Properties of MXene Products

Subjects: Physics, Condensed Matter
Contributor: Tomasz Blachowicz , Dariusz Wójcik , Maciej Surma , Mirosław Magnuski , Guido Ehrmann , Andrea Ehrmann

MXenes are two-dimensional layered materials containing early transition metal carbides, nitrides, and carbonitrides.

shielding effectiveness conductive coating magnetic properties

1. Different MXenes and Their Preparation

MXenes are two-dimensional layered materials containing early transition metal carbides, nitrides, and carbonitrides [1]. They are prepared by starting from so-called three-dimensional MAX phases, where MAX is the abbreviation of $M_{n+1}AX_n$ with (n = 1, 2, 3), and M denotes an early *d*-block transition metal (i.e., Ti, Sc, V, Cr, Ta, Nb, Zr, Mo, or Hf), A means a main group *sp* element especially from the groups 13 and 14, and X represents C and/or N [2]. By etching the *sp* element layers out of the MAX phases, two-dimensional MXenes (without the "A") remain [3]. MXenes have additional terminated functional groups (e.g., -OH, -O, -F) named "T", resulting in their general formula $M_{n+1}X_nT_x$ [4].

More than 60 of these MXenes have been found, yet with different metal or ceramic properties, depending on the chemical constitution [5]. One of the problems of MXenes is their susceptibility to oxidation in humid or aqueous environments, necessitating either excluding water vapor to reach them or increasing their stability against oxidation [6].

2. MXene Coatings

Due to their two-dimensional nature, MXenes are mostly applied in the form of coatings on textile fabrics, either solely or together with intrinsically conductive polymers, metals, or carbon-based fillers. Li et al. reported electromagnetic interference shielding combined with the potential applications of photothermal conversion and solar water evaporation, using a layer-by-layer assembly method on a textile fabric [7]. They combined SiO_2 nanoparticles/poly(dimethylsiloxane) (PDMS) and 1*H*,1*H*,2*H*,2*H*-perfluorooctyltriethoxysilane (PFOTES) to reach superhydrophobicity (i.e., a water contact angle larger than 160°) as well as MXene to reach a high conductivity of 1200 S/m, resulting in an EMI shielding of 36 dB.

Zheng et al. prepared bark-shaped MXene/textiles which showed not only high EMI shielding, but also good Joule heating and good piezoresistive sensing [8]. The bark-shape was suggested to enhance multiple interfaces scattering of EM waves to improve the EMI shielding effectiveness. To reach this shape, the authors used the pad-drying technology normally used in fabric dyeing to apply MXene flakes on a cellulose nonwoven. In their study, they synthesized $Ti_3C_2T_x$ MXene sheets, immersed a cellulose nonwoven into an aqueous MXene solution and used a padder to remove the excess water before drying, repeating this cycle 1–9 times. By increasing the number of pad-drying cycles from 3–9, the EMI shielding effectiveness could be increased from 3.2 dB to 36.3 dB in a range from 8.2 GHz–12.4 GHz (X-band) due to improving single conductive paths towards a conductive network, which was also visible in the decreased sheet resistance for larger numbers of pad-drying cycles.

Using a spray-drying procedure, Zhang et al. reported good electrical conductivity and low sheet resistance of 5 Ω already for low MXene loading of 6 wt% on a woven cotton fabric, resulting in efficient EMI shielding and well-balanced Joule heating as well as the possibility of using this fabric as a strain sensor to detect human motion [9]. Besides EMI shielding and thermal heating, Yu et al. also mentioned bactericidal activity of their Mxene-decorated, polydopamine (PDA) modified cellulose nonwovens [10]. They reached an EMI shielding of 38.6 dB in the X-band, good heating performance, and a very high bactericidal efficacy of more than 99.99% against *E. coli* and *S. aureus*.

Working on basalt fiber fabrics, Yu et al. used multilayer spray-drying to coat $Ti_3C_2T_x$ nanosheets and $Ti_3C_2T_x$/natural rubber layers, the latter protecting the inner $Ti_3C_2T_x$ coating and additionally formed conductive connections between the conductively coated basalt fibers [11]. The Mxene phase was prepared by etching Al from commercially available Ti_3AlC_2 powder, using LiF, followed by exfoliation by ultrasonication in an ice bath under Ar flow. With this procedure, a sheet resistance of (5 ± 3) Ω was reached with the maximum tested $Ti_3C_2T_x$ amount of 4 mg/cm^2, resulting in EMI shielding up to 41 dB in the X-band.

