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# Atomically isolated and unsaturated Sb sites created on $\text{Sb}_2\text{S}_3$ for highly selective NO electroreduction to $\text{NH}_3^\dagger$

 Kai Chen, Ying Zhang, Wenyu Du, Yali Guo and Ke Chu \*

$\text{Sb}_2\text{S}_3$  comprising an atomically isolated and unsaturated Sb ( $\text{Sb}_{\text{AIU}}$ ) site is demonstrated as a fascinating catalyst for highly selective electrochemical NO-to- $\text{NH}_3$  conversion (NORR). Theoretical calculations reveal the crucial function of  $\text{Sb}_{\text{AIU}}$  sites to favor the adsorption and activation of NO, accelerate the protonation energetics of the NO-to- $\text{NH}_3$  pathway and impede the coverage of  $\text{H}_2\text{O}/\text{H}$  species, thereby boosting both NORR activity and selectivity. Consequently, the developed  $\text{Sb}_{\text{AIU}}$ -rich  $\text{Sb}_2\text{S}_3$  catalyst exhibits an excellent NO-to- $\text{NH}_3$  faradaic efficiency of 93.7% and a high  $\text{NH}_3$  yield rate of  $168.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$ , representing the highest NORR selectivity among all reported NORR catalysts.

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## 1. Introduction

Ammonia is a pivotal chemical that is widely applied in many aspects of social and economic development.<sup>1–3</sup> Recently,  $\text{N}_2$  electrofixation emerged as a promising technology for green  $\text{NH}_3$  synthesis, whereas its efficiency is greatly limited by intractable issues of ultrastable  $\text{N}\equiv\text{N}$  bonds.<sup>4–10</sup> Alternatively, NO possesses a relatively low  $\text{N}=\text{O}$  bond energy and thus electrochemical NO-to- $\text{NH}_3$  conversion (NORR) represents a more prospective approach than  $\text{N}_2$  electrofixation for  $\text{NH}_3$  electrosynthesis.<sup>11–14</sup> Nevertheless, the NORR effectiveness is greatly retarded by the sophisticated five-electron reaction process and severe competition from the hydrogen evolution reaction (HER),<sup>1</sup> and it is imperative to explore efficient NORR electrocatalysts capable of boosting the NO-to- $\text{NH}_3$  pathway with high selectivity.<sup>15–20</sup>

Transition metal-based catalysts commonly exhibit high NORR activity owing to their partially occupied d-orbitals boosting NO adsorption.<sup>21–27</sup> Nevertheless, d-orbitals also favor the formation of metal-H bonds to trigger the competitive HER, giving rise to low NORR selectivity.<sup>28</sup> Promisingly, main group p-block metals (Sb, In, Bi, *etc.*) are catalytically inert in the HER because of their closed d-band shells.<sup>29</sup> Meanwhile, the partially occupied p-orbitals in p-block metals are confirmed to be active for  $\text{N}=\text{O}$  bond dissociation, making p-block metal-based materials promising as a new class of NORR catalysts.<sup>30–34</sup> P-block Sb-based catalysts are appealing

NORR candidates owing to the great capability of Sb sites to impede the HER and activate the nitrogen-containing molecules.<sup>35</sup> On the other hand, catalysts with atomically isolated sites are known to present outstanding catalytic performance because of their high atom utilization and optimal binding with intermediates and reactants.<sup>36–38</sup> Besides, defect engineering by creating vacancies or unsaturated sites is considered an effective strategy to tailor the electronic structure of catalysts with enhanced catalytic activities.<sup>39–41</sup> In view of the above, creating atomically isolated and unsaturated Sb sites is therefore an attractive strategy for designing high-efficiency NORR catalysts.

