Research Progress on MXene Nanomaterials for Organic Pollutants Removal

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Abstract. A new family of two dimensional (2D) carbides, nitrides and carbonitrides, intituled MXenes, sprung up since 2011. In possession of good hydrophilicity, controllable surface properties, excellent electrical conductivity and magnetic properties, it has been diffusely used in miscellaneous fields, such as energy storage, catalysis, medicine, adsorption and so on. At present, MXenes are primarily prepared through hydrofluoric acid, fluoride salts, alkali, and electrochemical etching, and chemical vapor deposition. The advantages and disadvantages of diversiform preparation methods are elaborated, and the application research progress on organic pollutants removal in recent years is illustrated. The adsorption and catalytic degradation mechanisms of MXene-based materials are analyzed. Moreover, difficulties and application strategies for the further development of MXene are described, which will provide the basis for its practical application in environmental pollutants.

Keywords: MXene, organic pollutants, adsorption, catalysis

1 Introduction

MXenes, belonging to inorganic two-dimensional transition metal-based components of carbides, nitrides and carbonitrides, are mainly prepared through etching layer A from the MAX phase. As shown in **Figure 1**[1], the MAX phase is a ternary carbide or nitride, and the chemical formula is $M_{n+1}AX_n$, where M stands for transition metals, A is an element of group IIIA or IVA, X is C and/or N, and n = 1, 2, 3. The M-X bond is much stronger than the M-A bond, as a result, the A layers undergo selective chemical etching without ruining the M-X bond, leading to weakly bonded $M_{n+1}X_n$ layers that can be easily splited through ultrasound. During the etching process, the surface of $M_{n+1}X_n$ units is always covered by functional groups, such as oxygen (=O), hydroxyl (-OH), and fluorine (-F). Hence, the chemical formula of MXene is summarized as $M_{n+1}X_nT_x$, where T_x stands for the surface functional group.

The unique physicochemical properties of MXene leads to its applications in all kinds of fields like energy storage and conversion, sensors, catalytic materials, and multifunctional polymer composite materials. On account of abundant functional groups, modifiable active sites, controllable surface chemical properties, adjustable energy gap, and high chemical and thermal stability, MXene has been the most promising nanomaterials for wastewater treatment

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and environmental renovation. Furthermore, they are gradually developing as high-efficiency adsorbents or catalysts for treating different organic contaminants. In this paper, the synthesis procedures are introduced, and the application and mechanism of MXenes in the field of organic pollution removal are analysed deeply. Ultimately, the emphasis and direction of future research are prospected.

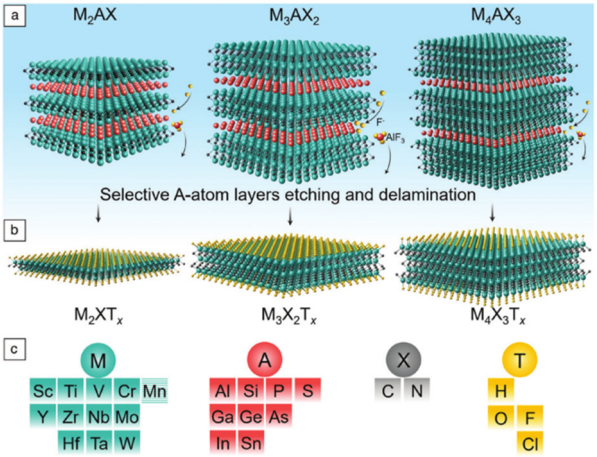

Fig.1. Structure diagram of MAX phase and MXene[1]

2 Synthetic methods of MXenes

Up to now, more than 100 MXene materials have been synthesized by theoretical prediction or experiments, and different synthesis methods have been studied to prepare MXene. **Figure 2**[2] shows the development timeline of the preparation methods, which were splited into top-down and bottom-up synthesis approaches.

