MXene-Based Membranes

Subjects: Materials Science, Characterization & Testing

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MXene (Figure 1a) is a younger member of the 2D family and has been widely fabricated into both laminar as well as pristine nanosheet membranes using different methods.

two-dimensional MXenes membrane antibacterial

1. Fabrication of MXene-Based Membranes

The ideal filtration membranes should be defect free, ultrathin, a dense film and mechanically robust with a high selectivity for small molecules along with good antifouling and antibacterial properties. Generally, methods such as spin coating, spray coating, vacuum filtration, Langmuir–Blodgett, drop casting, or direction evaporation and dip coating are used for the fabrication of 2D MXene lamellar membranes. Gogotsi et al. [1] used a vacuum filtration method for first time to prepare freestanding and PVDF-supported 2D $Ti_3C_2T_x$-based membranes. Such membranes demonstrated good hydrophilic properties because of the presence of the useful group in conjunction with excellent elasticity as well as a good mechanical strength, which is an ideal potential in separation membranes. Among these methods, the VF method is widely used for the fabrication of 2D MXene-based membranes due to its simplicity and ease of operation (**Figure 1**b). Ding et al. [2] also reported 2D MXene ($Ti_3C_2T_x$) with enhanced properties using a vacuum filtration method on a porous support whereas Kang et al. [3] fabricated MXene ($Ti_3C_2T_x$) and GO-based composite membranes by the same method. Sun and coworkers also fabricated GO/MXene lamellar membranes by the filtration method [4]. Wang and co-researchers worked out an improvement of the microstructure and physiochemical properties of an MXene membrane by mixing it with a polymer matrix. Recently, Wang et al. [5] reported $Ti_3C_2T_x$ lamellar membranes produced by employing a multivalent ion as a hydrogel pillar in the interlayer spacing. Researchers for obtaining the uniform composition mixed a solution of sodium alginate (SA) and MXene $Ti_3C_2T_x$; this composite, SA-$Ti_3C_2T_x$, was then used for the lamellar SA-$Ti_3C_2T_x$ membranes. Fascinatingly, a molecule of SA attached onto the MXene sheets by hydrogen bonding and Van der Waals forces. Finally, pillared SA-$Ti_3C_2T_x$ laminates were arranged by submerging an SA-Ti_3C_2Tx membrane into a solution of different types of multivalent cations such as Ca^{2+}, Ba^{2+}, Mn^{2+}, and Al^{3+}. The pillar membrane showed a homogeneous structure similar to a nacre-like composite and it considerably decreased the swelling effect. Liu et al. [6] fabricated Ti_3C_2Tx-CNT hybrid membranes using vacuum filtration (**Figure 1**c,d). Liu and coworkers also fabricated pristine Ti_3C_2Tx and CNT membranes for comparative studies using the VF method (**Figure 1**g,h). They improved the mechanical stability and permeance of MXene by incorporating CNTs into Ti_3C_2Tx nanosheets. Huang et al. [7] used a phase inversion process to fabricate a PES-Ni@MXene membrane by using an external field and incorporated magnetic Ni@MXene nanoparticles with the upper layer of the PES membrane during a wet phase inversion process. MXene-based lamellar membranes were also prepared by a layer-by-layer (LbL) method [8]. Tian et al. assembled a tris(2-aminoethyl) amine (TAEA) molecule and Ti_3C_2Tx MXene using an LbL assembly and obtained highly ordered multilayer of MXene/TAEA with an interlayer distance ~1 Å. This strategy was a good addition to fabricate MXene-based multilayered membranes for large-scale applications.

