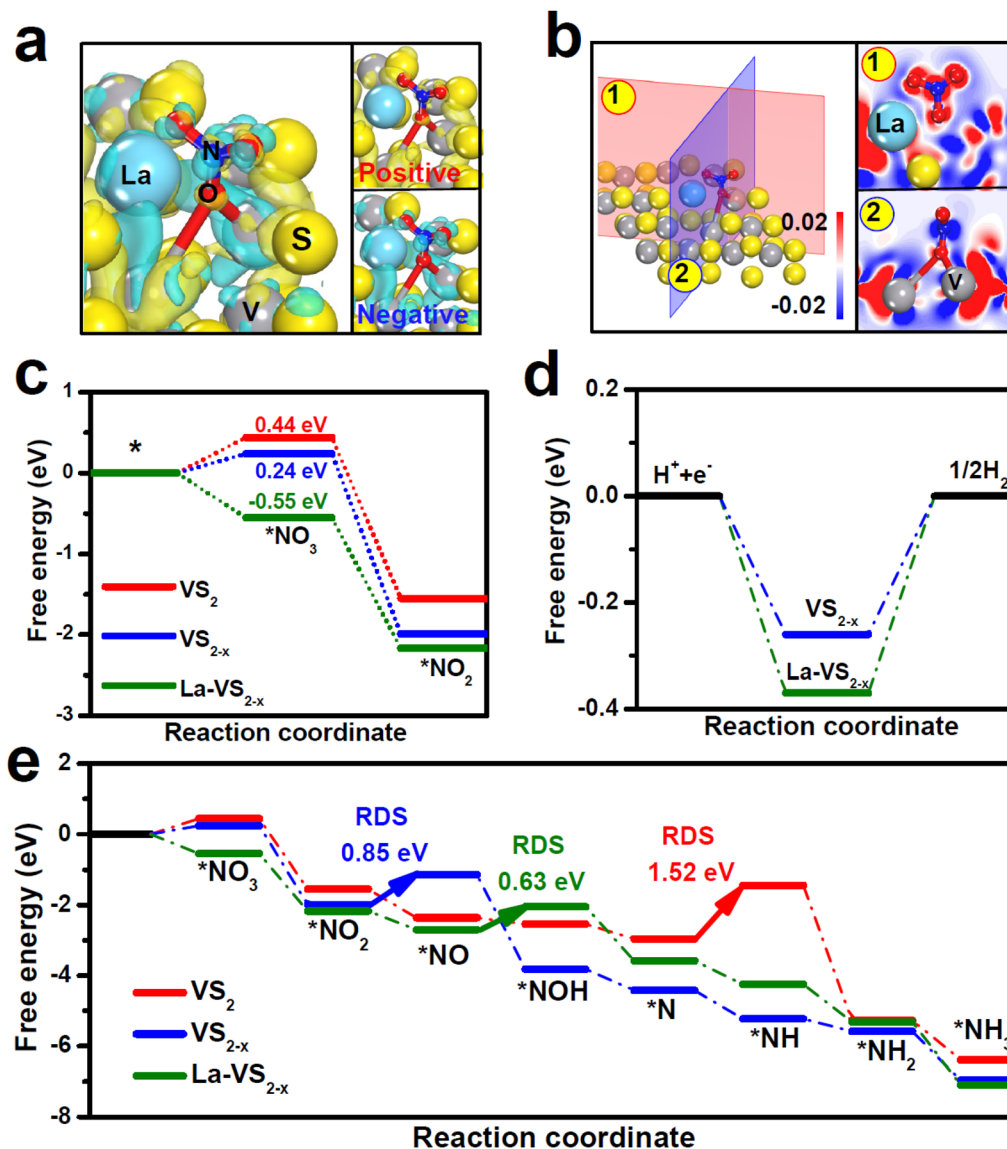


Fig. 4 (a) Differential charge density maps of  $\text{NO}_3^-$  adsorption on  $\text{La-VS}_{2-x}$  (yellow: accumulation, cyan: depletion) and (b) the corresponding electron location function maps (red: accumulation, blue: depletion). (c and d) Binding free energies of (c)  $\text{NO}_3^-$  and (d) H on different catalysts. (e) Gibbs free energy diagrams of the  $\text{NO}_3\text{RR}$  pathway of  $\text{VS}_2$ ,  $\text{VS}_{2-x}$  and  $\text{La-VS}_{2-x}$ , respectively.

### 3. Conclusion

In summary,  $\text{La-VS}_{2-x}$  is verified to be a highly active and selective  $\text{NO}_3\text{RR}$  catalyst. Theoretical computations reveal that the excellent  $\text{NO}_3\text{RR}$  performance of  $\text{La-VS}_{2-x}$  originates from the synergy of La-dopants and  $\text{V}_s$  to promote  $\text{NO}_3^-$  activation, suppress the HER and lower the energetic barriers. This work demonstrates the great potential of rare earth catalysts toward the efficient  $\text{NO}_3\text{RR}$  for  $\text{NH}_3$  electro-synthesis.

### Conflicts of interest

There are no conflicts of interest to declare.

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