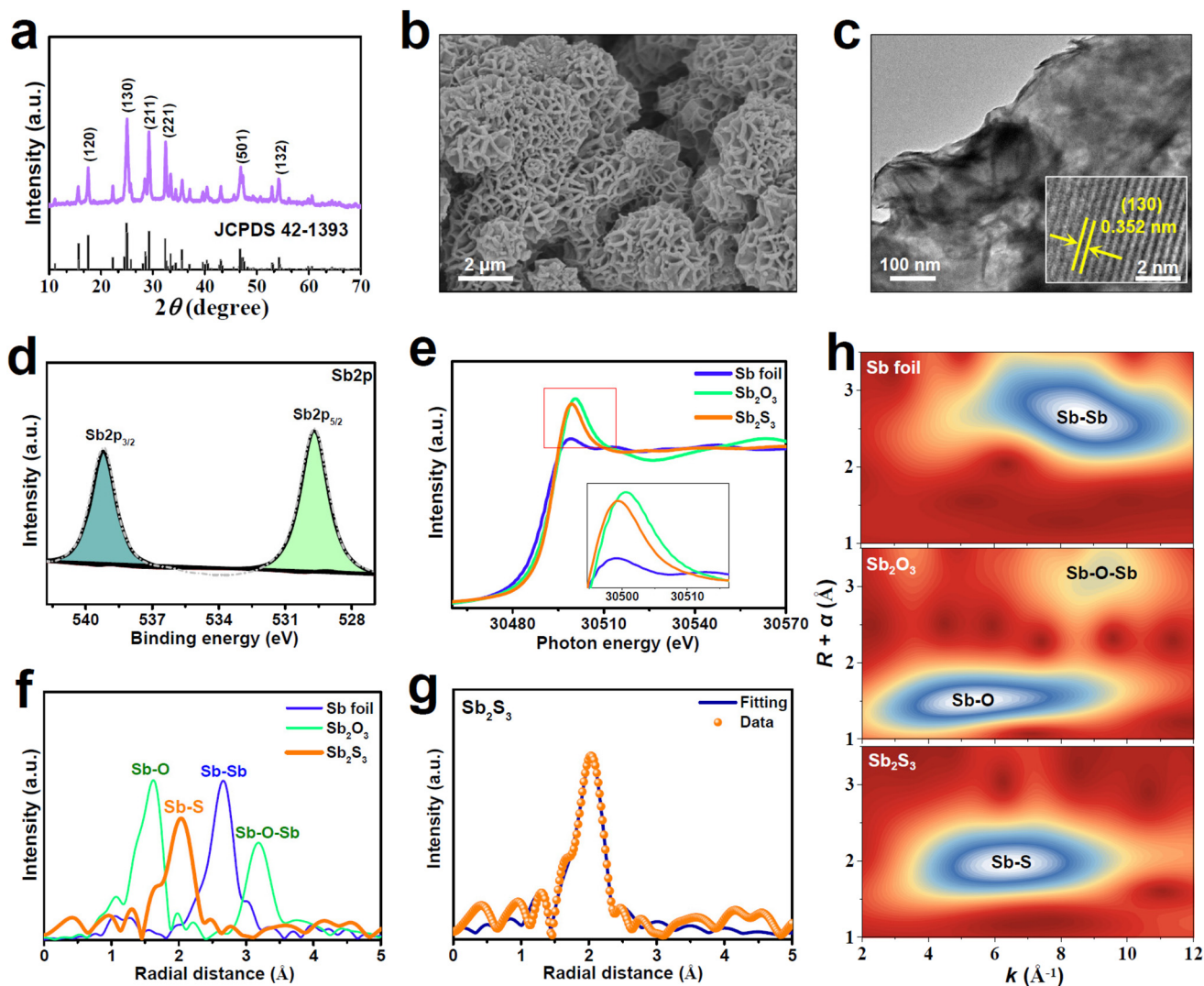
In this study, p-block  $\text{Sb}_2\text{S}_3$  is designed as a fascinating catalyst for highly selective NORR, which exhibits an excellent NO-to- $\text{NH}_3$  faradaic efficiency ( $\text{FE}_{\text{NH}_3}$ ) of 93.7% and a high  $\text{NH}_3$  yield rate of  $168.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$ , representing the highest NORR selectivity among all reported NORR catalysts. Detailed structural characterization and theoretical computations reveal that atomically isolated and unsaturated Sb sites created on  $\text{Sb}_2\text{S}_3$  play a crucial role in greatly enhancing the NORR activity and selectivity.

## 2. Results and discussion

A solvothermal method was utilized to synthesize  $\text{Sb}_2\text{S}_3$ . The XRD pattern of the as-synthesized  $\text{Sb}_2\text{S}_3$  (Fig. 1a) shows distinct peaks that are assigned to the pure orthorhombic  $\text{Sb}_2\text{S}_3$  phase with a good crystallinity. The SEM image of  $\text{Sb}_2\text{S}_3$  (Fig. 1b) shows a typical nanoflower morphology consisting of numerous vertically aligned nanosheets. The nanosheet feature can be further confirmed by the TEM image (Fig. 1c).

