Engineering vacancy and hydrophobicity of two-dimensional TaTe₂ for efficient and stable electrocatalytic N₂ reduction

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GRAPHICAL ABSTRACT

PUBLIC SUMMARY

- 2D TaTe₂ is produced in large quantities
- Jointly tuning the Te vacancies (V₉e) and surface hydrophobicity of 2D TaTe₂ enables efficient and stable electrocatalytic NRR with remarkable NH₃ faradic efficiency
- The edge plane of TaTe₂ and V₉e serve as the main active sites for NRR
- The free energy change at the potential-determining step on V₉e-TaTe₂ is comparable with the values at the top of the NRR volcano plots on various transition metal surfaces
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Demand for ammonia continues to increase to sustain the growing global population. The direct electrochemical N₂ reduction reaction (NRR) powered by renewable electricity offers a promising carbon-neutral and sustainable strategy for manufacturing NH₃, yet achieving this remains a grand challenge. Here, we report a synergistic strategy to promote ambient NRR for ammonia production by tuning the Te vacancies (V_{Te}) and surface hydrophobicity of two-dimensional TaTe₂ nanosheets. Remarkable NH₃ faradic efficiency of up to 32.2% is attained at a mild overpotential, which is largely maintained even after 100 h of consecutive electrolysis. Isotopic labeling validates that the N atoms of formed NH₃ originate from N₂. In situ X-ray diffraction indicates preservation of the crystalline structure of TaTe₂ during NRR. Further density functional theory calculations reveal that the potential-determining step (PDS) is \( \text{NH}_2 + \text{H}^+ + e^- \rightarrow \text{NH}_3 \) on V_{Te-TaTe₂} compared with that of \( \text{N}^+ + \text{N}_2 + \text{H}^+ + e^- \rightarrow \text{N}-\text{N}-\text{NH} \) on TaTe₂. We identify that the edge plane of TaTe₂ and V_{Te} serve as the main active sites for NRR. The free energy change at PDS on V_{Te-TaTe₂} is comparable with the values at the top of the NRR volcano plots on various transition metal surfaces.

INTRODUCTION

Nitrogen fixation is a key chemical transformation for sustainable development as ammonia (NH₃) is essential across modern industry and agriculture. The traditional fossil-fuel-powered Haber-Bosch process remains widely employed for artificial NH₃ synthesis. However, intense energy consumption (extreme reaction conditions of 300 °C–500 °C and 15–25 MPa),\(^{5-10}\) and massive emission of CO₂ (from the reformation of fossil fuels to produce the hydrogen gas feedstock) pose severe technological, environmental, and ecological challenges.\(^{5-10}\) The electrocatalytic N₂ reduction reaction (NRR), using intermittent electricity generated from renewable sources and water as the hydrogen source, is an attractive strategy for sustainable NH₃ production, and has recently sparked tremendous research interest.\(^{11}\) However, the cleavage of the inert N₂ molecule is difficult due to its strong dissociation energy (9.756 eV, i.e., \( \sim 941 \text{kJ mol}^{-1} \)), high first ionization energy (1,503 kJ mol\(^{-1}\)), and short N–N bond triple bond (1.098 Å).\(^{12-16}\) Another issue is that the major competitive reaction, the hydrogen evolution reaction (HER), has faster reaction kinetics and occurs under similar or even lower overpotentials during the NRR with aqueous electrolytes, causing severe energy efficiency losses.\(^{17}\) Therefore, the design and development of efficient electrocatalysts to break the N≡N bond to drive N₂ conversion while simultaneously suppressing HER is extremely desirable.\(^{18,19}\) Despite recent efforts, most catalytic systems reported suffer from low selectivity for NH₃ formation (typically less than 15% owing to the concomitant HER), large overpotential (or low energetic efficiency), and insufficient stability (usually <30 h), limiting practical use and technological commercialization.

