

Preparation of MXene and its application and research progress in supercapacitors

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Abstract: As a new type of two-dimensional nanomaterial, two-dimensional transition metal carbon/nitride (MXene) has attracted much attention because of its high specific surface area, high conductivity and solvability. MXene is often used as a basic material to construct macroscopic composites. In recent years, it has been used to manufacture MXene structural-functional integrated fiber materials and mqd derivatives of MXene, which has a wide application prospect in multifunctional fibers, energy conversion and storage (ECS), sensors, catalysis and lubrication, electromagnetic shielding (EMI), supercapacitors (SCs) and so on. And has achieved some results. In this paper, the international research progress of MXene materials in recent years is reviewed, and its structure, properties and preparation methods are summarized. On this basis, its development in the field of energy storage (such as supercapacitors) is summarized, the shortcomings in this field are pointed out, and the future development trend is prospected.

Keywords: Two-dimensional material; MXene; Supercapacitor; Surface active group.

1. Introduction

The application of renewable energy has attracted more and more attention in the fields of portability and wearability, and in the case that fossil energy may be exhausted. However, sustainable renewable energy sources such as wind energy, hydropower energy and solar energy have the characteristics of fluctuation and discontinuity. At the same time, with the demand of the country, the development of new energy equipment such as electric vehicles is getting faster and faster, which requires the development of an energy storage device with small volume, large capacity, relatively large volume specific energy and high cycle stability. In recent years, supercapacitor materials with high energy density and high cycle stability have been widely used in the field of energy storage, which has become the key to solve this problem.

Supercapacitors (SCs) generally include electric double layer capacitors (EDLC) and Faraday Pseudo-Capacitors.[3][39]The purpose of high power density, stable cycle performance, wide working voltage range, low working temperature and environmental protection is finally achieved by using high surface area electrode materials and thin media. The most important step in the research and development of batteries is the selection of electrode materials. However, because the two-dimensional layered nanomaterial has achieved nanometer level (0-100 nm) to a certain extent, and its thickness is much smaller than the other two dimensions, it has large specific surface area, good mechanical

properties and many surface active sites. At present, graphene, oxygen/hydroxide and carbon/nitride (MXene) have been widely used in two-dimensional systems.[38]. The development trend of high capacity and high power density batteries is to use two-dimensional materials with high specific surface area as battery electrode materials.

In 2011, Professor Naguib of Drexel University and his team developed a new type of two-dimensional layered material-MX gene. MXene is a new two-dimensional (2D) carbonitride compound with high conductivity (about 8000S/cm).[4][5][25]And has high specific capacity due to oxidation-reduction reaction between transition metal on its surface and electrolyte ions, and excellent electromagnetic shielding ability.

In this paper, the structure, properties and preparation methods of MXene are introduced in detail. Then, the progress and shortcomings in the research field of supercapacitors are emphatically summarized, and the future development of MXene is analyzed and prospected.

2. Introduction to MXene

MXene is a layered structure similar to graphene, with high specific surface area and good conductivity, and it is a new two-dimensional material with great application prospects.[25]. MXene is a transition metal carbide, nitride or carbonitride with $M_{n+1}X_nT_x$ ($n=1,2,3,4$) as the basic structural unit. X represents c and n, where m represents a pre-transition metal element; Tx is a kind of

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surface reactive end-capping groups, such as hydroxyl, hydroxyl, fluorine, chlorine and so on.[2]. Generally, in the process of preparing MXene, the A atom of MAX phase is selectively etched out, because the metal bonding strength of M-A of MAX species is weaker than the covalent bond of M-X, and the stability of M-X is higher than that of M-A, so MXene can be obtained by etching M-A.. The obtained MXene is divided into m layers and x layers. The MAX phase consists of more than 70 ternary metal carbides, nitrides and carbonitrides, and the general molecular formula is $M_{n+1}AX_n$ ($n=1,2,3$), with A as the main group (such as Al, Ga, In, Ti, Si, Ge, Sn, Pb, etc.). Compared with M-A, M-A is more metallic.[2][37].

