Oxygen vacancy engineering in spinel-structured nanosheet wrapped hollow polyhedra for electrochemical nitrogen fixation under ambient conditions

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Electrochemical nitrogen-to-ammonia conversion by the nitrogen reduction reaction (NRR) under ambient conditions is regarded as a potential approach to tackle the energy-intensive Haber–Bosch process with excessive CO2 emission. However, the NRR is still restricted by low faradaic efficiency and NH3 yield, which is due to the chemical inertness of N2 molecules. Then, the question on how to capture and activate N2 gas much more efficiently using electrocatalysts arises. Atomic surface engineering (such as Fe-, Co-, and Mo-based materials), nanostructures (such as one-dimensional nanostructures, two-dimensional ultrathin nanosheets, and three-dimensional hollow nanostructures) has become an efficient solution to obtain outstanding NRR electrocatalysts with a high faradaic efficiency due to the confined electro-active sites in the corresponding bulk. Therefore, constructing multilevel nanostructures (such as one-dimensional nanofibers/nanotubes, two-dimensional ultrathin nanosheets, and three-dimensional hollow nanostructures) has become an efficient solution to obtain outstanding NRR electrocatalysts with a high specific surface area, thus resulting to an increased number of active sites for efficient reactant adsorption.

Apart from this, the impeded NRR process is deeply rooted in the chemical inertness of N2 molecules. Then, the question on how to capture and activate N2 gas much more efficiently using electrocatalysts arises. Atomic surface engineering (such as defect engineering and doping engineering) is the best choice to regulate the electronic structure and alter the charge density distribution. Among various types of defects, the vacancy-type defect (such as oxygen vacancies) is regarded as a kind of point defect, which is caused by independent atoms escaping from the atomic surface. Up to now, several possible strategies have been discovered for generating oxygen vacancies in metal oxides, including chemical reduction, annealing in an oxygen poor atmosphere, and...
heterogeneous atom substitution. Furthermore, the oxygen vacancies created on the metal oxide surface could serve as trapping sites to capture and activate inert gas molecules of N₂. However, to our knowledge, the proper control of the oxygen vacancy content in the electrocatalytic N₂ reduction reaction is still in the rudimentary state.

To figure out the contribution of the oxygen vacancies in NRR applications, we conducted density functional theory (DFT) calculations by using NiCoO₄ with a perfect surface and oxygen vacancy-introduced surface as two models. As shown in Fig. 1, the introduction of oxygen vacancies in NiCoO₄ is beneficial for enhancing its stability towards NNH groups due to the presence of fewer coordination sites of Ni/Co cations around the vacancies. As further proved by the differential charge density of NiCoO₄ with oxygen vacancies, the bonded electrons can be delocalized to electron donors (Ni and Co elements) near the oxygen vacancies and be activated dramatically. As a result, the NiCoO₄ with oxygen vacancies exhibits a lower stabilization energy of 0.30 eV for NNH groups than NiCoO₄ with a perfect surface (0.61 eV), indicating the positive role of oxygen vacancies in the following nitrogen reduction reactions. In addition, the delocalized electrons on the surface of NiCoO₄ with oxygen-vacancies are easier to excite to the conduction band, which is favorable not only for enhanced conductivity but also for activation of N-related groups, by transferring their electrons into their antibonding orbitals. At the same time, the hollow carbon polyhedron is beneficial not only for electron transfer from buried carbon to the oxygen vacancy-rich NiCoO₄ surface for the fast NRR process, but also for increasing the number of active sites for the capture of NNH groups.

In this study, we design a series of highly efficient oxygen vacancy-rich spinel-structured nanosheets on hollow N-carbon polyhedra to facilitate the electrocatalytic N₂ reduction reaction. Taking the oxygen vacancy-rich NiCoO₄ on hollow N-carbon polyhedra (Vₒ-rich NiCoO₄@HNCP) as an example, it exhibited a high production yield (NH₃: 4.1 mg/g h) and faradaic efficiency: 5.3%, good selectivity at −0.25 V versus RHE, and high stability during the NRR process and is much more outstanding than the corresponding oxygen-vacancy-poor NiCoO₄ on hollow N-carbon polyhedra (Vₒ-poor NiCoO₄@HNCP). Furthermore, this oxygen vacancy engineering can also be applied in other spinel-structured nanosheets (such as ZnCo₂O₄ and Co₃O₄), which leads to a general solution for the design of advanced NRR electrocatalysts.

