Chemical preparation methods of MXenes materials and exploration and application of their chemical mechanisms

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Abstract. As a new generation of 2D materials, MXenes have demonstrated various application prospects in fields such as energy storage, electromagnetic interference shielding, sensing devices, medicine, seawater desalination, and environmental restoration due to their rich functional groups, adjustable interlayer spacing structure, and high electrical conductivity. In recent years, this has led to widespread exploration and research from the outside world. This article mainly focuses on the latest developments in the production of MXenes by Chemical Vapor Deposition (CVD) method, and briefly discusses the pseudocapacitive effects and photovoltaic effects of MXenes materials within the energy storage domain, highlighting their outstanding performance in potassium-ion supercapacitors and perovskite solar cells in the photovoltaic field.

Keywords: Chemical Vapor Deposition (CVD) method, MXenes materials, potassium-ion supercapacitors, perovskite solar cells

1. Introduction

MXenes materials are a type of organic two-dimensional transition metal carbides or nitrides, which exhibit great scalability by forming different chemical bonds, such as covalent bonds, metal bonds, ionic bonds, etc., through the metal and non-metal atoms they contain. For example, MXenes materials have great advantages in electrode materials for supercapacitors due to their long-lasting electrochemical stability, large specific surface area, and high conductivity. They have great commercial value and research application prospects. MAX phase is a layered nitride or carbide with hexagonal symmetry. Due to its combination of high conductivity properties of metals, staggered covalent layer stacking structure, and ceramic resistance to high temperature, acid, and alkali corrosion, it has become a substitute for titanium alloy materials and shows great competitive potential in the new generation of materials used in aerospace, nuclear industry, gas igniters, and other fields. MAX phase belongs to a vast family of solid materials, consisting of approximately 130 different materials. MXenes materials originate from a branch of MAX phase, and nearly 30 materials have been synthesized so far.

2. Overview of Chemical Vapor Deposition Method and MXenes

2.1. Chemical Vapor Deposition Method

Chemical Vapor Deposition (CVD) is a vapor-phase growth method for material preparation. It involves introducing one or several gases containing compounds or elemental gases that constitute the elements of the film into a reaction chamber containing a substrate. Solid films, heterostructures, and complete devices are deposited on the substrate surface through spatial gas phase chemical reactions [1-3]. The CVD technique is most extensively involved in the semiconductor industry for chip manufacturing, ranging from insulating materials to metals or alloy materials. The benefit of the CVD technique lies in its capacity to produce thin films of various materials and control the film thickness and interface matching degree by controlling the gas flow, achieving micro-assembly of multilayer films. Moreover, it has a rapid film formation rate, reaching several micrometers to several hundred micrometers per minute, achieving uniform composition and mass production while balancing efficiency and cost, which is unattainable by other thin-film technologies like Liquid Phase Epitaxy (LPE) or Molecular Beam Epitaxy (MBE). The CVD method is implemented through heating, plasma enhancement, photo-assistance, or under low-pressure conditions to facilitate the participation of gaseous substances in chemical reactions.

2.2. MXenes Material

MAX phases are a class of ternary layered compounds, universally characterized by the chemical formula $M_{n+1}AX_n$, where M is an early transition metal, A is a group III or IV element, and X is either carbon (C) or nitrogen (N), etc. Transition metal carbides or nitrides, such as Ti_3AlC_2, are typical examples of MAX phases. The successful exfoliation of Ti_3AlC_2 from MAX phases by professors Yury Gogotsi and Michel W. Barsoum has sparked significant interest in this new type of 2D material, which is known for its high electrical conductivity and flexible tunability. Over the past decade, researchers have discovered that MAX phases, represented by MoS_2, possess rich direct bandgap properties, promising broad applications in the field of photoelectrochemistry. However, this potential is greatly limited as the direct bandgap can only be achieved in monolayer structures and they are extremely unstable chemically in air.