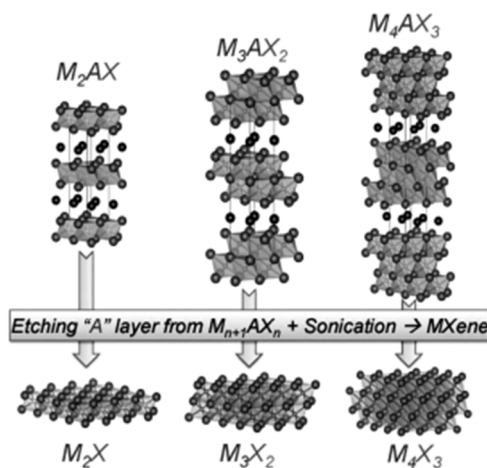


Fig. 1 structure of max phase and corresponding MXene[25]

At present, there are more than 60 kinds of MXene, more than 30 kinds have been synthesized, and more than 10 kinds can exist stably after calculation, such as Zr_2C , Ti_3N_2 , V_4C_3 and so on.[26]. MXene is a new type of ternary nitride. Up to now, only two materials, Ti_2N and TiN_3 , have been reported.[2]. The M-A bond of ternary nitride MXene is more stable than that of ternary carbide, and it is not easy to be etched.[2]. Although M in all the above MXENes is the same metal, there are still 26 MXENes with high stability by density functional theory (DFT) calculation.[26]. The system consists of $(TiV)_2C$, $(CrV)_3C_2$, $(CrV)_3C_2$, $(Cr_2V)_C_2$ and $(V_2Ti_2)C_3$.[2].

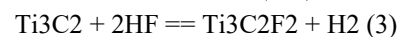
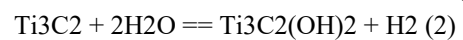
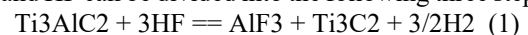
3. Preparation technology of MXene

Most synthesis methods of MXene are chemical etching, which makes use of the differences in chemical activity and stability of raw material elements or structural units to carry out selective stripping.[26]. Because the covalent bond of M-X is stronger than the metal bond of M-A, under the conditions of strong acid, molten salt and high temperature, the M-A bond can be broken, leaving only the M-X bond, thus preparing two-dimensional materials of MXene. The high-temperature heating method, although it can break the M-A bond, is generally not used because the twinning process will form a 3D structure similar to rock.[4][5]. Chemical etching is the mainstream preparation method. However, at present, ammonium

hydrogen fluoride, mixed solution of hydrochloric acid and lithium fluoride, hydrofluoric acid and other fluorides are mainly used in the market to prepare MXene thin films. These fluorides have strong electronic storage capacity in MXene thin films, and at the same time, the toxicity of fluoride itself will lead to safety problems in the preparation process. Therefore, it is urgent to develop a new method for preparing non-fluoride thin films. The following are several etching methods related to the preparation of MXene.

3.1 Etching based on HF and fluoride salt.

In 2011, Naguib et Al. etched Ti_3AlC_2 with HF to completely strip Al atoms in Ti_3AlC_2 , and obtained two-dimensional Ti_3C_2 nanosheets.[4][29]. The preparation of HF and HF can be divided into the following three steps:



Among these processes, the mechanism of etching and exfoliation processes is illustrated in fig. 3.