Results and discussion

According to the theoretical work, oxygen vacancy-rich NiCoO₄ on hollow N-carbon polyhedra (Vₒ-rich NiCoO₄@HNCP) was synthesized (Fig. S1†). As shown in Fig. 2a, the Vₒ-rich NiCoO₄@HNCP displays a regular geometrical shape with a maximum length of ~ 850 nm. A blurry interface between HNCP and Vₒ-rich NiCoO₄ nanosheets can be observed in the corresponding HRTEM image (Fig. 2b), with mixed phases of amorphous carbon and crystalline NiCoO₄, which is beneficial for the charge accumulation and transfer. As a result, the two parts of HNCP and Vₒ-rich NiCoO₄ nanosheets can be well connected with a shared electron transfer region. Meanwhile, the fringe spacing of Vₒ-rich NiCoO₄ is revealed to be ~0.23 nm in its HRTEM image (corresponding to the (311) plane), which demonstrates a negative role of oxygen vacancies in the crystalline NiCoO₄. As shown in the X-ray diffraction (XRD) pattern of Vₒ-rich NiCoO₄@HNCP (Fig. 2c), three typical peaks at 2θ = 36.9°, 43.0°, and 62.7° can be well indexed to the (311), (400) and (440) planes of spinel-structured NiCoO₄ (JCPDS card no. 73-1702), demonstrating its successful loading on the hollow nitrogen-doped carbon polyhedra. The nine-fold higher specific surface area (82.1 m² g⁻¹) of Vₒ-rich NiCoO₄@HNCP compared to the Vₒ-rich NiCoO₄ bulk (9.0 m² g⁻¹) (Fig. 2d) indicates its higher number of active sites, leading to shortened diffusion paths for reagents during the NRR process.

Further, for comparison, oxygen vacancy-poor NiCoO₄ on hollow N-carbon polyhedra (Vₒ-poor NiCoO₄@HNCP) was obtained by calcining the corresponding nickel–cobalt layered double hydroxide nanosheet wrapped hollow nitrogen-doped carbon polyhedra (Ni-Co LDH@HNCP) in an oxygen atmosphere, and a series of characterization experiments was conducted (Fig. S2–S8†). In the N 1s X-ray photoelectron spectroscopy (XPS) spectrum (Fig. 2e), the peaks at 400.6 eV, 399.7 eV, and 398.7 eV corresponded to the graphitic N, pyrrolic N, and pyridinic N of the HNCP template, which is beneficial for the efficient connection of both Vₒ-rich and Vₒ-poor NiCoO₄ nanosheets to form a charge-rich region. In addition, the nitrogen content was calculated to be 11.6 wt% (Fig. S9†). The binding energies of Co 2p3/2 (780 eV) and Co 2p1/2 (793 eV) for Vₒ-poor NiCoO₄@HNCP show negative shifts compared to those for Vₒ-rich NiCoO₄@HNCP (Fig. 2f). This indicates that some Co⁶⁺ ions in the NiCoO₄ nanosheets are reduced to Co⁴⁺ after introduction of oxygen vacancies due to the charge transfer from the Vₒ to the Co(Ni)–O bonds at the surfaces (Fig. S10†). In the O 1s XPS spectra (Fig. 2g), the peaks at 529.5, 531.1 and 532.5 eV are associated with Co(Ni)–O bonds (O1), oxygen vacancies or defects with lower oxygen coordination (O2), and surface adsorbed water molecules (O3), respectively. The proportion of the integral-area of the O2 peak in Vₒ-rich NiCoO₄@HNCP is much larger than that in Vₒ-poor NiCoO₄@HNCP.
NiCo$_2$O$_4$@HNCP, indicating the successful introduction of abundant oxygen vacancies in V$_o$-rich NiCo$_2$O$_4$@HNCP. In addition, the V$_o$ (O2) proportion in V$_o$-rich NiCo$_2$O$_4$@HNCP and the V$_o$-poor NiCo$_2$O$_4$ bulk increases from 33.0% to 68.2% as the annealing temperature increased from 200 to 300 °C (Fig. S11†), which means that the incorporated V$_o$ amount can be well controlled by adjusting the annealing temperature. This finding could be further confirmed using X-ray absorption near edge structure (XANES) of the O K-edge and Co L-edge. Fig. 2h shows the O K-edge XANES spectra of V$_o$-rich NiCo$_2$O$_4$@HNCP and V$_o$-poor NiCo$_2$O$_4$@HNCP. Meanwhile, attributed to the Co 2p to 3d transition and spin–orbit coupling, the Co L-edge spectra can be split into two parts, L3-edge and L2-edge (Fig. 2i). The lower peak intensity for both the Co L3-edge and L2-edge in V$_o$-rich NiCo$_2$O$_4$@HNCP indicates that more electrons would occupy the Co 3d orbitals, providing more crucial evidence for the presence of abundant V$_o$ on the surface of V$_o$-rich NiCo$_2$O$_4$@HNCP. A similar phenomenon is observed in the Ni L-edge spectrum (Fig. S14†). The generation of oxygen vacancies is due to the inadequate oxidation of NiCo$_2$O$_4$ in an oxygen-deficient atmosphere as compared to an oxygen atmosphere, leading to abundant partially unoxidized metal domains in the NiCo$_2$O$_4$ structure.\[55,56\]