Yao et al. also combined Mxene with a polymer network, here PDMS, to give a textile fabric EMI shielding, electro-thermal and photo-thermal conversion as well as pressure-sensing properties [12]. While different numbers of dip-coating cycles into a suspension of $Ti_3C_2T_x$ Mxene were examined, these coated textile fabrics were dipped into low cross-linked PDMS and thermally cured to reach adhesive properties. While samples without Mxene showed nearly no EMI shielding in the X-band, Mxene coated samples with 3–9 dip-coating cycles reached more than 30 dB along the whole X-band, mostly due to absorption.

Much higher EMI shielding values were even reported by Uzun et al. who used dip-coating of cotton and linen fabrics in $Ti_3C_2T_x$ Mxene dyes [13]. While 4 dip-coating cycles resulted in approx. 40 dB shielding in the X-band, 24 dip-coating cycles increased this value to approx. 80 dB. Interestingly, these values were decreased by only 8% and 13% for cotton and linen fabrics, respectively, after storing them for 2 years under ambient conditions.

Even higher values were reported from groups who combined Mxene coating with intrinsically conductive polymers, such as polyaniline (Pani), polypyrrole (Ppy), polythiophene, polyphenyl sulfide, polyacetylene, polyphenylene, polyphenylene vinylene, or poly (3,4-ethylene dioxythiophene) (PEDOT) [14]. Wang et al., e.g., applied Ppy-modified Mxene sheets on poly(ethylene terephthalate) (PET) textiles and subsequently coated them with silicone, resulting in high electrical conductivity around 1000 S/m and EMI shielding efficiency of approx. 90 dB as well as good Joule heating performance [15].

Combining Mxene with Pani nanowires on a carbon fiber fabric followed by PDMS coating resulted in a good conductivity of 325 S/m and EMI shielding effectiveness around 35 dB [16]. A 3D nanoflower structure from $Ti_3C_2T_x$/Pani was prepared by Li et al. by polymerization of aniline monomer on single-layer $Ti_3C_2T_x$ nanosheets, resulting in a shielding effectiveness of 52 dB in the X-band [17]. Previously, combining Mxenes and Pani in a layer-by-layer assembly, Yin et al. reached a conductivity of 25 S/m and an EMI shielding efficiency of 26 dB [18].

Other authors combined Mxene with metal, e.g., with Ag nanowires (Ag NWs), reaching an EMI shielding efficiency of 54 dB in the X-band [19], or with Fe_3O_4 hollow nanospheres, resulting in low sheet resistance of about 5 Ω and high EMI shielding effectiveness of 33 dB, enabling tuning the shielding mechanism between absorption and reflection [20]. Alternatively, combining MXene with carbon-based conductive materials is reported, e.g., a $Ti_3C_2T_x$/carbon nanotube (CNT) coated thermoplastic polyurethane nonwoven, leading to high EMI shielding around 43 dB [21].

As these examples show, there are many possibilities to apply MXene coatings on textile fabrics to prepare EMI shielding fabrics. However, only few reports about MXene fibers can be found in the literature. They are discussed in the next section.

3. MXene Fibers

One possibility to prepare MXene fibers is to use them as core or shell in coaxially spun fibers, as described by Liu et al. [22]. The authors prepared a cellulose spinning solution by dissolving cotton linter pulp with LiOH solution, urea, and distilled water, and received regenerated cellulose after putting the cellulose dispersion into an acetic acid coagulation bath. $Ti_3C_2T_x$ MXene was mixed with graphene oxide (GO) to prepare the other spinning solution. Both solutions were coaxially spun into a rotating bath, with cellulose or MXene/GO building the core. In this way, it was possible to prepare meter-long hollow fibers from regenerated cellulose and GO/MXene which could lift a mass of 100 g. These fibers were found to have conductivities up to 10^5 S/m. The EMI shielding effectiveness depended on the mesh grid spacing of woven or sewn structures prepared from these fibers, showing values around 27–33 dB for a single layer with the smallest grid spacing and up to more than 100 dB for 3 layers, building an only 12 µm thick MXene film. The same group also showed coaxial spinning of core-shell fibers with MXene core and aramid nanofiber shell [23]. In this way, they reached a conductivity of 3×10^5 S/m and an EMI shielding efficiency of 83 dB.

Zhou et al. suggested preparing compact MXene fibers by combining wet spinning from a MXene-glutaraldehyde (GA) solution with thermal drawing, resulting in significantly increased tensile strength and toughness, conductivity around 8×10^5 S/m and EMI shielding effectiveness of 50–60 dB in the X-band [24].

Instead of these filament-based approaches, Xiong et al. used short MXene fibers, produced by wet-spinning, to produce a MXene nonwoven by wet-assembly [25]. In this way, a strong interfiber bonding was reached. This MXene nonwoven showed high conductivity around 70,000 S/m and an EMI shielding effectiveness of 75 dB in the X-band.