School of Materials Science and Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China. E-mail: [chuk630@mail.lzjtu.cn](mailto:chuk630@mail.lzjtu.cn)

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**Fig. 1** Characterization of  $\text{Sb}_2\text{S}_3$ : (a) XRD pattern, (b) SEM image, (c) TEM image and HRTEM image (inset), (d) XPS  $\text{Sb}2p$  spectrum, (e)  $\text{Sb}$  K-edge XANES spectra, (f) EXAFS spectra and (h) WT profiles of  $\text{Sb}_2\text{S}_3$  and reference samples. (g) EXAFS fitting curve of  $\text{Sb}_2\text{S}_3$ .

As shown in the HRTEM image (Fig. 1c, inset), the lattice spacing of  $\text{Sb}_2\text{S}_3$  nanosheets is determined to be 0.352 nm, corresponding to the (130) facet of orthorhombic  $\text{Sb}_2\text{S}_3$ , in line with the XRD result (Fig. 1a). The XPS  $\text{Sb}$  spectrum of  $\text{Sb}_2\text{S}_3$  (Fig. 1d) can be split into  $\text{Sb}^{3+}2p_{3/2}$  (539.3 eV) and  $\text{Sb}^{3+}2p_{5/2}$  (529.8 eV), while the deconvolution of the  $\text{S}2p$  spectrum (Fig. S1†) shows two peaks of  $\text{S}2p_{1/2}$  (163.6 eV) and  $\text{S}2p_{3/2}$  (161.8 eV), in good accordance with those reported for  $\text{Sb}_2\text{S}_3$ .<sup>42–44</sup>

We employ X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) characterizations to further examine the valence states and coordination structures of  $\text{Sb}_2\text{S}_3$ . The  $\text{Sb}$  K-edge XANES spectra (Fig. 1e) show that the white line of  $\text{Sb}_2\text{S}_3$  is slightly lower than that of  $\text{Sb}_2\text{O}_3$ , suggesting the valence state of  $\text{Sb}$  to be smaller than the intrinsic  $\text{Sb}$  valence of  $\text{Sb}_2\text{S}_3$  (+3), which is caused by the presence of coordinatively unsaturated  $\text{Sb}$  sites in  $\text{Sb}_2\text{S}_3$ .

The  $\text{Sb}$  K-edge EXAFS spectra (Fig. 1f) show that  $\text{Sb}_2\text{S}_3$  exhibits a dominant peak at 2.03 Å assignable to the  $\text{Sb-S}$  bond, which largely differs from those of  $\text{Sb}$  foil ( $\text{Sb-Sb}$ : 2.66 Å) and  $\text{Sb}_2\text{O}_3$  ( $\text{Sb-O}$ : 1.62 Å,  $\text{Sb-O-Sb}$ : 3.18 Å), indicating that  $\text{Sb}_2\text{S}_3$  comprises the isolated state of  $\text{Sb}$  and no oxidized  $\text{Sb}$  species are present on  $\text{Sb}_2\text{S}_3$ . Likewise, the corresponding wavelet transform (WT) contour plots (Fig. 1h) show only one intensity maximum at 6.3 Å<sup>-1</sup> corresponding to the  $\text{Sb-S}$  coordination, suggesting the existence of atomically dispersed  $\text{Sb}$  atoms. The EXAFS fitting data (Fig. 1g and Table S1†) reveal the average coordination number (CN) of  $\text{Sb}_2\text{S}_3$  to be 4.2, much smaller than the crystallographic value of  $\text{Sb}_2\text{S}_3$  (CN = 5),<sup>45</sup> corroborating the existence of plentiful unsaturated  $\text{Sb}$  sites in  $\text{Sb}_2\text{S}_3$ . These XAS results reveal that the prepared  $\text{Sb}_2\text{S}_3$  naturally contains abundant atomically isolated and unsaturated  $\text{Sb}$  ( $\text{Sb}_{\text{ATU}}$ ) sites, which are considered to be catalytically active towards NORR.