Transition metal dichalcogenides (TMDs) are an emerging class of two-dimensional (2D) materials possessing direct and tunable band gaps.\(^{20-22}\) The interatomic binding in TMDs is strong due to covalent in-plane bonding. Nevertheless, the successive layers in TMD materials are bound through weaker van der Waals atomic binding in TMDs is strong due to covalent in-plane bonding. Nevertheless, the successive layers in TMD materials are bound through weaker van der Waals binding, which makes them suitable for electronic and optoelectronic applications.\(^{23}\) Especially in transition metal tellurides, the relatively low electronegativity of tellurium frequently leads to complex scenarios of competition between metals and non-metals for the bonding electrons. Compared with O, Se, and S chalcogenides, Te has more metallic character, which is a highly desired property for electrocatalysts.\(^{24-26}\) Two-dimensional TaTe₂ has been produced by chemical vapor deposition (CVD); however, the route has drawbacks, such as low yield and complicated operation steps, among others. Large-scale synthesis of 2D TaTe₂ remains a challenge. Furthermore, the catalytic properties of 2D TaTe₂ for NRR are unexplored to date.

Herein, we report efficient production of ultrathin metallic TaTe₂ nanosheets with tuned Te vacancies simply via liquid exfoliation of bulk TaTe₂. \( \gamma \)-Butyrolactone (\( \gamma \)-BL) was discovered to be an excellent organic solvent for the exfoliation. The specific surface area is maximized for a 2D structure, which affords a potentially high density of active sites and also increases surface accessibility to reactants. In addition, the in-plane electrical conductivity of TaTe₂ increased after exfoliation. This provides benefits in electrochemical reactions, where the higher conductivity usually ensures more efficient utilization of the electrical energy. Importantly, the as-prepared defective 2D TaTe₂ was found to be active for NRR, affording a remarkable NH₃ faradic efficiency (FE) in excess of 12% and an NH₃ yield rate of about 6.3 \( \mu \text{gNH}_3 \text{ h}^{-1} \text{ mgcat}^{-1} \) at a low applied potential of \(-0.12 \text{ V} \) versus the reversible hydrogen electrode (versus RHE). More interestingly, further surface modification of TaTe₂ nanosheets electrodes by tethering with trimethoxysilyl (1H,1H,2H,2H-heptadecyl)triethoxysilane (TMWHS) could limit the proton transfer on the electrode surface without interrupting the flow of non-polar moieties, thus enhancing the availability of N₂ on the electrode surface in relation to that of the protons. After such hydrophobic treatment of TaTe₂ nanosheets (denoted as 2D H-TaTe₂), the FE of NH₃ was markedly improved, approaching 32.2%, over 15.4 times compared with bulk TaTe₂. The 2D H-TaTe₂ catalytic performance was maintained even after 100 h of NRR electrolysis.

RESULTS AND DISCUSSION

Synthesis and structural characterization

We successfully prepared TaTe₂ nanosheets by liquid exfoliation of bulk TaTe₂ (Figures 1A and 1B) under ultrasound followed by centrifugation (CF) to remove poorly exfoliated aggregates. We discovered seven organic solvents that can effectively delaminate and disperse TaTe₂ (Table S1, Figure 1C), namely dimethyl sulfoxide, N-methylformamide, 1,3-dimethyl-2-imidazolidinone, \( \gamma \)-BL, tetrahydrofuran, cyclohexanone, and N-methyl-2-pyrrolidinone. \( \gamma \)-BL exhibited superior exfoliating capability. The mass of the TaTe₂ material after removal of the solvent for specific volumes of dispersions allowed one to estimate the stock dispersion concentration. A sample of the stock dispersion in \( \gamma \)-BL was serially diluted. The absorbance per unit-cell length for each diluted sample was then measured and plotted versus TaTe₂ dispersion concentration (Figure S1). The absorption coefficient (\( \alpha \)) at 400 nm was derived to be 554.9 mL mg\(^{-1}\) cm\(^{-1}\) by a straight line fit through the points. The resulting concentration (C) after CF was determined according to the Lambert-Beer law (\( A = \alpha C l \), where \( l \) is the cell length). The dispersion concentration increased steadily with the initial TaTe₂ concentration and reached as high as 4.5 mg mL\(^{-1}\) (Figure S2). The concentration of 4.5 mg mL\(^{-1}\) was chosen for further studies, as it is close to the saturation concentration of 5.3 mg mL\(^{-1}\) (Figure S2). Of interest is that about 80% of the TaTe₂ nanosheets maintained a stable dispersion against sedimentation for at least 20 days (Figure S4).

