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Introduction to Titanium Carbide (Ti_3C_2) MXenes for Energy and Environmental Applications

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1.1 Introduction

Transition metal carbide- and nitride-based materials were explored in the twentieth century as having high thermal resistance, chemically stable, hard, water resistance, and conductive characteristics. Since the 1970s, several designs of nanotextures have been proposed; however, there was a small increase in the surface area and the performance of these metal carbides and nitrides. A breakthrough in this field happened in 2011, with the discovery of 2D transition metal carbide and nitride nanotexture compounds, named titanium carbide ($Ti_3C_2T_x$) MXenes.

The general formula of MXene is $M_{n+1}X_nT_X$, which is derived from MAX materials. M stands for the early transitional metal elements such as Sc, Ti, Hf, Mo, Ta, V, Zr, Nb, and Cr. The "X" constitutes either carbon or nitrogen elements, and the acronym "A" represents the Al or Si layer and n ranges from 1 to 3. The chemical exfoliation of the A element of MAX results in the termination of the M surface with abundant functional groups, T_x, such as –F, –Cl, –OH, and –O [1, 2]. The first MXene material (titanium carbide MXene [$Ti_3C_2T_x$]) was synthesized in 2011 by Naguib et al. via chemical etching with hydrofluoric acid (HF) [3]. In general, 2D sheets have a thickness in the range of 1 nm; however, it can be altered by varying the number n in the MXene formula such as M_2XT, $M_3X_2T_x$, and $M_4X_3T_x$. Most of the MXenes (25 out of 29) are made of MAX materials by selective etching of the Al layer. A recent study showed that instead of Al and Si, transition metals of groups 8–12 of the periodic table (Fe, Cu, Zn, Cd, Ir, and Au) can also become the A layer of MAX phases.

Ti_3C_2 MXene, due to its 2D layered structure, has drawn attention worldwide in the area of energy storage and conversion applications [4–6]. This is due to its promising properties such as its higher specific area and terminal functional groups (OH, O, and –F). In photocatalytic applications, the Ti_3C_2 functional group aids in the formation of Schottky junctions for the trapping of electrons through a strong chemical connection at the semiconductor photocatalyst's interface and prevent the

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recombination of charge carriers produced by light. Due to Ti_3C_2 MXenes' better electron conductivity and increased reactivity, the exposed metallic active sites have an advantage. This causes efficient movement of charge carriers and separation of photogenerated electrons from holes [7–9]. Additionally, because of its diverse morphologies in terms of forms and dimensions, its application and photocatalyst activity capabilities have considerably changed and improved, which has expanded its use in photocatalytic energy conversions [10, 11]. The detailed information about the fundamental properties and characteristics of Ti_3C_2 MXenes has been discussed in Chapter 2.

The synthesis of Ti_3C_2 Mxenes is possible by using an etching agent under different operating conditions. Different etching agents are used for the removal of the Al layer in order to produce Ti_3C_2 in a variety of ways. The most often used techniques include electrochemical etching, molten salt etching, halogen etching, hydrofluoric acid etching, and acid F-salt etching. The detailed information related to synthesis and characterization of MXenes has been discussed in Chapter 3. The kind and concentration of the etching agent, reaction duration, intercalation agents, and synthesis conditions are only a few of the variables that have a significant impact on Ti_3C_2 etching [12]. These factors have the ability to change the structure, termination groups, defect morphology, conducting and semiconducting characteristics, and other features of Ti_3C_2 MXene. The features of the formed Ti_3C_2 can affect its quality, environmental stability, and other qualities [13, 14]. The conductive metal cores in the layered structure endow MXene with excellent metallic conductivities, and the modification of properties can lead to the formation of Ti_3C_2 MXene with the required properties for various applications in the field of energy conversion applications.