Electrocatalytic NORR measurements were carried out using a gas-tight H-type electrolytic cell containing 0.5 M  $\text{Na}_2\text{SO}_4$  solution.<sup>46</sup> Several colorimetric approaches (Fig. S2 and S3†) were performed to detect the liquid products, while the gaseous products were detected by gas chromatography. We conducted linear sweep voltammetry (LSV) measurement to initially assess the NORR activity of  $\text{Sb}_2\text{S}_3$ . It is displayed in

Fig. 2a that  $\text{Sb}_2\text{S}_3$  presents a noticeable current density ( $j$ ) enhancement in the NO-saturated electrolyte relative to the Ar-saturated one, proving that  $\text{Sb}_2\text{S}_3$  has a high NORR activity. We then quantitatively determined the NORR performance of  $\text{Sb}_2\text{S}_3$  with the integration of chronoamperometry (Fig. 2b) and colorimetric tests at various potentials. As shown in Fig. 2c, with increasing the potential, both the  $\text{NH}_3$  yield rate and

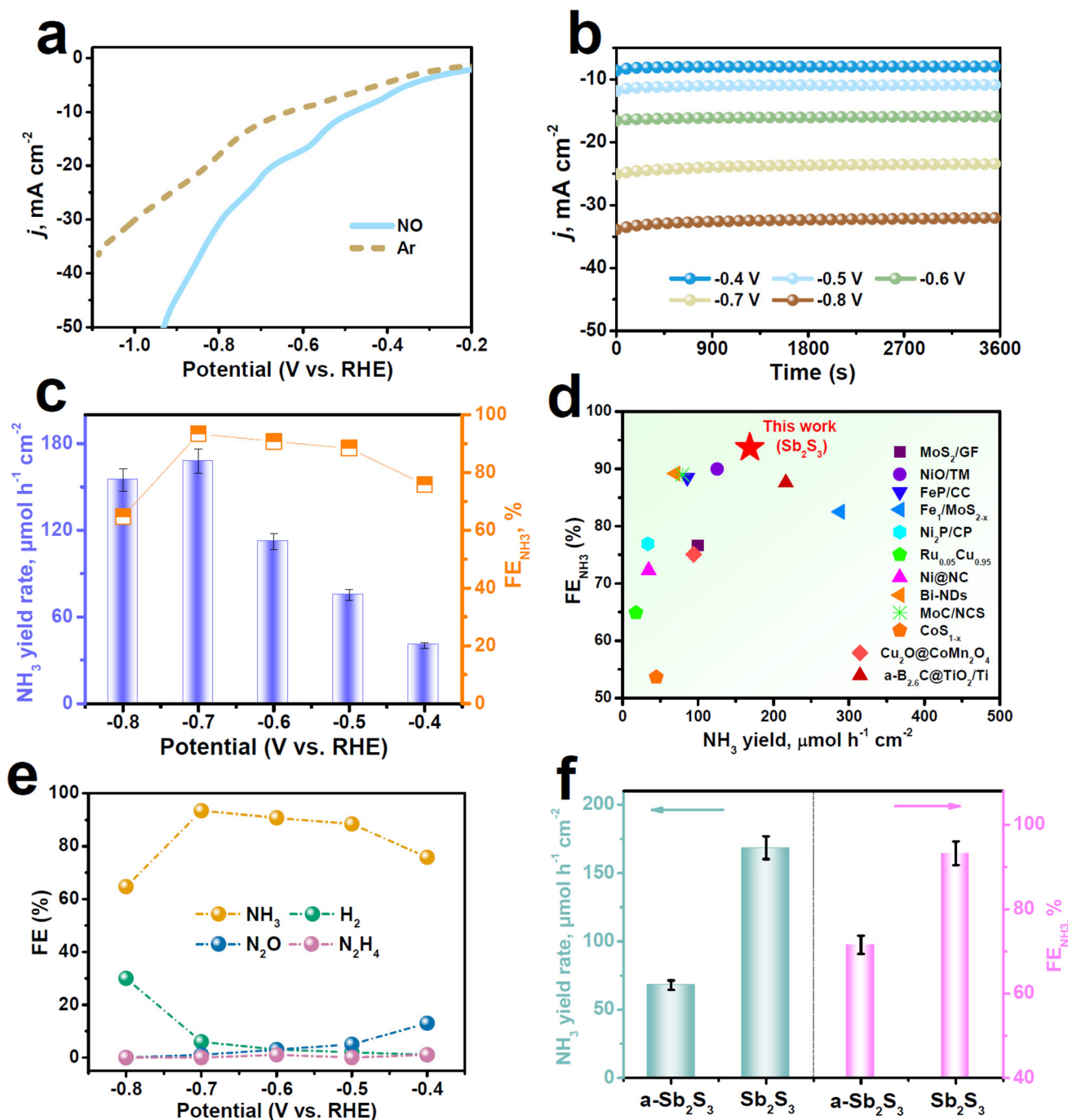
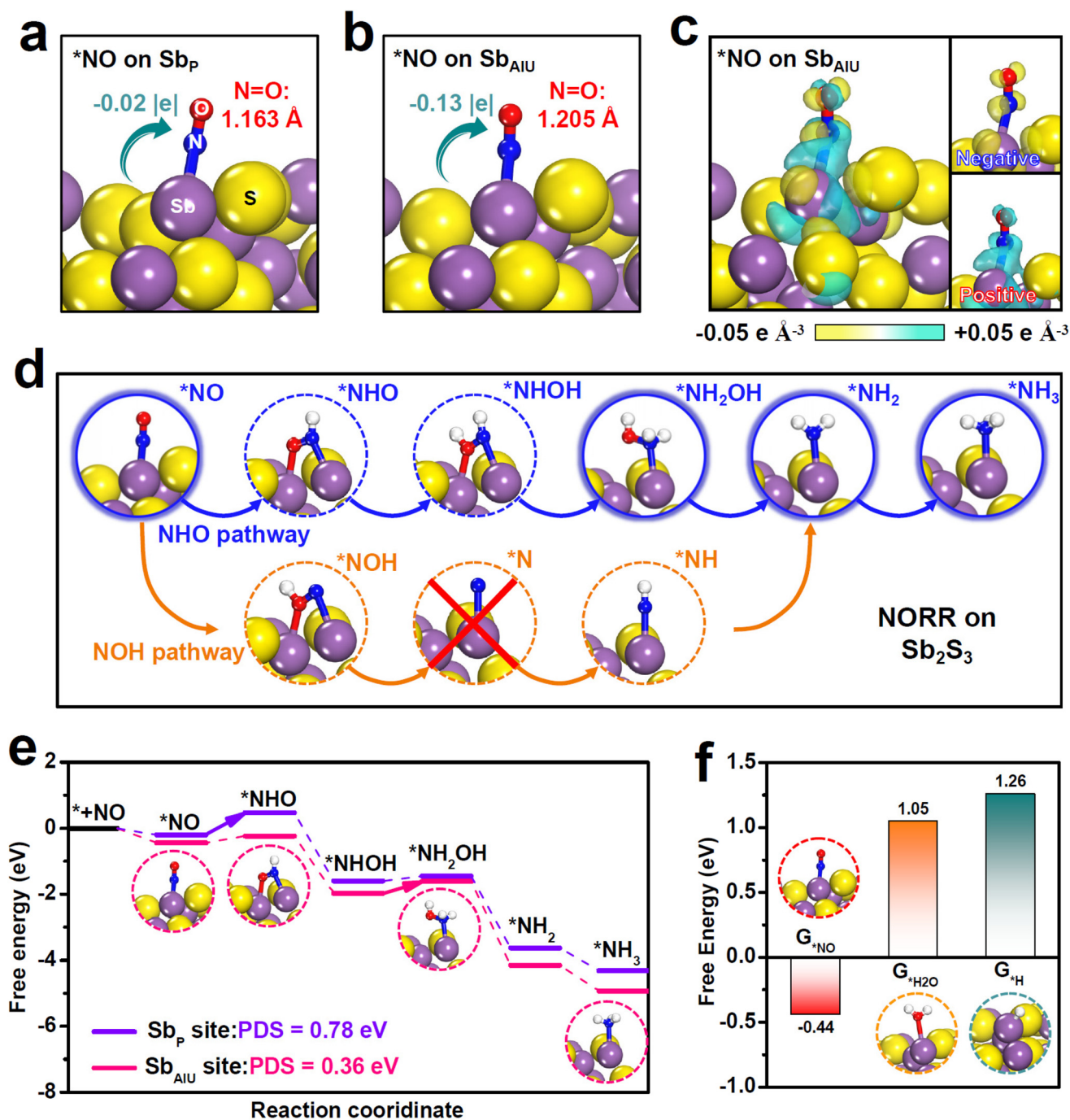


