Structure and Fabrication of MXene-Based Heterostructures

Subjects: Materials Science, Composites

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MXene, as an emerging family of 2D nanomaterials, exhibits excellent electrochemical, electronic, optical, and mechanical properties. MXene-based heterostructures have already been demonstrated in applications such as supercapacitors, sensors, batteries, and photocatalysts. Nowadays, increasing research attention is attracted onto MXene-based heterostructures, while there is less effort spent to summarize the current research status.

two-dimensional materials MXene heterostructures

1. Introduction

Since the discovery of graphene, a growing family of two-dimensional materials has been widely studied by researchers due to their extraordinary properties in optical, electrical, thermal, and mechanical aspects, as well as the wide application potential [1][2][3][4][5][6][7][8][9][10]. 2D layered materials mainly include the graphene-like family [11][12][13], 2D transition metal chalcogenides [14][15][16], the 2D oxide family [17][18], and layered materials with other structures [19][20]. In 2011, Gogotsi et al. [21] discovered a type of highly conductive 2D nitride and carbide, which were called MXenes. MXenes, as one of the major subfamilies of MAX phase materials, are stripped by etching and ultrasonic treatment to generate 2D transition metal carbides, carbonitrides, or nitride layers [22]. During the preparation of MXenes, the surface is often rich with functional groups (-O, -OH, and -F), which can bring different properties to MXenes. As a new family of 2D nanomaterials, MXene shows excellent electrochemical, electronic, optical, and mechanical properties [23][24] due to its graphene-like structure and mixed covalent/metallic/ionic character, hydrophilicity, and unique metal conductivity. Therefore, MXene materials have attracted wide attention in the world and have developed rapidly in the past decade [25][26][27]. In general, MXene is prepared by selectively etching a layer in the MAX phase using hydrofluoric acid (HF). In order to improve the quality of MXene, simplify the experimental steps, and reduce the toxicity of the reagents, various preparation methods, such as thermal reduction, UV-induced etching, and alkali treatment, have emerged [28][29][30][31]. Currently, the family of MXene materials continues to develop and an increasing expansion of the applications in energy storage batteries, sensors, catalysts, and other fields has been witnessed [32][33][34][35].

To date, although MXene-based materials have been demonstrated to be widely used in different areas, there are still some challenges [36]. For example, the application of MXenes in fabricating flexible energy storage devices is limited due to the difficulty in achieving a good balance between mechanical and electrochemical properties [37]. The serious stacking phenomenon of MXenes impedes the diffusion of carriers in the vertical direction, lowering the specific capacity of MXenes under a high current density [38]. The poor oxidation resistance of MXenes in the

application of the water-based flexible battery seriously affects its conductivity and cycling stability [39]. To overcome these shortcomings, different 2D nanomaterial structures are suggested to be spliced or stacked on top of each other, and as a result, many novel physical properties have been discovered.

In 2013, Geim and Grigoreva proposed for the first time a multilayer heterostructure, namely, van der Waals (vdW) heterostructure, which is formulated by using only the vertical vdW force between different layers to connect each 2D material and allow them to coexist in a stable way [40]. The discovery of 2D materials has breathed new life into the construction of heterogeneous structures. Traditional heterostructures are constructed by either doping homogenous materials, such as PN junctions of semiconductor silicon, or by epitaxial growth on lattice-matched substrate materials [41]. In this way, the material is severely limited, and serious dislocations and defects are easily formed at the interface, thus affecting the quality of the heterostructures. However, the 2D layered material has no dangling bonds on its surface, and different 2D atomic layers can be stacked together in selected order by means of weak van der Waals forces to form artificial heterostructures with atomically flat interfaces. Compared with traditional semiconductor heterostructures, 2D vdW heterostructures are not limited by lattice matching and material types, and can theoretically be stacked in any form (different types, angles, sequences, layers, etc.) like stacking wood [42][43][44]. The “arbitrary combination” of the van der Waals heterostructure allows these individual materials to be combined together while still maintaining the ultra-thin thickness [45]. Therefore, the emergence of vdW heterostructures offers a new structural platform for exploring new electronic and optoelectronic devices.

