Promoting N₂ electroreduction to ammonia by fluorine-terminating Ti₃C₂Tx MXene

Yu Ding¹, Junbo Zhang¹, Anxiang Guan¹, Qihao Wang¹, Si Li¹, Abdullah M. Al-Enizi², Linping Qian¹, Lijuan Zhang¹* and Gengfeng Zheng¹*

Abstract
Two-dimensional MXene-based materials are potential of presenting unique catalytic performances of electrocatalytic reactions. The surface functionalization of MXene-based catalysts is attractive for developing efficient electrocatalysts toward nitrogen reduction reaction. Herein, we reported a Ti₃C₂Tx MXene with a medium density of surface functionalized fluorine terminal groups, as an excellent N₂ reduction reaction electrocatalyst with enhanced adsorption and activation of N₂. The Ti₃C₂Tx MXene catalyst showed a production rate of ammonia as \(2.81 \times 10^{-5} \text{ μmol·s}^{-1}·\text{cm}^{-2}\), corresponding to a partial current density of 18.3 μA·cm⁻² and a Faradic efficiency of 7.4% at −0.7 V versus reversible hydrogen electrode in aqueous solutions at ambient conditions, substantially exceeding similar Ti₃C₂Tx MXene catalysts but with higher or lower densities of surface fluorine terminal groups. Our work suggests the capability of developing surface functionalization toolkit for enhancing electrochemical catalytic activities of two-dimensional MXene-based materials.

Keywords: MXene, Surface functionalization, Electrocatalysis, N₂ reduction reaction, Fluorine

1 Introduction
Artificial nitrogen fixation to ammonia (NH₃) plays a critical role in fabricating agricultural fertilizers and maintaining the earth’s ecosystems [1–3]. The traditional NH₃ synthesis in industry depends heavily on the Haber–Bosch process with high temperatures of 350–550 °C and pressures of 150–350 atm [4, 5]. In recent years, new strategies, such as biological [6], photocatalytic [7] and electrocatalytic [8–10] approaches, have been reported for ammonia synthesis. In particular, electrocatalytic nitrogen reduction reaction (N₂RR) can use water as hydrogen source and proceed in ambient conditions, suggesting an attractive feature of clean ammonia production with low carbon footprint [11]. Nevertheless, the development of N₂RR has been largely limited by its low current densities, limited Faradaic efficiency (FE) values, and slow NH₃ production rates, which are ascribed to the large reaction energy barriers during NH₃ adsorption and activation processes [12]. It is critical to design robust electrocatalysts that can efficiently adsorb, activate and convert N₂ into NH₃.

Two-dimensional (2D) materials, such as graphene [13], metal–organic frameworks [14], black phosphorus [15], have been drawing great attention of researchers for N₂RR, owning to their unique 2D structures and unconventional chemical properties [16]. MXenes, one of the novel 2D materials synthesized by selective etching of the aluminum layers from the precursor MAX phases [17], have been demonstrated with applications in supercapacitors [18], batteries [19], and electrochemical N₂RR [20–22]. For instance, Luo et al. [23] reported that Ti₃C₂Tx MXene on stainless steel mesh functioned as efficient N₂RR electrocatalysts with a FE of 5.78%. On the other hand, the terminal groups (Tx), mainly oxygen (O)-containing or fluorine (F)-terminations, can be tuned to affect the electrocatalytic performances of Ti₃C₂Tx MXene [24]. Previously, density functional theory (DFT)
calculations suggested that Ti₃C₂ MXene with O-containing terminal groups can combine N₂ more strongly than that with F-terminal groups [25]. The bond length of N₂ for Ti₃C₂ MXene with F-terminal groups was calculated to be slightly larger than that with O-containing terminal groups [26]. The computational calculations also indicated that a moderate proportion of F-termination on Ti₃C₂ MXene was theoretically beneficial to the adsorption and electrocatalytic activation of nitrogen. Thus, efforts are needed to develop efficient and tunable functionalization on the surface of Ti₃C₂Tx MXene to optimize its N₂RR performance and achieve highly selective NH₃ production.