Fig. 2 (a) LSV curves of  $\text{Sb}_2\text{S}_3$  in Ar/NO-saturated 0.5 M  $\text{Na}_2\text{SO}_4$ . (b) Chronoamperometry test of  $\text{Sb}_2\text{S}_3$  at various potentials, and the resulting (c)  $\text{NH}_3$  yield rates and  $\text{FE}_{\text{NH}_3}$ . (d) Comparison of  $\text{NH}_3$  yield rates and  $\text{FE}_{\text{NH}_3}$  between  $\text{Sb}_2\text{S}_3$  and the recently reported NORR catalysts. (e) FEs of different products on  $\text{Sb}_2\text{S}_3$  after NORR electrolysis at various potentials. (f)  $\text{NH}_3$  yield rates and  $\text{FE}_{\text{NH}_3}$  of  $\text{Sb}_2\text{S}_3$  and a- $\text{Sb}_2\text{S}_3$  at  $-0.7$  V.

$FE_{NH_3}$  of  $Sb_2S_3$  exhibit a volcanic shape and reach their highest values of  $168.6 \mu\text{mol h}^{-1} \text{cm}^{-2}$  and 93.7% at  $-0.7 \text{ V}$ , respectively. Strikingly, as shown in Fig. 2d (see Table S2 for details<sup>†</sup>), the  $FE_{NH_3}$  of  $Sb_2S_3$  shows the highest NORR selectivity among all the reported NORR catalysts, while its  $NH_3$  yield rate is also superior to those of most reported NORR catalysts. Meanwhile,

Fig. 2e shows that the FEs of N-containing side products ( $N_2O$  and  $N_2H_4$ ) are rather low at all considered potentials, in good accordance with the partial current density data (Fig. S4<sup>†</sup>), signifying the outstanding NO-to- $NH_3$  selectivity of  $Sb_2S_3$ . Regarding the NORR stability, the chronopotentiometric test presents a stable current density for at least 20 h of electrolysis



**Fig. 3** (a and b) Atomic structures of absorbed NO on (a) the  $Sb_P$  site and (b) the  $Sb_{AIU}$  site of  $Sb_2S_3$ . (c) Charge density difference of \*NO on the  $Sb_{AIU}$  site (yellow: accumulation; cyan: depletion). (d) Schematic of two NORR pathways (NHO and NOH) on  $Sb_2S_3$ . (e) Free energy profiles of the NORR process (NHO pathway) on  $Sb_P$  and  $Sb_{AIU}$ . (f) Binding free energies of \* $H_2O$ , \* $H$  and \*NO on  $Sb_{AIU}$ .

(Fig. S5†), and the resulting  $FE_{NH_3}$  shows very small attenuations, indicating the good long-term stability of  $Sb_2S_3$ . Besides, no remarkable fluctuations in the  $NH_3$  yield rate and  $FE_{NH_3}$  occur during the seven electrolysis cycles (Fig. S6†), proving the favorable cycling stability of  $Sb_2S_3$ .<sup>47–50</sup>

We conducted several experiments to verify the  $NH_3$  origin. First,  $NH_3$  is almost undetectable in the control colorimetric tests (Fig. S7†).<sup>32</sup> In addition, upon feeding  $^{15}NO$  gas, the resulting  $^1H$  nuclear magnetic resonance (NMR, Fig. S8†) spectra reveal the characteristic  $^{15}NH_4^+$  doublets, whereas feeding Ar gas leads to the absence of  $^{15}NH_4^+$  doublets.<sup>51–53</sup> Furthermore, the switching NO–Ar test (Fig. S9†) reveals significant  $NH_3$  production in NO cycles, whereas  $NH_3$  is nearly undetectable in Ar cycles. All these results validate that the produced  $NH_3$  stems from the electrochemical NORR process catalyzed by  $Sb_2S_3$ .

For comparison, we evaluated the NORR property of annealed  $Sb_2S_3$  (a- $Sb_2S_3$ ) with much reduced  $Sb_{AIU}$  (Fig. S10 and Table S1†) under identical measurement conditions at  $-0.7$  V. Impressively, Fig. 2f shows that the NORR performance of a- $Sb_2S_3$  is significantly poorer than that of the original  $Sb_2S_3$ , revealing that the  $Sb_{AIU}$  sites play a vital role in dramatically boosting the NORR property of  $Sb_2S_3$ . Electrochemical surface area (ECSA, Fig. S11 and S12†) measurements show that the ECSA-normalized NORR performances of the two catalysts (Fig. S13†) present the same trend as that shown in

Fig. 2f. Besides, both catalysts have comparable charge transport kinetics (Fig. S14†).<sup>54–57</sup> These findings demonstrate the intrinsic superior NORR property of  $Sb_2S_3$ .

