1. Introduction

MXene, an emerging family of 2D-layered transition-metal carbides/nitrides with a general chemical formula of $\text{M}_{n+1}\text{X}_n\text{T}_x$ ($n = 1–4$), has exhibited numerous attractive physical and chemical properties such as metallic conductivity,[1] water dispersibility,[2] high optical transparency,[3] good mechanical properties,[4] modifiable surface functional groups,[5] and tunable work function.[6] Since the discovery of MXene in 2011, the MXene family has exhibited superior performances in various applications such as energy storage,[7] electronics,[8] photothermal conversion,[9] electromagnetic interference shielding,[10] sensors,[11] water purification,[12] and desalination.[13] In addition to the superior performances, considering the abundant functional groups on the surface, MXene can be synthesized by a solution method and processed in the aqueous phase, which could provide low-cost and large-scale MXene applications.[14] The oxidation degradation by unsaturated metal atoms or dangling bonds at MXene edges and defects severely hinders the practical application of MXene. Herein, a passivation scheme for Ti$_3$C$_2$T$_x$ MXene is demonstrated by utilizing a sulfhydryl-containing molecule, $\beta$-mercaptoethanol (BME), which can significantly suppress the Ti$_3$C$_2$T$_x$ oxidation in various environments, including long-term storage of Ti$_3$C$_2$T$_x$ aqueous dispersions (2 m), single-layer Ti$_3$C$_2$T$_x$-based devices in humid air (2 m), and high-temperature environment (12 h). Notably, the nonionic BME does not cause aggregation but maintains the 2D morphology of Ti$_3$C$_2$T$_x$. A comprehensive investigation of the protection mechanism through density functional theory (DFT) calculations and experimental characterizations reveals that BME is adsorbed especially at the edges and surface defects of MXene (binding energy $\approx -1.70$ and $\approx -1.05$ eV), where the degradation starts. Further, the electron-donating effect of sulfhydryl groups tunes the work function of Ti$_3$C$_2$T$_x$ from 4.70 to 4.39 eV, resulting in improved carrier-transport performances in MoS$_2$ field-effect transistors owing to band alignment, where BME–Ti$_3$C$_2$T$_x$ serves as the source electrode. The described methodology can largely contribute to the ultralong service life of 2D Ti$_3$C$_2$T$_x$ without affecting its excellent properties, thereby promoting the practical application of this emerging material.

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Previous studies demonstrated effective strategies to delay the oxidation reaction of MXene, which can be roughly summarized into two categories: control of external factors that induce the oxidation reaction and stabilization of MXene by passivating the unsaturated Ti atoms at the defects and edges. For example, the oxidant of MXene, dissolved O₂ in water, can be removed by degassing using inert gases (Ar or N₂).[18] while another oxidant, H₂O₂, can be replaced by dispersing MXene in organic solvents.[19] However, the dispersions of MXene in organic solvents without additional additives generally lead to issues of low concentration and low dispersion stability.[20] Another factor of the oxidation reaction is the reaction rate. A low temperature (as low as −80 °C)[21] slows the oxidation reaction kinetics but has the disadvantages of high energy consumption and low efficiency. Overall, the control of external oxidation factors imposes harsh requirements on the application environment of MXene. In contrast, the method of stabilizing unsaturated Ti atoms has better adaptability because it improves the oxidation resistance of MXene. Mathis et al.[22] effectively reduced the defects in the Ti₃AlC₂ MAX phase precursor by adding excessive Al during synthesis, thereby largely eliminating the unsaturated Ti atoms in the surface defective part of the MXene sheet, although the edge Ti is still unsaturated. Natu et al.[23] raised polyphosphates by capping the edges of MXene to mitigate oxidation. Polyphosphate protection caused MXene aggregation, as high concentrations of salt destroyed the hydration layer of MXene. Zhao et al.[24] introduced a sodium L-ascorbate additive to mitigate the oxidation while preserving the 2D dispersion state of MXene, but the susceptibility to mold limited its application in an unsterilized environment. Therefore, the development of a low-energy-consumption method and material that do not require additional repeatable washing processes, especially to simultaneously provide protection in both the storage of dispersion and the application of solid-state MXene, is still crucial for both fundamental research and practical applications of MXene.

