

Enhanced Sulfonic Functionalization of MXene $\text{Ti}_3\text{C}_2\text{T}_x$ via Pre-Delamination Intercalation Strategy

(Pengubahsuaian Sulfonik yang Ditingkatkan bagi MXene $\text{Ti}_3\text{C}_2\text{T}_x$ melalui Strategi Interkalasi Pra-Delaminasi)

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ABSTRACT

This study details a novel method for surface functionalization of MXene $\text{Ti}_3\text{C}_2\text{T}_x$, achieving significantly higher yields of sulfonic and disulfonic functional groups compared to existing methods. A new method, designated M2, was developed for the surface functionalization where sulfonic and disulfonic acid groups were simultaneously introduced using different intercalant (TMAOH and NaOH) before delamination. The FTIR analysis show a new peak at $\sim 1000\text{ cm}^{-1}$ in the functionalized MXenes, indicating successful incorporation of SO_3H and $2(\text{SO}_3\text{H})$ functional groups. The XPS analysis showed functionalized of the Ti chemical environment together with detectable sulphur incorporation after surface functionalization. Survey XPS further showed higher sulphur atomic concentration via the M2 method, Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2, suggesting a higher degree of surface functionalization. The HR-TEM and XRD analyses, showed the surface functionalized MXenes to have an increase in d -spacing, indicating effective delamination, recorded with lattice spacing of $\sim 1.36\text{ nm}$. The sample Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 exhibited a more amorphous structure due to higher absorption of disulfonic acid groups and supported by SAED images. This method results in a functionalized MXene with a high density of functional groups, which serves as an ideal platform for further high-yield functionalization.

Keywords: Disulfonic; MXene; sulfonic; surface functionalization; $\text{Ti}_3\text{C}_2\text{T}_x$

ABSTRAK

Kajian ini memperincikan satu kaedah baharu untuk pengubahsuaian permukaan MXene $\text{Ti}_3\text{C}_2\text{T}_x$, yang berjaya mencapai hasil kumpulan berfungsi sulfonik dan disulfonik yang lebih tinggi berbanding kaedah sedia ada. Kaedah baharu ini, yang dinamakan sebagai kaedah M2, telah dibangunkan untuk kefungsi permukaan dengan kumpulan asid sulfonik dan disulfonik diperkenalkan secara serentak menggunakan agen interkalan yang berbeza (TMAOH dan NaOH) sebelum proses delaminasi. Analisis FTIR menunjukkan satu puncak baharu sekitar 1000 cm^{-1} pada MXenes yang diubah suai, menandakan kejayaan penggabungan kumpulan berfungsi SO_3H dan $2(\text{SO}_3\text{H})$. Analisis XPS mendedahkan pengubahsuaian persekitaran kimia Ti bersama-sama dengan penggabungan sulfur yang boleh dikesan selepas kefungsi permukaan. Survei XPS selanjutnya menunjukkan kepekatan atom sulfur yang lebih tinggi melalui kaedah M2, Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2, mencadangkan tahap kefungsi permukaan yang lebih tinggi. Analisis HR-TEM dan XRD pula menunjukkan peningkatan dalam jarak- d pada MXene yang diubah suai, menandakan proses delaminasi yang berkesan dengan jarak kekisi sekitar 1.36 nm . Sampel Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 turut menunjukkan struktur yang lebih amorfus, disebabkan oleh penyerapan kumpulan asid disulfonik yang lebih tinggi, seperti yang disokong oleh imej SAED. Kaedah baharu ini telah menghasilkan MXene yang berfungsi dengan ketumpatan kumpulan berfungsi yang tinggi, menjadikannya platform yang ideal untuk kefungsi lanjut dengan hasil yang tinggi.

Kata kunci: Disulfonik; MXene; pengubahsuaian permukaan; sulfonik; $\text{Ti}_3\text{C}_2\text{T}_x$

INTRODUCTION

Over the past decades, MXenes have emerged as a highly popular class of two-dimensional (2D) materials across diverse research fields due to their unique physicochemical properties. MXenes are composed of transitional metals,

nitrides/carbides and surface-terminating functional groups. Generally, MXene can be synthesised by selectively etching the A-layer from the parent MAX phase material, where M represents a transitional metal, A is an element such as Aluminium and X denotes carbon

and/or nitrogen, resulting in a layered structure materials with terminated surface filled with functional groups. The first MXene, $\text{Ti}_3\text{C}_2\text{T}_x$, was synthesised by Naguib et al. (2011) through the etching of aluminium from Ti_3AlC_2 . MXenes consist of hexagonal layers of transition metal and carbon/nitrogen, with surfaces terminated by functional groups such as -O, -OH and -F (Khazaei et al. 2019). To date, more than 46 varieties of MXenes have been reported, each with distinct properties and synthesis method. MXenes have shown great potential in various applications, including batteries (Huang et al. 2022; Li et al. 2020; Ming et al. 2021; Pan et al. 2019; Ren et al. 2019; Tang et al. 2020), supercapacitors (Wang et al. 2020; Wang et al. 2020; Zhou et al. 2020; Zhu et al. 2020), optoelectronics, biomedicine, solar panels, and fuel cells, due to their excellent electrical conductivity, high surface area, and tunable surface chemistry.

MXene is known for exhibiting a fascinating synergy of properties, which primarily stems from its layered structure and the terminated surface. These properties can vary depending on the elemental composition used in its structure. For instance, MXenes demonstrate excellent conductivities (Gao 2022; Shetti et al. 2023; Wang et al. 2021), high adsorption ability (Parey et al. 2021; Sun et al. 2021), unique reflective states (Feng et al. 2021) and superior energy storage capabilities (Zhang et al. 2019; Zhou et al. 2022). The 2D structure of MXene further improves these properties due to its large surface area, which is rich in functional groups (Liu et al. 2019).