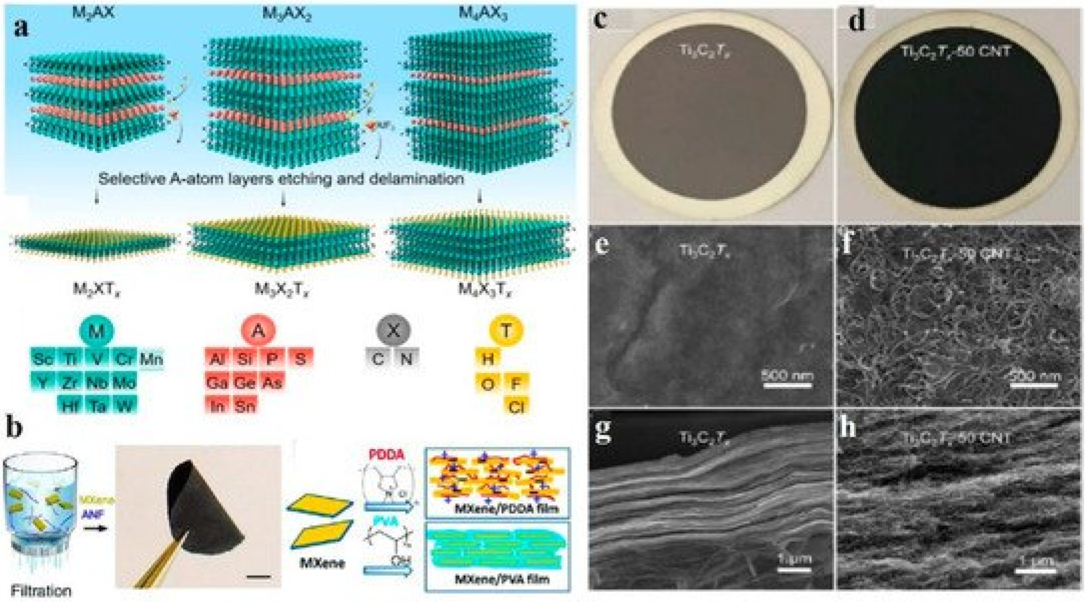

Figure 1. (**a**) MXene precursors and their common synthesis methods. Reprinted with permission from [9]. Copyright 2020 Springer Nature Group. (**b**) Fabrication of MXene/polymer-based composite membrane by the VF method. Reprinted with permission from [1]. Copyright 2015 American Chemical Society. (**c**,**d**) Fabrication of pristine Ti_3C_2Tx and Ti_3C_2Tx-CNT composite membranes. (**e**) The digital photograph of the solutions. (**f**) AFM study of Ti_3C_2Tx nanosheets. (**g**,**h**) Digital photos: surface; cross-sectional SEM images of pristine Ti_3C_2Tx, Ti_3C_2Tx-CNT, and CNT membranes, respectively. Reprinted with permission from [6]. Copyright 2020 American Chemical Society.

From the above studies, it was concluded that the vacuum filtration method was mostly used to fabricate MXene membranes. However, there are several disadvantages associated with the vacuum filtration method. It needs a large volume of solvent, takes long time, and is definitely difficult to scale up. Therefore, alternative methods such as the shear alignment method, printing method, and spin coating method should be utilized to fabricate state-of-the-art MXene-based laminar membranes with advanced physicochemical properties to fully utilize the power of this wonder material.