2. Structure of MXene-Based Heterostructures

The family of MXene materials has a great variety and excellent electrochemical, optical, and mechanical properties. However, the realization of the applications of MXene materials is often limited by some inherent drawbacks. To overcome these issues, many novel heterostructures have been constructed based on the special optical and electrical properties of an individual 2D crystal, generating synergetic photoelectric properties, and therefore, wide attention has been received from researchers on this topic [46][47][48][49]. Generally, 2D heterostructures can be divided into two types: vertical heterostructures and lateral heterostructures. Two kinds of MXene-based heterostructures are described as following.

2.1. Vertical Heterostructures

Vertical MXene-based heterostructures are synthesized by stacking independent monolayer 2D materials layer-by-layer through direct growth or the mechanical transfer method, which provides the heterostructure with a strong intralayer covalent bond and relatively weak interlayer vdW interaction, generating a system not limited by the lattice matching degree of the materials [50][51]. Due to the absence of suspended bonds and the weak vdW forces between the layered structures, the vertical MXene-based heterostructure can be easily constructed by stacking different materials. For instance, Yi et al. [52] fabricated MXene-GaN van der Waals heterostructures for photodetectors and LEDs. Dai et al. [53] designed vertical 2D $Ti_3C_2T_X$ MXene/V_2O_5 heterostructures by freeze-drying for the application of membrane electrodes. Vertical channels were formed in the heterostructures to promote rapid electron and ion transport throughout the electrode. Moreover, Yuan et al. [54] formed the BN/$Ti_3C_2T_x$

van der Waals heterostructure for lithium-ion batteries by high-energy ball milling, which played a series of roles in increasing the layer spacing, reducing the size of nanosheets, and maintaining the structural integrity. The experimental results showed that the heterostructure had excellent rate performance and long-term cycle stability.

Although vertical heterostructures have become one of the hottest research fields in recent years, there are two major problems limiting the applications of vertical heterostructures in various devices: (1) foreign pollutants are easily introduced during the preparation process; (2) the stacking direction is not controllable. The construction of lateral heterostructures can overcome these limitations.

2.2. Lateral Heterostructures

Lateral MXene-based heterostructures are generally prepared by seamlessly integrating 2D materials into one plane through direct growth, which can accurately control the direction and quality of the interface inside the 2D lateral heterostructures [55]. The 2D lateral heterostructure is connected by covalent bonds, which provide excellent intralaminar stability and improve the epitaxial quality.

Compared with vertical MXene-based heterostructures, the construction of 2D lateral heterostructures is more difficult in practice, and researchers cannot randomly choose the initial 2D materials to construct any heterostructure as researchers desire. Although the 2D lateral heterostructures are difficult to synthesize, the advantages of covalent bonding in the atomic plane and easy plane integration arouse people's great interest. Zeng et al. [56] prepared 2D lateral WC-graphene (WC-G) heterostructures based on a versatile approach, which demonstrated excellent chemical stability and reactivity, as seen in Figure 3. Currently, there are limited studies on 2D lateral MXene heterostructures, but due to the special properties and significant application potential, more research efforts on this topic can be expected in the coming years.

3. Fabrication of MXene-Based Heterostructures

Two-dimensional heterostructures can be prepared by deterministic transfer methods, CVD epitaxial growth methods, and self-assembly [57]. The various synthesis approaches of 2D heterostructures directly affect their physical and chemical properties, thus affecting their application fields [58]. Generally, the deterministic transfer method and CVD epitaxial growth method are most often used to construct 2D heterostructures [59]. PDMS, PPC, and PMMA are commonly used in deterministic transfer methods. As for the CVD epitaxial growth method, it is suitable for both vertical heterostructures and lateral heterostructures [60]. By adjusting the temperature, composition, velocity, and direction of the flow, different types of heterostructures can be prepared. Currently, three major preparing methods have been proposed for constructing MXene-based heterostructures, namely, the hydrothermal method [61], electrostatic self-assembly method [62], and chemical vapor deposition [63].

3.1. Hydrothermal Method

The hydrothermal method [64] refers to the method of preparing materials by dissolving and recrystallizing powders with water as the solvent in a sealed pressure vessel. The hydrothermal method has the advantages of relatively mild operating conditions, high crystallinity of products, environmental friendliness, and good dispersity. In addition, the cost of hydrothermal synthesis is lower in terms of instrumentation, energy, and material precursors compared to gas and solid-phase methods. MXene is dispersed in the liquid phase with another material to obtain a heterostructure under hydrothermal conditions [65]. Under the conditions of high temperature and high pressure, this method is able to improve the activity and manipulate the functional groups at the surface of MXene.