In this study, we demonstrate that β-mercaptoethanol (BME) can significantly inhibit the degradation of Ti₃C₂Tₓ MXene, in a colloidal dispersion, under humid air conditions, or even in a harsh 100 °C water. Ti₃C₂Tₓ was studied because it is the most representative and widely studied MXene, which can be attributed to the highest conductivity in the MXene family, rich surface groups for redox reactions and dispersibility in water, well-established methods for synthesis and material handling, etc.[25] BME was selected because the sulfhydryl groups (─SH) have strong electron-donating effects and are expected to have strong interactions with the partially positively charged unsaturated Ti atoms at the edges and defects of MXene. This is based on the classic strong interaction between ─SH and gold.[26] thereby eliminating active sites in the oxidation reaction. ─SH has a reducing ability to eliminate oxygen free radicals in water.[27] Moreover, compared with the reported ionic protective materials, the nonionic BME seldom destroys the hydration layer of MXene, while the hydrophilic hydroxyl tail is conducive to the good water dispersibility of BME–Ti₃C₂Tₓ MXene. Thus, 2D BME–Ti₃C₂Tₓ flakes can be easily obtained by spin-coating without any further treatments. The oxidation-suppressing effect of BME and the related mechanism was confirmed by various characterizations such as ultraviolet-visible–near-infrared (UV–vis–NIR) absorption spectroscopy, atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), Raman spectroscopy, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), electron paramagnetic resonance (EPR), and X-ray diffraction (XRD).

Using density functional theory (DFT) calculations and experimental characterizations, we propose that ─SH preferentially forms strong bonds (binding energy up to −1.70 eV) with unsaturated Ti atoms at the edges rather than at the surface of MXene, thereby suppressing the oxidation reaction. Furthermore, the electrical properties of BME–Ti₃C₂Tₓ were investigated by fabricating MXene-based field-effect transistors (FETs). BME–Ti₃C₂Tₓ exhibited better conductivity and considerably better humid air stability than those of pristine Ti₃C₂Tₓ. Finally, the work function of Ti₃C₂Tₓ was successfully tuned from 4.70 to 4.39 eV by the BME treatment because of the electron-donating effect of ─SH. BME–Ti₃C₂Tₓ served as a considerably better source electrode material than pristine Ti₃C₂Tₓ in MoS₂ FETs owing to the band alignment effect. The described methodology can largely contribute to the long-term storage of 2D MXene with a low energy consumption, which can likely improve the electronic properties of MXene, thereby promoting the practical application of MXene. In addition, the elucidation of the strong interaction of ─SH with MXene and improved stability of MXene at high temperatures is expected to inspire related studies and further expand the research field of MXene.