In the field of electrochemical applications, for example, graphene, despite its near-superconductive electrical conductivity (with electron mobility rates around $10^4–10^5$ cm² V^{-1} s^{-1} at room temperature[4]), faces a critical issue—it is a "zero-bandgap" semiconductor, meaning that electrical currents flow through it incessantly at high speeds. Efforts to improve its performance through quantum confinement, chemical modification, or doping have been explored[5-7], but the cost of introducing a bandgap far exceeds the commercial operational benefits, which iswhy graphene has not been commercialized in the semiconductor industry. Similar issues exist with other carbon nanomaterials. Meanwhile, the widely commercialized semiconductor materials also face numerous problems. For instance, first-generation Si materials have low electron mobility and conversion efficiency, suitable only for low-speed integrated circuits. The second-generation semiconductor materials like InGaPAs/GaAs, though they have better electron mobility, suffer from heavy metal ion pollution and resource scarcity. At this juncture, the MXenes material from the MAX family emerges, solving these issues. As a new type of environmentally friendly material composed of non-toxic and abundant elements like Ti, C, and N, whose degradation products are CO_2 and N_2, MXenes cause minimal environmental pollution. MXenes, based on the MAX phase with a structure similar to graphene, not only possess an adjustable direct bandgap unlike graphene but also offer advantages over silicon in terms of strength and weight, allowing for precise control of electron flow. Surface defects and strain capabilities provide significant advantages in the semiconductor chip industry. Unlike the single-layer bandgap structure of MAX phases, MXenes can be stacked in multiple layers. By leveraging a rich combination of chemical elements and surface functional groups for control, MXenes maintain stable chemical properties. Their unique layered structure, huge specific surface area, and high electrical conductivity, among other advantages, endow MXenes materials with

exceptional electrochemical performance, offering broad application prospects and development value in energy storage, electrocatalysis, sensing, and flexible wearable devices.

3. MXenes by Chemical Vapor Deposition

3.1. Traditional Methods for Preparing MXenes

There are two main traditional methods for preparing MXenes phases. The first method involves etching with fluorine-containing solutions: preparation using fluorine ion-containing acidic solutions and fluorine ion-containing salt solutions. However, this method poses significant hazards to human health and the environment. Inert F functional groups can reduce material performance and corrode the transition metal elements within the MXenes structure, and the by-products are not easily decomposed. The second method is etching with Lewis acidic molten salts [8]. Transition metal halides (e.g., $ZnCl_2$) act as Lewis acids in their molten state. These molten salts can generate strong electron-accepting ligands, which can thermodynamically react with the A elements in MAX phases for selective etching. Additionally, extensive research and discussions have been conducted on alkaline solution chemical etching and electrochemical etching in the preparation of MXenes materials, which will not be elaborated further here.

3.2. Preparing MXenes Materials by CVD Method

The precursor is key to the synthesis of MXenes materials. Traditional MXenes precursors involve high-temperature synthesis using raw materials such as ores, coal, and coke, or etching the A layers with hydrofluoric acid solutions or Lewis acidic molten salts. However, these methods produce a significant amount of waste, limiting the practicality of MXenes and contradicting the current pursuit of low-carbon, environmentally friendly goals.

Recently, Professor Dmitri V. Talapin from the University of Chicago discovered that cheap precursor materials from the MXenes family, such as metals and their halides and nitrides, can bypass the intermediate MAX phases and directly synthesize carpet-like MXenes using the CVD method [9]. MXenes (referred to as DS—MXenes) can be synthesized directly by high-temperature vaporization of a metal phase and various carbon sources (graphite, methane, etc.) or nitrogen sources. The surface groups can be removed by reduction or substitution methods. Moreover, the vertically aligned carpet-like structure of MXenes synthesized by this method exposes highly catalytically active edge sites. Chemical or electrochemical transformations can be applied by inserting different metal ions. For traditional MXenes synthesis methods, it is challenging to directly grow vertical MXenes flakes on substrates. Furthermore, based on the most attractive pseudocapacitance effect of MXenes materials, the author also compared the electrochemical characteristics of MXenes materials etched with molten Lewis acid salts (referred to as MS—MXenes) and DS—MXenes. It was found that DS—MXenes exhibited superior storage capacity to MS—MXenes while maintaining highly consistent electrochemical curves, including CV characteristic curves, under different voltages.
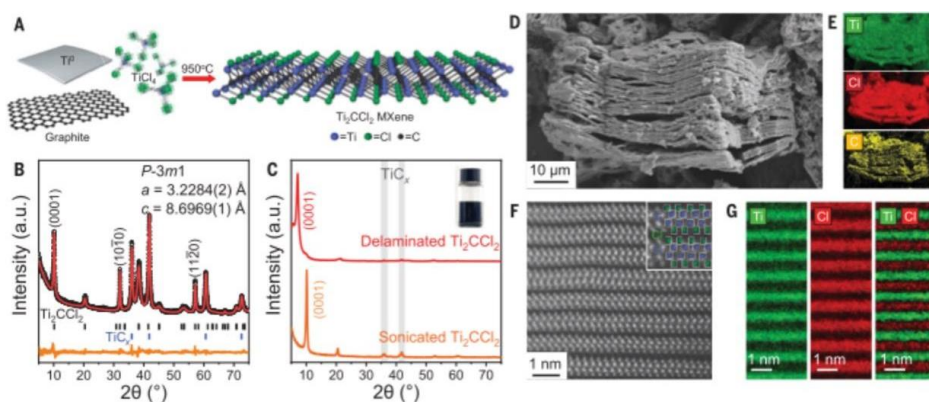