To reveal the role of oxygen vacancies in tuning the electronic structures of the NiCo$_2$O$_4$ nanosheets, DFT calculations were performed for different types of oxygen vacancies. Considering that there are two types of oxygen (e.g. surface and sub-surface oxygens) in the perfect crystallographic lattice of NiCo$_2$O$_4$ (Fig. 3a), we separately studied each situation regarding their density of states, formation possibility and adsorption ability towards the key NRR intermediates of NNH groups. The surface oxygen was removed first for building the...
surface oxygen vacancy (sur-\(V_o\)) model, as shown in Fig. 3b. We found that the d-band center of the sur-\(V_o\) model is \(-0.28\) eV, much closer to the Fermi level compared with that of the pristine NiCo\(_2\)O\(_4\) model (\(-0.34\) eV). This result indicates that oxygen vacancies can induce more activity of the metal atoms, that is, the adsorption strength of molecules and radicals over the metal atoms will be enhanced. As shown in Fig. 3c, we tested another type of oxygen vacancy, the sub-surface oxygen vacancy (sub-\(V_o\)) model, which has the closest d-band center (\(-0.24\) eV) to the Fermi level among the three models. In the subsequent calculation, we found that the possibility of the formation of these two types of oxygen vacancies is not the same (Fig. 3d). As a more positive formation energy denotes that a vacancy is more difficult to form, the results show that sub-\(V_o\) (2.47 eV) has a higher stability than sur-\(V_o\) (3.25 eV). Finally, we calculated the adsorption strength of the three models by using NNH as a probe and found that the sub-\(V_o\) model presents the most favorable energy (\(-0.03\) eV). The adsorption energy of the sur-\(V_o\) (0.30 eV) is also more negative than that of the pristine model (0.61 eV), indicating its enhanced adsorption ability, which is consistent with the d-band center results. According to the trend of formation energy, we can deduce that the sub-\(V_o\) is preferentially formed when the vacancy density is relatively low. Therefore, the adsorption enhancement will be significantly dependent on the vacancy density in the region of low vacancy density.