2. Results and Discussion

Figure 1a illustrates the aqueous dispersed 2D Ti₃C₂Tₓ nanosheets, the molecular structure of BME with highlighted lone pairs of electrons, and BME–Ti₃C₂Tₓ composite structure to prevent MXene attack by O₂ or H₂O. Aqueous Ti₃C₂Tₓ colloids were produced by etching the Al layer from Ti₃AlC₂ using HCl/LiF prior to removing extra acid and salts via centrifugation, as illustrated in Figure S2, Supporting Information (see Experimental Section).[14a] Regarding the mechanism of interaction between Ti₃C₂Tₓ and BME molecules, the S atoms of BME with lone pairs of electrons are considered to preferentially bind with the unsaturated Ti of MXene. The excess BME can also form strong bonds with the defective and perfect MXene surface, which is discussed in detail later. To suppress the oxidation reaction of Ti₃C₂Tₓ, the as-synthesized Ti₃C₂Tₓ colloid was separated and diluted with three aliquots of an aqueous BME solution (volume ratio of 1:3), which yielded final BME concentrations in the 10 mL Ti₃C₂Tₓ colloid of 0.005, 0.05, and 0.5 mol L⁻¹. An additional Ti₃C₂Tₓ suspension diluted by deionized water without BME was regarded as a control. Figure 1b shows images of the as-prepared pristine Ti₃C₂Tₓ colloid (0 d) and four Ti₃C₂Tₓ dispersions containing different amounts of BME after storage at room temperature (25 °C) for 28 d. The vials were shaken by hand and stood for around half an hour before taking photographs. Without BME, the Ti₃C₂Tₓ dispersion aged for 28 d was almost transparent, which indicates that the concentration was significantly reduced. This reveals the natural oxidation of MXene at room temperature. With the protection of BME, even with the minimum BME amount of 0.005 M, the dispersion exhibited a pitch-black color, similar to the original Ti₃C₂Tₓ. The concentration of Ti₃C₂Tₓ in these dispersions was monitored.
using UV–vis–NIR absorption spectra, as shown in Figure S3, Supporting Information. The absorbances of the Ti3C2Tx dispersions with 0.005 (0.005 BME–Ti3C2Tx), 0.05 (0.05 BME–Ti3C2Tx), and 0.5 M (0.5 BME–Ti3C2Tx) BME were approximately 1.92, 2.33, and 2.58 times that of Ti3C2Tx in pure water, respectively. Only a slight concentration attenuation and peak red shift were found in aged 0.5 BME–Ti3C2Tx compared to that in freshly synthesized pristine Ti3C2Tx, which demonstrates that BME can effectively restrain the oxidation of Ti3C2Tx. Figure 1c shows optical microscope (OM) images of a spin-coated Ti3C2Tx (left panel) and 0.05 BME–Ti3C2Tx (right panel) on Si/SiO2 substrates after storage in a humid air atmosphere (25 °C, relative humidity 50%) for 4 m. Without BME, Ti3C2Tx sheets were oxidized and finally disintegrated in humid air, leaving shiny TiO2 particles under OM light. By contrast, the spin-coated BME–Ti3C2Tx maintained its 2D structure after aging, and AFM microscopy further proved that BME–Ti3C2Tx retained its original morphology after 4 m (Figure S4, Supporting Information). This reflects the long-term stability of BME–Ti3C2Tx in humid air, and BME did not affect the dispersion of 2D Ti3C2Tx. Future MXene chemistry may involve high temperatures. Thus, we further analyzed the stabilities of Ti3C2Tx and BME–Ti3C2Tx in H2O at 100 °C. Figure 1d presents the relationship between the concentration of residual MXene and aging time, and the plots were well fitted by single-exponential decay (the dash lines). Based on the Lambert–Beer law, the concentration of residual MXene was estimated by the maximum absorption peak at ~750 nm in the UV–vis–NIR spectrum regardless of the gradual change in the extinction coefficient (Figure S5, Supporting Information). Without BME, Ti3C2Tx degraded extremely fast at the beginning, then tended to slow down as the oxide layer formed, and was almost completely oxidized in 100 °C H2O within 3 h. Under the protection of BME, 24.3%, 35.8%, and 60.5% of Ti3C2Tx survived in the 0.005, 0.05, and 0.5 M BME solutions after 12 h, respectively. Without or with a low amount of BME, the oxidation rate of MXene slows down with time, which is due to the gradual thickening of the oxidation layer hindering the oxidation reaction. While the almost linear degradation kinetics of 0.05 BME–Ti3C2Tx and the slow initial oxidation rate of 0.5 BME–Ti3C2Tx suggest that BME participates in the oxidation reaction and is likely to be oxidized preferentially to Ti3C2Tx. Additionally, the 0.5 BME–Ti3C2Tx after 12 h reaction at high temperature was further stored at room temperature for 14 d, and its UV–vis–NIR spectrum showed only negligible changes (Figure S6, Supporting Information), revealing that BME can still protect Ti3C2Tx after high temperature. Therefore, BME is expected to provide high-temperature chemical reactions and high-temperature applications of MXene.