Herein, we developed the surface modification of MXene-based catalysts to optimize the N₂RR performance. The fluorine-terminal groups on the MXene surface were modified by treating with different concentrations of fluorine-containing acids and subsequent alkalinization. Due to the combined effects including hydrogenation and N₂ activation, Ti₃C₂Tx MXene with a medium F-terminal group density (designated as Ti₃C₂Tx-medium F) exhibited the optimal electrocatalytic N₂RR performances. The NH₃ production rate was 2.81 × 10⁻⁵ μmol·s⁻¹·cm⁻² in 0.01 M Na₂SO₄ electrolyte at −0.7 V versus reversible hydrogen electrode in ambient conditions, corresponding to a FE of 7.4% and a partial current density up to 18.3 μA·cm⁻².

2 Experimental

Ti₃C₂Tx MXene nanosheets were synthesized via a fluorine-containing etching method [27, 28], which selectively etched the Al layers in Ti₃AlC₂ with fluorine-containing acid, followed by exfoliating steps to obtain Ti₃C₂Tx MXene nanosheets. To modify the density of fluorine terminal groups on the surface of Ti₃C₂Tx MXene, different fluorine-containing acids were used. In brief, 2 g of LiF was dissolved in 20 mL of 6 M HCl solution, and stirred for 5 min to form a high fluorine-containing acid environment to prepare the Ti₃C₂Tx MXene with high surface density of F-terminal groups; while 20 mL of 10% hydrofluoride acid (HF) was used to obtain a medium surface density of F-terminal groups. In order to further reduce the fluorine ratio of the terminal groups on the MXene surface, Ti₃C₂Tx MXene with medium density of fluorine-terminal groups was immersed into 0.5 M KOH solution to replace fluorine terminal groups by hydroxyl groups.

In our experiments, 1 g of Ti₃AlC₂ MAX precursor was slowly added into the aforementioned solutions respectively, and the obtained mixture was stirred for 24 h at room temperature to achieve different surface functionalization of fluorine or hydroxyl groups. Afterwards, the resulting solution was washed with deionized (DI) water and centrifuged at 3500 rpm for several times until pH of the solution was 6–7. To prepare few-layer Ti₃C₂Tx MXene nanosheets, the sediment was then dispersed in DI water and ultrasonicated for 30 min in ice bath with Ar gas bubbling. The few-layer Ti₃C₂Tx MXene solution was then obtained by centrifugation at 3500 rpm for 30 min. A polyvinyl difluoride (PVDF) membrane was utilized to filter Ti₃C₂Tx MXene product and the obtained powder was dried with membrane for 12 h at room temperature.

3 Results and discussion

The synthesis process of Ti₃C₂Tx MXene nanosheets included two successive steps [27, 28]: selective etching of aluminum (Al) layer on MAX phases with a fluorine-containing etching method, and delaminating of MXene layers by sonication (Fig. 1a). After these two steps of preparation, the original structure of Ti₃AlC₂ MAX phase (Additional file 1: Fig. S1) was transformed into few-layer, 2-dimensional Ti₃C₂Tx MXene (Fig. 1b). The surface of Ti₃C₂Tx MXene was covered by different terminal groups, mainly including O-containing groups (e.g., –O, –OH) and fluorine groups [29]. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping analysis showed that Ti, C, O, and F elements were evenly distributed on the obtained Ti₃C₂Tx MXene (Fig. 1c). The color of few-layer Ti₃C₂Tx MXene appeared as a blackish green color instead of pure black (Additional file 1: Fig. S2a), and the Tyndall scattering effect was also observed (Additional file 1: Fig. S2b). These two empirical phenomena indicated the formation of few-layer, sheet-like structure of Ti₃C₂Tx MXene.

The X-ray powder diffraction (XRD) pattern exhibited the characteristic peaks of Ti₃C₂Tx MXene, which differed greatly from the Ti₃AlC₂ MAX precursor (Fig. 1d). After etching, the peak (2θ ≈ 9.28°) on Ti₃AlC₂ MAX phase exhibited a negative shift to a low angle (2θ ≈ 5.89°), corresponding to the characteristic lattice (002) plane of Ti₃C₂Tx MXene [30]. No additional peaks were observed for Ti₃C₂Tx MXene except for the peaks of carbon paper. The differences of the XRD patterns between Ti₃C₂Tx MXene and Ti₃AlC₂ MAX indicated the successful etching of Al layers from Ti₃AlC₂ MAX phases.