Figure 1D shows powder X-ray diffraction (XRD) patterns of the starting TaTe₂ and as-obtained TaTe₂ nanosheets. The diffraction peaks at \(-3.3^\circ, 30.6^\circ, 31.2^\circ, \) and \(38.8^\circ\) in traces A and B can be well indexed to the respective (001), (−003), (310), and (−313) reflections of TaTe₂ (JCPDS no. 71-2197). This shows that the TaTe₂ lattice was preserved after exfoliation. However, dramatic weakening in the
relative intensity of the (001) was observed, suggesting loss of orientation in the plane as a consequence of exfoliation. The diffraction peak at 27.7° can be matched with tantalum oxide (JCPDS no. 19-1299), indicating partial oxidation under ultrasound liquid exfoliation. X-ray photoelectron spectroscopy (XPS) was employed to probe the surface chemical state of TaTe$_2$ nanosheets. The main peaks centered at 25.8 and 27.7 eV correspond to Ta 4f$^7/2$ and Ta 4f$^5/2$, respectively, denoting a main valence state of Ta$^{4+}$. The weak peaks appearing at 22.9 and 24.8 eV arise from TaO$_x$ defects. Two doublet peaks can be seen with Te 3d$^5/2$ at 572.8 and 576.1 eV and Te 3d$^3/2$ at 583.2 and 586.5 eV attributed to respective Te$^{2-}$ and Te$^{0}$. The effective restoring forces acting on the atoms increase concomitantly with layer number due to the interlayer van der Waals interaction, leading to a blue shift of the out-of-plane $A_{1g}$ vibration. This tendency indicates that TaTe$_2$ nanosheets become increasingly ultrathin. Further electron paramagnetic resonance (EPR) spectroscopy was employed to detect paramagnetic signals, allowing for analysis of the unsaturated sites with unpaired electrons in catalyst. Bulk TaTe$_2$ displayed weak EPR signals, suggesting low level of defects. By contrast, exfoliated TaTe$_2$ showed a symmetric pair of sharp peaks with the signal at $g = 2.003$, arising from trapped unpaired electrons by Te.
vacancies through adsorbed oxygen species from air ($O_2/C_0$), in accord with XPS results.

Bulk TaTe$_2$ and TaTe$_2$ nanosheets exhibited type II $N_2$ adsorption/desorption isotherms in the Brunauer-Deming-Deming-Teller classification (Figure S7). After exfoliation, the Brunauer-Emmett-Teller surface area and average single-point total pore volume rose from $<2.0 \text{ m}^2 \text{ g}^{-1}$ to $0.0112 \text{ cm}^3 \text{ g}^{-1}$ to $59.8 \text{ m}^2 \text{ g}^{-1}$ and $0.160 \text{ cm}^3 \text{ g}^{-1}$, respectively. The substantial increase in specific surface area benefits mass transport and improves surface accessibility to reactants, thus favoring NRR. We performed $N_2$ temperature-programmed desorption ($N_2$ TPD) to investigate the $N_2$ adsorption ability of TaTe$_2$. The $N_2$ TPD profiles of TaTe$_2$ nanosheets show two strong peaks at $338.6^\circ C$ and $411.0^\circ C$, and a mild peak at $97.4^\circ C$, arising from chemisorption and physisorption of $N_2$, respectively (Figure 1I). In comparison, only weak signals of physi- and chemisorbed $N_2$ on bulk TaTe$_2$ were detected, implying that TaTe$_2$ nanosheets possess more exposed active sites. The activation energy of desorption from the surface of TaTe$_2$ nanosheets was estimated to be about $32.6 \text{ kJ mol}^{-1}$, an indication of strong adsorption. The superior $N_2$ adsorption capacity and high bonding-affinity toward $N_2$ of 2D TaTe$_2$ definitely provide benefits for electrocatalytic $N_2$ reduction.