To illustrate the role of oxygen vacancies in the NRR, a two-compartment cell was assembled by employing \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP as the cathode catalyst with continuous \(N_2\) bubbling in a 0.1 M Na\(_2\)SO\(_4\) electrolyte. The highest average yields and corresponding faradaic efficiencies of \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP are achieved when the negative potential increases to \(-0.25\) V versus the reversible hydrogen electrode (RHE) and are calculated to be about 4.1 \(\mu\)g h\(^{-1}\) cm\(^{-2}\)/mol h\(^{-1}\) and 5.3\%, respectively (Fig. 4a and S15†). This production yield at \(-0.25\) V is also confirmed by the nuclear magnetic resonance (NMR) method as shown in Fig. S16–S18 and Table S1.† Beyond this negative potential, the \(NH_3\) yields and faradaic efficiencies decrease significantly because of the overwhelming competition from the hydrogen evolution reaction (HER). The NRR performance of the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP catalyst is much more outstanding than that of the \(V_o\)-poor NiCo\(_2\)O\(_4\)@HNCP catalyst (1.6 \(\mu\)g h\(^{-1}\) cm\(^{-2}\)/mol h\(^{-1}\) and 1.8\% at \(-0.25\) V), as well as other results under ambient conditions or at high temperatures and pressures (Table S2†). Note that no hydrazine is detected in the electrolyte (Fig. S19†). In addition, the charge amounts of the experimentally quantified \(NH_3\) and \(H_2\) gases and the calculated one (Fig. S20†) are roughly in agreement (S2 ≈ S3). These results indicate the high selectivity of the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP catalyst for \(NH_3\) generation except for \(H_2\) gas. For practical use, stability is another critical criterion to evaluate the NRR performance of a catalyst. As shown in Fig. 4b and S21–26,† the \(NH_3\) yield, faradaic efficiency, and current density of the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP catalyst are all stable without obvious fluctuation. As shown in Fig. S27† the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP catalyst displays ultra-stable properties in both \(NH_3\) yield and faradaic efficiency even after working for 100 h and is comparable to the recently reported catalysts but with a much longer practical life.‡ By using XRD and XPS analyses (Fig. S28†), the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP catalyst is found to exhibit an unchanged crystal structure and only slightly decreased oxygen vacancy content after working for 100 h, which demonstrates the relatively stable structure of \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP as an NRR catalyst. Due to the similar results of \(NH_3\) yield and faradaic efficiency after varying the nitrogen flow rate at \(-0.25\) V (Fig. 4c), the \(N_2\) diffusion process becomes a non-rate-determining step as it is an independent gas–solid interface. Moreover, by varying the reaction temperature of the NRR, both the \(NH_3\) yield and faradaic efficiency of the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP catalyst increase simultaneously (Fig. 4d). For instance, the NRR yield is about 2.5 times higher at 60 °C than at 0 °C, indicating that mass transfer plays a key role in enhancing the reaction rate of the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP catalyst. In accordance with the Arrhenius equation and Arrhenius plot (Fig. S29†), the apparent activation energy of \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP for the NRR is calculated to be 11.4 kJ mol\(^{-1}\). The UV/Vis absorption spectra of various samples (Fig. 4e) and photographs of \(NH_3\)-containing solutions before (Fig. S26†) and after working for 100 h (Fig. S27†) indicated that the \(V_o\)-rich NiCo\(_2\)O\(_4\)@HNCP remains stable during the NRR process.
and after staining with indophenol indicator (Fig. 4f) are exhibited. After comparing the EIS spectra (Fig. S30†) and the performance of the V<sub>r</sub>-rich NiCo<sub>2</sub>O<sub>4</sub> bulk (1.4 μg h<sup>−1</sup> cm<sup>−2</sup>/6.1 μg h<sup>−1</sup> mg<sup>−1</sup> and 1.6% at −0.25 V) in Fig. S31,† it could be seen that the hollow nitrogen-doped carbon polyhedron template in V<sub>r</sub>-rich NiCo<sub>2</sub>O<sub>4</sub>@HNCP is extremely vital for its enhanced NRR performance, due to the increased specific surface area (Fig. 2d) and well-formed interface between HNCP and V<sub>r</sub>-rich NiCo<sub>2</sub>O<sub>4</sub> nanosheets for charge accumulation/transfer. For the verification of the source of ammonia, a<sup>15</sup>N isotope labeling experiment using NMR (600 MHz) was performed. As shown in Fig. S32,† the <sup>1</sup>H NMR signals of <sup>14</sup>NH<sub>4</sub><sup>+</sup> produced <sup>14</sup>N triplets in the region of 6.8–7.1 ppm. Importantly, the <sup>1</sup>H NMR signal of <sup>15</sup>NH<sub>4</sub><sup>+</sup> only produced an <sup>15</sup>N doublet without the appearance of <sup>14</sup>N triplets in the same region, which demonstrates that the doped nitrogen atoms in the HNCP template are stable and do not escape from the structures. Therefore, the source of ammonia is the feed N<sub>2</sub> gas rather than the electrocatalyst.

