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# Utilizing the Wadsley-Roth structures in TiNb<sub>2</sub>O<sub>7</sub>@C microspheres for efficient electrochemical nitrogen reduction at ambient conditions

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# Abstract

The electrochemical nitrogen reduction reaction (NRR) is an attractive approach for sustainable ammonia production, which is anticipated as a potential carbon-neutral hydrogen carrier. However, compared to the competing HER, the NRR suffers from a major drawback of low selectivity and conversion efficiency due to the high negative potential driving the NRR. Therefore, developing optimal electrocatalysts that inhibit the HER and promote the NRR is crucial for electrochemical ammonia synthesis. In this study, we demonstrated that TiNb<sub>2</sub>O<sub>7</sub>@C (TNO@C) microspheres with Wadsley-Roth crystal structure as efficient NRR electrocatalysts. The prepared TNO@C microspheres were calcined at controlled temperatures, and their electrochemical performances were investigated in different electrolytes. The cationic size effects and the pH of the electrolytes were analyzed to influence the NRR activity actively. The prepared TNO@C900 electrocatalyst exhibits high faradaic efficiency (13.11%) and ammonia yield (0.62  $\mu$ mol h<sup>-1</sup> cm<sup>-2</sup>). The prepared TNO@C900 microspheres with Lewis acid sites of the Nb cations and the oxygen vacancy  $(V_o)$  coupled Ti cations can effectively improve the NRR performances of TNO@C electrocatalysts. Further, the in situ and theoretical analysis reveals the associative NRR pathway, and the purity and source of produced ammonia were carefully verified. This work elucidates that a controlled surface and morphology engineering strategy with appropriate NRR active elements can significantly increase the faradaic efficiency and ammonia yield.

**Keywords** NRR  $\cdot$  Wadsley-Roth crystal  $\cdot$  TiNb<sub>2</sub>O<sub>7</sub>  $\cdot$  Oxygen vacancies  $\cdot$  Cation effect

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# 1 Introduction

Modernized technical society has been obliged to adopt a renewable energy-based civilization, where green hydrogen is recognized as the essential eco-friendly approach. However, the use of ammonia as a hydrogen carrier for long-term hydrogen storage, which has been unsolved for decades, is recognized as a promising solution. Ammonia has a high energy density  $(5.52 \text{ kWh kg}^{-1})$  and gravimetric hydrogen content (17.6 wt%) and can be stored in liquid form by compression to approximately 0.9 MPa at ambient temperature [1]. Thus, ammonia has begun to receive international attention as a subject of discussion for energy storage and conversion to power the hydrogen economy. Industrially, the conversion of N<sub>2</sub> to NH<sub>3</sub> is carried out via the Haber-Bosch (HB) process at high temperatures and pressures (300-550 °C/150-250 atm), which consumes an enormous amount of energy, about 1.4% of the total energy used by mankind [2-4]. Therefore, developing an efficient and sustainable strategy to activate and convert abundant N<sub>2</sub> to ammonia under ambient conditions via electrochemical NRR is a potential solution to current clean energy development challenges [5].

The electrochemical NRR method requires water as a proton source to remove natural gas as in the HB process and proposes an eco-friendly and cost-effective approach for ammonia synthesis using renewable electricity. Despite its notable advantages, NRR is kinetically sluggish as it requires an energy of about 941 kJ mol<sup>-1</sup> to dissociate N<sub>2</sub> due to its strong triple bond [6]. Currently, transition metal catalysts are generally effective for activating linear gas molecules, such as N<sub>2</sub> [7–9]. Therefore, electrocatalysts are appropriately designed with transition metals to selectively activate N<sub>2</sub> molecules by utilizing the lone electron pairs in the molecule that exhibit Lewis basic properties.

The electrocatalysts can be fabricated with metallic or non-metallic candidates imposing a Lewis acidic character to uptake the N<sub>2</sub> molecule. Several important candidates include early transition metals and main group elements, which impose Lewis acidic nature to selectively activate the triple bonds of N<sub>2</sub> facilitating NRR. Notably, Ti, V, Nb, and Mo of the early transition metals-based electrocatalysts were crucially analyzed for effective NRR performances (Table S1). The early transition metal-based electrocatalyst not only enhances N2 adsorption but also suppresses the kinetically favorable hydrogen evolution due to the abundant presence of protons in aqueous electrolyte. However, achieving a high yield of NH<sub>3</sub> and efficiency via electrocatalytic NRR is challenging because it requires the high catalytic activity of an electrocatalyst to effectively activate the stable triple bond of N<sub>2</sub> and inhibit the competitive hydrogen evolution reaction (HER) [1]. To

overcome the efficiency problem, optimal electrocatalysts are desired to enable enhanced NRR activity and selectivity. Additionally, suppressing HER by choosing various electrolytes has a huge impact by kinetically affecting the proton availability over the electrocatalyst surface. The pH of the electrolytes and the cation effects with diversified hydration shells impose kinetic effects on the NRR performance of the electrocatalyst [2]. Hence, a higher ammonia yield and FE can be achieved by choosing the appropriate electrolytes. According to the acceptance-donation mechanism, the unoccupied d-orbitals of the transition metal atoms will accept an electron from the N<sub>2</sub> orbitals. They will donate a d-electron to the anti-bonding orbitals of N<sub>2</sub>. Finally, this electron transfer weakens the N≡N bond and activates N<sub>2</sub> for the further reduction process. However, transition metal-based catalysts still face challenges such as low selectivity, low Faraday efficiency (FE), and inefficient productivity [3-5].

Notably, early transition metal, Nb-based materials are cautiously explored as promising electrocatalysts to achieve high ammonia yield and higher selectivity towards NRR [6]. Reports on Nb-based electrocatalysts include the works on Nb<sub>2</sub>O<sub>5</sub> nanofibers [7], NbO<sub>2</sub> nanorods [8], Nb<sub>2</sub>O<sub>5</sub> nanowire arrays [9], Nb<sub>3</sub>O<sub>7</sub>(OH)/CFC [10], NbSe<sub>2</sub> nanosheets [11], Nb<sub>2</sub>O<sub>5</sub> nanochannel film [12], and Nb<sub>2</sub>CT<sub>x</sub> MXene [13]. Niobium oxides as an electrocatalyst show a consistent performance with a significant FE, which can be attributed to sufficient HER suppression in the electrocatalyst. Kong et al. [9] reported the Nb<sub>2</sub>O<sub>5</sub> nanowire arrays in an acidic environment, which provided an ammonia yield of about  $1.58 \times 10^{-10}$  mol s<sup>-1</sup> cm<sup>-2</sup> at an FE of about 2.26% [9]. However, a low yield and FE were experienced, which show higher HER from the electrocatalyst. Wang et al. [11] reported the Nb<sub>2</sub>O<sub>5</sub> nanochannel films as the NRR electrocatalysts with a maximum ammonia yield and FE of about  $2.52 \times 10^{-10}$  mol s<sup>-1</sup> cm<sup>-2</sup> and 9.81%, respectively, in neutral electrolytes. The superior activity of the electrocatalysts can be attributed to the rich oxygen vacancies in the electrocatalysts but suffers from structural transformations. This adequately exposes the instability of the electrocatalyst. To account for the increased conductivity, Zhang et al. [13] reported the MXene-based Nb<sub>2</sub>CT<sub>x</sub> which after exfoliation and etching formed layers of Nb<sub>2</sub>O<sub>5</sub>/C. The Nb<sub>2</sub>O<sub>5</sub> NP on carbon sheets exhibited an ammonia yield and FE of about 29.1  $\mu$ g h<sup>-1</sup> cm<sup>-2</sup> and 11.5%, respectively. One important drawback of the MXene nanosheets is the feasible degradation of the sheets in presence of water and oxygen [14].

Besides, Ti-based electrocatalysts are developed that deliver significant electrocatalytic activity for NRR. The oxidation states of Ti-based catalysts, oxygen vacancy engineering, and the efficient support activity of  $TiO_2$  supplement the NRR performance in diverse electrocatalysts. For instance, Li et al. [15] designed the  $TiO_2$  catalyst by

tuning the oxidation states of Ti via a dual anion substitution strategy. The prepared NS-TiO<sub>2</sub>/C with N and S anions effectively regulated the oxidation states of Ti which boosts the NRR efficiency to about 25.49%. The substitutional and interstitial bonds of Ti-N and Ti-S in the anatase TiO<sub>2</sub> generate oxygen vacancies and highly active Ti<sup>3+</sup> species, which infer better electronic conductivity and efficient N2 activation. Similarly, Wu et al. [16] designed the Cu-TiO<sub>2</sub> electrocatalyst where the mixed valent Cu atoms modulate the oxygen vacancy concentration and formation of Ti<sup>3+</sup> defect sites, which reveal highly efficient NRR performances. DFT studies for Cu-TiO<sub>2</sub> revealed that with the formation of  $Ti^{3+}$ states, multiple oxygen-vacant sites are created and lie below the Fermi level. Therefore, tuning the oxidation states of Ti and oxygen vacancy engineering in Ti-based catalysts enhances the NRR performance. Additionally, Ti oxides are also used as supports for various catalysts like Au/TiO<sub>2</sub> [17],  $TiO_2/Ti_3C_2T_x$  [18], Pd/TiO\_2 [19], and Ru/TiO\_2 [20].

In order to achieve higher NRR catalytic performance by realizing a stable structure and improved electronic conductivity, we propose the Wadsley-Roth shear crystallographic structure for the NRR applications. The Wadsley-Roth crystal structure is a type of layered crystal structure, which consists of stacked layers of atoms or molecules. In this structure, the layers are made up of hexagonal rings of atoms arranged in a honeycomb pattern. These rings are connected by bridges of atoms that form channels or pores throughout the structure. The Wadsley-Roth crystal structure is widely used in materials science and engineering because of its unique properties, such as high surface area, tunable pore size, stability, selectivity, and versatility. The TiNb<sub>2</sub>O<sub>7</sub> (TNO) structures belong to the Wadsley-Roth family of crystal structures, which have been identified as important electrode materials for electrochemical applications [21–23]. The significance of the TNO structures in the electrochemical application is due to the presence of multiple redox couples and improved electron conductivity [21, 24–32]. The presence of multiple redox couples in TNO provides the necessary active sites for the N<sub>2</sub> reduction reaction. On considering the structural properties, TiNb<sub>2</sub>O<sub>7</sub> exhibits a monoclinic C2/m phase with Ti and Nb cations present on the octahedral sites of a ReO<sub>2</sub>-type shear crystallographic structure [29-32]. Besides, the structures have been studied under various calcination temperatures, which show outstanding stability and porous structures [21]. Since oxygen vacancies can affect the properties of a material, such as electrical conductivity, magnetic properties, or catalytic activity, the potential for redox activity can be further increased by imposing higher oxygen vacancies in the TNO crystal structure [25, 28, 33, 34]. In this work, we report the electrochemical NRR performances of the Wadsley-Roth crystal structures in TiNb<sub>2</sub>O<sub>7</sub>@C (TNO@C) microspheres. The TNO@C microspheres were prepared by the facile hydrothermal procedure and calcined at various temperatures to attain the optimum electrocatalyst. In addition, the calcined TNO@C electrocatalysts were studied for electrocatalytic NRR under various electrolytes.

# 2 Experimental section

# 2.1 Materials

Titanium isopropoxide (TTIP), niobium chloride (NbCl<sub>5</sub>), urea, oleic acid, polyvinylidene difluoride (PVDF), N-methyl 2-pyrrolidine (NMP), and carbon black were purchased commercially. All the chemicals purchased were of analytical grade and used without further purification.

#### 2.2 Synthesis of TiNb<sub>2</sub>O<sub>7</sub> microspheres

The TiNb<sub>2</sub>O<sub>7</sub> (TNO@C) electrocatalysts were prepared by the facile hydrothermal method, followed by calcination. A stoichiometric amount of TTIP, NbCl<sub>5</sub>, and urea was dissolved into 20 mL of ethanol separately. Subsequently, the solution containing urea and NbCl<sub>5</sub> was added to the TTIP solution and stirred for 30 min. In order to achieve a uniform carbon coating on the TiNb2O7 particles, oleic acid which acts as a carbon source and capping agent was added to the starting precursor solution. Then, the solution was transferred to the 80-mL Teflon-lined stainless steel autoclave container that was kept at 200 °C for 24 h. At the end of the process, the obtained white color powder was washed several times using distilled water and ethanol and dried at 80 °C for 12 h. Finally, the sample was calcinated at 800 °C for 3 h under an Ar atmosphere to attain the crystalline TiNb<sub>2</sub>O<sub>7</sub>@C microspheres. The prepared samples were denoted as TNO@C700, TNO@C800, and TNO@C900, relating to their experimental conditions, respectively.

#### 2.3 Characterization of the materials

The crystal structure and phase formation of the samples were identified using powder X-ray diffraction (XRD) (Rint 1000, Rigaku, Japan) with Cu K $\alpha$  radiation ( $\lambda$  = 1.5418 Å). X-ray photoelectron spectroscopy (XPS) analysis (K-ALPHA +, Thermo scientific, USA) was performed to determine the oxidation states and analyze the chemical bonding between the surface elements. The morphologies of the samples were investigated through scanning electron microscopy (SEM) (JSM-7500F, JEOL, Japan) and transmission electron microscopy (TEM) (JEM-2100F, JEOL, Japan). The energy-dispersive X-ray spectroscopy (EDX) for elemental mapping characterizations was investigated through high-resolution TEM (HRTEM).