Transmission electron microscopy (TEM) images showed the formation of thin TaTe$_2$ flakes with lateral sizes in the range of $200 \text{ nm}$ to $1 \mu \text{ m}$, randomly stacking on top of each other (Figures 2A–2C and S8). Figure 2D reveals a set of interference fringes, with the fast Fourier transform showing $d$-spacings of $0.29$ and $0.22 \text{ nm}$, and a mutual angle between the planes of $94^\circ$. These are in excellent agreement to $1T$ TaTe$_2$ viewed down the $[15-6]$ axis, and with the $0.29 \text{ nm}$ spacing corresponding to a $(111)$ plane. The existing oxygen means that TaTe$_2$ flakes were weakly oxidized on the surface, with disordered edges observed for many of the nanosheets (Figures 2B, 2I, and S8A). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observation (Figure 2E) together with in situ energy-dispersive X-ray spectroscopy mapping (Figures 2F–2H) indicated that TaTe$_2$ nanosheets were composed of Ta, Te, and a small amount of oxygen. Ta M and O K could only be detected in the electron energy loss spectroscopy spectrum (Figure 2J), and the Ta/O atomic ratio was about $0.61$, corresponding to TaO$_x$ in the XRD pattern. Shown in Figure 2K are the tapping-mode atomic force microscopy images of 2D TaTe$_2$ exfoliated in $\gamma$-BL at a concentration of $0.4 \text{ mg mL}^{-1}$ deposited on an SiO$_2$/Si substrate. The Innovation 3(1): 100190, January 25, 2022.
a contact angle of 57.5°. In stark contrast, after hydrophobic treatment, the hydrophilic electrode showed an increased contact angle of 147.2°, indicating a hydrophobic feature of 2D H-TaTe2. The TaTe2 nanosheets before and after hydrophobic modification were examined for NRR using a classic two-compartment H-type cell separated by a cation-exchange membrane (Nafion 117) with continuous N2 bubbling (Figure S10).

Particular care was taken when carrying out NRR to avoid false positives from background NH3 in the system or external contamination. Prior to NRR measurements, the N2 feeding gas was pre-purified to eliminate possible NH3 and labile nitrogen-containing contaminants (such as nitric oxides, nitrites, or nitrates). Spectrophotometric tests verified that almost no NO2− and NO3− existed in the N2-purged electrolyte (Figures S11–S13). To evaluate the NRR activity, electrochemical tests were conducted in 0.1 M HCl solutions saturated with purified N2 or Ar (Figure S14) as used as a feed gas. Linear sweep voltammetry curves of bulk TaTe2, 2D TaTe2, and H-TaTe2 revealed an onset cathodic current related to hydrogen evolution under both Ar and N2 conditions (Figure 3B). The 2D H-TaTe2 exhibited a lower current density compared with 2D TaTe2 in 0.1 M N2-purged HCl, resulting from weak binding of hydrogen atoms on the hydrophobic surface. The NRR was found to take place with an overpotential as low as considerably higher than that of a recently reported liquid H2O droplet plasma system. The NH3 FE first decreased from −0.02 to −0.07 V because the HER tended to dominate over NRR at low overpotentials, but increased with applied potentials upon stepping the voltage from −0.07 to −0.12 V, beyond which the FE for NH3 formation drastically declined owing to more severe competition which could shift the reaction selectivity toward the HER. Moreover, at high current densities the available amounts of N2 may become mass transport determined and decreased as a result of NRR. Among others, the wetted surface area within the electrode itself and occupation of active sites by H + (decreasing the surface coverage of N2) increased as a function of the applied reductive potential, which would also intensify the HER. The NH3 FE attained was up to 17.3% at −0.17 V, over seven times higher than that of bulk TaTe2. Notably, H-TaTe2 nanosheets reached an NH3 FE exceeding 32.0% with an NH3 formation rate of 18 µmol h−1 mgcat−1 at −0.12 V. The NH3 FE could be further improved to 36.2% at −0.17 V, over 15 times higher than that of bulk TaTe2 (Figure 3D). The NH3 partial geometric current density of 2D H-TaTe2 was 10.8 µA cm−2, 2.3 times higher than that of bulk TaTe2 (Figure 3E). The cathodic energy efficiency at
0.28 mA cm$^{-2}$ was evaluated to be $\sim$24.8% (Figure S20). The N$_2$ reduction performance was found to be most optimal at pH 1.0 (Figure S21) and a working electrode loading density of 0.5 mg TaTe$_2$ cm$^{-2}$ (Figure S22). Alternatively, both NH$_3$ production rate and FE were observed to increase with an increase of centrifugation speed from 500 to 1,000 rpm (Figure S23), indicating that increase in vacancy concentration led to improvement of NRR activity. Whereas further increase of centrifugation speed from 1,000 to 3,000 rpm to induce more defects (i.e., V$_{Te}$) resulted in decreased NRR performance. This may be due to lowering in electric conductivity and simultaneously enhanced HER. It is worth noting that the 2D H-TaTe$_2$ nanosheets outperform most previously reported transition metal- and precious metal-based electrocatalysts in terms of NH$_3$ FE (Table S2).