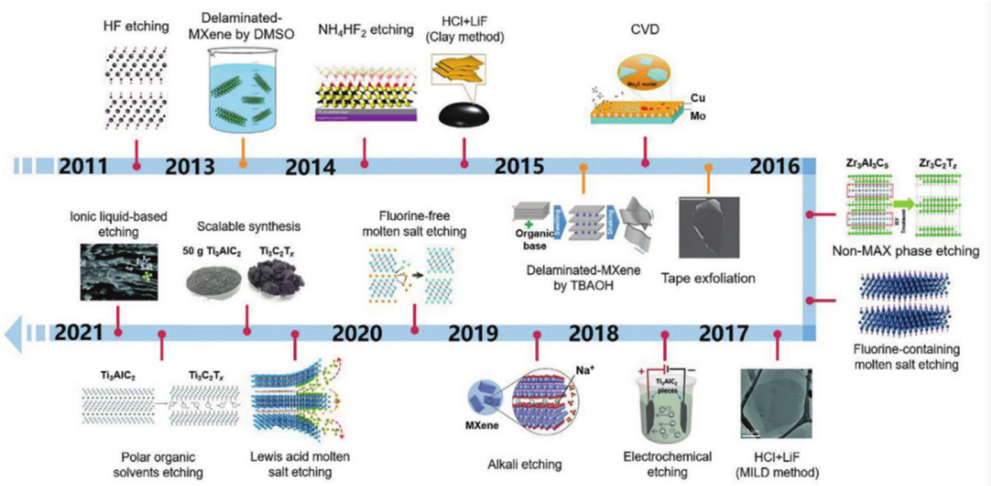

Fig. 2. Timeline of the development of MXene synthetic methods [2]

2.1 The top-down approaches

The top-down preparation approach is the mainstream route for the preparation of MXenes. That is, layer A is removed from the structure through chemical liquid phase etching, and a new two-dimensional structure is obtained. The synthesis of MXenes by chemical etching is dependent on the etching conditions used, including the strength and concentration of chemical etching agents, etching temperature and etching time.

Fluorine-containing etching approaches include HF etching method, in-situ HF etching method, fluorine-containing molten salt etching method, etc. Because of the diversity of M-A and M-X bonding and extremely corrosive of HF, HF etching is widely used to prepare most MXenes, including Ti_2C, Mo_2C, Nb_2C, V_2C, Hf_3C_2, Mo_2TiC_2, Nb_4C_3, Mo_4VC_4, and many other MXenes. However, high concentration of HF is highly toxic, which can easily penetrate the skin, muscle tissue and bone, so that the operation has a certain risk. In-situ synthesis of HF can be used to avoid or minimize the employment of high concentrations of HF, of which the most extensively utilized is a mixture of HCl and fluoride salts. Professor Yury led a team to conduct a series of studies. In 2014, a relatively mild minimum intensity layer deposition (MILD) method was used for the first time, which was LiF and HCl etching and centrifugation to prepare single-layer MXene and the surface end groups were mainly -OH or -O [3]. An in-depth study was conducted on atomic defects in single-layer $Ti_3C_2T_x$, and it was found that the concentration of titanium vacancies can be adjusted by regulating the concentration of the etchant. The conductivity of single-layer $Ti_3C_2T_x$ is equivalent to that of graphene. In addition, other fluoride salts (NaF, KF, and NH_4F), as well as diverse LiF/HCl molar ratios and HCl concentrations can also be used to synthesize MXenes with different structures and functions. In 2016, Gogotsi team innovatively reported nitride MXenes with different terminals ($Ti_4N_3T_x$, T_x=O>F>OH) by heating Ti_4AlN_3 in molten fluoride salts[4]. After reacting at 550 °C for 30 min, the Al layer was successfully removed from Ti_4AlN_3, and the multi-layer $Ti_4N_3T_x$ particles were layered into small and single layers, indicating the probability of synthesizing nitride MXenes by molten fluoride salt approach.