The single-Ti_3C_2 MXenes have less photocatalytic activity due to conductive characteristics; thus, they are commonly used as a cocatalysts with semiconductor materials. Ti_3C_2 MXenes can be combined with a variety of materials for use in energy conversion applications because of the several benefits such as (i) numerous functional beneficial characteristics for the construction of an intimate contact interface with other semiconductors; and (ii) the bandgap alignment of Ti_3C_2 modulated for tuning the surface chemistry [15–17]. A detailed discussion about the synthesis and characterization of MXenes based heterojunction formation has been given in Chapter 4. The layered Ti_3C_2 MXene structure, which resembles an accordion, may be transformed into different dimensions, including a three-dimensional structure, very thin two-dimensional nanosheets, one-dimensional (1D) nanorods and nanowires, and zero-dimensional (0D) quantum dots [18–21]. A range of 2D, 0D, and 1D photocatalyst materials may also be loaded onto Ti_3C_2 MXene to provide efficient, renewable solar fuel [22, 23]. For the production of Ti_3C_2 MXene-based composite photocatalysts, a number of techniques have been published in the literature. The mechanical mixing, self-assembly, in situ semiconductor decorating over the MXene surface, and the in situ oxidation approach are the most often utilized techniques [24–27].

Titanium dioxide material is considered the most extensively investigated photocatalysis material owing to its photocatalytic activity, good chemical stability, abundancy, and low cost. However, because of its wide bandgap energy (3.2 eV), the TiO_2 photocatalyst is UV-active only and functions poorly under visible light, thus lowering its photoactivity [28, 29]. Recently, titanium carbides (MXenes) have gained significant concern in improving the photocatalytic activity of semiconductors, in particular TiO_2, due to their exceptional chemical and physical properties. In Chapter 5, the properties and characteristics of the benchmark TiO_2 photocatalysts and the highly conductive 2D MXene (Ti_3C_2) materials are discussed. The role of MXene in enhancing the photocatalytic performance of TiO_2 photocatalysts is summarized in three main sections; the formation of Schottky heterojunctions, enhancing light harvesting; and enhancing reactant adsorption. Finally, Chapter 5 discloses the recent developments of MXene/TiO_2 nanocomposites for environmental remediation and energy production applications such as photocatalytic CO_2 reduction, photocatalytic H_2 production, and pollutant photodegradation.

Due to the appropriate construction, non-toxicity, and high reduction capacity, graphitic carbon nitride (g-C_3N_4) is regarded as an ideal element for hydrogen production in the visible light spectrum. However, they have a higher recombination of charged carriers, which significantly limits g-C_3N_4 photocatalytic efficacy. The performance of g-C_3N_4 with fast charge carrier separation can be effectively achieved by constructing composites with MXenes. In this perspective, 2D/2D heterojunction of g-C_3N_4 with Ti_3C_2 can be achieved. Due to its tunable terminal groups, metallic conductivity, layered structure, and simple morphological arrangement, Ti_3C_2 MXene as a cocatalyst could boost photocatalytic performance [16, 17]. The detailed information about the Ti_3C_2 coupled g-C_3N_4 composite has been discussed in Chapter 6.

In recent years, metal-organic frameworks (MOFs) have been explored for photocatalytic applications because of their high specific surface area, tunable bandgap, changeable crystalline structures, adjustable chemistry, and functionality. Furthermore, MOFs have outstanding physical qualities which can be employed for adsorption processes in environmental applications [30, 31]. However, the crystalline architecture of MOFs inherently introduces structural flaws such as electron-hole recombination centers and low electrical conductivity, limiting their efficiency in photocatalytic water splitting [32, 33]. Ti_3C_2 MXenes are permissive materials that can be used with MOFs for energy and environmental applications. Notably, conductive TiC MXenes may improve charge carrier transport efficiency and allow for fine-tuning of catalytic performance in MXene/MOF multicomponent catalyst systems [34]. Chapter 7 discloses detailed information about the Ti_3C_2-based MOF composites for energy and environmental application.

Currently, several two-dimensional (2D) materials have been employed to improve the catalytic performance by virtue of their non-toxic behavior, high durability, and huge surface area. Layered double hydroxides (LDHs) have been widely utilized in energy storage and conversion application due to their unique properties. For example, the Fe-, Co-, and Ni-based LDHs have demonstrated efficient performance in the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER); and the space of the layered structure can be used as storage sites for Li^+ in Li-ion batteries. However, the LDHs still endure the poor performance owing to the shortage of active sites and effective electronic transport. Among these 2D materials, LDH and titanium carbide MXene (TiC MXene) having highly active sites with high density and high uniformity can work as ideal models to modify the important parameters for energy storage and environmental applications. The detailed information about the recent development in LDH-based materials and their Ti_3C_2-based composites has been discussed in Chapter 8.