Scanning electron microscopy (SEM) images showed that all the synthesized Ti₃C₂Tx MXene were 2D sheet-like structures (Additional file 1: Fig. S3). The ratio of F-terminal groups to all the surface groups of Ti₃C₂Tx MXene was measured by EDS profiles (Additional file 1: Fig. S4), which was calculated as 82% (designated as Ti₃C₂Tx-high F, indicating that it was etched by a high-concentration fluorinated acid) and 48% (designated as Ti₃C₂Tx-medium F, indicating that it was etched by a medium-concentration fluorinated acid). To further
decrease the ratio of fluorine groups on the surface of MXene, an alkalinization treatment was conducted to Ti$_3$C$_2$T$_x$-medium F MXene (Experimental section), and the fluorine proportion was reduced to 24% (designated as Ti$_3$C$_2$T$_x$-low F).

To investigate the structures of Ti$_3$C$_2$T$_x$ MXene with different amounts of fluoride, Raman and X-ray photoelectron spectroscopy (XPS) were conducted to qualitatively investigate the fluorine ratio in all the terminal groups. As shown in the Raman spectra (Fig. 2a), the relative intensity of vibrational modes for Ti$_3$C$_2$T$_x$ indicated the densities of terminal groups on MXene. The Raman shifts at 205 and 366 cm$^{-1}$ were respectively associated to the A$_{1g}$ and E$_g$ vibration modes of the C–Ti–O structure. The Raman peak at 614 cm$^{-1}$ corresponded to the C–Ti–OH structure [23], and the Raman peak at 706 cm$^{-1}$ represented the A$_{1g}$ vibrations of carbon. The relatively large intensity of the characteristic Raman peaks at 205, 614, and 366 cm$^{-1}$ corresponded to the O-containing terminal groups, and suggested that the densities of O-terminal groups were in the order of Ti$_3$C$_2$T$_x$-low F > Ti$_3$C$_2$T$_x$-medium F > Ti$_3$C$_2$T$_x$-high F. This trend also confirmed that the densities of F-terminal groups followed the order as: Ti$_3$C$_2$T$_x$-high F > Ti$_3$C$_2$T$_x$-medium F > Ti$_3$C$_2$T$_x$-low F.

The survey XPS spectra of all the Ti$_3$C$_2$T$_x$ MXene samples with different densities of fluorine terminal groups exhibited same element peaks (Fig. 2b), which assigned to F 1 s, O 1 s, Ti 2p and C 1 s, respectively. Among these samples, Ti$_3$C$_2$T$_x$ MXene-high F showed the highest intensity of F 1 s and the lowest intensity of O 1 s, indicating the highest ratio of fluorine terminal groups among these samples, in good accord with the EDX result. The F 1 s XPS spectra presented two main peaks at 684.5 and 685.9 eV (Fig. 2c), corresponding to the F–Ti and F–C bonds, respectively. For the O 1 s spectra (Additional file 1: Fig. S5), the peaks at 529.3, 531.2 and 533.4 eV were ascribed to C–Ti–O, C–Ti–OH species, and the adsorbed H$_2$O on the MXene surface. With the increased concentrations of alkali solutions, the density of C–Ti–O species on the MXene surface increased and the fluorine terminal groups decreased. For the Ti 2p XPS spectrum (Fig. 2d), four doublets were fitted to indicate the valence and bond structures of Ti. The peaks centered at 454.4 and 460.6 eV referred to Ti$^{3+}$; the peaks at 455.0 and 461.7 eV were assigned to Ti$^{2+}$; the peaks at 456.2 and 462.9 eV were associated with the Ti–C bond; the peaks at 458.4 and 464.3 eV were ascribed to the Ti–O bond; and the peak at 459.5 eV was attributed to the Ti–F bond. The relative intensities of Ti–O and Ti–F bonds also indicated that the fluorine terminal group density on the MXene surface followed the order of Ti$_3$C$_2$T$_x$-high F > Ti$_3$C$_2$T$_x$-medium F > Ti$_3$C$_2$T$_x$-low F.