In MXene, both the terminated surface and the transitional metals components contribute significantly to its properties. Variations in MXene properties have been observed when different types of MAX phase materials are used and/or when different methods employing various etchants are applied. The choice of synthesis method and etchant affects the nature of the terminal surface, while the type of MAX phase material determines the transition metal content (Lim et al. 2022). For example, MXene $\text{Ti}_3\text{C}_2\text{T}_x$ contains -OH, -O and -F terminal groups, originating from the use of hydrofluoric acid as the etchant, while the titanium element is derived from the parent MAX phase Ti_3AlC_2 used during synthesis. Furthermore, the concentration of terminal groups can vary depending on the synthesis approach. In the *in-situ* HF etching method, hydrofluoric acid is generated via the reaction of LiF and HCl. In this process, Ti_3AlC_2 is mixed with a LiF–HCl solution and stirred for 48 h, during which etching occurs concurrently with the generation of HF. It has been reported that this *in-situ* method yields a higher concentration of -F terminal groups compared to direct etching using HF (Ghidiu et al. 2014). This ability to control the surface chemistry through the selection of etchants is especially critical when considering further surface functionalization.

Surface functionalization of MXene was first demonstrated when it was observed that the terminal

groups O and F were completely replaced by -OH groups after washing the MXene powder with alcohol, resulting in OH-terminated MXene. This OH-terminated MXene exhibited a lower potential difference compared to the parent MXene, suggesting a shift toward semiconducting behavior (Khazaei et al. 2015). Additionally, the OH-terminated MXene displayed altered properties, such as reduced work function and conductivity. These observations indicate that variations in terminal groups significantly influence the physicochemical properties of MXene, thereby opening up new opportunities for tailoring MXene for specific functional applications. Subsequent research has employed various surface functionalization strategies to fine-tune MXene properties, facilitating the development of advanced materials for targeted applications. Surface functionalized MXenes have been successfully applied in diverse fields, including batteries, biomedical devices (Huang et al. 2020), electrocatalysis (Bai & Guan 2022), fuel cells (Xue et al. 2024), and capacitors (Zhu et al. 2021).

Surface functionalizations are typically performed on few-layer MXene to increase the number of functional groups. By default, few-layer MXene possesses a larger surface area than multilayer MXene, making it fundamentally more attractive for surface functionalization (Li & Song 2023). The fewer the layer in the MXene, the higher the surface-to-volume ratio (Naguib et al. 2012; Saha et al. 2021). Surface functionalization in few-layer MXene focuses on substituting the existing functional groups on the terminated surface. This substitution process relies on using functional groups with higher electronegativity to replace those with weaker electronegativity. For example, in the case of $\text{Ti}_3\text{C}_2\text{T}_x$, the O groups exhibit relatively low electronegativity, while F is considered the least stable (Zhang et al. 2022; Zhang et al. 2019). In contrast, multilayer MXene generally contains a lower concentration of terminal functional groups due to its layered structure (Natu et al. 2022). This may result from poor penetration of the etchant during synthesis or from layers not being adequately exposed to the etchant (Munir et al. 2020). Both factors can lead to incomplete etching and, consequently, a reduced concentration of surface functional groups. Therefore, it is standard practice to delaminate MXene prior to surface functionalization, as this increases the overall surface area and enhances the degree of functionalization (Nikhil et al. 2023).

However, there is a theoretical advantage to using multilayer MXene. It is hypothesized that the interlayer regions contain a minimal number of functional groups, implying that additional space remains available for further functionalization due to the limited spacing between layers (Cheng et al. 2021; Zhang et al. 2023). During delamination, surface functionalization can occur as these previously unoccupied spaces become filled with functional groups present in the solution. The nature

of these groups is determined by the intercalant solution used. Common intercalants typically introduce OH and O groups, which do not alter the fundamental composition of the MXene. Consequently, the most commonly observed changes involve variations in the concentration of F terminations, as well as changes in the thickness and the number of MXene layers. Theoretically, pre-saturating the intercalant solution with desired functional groups before and during delamination could enhance the absorption of these groups, thereby increasing the degree of functionalization (Garg, Agarwal & Agarwal 2020; Zeng et al. 2023).

This indicates that the possibility of producing MXene with specific desired properties can be controlled by tailoring its surface terminations. To test this hypothesis, the present study incorporates sulfonic groups (SO_3H) from sulfonic acids and disulfonic groups ($2\text{SO}_3\text{H}$) from disulfonic acids via two approaches. Method 1 (M1) refers to the conventional surface functionalization technique, while Method 2 (M2) represents an improved approach involving simultaneous surface functionalization and delamination, using two different types of intercalants. The M2 method aims to produce surface functionalized MXene with a higher concentration of specific functional groups. The main difference between M1 and M2 is that M1 functionalization is done after the complete delamination of MXene, while functionalization in M2 is done during/before full delamination occurs. The approach of M2 focuses on the abundance of functional groups present in the solution prior to full delamination occurring/induced. The sulfonic functionalization was introduced with the goal of enhancing the material's potential for application in proton exchange membrane fuel cells (PEMFCs). The surface functionalization of MXene with sulfonic groups was first reported by Zhang et al. (2017) using the conventional M1 method. This study further investigates the role of intercalants in facilitating the substitution of new functional groups on the MXene surface. The intercalants used were tetramethylammonium hydroxide (TMAOH) and sodium hydroxide (NaOH), each offering distinct intercalation mechanisms. TMAOH, with its large molecular size, intercalates by wedging between the layers, thereby increasing the interlayer spacing and enabling partial delamination through simple stirring. In contrast, NaOH, due to its smaller molecular size, penetrates more deeply between the layers without causing complete delamination, which may be advantageous in strategies that rely on partial delamination (Deysher et al. 2020).

MATERIALS AND METHODS

MATERIALS

The chemicals used for the surface functionalization were sulfanilic diazonium salt, which was prepared for the

sulfonic functionalization, and amino naphthalenedisulfonic acid, which was used as purchased from Sigma-Aldrich, for the disulfonic acid functionalization. The MXene used in this study is multilayer $\text{Ti}_3\text{C}_2\text{T}_x$, purchased from ACS Material. The intercalants used were tetramethylammonium hydroxide (TMAOH) and sodium hydroxide (NaOH). TMAOH was used as received, while NaOH (5 wt%) pellets were first dissolved in deionized (DI) water to obtain NaOH solution.