Perovskites, on the other hand, are an interesting class of photocatalysts since they can be synthesized under benign circumstances and a broad range of catalytic properties can be controlled. They have broad-spectrum activity, enabling their use for a variety of purposes, including the production of value-added compounds for expanding chemical feedstocks and lowering atmospheric CO_2 emissions [35]. However, perovskites have drawbacks such as high electron-hole recombination and limited specific surface area [36]. As a result, a variety of techniques have been devised to increase the photocatalytic efficiency of perovskites. In this regard, MXene, because of their exceptional conductive and photothermal properties, is one of the fastest-growing research domains among all existing 2D materials [37]. Ti_3C_2 MXene-based semiconductors as a mediator or heterojunction have been accepted as a viable strategy for promoting charge separation and enhancing the photostability of the final product. More interestingly, it is possible to increase light absorption with improved photoactivity and stability by combining MXene multilayer materials with perovskite [38]. Chapter 9 discloses detailed information about the application of perovskites-based MXenes for energy and environmental applications.

With the popularization of electric automobiles and handy electronic devices, the development and improvement of electrochemical energy storage devices (EESD) are needed to meet the required power and energy density. Also, harnessing energy from renewable energy sources, such as solar, wind, and hydro energy, greatly depends on weather conditions (tide, wind, and sun), and these conditions are not continuous due to environmental weather conditions. Hence, highly performing energy storage devices are required to save the energy generated. MXenes due to their intrinsic structure and properties have received increasing attention and have the advantages of being employed in particular as an electrode material for electrochemical energy storage devices. Detailed information about energy storage performances of MXenes has been discussed in Chapter 10.

1.2 Layout of the Book

The introduction of titanium carbide (Ti_3C_2) MXenes has been discussed in Chapter 1. Chapter 2 describes the fundamentals, properties, and characteristics of titanium carbide MXenes ($Ti_3C_2T_x$). The synthesis and characterization of titanium carbide (Ti_3C_2) MXenes have been discussed in Chapter 3. The synthesis and characterization of Ti_2C_3-MXene-based composites for energy storage and conversion have been presented in Chapter 4. Titanium carbide MXene-based titanium dioxide composites for energy and environmental applications are discussed in Chapter 5. MXene-based graphitic carbon nitride composites for energy and environmental applications have been discussed in Chapter 6. The titanium carbide MXene-based MOF composites for energy and environmental applications are discussed in Chapter 7. Chapter 8 depicts titanium carbide (TiC) MXene-based layered double hydroxide (LDH) composites for energy and environmental applications. Chapter 9 discusses titanium carbide MXene-based perovskite composites for energy and environmental applications. Finally, titanium carbide-based MXenes for energy storage applications have been discussed in Chapter 10.

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References

1 Tahir, M. and Tahir, B. (2022). Constructing S-scheme 2D/0D g-C_3N_4/TiO_2 NPs/MPs heterojunction with 2D-Ti_3AlC_2 MAX cocatalyst for photocatalytic CO_2 reduction to CO/CH_4 in fixed-bed and monolith photoreactors. *J. Mater. Sci. Technol.* 106: 195–210.

2 Tahir, M., Sherryna, A., Mansoor, R. et al. (2022). Titanium carbide MXene nanostructures as catalysts and cocatalysts for photocatalytic fuel production: a review. *ACS Appl. Nano Mater.* 5 (1): 18–54.

3 Naguib, M., Kurtoglu, M., Presser, V. et al. (2011). Two-dimensional nanocrystals produced by exfoliation of Ti_3AlC_2. *Adv. Mater.* 23 (37): 4248–4253.

4 Aghamohammadi, H., Amousa, N., and Eslami-Farsani, R. (2021). Recent advances in developing the MXene/polymer nanocomposites with multiple properties: a review study. *Synth. Met.* 273.