2. Antibacterial Activity of MXene-Based Membranes

Pathogenic contamination is considered to be the most harmful issue worldwide and is responsible for various kinds of waterborne diseases [10]. It is directly responsible for the biofouling of any water filtration membrane; therefore, it is important that a membrane should be tested against antibacterial properties. Up to date, several bactericidal nanomaterials including graphene, TMDCs, and MXenes have been explored to meet these challenges. The antibacterial activity of graphite, graphite oxide, GO, rGO, MoS_2, and WS_2 against Gram-negative and Gram-positive bacteria have already been tested. Recently, MXenes with unique hydrophilic properties, a good adsorption, an ideal surface functionality, and excellent biocompatibility and photothermal properties have been widely tested for wastewater treatment and desalination, water purification, ion separation and other applications, as shown in **Table 1**. MXenes are expected to be resistant to biofouling and offer bactericidal properties [11]. However, very few studies [11][12][13][14][15][16][17][18][19] have been carried out in this direction. An initial work by Rasool et al. [17] reported that Ti_3C_2Tx membranes could be an ideal platform for antibacterial studies (**Figure 5**a–d). Rasool et al. [17] further used $Ti_3C_2T_x$-based membranes to measure the antibacterial properties against *Escherichia coli* (*E. coli*) and *Bacillus subtilis (B. subtilis*) by using bacterial growth curves based on optical densities (OD) and colony growth on agar nutritive plates (**Figure 5**b,c). The membranes showed a high antibacterial efficiency against both Gram-negative *E. coli* and Gram-positive *B. subtilis* compared with the GO membranes. Concentration-dependent antibacterial activity was observed and more than 98% of bacterial cell viability loss was found at 200 µg/mL in $Ti_3C_2T_x$ for both bacterial cells within 4 h of exposure, as confirmed by a colony-forming unit (CFU) and regrowth curve (**Figure 5**d,e). In another study, $Ti_3C_2T_x$/PVDF composite membranes were tested to measure the antibacterial rate of *E. coli* and *B. subtilis* [11]. The composite membranes showed a ~73% and ~63% antibacterial rate for *B. subtilis* and *E. coli*, respectively, compared with the control PVDF membranes [11]. Additionally, the $Ti_3C_2T_x$ membrane showed over a 99% growth inhibition of both bacteria under the same conditions. Mayerberger et al. [12] demonstrated Ti_3C_2Tz/chitosan composite nanofiber membranes for a passive antibacterial wound dressing application. The as-prepared composite membrane showed a 95% and 62% reduction in the colony-forming units of Gram-negative *E. coli* and Gram-positive *Staphylococcus aureus* (*S. aureus*), respectively. Jastrzebsa and coworkers also reported the antimicrobial properties of a Ti_3C_2 MXene-based nanocomposite, i.e., $Ti_3C_2/SiO_2/Ag$, $Ti_3C_2/Al_2O_3/Ag$, and $Ti_3C_2/SiO_2/Pd$ [13]. They also demonstrated the outstanding bioactive properties of Ti_2C and Ti_3C_2 MXenes against a Gram-negative bacterial strain [19]. Recently, Zhu et al. [15] evaluated the effect of near-infrared (NIR) light on the antibacterial activities of silver (Ag), $Ti_3C_2T_x$, and an $Ag/Ti_3C_2T_x$ composite. The as-prepared $Ag/Ti_3C_2T_x$ composite showed a high efficacy against Gram-positive *S. aureus* and Gram-negative *E. coli* bacteria in an in vitro antibacterial test. Upon NIR irradiation, the antimicrobial effect of $Ag/Ti_3C_2T_x$ significantly strengthened compared with the pristine Ag and $Ti_3C_2T_x$. The growth of *E. coli* was completely inhibited during the initial 0–6 h by 200 µg/mL of $Ti_3C_2T_x$ due to the photothermal heat produced killing the bacteria in the surrounding area. The $Ag/Ti_3C_2T_x$ composite exhibited the best antibacterial activities with the same dose of pristine Ag and $Ti_3C_2T_x$. After NIR irradiation, the $Ti_3C_2T_x$ composite could completely restrain the *E. coli* growth when used at 100–200 µg/mL.