PREPARATION AND DELAMINATION OF MXene

The preparation of sulfonic acid functional group solutions involved the synthesis of sulfanilic diazonium salt. This was achieved by suspending sulfanilic acid in cooled deionized (DI) water (0–5 °C), followed by the addition of cooled hydrochloric acid (HCl) solution (0–5 °C). The mixture was stirred for 15 min, after which a cooled sodium nitrate solution (0–5 °C) was added dropwise. The resulting mixture was stirred for an additional 30 min. The sulfanilic diazonium salt obtained was then used for the surface functionalization of MXene. For disulfonic acid functionalization, an aqueous solution of amino-naphthalenedisulfonic acid, with the ratio of the weight of amino-naphthalenedisulfonic acid to MXene is 1:1, prepared by simple dissolution in 10 mL of DI water.

In this study, the MXene underwent intercalation prior to surface functionalization. Two different intercalants were used to determine their efficacy in facilitating the incorporation or substitution of functional groups. The intercalants used were tetramethylammonium hydroxide (TMAOH), recognized as one of the most effective agents for MXene delamination due to its large cation size, which increases the interlayer spacing; the sodium hydroxide (NaOH), a smaller cation with higher charge density, which allows deeper layer penetration (Barmann et al. 2021). A fixed intercalation reaction time of 12 h was employed, with the intercalant used in excess relative to the MXene powder by weight. The 12-h reaction time was chosen based on that TMAOH reportedly only needs a few hours (2 h and above) and NaOH reported to need between 8 h–12 h (Maleski et al. 2021; Nóbrega et al. 2006). Hence, 12 h were chosen to allow fair reaction time for both intercalants.

For sulfonic functionalizations, two distinct methods were implemented to evaluate MXene's absorption behavior toward the introduced functional groups. In Method 1 (M1), the intercalated MXene was first centrifuged and dried, then fully delaminated before undergoing the surface functionalization process. Samples prepared via this approach are denoted as $\text{TM-Ti}_3\text{C}_2\text{T}_x\text{-S1-M1}$, $\text{TM-Ti}_3\text{C}_2\text{T}_x\text{-S2-M1}$, $\text{Na-Ti}_3\text{C}_2\text{T}_x\text{-S1-M1}$, and $\text{Na-Ti}_3\text{C}_2\text{T}_x\text{-S2-M1}$, where S1 represents sulfonic acid functionalization and S2 denotes disulfonic acid functionalization. In contrast, Method 2 (M2) adopts an improved approach, the intercalated MXene

was directly subjected to surface functionalization without separating excess intercalant or reactants. Sonication was performed afterward. Samples prepared by this method are denoted as TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M2, TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2, Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M2, and Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2. In this naming scheme, M2 refers to the improved, simultaneous functionalization–delamination method.

SURFACE FUNCTIONALISATION OF MXene

For sulfonic functionalization, two methods were employed to study the interaction efficiency of different intercalants and the ability of MXene $\text{Ti}_3\text{C}_2\text{T}_x$ to absorb new functional groups. In Method 1 (M1), the delaminated MXene was used after removing the excess intercalant. This was achieved by applying sonication to induce delamination, a standard delamination procedure. Samples produced using this method are labeled M1. In Method 2 (M2), the MXene was used prior to sonication and without removing the excess intercalant. In this method, delamination and functionalization occurred simultaneously. Samples produced through this enhanced approach are labeled M2. The aim of this method was to observe the MXene's ability to

absorb functional groups on its terminated surface when immersed in a solution rich in functional groups prior to sonication-induced delamination.

Functionalisation was performed by reacting the MXene with sulfonic group solutions: sulfanilic diazonium salt for sulfonic group functionalization (denoted as S1) and amino-naphthalenedisulfonic acid for disulfonic group functionalization (denoted as S2). Both reactions were allowed to proceed for 4 hours to maintain a constant reaction time.

In Method 1, delaminated MXene was reacted with the sulfonic group solution for 4 h, followed by centrifugation, vacuum filtration, and drying in a vacuum oven at 60 °C overnight. In Method 2, the MXene was reacted with the sulfonic group solution during the final 4 h of the 12-h intercalation period, followed by sonication, centrifugation, vacuum filtration, and drying in a vacuum oven at 60 °C overnight. Figure 1 shows the flow diagram of the steps taken.

All prepared samples were then analyzed using HR-TEM and XRD to examine the morphological changes in the surface-functionalized MXene. XPS, XRD, and FTIR analyses were performed to investigate the formation of new bonds and the successful incorporation of functional groups. SEM and XRD