In addition, there are various fluorine-free etching methods available. The electrochemical etching method for preparing MXene uses MAX phase as the working electrode, selectively removing the Al atomic layer under a certain voltage. NaCl, $FeCl_3$, NaOH, etc. can be used as electrolysis systems to obtain carbide derived carbon (CDC) from MAX phase. Electrochemical etching is an environmental-friendly, safe and low energy synthesis approach, but the existence of CDC layer and the internal MAX phase is difficult to be etched is still a challenge. Although the use of HF can be averted using modified acid etching, the presence of H^+ and F^- in the system may still lead to the release of HF, and the F-attack layer A is only suitable for the removal of alkaline or amphoteric elements. Therefore, the development of new fluorine-free solution etching methods to remove layer A is essential for the development of safe and green MXene preparation routes [5].

2.2 The bottom-up approaches

In recent years, multifarious bottom-up preparation approaches have also been exploited, involving chemical vapor deposition (CVD), atomic layer deposition (ALD), template method, and plasma enhanced pulsed laser deposition (PEPLD). It was reported that the growth of high-quality ultra-thin α-Mo_2C (~3 nm) through CVD method using double metal foil as

growth substrate [6]. Compared with CVD method, template method has a significant advantage of higher yield. 2D transition metal oxide (TMOs) nanosheets are utilized as templates, which are then carbonized or nitrided to synthesize MXenes, the structure of which depends on the 2D TMOs used. Materials prepared by bottom-up methods have higher crystal quality compared to selective etching processes, but so far none of these methods have produced a single layer of MXene, but rather an ultra-thin film composed of several layers.

3 Degradation mechanism

Nano-composites prepared with MXenes modified by TiO_2, Ag_2O, PdO_2, Au, etc., or MXenes combined with MnO_2, Fe_3O_4 and other metal oxides can effectively degrade various organic pollutants, which are mainly removed using three different ways: (i) adsorption and complexation, (ii) photocatalytic degradation by in situ free radical production, and (iii) catalytic degradation by advanced oxidation engineering (AOPs).

3.1 Adsorption and complexation

The advantages, including negatively charged surface, layered morphology, and surface adjustability, of MXene have attracted attention to its application in the adsorption of organic pollutants. Due to electrostatic attraction, multi-layer MXene can efficiently and selectively adsorb the cationic dye methylene blue (MB) in aqueous solutions, but the adsorption performance of anionic dye acid Blue 80 (AB80) is average[7]. MXene-based adsorbents exhibit degradation properties to different ionic dyes with the presence of appropriate catalysts. Under ultraviolet irradiation, the degradation rate of AB80 and MB was 62% and 81%, respectively, while the degradation rate of MB was only 18% in the dark.

Nano Fe_2O_3 grains was embedded into the inner layer of MXene to increase the number of available activation layers. Then magnetic nano Fe_3O_4 was embedded into MXene matrix and combined with its Ti-O terminal to prepare sandwich-like MXene/magnetic nanocomposites, which can efficiently remove phosphate from water [8]. The different adsorption properties at different hybrid ratios indicate that the best synergistic effect occurs when MXene:Fe_3O_4=2:1, confirming the synergistic adsorption of bimetallic oxides by ferric oxide intercalation and terminal titanium hydroxide hybridization. Guo et al.[9] synthesized Ti_3C_2-MoS_2 using a hydrothermal method, which achieved adsorption equilibrium for the organic pesticide paraquat (PQ) within 30 min. The specific surface area increased significantly and the adsorption capacity augmented from 8.7 mg/g to 105.5 mg/g due to the introduction of flowerlike MoS_2. The adsorption process follows freundlich isothermal model and quasi-second-order kinetic model, which manifests that there are both physical adsorption and chemical adsorption in the adsorption process.

3.2 Photocatalytic degradation

Photocatalysis is a low-cost and environmentally friendly technology that purifies contaminants in wastewater to form H_2O and CO_2.