# 2.4 Calculation of the strain in TNO@C samples

The strain in the TNO@C samples was calculated using the William-Hall (W–H) method using the following equation (Eq. 1).

$$\beta \cos\theta = \frac{k\lambda}{D} + \varepsilon(4\sin\theta) \tag{1}$$

where  $\beta$  is the full-width at half maximum (FWHM) value calculated from the XRD patterns,  $\theta$  is the half of the diffraction angle of the corresponding diffraction peaks, *k* is the Scherrer constant (*k*=0.94),  $\lambda$  is the wavelength of the incident X-rays, *D* is the interplanar spacing, and  $\varepsilon$  is the slope of the equation resembling the strain in the sample. The W–H equation forms a straight line in the graph plotted for  $4\sin\theta$  vs.  $\beta$ cos $\theta$  [35].

# 2.5 Fabrication of the electrode

The working electrode was prepared by brush-coating the homogeneous slurry of TNO@C on a precleaned carbon cloth substrate. The carbon cloth substrate was cut into a geometric area of  $1 \times 1$  cm<sup>2</sup> and was cleaned with diluted HCl solution (for the ratio of 1:4) for 5 min. After washing thoroughly with DI water to remove the residual acid solution, the substrates were dried. The homogeneous slurry was prepared by mixing the active material of TNO@C powder, carbon black, and PVDF in the ratio of 8:1:1 using 0.2 mL of NMP. The obtained slurry was coated over the precleaned substrates using a paintbrush and dried overnight at 80 °C in a vacuum oven. The mass loading on the coated electrode was approximately ~ 1 mg cm<sup>-2</sup>.

#### 2.6 Electrochemical measurements

Electrochemical tests were performed in a three-electrode cell configuration with the VMP3-Biologic multi-channel potentiostat. Fifty milliliters of various electrolytes (0.1 M KOH, 0.1 M  $Na_2SO_4$ , 0.1 M LiClO<sub>4</sub>) was saturated with Ar or  $N_2$  gas for 30 min prior to the electrochemical measurements. Pt wire and the carbon cloth were used as the counter electrode and working electrode. Hg/HgO and saturated calomel electrode (SCE) were used as the reference electrode for alkaline (0.1 M KOH) and neutral (0.1 M  $Na_2SO_4$  and 0.1 M LiClO<sub>4</sub>) electrolytes, respectively. The observed reference electrode potential was converted to reversible hydrogen electrode (RHE) potential through the following equation (Eq. 2).

 $E(RHE) = E(Obv.Ref.Potential) + E^{o}(Std.Ref.Potential) + 0.0591pH$ (2)

 $N_2$  gas was continuously fed into the electrochemical cell during the experiments. Chronoamperometry (CA)

measurements were taken at various potentials from -0.35 to 0 V vs. RHE for 2 h.

#### 2.7 Determination of the produced ammonia

The produced NH<sub>3</sub> was spectrophotometrically determined using the salicylate method. After each electrochemical measurement, 5.0 mL of the sample solution was first taken from the electrolyte with the micropipette. Afterward, a fresh test solution (sodium salicylate, NaOH, sodium nitroferricyanide, and NaOCl) purchased from API Co. was added to the sampled electrolyte. After the electrolyte was allowed to stand at room temperature for 10 min, the absorption spectrum was recorded with a UV-vis spectrophotometer (P4300 Evolution 220 Spectrophotometer). The concentration of the sample was determined using the absorbance obtained at a wavelength around ~ 680 nm. The NH<sub>3</sub>/NH<sub>4</sub><sup>+</sup> concentration–calibration curve was constructed using standard NH<sub>4</sub>OH solution through a series of ammonia concentrations ranging from 0 to 8 ppm, as shown in Fig. S1. The fitting curve (absorbance intensity  $= 0.12963 \times \text{ammonia}$ concentration + 0.00706) shows a good linear relationship between the absorbance value and the NH<sub>3</sub> concentration.

# 2.8 Calculation of the yield rate of ammonia production and faradaic efficiency (FE)

The yield rate of ammonia production and faradaic efficiency are calculated using Eqs. 3 and 4, respectively.

Ammonia yield rate, 
$$r_{\rm NH_3}(\mu {\rm mol} {\rm h}^{-1}{\rm cm}^{-2}) = \frac{\left[{\rm NH}_4^+\right] \times V}{t \times A}$$
(3)

Faradaic efficiency, FE (%) = 
$$\frac{3F \times r_{\rm NH_3}}{J}$$
 (4)

where,  $r_{\rm NH_3}$  is the yield rate of ammonia production (mol h<sup>-1</sup> cm<sup>-2</sup>), [NH<sub>4</sub><sup>+</sup>] is the concentration of the produced ammonium ion (mol L<sup>-1</sup>), *V* is the volume of the electrolyte solution (mL), *t* is the time of NRR electrolysis (hours), *A* is the overall electrode area (cm<sup>2</sup>), *J* is the current density (mA cm<sup>-2</sup>) at the corresponding applied potential, and *F* is the Faraday constant (96 485 C mol<sup>-1</sup>).

#### 2.9 Computational details

All electronic energies and forces were calculated with density functional theory (DFT) calculation using the Vienna Ab initio Simulation Package (VASP) with projector augmented wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) functional with D3 dispersion correction was used to describe the electronic exchange and correlation. A 550 eV plane-wave kinetic energy cutoff was chosen. The Brillouin zone was sampled with  $3 \times 3 \times 1$  based on the Gamma-centered scheme. Electron and geometry convergence thresholds were set to  $10^{-6}$  eV and  $5 \times 10^{-2}$  eV/Å, respectively. The slab included a 15-Å-thick vacuum layer along with the z-direction. The top two layers of the slab and adsorbates were allowed to relax until the relaxation, whereas the bottom two layers were fixed during the optimization process. The electronic structure was also studied with the inclusion of a Hubbard *U* correction (DFT + *U*). *U* values of 5.2 eV were applied to Ti and Nb. An exchange parameter, *J*, of 1 eV was applied in both cases, and The Brillouin zone was sampled with  $6 \times 6 \times 1$ .

The surface established for the TiNb<sub>2</sub>O<sub>7</sub> Slab model is (110), which was established through XRD and TEM analysis. DFT calculations on (110) were performed to investigate the NRR mechanisms over TNO@C at U=0 V and pH 7. The Gibbs free energy change was calculated at 298 K and 1 atm, and the (H<sup>+</sup> + e<sup>-</sup>) pair was considered to have half the chemical potential of H<sub>2</sub> at pH 0. To compare experiments and calculations, we investigated the NRR reaction at pH 7, which was used in the experiments, and for each step, the Gibbs free energy change and adsorption energy were calculated as follows.

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S - neU + \int_{0}^{T} C_{V} dT - k_{B} \ln 10 \times ph$$
(5)

$$\Delta E_{\text{adsorption}} = E_{\text{slab}+\text{adsorbate}} - \left(E_{\text{slab}} + E_{\text{adsorbate}}\right) \tag{6}$$

Here,  $\Delta E$  is the change of electronic energy,  $\Delta S$  is the change of zero-point correction energy, *T* is absolute temperature,  $\Delta S$  is the change of entropy, *n* is the number of transferred electrons in each step,  $k_{\rm B}$  is the Boltzmann constant, and  $C_{\rm V}$  is the heat capacity.  $\Delta ZPE$ ,  $\int_0^T C_{\rm V} dT$ , and  $\Delta S$  can all be derived from the vibrational frequencies of the adsorbed species. For the adsorption energy ( $\Delta E_{\rm adsorption}$ ) calculation,  $E_{\rm slab+adsorbate}$  is the total energy of the system after adsorption,  $E_{\rm slab}$  is the total energy of the bare surface, and  $E_{\rm adsorbate}$  is the total energy of adsorbate in the gas phase.

# **3** Results and discussion

# 3.1 Physicochemical characterization of TNO@C microspheres

The TiNb<sub>2</sub>O<sub>7</sub> (TNO@C) microspheres were synthesized by a facile surfactant-assisted hydrothermal method followed by calcination, as shown in Fig. 1a. The phase structures and crystallinity of the TNO@C samples were analyzed from the X-ray diffraction (XRD) studies [29, 32]. Figure 1b displays the XRD patterns of the as-prepared TNO, TNO@ C700, TNO@C800, and TNO@C900 samples with varying calcination temperatures. The pre-dominant peaks observed

Fig. 1 a Schematic representation of the synthesis route of TNO@C electrocatalyst. b XRD patterns of the prepared TNO@C electrocatalysts under various calcination temperatures from 700 to 900 °C. c William-Hall (W–H) plot of TNO@C electrocatalyst calculated from XRD



for TNO@C700, TNO@C800, and TNO@C900 electrocatalysts at  $2\theta = 24^{\circ}$ ,  $26^{\circ}$ ,  $32.5^{\circ}$ ,  $44^{\circ}$ ,  $48^{\circ}$ , and  $55^{\circ}$  correspond to the lattice planes of (110), (003), (51 $\overline{2}$ ), (005), (020), and (111 $\overline{3}$ ), respectively. The XRD patterns are ascertained to match the standard powder diffraction file (JCPDS: 98–000-6120) [22, 29, 32]. The observed lattice planes are indexed to the monoclinic ReO<sub>2</sub> type crystal structure with the C2/m space group of TiNb<sub>2</sub>O<sub>7</sub>. The obtained XRD patterns for TNO@C match well with the Wadsley-Roth structures of TiNb<sub>2</sub>O<sub>7</sub>. The Wadsley-Roth structures have distributed Ti and Nb metal ions at the octahedral positions linked by edges and corners of the TiNb<sub>2</sub>O<sub>7</sub> lattice, as reported in previous literature [29, 32, 36, 37]. No impure phases of Nb<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, or any Ti-Nb-oxides can be noted from the XRD peaks, which show pure phase formation of TiNb<sub>2</sub>O<sub>7</sub>.

From the XRD patterns, we notice that the as-prepared TNO samples exhibit a broad, amorphous peak that indicates lower crystallinity due to oleic acid structures. During calcination, sharp peaks evolve steadily from the as-prepared sample, which shows increasing crystallinity of TNO@C with increasing calcination temperatures. The TNO@ C700 and TNO@C800 samples show semi-crystalline peaks, which is attributed to the partial crystallization of the TNO@C samples and imperfect carbonization of the surface. Besides, with a further increase in calcination temperature to 900 °C, the TNO@C samples were better crystallized, as more intense and sharp diffraction peaks were observed for TNO@C900. Therefore, the XRD results for TNO@C confirmed the formation of a Wadsley-Roth crystal structure with a  $\text{ReO}_2$ -type monoclinic phase on  $\text{TiNb}_2\text{O}_7$ with a C2/m space group and that calcination at higher temperatures produced TNO@C with higher crystallinity. The Williamson-Hall (W-H) plots for the TNO@C electrocatalysts show the strain evolution in the sample calculated using the W–H equation (Fig. 1c). The W–H equation resembles a linear form in which the slope relates to the strain in the sample, and the intercept of the equation relates to the interplanar distance [35, 38]. The W-H plots for TNO@C700 and TNO@C800 samples reveal a negative slope, which indicates the compressive nature of strain (lattice contraction) in the sample. The larger the slope value results in the higher strain in the TNO@C samples. On the contrary, the TNO@C900 sample elucidates a positive strain due to lattice expansion at higher calcination temperatures. Lattice expansion explains the formation of highly accessible pores in crystals that enhance mass transport [39, 40].

The morphology and microstructure of the TNO@C samples were analyzed by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). The FESEM images of the prepared TNO@C samples reveal a uniform monodisperse microsphere morphology and confirm that the surface roughness increases with increasing calcination temperature. The FESEM images of

the as-prepared TNO samples initially show smooth spherical surfaces, as shown in Fig. 2a. However, it is noted that for increasing calcination temperatures, the TNO microspheres become rough due to the decomposition of the surface carbon structures with the lattice oxygen. Consequently, the FESEM images of the TNO@C700 and TNO@ C800 samples show a gradual increase in roughness due to the high-temperature decomposition of the carbon structures on the surface (Fig. 2b, c). Furthermore, the TNO@ C900 microspheres reveal highly rough surfaces due to the decomposition of the carbon structures with the lattice oxygen atoms (Fig. 2d) [41, 42]. The morphological evolution of the TNO@C microspheres is initiated by treating the homogenous mixture of Ti and Nb precursors in ethanol and oleic acid via the hydrothermal method. Here, the oleic acid plays an important role as the capping agent to achieve uniform morphology of the TNO@C microspheres and to avoid agglomeration after growth [43]. Thus, the addition of oleic acid confines the nucleated TNO@C microspheres by altering the surface energies of the microspheres to induce growth in the specified direction. Moreover, the micelle-like structures of oleic acid are supported on the surface of the TNO@C microspheres, which separates adjacent spheres from agglomeration [43]. Hence, the as-prepared monodispersed TNO@C microspheres with uniform size and morphology are achieved by the initial hydrothermal procedure. Secondly, the as-prepared TNO@C microspheres are calcined at high temperatures under Ar atmosphere, which results in the crystallization of the sample. The increasing calcination temperatures (700 °C, 800 °C, and 900 °C) have a direct impact on the decomposition of the oleic acid structures into carbon layers on the surface and crystallization of the TNO@C microspheres. During calcination under the Ar atmosphere, the carbon layers are partially oxidized with the lattice oxygen, which removes an oxygen atom from the lattice sites, forming  $CO_2$  gas [44]. The evolution of  $CO_2$  with the lattice oxygen results in the highly rough surfaces of the TNO@C900 samples. In addition, the increasing calcination temperature crystallizes the TNO@C microspheres and exposes the TNO surfaces due to the decomposition of the carbon layers, as noted from the crystalline peaks in XRD patterns.