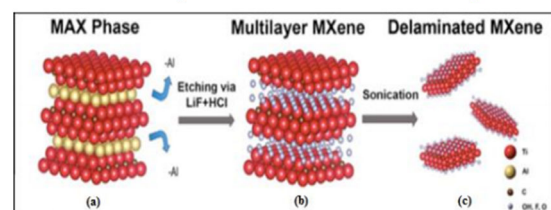


Fig. 2 Etching spalling mechanism diagram of Ti_3AlC_2 material (a) Ti_3AlC_2 structure diagram; (b) replacing Al atoms after acid etching with -OH groups; (c) hydrogen bonds between layers are broken under the action of ultrasonic waves, and the layers are separated.[29][32]

From the above equation, we can see that the surface of the two-dimensional nano-material MXene prepared by this method is rich in hydroxyl or fluorine groups, and the mechanical and thermodynamic stability of the material is improved by modifying its surface functional groups. At the same time, theoretically, the energy and width of the material can be adjusted by adjusting the surface functional groups of the material, so as to adjust the conductivity of the material.[26]. In addition, MXene materials with different properties can be prepared by adjusting the concentration, temperature and etching time of acidic solution. The experimental results show that the optimum preparation temperature of Ti_3C_2Tx MXene is around 55OC. During hydrofluoric acid etching, cations can play an insertion role, which increases the interlayer spacing of MXene films. In the preparation process, etching and stripping can be carried out simultaneously. Ghidui et al. etched with lithium fluoride and hydrochloric acid in addition to hydrofluoric acid, and finally obtained Ti_3C_2 similar to clay.[13][26]. Halim et al. grew Ti_3AlC_2 thin films by magnetron sputtering. However, the mixture of hydrogen fluoride and hydrogen chloride is essentially a strong acid turned into a weak acid, so hydrogen fluoride is finally at work.[12][26].

3.2 Other methods.

In addition to the above preparation methods, the latest research theory also uses chemical vapor deposition (CVD) to prepare nano-scale ultrafine structures. Xu et al. prepared large-area and high-quality two-dimensional AlphaMo₂C single crystal and some transition metal carbides such as W₂C and WC by chemical vapor deposition.[17][2]. Du et al. took the lead in putting forward a new idea of "topological transformation" in the world. Single-layer chalcogenides can be synthesized in large quantities by using non-Van der Waals systems (such as carbides, nitrides and carbon-nitrides (such as MAX phase)), which opens up a new idea for building MXene.[2][25].

4. Application of MXene in supercapacitors

As analyzed above, MXene materials have been widely used as electrode materials in supercapacitors because of their excellent conductivity and large specific surface area, and have a good development prospect. At present, the research direction of MXene for supercapacitors can be roughly summarized as the application of a single MXene electrode material in SCs. In view of the problem that MXene sheet structure is easy to accumulate, the MXene material is modified or compounded with other materials to make composite thin film materials. Of course, the application of MXene in hybrid supercapacitors is also developing rapidly.

4.1 Pure MXene electrode material.

Lukatskaya et al. discovered for the first time that cations (K⁺, Na⁺, Mg²⁺, etc.) in Ti₃C₂T_x MXene will be self-intercalated, but the specific mechanism is not clear.[36]. Lukatskaya et al. used dimethyl sulfoxide (DMSO) to separate Ti₃C₂, then used ultrasonic wave to form a thinner layer, then centrifuged, filtered and dried it, and finally made a "Ti₃C: paper" electrode with a thickness of 2-20 microns. In KOH solution, under the condition of 2 mV/s, the capacity of this unbonded electrode can reach 340 F/cm³, and it will not produce any loss during 10000 times of charge and discharge.[14][26]. Ghidui et al. etched Ti₃AlC₂ with lithium fluoride and hydrochloric acid to obtain slurry Ti₃C₂, and then rolled the slurry Ti₃C₂ into a thin sheet with a roller, thereby directly making the slurry Ti₃C₂ into an electrode. The electrode has a volume specific capacitance of 900 mV/cm³ at a scanning speed of 2 mV/sec in a sulfuric acid solution of 2 mV/sec, and a volume specific capacitance of 730 mV/cm³ at a scanning speed of 100 mV/sec. Ghidui et al. determined the electrochemical properties of the prepared self-supporting Ti₃C₂ electrode material.[13][2]. As can be seen in figure 6. At 2 mV/s, the material has a specific capacity of 900 F/cm³, good rate characteristics and a cycle life of 10,000 times.