Figure 1. Several chemical synthesis processes and characteristics image of DS—MXenes [9].
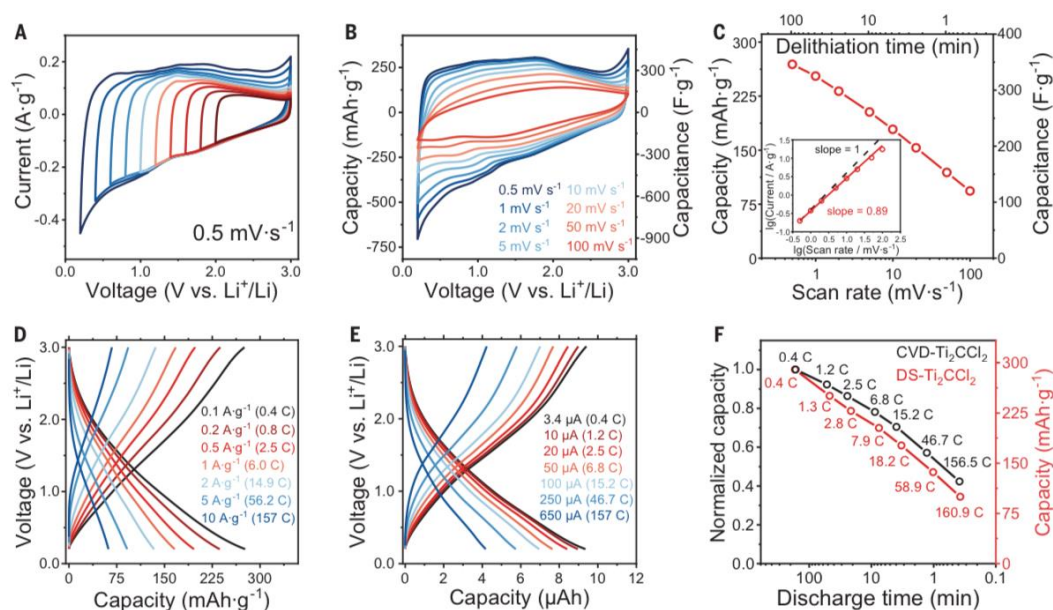
Figure 2. Electrochemical Energy Storage Performance Parameters of DS—MXenes [9].

4. Applications of MXenes

4.1. *MXenes in the Field of Energy Storage for Supercapacitors*

4.1.1. Potassium-Ion Supercapacitors. Faradaic pseudocapacitance is a type of supercapacitor that lies between traditional capacitors and batteries. Unlike conventional batteries, which convert electrical energy into chemical energy for storage through charging and discharging, pseudocapacitors store charge in two ways: one is through charge storage on the double layer; the other involves fast and reversible redox reactions of ions in the electrolyte within the electrode's active material. Potassium-ion capacitors, a type of pseudocapacitor within supercapacitors, possess many advantages, including long life, high energy density, large theoretical capacity, compact size, and widespread availability. However, a current issue with potassium-ion supercapacitors is the large atomic size of potassium ions. Repeated charging and discharging can cause crystal volume expansion, leading to the collapse of the lattice structure. This means that the structural stability of potassium-ion electrodes during the insertion/extraction process is poor, affecting the performance and cycle life of the electrodes. Therefore, there is an urgent need to find a material that can maintain lattice structure stability and limit the volume expansion of K ions.