Subsequently, the TEM images of the TNO@C900 in Fig. 2e reveal the TNO nanoparticle assembled solid microspheres with a diameter of nearly ~ 3  $\mu$ m. Besides, the high-resolution TEM (HRTEM) images in Fig. 2f show the periodic arrangement of all the lattice planes oriented in the same direction. The amorphous layer, as observed from the HRTEM images, corresponds to the carbon layer. The carbon layer is formed during the pyrolysis of the as-prepared TNO microspheres. The presence of the surfactants (oleic acid) during synthesis acts as a capping agent to facilitate uniform growth of the TNO microspheres



**Fig.2** FESEM images of **a** as-prepared TNO, **b** TNO@C700, **c** TNO@C800, and **d** TNO@C900, respectively. **e** TEM image of the TNO@C900 microsphere, **f**, **g** HRTEM images of the TNO@C900

[45, 46]. The high-temperature pyrolysis of the prepared electrocatalyst causes the evolution of volatile elements, resulting in the formation of a carbon layer on the surface of TNO@C microspheres. The magnified HRTEM image in Fig. 2g reveals the lattice fringes with an interlayer spacing of about 0.37 nm assigned to the most dominant (110) plane of the monoclinic TiNb<sub>2</sub>O<sub>7</sub> crystal structure [29, 30, 47]. The selected area electron diffraction (SAED) patterns for the TNO@C900 microspheres exhibit a typical polycrystalline pattern due to the presence of carbon layers on the surface, as shown in Fig. 2h. The carbon layer is formed as a result of high-temperature pyrolysis of surfactants (oleic acid). Besides, the sharp spots in the SAED patterns correspond to the single-crystalline nature of the TNO@C samples [48]. Hence, the results are consistent with the XRD patterns, which further confirms the crystalline nature of TNO@C900 samples with monoclinic structure. The energy-dispersive X-ray spectrum (EDX) (Fig. 2i-m) shows the uniform elemental distributions of Ti, Nb, O, and C on the TNO@C900 sample. The presence of C is due to the decomposed oleic acid on the surface during the synthesis of the TNO@C microsphere.

The chemical composition and oxidation states of the TNO@C samples under various calcination temperatures were analyzed using X-ray photoelectron spectroscopy

microsphere under various magnifications, **h** SAED patterns of the TNO@C900 microspheres, and **i**–**m** EDX elemental mapping images of TNO@C900 microspheres

(XPS). The high-resolution XPS spectrum of Ti 2p in Fig. 3a displays peaks at 458.2 eV and 464.06 eV, which correspond to Ti  $2p_{3/2}$  and Ti  $2p_{1/2}$ , respectively [27, 49]. The deconvoluted peaks for Ti 2p<sub>3/2</sub> indicate the contributions from Ti<sup>3+</sup> and Ti<sup>4+</sup> at 457.96 eV and 458.59 eV, respectively. The slight deviations in Ti 2p<sub>3/2</sub> peaks elucidate the changes in oxidation states of the sample during the variation in calcination temperatures [34]. A similar trend in the peak difference was analyzed for the Ti  $2p_{1/2}$  peaks, with signals arising for  $Ti^{3+}$  and  $Ti^{4+}$  at 463.34 eV and 464.35 eV, respectively. For TNO@C900 with a high calcination temperature, the cations change from Ti<sup>4+</sup> to Ti<sup>3+</sup>, resulting in a downshift in the spectrum. The relatively higher peak intensity for Ti<sup>4+</sup> indicates the surface dominant tetravalent Ti states present in the octahedral sites of the TNO@C crystal structure [50]. Similarly, the spectra of Nb 3d in Fig. 3b show two broad peaks at 206.78 eV and 209.53 eV corresponding to Nb 3d<sub>5/2</sub> and Nb 3d<sub>3/2</sub>, respectively, for TNO@C900 [27]. The deconvoluted peaks referring to 206.45 eV and 209.23 eV correspond to the Nb<sup>4+</sup> species, and the peaks at 207.09 eV and 209.86 eV correspond to the Nb<sup>5+</sup> species, respectively [8]. It is observed that the peaks of Nb  $3d_{5/2}$  and Nb  $3d_{3/2}$ shift to lower binding energy with increasing calcination temperatures, indicating the partial reduction of Nb<sup>5+</sup> to  $Nb^{4+}$  forming a defective Ti/NbO<sub>6-x</sub> octahedra [34].

**Fig. 3** High-resolution XPS spectra for **a** Ti 2p, **b** Nb 3d, **c** O 1 s, and **d** C 1 s of the TNO microspheres under various calcination temperatures, respectively



The partial reduction in the TNO@C900 sample creates oxygen vacancies in the sample around Nb<sup>4+</sup> ions with electron accumulation on the defective sites [34, 51-54]. Moreover, the Nb<sup>5+</sup> cations have been found to achieve stable octahedral positions in the TNO@C structures, by which they are inferred to be weak active sites for redox reactions [29]. The Nb<sup>4+</sup> sites form a defective octahedron with a lower binding energy shift, which imposes point defects in the TiNb<sub>2</sub>O<sub>7</sub> structure [34]. Therefore, the presence of transition metals such as Ti coupled with the oxygen vacancy and Nb forming a defective octahedron provide partially occupied d-orbitals that are ascribed as effective active sites for N2 adsorption and reduction. Moreover, the stable defective octahedral positions offered by the Wadsley-Roth structure for the Ti and Nb elements reveal sufficient oxygen vacancies, which improve the redox activity of the material. Thus, the presence of Ti<sup>4+</sup> and Nb<sup>4+</sup> cations with modified electron densities can be anticipated as the major active sites in the TNO@C electrocatalysts.

The O1s spectra of TNO@C900 show peaks at 529.45 eV, 530.10 eV, 530.77 eV, and 531.82 eV, corresponding to O-M interactions (M=Nb or Ti), lattice oxygen anions of Ti and Nb octahedra [31, 33, 55, 56], oxygen vacancies (V<sub>o</sub>), and the unreactive carbonyl group, respectively (Fig. 3c) [49, 55, 57, 58]. The non-lattice oxygen signal at 530.77 eV represents O species weakly adsorbed on oxygen vacancies (V<sub>o</sub>) formed during calcination [8, 41, 58], and it was found that increasing the calcination temperature to 900 °C resulted

in a relative decrease in the lattice oxygen anion peak at 530.10 eV compared to the oxygen vacancy peak ( $V_o$ ) at 530.77 eV. This relative peak difference is due to the higher cationic valence states with oxygen vacancies.

The weak peak at 528.6 eV in TNO@C700 corresponds to impure bulk dissolved oxygen species that are converted to lattice oxygen atoms by increasing the calcination temperatures [59]. The functional groups (-COOH) incorporate lone pair of electrons into the metal ions forming a metal oleate complex which forms the desired metal oxide nanoparticles. The presence of the dissolved oxygen as  $O^{2-}$  is formed due to the interaction with the metal d-band and the oxygen species impersonating as a metallic character rather than the usual metal oxides [60, 61]. As suggested in previous literature, charge transferred from the metal to the oxygen species, resulting in the formation of bulk  $O^{2-}$  [61, 62]. Hence, it is suggested that the presence of  $O^{2-}$  in TNO@C700 is due to the dissolved oxygen species formed as a result of strong metal d-band interaction with the oxygen species. In addition, dissolved oxygen species have been noticed to desorb from materials at temperatures above 800 °C [63]. Thus, the increase in oxygen vacancies in the TNO@C electrocatalysts causes point defects between metal ions bonded by the oxygen atoms. The oxygen vacancies promote electron delocalization in the TNO@C900 sample, which increases the electronic conductivity [34]. The repulsion between two adjacent cations due to oxygen vacancies causes lattice strain in TNO@C electrocatalysts [64, 65]. Therefore, the lattice strain induced by the point defects is high in TNO@C900 electrocatalysts, which supports the W–H plots for the TNO@C electrocatalysts.

From the C1s spectra for TNO@C900, peaks at 283.72 eV, 284.67 eV, 285.94 eV, and 288.16 eV arise from interactions between metal ions and the carbon layer, C-C bonds on the surface sp3 bonded carbon, C-O interactions with the lattice oxygen, and the unreactive carbonyl groups, respectively (Fig. 3d). The peak at 283.72 eV finds a relatively increased peak intensity from 800 to 900 °C, which is attributed to the higher M-C bonds on the microspheres. Furthermore, the peak at 282 eV for TNO@C700 corresponds to the M-C-O bonds [66]. The gradual increase in calcination temperature elucidates the reduction of M-C-O bonds to M-C with higher peak intensity, indicating the formation of oxygen vacancies and higher M-C interactions [67]. At high temperatures, the peaks for M-C are relatively higher suggesting the formation of  $MC_x$  moieties [68]. The presence of stronger M-C bonds facilitates electron transfer from the active sites to the conductive carbon layer improving the electrocatalytic activity. However, the bulk presence of the metal carbides was not observed in Ti 2p and Nb 3d spectra and in XRD. The presence of this bond is beneficial for efficient charge transfer in the system.

In addition, the peaks around 284.67 eV correspond to the sp3 C-C interactions from the carbon layer on the TNO@C surface [69]. The peak for C–C becomes relatively sharper as the temperature increases from 700 to 800 °C due to the formation of ordered carbon structures [70]. However, the intensity of the C-C peak decreases at 900 °C due to CO<sub>2</sub> evolution with lattice oxygen at higher temperatures, forming oxygen vacancies, which corroborates the results from the O 1 s spectra [41, 71]. The relatively higher Ti-C peak intensity and the lower C-C peak intensity for 900 °C validate the higher crystallinity of the TNO@C900 samples as inspected from the XRD patterns. The peak at 285.94 eV corresponds to the lattice oxide interaction with the carbon layer, which shows a higher peak intensity for TNO@C900, suggesting an increased stability of TNO with the carbon layer [72, 73]. Thus, from the XPS results, we interpret the active sites for the N2 reduction reaction with modified electronic states.

The Ti<sup>4+</sup> and the Nb<sup>4+</sup> together with the oxygen vacancies can impose adsorption sites for N<sub>2</sub>, and this readily provides electrons for protonation. The oxygen vacancies are anticipated to trap the lattice electrons in the meta-stable state which is exploited during N<sub>2</sub> activation for NRR. In addition, the carbon networks on the surface of the microspheres provide excellent electron conduction pathways. Thus, the TNO@C microspheres were analyzed to be active for efficient NRR performances.

Overall, the TNO@C microspheres exhibit crystallization and lattice expansion due to strain effects as the calcination temperature increases. Thus, defective Ti<sup>4+</sup> and Nb<sup>4+</sup> octahedral sites and oxygen vacancies increase in TNO@ C900 samples fired at higher temperatures. The point defects create a lattice strain, resulting in lattice expansion in the TNO@C900 sample due to crystallization at high temperatures. The Ti<sup>4+</sup> cations support oxygen vacancies, and the reduction of Nb5+ ions to Nb4+ creates electron accumulation sites that serve as Lewis acid sites for N<sub>2</sub> adsorption. In addition, the oxygen vacancies and surface carbon structure promote higher electronic conductivity in TNO@C900 samples. Therefore, TNO@C900 samples with the Wadsley-Roth crystal structure are expected to exhibit higher NRR activity due to the extended lattice caused by the positive strain, Ti<sup>4+</sup>, and Nb<sup>4+</sup> active sites, intrinsic oxygen vacancies, and surface carbon network.