For further detailed insights into the structure–activity relationship between the V<sub>r</sub>-rich NiCo<sub>2</sub>O<sub>4</sub>@HNCP catalyst and its enhanced NRR properties, DFT calculation was carried out from the perspective of thermodynamic and kinetic acceleration. First, from the thermodynamic point of view, the electrons that previously occupied the O 2p orbital would partially delocalized to the neighboring Ni/Co cations after introduction of oxygen vacancies, which suggests that a surface with oxygen vacancies is much more activated. Meanwhile, a rational model for the V<sub>r</sub>-rich NiCo<sub>2</sub>O<sub>4</sub>@HNCP catalyst was constructed by aligning optimized V<sub>r</sub>-rich NiCo<sub>2</sub>O<sub>4</sub> with highly conductive nitrogen-doped carbon (Fig. 4g and S33†). After analysis in detail,
abundant charges accumulated on the blurry interface between \( V_{o}\)-rich NiCo\(_2\)O\(_4\) and nitrogen-doped carbon, leading to the successful generation of highly active regions for the electro-catalytic process. As shown in Fig. S34 and S35,\(^\dagger\) the electrons are prone to transfer from nitrogen-doped carbon to \( V_{o}\)-rich NiCo\(_2\)O\(_4\) due to their inconsistent charge distribution. In turn, the Ni/Co cations show increased electronic states of the orbital around the Fermi level, which is beneficial for activation of \( \text{N}_2 \) and formation of an N-catalyst bond. From the kinetic point of view, the hollow nitrogen-doped carbon polyhedron template endows the \( V_{o}\)-rich NiCo\(_2\)O\(_4\) nanosheets with a higher specific surface area with more exposed active sites for adsorption/activation of N-related species. Attributed to the structural merits of the \( V_{o}\)-rich NiCo\(_2\)O\(_4@\)HNCP catalyst, a possible NRR mechanism is depicted in Fig. 4h and i. Firstly, the \( \text{N}_2 \) gas can be easily adsorbed on the surface of the \( V_{o}\)-rich NiCo\(_2\)O\(_4@\)HNCP catalyst to form chemisorbed Co[Ni]–N\(_2\) bonds, which can be denoted as \( \text{N}_2(g) \rightarrow \text{N}_2^* \) (here, the asterisk \( \ast \) denotes an adsorption site). After full structural relaxation, two energetically favorable configurations were found: end-on and side-on. On the \( V_{o}\)-poor NiCo\(_2\)O\(_4\) surface, an \( \text{N}_2 \) molecule was more likely to anchor in the end-on configuration with a Co–N bond length of 1.84 \( \text{Å} \) (Fig. S36a\(^\dagger\)), whereas, on the \( V_{o}\)-rich NiCo\(_2\)O\(_4\) surface, two Co–N bonds (1.20 \( \text{Å} \) in length) in the side-on configuration are formed with an elongated N–N bond length from 1.12 \( \text{Å} \) to 1.16 \( \text{Å} \) (Fig. S36b\(^\dagger\)). When taking \( \Delta E_{\text{ZPE}} \) and entropy into consideration, the \( \Delta G \) values for \( \text{N}_2 \) adsorption are –0.05 eV for the \( V_{o}\)-rich NiCo\(_2\)O\(_4\) surface and –0.57 eV for the \( V_{o}\)-poor NiCo\(_2\)O\(_4\) surface, respectively. Secondly, six consecutive protonation and reduction processes on the \( V_{o}\)-rich(poor) NiCo\(_2\)O\(_4\) surfaces were further proposed with atomic configurations at various states of each elementary step (Fig. S37\(^\dagger\)). As discussed in Fig. 4i and Table S3,\(^\dagger\) the free energies of all these states were slightly downhill for the \( V_{o}\)-rich NiCo\(_2\)O\(_4\) surface compared to the \( V_{o}\)-poor NiCo\(_2\)O\(_4\) surface, which also proves that the successful introduction of oxygen vacancies in NiCo\(_2\)O\(_4\) is beneficial for the nitrogen reduction reaction process theoretically.