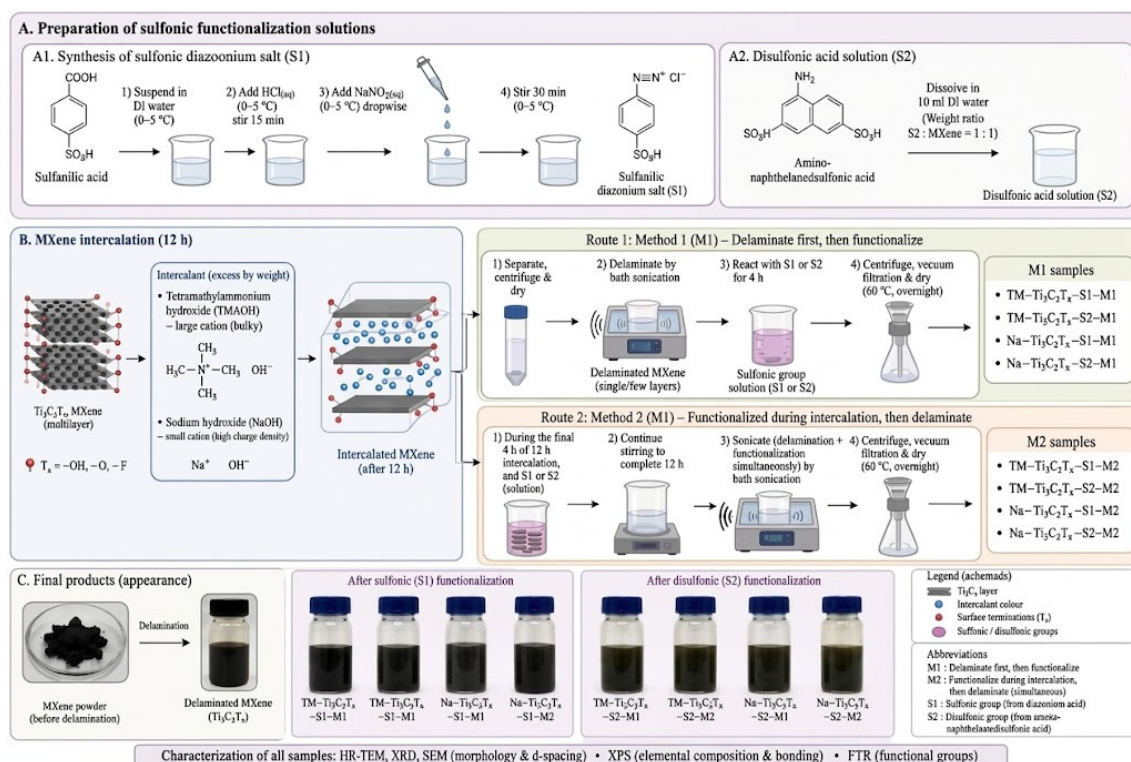


FIGURE 1. Schematic illustration of the preparation and surface functionalization of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene using sulfonic (S1) and disulfonic (S2) acid functionalization solutions via two approaches: (M1) delamination followed by surface functionalization and (M2) simultaneous functionalization during the intercalation process. The diagram was created with assistance from ChatGPT (OpenAI 2026)

were also used to confirm the extent of delamination by examining the physical morphology and determining the new d-spacing of the resultant MXene structures. The presence of new functional groups and the bonding characteristics were further validated through XPS and FTIR spectra.

RESULTS AND DISCUSSIONS

FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

In the FTIR spectrum of pristine MXene ($\text{Ti}_3\text{C}_2\text{T}_x$), characteristic broad stretching bands are observed in the range of $650\text{--}950\text{ cm}^{-1}$, attributed to Ti-based species. A sharp and intense absorption band around $\sim 1240\text{ cm}^{-1}$ corresponds to C–O stretching, while additional stretching bands between $\sim 1900\text{--}2400\text{ cm}^{-1}$ are assigned to C=O bonds. It should be noted that the FTIR spectra of MXene may vary between synthesis batches, depending on the specific etching conditions and parameters applied to the MAX phase material.

FTIR analysis in this study was employed to confirm the presence of newly introduced functional groups, particularly SO_3H and $2(\text{SO}_3\text{H})$. In pristine $\text{Ti}_3\text{C}_2\text{T}_x$ MXene, the detectable termination groups include O, OH, and F. From the FTIR results shown in Figure 2, the appearance of a new stretching band around $\sim 1056\text{ cm}^{-1}$ indicates the presence of S=O stretching,

confirming successful incorporation of sulfonic species. This intensity of this band increased significantly in samples functionalized with disulfonic groups ($2\text{SO}_3\text{H}$) and was slightly enhanced when the M2 functionalization method was employed.

Additionally, stretching bands associated with C–H ($\sim 680\text{--}800\text{ cm}^{-1}$), broad O–H stretching ($\sim 3600\text{ cm}^{-1}$), and C=C ($\sim 1650\text{ cm}^{-1}$) were also intensified. These can be attributed to the benzene ring and hydroxyl groups present in the sulfanilic diazonium salt and amino-naphthalenedisulfonic acid used for functionalization. The S=O stretching band around $\sim 1056\text{ cm}^{-1}$ was notably more pronounced in MXene samples functionalized using NaOH as the intercalant.

Overall, these observations confirm the successful surface functionalization of MXene. However, minimal changes were observed in the band intensities between the two functionalization methods, indicating that while incorporation occurred, the extent of bonding may not differ drastically across synthesis approaches. From the FTIR results, it can be concluded that the surface functionalization was successful, as new sulphur-containing bonds were detected. To further confirm these findings, XPS analysis was performed. These results are consistent with previously reported data by Wang et al. (2016) on Nafion–MXene composites. It is important to note that FTIR analysis of MXene can be challenging due to its strong near-infrared (NIR)