Further characterizations were performed to investigate the antioxidation effect of BME using the aforementioned Ti3C2Tx and 0.05 BME–Ti3C2Tx samples. AFM images of pristine Ti3C2Tx and Ti3C2Tx–28 (Ti3C2Tx in water after 28 d), and BME–Ti3C2Tx–28 (Ti3C2Tx in the 0.05 M BME solution after 28 d) are presented in Figure 2a from left to right, respectively, with relevant height profiles. The 2D nature of the Ti3C2Tx monolayer was confirmed by the AFM image with a height of 1.65 nm.[28] While the Ti3C2Tx–28 lost the 2D feature, exhibiting many particles with sizes of dozens of nanometers. With the protection of BME, even after storage at room temperature for 28 d, the 2D feature of the Ti3C2Tx nanosheet was completely retained. The
The height of BME–Ti$_3$C$_2$Tx increased to 2.17 nm owing to excessive BME adsorption on the surface of Ti$_3$C$_2$Tx. Further, the oxidation states of the Ti$_3$C$_2$Tx nanosheets were studied using XPS. Figure 2b shows high-resolution XPS spectra of Ti 2p in pristine Ti$_3$C$_2$Tx, Ti$_3$C$_2$Tx–28, and BME–Ti$_3$C$_2$Tx–28. The Ti 2p spectra were fitted to Ti─C, Ti$^{2+}$, Ti$^{3+}$, TiO$_2$, and C─TiF$_x$ peaks. The peak at a ≈ 459.00 eV can be attributed to TiO$_2$, which indicates the oxidation degree of MXene.[29] For both pristine Ti$_3$C$_2$Tx and BME–Ti$_3$C$_2$Tx–28 samples, the small TiO$_2$ peaks reflect the low atomic percentage in the Ti 2p region of ≈10.04 and 12.45 atom%, respectively (Table S1, Supporting Information, presents the atomic ratio obtained by the Ti 2p peak fitting). Nevertheless, for the sample stored in pure water for 28 d, the high TiO$_2$ peak reflects a considerably higher atomic percentage of ≈58.32 atom % in the Ti 2p region, which reveals the severe oxidation of Ti$_3$C$_2$Tx in water without BME (Figure S7, Supporting Information, depicts the C 1s and O 1s core levels). To further analyze the effectiveness of BME in stabilizing the Ti$_3$C$_2$Tx lattice, TEM measurements were conducted to characterize the morphologies of pristine Ti$_3$C$_2$Tx, Ti$_3$C$_2$Tx–28, and 0.005 and 0.05 BME–Ti$_3$C$_2$Tx–28, as shown in Figure 2c and S8, Supporting Information. After oxidation in pure water for 28 d, a large number of aggregated large particles appeared on the surface of the survived Ti$_3$C$_2$Tx, consistent with the AFM image, which are probably TiO$_2$ particles based on the XPS analysis. The Ti$_3$C$_2$Tx nanosheet in the BME solution stored for 28 d still maintained its 2D structure, with an intact lattice like that of a pristine Ti$_3$C$_2$Tx nanosheet according to the fast Fourier transform pattern (inset of Figure 2c).[30] In addition, Raman spectroscopy was used to monitor the oxidation state of Ti$_3$C$_2$Tx, as shown in Figure S9, Supporting Information. The characterized A$_{1g}$ (Ti, O, C) vibrational mode of Ti$_3$C$_2$Tx was detected at ≈200 cm$^{-1}$ in pristine Ti$_3$C$_2$Tx, Ti$_3$C$_2$Tx–28, and 0.05 BME–Ti$_3$C$_2$Tx–28. Another obvious peak at ≈150 cm$^{-1}$ appeared only in the Ti$_3$C$_2$Tx–28 sample and was attributed to the E$_{1g}$ mode of anatase TiO$_2$ formed by the oxidation reaction.[17a,31] Furthermore, the 0.05 BME–Ti$_3$C$_2$Tx sample stored as long as 2 m (BME–Ti$_3$C$_2$Tx–60) was also characterized by the AFM, XPS, TEM, and Raman in Figure S10, Supporting Information. The 60 d sample retains typical features of Ti$_3$C$_2$Tx although the oxidation degree is increased compared to 0.05 BME–Ti$_3$C$_2$Tx–28 (as discussed in the Supporting Information), indicating that Ti$_3$C$_2$Tx can survive for 2 m under the protection of BME.