# 3.2 Electrochemical NRR performances of TNO@C electrocatalysts

The electrochemical NRR experiments for TNO@C700, TNO@C800, and TNO@C900 samples were carried out in a three-electrode setup under ambient conditions. The linear sweep voltammetry (LSV) curves for different electrocatalysts are shown in Fig. 4a, which shows an early onset potential for TNO@C900 under N2-saturated 0.1 M Na2SO4 electrolyte. The high current density reveals the N<sub>2</sub> reduction activity of the TNO@C electrocatalysts to produce ammonia. The TNO@C electrocatalysts were subjected to chronoamperometric (CA) tests for 2 h under N2-saturated electrolyte within the potential range of -0.25 to -0.1 V (vs. RHE) (Fig. S2). After 2 h of electrolysis, the electrolytes were collected and stained by the salicylate method to perform UV-absorption tests. The absorption intensity for various potentials was compared with the concentration-calibration curves derived from standard ammonia solutions to analyze the concentration of ammonia produced (Fig. S1a and S1b). As shown in Fig. 4b and S3, the ammonia yields of TNO@C700, TNO@C800, and TNO@ C900 were 0.11  $\mu$ mol h<sup>-1</sup> cm<sup>-2</sup>, 0.18  $\mu$ mol h<sup>-1</sup> cm<sup>-2</sup>, and  $0.62 \text{ }\mu\text{mol }h^{-1} \text{ cm}^{-2}$ , respectively, with TNO@C900 having the highest. The FEs were also 7.6%, 8%, and 13.11%, respectively, with TNO@C900 being the most efficient, showing superior NRR performance compared to TNO@ C700 and TNO@C800 electrocatalysts. However, HER dominates at more negative potentials. Hence, a high ammonia yield rate and FE can be noticed at particular applied potentials. Error bars display the standard deviation for ammonia yield and FE for TNO@C electrocatalyst from three independent electrochemical NRR electrolysis tests.



Fig.4 a LSV polarization curves of the TNO@C electrocatalysts under various calcination temperatures; **b** corresponding ammonia yield and FE of prepared TNO@C electrocatalysts for various calcination temperatures. **c** LSV polarization curves of the TNO@C900 electrocatalyst under  $N_2$ - and Ar-saturated 0.1 M  $Na_2SO_4$  electrolyte, **d** LSV polarization curves of the TNO@C900 electrocatalyst under

various electrolytes, **e** ammonia yield and FE for TNO@C900 electrocatalyst at the various potentials, **f** <sup>1</sup>H NMR spectra of TNO@C900 electrocatalyst at -0.2 V (vs. RHE) in <sup>15</sup>N<sub>2</sub>-saturated electrolyte, **g** long-term stability, and **h** cyclic NRR test for the TNO@C900 electrocatalyst

The high activity of TNO@C900 is attributed to the synergistic interaction of the extended lattice, the cationic Nb<sup>4+</sup> and Ti<sup>4+</sup> metal active sites, and their high accessibility due to the surface carbon structure. Besides, TiNb<sub>2</sub>O<sub>7</sub>, covered with an amorphous carbon layer, incorporates higher electron conductivity to and from the electrocatalytic active sites. The amorphous layer is highly porous due to the evolution of volatile compounds from the skeleton of the surfactants (oleic acids) used in synthesis as a result of high-temperature annealing. This porous carbon layer over TiNb<sub>2</sub>O<sub>7</sub> additionally promotes mass transport towards the active sites.

The combined activity of oxygen vacancies and metal active sites results in improved NRR performance [74]. In contrast, XPS analysis of TNO@C700 showed a high

density of oxygen vacancies, but relatively low NRR performance. The poor performance can be ascribed to the concealment of the metal active sites by the surfactants present on the surface. The presence of oxygen vacancies assists the metal ions in N<sub>2</sub> reduction; however, the oxygen vacancy alone cannot perform NRR. Even though TNO@C800 had a relatively low oxygen vacancy peak, it showed relatively improved ammonia yield and FE due to the exposed metal active sites. TNO@C900 exhibited the highest NRR electrocatalytic activity due to the exposure of metal active centers and the synergistic activity of many oxygen vacancies.

To clearly verify NRR activity, the LSV curves for the TNO@C900 electrocatalyst under Ar- and  $N_2$ -saturated 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte were performed, as shown in

Fig. 4c. For the Ar-saturated electrolytes, at more negative potentials, HER takes place at more negative potentials, which is observed from the higher current density with an onset potential. In the case of the N<sub>2</sub>-saturated electrolytes, the onset potentials shift to a lower value, indicating an enhanced current density, which reveals the feasible N<sub>2</sub> reduction performances [75].

The NRR performances of the TNO@C900 electrocatalyst were evaluated under three different electrolytes such as 0.1 M Na<sub>2</sub>SO<sub>4</sub>, 0.1 M KOH, and 0.1 M LiClO<sub>4</sub>. The variation of the electrocatalytic activity due to various electrolytes can be elucidated from the pH of the electrolyte and the effects of the cationic sizes. The LSV curves in Fig. 4d of the TNO@C900 electrocatalysts performed under different electrolytes show lower onset potentials in the order  $Na_2SO_4 < KOH < LiClO_4$ . The  $Na_2SO_4$  electrolyte and KOH electrolytes display early onset potentials and higher current densities than the LiClO<sub>4</sub> electrolyte. The lower current densities for LiClO<sub>4</sub> are due to the lower charge transfer reactions for NRR under the LiClO<sub>4</sub> electrolyte. Na<sub>2</sub>SO<sub>4</sub> and LiClO<sub>4</sub> are pH-neutral electrolytes, while KOH electrolytes are alkaline. For better electrocatalytic NRR performances, the electrolysis cell must be able to mitigate the competing HER which has been found to be significantly suppressed in pH-neutral aqueous electrolytes [76]. Thus, by providing sufficient protons to the electrocatalyst surface, good  $N_2$ reduction with high FE occurs in the Na<sub>2</sub>SO<sub>4</sub> electrolyte. The size of the cation plays an important role, with better activity in Na<sub>2</sub>SO<sub>4</sub> electrolytes than in LiClO<sub>4</sub> electrolytes. In general, the larger the cation size, the higher the HER suppression on the electrocatalyst surface due to the deformation of the Helmholtz plane by cation adsorption [77–79]. Thus, the Na<sub>2</sub>SO<sub>4</sub> electrolyte behaves as an optimal electrolytic medium for efficient NRR activities.

The reduction performances in Ar saturation can be ascribed to the hydrogen evolution from the electrocatalyst surface in the absence of N<sub>2</sub>. It is analyzed that at N<sub>2</sub> saturation, NRR is dominant, whereas HER is suppressed. However, at more negative potentials, HER dominates. Hence, a high ammonia yield rate and FE can be inspected at certain applied potentials. The CA tests were performed on the TNO@C900 electrocatalyst for 2 h, followed by the salicylate method for ammonia determination on the spent electrolyte (Fig. S6a). The UV-vis curves show an absorption peak at 677 nm, indicating the presence of ammonia by NRR in the electrolyte used (Fig. S6b). The TNO@ C900 electrocatalyst exhibits a maximum ammonia yield  $(0.62 \ \mu mol \ h^{-1} \ cm^{-2})$  and the highest FE of about ~ 13.11% for -0.20 V vs. RHE, which is superior to the performances at other applied potentials (Fig. 4e). The small amounts of  $NH_3$  formed at - 0.25 V (vs. RHE) could be attributed to the competitive adsorption of H<sup>+</sup> species on the electrode surface to perform HER.

The maximum FE and ammonia yield for 0.1 M LiClO<sub>4</sub> are calculated to be 2.3% and 0.4 µmol h<sup>-1</sup> cm<sup>-2</sup> and for 0.1 KOH are 0.39% and 0.16 µmol h<sup>-1</sup> cm<sup>-2</sup>, respectively (Figs. S7, S8). As observed from the ammonia yield and FE plots, electrolytes with variable cations and pH reveal maximum ammonia yield and FE for 0.1 M Na<sub>2</sub>SO<sub>4</sub> than 0.1 M LiClO<sub>4</sub> and 0.1 M KOH. In the case of neutral and alkaline pH, neutral electrolytes deliver higher ammonia yield and FE compared to alkaline electrolytes due to the limited availability of hydroxyl ions, which effectively interact with the active sites than N<sub>2</sub> molecules. Therefore, electrolytes containing neutral pH deliver higher ammonia production performances, as observed from the previous study [80]. Besides, the cation effects play a crucial role in enhancing electrocatalytic activity.

The possible sources of N other than from  $N_2$  feeding gas are N atoms from the electrocatalyst surface and the NO<sub>x</sub> impurities in N<sub>2</sub> feeding gas and electrolyte which can lead to overestimation of the electrocatalyst performance. The NRR performances of TNO@C900 electrocatalysts were performed under static N2-saturated electrolyte, which revealed almost similar ammonia yield and insignificant difference in FE compared to NRR under N<sub>2</sub> flow (Fig. S9). Besides, the N<sub>2</sub>-saturated electrolyte was analyzed for NO<sub>x</sub> contaminants via high-purity liquid chromatography (HPLC) analysis, which does not exhibit any hint of the NO<sub>x</sub> impurities in the N<sub>2</sub> feeding gas compared to the standard data for  $NO_3^-$  and  $NO_2^-$  (Fig. S10). The insignificant differences in ammonia yield and FE may be due to the deviation in N<sub>2</sub> concentration within the N<sub>2</sub>-saturated electrolyte during NRR electrolysis. Hence, the control study with N2-saturated electrolyte and HPLC analysis ensures that ammonia production is from N<sub>2</sub> feeding gas by NRR and rather than from NO<sub>x</sub> impurities.

To investigate the electrocatalytic activities in the TNO@ C900 further, <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were performed after 5-h and 25-h reaction times with  ${}^{15}N_2$  feeding gas under Ar atmospheric conditions, respectively (Fig. 4f). The <sup>1</sup>H NMR indicated a doublet coupling for  ${}^{15}\text{NH}_4^+$  and a triplet coupling for  ${}^{14}\text{NH}_4^+$ , with  ${}^{15}\text{N}_2$ and  ${}^{14}N_2$  functioning as the corresponding N<sub>2</sub> sources [11]. Notably, the Ar-saturated electrolyte reveals the absence of doublet or triplet peaks, indicating the absence of ammonia without N<sub>2</sub> feeding gas. Thereby, <sup>1</sup>H NMR results substantiate the hypothesis that the produced NH<sub>3</sub> originates from the electrocatalytic conversion of the supplied N<sub>2</sub> over the TNO@C900 electrocatalyst. If the produced ammonia were from other N sources or by electrode degradation, the <sup>1</sup>H NMR spectra would result in the co-existence of doublet and triplet peaks for the electrocatalytic conversion of  ${}^{15}N_2$ feeding gas and other undesired N sources. Hence, the control experiments under Ar and N2 saturation conditions and under <sup>15</sup>N<sub>2</sub> feeding gas reveal the ammonia production of TNO@C900 completely by  $N_2$  feeding gas reduction neither due to the NO<sub>x</sub> contaminants in the electrolyte or feeding gas nor by catalytic degradation of the electrode.

Furthermore, long-term and cyclic stability tests were conducted to scrutinize the durability of the catalysts. The current density in the *i*-t curve, determined using the long-term CA method over a duration of 10 h at -0.2 V (vs. RHE), exhibited consistent stability (Fig. 4g). After completing 12 cycles (Fig. 4h), no substantial changes in the ammonia yield rate and FE were inspected, implying that the TNO@C900 composites possess exceptional electrochemical stability. The TNO@C900 electrocatalyst was characterized with XPS, XRD, and FESEM analysis after NRR stability tests. The XPS analysis in Fig. S11 shows that the characteristic peaks of Ti 2p and Nb 3d shifted to their higher oxidation states relative to the sample before the NRR test. This positive shift is due to electron transfer from metal sites into N<sub>2</sub> species during NRR electrolysis [81]. Besides, the O 1 s spectra reveal the formation of C-O bonds due to surface oxidation of TNO@C900 during NRR electrolysis. The M-O bonds corresponding to lattice oxygen anions of Ti and Nb octahedra had disappeared which may be due to the interaction of N2 atoms within the Ti and Nb lattice. However, the M-O bonds for Ti-O and Nb-O species experience a slight shift to higher binding energy without any change in intensity. Thereby, the oxide structure of TNO@C900 holds structural integrity with minor oxidative changes during NRR electrolysis. The C 1 s spectra consequently reveal the peak intensity reduction of C-C bonds, which agrees with the surface oxidation forming C-O bonds in O 1 s spectra. Notably, the M-C bonds significantly disappeared after NRR electrolysis which may correspond to the activity of metal sites towards N2 adsorption and activation during NRR. However, the carboxyl species (O = C - O)has a relatively higher intensity due to the oxidation of the C species. The O = C - O bonds reveal a peak shift to high binding energy due to the adsorption of intermediates and increased surface oxidation during NRR [82-84]. Hence, the XPS results elucidate that the oxide phase of TNO@C900 is undisturbed but a thin oxide layer is formed due to surficial oxidation after NRR electrolysis.

However, the XRD results in Fig. S12 after the NRR stability test reveal insignificant changes to the crystal phase of TNO@C900 electrocatalysts. The XRD analysis confirms that the bulk TNO@C900 did not show any structural variations, and the surface oxidation changes, as analyzed in XPS, have occurred as a result of NRR. Besides, morphological analysis by FESEM after NRR tests has revealed a negligible structural change to the surface, further elucidating the structural robustness of TNO@C900 electrocatalysts (Fig. S13). The enhanced electrocatalytic activity of the TNO@C900 is due to the positive strain and the oxygen vacancy-induced catalytic active centers of Ti<sup>4+</sup> and Nb<sup>4+</sup>, which participate in the N<sub>2</sub> reduction reaction. As shown in Fig. S14 and Table S1, TNO@C900 exhibits better NRR activity at high FE compared to other previously reported electrocatalysts [7, 9, 12, 54, 74, 81, 85–94]. This is attributed to the enhanced performance of the Ti and Nb cation sites supporting the oxygen vacancies in the Wadsley-Roth structured TiNb<sub>2</sub>O<sub>7</sub> electrocatalyst and the carbon layer acting as a conductive support.