To probe possible interference, if any, from the environment and assess the origin of the detected NH$_3$, a set of rigorous control and verification experiments (for multiple repeats at each condition) were carried out. Almost no NH$_3$ was obtained either in Ar-saturated solution (under the same conditions as the NRR experiments), or in the absence of catalyst, or with just the background Na$_2$SO$_4$ solution binder, or at an open circuit potential (Figures 3F and 3G). Isotopic labeling using $^{15}$N$_2$ in combination with isotope-sensitive proton nuclear magnetic resonance ($^1$H NMR) was further performed. The $^1$H NMR spectrum of the NRR product exhibited a doublet coupling ($\sim$73 Hz) typical for $^{15}$NH$_4^+$ compared with a triplet coupling ($\sim$52 Hz) for $^{14}$NH$_4^+$ (Figure 3G). The absolute dominant $^{15}$NH$_4^+$ doublets confirmed that the N in NH$_3$ stemmed from the gaseous N$_2$ supplied. In addition, we would like to emphasize that the TaTe$_2$ catalysts neither contain nitrogen in their structures nor are prepared from nitrates, nitrides, or ammonium precursors, excluding extraneous nitrogen sources. These strongly suggest that the NH$_3$ was generated from the reduction of dissolved N$_2$ accelerated by the 2D TaTe$_2$ electrocatalyst.

To evaluate the stability of 2D H-TaTe$_2$, we conducted alternating electrolysis between Ar and N$_2$-saturated electrolytes, which showed that the NH$_3$ evolved remained essentially unchanged for three cycles (Figure 4A). TaTe$_2$ nanosheets also exhibited good stability with nearly constant NH$_3$ yield rates, FEs, and partial geometric current densities ($J_{NH3}$) for 20 times by use of 20 batches of 2D H-TaTe$_2$ at $-0.12$ V (Figure 4B). Strikingly, negligible decay in $J_{NH3}$ occurred even after continuous electrolysis for 100 h, indicating considerable catalytic stability of 2D H-TaTe$_2$ (Figure 4C). After 100 h of NRR, the catalytic performance of post-NRR 2D H-TaTe$_2$ and TaTe$_2$ in fresh N$_2$-saturated electrolyte was also determined. As displayed in Figure 4D, there are no obvious decreases in both NH$_3$ yield and FE at $-0.12$ V, suggesting that H-TaTe$_2$ nanosheets still maintained high activity after long-term use. No obvious leaching of TaTe$_2$ into the electrolyte ($<0.06$ wt %) was observed even after 100 h of electrolysis by inductively coupled plasma atomic emission spectroscopy analysis. The stability of TaTe$_2$ nanosheets was also investigated by in situ XRD analysis (Figures 5A and S24). It can be clearly seen that the peaks corresponding to TaTe$_2$ remained consistent throughout the entire electrolysis, accounting for the good durability of such V$_{Te}$-rich TaTe$_2$. Post characterization by XRD analysis (Figures 5A and S24) confirmed the presence of the TaTe$_2$ phase.

To further investigate the origin of the detected NH$_3$, an in situ XRD analysis was carried out (Figures 5A and S24). It can be clearly seen that the peaks corresponding to TaTe$_2$ remained consistent throughout the entire electrolysis, suggesting the presence of the TaTe$_2$ phase. Post characterization by XRD analysis (Figures 5A and S24) confirmed the presence of the TaTe$_2$ phase.
TaTe$_2$ nanosheets possess more rapid reaction kinetics, and the for bulk TaTe$_2$, in accordance with its observed superior NRR activity. Nyquist plots (Figure 5C) revealed a significantly lower charge transfer resistance for H-TaTe$_2$ and TaTe$_2$ nanosheets than that of bulk TaTe$_2$ (Figure S26), the most stable vacancy site is considered. EPR characterization (Figure 1H) showed preservation of defects in 2D TaTe$_2$ even after electrolysis, accounting for maintenance of the NRR performance.