In-situ TiO_2/MXene. In recent years, the use of semiconductor photocatalysts and UV-visible energy for photocatalytic decomposition of pollutants has become more and more important. Excellent light capture ability, high transfer efficiency, and fast reaction dynamics generate

efficient photocatalytic performance. Due to the low cost, easy production, and strong availability of TiO_2-based photocatalysts, they are the most common. MXenes have extensive hydrophilic functional groups (-O and -OH), making it easy to establish strong and sufficient connections with semiconductors. The Ti sites with strong redox activity promote the reduction reaction of electrons and generate more •OH radicals. In addition, its outstanding metal conductivity makes it an efficient carrier for carrier transfer, which is profitable to the separation of carriers. It is conducive to combine it with TiO_2 to make the photocatalytic performance of the catalyst to get better. Wojciechowski et al.[10] recombined Ti_2C-MXene and six nanomaterials (i.e. MXene modified with TiO_2, Ag_2O, Ag, PdO, Pd, and Au) as photocatalysts to degrade salicylic acid (SA) under UV irradiation. The degradation rate of SA was 86% -97% after 3 h. The band gap of the materials measured through the tauc method is within the range of 0.90 to 1.31 eV. On account of the metallic property of Ti_2C, the lifetime of photo created electrons migrating from the TiO_2 conduction band to MXene surface was extended. In addition, photocatalysts for dye degradation include ZnO, Ag_3PO_4, $ZnFe_2O_4$, $BiVO_4$, etc. Iqbal et al.[11] prepared $BiFeO_3/Ti_3C_2$ nano-hybrid through solvothermal method. The band gap tuning of the hybrid can reach 1.96 eV, and the specific surface area has reached 147 m^2 /g. The photocatalytic degradation efficiency of congo red (CR) and acetophenone can reach 100% in 42 min and 150 min, respectively. Large specific surface area and low electron-cavity recombination rate are the factors leading to rapid and efficient degradation of organic contaminants.

MXene heterostructure. Combining with metal oxides or semiconductor materials, MXene can form heterojunction structures with effective electron hole separation and good photocatalytic performance, and photocarrier separation and transport regulation are important factors affecting the photocatalytic efficiency. Wu et al.[12] prepared a novel NH_2-MIL-125 (Ti) (TiO_2)/Ti_3C_2 nanocomposite through solvothermal approach. The optimized nanocomposite showed a 1.65-fold increase in H_2O_2 yield under visible light irradiation, and the degradation efficiency of tetracycline hydrochloride (TC-HCl) reached 83% for 1 h. This material was a dual heterostructure, whose electrons generated by NH_2-MIL-125 (Ti) (TiO_2) are transferred to Ti_3C_2, which not only increases the carrier density but also significantly accelerates the separation and transfer of interfacial charges, improving photocatalytic activity. Free radical capture experiments and ESR spectra confirm that ·OH and h^+ are the main active substances in photocatalytic activity. Except as binary compounds based on MXenes, the probe of ternary heterostructures has become a trend in the area of photocatalysis. Examples include TiO_2@Ti_3C_2/g-C_3N_4 ternary heterostructure, CdS@Ti_3C_2@TiO_2 composite, core-shell In_2S_3/ TiO_2@$Ti_3C_2T_x$ hybrid, BiOI/(001)TiO_2/Ti_3C_2 hybrid, g-C_3N_4 /Ti_3C_2/$MoSe_2$ Type z heterojunction.

Photofenton reaction. Photofenton catalytic reaction is a process in which H_2O_2 generates hydroxyl radical (•OH) under the synergistic catalysis of photoelectrons generated by ultraviolet excitation and Fe^{2+}. •OH has strong oxidation and electrophilic addition performance, and can oxidize and decompose most organic matter into small molecule substances. However, in this system, the light utilization rate is low, the energy consumption is large, and the high concentration of H_2O_2 will cause water pollution, which is generally only suitable for the treatment of medium and low concentration of organic wastewater. Zhao et al.[13] prepared MXene/MIL(Fe) photocatalyst with heme-like structure by metal replacement and bottom-up synthesis method. Fe sites were highly dispersed embedded in the highly

conductive MXene structure to build the Fe-porphyrin heme-like structure with high oxygen carrying capacity. The rapid in-situ generation of H_2O_2 was realized under light, and the efficient degradation of thiacloprid (TCL) was realized in the zero H_2O_2 addition system. Compared to MIL-100 (Fe), H_2O_2 formation rate of MXene/MIL-100 (Fe) was 12 times higher (up to 1175.2 μmol/L), the degradation rate of TCL was 24 times higher, and the mineralization rate was 3.7 times higher.