# 3.3 Mechanism of NRR on the TNO@C electrocatalyst

The XPS characterization results indicate that the TNO@C structures contain oxygen vacancies along with the Ti<sup>4+</sup> and Nb<sup>4+</sup> cations, which are considered active sites for N<sub>2</sub> adsorption and reduction. The gaseous nitrogen is initially adsorbed on the electrocatalyst surface and is readily protonated by the proton-coupled electron transfer (PCET) steps that finally release ammonia from the surface. N<sub>2</sub> is adsorbed on the Nb and Ti cationic sites by the *acceptance-donation* mechanism, as shown in Fig. 5a. The N atom in its ground state has the highest occupied molecular orbital (HOMO) in  $3\sigma_g$  (bonding orbitals) and the lowest unoccupied molecular orbital (LUMO) in  $1\pi_g^*$  (anti-bonding orbitals) [2]. Moreover, the TNO@C structures have been studied to provide both Nb<sup>4+</sup> and Ti<sup>4+</sup> cationic sites with a d-electron in the Nb<sup>4+</sup> site and the V<sub>o</sub>-assisted Ti<sup>4+</sup> site [7, 8].

On the other hand, the unoccupied d-orbitals of the Nb cationic sites accept an electron from the  $3\sigma_{\sigma}$  orbitals. An electron from the occupied d-orbital of the metal site is donated to the  $1\pi_{\sigma}^{*}$  anti-bonding orbitals. This electron transfer activates the N<sub>2</sub> triple bond, resulting in the elongation of the bonds. The activated N2 is readily protonated by six proton-coupled electron transfer (PCET) steps to evolve NH<sub>3</sub> from the surface. Previous studies suggest that the  $\pi$ -back donation process is feasible in Nb<sup>4+</sup> ions due to a d-electron in its orbitals, as shown in Eq. 7 [8]. On the other hand, the defective Ti<sup>4+</sup> with surface oxygen vacancies  $(V_0 - TiO_2)$  can act as efficient Lewis acid sites for NRR. The oxygen vacancies  $(V_0)$  trap the electrons from the lattice in the meta-stable state  $(V_0 \bullet)$  [95]. The electrons from N<sub>2</sub> are accepted into the unoccupied d-orbitals of Ti<sup>4+</sup> states. The trapped electrons from  $V_0 \bullet$  are then donated to the antibonding  $\pi^*$  orbitals during the acceptance-donation mechanism, as in Eq. 8. The corresponding N<sub>2</sub> activation reactions at the Nb<sup>4+</sup> and Ti<sup>4+</sup> cationic sites are listed below.

$$Nb^{4+} + N_2 \to Nb^{4+} * -(N = N) \bullet$$
 (7)

$$(V_o \bullet -Ti^{4+}) + N_2 \to (V_o - Ti^{4+}) - N = N \bullet$$
 (8)



Fig. 5 a Illustration of the acceptance-donation mechanism on  $N_2$  molecule at the cationic active sites in TNO@C electrocatalyst. b Representation of the ammonia formation by associative alternating and distal pathways on the active sites of TNO@C electrocatalysts

where  $_*$  denotes the transferred  $\sigma$ -electron from N<sub>2</sub> during the *acceptance-donation* mechanism, and  $V_0 \bullet$  denotes the oxygen vacancy with a trapped electron in the meta-stable state. Later, the adsorbed N atoms are ready for protonation, which involves six PCET steps to produce ammonia (NH<sub>3</sub>). The protonation mechanism of the adsorbed N<sub>2</sub> follows either the associative alternating or the associative distal pathway, as shown in Fig. 5b. In the associative alternating pathway, protonation of the adsorbed N2 occurs on alternating N atoms (Eqs. 9-14). Eventually, the desorption of ammonia from both N atoms occurs in the subsequent steps of protonation (Eqs. 13 and 14). In the associative distal pathway, however, N2 protonation occurs in a serial manner (Eqs. 15–20). First, one N atom is protonated completely to form ammonia, which desorbs in the third step after the first protonation (Eq. 17), and then, proton addition begins at the second N atom. The second ammonia molecule is desorbed from the surface in the sixth step after the first protonation (Eq. 20). The detailed associative alternating and distal pathways for the Nb<sup>4+</sup> active sites are described below in Eqs. 9, 10, 11, 12, 13, 14 and 15, 16, 17, 18, 19, 20 respectively.

Associative alternating pathway:

$$Nb^{4+} * -(N = N) \bullet +H^{+} + e^{-} \to Nb^{4+} * -(N = N)H(First protonation)$$
(9)

$$Nb^{4+} * -(N = N)H + H^{+} + e^{-} \rightarrow Nb^{4+} * -(NH = NH)$$
(10)

$$Nb^{4+} * -(NH = NH) + H^{+} + e^{-} \rightarrow Nb^{4+} * -(NH - NH_2)$$
(11)

$$Nb^{4+} * - (NH - NH_2) + H^+ + e^- \rightarrow Nb^{4+} * - (NH_2 - NH_2)$$
(12)

$$Nb^{4+} * - (NH_2 - NH_2) + H^+ + e^- \rightarrow Nb^{4+} * - (NH_2 - -NH_3)(NH_3 \text{ desorption})$$
(13)

$$Nb^{4+} * - (NH_2) + H^+ + e^- \rightarrow Nb^{4+} * - - (NH_3) (NH_3 \text{ desorption})$$
  
(14)

Associative distal pathway:

$$Nb^{4+} * -(N = N) \bullet +H^{+} + e^{-} \rightarrow Nb^{4+} *$$
  
-(N = N)H(First protonation) (15)

$$Nb^{4+} * -(N = N)H + H^{+} + e^{-} \rightarrow Nb^{4+} * -(N = NH_2)$$
(16)

$$Nb^{4+} * - (N = NH_2) + H^+ + e^- \to Nb^{4+} * -(N - -NH_3)(NH_3 \text{ desorption})$$
(17)

$$Nb^{4+} * -(N) + H^{+} + e^{-} \rightarrow Nb^{4+} * -(NH)$$
 (18)

$$Nb^{4+} * -(NH) + H^{+} + e^{-} \rightarrow Nb^{4+} * -(NH_2)$$
 (19)

 $Nb^{4+} * -(NH_2) + H^+ + e^- \rightarrow Nb^{4+} * - -(NH_3)$  (NH<sub>3</sub> desorption) (20)

The Ti<sup>4+</sup> active sites follow a similar trend for NRR as the Nb<sup>4+</sup> sites, which protonate the adsorbed N<sub>2</sub> through the six PCET processes (Eq. 21) either by associative alternating or associative distal pathway.

$$(V_o - Ti^{4+}) - N = N \cdot +6H_2O$$
  
+ 6 e<sup>-</sup>  $\rightarrow (V_o - Ti^{4+}) + 2NH_3 + 6 OH^-$  (21)

Hence, the TNO@C electrocatalyst was shown to have efficient NRR activity. The higher ammonia yields and FE for the TNO@C900 electrocatalysts are due to the exposed Ti<sup>4+</sup> and Nb<sup>4+</sup> cationic sites actively involved in NRR. Furthermore, the carbon layer present on the surface of the TNO@C electrocatalysts provides a conductive pathway for electrons to the active sites, and the rough surfaces with high accessibility promote higher mass transport. NRR is facilitated by the series of proton-coupled electron transfer steps that follow either the associative alternating pathway or the associative distal pathway. Therefore, the adsorption sites for the TNO@C900 electrocatalysts are the Nb<sup>4+</sup> and Ti<sup>4+</sup> cation sites. The Nb<sup>4+</sup> ion with an occupied d-orbital electron and the Ti<sup>4+</sup> ion with a trapped electron at the oxygen vacancy contribute to the efficient N<sub>2</sub> reduction of the TNO@C900 electrocatalyst.

# 3.4 Electrochemical characterization of the TNO@C electrocatalysts

The electrochemical characterization of the TNO@C electrocatalysts in 0.1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte was also investigated. The double layer capacitance ( $C_{dl}$ ) values for the TNO@C electrocatalysts are derived from the CV curves at various scan rates in the non-faradaic region (Figs. S15-17) [93]. The  $C_{dl}$  values represent the active sites exposed on the surface, which are used to estimate the ECSA of the corresponding TNO@C electrocatalyst [94].

The plots in Fig. 6a illustrate the higher  $C_{dl}$  values for TNO@C900 electrocatalysts (0.58 mF), which is almost double that of TNO@C700 (0.33 mF) and TNO@C800 (0.36 mF), respectively. The low  $C_{dl}$  values of TNO@C700 and TNO@C800 are believed to be due to the partial crystallization of TNO@C microspheres and incomplete carbonization of the TNO@C microsphere surface. The ECSA values derived from  $C_{dl}$  for TNO@C700, TNO@C800, and TNO@C900 electrocatalysts are 8.25 cm<sup>2</sup>, 9 cm<sup>2</sup>, and 14 cm<sup>2</sup>, respectively, showing that TNO@C900 electrocatalyst has many active sites for NRR.

Electrochemical impedance spectroscopy (EIS) was used to analyze the charge transfer kinetics provided by the TNO@C electrocatalyst. As shown in Fig. 6b and Table S2, TNO@C900 exhibits lower solution resistance ( $R_1$ ) and charge transfer resistance ( $R_2$ ) compared to other catalysts, and the diffusion parameter in the low-frequency region controlled by the Warburg impedance factor (w3) also shows a steep increase in the case of TNO@C900, confirming that fast ion diffusion occurs in TNO@C900 [95]. This is believed to be due to the high surface roughness and electrical conductivity of TNO@C900 compared to TNO@C700 and TNO@C800 and the high surface-active area due to the cationic sites of Ti and Nb.

The potential-dependent impedance of the TNO@C900 electrocatalyst was analyzed to confirm the effective electrochemical performance of the electrocatalyst. The EIS spectra in Fig. 6c reveal a higher charge transfer resistance at 0 V vs. open circuit voltage (OCV), where the desired NRR does not occur. Thus, as the negative potentials increase with respect to the RHE, the charge transfer resistance decreases. The lowest resistance value is observed at -0.2 V vs. RHE for TNO@C900, which is ascribed to the highest ammonia yield and FE as observed in previous NRR studies. Therefore, in the TNO@C900 electrocatalysts, under N<sub>2</sub>-saturated electrolyte and at negative potentials of about -0.2 V vs. RHE, a fast charge transfer between the electrode surface and the reactants is observed [96, 97]. Bode plots of frequency vs. phase angle were analyzed at various applied potentials (Fig. 6d). The plots show the unaltered curves at higher frequencies, which remain the same for decreasing potentials. The change in the low-frequency region elucidates the changes in the charge transfer resistance with respect to the applied potentials [96]. Besides, the lower curve area for the bode plots was observed for -0.2 V vs. RHE, which indicates higher charge transfer reactions [98]. Thus, the bias-dependent impedance spectra indicate the shift of the relaxation frequency from the lower frequency region to the higher frequency region.

The relaxation frequency shift is accompanied by a decrease in the absolute values of the real (Z') and imaginary (Z'') parts of the impedance, which is consequently reflected in the Bode plots [99]. Therefore, the EIS analysis for the TNO@C900 electrocatalysts shows a lower charge transfer resistance and a higher NRR performance at -0.2 V vs. RHE. In addition, the Bode plots confirm the higher NRR activity and the charge transfer dependence of TNO@C900 in the high-frequency region. As a result, the enhanced charge transfer kinetics is due to the oxygen vacancy supported Ti<sup>4+</sup> and defective Nb<sup>4+</sup> cationic sites which perform efficient N2 reduction activity. Also, the oxygen vacancyinduced lattice strain and the carbon layer on the TNO@ C900 microspheres contribute to the lower charge transfer resistance of the electrocatalyst [25]. From the electrochemical characterization results, we infer that the TNO@C900 electrocatalyst exhibits better NRR performance due to (1) rough and defective surface with large ECSA, (2) cationic active sites, (3) vacancy-induced strain effect, and (4) beneficial carbon layer on TNO@C microspheres.



Fig.6 a Linear fit of the capacitive currents vs. the scan rate for TNO@C700, TNO@C800, and TNO@C900 electrocatalysts. b Nyquist plots of the TNO@C700, TNO@C800, and TNO@C900, electrocatalysts (inset: equivalent circuit model for TNO@C elec-

trocatalysts). **c** Nyquist plots of the TNO@C900 electrocatalysts under various applied potentials. **d** Corresponding Bode plots for the TNO@C900 electrocatalysts under various applied potentials

In a nutshell, the Wadsley-Roth crystal system of the ReO<sub>2</sub> type monoclinic structure in TiNb<sub>2</sub>O<sub>7</sub> electrocatalyst exhibits higher activity towards NRR due to the early transition metal active sites, high exposure of active sites, and oxygen vacancies. The Ti<sup>4+</sup> and Nb<sup>4+</sup> cations on the octahedral sites with oxygen vacancies are described as acidic Lewis sites for N<sub>2</sub> adsorption and protonation. In the Wadsley-Roth structures, excluded oxygenated space that provides a favorable environment for nitrogen adsorption. The defect and space of the Wadsley-Roth structure were optimized through control of the crystallinity, which is dependent on the calcination temperature. The TNO@C900 electrocatalysts form the desired crystalline structure when calcined at 900 °C, revealing the rough surface of the TNO@C microspheres. Thus, the superior NRR performance of TNO@

C900 is attributed to the well-defined Wadsley-Roth crystal structure and the inherent oxygen vacancies in the sample, as inspected in the material characterization.