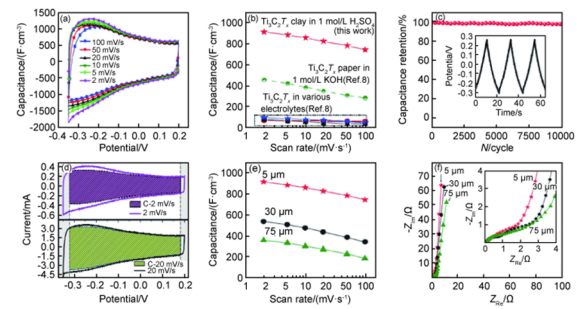


Fig. 3 electrochemical characteristics of ti3c2tx material (a) cyclic voltammety (CV) curves of ti3c2tx at various scanning speeds; (b) The rate characteristics of Ti₃C₂T_x in various electrolytes; (c) The capacitance hypertension ratio of Ti₃C₂T_x during constant current charging/discharging is 10 A/g; (d) CV curves of Ti₃C₂T_x at scanning speeds of 2 mV/s and 20 mV/s; (e) Capacitor maintenance coefficient of Ti₃C₂T_x with different electrode thicknesses; (f) Impedance curves of Ti₃C₂T_x on electrodes with different thicknesses.[2]

MXene is a kind of supercapacitor material with great development potential, but its problems such as easy agglomeration, accumulation and oxidation seriously restrict its application in batteries. In addition, the surface functional groups of MXene will also affect the conductivity and cycle stability of the material.[35]. Based on this, this project intends to carry out related research from several aspects such as surface modification, structural regulation, ion/molecule insertion/doping, and antioxidant modification.

4.1.1 Structural control.

At present, the structural regulation of MXene is mainly realized by core-shell and porous methods. Xu et al. used the current collector Ni as the carrier, and loaded MXene nano-sheets on its surface to prepare a new type of wearable flexible fiber substrate. The substrate does not need any binder, and its specific capacity reaches 140 F/g in 1 mol/L KOH solution.[17][25]. Li et al. found that three-dimensional Ti₃C₂ aerogels have high specific surface area (176.3m²/g) and special pore structure. The electrode was tested in 1 mol/L KOH electrolyte with a scanning speed of 2 mV/s, and a high surface capacity of 1012.5 mF/cm² was obtained.[16][25]. The above research results show that by adjusting the micro-morphology of MXene, the lamellar rearrangement of MXene can be effectively reduced, the specific surface area can be increased, the active sites can be increased, the ion transport channel can be shortened, and the ion intercalation/deintercalation can be accelerated, thus greatly improving the electrochemical performance of MXene, which is an important means to improve the rate performance of MXene.[25]

4.1.2 Intercalation Modification and Doping Modification.

Insertion modification of MXene usually does not change its surface functional groups, but only increases its interlayer distance; By doping modification, the

functional groups on the surface of the material can be changed. Both methods can improve the related performance of MXene. By introducing cations, organic compounds, etc. between the layers of MXene, the interlayer spacing of MXene is increased, the active sites of MXene are increased, and its electrochemical, adsorption, mechanical and other properties are improved. Li et al. introduced Na⁺ ions into MXene (Si-Ti₃C₂Tx), which increased the specific surface area of MXene, increased the surface active sites of MXene, and formed hydrogen bonds with ciprofloxacin (CPX), which was electrocatalytic decomposed into CO₂ and H₂O.[31]. The reaction process is shown in fig. 7. In the second cycle, the removal rate of chlorinated hydrocarbons can reach ninety-seven percent.