3.3 Catalytic degradation by AOPs

Free radicals are generated by AOPs in the reaction through electro-optical irradiation, catalysts, etc., and then through the addition, substitution, electron transfer, and bond breaking between free radicals and organic compounds, so that the macromolecules in the water body are oxidized and degraded into non-toxic small particles, and even directly degraded into CO_2 and H_2O. Sulfate radical advanced oxidation technology (SR-AOPs) is a new wastewater treatment technology, its working principle is mainly based on persulfate (including persulfate PMS and persulfate PDS) molecules to break the peroxide bond to initiate a chain reaction. Oxygen-containing species such as persulfate radical (SO_4^{-}•), hydroxyl radical (OH^{-}•), superoxide radical (O_2^{-}•) and singlet oxygen ($^1O_2$) are produced.

Ding et al. studied the activation of $Ti_3C_2T_X$ and $Fe_2CoTi_3O_{10}$-MXene composites on PMS, and thus degraded 2, 4-dichlorophenoxyacetic acid (2,4-D). The efficiency of electron transfer generally improved through the small HOMO-LUMO gap and the good compatibility between the superoxide LUMO and the HOMO of the low-dimensional catalyst, which leads to the production of ROS through the break of the peroxygen bond, compared to the bulk form as an activator. The activation of peroxonosulfate and the production of active free radicals resulted in the reaction kinetics being about 376 times higher and the degradation of 2,4-D significantly increased. Moreover, PMS activation was also found to be effective in the degradation of SA. In the meanwhile, α-Fe_2O_3 /MXene composite was prepared using hydrothermal method and served as PMS activator to degrade SA, with a pollutant removal rate of 97% and a mineralization rate of 68.5%. EPR analysis verified the genegration of sulfates and hydroxyl radicals, which contribute to the degradation of SA [14].

4 Application prospects of MXenes for Organic Pollutants Removal

The large number of functional groups exposed on the surface of layered MXenes provide sufficient active sites for the adsorption of organic contaminants, and the specific surface area is crucial in the adsorption capacity of MXenes. Therefore, its adsorption performance can be effectively improved by adjusting surface functional groups, interlayer insertion, and self-assembly. The separation and transportation regulation of photo carriers are important factors affecting photocatalytic efficiency. MXene as a carrier can enlarge the photo generation rate of photocatalytic active substances, resulting in higher electron hole pair generation rate, wider photon absorption, enhanced surface redox performance of photocatalysts, and improved photocatalytic activity. Through the small HOMO-LUMO gap and the good compatibility between superoxide LUMO and catalyst HOMO, the electron transfer efficiency of advanced oxidation processes (AOPs) can be improved, the activation efficiency of activators can be enhanced, and the reaction kinetics rate can be improved. Organic pollutants can be

mineralized into carbon dioxide and water, making it an environmentally friendly process. In addition, it can also be made into two-dimensional composite materials or three-dimensional porous structures, further improving performance.

5 Conclusion

In recent years, two-dimensional MXenes have been prepared by various methods. The top-down strategy, more widely used, mainly contains chemical liquid etching, hydrothermal method, and melting method. The bottom-up strategy involves auxiliary solvothermal method, template method, and CVD method. The MXene synthesized using these approaches has a unique layered structure, excellent hydrophilicity, and controllable surface chemical properties, which can degrade organic pollutants through adsorption and catalysis. There are several problems in the preparation process. For example, high toxicity of chemical etching solution poses a certain threat to the environment and human body. It is very necessary for researching more environmentally friendly, safe, and friendly preparation methods. Moreover, the prepared substance may produce structural defects due to etching, which affects its performance. The stability of MXene is poor, and the functional groups on the surface are easily removed during calcination. Solving these problems is of benefit for further development of high-performance MXene-based nanomaterials.

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