4.1.2. MXenes Materials and Potassium-ion Supercapacitors. Pseudocapacitive Effect of MXenes Electrodes in Potassium-ion Supercapacitors. Currently, the storage method in the new energy vehicle sector is primarily lithium batteries, which face several issues such as long charging times, short range, low battery life, and a propensity for thermal runaway leading to explosions during charging. From a low-cost and recyclable perspective, pseudocapacitance formed by sodium and potassium ions holds the most promise for replacing lithium-ion batteries. Recently, Professor Zhi Chunyi who comes from City University of Hong Kong and his research team [10] have constructed high-performance aqueous potassium-ion supercapacitors using MXenes electrodes. By leveraging the adjustable interlayer spacing and improved structural stability of MXenes materials and comparing the potassium ion capture and release behavior of three different MXenes electrode materials (namely Nb_2C, Ti_2C, and Ti_3C_2), they explored their electrochemical performance to enhance potassium-ion supercapacitors.
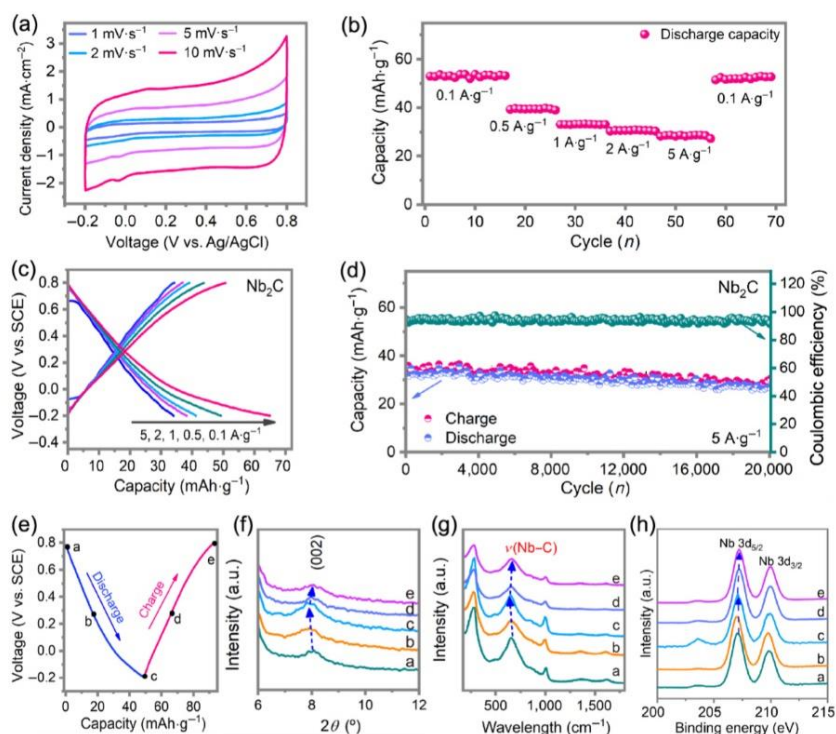
Figure 3. The MXenes electrodes performance characterization of electrochemistry for potassium ion storage (a) Several scan rates of C-V characteristic curves (b) Rate performance curves corresponding to different current densities (c) C-V curves of Nb_2C under several kinds of current densities (d) Coulombic efficiency performance (e)-(h) Tracing characterization images of Nb_2C electrodes [10].

Through experimental comparison, the author confirmed the contribution of MXenes materials in the potassiation/de-potassiation process towards achieving long-term stable cycling and rapid energy storage. Among them, the capacitive performance characteristics of Nb_2C MXenes material with potassium ions were the most outstanding, has a maximum power density approach 2336 $W·kg^{-1}$ and an energy density reach 24.6 $Wh·kg^{-1}$. After 30,000 cycles at 5 $A·g^{-1}$, the volume could still maintain 94.6%. Although lithium batteries have higher energy density, their power density is only 250-340 $W·kg^{-1}$ [10], which is inferior to MXenes-potassium ion supercapacitors in terms of reaction rate. This experiment fully demonstrated the pseudocapacitive effect inherent in MXenes materials. Compared to previous supercapacitors with pseudocapacitive effects, MXenes materials contribute significantly to extending the lifespan of supercapacitors without sacrificing cycle stability for higher energy density.