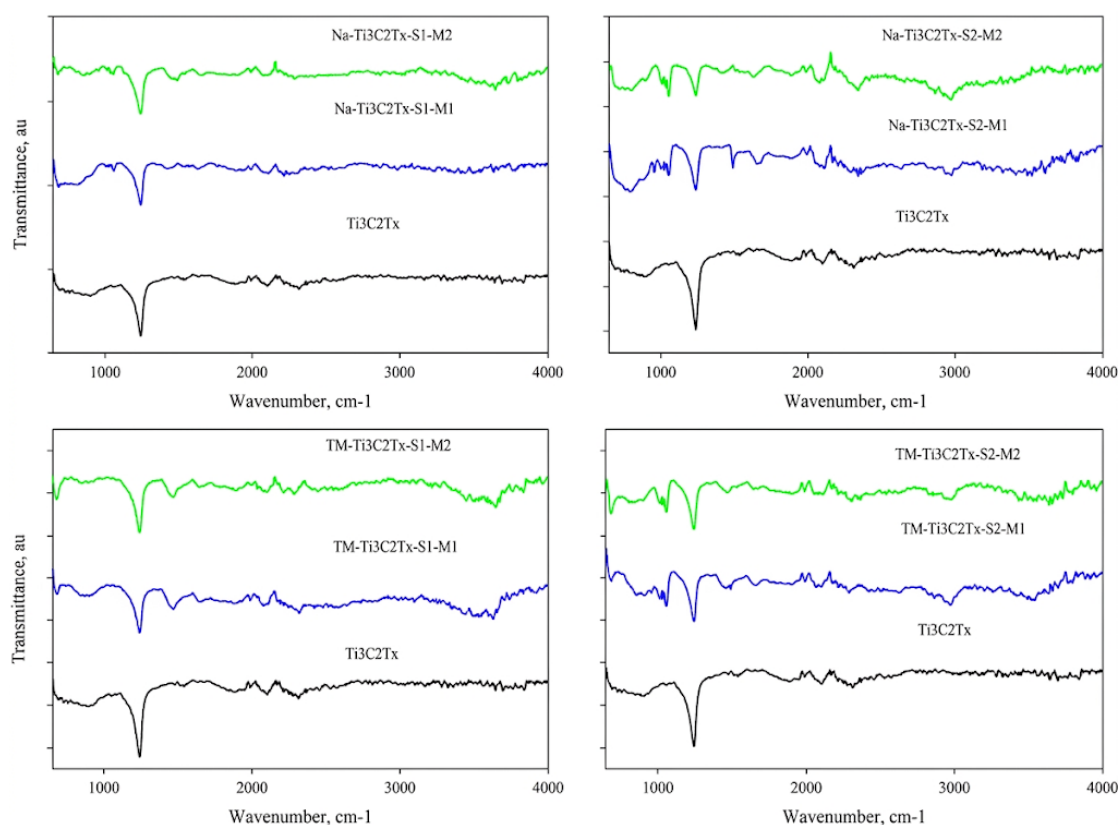


FIGURE 2. FTIR spectra of pristine and surface-functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ MXene samples

absorption, which arises from the unique properties of free-electron absorption and surface plasmon resonance (Maleski et al. 2021). Nevertheless, the observed FTIR spectra in this study are indicative of the successful incorporation of new functional groups onto the surface of the functionalized MXenes.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

Table 1 summarizes the sulphur atomic percentages obtained from the XPS survey spectra for the sulfonic (S1) and disulfonic (S2) functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ samples. No sulphur was detected in pristine $\text{Ti}_3\text{C}_2\text{T}_x$, confirming that sulphur was introduced exclusively through the surface functionalization process. Following functionalization, sulphur was detected in all functionalized samples, indicating the successful incorporation of sulphur-containing functional groups onto the MXene surface.

For the S1 functionalization, the sulphur atomic percentage increased from 0.00 at.% for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M1 to 0.10 at.% for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M2. A similar trend was observed for the NaOH-intercalated samples, where sulphur increased from 0.17 at.% (Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M1) to 0.25 at.% (Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M2). Likewise, the disulfonic acid (S2) functionalized samples exhibited consistently higher sulphur contents than their corresponding M1 samples, increasing from 0.00 at.% for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M1, to 0.26 at.% for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 and from 0.42 at.% for Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M1, to 0.67 at.% for Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2. These results demonstrate that the proposed M2 functionalization strategy consistently enhances sulphur incorporation compared with the conventional post-delamination (M1) approach.

The higher sulphur content obtained by the M2 method can be attributed to the simultaneous

intercalation and functionalization process, which allows sulphur-containing molecules to access the expanding interlayer galleries during delamination. This process increases the availability of active surface sites for functionalization before complete exfoliation occurs, thereby promoting more efficient incorporation of sulfonic and disulfonic functional groups throughout the MXene structure. In contrast, the M1 method performs surface functionalization after delamination, where some reactive Ti surface sites may already be occupied by oxygen-containing terminations or become less accessible due to restacking, resulting in lower sulphur incorporation.

Furthermore, the NaOH-intercalated samples consistently exhibited higher sulphur contents than the TMAOH intercalated counterparts for both S1 and S2 functionalizations. This observation suggests that NaOH intercalation provides a more favorable environment for subsequent functional group incorporation, likely due to the ability to expand the interlayer spacing without fully delaminating like TMAOH, which improved accessibility of surface Ti sites during the functionalization process (Deysher et al. 2020).

To further investigate the influence of surface functionalization on the elemental composition of $\text{Ti}_3\text{C}_2\text{T}_x$, the atomic percentages obtained from the XPS survey spectra are summarized in Table 2. Compared with pristine $\text{Ti}_3\text{C}_2\text{T}_x$, both functionalized samples exhibit a noticeable increase in oxygen content accompanied by a substantial reduction in fluorine concentration. The oxygen atomic percentage increased from 17.32 at.% in pristine $\text{Ti}_3\text{C}_2\text{T}_x$ to 26.35 and 35.19 at.% for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 and Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2, respectively, whereas the fluorine content decreased from 17.21 to 5.41 and 4.12 at.%.

TABLE 1. Sulphur atomic percentage of sulfonic and disulfonic functional groups in functionalized MXene samples from XPS survey spectra

Sample (S1)	Sulfonic (at. %)	Sample (S2)	Disulfonic (at. %)
TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M1	0.00	TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M1	0.00
TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M2	0.10	TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2	0.26
Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M1	0.17	Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M1	0.42
Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S1-M2	0.25	Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2	0.67

TABLE 2. Surface elemental composition (atomic %) of pristine and disulfonic-functionalized $\text{Ti}_3\text{C}_2\text{T}_x$ obtained from XPS survey spectra

Sample	Ti 2p (%)	C 1s (%)	F 1s (%)	O 1s (%)	S 2p (%)
MXene	16.83	48.64	17.21	17.32	0.00
TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2	17.52	50.47	5.41	26.35	0.26
Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2	14.5	45.52	4.12	35.19	0.67

The reduction in fluorine concentration suggests partial replacement of native fluorine terminations generated during HF etching by oxygen-containing functional groups during the surface functionalization process, which is due to -F terminated surface is the least stable. Simultaneously, the increased oxygen content is consistent with the introduction of sulfonic/disulfonic groups, which contain multiple oxygen atoms and therefore contribute to the overall oxygen concentration detected by XPS.

Sulphur was absent in pristine $\text{Ti}_3\text{C}_2\text{T}_x$ but became detectable after surface functionalization, reaching 0.26 at.% and 0.67 at.% for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 and Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2, respectively. Although the sulphur concentration is relatively low, its absence in pristine MXene and subsequent appearance after functionalization provide direct evidence that sulphur-containing functional groups were successfully introduced onto the MXene surface. The higher sulphur content observed for the NaOH-intercalated sample further supports the improved functionalization efficiency of the M2 strategy.

The elemental composition trends observed in Table 2 are also consistent with the FTIR and Ti 2p XPS analyses. FTIR confirms the presence of sulphur-containing functional groups through characteristic S=O vibrations, while the Ti 2p spectra indicate functionalization of the titanium chemical environment after functionalization. Collectively, these complementary characterizations demonstrate the successful incorporation of sulphur-containing sulfonic/disulfonic functional groups onto $\text{Ti}_3\text{C}_2\text{T}_x$.