Another path was suggested by Zheng et al. who prepared a core–shell aerogel from reduced graphene oxide (rGO) with MXene by wet-spinning and freeze-drying [26]. In this way, they reached an EMI shielding effectiveness up to 83 dB which degraded by only 17% after 120 days.

As these few examples show, MXene fibers are challenging to produce and thus are less often prepared for EMI shielding applications. Carbon fibers and metal wires, on the other hand, are commercially available in diverse qualities and diameters; however, EMI shielding is nevertheless mostly reached by functionalizing textile fabrics with carbon or metal containing coatings.

References

1. Naguib, M.; Mochalin, V.N.; Barsoum, M.W.; Gogotsi, Y. MXenes: A new family of two-dimensional materials. Adv. Mater. 2014, 26, 992–1005.
2. Barsoum, M.W. The Mn+1AXn phases: A new class of solids. Prog. Solid State Chem. 2000, 28, 201–281.
3. Sinha, A.; Dhanjai; Zhao, H.M.; Huang, Y.J.; Lu, X.B.; Chen, J.P.; Jain, R. MXene: An emerging material for sensing and biosensing. TrAC Trends Anal. Chem. 2018, 105, 424–435.
4. Zhang, C.; McKeon, L.; Kremer, M.P.; Park, S.-H.; Ronan, O.; Seral-Ascasco, A.; Barwich, S.; Coileáin, C.Ó.; McEvoy, N.; Nerl, H.C.; et al. Additive-free MXene inks and direct printing of micro-supercapacitors. Nat. Commun. 2019, 10, 1795.
5. Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M.W. Two dimensional transition metal carbides. ACS Nano 2012, 6, 1322–1331.
6. Lee, Y.H.; Kim, S.J.; Kim, Y.-J.; Lim, Y.H.; Chae, Y.J.; Lee, B.J.; Kim, Y.-T.; Han, H.; Gogotsi, Y.; Ahn, C.W. Oxidation-resistant titanium carbide MXene films. J. Mater. Chem. A 2020, 8, 573–581.
7. Li, E.; Pan, Y.M.; Wang, C.F.; Liu, C.T.; Shen, C.Y.; Pan, C.F.; Liu, X.H. Asymmetric Superhydrophobic Textiles for Electromagnetic Interference Shielding, Photothermal Conversion, and Solar Water Evaporation. ACS Appl. Mater. Interfaces 2021, 13, 28996–29007.
8. Zheng, X.H.; Wang, P.; Zhang, X.S.; Hu, Q.L.; Wang, Z.Q.; Nie, W.Q.; Zou, L.H.; Li, C.L.; Han, X. Breathable, durable and bark-shaped MXene/textiles for high-performance wearable pressure sensors, EMI shielding and heat physiotherapy. Compos. A Appl. Sci. Manuf. 2022, 152, 106700.
9. Zhang, X.S.; Wang, X.F.; Lei, Z.W.; Wang, L.L.; Tian, M.W.; Zhu, S.F.; Xiao, H.; Tang, X.N.; Qu, L.J. Flexible MXene-Decorated Fabric with Interwoven Conductive Networks for Integrated Joule Heating, Electromagnetic Interference Shielding, and Strain Sensing Performances. ACS Appl. Mater. Interfaces 2020, 12, 14459–14467.