Theoretical computations were carried out to shed light on the boosted NORR property of  $Sb_2S_3$ . To start, we evaluated the adsorption behaviors of the NO molecule on two sites of  $Sb_2S_3$ , namely the pristine Sb ( $Sb_P$ ) site and the  $Sb_{AIU}$  site, as the NO adsorption is the initial critical step to trigger the NORR.<sup>46</sup> Upon absorbing NO on the  $Sb_P$  site (Fig. 3a),  $^*NO$  exhibits a rather small N=O elongation (1.163 Å, 1.159 Å for original NO) with negligible  $Sb_P$ -to- $^*NO$  electron transfer ( $-0.02$  |e|), which means poor NO adsorption on the  $Sb_P$  site. As a sharp comparison,  $^*NO$  on the  $Sb_{AIU}$  site (Fig. 3b) presents dramatic N=O bond elongation (1.205 Å) and  $Sb_{AIU}$ -to- $^*NO$  electron transfer ( $-0.13$  |e|), indicating largely improved NO adsorption on  $Sb_{AIU}$ . Additionally, the charge density difference (Fig. 3c) clearly shows strong  $^*NO/Sb_{AIU}$  electronic interactions, where both remarkable positive and negative charge aggregations can be seen on  $^*NO$ , proving that  $Sb_{AIU}$  enables powerful NO activation *via* a “donation–backdonation” mechanism.

To investigate the entire NORR process, we initially conducted online differential electrochemical mass spectrometry (DEMS) measurements to experimentally probe the reaction intermediates formed on  $Sb_2S_3$  during the NORR electrolysis. The online DEMS spectra (Fig. S15†) reveal the generation of distinct  $NH_3$  ( $m/z = 17$ ) and  $NH_2OH$  ( $m/z = 33$ ) signals.

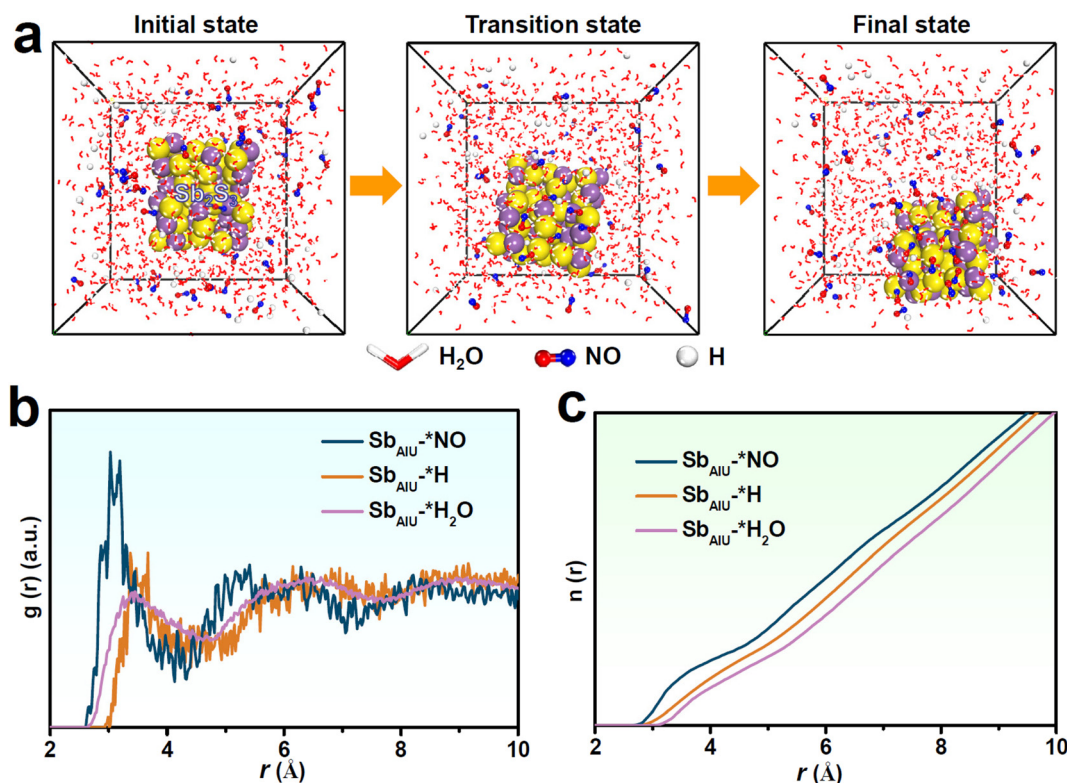


Fig. 4 (a) Initial, transition and final simulated states of the dynamic adsorption process of  $^*H_2O$ ,  $^*H$  and  $^*NO$  on  $Sb_{AIU}$ , and the corresponding (b) RDF and (c) integrated RDF curves of the interactions between  $Sb_{AIU}$  and  $^*NO$ ,  $^*H$  and  $^*H_2O$ .