The high-resolution Ti 2p spectra of pristine $\text{Ti}_3\text{C}_2\text{T}_x$, TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2, and Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 are presented in Figure 3. Prior to peak fitting, all spectra were charge-corrected using the adventitious carbon C 1s peak at 284.8 eV as the reference. A uniform binding-energy correction was applied to all spectra to compensate for instrumental calibration offsets and sample charging effects before deconvolution (Greczynski & Hultman 2020). Therefore, the discussion focuses primarily on the relative evolution of the Ti 2p components rather than their absolute binding energies.

The pristine $\text{Ti}_3\text{C}_2\text{T}_x$ spectrum exhibits three dominant Ti 2p components centered at approximately 452.5, 458.4, and 462.3 eV, which are characteristic of Ti-C and oxidized Ti surface environments commonly observed in etched MXene materials (Natu et al. 2022). Following disulfonic acid functionalization, an additional Ti component appears at approximately 456-457 eV, accompanied by an increased contribution of the higher binding-energy Ti components and a reduction in the relative intensity of the lower binding-energy Ti component. These spectral changes are more pronounced for Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 than for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2, indicating a progressive functionalization

of the local Ti chemical environment with increasing sulphur incorporation.

Among the functionalized samples, Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 exhibits the largest change in the Ti 2p spectrum, followed by TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2. This trend agrees well with the sulphur atomic percentages obtained from the XPS survey spectra, where sulphur increased from 0 at.% in pristine $\text{Ti}_3\text{C}_2\text{T}_x$ to 0.26 at.% for TM- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 and 0.67 at.% for Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2. The higher sulphur content in the NaOH-treated sample indicates a higher degree of surface functionalization.

The increased contribution of the higher binding-energy Ti components is consistent with stronger interactions between surface Ti atoms and oxygen-containing sulfonic/disulfonic groups, resulting in a more oxidized Ti chemical environment (Bargiela et al. 2024). This interpretation is consistent with the FTIR results, which confirm the presence of sulphur-containing functional groups, and together demonstrates the successful surface functionalization of $\text{Ti}_3\text{C}_2\text{T}_x$.

X-RAY DIFFRACTION XRD

XRD analysis was employed to determine the crystallinity of the resultant MXene and to evaluate the success of the delamination process. Based on the results shown in Figures 4 and 5, the structure of all functionalized MXenes exhibits a trend toward increased amorphousness, particularly in the samples functionalized using Method 2 (M2). This amorphization is attributed to the incorporation of benzene rings from sulfanilic diazonium salt and amino naphthalenedisulfonic acid.

Notably, the sample Na- $\text{Ti}_3\text{C}_2\text{T}_x$ -S2-M2 showed the most pronounced amorphous character, consistent with observations from SAED (Selected Area Electron Diffraction) scans presented in Figure 6. Furthermore, a noticeable shift in the (002) peak was observed. In pristine MXene, the (002) peak is typically located around 9° (2 θ), but in the functionalized samples, it shifted to around 6° - 7° (2 θ), indicating an increase in *d*-spacing. This shift is consistent with delamination processes, as reported by Alhabeab et al. (2017) and further supports the successful intercalation and surface functionalization of the MXene.

HIGH RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HR-TEM)

The TEM images show ultrathin, layered structures characteristic of exfoliated $\text{Ti}_3\text{C}_2\text{T}_x$ MXene (Figure 6). The HR-TEM images show clear lattice fringes with an interlayer spacing of approximately 1.0 nm, corresponding to the (002) planes of $\text{Ti}_3\text{C}_2\text{T}_x$, in agreement with XRD analysis. The shifts observed in the XRD scans suggest that the interlayer distance has increased to around 1.26-1.47 nm. To validate this, HR-TEM was employed. As shown in Figure 6, the interlayer spacing