To gain insight into the outstanding activity of TaTe$_2$ nanosheets, the Tafel plot and electrochemical impedance were evaluated. The Tafel slope was ~146.3 mV dec$^{-1}$ for 2D H-TaTe$_2$, ~163.5 mV dec$^{-1}$ for TaTe$_2$ nanosheets, much lower than that of bulk TaTe$_2$ (~269.5 mV dec$^{-1}$) (Figure S8B). This implies that exfoliated TaTe$_2$ nanosheets possess more rapid reaction kinetics, and the first electron transfer process to yield $^*\text{N}-\text{NH}$ ($^*$ represents the surface adsorbed species) is the rate-determining step. Nyquist plots (Figure 5C) revealed a significantly lower charge transfer resistance for H-TaTe$_2$ and TaTe$_2$ nanosheets than that of bulk TaTe$_2$ in accordance with its observed superior NRR activity. To understand the reaction mechanism for NRR and origin for enhanced NRR activity on TaTe$_2$ nanosheets, we conducted DFT calculations. We used monodispionic-TaTe$_2$, which agrees with the as-obtained crystalline structure of TaTe$_2$ from the XRD results (Figure 1D). The (~603) facet, which is the basal plane of the exfoliated TaTe$_2$, was considered. EPR characterization (Figure 1H) identified the emerging Te vacancy ($V_{603}$) after exfoliation, and thus we also considered the NRR activity at $V_{603}$ sites. $V_{603}$ site is modeled by eliminating one Te atom in TaTe$_2$ (~603) (Figure S26), the most stable vacancy site is considered, denoted as $V_{603}$-TaTe$_2$ (~603). The TEM and STEM images (Figures 2B and 2I) showed the disordered edges. Making a representative DFT model for amorphous solid is limited due to the need for reasonable calculation times. Alternatively, we used the crystalline edge of TaTe$_2$(010) instead, assuming that the local moiety of the amorphous edge to be similar to the crystalline edge. To investigate the effect of the TaO$_x$ in the edge site, we modeled the oxygen atom containing TaTe$_2$(010) edge sites. Also, we constructed Te(10-10) facet to consider the remaining Te which were found in XPS (Figure 1F). The optimized geometries of calculation models are shown in Figures S28 and S27. We consider surface Ta atom as an active site in TaTe$_2$(010) and $V_{603}$-TaTe$_2$ (~603). For TaTe$_2$ (~603), Te atom is regarded as an active site since Ta atom is not exposed.

Among the many intermediate steps in NRR, we first focused on $^*\text{N}-\text{NH}$ formation. This has been identified as the largest free energy demanding step in various catalysts and, hence, the $^*\text{N}-\text{NH}$ formation energy is a good descriptor for estimating the NRR activity. We compared the $^*\text{N}-\text{NH}$ formation free energy on (~603), $V_{603}$-TaTe$_2$ (~603), and TaTe$_2$(010), obtained by $G(\text{N}_2) – G(^*\text{NH}) – G(\text{NH}_3)$ and $G(^*\text{N}_2) – G(^*\text{NH}) – G(\text{NH}_3)$ (Figure 6B). This result indicates that the Ta atom site rather than Te atom facilitates $^*\text{N}-\text{NH}$ formation and plays an important role in enhancing N$_2$ activation. Meanwhile, the $^*\text{N}-\text{NH}$ formation energies of Te(10-10) (~3.41 eV) and TaO$_x$ (~1.62–3.44 eV) are higher than that of $V_{603}$-TaTe$_2$ (~0.82 eV) or TaTe$_2$(010) (~1.47 eV) (Figure S27C). Thus, the Te and TaO$_x$ are less reactive for NRR than $V_{603}$-TaTe$_2$ and TaTe$_2$(010), which qualitatively agrees with the experimental result (Figure S1B). We further conducted DFT calculations with the oxygen-doped TaTe$_2$(010), which showed the reliable $^*\text{N}-\text{NH}$ formation energy (~1.66 eV, 1.63 eV) to consider the effect of the oxygen.

Next, we obtained a free energy diagram for NRR and identified the lowest free energy pathway. The NRR activity is estimated by comparing the free energy change at the potential-determining step (PDS), the largest free energy requiring electrochemical step. The PDS is $^*\text{N}_2 + (H^+ + e^-) \rightarrow ^*\text{N}-\text{NH}$ on TaTe$_2$ (~603) and TaTe$_2$(010) (Figures S28 and 6D), while that on $V_{603}$-TaTe$_2$ (~603) is $^*\text{N}_2 + (H^+ + e^-) \rightarrow ^*\text{NH}_2$ (Figure 6C). We noted that a stronger N bind-
energy in the free energy diagram of $V_{2\alpha}TaTe_2(-603)$ and $TaTe_2(010)$. This result matches the Tafel slope analysis, which reveals that the rate-determining step is the first electron transfer step.