To reveal the mechanism by which BME mitigates the Ti$_3$C$_2$Tx degradation, DFT calculations[32] were performed to investigate...
the interaction between $-\text{SH}$ groups of BME and Ti$_3$C$_2$T$_x$, including the positively charged unpassivated titanium atoms at the edge, the typical single Ti atom defect site and functional groups on the surface of Ti$_3$C$_2$T$_x$. Figure 3a presents the optimal structure of BME at the edge of the OH-terminated Ti$_3$C$_2$T$_x$ based on DFT calculations (refer to the DFT calculations in Experimental Section for details). The sulfur atom was aligned between two unsaturated titanium atoms with a Ti$-\text{S}$ bond with a bond length of 2.50 Å and binding energy of $-1.70$ eV. The OH-terminated MXene plays a major role in the oxidation reaction because the stability of MXene follows $\text{OH} < -\text{F} < -\text{O}$ as the respective groups.$[33]$ In addition, most $-\text{OH}$ functional groups disappeared in the O 1s core level of Ti$_3$C$_2$T$_x$–28 (Figure 2b). The three optimized BME adsorption conformations on the surface of OH-terminated Ti$_3$C$_2$T$_x$ are shown in Figure S11, Supporting Information. The $-\text{SH}$ groups of BME tend to interact with the Ti$_3$C$_2$(OH)$_2$ surface through the S···H hydrogen bond at a binding energy of $-0.68$ eV. In addition, as the number of $-\text{O}$ groups in the proposed MXene was large according to the XPS O 1s peak, the interaction between the BME and Ti$_3$C$_2$O$_2$ has been presented and discussed in Figure S12, Supporting Information. BME is preferentially adsorbed to the edge of MXene rather than to the surface for either Ti$_3$C$_2$(OH)$_2$ or Ti$_3$C$_2$O$_2$. Thus, it can effectively mitigate the oxidation of MXene because the oxidation reaction starts at the edge rather than at the perfect surface. The other oxidation reaction site is the defect on the surface of MXene. Therefore, we constructed a typical single Ti atom defect in Ti$_3$C$_2$O$_2$ and calculated the interaction between the BME and the defect site.$[34]$ As shown in Figure S13, Supporting Information, both $-\text{SH}$ and $-\text{OH}$ of BME have a strong binding energy, exceeding 1 eV on the defect of MXene. It is stronger than that in the case of a perfect surface and BME can still strongly bind to the edge of the defective MXene. Furthermore, the Ti$-\text{S}$ bond was experimentally proved. As shown in Figure 3b, the S 2p peaks in the XPS spectra of the aged 0.005 BME–Ti$_3$C$_2$T$_x$ sample provide further evidence of the interaction between $-\text{SH}$ and Ti$_3$C$_2$T$_x$. The peak at 162.5 eV and its shoulder at 163.6 eV is a vital signal, which represents the bound S atom with the bare Ti atom (i.e., forming Ti$-\text{S}$ bonds) at the edge or defect of Ti$_3$C$_2$T$_x$.$[35]$ The peaks at 163.4 eV (164.6 eV for S 2p$_{1/2}$) were assigned to the disulfide bonds originated by the oxidation of thiol groups and unbound thiol groups.$[36]$ Figure S14a–c, Supporting Information, shows the binding energies of the S 2p core levels in the XPS spectra of the pristine Ti$_3$C$_2$T$_x$, 0.05 and 0.5 BME–Ti$_3$C$_2$T$_x$ respectively. The XRD patterns shown in Figure 3c reveal the (002) peaks of pristine Ti$_3$C$_2$T$_x$ and BME–Ti$_3$C$_2$T$_x$ in the range of 4°–30°, corresponding to the d spacing between the Ti$_3$C$_2$T$_x$ layers.$[37]$ As the amount of BME increases, the interlayer spacing of Ti$_3$C$_2$T$_x$ increases from 1.27 nm for the pristine Ti$_3$C$_2$T$_x$ to 1.28, 1.46, and 1.48 nm for the 0.005, 0.05, and 0.5 BME–Ti$_3$C$_2$T$_x$ respectively (Table S2, Supporting Information, summarizes the layer distances). Notably, the layer spacings of the pristine Ti$_3$C$_2$T$_x$ and 0.005 BME–Ti$_3$C$_2$T$_x$ are almost equal, because a small amount of BME is preferentially combined with the edge of Ti$_3$C$_2$T$_x$. The 0.2 nm increase in layer spacing for 0.05 BME–Ti$_3$C$_2$T$_x$ compared to pristine Ti$_3$C$_2$T$_x$ may result from more BME adsorbed on the defective (preferentially) and perfect

**Figure 3.** a) Configuration structure of the BME adsorbed to the Ti$_3$C$_2$(OH)$_2$ edge with the corresponding Ti$-\text{S}$ bond length and binding energy ($E_b$). b) S 2p XPS spectra of 0.005 BME–Ti$_3$C$_2$T$_x$. c) X-ray diffraction (XRD) patterns of pristine Ti$_3$C$_2$T$_x$ and BME–Ti$_3$C$_2$T$_x$ (0.005, 0.05, and 0.5) in a range of diffraction angles from 4° to 30°. d) Schematic of the pristine Ti$_3$C$_2$T$_x$/BME–Ti$_3$C$_2$T$_x$-based field-effect transistor (FET) device. e) Conductivity changes of Ti$_3$C$_2$T$_x$ and 0.005 and 0.05 BME–Ti$_3$C$_2$T$_x$ flakes on SiO$_2$ substrates in humid air over time.
Ti$_3$C$_2$Tx surface, but some BME molecules may be removed during the drying process of prepared XRD samples. The (002) peak of 0.5 BME–Ti$_3$C$_2$Tx split into two peaks at 5.98° and 4.72° by the uneven intercalation of excessive BME. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were conducted to analyze the thermal stability of the BME–Ti$_3$C$_2$Tx and, in particular, the desorption process of BME. Figure S15a, Supporting Information, shows an additional weight loss of ≈3% occurred at 160–210 °C in BME–Ti$_3$C$_2$Tx as compared with pristine Ti$_3$C$_2$Tx, which was related to the evaporation and desorption of BME. The DSC peaks (Figure S15b, Supporting Information) of BME–Ti$_3$C$_2$Tx at 102.7, 160.4, 176.7, and 209.5 °C could be attributed to the evaporation of H$_2$O and free BME, and to the desorption of BME on the surface and at the edge of Ti$_3$C$_2$Tx, respectively. Electron paramagnetic resonance (EPR) was used to study the single electrons in pristine Ti$_3$C$_2$Tx and BME–Ti$_3$C$_2$Tx, as shown in Figure S16, Supporting Information. Consistent with the previous study,[38] both pristine Ti$_3$C$_2$Tx and BME–Ti$_3$C$_2$Tx showed negligible EPR signals, indicating that the strong binding energy between BME and Ti$_3$C$_2$Tx edges originated from the electron donation of sulfhydryl groups rather than any possible radical reaction.