We further studied the NRR activity of other spinel-structured nanosheet wrapped HNCP, such as ZnCo\(_2\)O\(_4@\)HNCP and Co\(_3\)O\(_4@\)HNCP, in which oxygen vacancies were deliberately introduced. It should be noted that the XPS O 1s spectra (Fig. S38\(^\dagger\)) reveal that abundant oxygen vacancies were successfully introduced into the surface of both the \( V_{o}\)-rich ZnCo\(_2\)O\(_4@\)HNCP and \( V_{o}\)-rich Co\(_3\)O\(_4@\)HNCP catalysts. As shown in Fig. 5a, all the catalysts with abundant oxygen vacancies showed a higher NH\(_3\) yield rate and faradaic efficiency than their \( V_{o}\)-poor counterparts in 0.1 M Na\(_2\)SO\(_4\). Taking \( V_{o}\)-rich ZnCo\(_2\)O\(_4@\)HNCP and its \( V_{o}\)-poor counterpart as examples, the NH\(_3\) yield rate and faradaic efficiency for the \( V_{o}\)-rich ZnCo\(_2\)O\(_4@\)HNCP catalyst were 3.7 \( \mu \text{g} \text{ h}^{-1} \text{ cm}^{-2}/16.0 \mu \text{g} \text{ h}^{-1} \text{ mg}^{-1} \) and 3.6%, respectively, which are much more outstanding than those of the \( V_{o}\)-poor ZnCo\(_2\)O\(_4@\)HNCP catalyst (1.6 \( \mu \text{g} \text{ h}^{-1} \text{ cm}^{-2}/6.9 \mu \text{g} \text{ h}^{-1} \text{ mg}^{-1} \) and 1.7% at –0.25 V). Besides, the time-dependent curves of various catalysts at –0.25 V (Fig. 5b) exhibited excellent stability, indicating the stable vacancy structure in both the \( V_{o}\)-rich ZnCo\(_2\)O\(_4@\)HNCP and \( V_{o}\)-rich Co\(_3\)O\(_4@\)HNCP catalysts during the NRR process.

Conclusions and outlook

In summary, we uncovered the positive role of oxygen vacancies in spinel-structured nanosheets on hollow N-carbon polyhedra (e.g. \( V_{o}\)-rich NiCo\(_2\)O\(_4@\)HNCP, \( V_{o}\)-rich ZnCo\(_2\)O\(_4@\)HNCP, and \( V_{o}\)-rich Co\(_3\)O\(_4@\)HNCP) towards the electrocatalysis of the nitrogen reduction reaction. For example, the \( V_{o}\)-rich NiCo\(_2\)O\(_4@\)HNCP catalyst showed higher production yield (NH\(_3\): 4.1 \( \mu \text{g} \text{ h}^{-1} \text{ cm}^{-2}/17.8 \mu \text{g} \text{ h}^{-1} \text{ mg}^{-1} \) and faradaic efficiency: 5.3%), good selectivity and high stability when compared with its \( V_{o}\)-poor counterpart (NH\(_3\): 1.6 \( \mu \text{g} \text{ h}^{-1} \text{ cm}^{-2}/6.9 \mu \text{g} \text{ h}^{-1} \text{ mg}^{-1} \) and faradaic efficiency: 1.8%). As revealed by DFT calculations, the oxygen vacancies enhance the reactivity of the active sites, leading to reduced stabilization energy of NNH groups. Meanwhile, the HNCP template increased the number of active sites for facilitating the reaction on the surface of \( V_{o}\)-rich NiCo\(_2\)O\(_4\) nanosheets and improved the conductivity for interfacial electron transfer between \( V_{o}\)-rich NiCo\(_2\)O\(_4\) and HNCP. Systematic study from both theoretical and experimental aspects further confirmed the superior kinetics for NH\(_3\) production using \( V_{o}\)-rich NiCo\(_2\)O\(_4@\)HNCP. Therefore, this work provides a guideline for the rational design of novel and highly efficient catalysts towards \( \text{N}_2 \) electrochemical reduction by increasing the surface area and introducing surface oxygen vacancies in spinel-structured nanosheets simultaneously.

Experimental section

Details of the synthetic procedures, characterization and theoretical calculation methods can be found in the ESI\(^\dagger\).

Conflicts of interest

The authors declare no conflict of interest.

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Fig. 5 (a) Average NH\(_3\) yields and faradaic efficiency of other spinel-structured nanosheet wrapped HNCP (ZnCo\(_2\)O\(_4@\)HNCP and Co\(_3\)O\(_4@\)HNCP) with and without oxygen vacancies after chronocoulometry testing at –0.25 V versus RHE. (b) Time-dependent current density curves of various catalysts for the NRR at –0.25 V versus RHE.
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