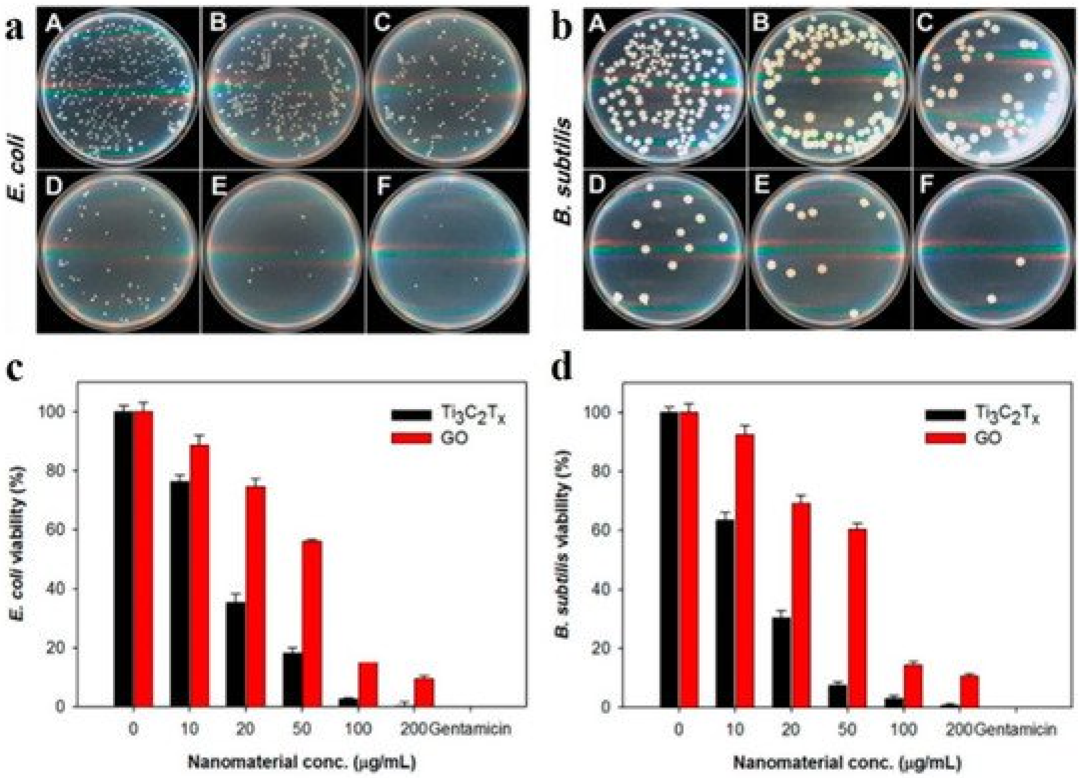

Figure 5. $Ti_3C_2T_x$ nanosheet membranes. (**a**) Antibacterial activities of $Ti_3C_2T_x$ membranes in an aqueous solution against *E. coli* and (**b**) *B. subtilis* with different concentrations, i.e., 0 µg/mL (**A**), 10 µg/mL (**B**), 20 µg/mL (**C**), 50 µg/mL (**D**), 100 µg/mL (**E**), and 200 µg/mL (**F**), respectively. (**c**,**d**) Cell viability measurement and comparison studies of $Ti_3C_2T_x$ and GO membranes against *E. coli* and *B. subtilis* bacterial strains. Bacterial suspensions (107 CFU/mL) were incubated with different concentrations (0–200 µg/mL) of $Ti_3C_2T_x$ and GO membranes at 35 °C for 4 h at a speed of 150 rmp. Reprinted with permission from [17]. Copyright 2016 American Chemical Society.

Table 1. MXene-based membranes for the separation of ions, molecules, and pathogens from water.

Table 1. MXene-based membranes for the separation of ions, molecules, and pathogens from water.

Type of Membrane	Fabrication Method	Feed Solution/Concentration	Rejection (%)	Permeability (Lm^{-2} h^{-1} bar^{-1})	Ref.
Ti_3C_2Tx	Vacuum filtration	RB	85	1084	[2]
		EB	90		
		CC (Each 10–20 mg/L)	97		
Ti_3C_2Tx	Vacuum filtration	NaCl (10,000 mg/L)	56–64	10	[20]
		BSA (2000 mg/L)			

Type of Membrane	Fabrication Method	Feed Solution/Concentration	Rejection (%)	Permeability (Lm^{-2} h^{-1} bar^{-1})	Ref.
Ti_3C_2Tx	Vacuum filtration	CR	92	405	[21]
		GN	80		
		MgCl2	2.3		
		Na2SO4	13.2		
		NaCl (Each 100–1000 mg/L)	13.8%		
Ti_3C_2Tx	Vacuum filtration	*E. coli*	>99	37.4	[11]
		B. subtilis	>99		
Ti_3C_2Tx	Vacuum filtration	Na_2SO_4	50–99	5–15.25	[22]
		Mg_2SO_4			
		$MgCl_2$			
		NaCl			
		$VOSO_4$			
Ti_3C_2Tx-Ag	Vacuum-assisted filtration	RB	79.9	~420	[23]
		MG	92.3		
		BSA (50–100 mg/L)	>99%		
Ti_3C_2Tx-GO	Vacuum filtration	BB	95.4	~25 L	[3]
		Rose Bengal	94.6		
		MLB	40		
		MLR	5		
		MgSO4	<1		
		NaCl (Each 10 mg/L)			
Ti_3C_2Tx-GO	Vacuum filtration	RB	>97 (dyes)	89.6	[24]
		MB			

Type of Membrane	Fabrication Method	Feed Solution/Concentration	Rejection (%)	Permeability (Lm^{-2} h^{-1} bar^{-1})	Ref.
		CV			
		NR (Each 10 mg/L)			
		Na_2SO_4	61		
		NaCl (Each 5 mM)	23		
Ti_3C_2Tx-GO	Vacuum filtration	Chrysoidine G	>99% (dyes)	71.9	[25]
		MLB			
		NR			
		CV			
		BB			
		HA			
		BSA			
		Na_2SO_4	61		
		NaCl (Each 10 mg/L)	23		
Ti_3C_2Tx-GO	Vacuum filtration	MO	>95	~8.5–11	[22]
		MLB			
		Acid yellow 14			
		IC			
		Eosin (Each 10 mg/L)			
Ti_3C_2Tx-TiO_2	Spin coating	Dextran (3000 mg/L)	>95	~90	[26]

CC: cytochrome C; MLB: methylene blue; RB: rhodamine B; EB: Evan blue; MO: methyl orange; IC: indigo carmine; HA: humic acid; BB: brilliant blue; NR: neutral red; CV: crystal violet; CR: Congo red; GN: gentian violet; MG: methyl green; MLR: methylene red.

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