Deformation induced by point defects shows lattice expansion due to the higher crystallinity of the TNO@ C900 sample. The cationic active sites of Ti<sup>4+</sup> and Nb<sup>4+</sup> from the TNO@C900 sample with large ECSA and lower charge transfer resistances are recognized as the active sites for NRR. Since N<sub>2</sub> is Lewis basic with a higher electron number, it is expected to be adsorbed on Lewis acidic site of Ti<sup>4+</sup> and Nb<sup>4+</sup> to perform the acceptance-donation mechanism. In addition, the innate oxygen vacancies and the surface carbon structures incorporate high electron conductivity for feasible electron transport to the active sites for N<sub>2</sub> reduction [25]. Furthermore, the NRR performances have been extended to analyze the effect of electrolytes that create the environment for NRR electrolysis. Among various electrolytes,  $Na_2SO_4$  was found to drive the reaction feasibly with swift ion transport and control of the local pH of the electrode surface. The higher FE of 13.11% is due to the enhanced selectivity of the TNO@C900 sample over Ti and Nb cationic sites due to their significant affinity towards  $N_2$  adsorption. The effect of the  $Na_2SO_4$  electrolyte is crucial in providing sufficient protons for  $N_2$  protonation and limiting the direct adsorption of H<sup>+</sup> on the catalyst surface to inhibit HER. The electrochemical characterization results show that the higher ECSA and lower charge transfer resistance improve the electrode kinetics for the TNO@C900 electrocatalyst.

# 3.5 Mechanistic study on TNO@C using in situ FT-IR spectroscopy and DFT analysis

In situ vibrational spectroscopy analysis using Fourier transform-infrared (FT-IR) spectroscopic studies of the electrode surface during NRR electrolysis reveals stretching, bending, and wagging of the N–H species which explains the nature of NRR intermediates and the probable NRR pathway. In situ FT-IR spectroscopy studies for TNO@C900 are performed to observe the formation of NH intermediates on the electrode surface for NRR potentials within 0 to -0.4 V vs. RHE. The peaks observed in Fig. 7 at 1103, 1255, 1430, 1513, 1634, 3230, and 3300 cm<sup>-1</sup> correspond to the symmetric and asymmetric vibrations of N–H, N–N, and H–O-H species.

The FT-IR spectroscopy analysis in Fig. 7a shows a peak at 1103 cm<sup>-1</sup>, corresponding to the N-N stretching vibration of the N<sub>2</sub> molecules [100]. The peaks at 1634 cm<sup>-1</sup> and 3307/3518 cm<sup>-1</sup> correspond to H–O-H species that serve as the proton source for NRR during PCET reactions [100–102]. Notably, the peaks at 1430 and 3248 cm<sup>-1</sup> correspond to the asymmetric deformation and symmetric stretching modes of the H–N–H bond of the NH<sub>4</sub><sup>+</sup> species, respectively. Besides, the peaks at 1255 and 1513 cm<sup>-1</sup> correspond to the -NH<sub>2</sub> wagging mode and H–N–H bonding vibrations [101, 103].

The wide band of peaks around  $3000-3450 \text{ cm}^{-1}$  (3161, 3278, 3340, 3361, 3435) corresponds to the vibration modes of adsorbed NH<sub>x</sub> species [104]. Additionally, the peaks at 2371 cm<sup>-1</sup> correspond to the adsorbed CO<sub>2</sub> molecules present on the electrode surface from the electrolyte or atmosphere [105]. The negligible peaks for open circuit potential (OCP) suggest that ammonia is not innately present in the electrolyte compartment. Hence, in situ FT-IR reveals the existence of N–N stretching, -NH<sub>2</sub> wagging, H–N–H bending, and stretching of NH<sub>x</sub> species that confirm ammonia is produced via the associative mechanism

of electrochemical NRR. Comparing the obtained results with ammonia yield plots for TNO@C900, the increase in H–O-H adsorption corresponds to HER at higher potentials.

In addition, time-dependent in situ FT-IR studies in Fig. 7b are performed at -0.25 V vs. RHE every 1 min for 60 min to observe the evolution of NRR. As observed, the peak at 1435 cm<sup>-1</sup> gradually over the period, indicating the production of NH<sub>3</sub> via electrochemical NRR activity [101]. The gradual increase in peak intensity for asymmetric and symmetric stretching modes of N-H species explains that N<sub>2</sub> is electrochemically reduced to ammonia over time. Further, in situ Raman analysis revealed the bonding vibrations of the intermediates formed over the TNO@C900 surface during NRR. Similar to in situ FT-IR spectra, the in situ Raman analysis reveals the N-N stretching and bonding vibrations of N<sub>2</sub>H<sub>v</sub> intermediates. As observed in Fig. 7c and d, the peaks at 980 and 993 cm<sup>-1</sup> correspond to the adsorbed sulfate radical species  $(SO_4^{2-})$  and NH<sub>3</sub> adsorption, respectively. Besides, the peaks at 1125, 1079, and 1198 cm<sup>-1</sup> correspond to the N-N stretching and NH<sub>2</sub> adsorption vibrations of the  $N_2H_v$  intermediates, respectively. Therefore, the in situ FT-IR and Raman analysis reveal the strong nitrogen reduction on the catalyst surface, which suggests the selectivity of ammonia formation towards associative NRR mechanism.

Further DFT analysis is performed to calculate the surface free energy and adsorption energies of the N2 and intermediate N-H species on active sites to estimate the probable NRR pathway. The (110) surface of the as-formed TNO@C catalyst can be an active site for both the adsorption of N<sub>2</sub> for NRR and H for HER through the transfer of electrons from Ti and Nb sites. Therefore, to determine how well the adsorption of  $N_2(g)$  and H occurs, adsorption energy calculations were performed for the possible Ti and Nb sites on the (110) surface (Fig. S18a, S18b). N<sub>2</sub>(g) and H were adsorbed on top of each active site, Nb and Ti, and the most stable sites for each active site for nitrogen gas were found to be -0.77 eV and -0.64 eV on Ti and Nb(4) sites, and the most stable adsorption energy for H was found to be -0.72 eV on Nb(4) site. These stable adsorption energies at Ti and Nb(4) sites are due to the empty space caused by the Wadsley-Roth structure on the TiNb<sub>2</sub>O<sub>7</sub>(110) surface, which makes the adsorption of both N<sub>2</sub> and H better, but leads to stable adsorption for different sites, especially for the adsorption of H. The adsorption energy at the site shows that the adsorption of  $N_2(g)$  is more stable except for the Nb(4) site, which confirms that the adsorption of  $N_2(g)$  is better than the adsorption of H, which can lead to better NRR than HER (Fig. S18c).

The change in the distribution of electrons was calculated for the (110) surface of the TNO@C catalyst to confirm the transfer of electrons for adsorption. The adsorption of N<sub>2</sub> at each site breaks the  $\pi$ -bond of the molecule, allowing it to bond to the surface of the catalyst. This bonding requires



Fig. 7 a Potential-dependent and b time-dependent in situ FT-IR spectroscopy for TNO@C900

electrons between the  $N_2$  and the catalyst, which are provided by each Ti and Nb site in different ways. To confirm this, nitrogen molecules were absorbed on the Ti and Nb(4) sites with the most stable adsorption energies (Fig. S19a, S19b). The charge density difference analysis results show the direction of electron transfer and, thus, the way each site donates electrons. At the Ti site, the density of electrons at the Ti site is also enriched by meta-stable electrons around the Ti site, and it is confirmed that the adsorption of nitrogen molecules occurs favorably due to these enriched electrons. For the Nb site, it is shown that the d-electron of Nb is involved in the adsorption, which reduces the charge density at the site itself (Fig. 8a, b). The free energy graphs for NRR and HER for the active site with the most stable adsorption energy explain the overall reaction by investigating the intermediate reactions.

For each NRR and HER reaction, the Gibbs free energy was investigated for Ti and Nb(4) sites with stable adsorption energies for NRR, and for HER, the Gibbs free energy at Nb(4) was investigated under U=0 V condition (Fig. 8c–e). When checking the investigated Gibbs free energy, HER was found to have a limiting potential  $(U_{\rm I})$  value of -0.65 V in Fig. 8c, and NRR was found to have values of -0.91 V and -0.78 V for Ti and Nb sites, respectively, in the  $NH_2^* + (H^+ + e^-) \rightarrow NH_3^*$  step (Fig. 8d, e). In the comparison of NRR and HER, the dominant reaction of HER is related to the coverage of H\*, which is investigated for the binding energy. Below -0.2 V, the NRR reaction is favored due to the favorable adsorption of  $N_2$ , but above -0.2 V, the HER reaction is judged to be increasingly favorable, and this is due to the increase in the adsorption of H and the dominance of the HER reaction through high coverage, resulting in a decrease in NRR reactivity.

#### **4** Conclusion

In summary, we have demonstrated the efficient NRR performance of TiNb<sub>2</sub>O<sub>7</sub> (TNO@C) microspheres belonging to the Wadsley-Roth crystal structure family. After synthesis by a facile hydrothermal method, TNO@C microspheres calcined at different temperatures successfully formed a ReO<sub>2</sub>-type monoclinic crystal structure with the C2/m phase of TiNb<sub>2</sub>O<sub>7</sub>. The calcined TNO@C samples were prepared as microspheres with uniformly sized rough surfaces and exhibited distinct lattice planes. TNO@C900 calcined at 900 °C exhibited superior NRR performance compared to TNO@C700 and TNO@C800 because Ti<sup>4+</sup> and Nb<sup>4+</sup> ions with excessive oxygen vacancies in the octahedral sites of TiNb<sub>2</sub>O<sub>7</sub> promoted the electrocatalytic activity. In addition, NRR was measured with different electrolytes, and it was found that Na<sub>2</sub>SO<sub>4</sub> electrolyte was more active in NRR compared to KOH and LiClO<sub>4</sub>. As a result, the TNO@C900 sample exhibited an ammonia yield of up to  $0.62 \,\mu\text{mol}\,\text{h}^{-1}\,\text{cm}^{-2}$ and an FE of 13.11% in 0.1 M Na2SO4 electrolyte. This excellent NRR performance of TNO@C900 is attributed to the deformation effect caused by the rough surface, crystallized carbon layer, cationic active sites, and oxygen vacancies in the TiNb<sub>2</sub>O<sub>7</sub> Wadsley-Roth structure. In addition, the electrolyte pH in the electrochemical NRR system also has a great influence on the NRR performance. Therefore, this experimental study on the NRR performance of the Wadsley-Roth structure will enrich the knowledge of the design and development of active electrocatalysts and systems. Future studies can focus on modifying the TiNb2O7 structure through doping and heterostructured strategies to increase the active centers. Thus, the Wadsley-Roth crystal structure provides a



**Fig. 8 a**, **b** Iso-surface of charge density difference at the (110) plane. **c–e** Gibbs free energy diagram for HER and NRR on the various reaction sites

stable structure that is insensitive to deformation and can be chosen as a reliable electrocatalyst in modern applications.

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# Declarations

Conflict of interest The authors declare no competing interests.