In practical applications, MXene-based heterostructures with rich functions are usually required. A hydrothermal environment can control the functional groups on the surface of MXene-based heterostructures, so as to improve their activity. Qiao et al. [66] designed and fabricated Ti_3C_2/CdS heterostructures for use as highly efficient co-catalysts by a hydrothermal strategy. The characterization results showed that the Ti_3C_2/CdS heterostructure was spontaneously decorated with a large number of hydrophilic functional groups (-OH and -O). In addition, the CdS/Ti_3C_2 heterostructure with a cauliflower structure showed ultra-high visible light photocatalytic activity and has great application potential in the field of photocatalysis. Wang et al. [67] constructed a 1T-MoS_2/Ti_3C_2 MXene heterostructure for a supercapacitor via the hydrothermal method and studied the electrochemical storage mechanism of the heterostructure. The experimental results showed that the supercapacitor based on 1T-MoS_2/Ti_3C_2 MXene heterostructure had a high capacitance ratio and excellent rate performance, and maintained an excellent cycling stability after tens of thousands of cycles because of the synergistic effect between MoS_2 and MXene.

Under the hydrothermal environment, the functional groups on the surface of MXenes are improved. Due to the electrostatic interaction and other effects, the second phase dispersed in the liquid phase can grow in situ on the surface of MXene, and the two kinds of materials are in close contact to form a heterostructure, which has strong interface interaction, excellent electron transfer ability, and can provide a large interface contact area at the interface. Cao et al. [68] successfully prepared a novel 2D/2D Ti_3C_2/Bi_2WO_6 heterostructure through a hydrothermal strategy. The synthesized Ti_3C_2/Bi_2WO_6 heterostructure showed an excellent ability forphotocatalytic reduction of CO_2, which was mainly due to the improvement of the specific surface area and pore structure of the synthesized heterostructure, as well as the short charge-transfer distance and large interface contact area.

3.2. Electrostatic Self-Assembly Method

Electrostatic self-assembly [69] uses the electrostatic interaction of two nanomaterials with opposite charges in an aqueous solution for self-assembly, so as to form nanoscale ultra-thin polymer materials. Among many self-assembly methods, electrostatic self-assembly has a wide range of applications, owing to its simplicity and controllable thickness [70]. As a common method for constructing two-dimensional heterostructures, a variety of MXene-based heterostructures have been constructed via electrostatic self-assembly and have been applied in many fields [64]. However, electrostatic self-assembly is less stable due to the electrostatic interaction and hydrogen bonding.

The layer-by-layer stacking of the layered structure can re-stack the nanosheets with different functional properties into heterogeneous structures, which undoubtedly makes full use of the characteristics of each heterogeneous component and presents superior electrochemical performance coordinated with the mechanical structure. In 2019, Liu et al. [71] reported the heterostructure synthesis of MXenes@C for magnesium-ion storage via electrostatic interactions between negatively charged 2D MXene nanosheets and positively charged 3D carbon nanospheres, which could effectively prevent the re-stacking of MXene nanosheets, so as to promote the transmission of electrolytes and shorten the ion diffusion path. Tests revealed that the magnesium-ion storage battery exhibited high reversible specific capacity, outstanding rate capacity, and excellent cycle stability. Moreover, Wen et al. [72] prepared three-dimensional hierarchical nMOF-867/$Ti_3C_2T_x$ heterostructures for lithium–sulfur batteries via electrostatic self-assembly. The lithium−sulfur battery based on the nMOF-867/$Ti_3C_2T_x$ heterostructures had strong conductivity and could reduce the volume expansion during cycling. This work provided the inspiration for preparing high-performance lithium-sulfur batteries based on MXene-based heterostructures. Electrostatic self-assembly uses MXenes with functional groups on the surface and materials with opposite surface charges to construct heterostructures by electrostatic attraction. As a simple, easily operated method, it can effectively open the middle layer and prevent the re-stacking of MXene nanosheets, thus providing an effective charge-transfer channel and shortening the ion diffusion path.