5 Verger, L., Xu, C., Natu, V. et al. (2019). Overview of the synthesis of MXenes and other ultrathin 2D transition metal carbides and nitrides. *Curr. Opin. Solid State Mater. Sci.* 23 (3): 149–163.

6 Xie, X., Zhang, N., Tang, Z.-R. et al. (2018). $Ti_3C_2T_x$ MXene as a Janus cocatalyst for concurrent promoted photoactivity and inhibited photocorrosion. *Appl. Catal. B* 237: 43–49.

7 Xu, Y., Wang, S., Yang, J. et al. (2018). Highly efficient photoelectrocatalytic reduction of CO_2 on the Ti_3C_2/g-C_3N_4 heterojunction with rich $Ti^{3+}$and pyri-N species. *J. Mater. Chem. A* 6 (31): 15213–15220.

8 Li, X., Wang, C., Cao, Y., and Wang, G. (2018). Functional MXene materials: progress of their applications. *Chem. Asian J.* 13 (19): 2742–2757.

9 Pang, J., Mendes, R.G., Bachmatiuk, A. et al. (2019). Applications of 2D MXenes in energy conversion and storage systems. *Chem. Soc. Rev.* 48 (1): 72–133.

10 Dong, Y., Zheng, S., Qin, J. et al. (2018). All-MXene-based integrated electrode constructed by Ti_3C_2 nanoribbon framework host and nanosheet interlayer for high-energy-density Li–S batteries. *ACS Nano* 12 (3): 2381–2388.

11 Xiong, D., Li, X., Bai, Z., and Lu, S. (2018). Recent advances in layered $Ti_3C_2T_x$ MXene for electrochemical energy storage. *Small* 14 (17): 1703419.

12 Tahir, M., Khan, A.A., Tasleem, S. et al. (2023). Recent advances in titanium carbide MXene-based nanotextures with influential effect of synthesis parameters for solar CO_2 reduction and H_2 production: a critical review. *J. Energy Chem.* 76: 295–331.

13 Alhabeb, M., Maleski, K., Anasori, B. et al. (2017). Guidelines for synthesis and processing of two-dimensional titanium carbide ($Ti_3C_2T_x$ MXene). *Chem. Mater.* 29 (18): 7633–7644.

14 Munir, S., Rasheed, A., Rasheed, T. et al. (2020). Exploring the influence of critical parameters for the effective synthesis of high-quality 2D MXene. *ACS Omega* 5 (41): 26845–26854.

15 Tang, R., Xiong, S., Gong, D. et al. (2020). Ti_3C_2 2D MXene: recent progress and perspectives in photocatalysis. *ACS Appl. Mater. Interfaces* 12 (51): 56663–56680.

16 Tahir, M., Ali Khan, A., Tasleem, S. et al. (2021). Titanium carbide (Ti_3C_2) MXene as a promising co-catalyst for photocatalytic CO_2 conversion to energy-efficient fuels: a review. *Energy Fuels* 35 (13): 10374–10404.

17 Tahir, M. (2021). Binary Ni_2P/Ti_3C_2 multilayer cocatalyst anchored TiO_2 nanocomposite with etchant/oxidation grown TiO_2 NPs for enhancing photocatalytic H_2 production. *Energy Fuels* 35 (17): 14197–14211.

18 Liu, J., Xu, H., Xu, Y. et al. (2017). Graphene quantum dots modified mesoporous graphite carbon nitride with significant enhancement of photocatalytic activity. *Appl. Catal., B* 207: 429–437.

19 Li, K., Liang, M., Wang, H. et al. (2020). 3D MXene architectures for efficient energy storage and conversion. *Adv. Funct. Mater.* 30 (47): 2000842.

20 Li, Z., Wang, L., Sun, D. et al. (2015). Synthesis and thermal stability of two-dimensional carbide MXene Ti_3C_2. *Mater. Sci. Eng., B* 191: 33–40.

21 Zeng, Z., Yan, Y., Chen, J. et al. (2019). Boosting the photocatalytic ability of Cu_2O nanowires for CO_2 conversion by MXene quantum dots. *Adv. Funct. Mater.* 29 (2): 1806500.