To quantitatively study the humid air stability and electrical properties of single-layer pristine Ti$_3$C$_2$Tx and BME–Ti$_3$C$_2$Tx, FET devices were fabricated using MXene as a channel. Two Au electrodes were thermally deposited to contact MXene on the Si/SiO$_2$ substrate, as shown in Figure 3d. The transfer and output characteristics of the pristine Ti$_3$C$_2$Tx and BME–Ti$_3$C$_2$Tx-based FETs are presented in Figure S17a,b, Supporting Information, respectively. Consistent with the transfer curve, the output curve exhibits a slight n-type characteristic, and the ultra-linear I$_d$–V$_d$ plot indicates Ohmic contact between the Au electrodes and (BME–)Ti$_3$C$_2$Tx; thus, the conductivity can be directly calculated from the current. Figure 3e shows the changes in electrical conductivity of pristine Ti$_3$C$_2$Tx and BME–Ti$_3$C$_2$Tx over time for 28 and 60 d, respectively. Previous studies[39] have extensively demonstrated the effect of molecular doping on the Ti$_3$C$_2$Tx conductivity, and the current experiments indicate that incorporating BME with Ti$_3$C$_2$Tx slightly improves the conductivity from 3534.1 to 4371.7 and 4514.9 S cm$^{-1}$ for 0.005 and 0.05 BME–Ti$_3$C$_2$Tx, respectively. In addition, Ti$_3$C$_2$Tx degenerates into an insulator (0.015 S cm$^{-1}$) after 7 d owing to oxidation, whereas 0.005 and 0.05 BME–Ti$_3$C$_2$Tx retain excellent conductivities (96.5 and 1082.8 S cm$^{-1}$) even after 28 d. Furthermore, 0.05 BME–Ti$_3$C$_2$Tx retains a strong conductivity of 92.6 S cm$^{-1}$ after 60 d, confirming the remarkable stability of BME–Ti$_3$C$_2$Tx in humid air. The degradation of BME–Ti$_3$C$_2$Tx in air also followed...
the exponential decay, and the accelerated degradation rate over time may be due to the gradual desorption of BME. Those results demonstrate that BME–Ti3C2Tx can be easily fabricated onto 2D flakes on SiO2 substrates, and the potential of BME to continuously protect Ti3C2Tx in subsequent applications.

Figure 4a presents work function maps of the pristine Ti3C2Tx and 0.005 BME–Ti3C2Tx sheets on the Si substrates obtained by Kelvin probe force microscopy (KPFM) measurements. An evident color contrast is observed, from red (pristine Ti3C2Tx) to baby blue (BME–Ti3C2Tx), indicating the successful tuning of the work function. The bottom panel of Figure 4a shows work function distributions in the selected area of the pristine Ti3C2Tx (red), Si substrate (green), and 0.005 BME–Ti3C2Tx (blue), and their average work function distributions determined by Gaussian fitting are 4.70, 4.49, and 4.39 eV, respectively. The change of work function can be attributed to the electron-donating effect of BME, which changes the surface dipole moment of Ti3C2Tx and the doping of the conductive layer. Figure S18a,b, Supporting Information, presents a work function map of 0.05 BME–Ti3C2Tx and statistical work function (4.40 eV), which indicates that the doping of Ti3C2Tx is saturated by 0.05 M BME. Owing to the 0.31 eV amplitude modulation, the work function of BME–Ti3C2Tx is very close to the conduction band (CB) or lowest unoccupied molecular orbital of the n-type 2H-phase MoS2.