#### References

- Singh AR, Rohr BA, Schwalbe JA, Cargnello M, Chan K, Jaramillo TF, Chorkendorff I, Nørskov JK (2017) Electrochemical ammonia synthesis—the selectivity challenge. ACS Catal 7:706–709
- 2. Rao CNR, Ranga Rao G (1991) Nature of nitrogen adsorbed on transition metal surfaces as revealed by electron spectroscopy and cognate techniques. Surf Sci Rep 13:223–263
- Feng J, Pan H (2020) Electronic state optimization for electrochemical N2 reduction reaction in aqueous solution. J Mater Chem A 8:13896–13915
- 4. Qian Y, Liu Y, Zhao Y, Zhang X, Yu G (2020) Single vs double atom catalyst for N2 activation in nitrogen reduction reaction: a DFT perspective. EcoMat 2:e12014
- Yin H, Gan L-Y, Wang P (2020) The identification of optimal active boron sites for N2 reduction. J Mater Chem A 8:3910–3917
- Liu D, Chen M, Du X, Ai H, Lo KH, Wang S, Chen S, Xing G, Wang X, Pan H (2021) Development of electrocatalysts for efficient nitrogen reduction reaction under ambient condition. Adv Funct Mater 7:2008983
- Han J, Liu Z, Ma Y, Cui G, Xie F, Wang F, Wu Y, Gao S, Xu Y, Sun X (2018) Ambient N2 fixation to NH3 at ambient conditions: Using Nb2O5 nanofiber as a high performance electrocatalyst. Nano Energy 52:264–270
- Huang L, Wu J, Han P, Al-Enizi AM, Almutairi TM, Zhang L, Zheng G (2019) Electrocatalyst toward 32% faradaic efficiency for N2 fixation. Small Methods 3:1800386
- Kong W, Liu Z, Han J, Xia L, Wang Y, Liu Q, Shi X, Wu Y, Xu Y, Sun X (2019) Ambient electrochemical N2- to-NH3 fixation enabled by Nb2O5 nanowire array. Inorg Chem Front 6:423–427
- Wu T, Han M, Zhu X, Wang G, Zhang Y, Zhang H, Zhao H (2019) Experimental and theoretical understanding on electrochemical activation and inactivation processes of Nb3O7(OH) for ambient electrosynthesis of NH3. J Mater Chem A 7:16969–16978
- Wang Y, Chen A, Lai S, Peng X, Zhao S, Hu G, Qiu Y, Ren J, Liu X, Luo J (2020) Self-supported NbSe2 nanosheet arrays for highly efficient ammonia electrosynthesis under ambient conditions. J Catal 381:78–83
- Wang J, Kang S, Zhu X, Wang G, Zhang H (2021) Highly ordered Nb2O5 nanochannel film with rich oxygen vacancies for electrocatalytic N2 reduction: Inactivation and regeneration of electrode. Chin Chem Lett 32:2833–2836
- Zhang M, Yin H, Jin F, Liu J, Ji X, Du A, Yang W, Liu Z (2022) Vacancy engineering of oxidized Nb2CTx MXenes for a biased nitrogen fixation. Green Energy Environ
- Seyedin S, Zhang J, Usman KAS, Qin S, Glushenkov AM, Yanza ERS, Jones RT, Razal JM (2019) Facile solution processing of stable MXene dispersions towards conductive composite fibers. Glob Challenges 3:1900037
- Li Q, Fang C, Yang Z, Yu B, Takabatake M, Motokura K, Sun X, Yang Y (2022) Modulating the oxidation state of titanium via dual anions substitution for efficient N2 electroreduction. Small 18:2201343
- 16. Wu T, Zhao H, Zhu X, Xing Z, Liu Q, Liu T, Gao S, Lu S, Chen G, Asiri AM, Zhang Y, Sun X (2020) Identifying the origin of Ti3+ activity toward enhanced electrocatalytic N2 Reduction over TiO2 nanoparticles modulated by mixed-valent copper. Adv Mater 32:2000299

- 17. Shi M-M, Bao D, Wulan B-R, Li Y-H, Zhang Y-F, Yan J-M, Jiang Q (2017) Au sub-nanoclusters on TiO2 toward highly efficient and selective electrocatalyst for N2 conversion to NH3 at ambient conditions. Adv Mater 29:1606550
- Fang Y, Liu Z, Han J, Jin Z, Han Y, Wang F, Niu Y, Wu Y, Xu Y (2019) High-performance electrocatalytic conversion of N2 to NH3 using oxygen-vacancy-rich TiO2 in situ grown on Ti3C2Tx MXene. Adv Energy Mater 9:1803406
- Lv J, Tian Z, Dai K, Ye Y, Liang C (2019) Interface and defect engineer of titanium dioxide supported palladium or platinum for tuning the activity and selectivity of electrocatalytic nitrogen reduction reaction. J Colloid Interface Sci 553:126–135
- Cai W, Jiang Y-F, Zhang J, Yang H, Zhang J, Xu C-Q, Liu W, Li J, Liu B (2022) Ruthenium/titanium oxide interface promoted electrochemical nitrogen reduction reaction. Chem Catal 2:1764–1774
- Guo B, Yu X, Sun X-G, Chi M, Qiao Z-A, Liu J, Hu Y-S, Yang X-Q, Goodenough JB, Dai S (2014) A long-life lithium-ion battery with a highly porous TiNb2O7 anode for large-scale electrical energy storage. Energy Environ Sci 7(2220):2226
- 22. Jayaraman S, Aravindan V, Suresh Kumar P, Chui Ling W, Ramakrishna S, Madhavi S (2014) Exceptional performance of TiNb2O7 anode in all one-dimensional architecture by electrospinning. ACS Appl Mater Interfaces 6:8660–8666
- 23. Wu X, Lou S, Cheng X, Lin C, Gao J, Ma Y, Zuo P, Du C, Gao Y, Yin G (2018) Unravelling the interface layer formation and gas evolution/suppression on a TiNb2O7 anode for lithium-ion batteries. ACS Appl Mater Interfaces 10:27056–27062
- 24. Zhou X, Zeng P, Yu H, Guo C, Miao C, Guo X, Chen M, Wang X (2022) Engineering a TiNb2O7-based electrocatalyst on a flexible self-supporting sulfur cathode for promoting Li-S battery performance. ACS Appl Mater Interfaces 14:1157–1168
- 25. Zhu W, Zou B, Zhang C, Ng DHL, El-Khodary SA, Liu X, Li G, Qiu J, Zhao Y, Yang S, Lian J, Li H (2020) Oxygen-defective TiNb2O7-x nanochains with enlarged lattice spacing for high-rate lithium ion capacitor. Adv Mater Interfaces 7:2000705
- 26. Hu L, Lin C, Wang C, Yang C, Li J, Chen Y, Lin S (2016) TiNb2O7 nanorods as a novel anode material for secondary lithium-ion batteries. Funct Mater Lett 09:1642004
- 27. Lee Y-S, Ryu K-S (2017) Study of the lithium diffusion properties and high rate performance of TiNb6O17 as an anode in lithium secondary battery. Sci Rep 7:16617
- Zhang Y, Zhang M, Liu Y, Zhu H, Wang L, Liu Y, Xue M, Li B, Tao X (2020) Oxygen vacancy regulated TiNb2O7 compound with enhanced electrochemical performance used as anode material in Li-ion batteries. Electrochim Acta 330:135299
- 29. Ise K, Morimoto S, Harada Y, Takami N (2018) Large lithium storage in highly crystalline TiNb2O7 nanoparticles synthesized by a hydrothermal method as anodes for lithium-ion batteries. Solid State Ionics 320:7–15
- 30. Li H, Shen L, Pang G, Fang S, Luo H, Yang K, Zhang X (2015) TiNb2O7 nanoparticles assembled into hierarchical microspheres as high-rate capability and long-cycle-life anode materials for lithium ion batteries. Nanoscale 7:619–624
- 31. Lou S, Cheng X, Zhao Y, Lushington A, Gao J, Li Q, Zuo P, Wang B, Gao Y, Ma Y, Du C, Yin G, Sun X (2017) Superior performance of ordered macroporous TiNb2O7 anodes for lithium ion batteries: Understanding from the structural and pseudocapacitive insights on achieving high rate capability. Nano Energy 34:15–25
- 32. Griffith KJ, Seymour ID, Hope MA, Butala MM, Lamontagne LK, Preefer MB, Koçer CP, Henkelman G, Morris AJ, Cliffe MJ, Dutton SE, Grey CP (2019) Ionic and electronic conduction in TiNb2O7. J Am Chem Soc 141:16706–16725
- Yu Z, Waclawik ER, Wang Z, Gu X, Yuan Y, Zheng Z (2017) Dual modification of TiNb2O7 with nitrogen dopants and oxygen

vacancies for selective aerobic oxidation of benzylamine to imine under green light. J Mater Chem A 5:4607–4615

- Choi H, Kim T, Park H (2022) Defect engineering of TiNb2O7 compound for enhanced Li-ion battery anode performances. Electrochim Acta 404:139603
- 35. Maniammal K, Madhu G, Biju V (2017) X-ray diffraction line profile analysis of nanostructured nickel oxide: shape factor and convolution of crystallite size and microstrain contributions. Phys E: Lowdimensional Syst Nanostruct 85:214–222
- 36. Yang Y, Li Y, Liu K, Zhang K, Jin S, Bao Y, Fan Y, Yang Z, Zhang R, Jin B, Liu G (2021) Hierarchical porous TiNb2O7@Ndoped carbon microspheres as superior anode materials for lithium ion storage. Int J Hydrogen Energy 46:3425–3436
- Yu L, Lv J, Zhou Z, Li Y, Wei M (2021) Hierarchical structure TiNb2O7 microspheres derived from titanate for high-performance lithium-ion batteries. CrystEngComm 23:4905–4909
- Gholizadeh AJJOAM (2015) X-ray peak broadening analysis in LaMnO3+ δ nano-particles with rhombohedral crystal structure. Processing 3:71–83
- 39. Hsu W-D, Yang P-W, Chen H-Y, Wu P-H, Wu P-C, Hu C-W, Saravanan L, Liao Y-F, Su Y-T, Bhalothia D, Chen T-Y, Chang C-C (2021) Preferential lattice expansion of polypropylene in a trilayer polypropylene/polyethylene/polypropylene microporous separator in Li-ion batteries. Sci Rep 11:1929
- 40. Ren Y, Zhou X, Tang J, Ding J, Chen S, Zhang J, Hu T, Yang X-S, Wang X, Yang J (2019) Boron-doped spherical hollow-porous silicon local lattice expansion toward a high-performance lithium-ion- battery anode. Inorg Chem 58:4592–4599
- 41. Gupta A, Mittal M, Singh MK, Suib SL, Pandey OP (2018) Low temperature synthesis of NbC/C nanocomposites as visible light photoactive catalyst. Sci Rep 8:13597
- 42. Mousavi SM, Mahjoub AR, Abazari R (2015) Green synthesis of ZnO hollow sphere nanostructures by a facile route at room temperature with efficient photocatalytic dye degradation properties. RSC Adv 5:107378–107388
- Gulati S, Sachdeva M, Bhasin KK (2018) Capping agents in nanoparticle synthesis: surfactant and solvent system. AIP Confe Proc 1953:030214
- 44. Oskouei HI, Aghamohammadi H, Eslami-Farsani R (2022) Electrochemical performance of TiNb2O7 nanoparticles anchored with different contents of MWCNTs as anode materials for Li-ion batteries. Ceram Int 48:14717–14725
- 45. Song HJ, Sung M-C, Yoon H, Ju B, Kim D-W (2019) Ultrafine α-phase molybdenum carbide decorated with platinum nanoparticles for efficient hydrogen production in acidic and alkaline media. Adv Sci 6:1802135
- 46. McCarthy SA, Ratkic R, Purcell-Milton F, Perova TS, Gun'ko YK (2018) Adaptable surfactant-mediated method for the preparation of anisotropic metal chalcogenide nanomaterials. Sci Rep 8:2860
- 47. Yang Y, Yue Y, Wang L, Cheng X, Hu Y, Yang Z-Z, Zhang R, Jin B, Sun R (2020) Facile synthesis of mesoporous TiNb2O7/C microspheres as long-life and high-power anodes for lithium-ion batteries. Int J Hydrogen Energy 45:12583–12592
- 48. Shen S, Guo W, Xie D, Wang Y, Deng S, Zhong Y, Wang X, Xia X, Tu J (2018) A synergistic vertical graphene skeleton and S–C shell to construct high-performance TiNb2O7-based core/shell arrays. J Mater Chem A 6:20195–20204
- 49. Qi M, Chao D, Sun W, Yin J, Chen M (2020) Three-dimensional TiNb2O7 anchored on carbon nanofiber core-shell arrays as an anode for high-rate lithium ion storage. RSC Adv 10:6342–6350
- Gong S, Jiang Z, Zhu S, Fan J, Xu Q, Min Y (2018) The synthesis of graphene-TiO2/g-C3N4 super-thin heterojunctions with enhanced visible-light photocatalytic activities. J Nanoparticle Res 20:310