In recent years, due to its simplicity, electrostatic self-assembly has also been adopted to synthesize photocatalysts with high photocatalytic activity. Hu et al. [73] synthesized 2D/2D Ti_3C_2/porous g-C_3N_4 (TC/PCN) photocatalysts through a facile electrostatic self-assembly method by integrating the merits of g-C_3N_4 and Ti_3C_2. The synthesized heterostructures exhibited exceptional performance compared with pure PCN and the observed activity had no significant decrease after four cyclic experiments. In another experiment, boron-doped graphite carbonitride (g-C_3N_4) and few-layer Ti_3C_2 MXene were combined to construct heterostructures by electrostatic self-assembly for enhanced photocatalytic reduction of CO_2 [74]. The optimized composite structure had excellent photocatalytic activity and stability. The yields of CO and CH_4 were 3.2 times and 8.9 times higher than that of a bare g-C_3N_4, respectively. Zhuang et al. [75] successfully prepared TiO_2/Ti_3C_2 heterostructures by the electrostatic self-assembly technique. The maximum hydrogen production rate was 2.8 times larger than that of pure TiO_2 nanofibers, and the nanocomposite maintained a good hydrogen production cycle capacity, owing to the heterogeneous interface between TiO_2 and Ti_3C_2 nanosheets.

3.3. Chemical Vapor Deposition (CVD)

Chemical vapor deposition mainly uses one or several gas-phase compounds or elements containing film elements to generate film on the substrate surface by chemical reaction. In the CVD process, parameters such as pressure, temperature, gas flow rate, and catalyst type can be adjusted to achieve fine control of the size, layer number, morphology, and quality of 2D lattices. Chemical vapor deposition (CVD) has been widely used in the preparation of heterostructures owing to its low cost, extensibility, and full controllability. The synthesis of vertical and lateral heterostructures from different 2D materials can result in many excellent physical properties and has been applied in the fields of batteries, catalysts, and sensors, which largely depends on the arrangement, quality, and interface of the combined 2D layered crystals.

Based on a one-step CVD method, Zeng et al. [56] reported the embedding of a 2D WC crystal into graphene to fabricate 2D WC-graphene lateral heterostructures on metal gallium (Ga) by integrating a liquid metal-based co-segregation strategy. The as-synthesized heterostructure exhibited excellent catalytic potential, which provided a good reference for fabricating other high-quality in-plane 2D transition metal carbide-based structures. In general, the heterostructures of graphene and other 2D materials are fabricated by stacking, which leads to random arrangement, weak interface interactions, and inevitable interface pollutants during the preparation process. Xu et al. [76] constructed high-quality graphene/α-Mo_2C crystal vertical heterostructures with uniformly well-aligned lattice orientation and strong interface coupling by a two-step CVD method. During the two-step CVD, the researchers maintained a constant atmosphere to avoid defects, thus forming high-quality heterostructures.

At present, chemical vapor deposition (CVD) has been widely used to prepare vertical and lateral heterostructures. Compared with the stacking method, the MXene-based heterostructures prepared by CVD can obtain a very clean interface. In addition, high-quality MXene-based heterostructures can be synthesized by carefully controlling the preparation parameters. What's more, the synthesized heterostructures have a strong interface interaction.

Among the three common synthesis approaches of MXene-based heterostructures, the hydrothermal method has the advantages of relatively mild operating conditions, environmental friendliness, good dispersion, and low cost. At the same time, the activity of heterostructures can be improved and the functional groups on the surface of MXenes can be manipulated in the hydrothermal environment. Electrostatic self-assembly is widely used because of its simple preparing procedures and controllable thickness. However, the surface of the constituent materials needs to be pretreated. In the CVD process, the parameters such as pressure, temperature, gas flow rate, and catalyst type can be adjusted to realize the fine control of the size, layer number, morphology, and quality of MXene-based heterostructures, and CVD is applicable to synthesize both vertical and lateral heterostructures. The high-quality heterostructures synthesized by the aforementioned three methods are able to provide a large interface contact area and a short charge-transfer distance at the interface, as well as prevent the stacking of MXene layers, generating an improved interfacial carrier transport.

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