As summarized in Figure S30, the free energy change at PDS increases in the order of $TaTe_2(010) < V_{2\alpha}TaTe_2(-603) < TaTe_2(-603)$. Interestingly, the free energy change at PDS on $TaTe_2(010)$ and $V_{2\alpha}TaTe_2(-603)$ is decreased by $\sim 1.8$ eV compared with that of $TaTe_2(-603)$, indicating that the exposed Ta atoms in $TaTe_2$, rather than surface Te atom, act as the major active sites for NRR. We note that the free energy change at PDS on $TaTe_2(010)$ and $V_{2\alpha}TaTe_2(-603)$ (0.95 eV) is comparable with the values ($\sim 1.0$ eV) at the top of the NRR volcanoes on various transition metal surfaces. In the case of oxygen-doped $TaTe_2(010)$ planes, the PDS is $\Delta G_{\text{PDS}}^{\text{Ta}} = 4.7$ eV at an applied potential of $\sim 0.4$ V. Facile modification of $TaTe_2$ electrodes by using trimethoxy(1H,1H,2H,2H perfluorodecyl) silane substantially inhibited the parasitic HER and greatly increased the FE for NH$_3$ formation, reaching $\sim 92\%$ at $\sim 0.4$ V with an NH$_3$ yield rate of $5.8$ mmol g$^{-1}$ h$^{-1}$. The NH$_3$ FE was further improved to $\sim 36\%$ at $\sim 0.17$ V, over 15.4 times higher than on bulk TaTe$_2$. Of particular interest is the H-TaTe$_2$ nanosheets retained NRR performance even after 100 h of operation. DFT calculations showed that the exposed Ta atom sites dramatically enhanced N binding and decreased the free energy change at PDS, thereby boosting N$_2$ reduction. We envision that the integrative strategy by engineering anion vacancies and surface hydrophobicity of 2D TMDs will offer profound implications for design and prepration of efficient NRR electrocatalysts.

CONCLUSIONS

In summary, we have demonstrated high yield of stably dispersed few-layer metallic TaTe$_2$ nanosheets rich in Te vacancies by ultrasonication of bulk TaTe$_2$ in H$_2$-butylpyrrolactone. The defective 2D TaTe$_2$ efficiently facilitated electrochemical N$_2$ fixation, delivering a large NH$_3$ FE ($\sim 12.9\%$) and high NH$_3$ formation rate ($\sim 0.3$ mmol g$^{-1}$ h$^{-1}$) at an applied potential of $\sim 0.12$ V. Facile modification of TaTe$_2$ electrodes by using trimethoxy(1H,1H,2H,2H perfluorodecyl) silane substantially inhibited the parasitic HER and greatly increased the FE for NH$_3$ formation, reaching $\sim 92\%$ at $\sim 0.4$ V with an NH$_3$ yield rate of $5.8$ mmol g$^{-1}$ h$^{-1}$. The NH$_3$ FE was further improved to $\sim 36\%$ at $\sim 0.17$ V, over 15.4 times higher than on bulk TaTe$_2$. Of particular interest is the H-TaTe$_2$ nanosheets retained NRR performance even after 100 h of operation. DFT calculations showed that the exposed Ta atom sites dramatically enhanced N binding and decreased the free energy change at PDS, thereby boosting N$_2$ reduction. We envision that the integrative strategy by engineering anion vacancies and surface hydrophobicity of 2D TMDs will offer profound implications for design and preparation of efficient NRR electrocatalysts.

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AUTHOR CONTRIBUTIONS

Z.S. supervised the project. Z.S. and Z.Z. conceived the idea. Z.Z., X.H., and Z.L. conducted synthesis and electrocatalytic experiments. S.H. and A.W.R. carried out the electron microscopy. H.Z. and T.W.B.L. measured in situ XRD. J.P., C.C., and Y.J. performed DFT analysis. Z.S., Z.Z., J.P., and Y.J. wrote the manuscript and A.W.R. polished the language.

DECLARATION OF INTERESTS

The authors declare no competing interests.

SUPPLEMENTAL INFORMATION

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