Specifically, N ( $m/z = 14$ ), which is the key intermediate involved in the NOH pathway, is absent in the NORR electrolysis, demonstrating that  $\text{Sb}_2\text{S}_3$  preferentially undergoes the NHO pathway to drive the NORR process,<sup>58</sup> as illustrated in Fig. 3d. As displayed in the free energy profiles of the energetic-preferred NHO pathway (Fig. 3e and Fig. S16<sup>†</sup>), the  $\text{Sb}_p$  site exhibits a large energy barrier of 0.78 eV to drive the first protonation step of  $^*\text{NO} \rightarrow ^*\text{NOH}$  as the potential-determining step (PDS). In stark contrast, by virtue of powerful NO activation, the  $\text{Sb}_{\text{AIU}}$  site presents a largely reduced barrier of 0.21 eV for the same  $^*\text{NO} \rightarrow ^*\text{NOH}$ , suggesting that the initial protonation step can be greatly boosted on the  $\text{Sb}_{\text{AIU}}$  site. The PDS of  $\text{Sb}_{\text{AIU}}$  is changed to  $^*\text{NHOH} \rightarrow ^*\text{NH}_2\text{OH}$  with only 0.36 eV uphill, corroborating the significantly enhanced NORR energetics over the  $\text{Sb}_{\text{AIU}}$  site that renders a high NORR activity of  $\text{Sb}_2\text{S}_3$ . We then investigated the catalytic behavior of the  $\text{Sb}_{\text{AIU}}$  site towards the HER, which is the main competitive reaction for NORR.<sup>24</sup> The calculated binding free energies ( $G$ ) of various species (Fig. 3f) show that  $G_{^*\text{NO}}$  (−0.44 eV) is much more negative than  $G_{^*\text{H}_2\text{O}}$  (1.05 eV) and  $G_{^*\text{H}}$  (1.26 eV), demonstrating that the  $\text{Sb}_{\text{AIU}}$  site preferentially absorbs NO over  $\text{H}_2\text{O}/\text{H}$  species to impede the competing HER.

Molecular dynamics (MD) simulations were conducted to further examine the competitive adsorption of NO and  $\text{H}_2\text{O}/\text{H}$  on  $\text{Sb}_{\text{AIU}}$ . After simulation, the snapshots (Fig. 4a) show prominent NO aggregation on  $\text{Sb}_{\text{AIU}}$  together with an enhanced  $\text{Sb}_{\text{AIU}}-^*\text{NO}$  interaction over  $\text{Sb}_{\text{AIU}}-^*\text{H}_2\text{O}$  and  $\text{Sb}_{\text{AIU}}-^*\text{H}$  interactions, as displayed in the radial distribution function (RDF, Fig. 4b) curves and the corresponding integrated RDF curves (Fig. 4c),<sup>58–62</sup> proving a high tendency of  $\text{Sb}_{\text{AIU}}$  for the adsorption and coverage of NO over  $\text{H}_2\text{O}/\text{H}$ , which is greatly favorable for HER suppression to obtain a high NORR selectivity.

### 3. Conclusion

In summary,  $\text{Sb}_{\text{AIU}}$ -rich  $\text{Sb}_2\text{S}_3$  has been corroborated as a high-performing p-block metal catalyst for NORR. Theoretical computations reveal the critical role of  $\text{Sb}_{\text{AIU}}$  sites in promoting the activation and protonation of NO, while concurrently prohibiting the coverage of  $\text{H}_2\text{O}/\text{H}$  species. This work not only highlights the critical design of atomically isolated and unsaturated sites to dramatically enhance the catalytic NORR activity and selectivity, but also demonstrates the promising prospects of p-block metal elements in the design of high-efficiency NORR electrocatalysts.

### Conflicts of interest

There are no conflicts of interest to declare.

### Acknowledgements

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