22 Fu, Y., Li, Z., Liu, Q. et al. (2017). Construction of carbon nitride and MoS_2 quantum dot 2D/0D hybrid photocatalyst: direct Z-scheme mechanism for improved photocatalytic activity. *Chin. J. Catal.* 38 (12): 2160–2170.

23 Feng, A., Yu, Y., Wang, Y. et al. (2017). Two-dimensional MXene Ti_3C_2 produced by exfoliation of Ti_3AlC_2. *Mater. Design* 114: 161–166.

24 Li, Z. and Wu, Y. (2019). 2D early transition metal carbides (MXenes) for catalysis. *Small* 15 (29): 1804736.

25 Yang, C., Tan, Q., Li, Q. et al. (2020). 2D/2D Ti_3C_2 MXene/g-C_3N_4 nanosheets heterojunction for high efficient CO_2 reduction photocatalyst: dual effects of urea. *Appl. Catal., B* 268: 118738.

26 Su, T., Hood, Z.D., Naguib, M. et al. (2019). 2D/2D heterojunction of Ti_3C_2/g-C_3N_4 nanosheets for enhanced photocatalytic hydrogen evolution. *Nanoscale* 11 (17): 8138–8149.

27 Su, T., Peng, R., Hood, Z.D. et al. (2018). One-step synthesis of $Nb_2O_5/C/Nb_2C$ (MXene) composites and their use as photocatalysts for hydrogen evolution. *ChemSusChem* 11 (4): 688–699.

28 Tahir, B., Tahir, M., and Amin, N.S. (2015). Gold–indium modified TiO_2 nanocatalysts for photocatalytic CO_2 reduction with H_2 as reductant in a monolith photoreactor. *Appl. Surf. Sci.* 338: 1–14.

29 Tahir, M. and Tahir, B. (2021). In-situ growth of TiO_2 imbedded $Ti_3C_2T_A$ nanosheets to construct PCN/$Ti_3C_2T_A$ MXenes 2D/3D heterojunction for efficient solar driven photocatalytic CO_2 reduction towards CO and CH_4 production. *J. Colloid Interface Sci.* 591: 20–37.

30 Liu, X., Shan, Y., Zhang, S. et al. (2022). Application of metal organic framework in wastewater treatment. *Green Energy Environ.* 8 (3): 698–721.

31 Lin, S., Song, Z., Che, G. et al. (2014). Adsorption behavior of metal–organic frameworks for methylene blue from aqueous solution. *Microporous Mesoporous Mater.* 193: 27–34.

32 Liu, S., Zhang, C., Sun, Y. et al. (2020). Design of metal-organic framework-based photocatalysts for hydrogen generation. *Coord. Chem. Rev.* 413: 213266.

33 Reddy, C.V., Reddy, K.R., Harish, V.V.N. et al. (2020). Metal-organic frameworks (MOFs)-based efficient heterogeneous photocatalysts: synthesis, properties and its applications in photocatalytic hydrogen generation, CO_2 reduction and photodegradation of organic dyes. *Int. J. Hydrogen Energy* 45 (13): 7656–7679.

34 Sharma, K., Hasija, V., Patial, S. et al. (2022). Recent progress on MXenes and MOFs hybrids: structure, synthetic strategies and catalytic water splitting. *Int. J. Hydrogen Energy*.

35 Tabish, A., Varghese, A.M., Wahab, M.A., and Karanikolos, G.N. (2020). Perovskites in the energy grid and CO_2 conversion: current context and future directions. *Catalysts* 10 (1): 95.

36 Xiang, S., Zhang, Z., Gong, C. et al. (2018). $LaFeO_3$ nanoparticle-coupled TiO_2 nanotube array composite with enhanced visible light photocatalytic activity. *Mater. Lett.* 216: 1–4.

37 Lin, H., Gao, S., Dai, C. et al. (2017). A two-dimensional biodegradable niobium carbide (MXene) for photothermal tumor eradication in NIR-I and NIR-II biowindows. *J. Am. Chem. Soc.* 139 (45): 16235–16247.

38 Tasleem, S. and Tahir, M. (2020). Current trends in strategies to improve photocatalytic performance of perovskites materials for solar to hydrogen production. *Renewable Sustainable Energy Rev.* 132: 110073.