Doping MXene can effectively increase the interlayer distance and lay a foundation for its application in the fields of batteries and energy storage. However, the electrochemical performance of fluorine-terminated MXene prepared by existing etching methods in supercapacitors is not ideal. Therefore, in addition to intercalation modification, MXene also needs doping modification.

By introducing carbon, nitrogen, sulfur and other elements into MXene, and introducing chemical bonds into MXene, its conductivity is enhanced and its surface wettability is improved, thus increasing its reactive sites. At the same time, the collaborative optimization of MXene is realized by post-heat treatment; By doping transition metal elements in MXene, MXene has good catalytic performance for hydrogen evolution. As shown in fig. 8, LU et al. have fully studied the nitrogen doping mechanism of MXene.[25][31]

degradation of MXene, it is often necessary to conduct waterproof and insulation treatment. Taking MXene as the research object, MXene was treated with alkali by physical and chemical methods to improve the order of MXene crystals and reduce the content of functional groups such as hydroxyl and fluorine, and the MXene materials with high conductivity, high hydrophobicity and high conductivity were prepared. Chemical method can effectively isolate MXene from water by means of polyanion adsorption and polymer coating.[31]

4.2 MXene composite film material.

MXene is a new material which combines the advantages of many materials and has great potential.

4.2.1 And carbon composite

Graphene, carbon nanotubes (CNT), carbon nanofibers, carbon aerogels and other carbon materials are excellent conductive materials. They have excellent conductivity and are excellent conductive materials.[25]. Zhao et al. obtained the sandwich-shaped Ti₃C₂Tx/ carbon nanotube (CNT) composite electrode material by alternating suction filtration. It is in 1 mol/L MgSO₄ aqueous electrolyte, at a scanning speed of 2 mv/s.[26] The volume specific capacitance is 390 f/cm³, and it is 280 F/cm³ at a scanning speed of 200 mv/s.[26]. In addition, Linetal's previous work also found that sandwich composite electrode materials have better electrochemical properties than random hybrid composite structures.

4.2.2 Compounding with metal oxide.

Transition metal oxide (TMO) is superior to carbon in theoretical capacity and safety, but it will have large volume expansion during charging and discharging, and its conductivity is low.[34]. However, if it is compounded with MXene, the performance of the two can be supplemented, thus improving the comprehensive properties of the material.[25]. Jiang loaded MnO₂ on Ti₃C₂Tx by chemical deposition, and obtained MnO₂/Ti₃C₂Tx composites.[25] The composite material has the highest specific capacity of 130.5 F/g at 0.2 A/g, which is equivalent to twice the same current density.[25]. Peng et al. used the strong electrostatic attraction between WO₃ nanorods (WNR) and Ti₃C₂Tx (MXene) to compound WO₃/MXen, so that it could obtain more than 5,000 cycles in the system of 1A/g current density and 0.5 mol/LH₂SO₄, and its specific capacity reached 297 f/g. Through the above research, we found that the addition of TMOs can greatly improve its specific capacity, and at the same time, the advantages of two-dimensional layered MXene and TMOs complement each other, which can ensure the volume stability of TMOs.[25]

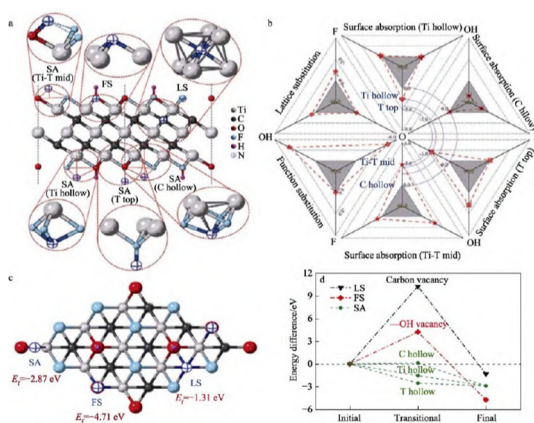


Fig. 4 simulation of nitrogen dopant in ti3c2: atomic structure of Ti₃C₂Tx with all nitrogen dopants (a); Calculation of generating capacity (b) (shaded with positive and negative values); It has a nitrogen atom (top view) (c) in the most favorable position of the energy of Ti₃C₂ supermonomer; Calculation of Transition State Energy Levels (D)[31]