Figure 4b presents a schematic band diagram of the pristine Ti3C2Tx, BME–Ti3C2Tx, and multi-layered MoS2. The work function of BME–Ti3C2Tx matches the CB of MoS2 (≈4.4 eV), which facilitates the barrier-free injection of electrons. In contrast, when electrons are injected from the pristine Ti3C2Tx into MoS2, an energy barrier must be overcome. In the case of hole transport, BME–Ti3C2Tx encounters larger obstacles than pristine Ti3C2Tx to inject holes into the valence band (VB, ≈6.2 eV) of MoS2. To verify this claim, MoS2 FET devices were fabricated to compare the qualities of pristine Ti3C2Tx and BME–Ti3C2Tx as source electrodes, as shown in Figure 4c. The fabrication is described in Experimental Section. The bottom panel of Figure 4c shows an OM image of a typical MoS2 FET device with a BME–Ti3C2Tx source electrode. Figure 4d compares the transfer curves of the as-fabricated FETs using Ti3C2Tx (black curve) and BME–Ti3C2Tx (blue curve) electrodes. The BME–Ti3C2Tx exhibits a high on/off ratio of 106 with an ON current 10 times higher than that of pristine Ti3C2Tx. Figure S20, Supporting Information, depicts the output curves at various gate voltages. A nonlinear I–V curve for a low Vg is observed in the pristine Ti3C2Tx based FETs, indicating a typical Schottky contact, while a linear I–V curve supports Ohmic contact between BME–Ti3C2Tx and MoS2.

In addition, Figure S21, Supporting Information, shows that the performance of the FETs with the monolayer BME–Ti3C2Tx electrodes is comparable to that of conventional thick Cr/Au (5/50 nm) electrodes, demonstrating the potential of BME–Ti3C2Tx as a 2D electrode in future electronics.

3. Conclusion

We have demonstrated that the BME treatment could suppress the oxidation of Ti3C2Tx, MXene, in the colloidal dispersion (2 m), under humid air conditions (2 m), or even in harsh 100 °C water (12 h). The absorption mechanism between BME and Ti3C2Tx was investigated by comprehensive DFT calculations and experimental characterizations, revealing BME has strong interaction with both the edge (through Ti–S bond, binding energy –1.70 eV) and defect (by hydrogen bond, binding energy –1.05 eV) of Ti3C2Tx, which significantly suppresses the degradation of Ti3C2Tx. The work function of Ti3C2Tx was successfully tuned from 4.70 to 4.39 eV by the BME treatment because of the electron-donating effect of sulphydryl groups. BME–Ti3C2Tx showed excellent electrical properties and much better humid air stability than Ti3C2Tx in as-fabricated FET devices, and served as a better source electrode material than pristine Ti3C2Tx in n-type MoS2 FETs because of the band alignment effect. The described methodology can largely contribute to the long-term storage and service life of Ti3C2Tx and simultaneously cover every aspect (in comparison to recently published antioxidant methods, see Table S3, Supporting Information), thus promoting the practical application of MXene. In addition, the elucidation of the strong interaction between sulphydryl groups with MXene and the improved stability of MXene at high temperatures are expected to inspire related studies and further expand the research field of MXene.

4. Experimental Section

Synthesis of Ti3C2Tx: To remove the Al layer in Ti3AlC2 by chemical etching, 1 g of Ti3AlC2 was slowly added to the etchant (precooled to below 5 °C) containing 1.6 g of LiF (Sigma Aldrich), 5 mL of deionized H2O, and 15 mL of 12 M HCl (hydrochloric acid, Sigma Aldrich) in a 100 mL Teflon beaker. The mixture of a Teflon stirring bar was treated by N2 blowing and then sealed prior to being placed in an ice bath and stirred at 500 rpm for 1 h. Subsequently, the reaction was continued at 25 °C for 36 h. The product was then washed with centrifugation (5–6 cycles, at 3500 rpm) and manual shaking until the pH of the supernatant became neutral. The mixture was then centrifuged at 3500 rpm for 1 h, and the resulting colloid and swollen upper black precipitate were collected for follow-up experiments. The concentration of the as-prepared Ti3C2Tx dispersion was determined to be approximately 13 mg mL−1 by the freeze-drying technology.

Protection of Ti3C2Tx by BME: Typically, in a 10 mL vial, 2.5 mL of Ti3C2Tx obtained as described earlier was diluted with 7.5 mL of deionized water or BME solution, which yielded final BME concentrations in the 10 mL Ti3C2Tx colloid of 0.005, 0.05, and 0.5 mol L−1. The ratios of BME and Ti3C2Tx were ≈0.12:1 (0.005 BME–Ti3C2Tx), 1:1 (0.05 BME–Ti3C2Tx), and 12:1 (0.3 BME–Ti3C2Tx), respectively. Thereafter, manual shaking was performed for ≈10 min to thoroughly mix Ti3C2Tx and BME, followed by sonication in an ice water bath for 3 min to separate the oxidized Ti3C2Tx maximally. The floating impurities on the dispersion surface were carefully removed and, finally, the vials were capped and stored in a dark place.