The capability of different F-terminating surface functionalizations of Ti$_3$C$_2$T$_x$ MXene for enhancing the N$_2$RR catalytic activity was then investigated. All the
electrochemical tests were conducted in N₂-saturated 0.01 M Na₂SO₄ electrolyte, and all the potentials presented in this work were converted as values versus reversible hydrogen electrode (RHE). The linear sweep voltammetry (LSV) curves of Ti₃C₂Tx MXene with different proportions of fluorine terminal groups were recorded (Fig. 3a). The experimental overpotentials of Ti₃C₂Tx MXene displayed the following order of Ti₃C₂Tx-high F > Ti₃C₂Tx-medium F > Ti₃C₂Tx-low F at −10 mA·cm⁻² current density, which was associated with the hydrogenation step during electrochemical reduction. Owning to the different densities of F-termination on the MXene surface, the hydrogenation step could be inhibited [31]. The Ti₃C₂Tx-high F sample had the highest density of fluorine terminal groups, resulting in the inhibition of H⁺ adsorption [32] and eventually the decline of N₂RR activity. In contrast, Ti₃C₂Tx-low F had a low density of fluorine terminal groups and abundant O-containing termination, and presented the highest hydrogen evolution reaction (HER) performance but low N₂ adsorption and activation capabilities. In comparison, Ti₃C₂Tx-medium F MXene had a medium density of fluorine terminal groups, and presented the highest N₂RR electrocatalytic activity.

The Ti₃C₂Tx-medium F MXene catalyst was further tested in both Ar-saturated and N₂-saturated electrolytes (Fig. 3b). The current density in N₂-saturated electrolyte (red curve) exceeded that in Ar-saturated electrolyte (black curve) in the voltage range between −0.4 and −0.8 V, indicating the occurrence of electrochemical N₂RR on the catalyst surface. Both the chronoaempoerometric tests and the salicylic acid indicator method were adopted to determine the amount of produced NH₃. All the yields of ammonia were calculated from the standard curves (Additional file 1: Fig. S6). In addition, each experiment was also conducted in Ar-saturated electrolyte to serve as the background. The corrected rate of NH₃ yield (YR_corrected) was calculated from the following...
equation: $Y_{R_{corrected}} = Y_{R_{N2}} - Y_{R_{Ar}}$. The NH$_3$ yield rate from Ti$_3$C$_2$T$_x$-medium F MXene was calculated based on the corresponding UV–Vis absorption spectra at the potential range between −0.4 and −0.8 V (Fig. 3c). The value of average background ($Y_{R_{Ar}}$) was calculated as $(2.03 \pm 0.2) \times 10^{-5}$ μmol·s$^{-1}$·cm$^{-2}$. As shown in Fig. 3d, the maximum FE for NH$_3$ production by Ti$_3$C$_2$T$_x$-medium F MXene was 42.7% at −0.5 V, while the highest NH$_3$ partial current density after background correction was 18.3 μA·cm$^{-2}$ at −0.7 V, corresponding to an FE of 7.4% and the NH$_3$ production rate of $2.81 \times 10^{-5}$ μmol·s$^{-1}$·cm$^{-2}$.

The chronoamperometry curves and the corresponding UV–Vis absorption spectra over Ti$_3$C$_2$T$_x$ MXene with different densities of F-terminal groups at all applied potentials were displayed (Additional file 1: Fig. S7). Compared to Ti$_3$C$_2$T$_x$ MXene counterparts with higher or lower surface densities of fluorine terminal groups (i.e., Ti$_3$C$_2$T$_x$-high F and Ti$_3$C$_2$T$_x$-low F), the Ti$_3$C$_2$T$_x$-medium F MXene catalyst covered with medium fluorine terminal group density exhibited the highest N$_2$RR catalytic performance (Fig. 4a, b). The corrected NH$_3$ yield rate ($Y_{R_{corrected}}$) with Ti$_3$C$_2$T$_x$-medium F catalyst ($2.81 \times 10^{-5}$ μmol·s$^{-1}$·cm$^{-2}$) was 1.6 and 1.7 times higher than that of Ti$_3$C$_2$T$_x$-high F ($1.75 \times 10^{-5}$ μmol·s$^{-1}$·cm$^{-2}$) and Ti$_3$C$_2$T$_x$-low F ($1.67 \times 10^{-5}$ μmol·s$^{-1}$·cm$^{-2}$) at −0.7 V.