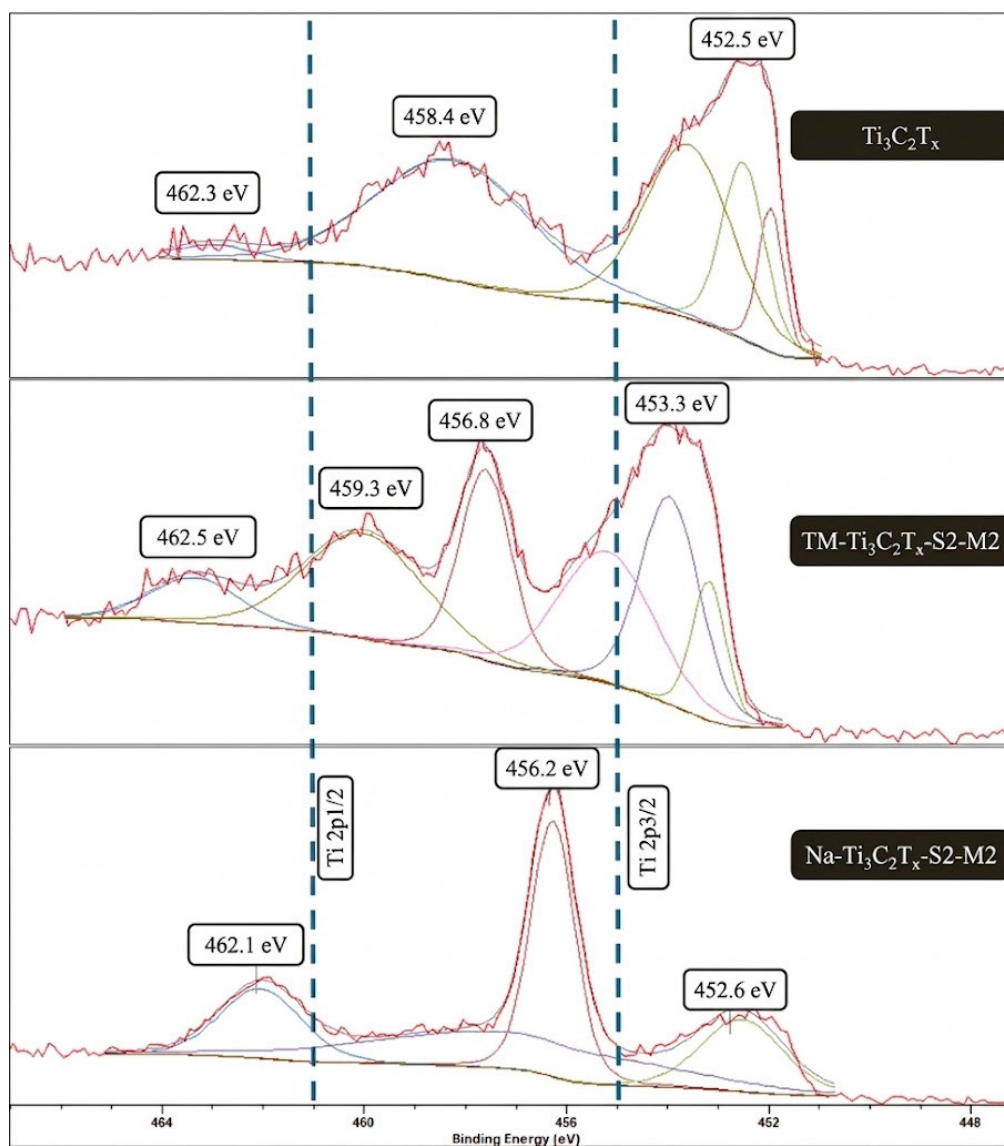


FIGURE 3. Ti 2p XPS spectra of $\text{Ti}_3\text{C}_2\text{T}_x$, $\text{TM-Ti}_3\text{C}_2\text{T}_x\text{-S2-M2}$, and $\text{Na-Ti}_3\text{C}_2\text{T}_x\text{-S2-M2}$