Device Fabrication: The highly doped n-type Si and thermally grown 285 nm thick SiO2 served as the bottom gate and dielectric layer, respectively. The ten times diluted pristine Ti3C2Tx or BME–Ti3C2Tx dispersion was spin-coated on the O2 plasma-treated substrate. An MXene flake with a regular shape was selected through OM and determined as a monolayer through AFM. For the fabrication of MXene-based FET devices, poly (methyl methacrylate) (PMMA) was coated onto the pristine Ti3C2Tx flakes mechanically exfoliated from bulk MoS2 crystals. High-quality MoS2 flakes with suitable sizes (thicknesses ≈ 20 nm) were attached to a polydimethylsiloxane (PDMS)
stamp on a glass slide and then transferred onto the selected MXene (using low-temperature AFM) surface in a nitrogen-filled glove box. After staining, the resulting pristine Ti3C2Tx/BME–Ti3C2Tx/MoS2 samples were immediately spin-coated with PMMA solution and patterned with EBL to control the channel length as ~2 μm. Finally, 5/10 nm thick Cr/Au electrodes were deposited as the source and drain electrodes at a low pressure ~10–6 Torr at a speed of 1 Å s–1. Subsequently, a metal lift-off process was performed. The electrical properties of the devices were measured using a Keithley 4200 parameter analyzer at a pressure of 10–12 Torr.

Sample Characterization: The surface morphologies of the pristine Ti3C2Tx and BME–Ti3C2Tx flakes were characterized by OM, AFM, and TEM. The thicknesses of the MXene and BME–spin-coated-MXene flakes were measured using AFM (Park System Corp.). The work function was measured using the KPFM method in an AFM–Raman measurement system equipped with a Kelvin probe (NTegra Spectra, NT-MDT 830). The contact potential difference (ΔVCOP) was calculated based on work function measurements collected from the KPFM tip and the sample according to the Equation εAVCP = Φtip – Φsample, where Φtip is the work function of the tip, Φsample is the work function of the sample, and ε is the electric charge. Φtip was calibrated at 4.75 eV using the KPFM measurements collected from highly ordered pyrolytic graphite. Optical images were obtained using an OM (Olympus BX51). TEM images were acquired by low-resolution TEM with an incident electron beam energy of 80 keV (TEM 2100 F, JEOL). The chemical compositions were probed using XPS (ESCA2000, VG Microtech Inc.) in an ultrahigh vacuum with an Mg Kα X-ray source. The absorption properties of the pristine Ti3C2Tx and BME–Ti3C2Tx dispersion were observed using UV–vis–NIR spectroscopy with injection from a deuterium and tungsten lamp (Shimadzu UV–3600). Raman spectra were acquired using a Raman microscopy system (Kaiser Optical Systems model RXN) fitted with a 532 nm laser. The thermal stability was explored by using a DSC–TGA thermal analyzer (SDT650) in the presence of nitrogen gas. XRD patterns were acquired using Cu KR radiation at a wavelength of 0.1541 nm. EPR signals were obtained using X-band CW-EPR at RT with a microwave power of 1 mW, microwave frequency of 9.64 GHz, modulation frequency of 100 kHz, and modulation amplitude of 10 G.

DFT Calculation Methods: To probe the interactions between BME and Ti3C2Tx in the BME–Ti3C2Tx hybrid system, DFT calculations were performed using the DMOl3 code. The generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE) functional and DFT semi-core pseudo-potential double numerical atomic basis set plus polarization were employed. Owing to the poor description of the weak van der Waals interactions of the popular PBE functional, an empirical dispersion-corrected DFT approach proposed by Grimme was used. The optimal geometric convergence criteria of energy, force, and displacement were 1.0 × 10−3 Ha, 0.002 Ha Å−1, and 0.005 Å, respectively. The k-point grid was set to be 1 × 3 × 1 for structural optimization. The vacuum thickness was set to be more than 20 Å to avoid interactions between neighboring layers. A supercell consisting of 3 × 2 Ti3C2O2 nanoribbons was selected to adsorb BME on the edge and surface for the simulation. A vacuum gap larger than 20 Å was added to the other two nonperiodic directions (y- and z-axes). To quantitatively describe the interaction strength between BME and Ti3C2Tx, the binding energy was defined as EΣ = Etotal − E(BME) − E(Ti3C2Tx), where Etotal, E(BME), and E(Ti3C2Tx) denote the energies of BME–Ti3C2Tx/BME, and pristine Ti3C2Tx flake, respectively.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
MXene, stability, Ti–S bond, work function, β-mercaptopetoethanol

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