10. Yu, Z.C.; Deng, C.; Seidi, F.; Yong, Q.; Lou, Z.C.; Meng, L.C.; Liu, J.W.; Huang, C.; Liu, Y.Q.; Wu, W.B.; et al. Air-permeable and flexible multifunctional cellulose-based textiles for bio-protection, thermal heating conversion, and electromagnetic interference shielding. J. Mater. Chem. A 2022, 10, 17452–17463.
11. Yu, J.; Cui, Z.L.; Lu, J.Y.; Zhao, J.L.; Zhang, Y.; Fan, G.Q.; Liu, S.Y.; He, Y.B.; Yu, Y.H.; Qi, D.M. Integrated hierarchical macrostructures of flexible basalt fiber composites with tunable electromagnetic interference (EMI) shielding and rapid electrothermal response. Compos. B Eng. 2021, 224, 109193.
12. Yao, D.J.; Tang, Z.H.; Liang, Z.H.; Zhang, L.; Sun, Q.-J.; Fan, J.M.; Zhong, G.K.; Liu, Q.-X.; Jiang, Y.-P.; Tang, X.-G.; et al. Adhesive, multifunctional, and wearable electronics based on MXene-coated textile for personal heating systems, electromagnetic interference shielding, and pressure sensing. J. Coll. Interface Sci. 2023, 630, 23–33.
13. Uzun, S.; Han, M.K.; Strobel, C.J.; Hantanasirisakul, K.; Goad, A.; Dion, G.; Gogotsi, Y. Highly conductive and scalable Ti3C2Tx-coated fabrics for efficient electromagnetic interference shielding. Carbon 2021, 174, 382–389.
14. Taghizadeh, A.; Taghizadeh, M.; Jouyandeh, M.; Khodadadi Yazdi, M.; Zarrintaj, P.; Saeb, M.R.; Lima, E.C.; Gupta, V.K. Conductive polymers in water treatment: A review. J. Mol. Liq. 2020, 312, 113447.
15. Wang, Q.-W.; Zhang, H.-B.; Liu, J.; Zhao, S.; Xie, X.; Liu, L.X.; Yang, R.; Koratkar, N.; Yu, Z.-Z. Multifunctional and Water-Resistant MXene-Decorated Polyester Textiles with Outstanding Electromagnetic Interference Shielding and Joule Heating Performances. Adv. Funct. Mater. 2019, 29, 1806819.
16. Yin, G.; Wang, Y.; Wang, W.; Qu, Z.J.; Yu, D. A Flexible Electromagnetic Interference Shielding Fabric Prepared by Construction of PANI/MXene Conductive Network via Layer-by-Layer Assembly. Adv. Mater. Interfaces 2021, 8, 2001893.
17. Li, J.; Li, Y.X.; Yang, L.Y.; Yin, S.G. Ti3C2Tx/PANI/Liquid Metal Composite Microspheres with 3D Nanoflower Structure: Preparation, Characterization, and Applications in EMI Shielding. Adv. Mater. Interfaces 2022, 9, 2102266.
18. Yin, G.; Wang, Y.; Wang, W.; Yu, D. Multilayer structured PANI/MXene/CF fabric for electromagnetic interference shielding constructed by layer-by-layer strategy. Coll. Surf. A Physicochem. Eng. Asp. 2020, 601, 125047.
19. Liu, L.-X.; Chen, W.; Zhang, H.-B.; Wang, Q.-W.; Guan, F.L.; Yu, Z.-Z. Flexible and Multifunctional Silk Textiles with Biomimetic Leaf-Like MXene/Silver Nanowire Nanostructures for Electromagnetic Interference Shielding, Humidity Monitoring, and Self-Derived Hydrophobicity. Adv. Funct. Mater. 2019, 29, 1905197.

20. Zheng, X.H.; Tang, J.H.; Cheng, L.Z.; Yang, H.W.; Zou, L.H.; Li, C.L. Superhydrophobic hollow magnetized Fe3O4 nanospheres/MXene fabrics for electromagnetic interference shielding. J. Alloy. Comp. 2023, 934, 167964.

21. Zhang, D.B.; Yin, R.; Zheng, Y.J.; Li, Q.M.; Liu, H.; Liu, C.T.; Shen, C.Y. Multifunctional MXene/CNTs based flexible electronic textile with excellent strain sensing, electromagnetic interference shielding and Joule heating performances. Chem. Eng. J. 2022, 438, 135587.

22. Liu, L.-X.; Chen, W.; Zhang, H.-B.; Zhang, Y.; Tang, P.P.; Li, D.Y.; Deng, Z.M.; Ye, L.X.; Yu, Z.-Z. Tough and electrically conductive Ti3C2Tx MXene–based core–shell fibers for high–performance electromagnetic interference shielding and heating application. Chem. Eng. J. 2022, 430, 133074.

23. Liu, L.-X.; Chen, W.; Zhang, H.-B.; Ye, L.X.; Wang, Z.G.; Zhang, Y.; Min, P.; Yu, Z.-Z. Super-Tough and Environmentally Stable Aramid. Coaxial Fibers with Outstanding Electromagnetic Interference Shielding Efficiency. Nano-Micro Lett. 2022, 14, 111.

24. Zhou, T.Z.; He, Y.Z.; He, B.; Wang, Z.; Xiong, T.; Wang, Z.X.; Liu, Y.T.; Xin, J.W.; Qi, M.; Zhang, H.Z.; et al. Ultra-compact MXene fibers by continuous and controllable synergy of interfacial interactions and thermal drawing-induced stresses. Nat. Commun. 2022, 13, 4564.

25. Xiong, J.H.; Zheng, H.W.; Ding, R.J.; Li, P.Y.; Liu, Z.L.; Zhao, X.; Xue, F.H.; Chen, Z.; Yan, Q.; Peng, Q.Y.; et al. Multifunctional non-woven fabrics based on interfused MXene fibers. Mater. Des. 2022, 223, 111207.

26. Zheng, X.H.; Tang, J.H.; Wang, P.; Wang, Z.Q.; Zou, L.H.; Li, C.L. Interfused core-shell heterogeneous graphene/MXene fiber aerogel for high-performance and durable electromagnetic interference shielding. J. Coll. Interface Sci. 2022, 628, 994–1003.