- Zhao Z, Tan H, Zhao H, Lv Y, Zhou L-J, Song Y, Sun Z (2014) Reduced TiO2 rutile nanorods with welldefined facets and their visible-light photocatalytic activity. Chem Commun 50:2755–2757
- Liu Y, Deng P, Wu R, Zhang X, Sun C, Li H (2021) Oxygen vacancies for promoting the electrochemical nitrogen reduction reaction. J Mater Chem A 9:6694–6709
- 53. Cheng S, Gao Y-J, Yan Y-L, Gao X, Zhang S-H, Zhuang G-L, Deng S-W, Wei Z-Z, Zhong X, Wang J-G (2019) Oxygen vacancy enhancing mechanism of nitrogen reduction reaction property in Ru/TiO2. J Energy Chem 39:144–151
- 54. Liu Y, Deng P, Wu R, Geioushy RA, Li Y, Liu Y, Zhou F, Li H, Sun C (2021) BiVO4/TiO2 heterojunction with rich oxygen vacancies for enhanced electrocatalytic nitrogen reduction reaction. Front Phys 16:53503
- Deng X, Verdaguer A, Herranz T, Weis C, Bluhm H, Salmeron M (2008) Surface chemistry of Cu in the presence of CO2 and H2O. Langmuir 24:9474–9478
- Parkinson CR, Walker M, McConville CF (2003) Reaction of atomic oxygen with a Pt(111) surface: chemical and structural determination using XPS, CAICISS and LEED. Surf Sci 545:19–33
- Zhang Y, Chen Z, Lu Z (2018) A facile method for the preparation of colored Bi4Ti3O12-x nanosheets with enhanced visiblelight photocatalytic hydrogen evolution activity. Nanomaterials 8
- Bera RK, Park H, Ryoo R (2019) Co3O4 nanosheets on zeolitetemplated carbon as an efficient oxygen electrocatalyst for a zincair battery. J Mater Chem A 7:9988–9996
- 59. Jones TE, Rocha TCR, Knop-Gericke A, Stampfl C, Schlögl R, Piccinin S (2015) Thermodynamic and spectroscopic properties of oxygen on silver under an oxygen atmosphere. Phys Chem Chem Phys 17:9288–9312
- Gawli Y, Badadhe S, Basu A, Guin D, Shelke MV, Ogale S (2014) Evaluation of n-type ternary metal oxide NiMn2O4 nanomaterial for humidity sensing. Sensors Actuators B: Chem 191:837–843
- 61. Campbell CT, Foyt DC, White JM (1977) Oxygen penetration into the bulk of palladium. J Phys Chem 81:491–494
- 62. Zemlyanov D, Aszalos-Kiss B, Kleimenov E, Teschner D, Zafeiratos S, Hävecker M, Knop-Gericke A, Schlögl R, Gabasch H, Unterberger W, Hayek K, Klötzer B (2006) In situ XPS study of Pd(111) oxidation. Part 1: 2D oxide formation in 10–3mbar O2. Surf Sci 600:983–994
- Leisenberger FP, Koller G, Sock M, Surnev S, Ramsey MG, Netzer FP, Klötzer B, Hayek K (2000) Surface and subsurface oxygen on Pd(111). Surf Sci 445:380–393
- 64. Du M, Miao Z, Li H, Zhang F, Sang Y, Wei L, Liu H, Wang S (2021) Oxygen-vacancy and phosphate coordination triggered strain engineering of vanadium oxide for high-performance aqueous zinc ion storage. Nano Energy 89:106477
- 65. Sun X, Wu K-H, Sakamoto R, Kusamoto T, Maeda H, Ni X, Jiang W, Liu F, Sasaki S, Masunaga H, Nishihara H (2017) Bis(aminothiolato)nickel nanosheet as a redox switch for conductivity and an electrocatalyst for the hydrogen evolution reaction. Chem Sci 8:8078–8085
- Fei R, Yang L (2014) Strain-engineering the anisotropic electrical conductance of few-layer black phosphorus. Nano Lett 14:2884–2889
- 67. Zhang Q, Bao N, Wang X, Hu X, Miao X, Chaker M, Ma D (2016) Advanced fabrication of chemically bonded graphene/ TiO2 continuous fibers with enhanced broadband photocatalytic properties and involved mechanisms exploration. Sci Rep 6:38066
- Zhang H, Geng S, Ouyang M, Yadegari H, Xie F, Riley DJ (2022) A self-reconstructed bifunctional electrocatalyst of

pseudo-amorphous nickel carbide @ iron oxide network for seawater splitting. Adv Sci 9:2200146

- 69. Bayeh AW, Kabtamu DM, Chang Y-C, Chen G-C, Chen H-Y, Lin G-Y, Liu T-R, Wondimu TH, Wang K-C, Wang C-H (2018) Synergistic effects of a TiNb2O7–reduced graphene oxide nanocomposite electrocatalyst for high-performance all-vanadium redox flow batteries. J Mater Chem A 6:13908–13917
- Smith M, Scudiero L, Espinal J, McEwen J-S, Garcia-Perez M (2016) Improving the deconvolution and interpretation of XPS spectra from chars by ab initio calculations. Carbon 110:155–171
- Ou G, Liu W, Yao L, Wu H, Pan W (2014) High conductivity of La2Zr2O7 nanofibers by phase control. J Mater Chem A 2:1855–1861
- 72. Bazylewski P, Boukhvalov DW, Kukharenko AI, Kurmaev EZ, Hunt A, Moewes A, Lee YH, Cholakh SO, Chang GS (2015) The characterization of Co-nanoparticles supported on graphene. RSC Adv 5:75600–75606
- 73. Skorupska M, Kamedulski P, Lukaszewicz JP, Ilnicka A (2021) The improvement of energy storage performance by sucrosederived carbon foams via incorporating nitrogen atoms. Nanomaterials 11
- 74. Lai F, Feng J, Ye X, Zong W, He G, Yang C, Wang W, Miao Y-E, Pan B, Yan W, Liu T, Parkin IP (2020) Oxygen vacancy engineering in spinel-structured nanosheet wrapped hollow polyhedra for electrochemical nitrogen fixation under ambient conditions. J Mater Chem A 8:1652–1659
- Guha A, Narayanaru S, Kaley NM, Krishna Rao D, Mondal J, Narayanan TN (2019) Mechanistic insight into high yield electrochemical nitrogen reduction to ammonia using lithium ions. Mater Today Commun 21:100700
- 76. Kani NC, Prajapati A, Collins BA, Goodpaster JD, Singh MR (2020) Competing effects of pH, cation identity, H2O saturation, and N2 concentration on the activity and selectivity of electrochemical reduction of N2 to NH3 on electrodeposited Cu at ambient conditions. ACS Catal 10:14592–14603
- 77. de Salles M, Pupo M, Kortlever R (2019) Electrolyte effects on the electrochemical reduction of CO2. ChemPhysChem 20:2926–2935
- Singh MR, Kwon Y, Lum Y, Ager JW, Bell AT (2016) Hydrolysis of electrolyte cations enhances the electrochemical reduction of CO2 over Ag and Cu. J Am Chem Soc 138:13006–13012
- Zhu Y, Yin J, Zheng X, Emwas A-H, Lei Y, Mohammed OF, Cui Y, Alshareef HN (2021) Concentrated dual-cation electrolyte strategy for aqueous zinc-ion batteries. Energy Environ Sci 14:4463–4473
- Wang J, Yu L, Hu L, Chen G, Xin H, Feng X (2018) Ambient ammonia synthesis via palladium-catalyzed electrohydrogenation of dinitrogen at low overpotential. Nat Commun 9:1795
- 81. Wang H, Si J, Zhang T, Li Y, Yang B, Li Z, Chen J, Wen Z, Yuan C, Lei L, Hou Y (2020) Exfoliated metallic niobium disulfate nanosheets for enhanced electrochemical ammonia synthesis and Zn-N2 battery. Appl Catal B: Environ 270:118892
- Greczynski G, Hultman L (2021) The same chemical state of carbon gives rise to two peaks in X-ray photoelectron spectroscopy. Sci Rep 11:11195
- Smykalla L, Shukrynau P, Korb M, Lang H, Hietschold M (2015) Surface-confined 2D polymerization of a brominated coppertetraphenylporphyrin on Au(111). Nanoscale 7:4234–4241
- 84. Linic S, Piao H, Adib K, Barteau MA (2004) Ethylene epoxidation on Ag: identification of the crucial surface intermediate by experimental and theoretical investigation of its electronic structure. Angew Chem Int Ed 43:2918–2921
- 85. Wu D, Wang H, Huang H, Zhang R, Ji L, Chen H, Luo Y, You J, Tang D, Zhang Z, Sun X (2019) Ambient electrochemical N2 reduction to NH3 under alkaline conditions enabled by a layered K2Ti4O9 nanobelt. Chem Commun 55:7546–7549

- 86. Zhang J, Yang L, Wang H, Zhu G, Wen H, Feng H, Sun X, Guan X, Wen J, Yao Y (2019) In situ hydrothermal growth of TiO2 nanoparticles on a conductive Ti3C2Tx MXene nanosheet: a synergistically active Ti-based nanohybrid electrocatalyst for enhanced n2 reduction to nh3 at ambient conditions. Inorg Chem 58:5414–5418
- 87. Li T, Yan X, Huang L, Li J, Yao L, Zhu Q, Wang W, Abbas W, Naz R, Gu J, Liu Q, Zhang W, Zhang D (2019) Fluorine-free Ti3C2Tx (T = O, OH) nanosheets (~50–100 nm) for nitrogen fixation under ambient conditions. J Mater Chem A 7:14462–14465
- Xiao L, Zhu S, Liang Y, Li Z, Wu S, Luo S, Chang C, Cui Z (2021) Nanoporous nickel–molybdenum oxide with an oxygen vacancy for electrocatalytic nitrogen fixation under ambient conditions. ACS Appl Mater Interfaces 13:30722–30730
- Yesudoss DK, Chun H, Han B, Shanmugam S (2022) Accelerated N2 reduction kinetics in hybrid interfaces of NbTiO4 and nitrogen-doped carbon nanorod via synergistic electronic coupling effect. Appl Catal B: Environ 304:120938
- 90. Kong W, Gong F, Zhou Q, Yu G, Ji L, Sun X, Asiri AM, Wang T, Luo Y, Xu Y (2019) An MnO2–Ti3C2Tx MXene nanohybrid: an efficient and durable electrocatalyst toward artificial N2 fixation to NH3 under ambient conditions. J Mater Chem A 7:18823–18827
- 91. Chen H, Wu T, Li X, Lu S, Zhang F, Wang Y, Zhao H, Liu Q, Luo Y, Asiri AM, Feng Z-S, Zhang Y, Sun X (2021) Modulating oxygen vacancies of TiO2 nanospheres by Mn-doping to boost electrocatalytic N2 reduction. ACS Sustain Chem Eng 9:1512–1517
- Young SD, Ceballos BM, Banerjee A, Mukundan R, Pilania G, Goldsmith BR (2022) Metal oxynitrides for the electrocatalytic reduction of nitrogen to ammonia. J Phys Chem C 126:12980–12993
- Zhao L, Xiong Y, Wang X, Zhao R, Chi X, Zhou Y, Wang H, Yang Z, Yan Y-M (2022) Shearing sulfur edges of VS2 electrocatalyst enhances its nitrogen reduction performance. Small 18:2106939
- Cheng H, Ding L-X, Chen G-F, Zhang L, Xue J, Wang H (2018) Molybdenum carbide nanodots enable efficient electrocatalytic nitrogen fixation under ambient conditions. Adv Mater 30:1803694
- 95. Yang L, Wu T, Zhang R, Zhou H, Xia L, Shi X, Zheng H, Zhang Y, Sun X (2019) Insights into defective TiO2 in electrocatalytic N2 reduction: combining theoretical and experimental studies. Nanoscale 11:1555–1562
- Janani G, Surendran S, Choi H, An T-Y, Han M-K, Song S-J, Park W, Kim JK, Sim U (2022) Anchoring of Ni12P5 microbricks in nitrogen- and phosphorus-enriched carbon frameworks:

engineering bifunctional active sites for efficient water-splitting systems. ACS Sustain Chem Eng 10:1182–1194

- 97. Choi H, Surendran S, Kim D, Lim Y, Lim J, Park J, Kim JK, Han M-K, Sim U (2021) Boosting eco-friendly hydrogen generation by urea-assisted water electrolysis using spinel M2GeO4 (M = Fe, Co) as an active electrocatalyst. Environ Sci: Nano 8:3110–3121
- Bhat KS, Nagaraja HS (2020) Hydrogen evolution reaction at extreme pH conditions of copper sulphide micro-hexagons. J Sci: Adv Mater Devices 5:361–367
- 99. Pandey K, Yadav P, Singh D, Gupta SK, Sonvane Y, Lukačević I, Kim J, Kumar M (2016) First step to investigate nature of electronic states and transport in flower-like MoS2: combining experimental studies with computational calculations. Sci Rep 6:32690
- 100. Song P, Wang H, Cao X, Liu N, Wang Q, Wang R (2019) Ambient electrochemical N2 reduction to NH3 on nitrogen and phosphorus co-doped porous carbon with trace iron in alkaline electrolytes. ChemElectroChem 7:212–216
- 101. Lee J, Liu X, Kumar A, Hwang Y, Lee E, Yu J, Kim YD, Lee H (2021) Phase-selective active sites on ordered/disordered titanium dioxide enable exceptional photocatalytic ammonia synthesis. Chem Sci 12:9619–9629
- 102. Wen W, Yan P, Sun W, Zhou Y, Yu X-Y (2023) Metastable phase Cu with optimized local electronic state for efficient electrocatalytic production of ammonia from nitrate. Adv Funct Mater 33:2212236
- 103. Sun Y, Han Y, Zhang X, Cai W, Zhang Y, Zhang Y, Li Z, Li B, Lai J, Wang L (2022) TiO1.8 with lattice H for effective electrocatalytic nitrogen fixation. Appl Catal B: Environ 319:121933
- 104. Mao C, Li H, Gu H, Wang J, Zou Y, Qi G, Xu J, Deng F, Shen W, Li J, Liu S, Zhao J, Zhang L (2019) Beyond the thermal equilibrium limit of ammonia synthesis with dual temperature zone catalyst powered by solar light. Chem 5:2702–2717
- Ye J-Y, Jiang Y-X, Sheng T, Sun S-G (2016) In-situ FTIR spectroscopic studies of electrocatalytic reactions and processes. Nano Energy 29:414–427

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