4.1.3 Anti-oxidation modification.

In the medium of water and air, MXene is easy to be oxidized by Ti to produce TiO₂, which diffuses from outside to inside, resulting in the destruction of MXene structure. Therefore, in order to prevent the oxidative

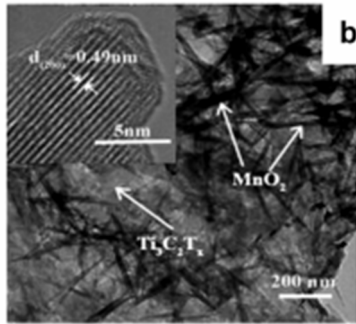


Fig. 5 TEM image of nano MnO₂/Ti₃C₂T_x[25][33]

4.2.3 Compounding with polymer.

The introduction of polymers (such as polyaniline, polydimethyl acrylic acid, etc.) can effectively increase the interlayer spacing of MXene. As a carrier, it can effectively inhibit the stacking of layers, expose more surface active sites, shorten the ion diffusion channel of electrolyte, accelerate charge transfer, accelerate Ferrari reaction, and enhance its mechanical properties and stability.[25]. For example, Ling et al. used MXene with atomic layer thickness as the building block, and realized the controllable preparation of MXene/polymer composite films for the first time by self-assembly chemistry.[26]. The Ti₃C₂T_x/PDA composite electrode prepared by Wang has a specific surface area capacity of 75 mF/cm², and it can still maintain a specific surface area of 95.5% after 10,000 cycles.[25].

5. Conclusion and prospect

In this paper, firstly, the structure and properties of MXene materials are introduced, and the existing preparation methods are summarized in detail. At present, most of the preparation of MXene adopts chemical etching method, and fluorine-containing compounds account for the majority. However, there is a certain danger, and more efficient and safer etching methods in the future need to be further studied by scholars. Secondly, the applications of various MXene in supercapacitors are reviewed. In the preparation process of monolayer two-dimensional nano-material MXene, there are usually defects such as easy accumulation, so it is necessary to improve its related properties by doping and intercalation. In addition, in order to solve the problem that Ti atoms on the surface of MXene are easy to be oxidized, the oxidation resistance of MXene is also improved from two aspects: physical alkaline annealing and chemical coating. Based on the comprehensive advantages of each material, composite MXene thin film material is the thriving development direction of supercapacitor pseudocapacitor in the future. However, the research of MXene still faces the following problems: (1) More than 150 kinds of MAX phases are known, but only more than 30 kinds of MXene have been developed, and most of them are Ti₃C₂T_x limited by element A. The preparation and research of other kinds of

MXene need further breakthrough. (2) The surface active groups of 2)MXene materials have great influence on the properties and electrochemical properties of the materials. However, after the surface functional groups are completely removed, the characteristics of this material are only theoretical speculation, and its actual characteristics need further study. (3) At present, the synthesis of MXene mostly needs to use some corrosive drugs, and its yield is low, which is easily disturbed by external conditions. How to realize efficient and safe large-scale production and industrialization of MXene is an urgent problem to be solved. (4) At present, the application of MXene material library in SCs is still in the primary stage, and it is urgent to develop the preparation technology, structural design and functional method of Ti₃C₂T_x electrode with high cost performance and high yield.[22].

However, based on the excellent performance of MXene materials and the continuous exploration of energy storage in recent years, the research of MXene materials in super capacitor (SCs) still has a very broad application prospect, and the country is also vigorously promoting the research and development of sustainable green pollution-free energy.

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