The electrochemical stability of the Ti$_3$C$_2$T$_x$-medium F MXene catalyst was further interrogated. As shown in Fig. 4c, the total electrolysis current density in N$_2$-saturated electrolyte was maintained relatively stable over 18 h. Moreover, cycling test of six continuous times was conducted, and the corresponding chronoamperometric measurements and UV–Vis absorption spectra were examined after each cycle (Additional file 1: Fig. S7e, f). Both of NH$_3$ production rate ($2.67 \pm 0.16 \times 10^{-5}$ μmol·s$^{-1}$·cm$^{-2}$) and the FE values ($7.5\pm 0.5\%$) were within the error range of 7.4% after the continuous chronoamperometric measurement for 6 times, with 1 h of measurement each time (Fig. 4d), which suggesting the excellent durability of Ti$_3$C$_2$T$_x$-medium F MXene. Furthermore, the XRD patterns of Ti$_3$C$_2$T$_x$ MXene before and after electrochemical nitrogen reduction reaction were also displayed (Additional file 1: Fig. S8), the unvaried peak position of XRD patterns also testified the stable crystal phases and structure of Ti$_3$C$_2$T$_x$ MXene. Thus, Ti$_3$C$_2$T$_x$-medium F MXene with a medium density of...
surface fluorine terminal groups was demonstrated as an optimal catalyst for N$_2$RR.

4 Conclusions
In summary, we demonstrated the surface functionalization of fluorine terminal groups on MXene to tune the N$_2$RR catalytic activity at ambient conditions, in which different densities of surface fluorine terminal groups allowed to affect the capability of N$_2$ adsorption and activation. The Ti$_3$C$_2$T$_x$ MXene catalyst with a medium F-termination proportion (Ti$_3$C$_2$T$_x$-medium F) showed the optimal N$_2$RR activity, with the highest NH$_3$ yield rate of 2.81 × 10$^{-5}$ μmol·s$^{-1}$·cm$^{-2}$ at −0.7 V, substantially exceeding that of Ti$_3$C$_2$T$_x$-high F and Ti$_3$C$_2$T$_x$-low F. Further study and development of surface functionalization toward N$_2$ adsorption and activation can serve as a powerful toolkit for improving artificial N$_2$ fixation.

Supplementary Information
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Additional file 1. Fig. S1. (a-c) SEM images and (d) EDS elemental analysis profile of Ti$_3$AlC$_2$ MAX. Fig. S2. (a) The blackish green color and (b) the Tyndall scattering effect of Ti$_3$C$_2$Tx MXene solution. Fig. S3. SEM images of (a-c) Ti$_3$C$_2$Tx-high F; (d-f) Ti$_3$C$_2$Tx-medium F and (g-i) Ti$_3$C$_2$Tx-low F. Fig. S4. EDS elemental analysis profiles of (a) Ti$_3$C$_2$Tx-high F; (b) Ti$_3$C$_2$Tx-medium F; (c) Ti$_3$C$_2$Tx-high F, and (d) the element analysis of all MXene samples. Fig. S5. (a) O 1s and (b) C 1s XPS spectra of Ti$_3$C$_2$Tx-high F, Ti$_3$C$_2$Tx-medium F and Ti$_3$C$_2$Tx-high F MXene samples. Fig. S6. (a) UV-Vis absorption spectra of standard ammonia solutions with salicylic acid indicator. (b) Standard curves for determination of ammonia concentrations: y = 0.5408x – 0.0035, R$^2$ = 0.995. Fig. S7. (a, c) Chronoamperometry curves of N$_2$RR in 0.01 M Na$_2$SO$_4$ solution at corresponding potentials: (a) Ti$_3$C$_2$Tx-high F and (c) Ti$_3$C$_2$Tx-low F. (b, d) UV-Vis absorption spectra of (b) Ti$_3$C$_2$Tx-high F and (d) Ti$_3$C$_2$Tx-low F after N$_2$RR electrolysis at different potentials for 1 h. (e) Chronoamperometry curves and (f) UV-Vis absorption spectra of N$_2$RR over Ti$_3$C$_2$Tx-medium F at the potential of −0.7 V for 6 times. Fig. S8. XRD patterns of Ti$_3$C$_2$Tx MXene (on carbon paper, CP) before and after electrochemical nitrogen reduction reaction at the potential of −0.7 V. Table S1. Comparison of the electrochemical N$_2$RR performances for MXene-based catalysts.

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Authors’ contributions
GZ and LZ proposed, designed, and supervised the project. GZ, LZ, and YD wrote the manuscript. YD, LZ, AG, QW, SL, AMA and LQ performed the experiments and analyzed the data. All authors read and approved the final manuscript.
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Availability of data and materials
The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests
The authors declare that they have no competing interests.

Author details
1 Laboratory of Advanced Materials, Department of Chemistry, Faculty of Chemistry and Materials Science, Fudan University, Shanghai 200438, China. 2 Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia.

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