Contribution of MXenes Materials to the Cycle Stability of Potassium-ion Supercapacitors. The contribution of MXenes in preventing crystal collapse and suppressing dendrite growth has been widely verified in Na-ion and Li-ion capacitors, but there are relatively few experiments related to preventing K dendrite growth. However, the experimental team led by Haodong made a new discovery regarding the volume expansion and dendrite growth issues of potassium ions — by designing the (a- TI_3C_2) nanoribbon framework, they effectively suppressed the volume change and dendrite growth of potassium ions [11]. The a- TI_3C_2 MXenes framework, with its high electrical conductivity, wide specific surface area, abundant porous structure, and potassium-friendly functional groups, provided conditions for uniform deposition of potassium ions, achieving 99.4% Coulombic efficiency and 300 cycles of sustained stability [11]. It is evident from the figures that the F and O functional groups contained in the a- TI_3C_2 material are most beneficial for the uniform deposition of potassium ions. Moreover, the experiment also compared the effects of uniform potassium ion deposition between bare copper electrodes and a- TI_3C_2 electrodes. Compared to the rough surface of copper electrodes, which causes

uneven distribution of potassium ions, a- TI_3C_2 provides uniform active sites for potassium, further demonstrating the advantages of MXenes materials in suppressing dendrite growth and extending the lifespan of supercapacitors.
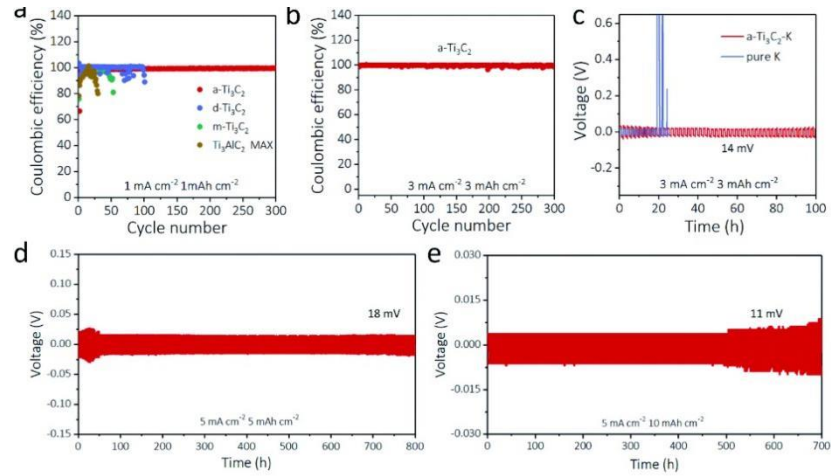

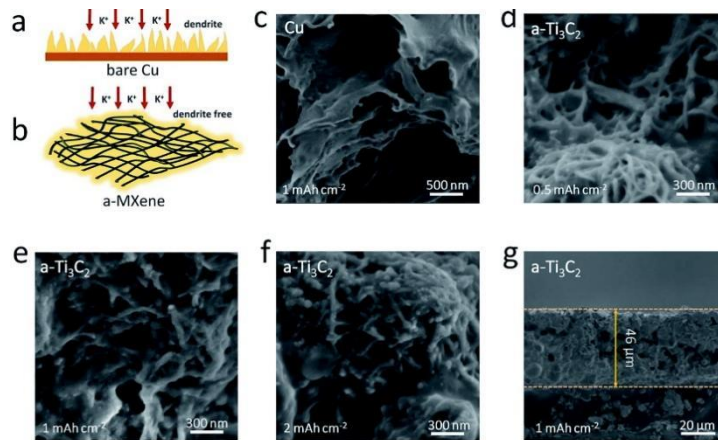**Figure 4.** Impact of cycling number and time on K dendrite growth [11].

Figure 5. Characterization images of K plating on a-TI_3C_2 electrodes and copper electrodes [11].

4.2. Applications of MXenes Materials in the Photovoltaic Field

4.2.1. Solar Cells and Photovoltaic Effect. Given that solar energy is an inexhaustible and immense source of power, harnessing solar energy is a significant topic in the current energy field, with the photovoltaic effect being one of the most crucial mechanisms for solar energy utilization. The principle of solar cells lies in using the photoelectric effect to transfer solar energy into electrical energy directly for storage, essentially functioning as a diode under sunlight. Ideal solar cell materials possess high photoelectric conversion efficiency, are conducive to large-scale industrial production, exhibit stable chemical properties, and do not pollute the environment. Currently, commercial solar cell materials are mainly categorized into silicon wafers, copper indium gallium selenide (CIGS), and perovskites. The goal of the new generation (third-generation) solar cells is to enhance photoelectric conversion efficiency while considering production costs and environmental protection. Organic solar cells, overcoming the high cost of first-generation and the low conversion efficiency of second-generation thin-film solar cells, feature abundant raw materials, non-toxicity, stable performance, and no environmental harm, making them a popular material in recent solar cell development.