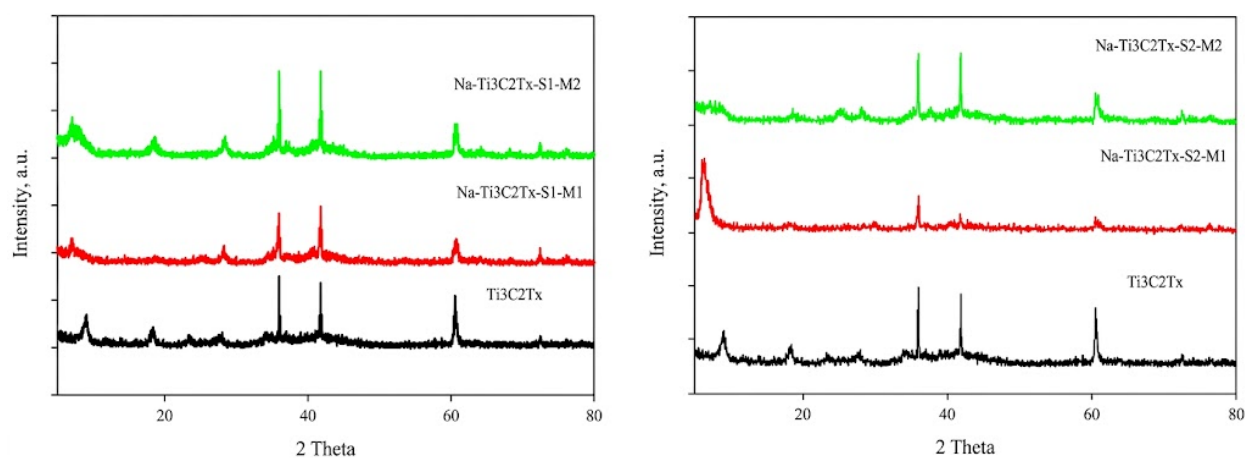


FIGURE 4. XRD patterns of MXene functionalized with NaOH intercalant

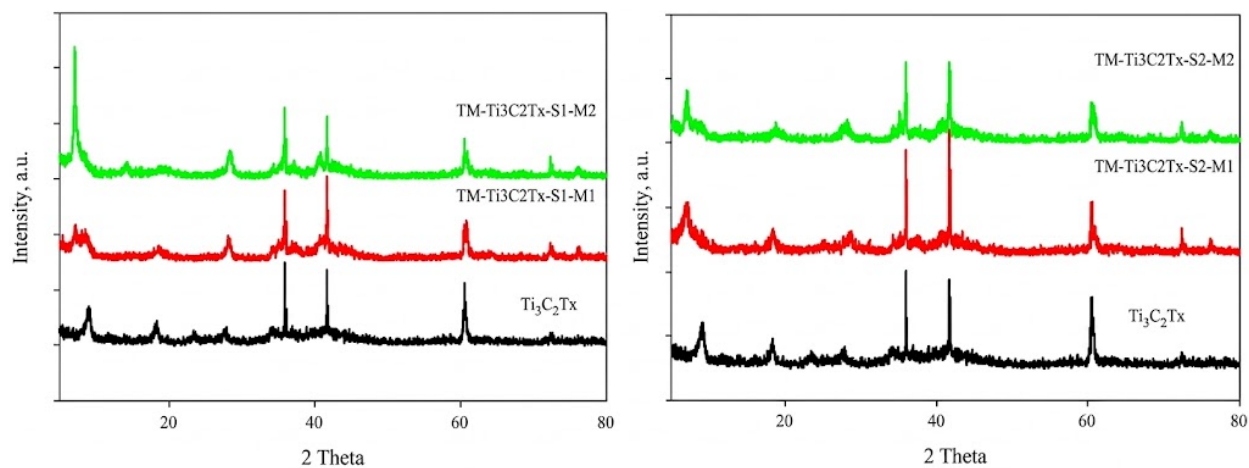


FIGURE 5. XRD patterns of MXene functionalized with TMAOH intercalant

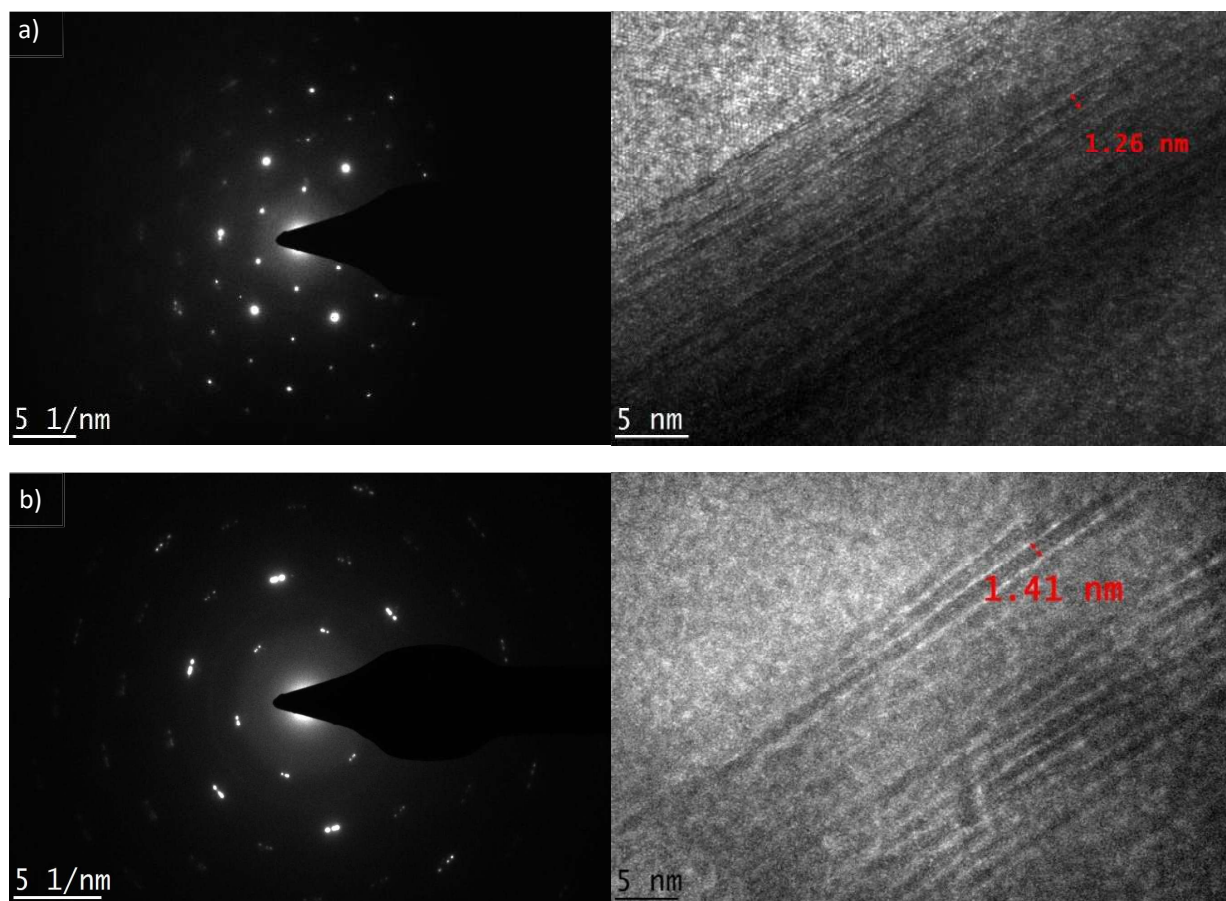


FIGURE 6. Side-by-side comparison of SAED patterns and HR-TEM images of $\text{Na-Ti}_3\text{C}_2\text{T}_x\text{-S}_2\text{-M1}$ and $\text{Na-Ti}_3\text{C}_2\text{T}_x\text{-S}_2\text{-M2}$. (a) SAED and HR-TEM images of $\text{Na-Ti}_3\text{C}_2\text{T}_x\text{-S}_2\text{-M1}$ showing an interlayer spacing of 1.26 nm. (b) SAED and HR-TEM images of $\text{Na-Ti}_3\text{C}_2\text{T}_x\text{-S}_2\text{-M2}$ showing an expanded interlayer spacing of 1.41 nm

measured from the images was ~ 1.26 nm for Na-Ti₃C₂T_x-S2-M1 and ~ 1.41 nm for Na-Ti₃C₂T_x-S2-M2, aligning with the XRD results and confirming successful delamination of the functionalized MXene.

The SAED (Selected Area Electron Diffraction) patterns further support these findings. They display hexagonal diffraction spots, confirming the crystalline nature of the Ti₃C₂T_x nanosheets. Notably, the SAED pattern of Na-Ti₃C₂T_x-S2-M2 (Figure 6(b)) appears more diffuse compared to Na-Ti₃C₂T_x-S2-M1 (Figure 6(a)), indicating a transition toward a more amorphous structure. This transformation is likely due to the incorporation of benzene rings from the disulfonic acid functional groups, suggesting more extensive surface functionalization in the Na-Ti₃C₂T_x-S2-M2 sample.

CONCLUSION

In conclusion, the surface functionalization of MXene with sulfonic and disulfonic groups was successfully achieved. The proposed method (M2) resulted in a higher yield of sulphur-containing functional groups, as evidenced by XPS analysis. MXene samples functionalized via M2 exhibited a significantly greater concentration of S groups compared to those functionalized using the conventional M1 approach, indicating more efficient incorporation. This improvement can be attributed to the fact that in M2, functionalization occurred prior to delamination, allowing more functional groups to be absorbed during the separation of MXene layers. FTIR analysis further supports this, sulphur-containing functional groups peaks were observed in M2-functionalized samples. Delamination was confirmed by XRD results, which showed an increase in *d*-spacing, indicated by a shift in the (002) peak from $\sim 9^\circ$ to $\sim 6\text{--}7^\circ$. This was corroborated by HR-TEM images, with an interlayer distance of approximately 1.41 nm observed in the Na-Ti₃C₂T_x-S2-M2 sample. Overall, M2 demonstrated superior functionalization efficiency compared to the standard M1 method, primarily due to the abundance of functional groups present prior to delamination. Additionally, NaOH was found to be a more effective intercalant than TMAOH, likely due to the smaller size of Na⁺ ions, which do not induce premature delamination before sonication.

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