4.2.2. MXenes Materials and Solar Cells. With outstanding characteristic of electrical conducting and the transparency, MXenes materials present significant advantages as transparent electrodes and efficient electron-hole transport layers both in organic and various solar cells, thus offering immense prospects in solar cell materials.

Recently, Wang's team controlled the oxidation level of $Ti_3C_2T_x$ MXenes, categorizing them into $Ti_3C_2T_x$, lightly oxidized $Ti_3C_2T_x$ (abbreviated as LO- $Ti_3C_2T_x$), heavily oxidized $Ti_3C_2T_x$ (abbreviated as HO- $Ti_3C_2T_x$), and heavily oxidized with initial composite $Ti_3C_2T_x$ (HO- $Ti_3C_2T_x$ @ $Ti_3C_2T_x$) [11-12]. Through DFT calculations, they analyzed the current-voltage characteristics and energy level and work function curves of perovskite solar cells with different oxidation levels of $Ti_3C_2T_x$. They found that appropriately oxidized $Ti_3C_2T_x$ MXenes not only effectively reduce defects in the fabricated films and enhance the energy level matching with other components but can also change the material's chemical properties from metallic to semiconducting upon heavy oxidation, ultimately achieving a photoelectric conversion efficiency of 18.29%. Based on this, the team fabricated perovskite solar cells using MXenes materials solely as the electron transport layer. Compared to traditional electron transport materials like TiO_2 and ZnO, which face charge transport mismatch, complicated high-temperature annealing processes, and high energy input leading to constraints in the low-cost, large-scale commercial application of perovskite solar cells (PSCs), this discovery offers new options for low-temperature preparation, large area, flexible photovoltaic devices, and high conductivity applications.
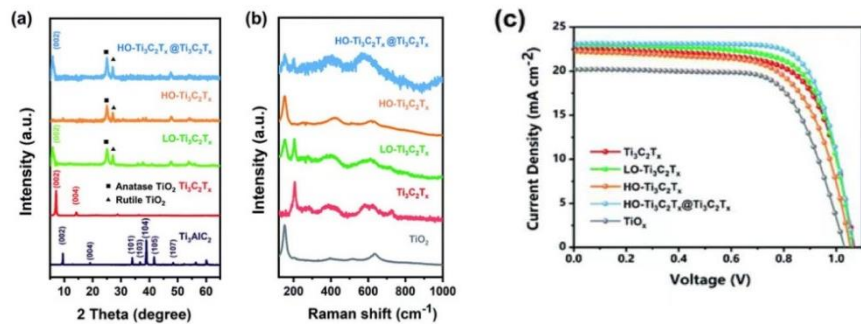

Figure 6. Chemical characterization and J-V curves of $Ti_3C_2T_x$ materials with different oxidation levels [12].

Table 1. Photovoltaic characteristic parameters of perovskite solar cells with several layers of electron transport [12].

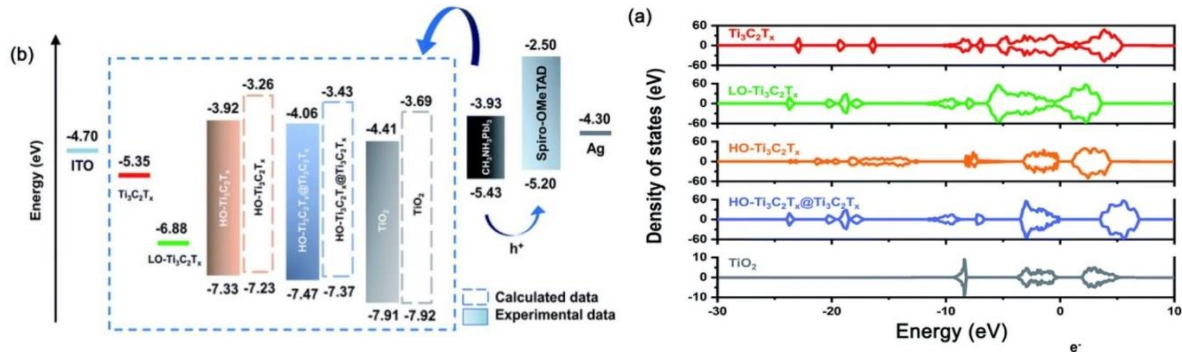| ETL	V_{OC}(V)	J_{SC}(mA·cm^{-2})	FF(%)	PCE(%)
$Ti_3C_2T_x$	1.07	22.35	69	16.50
LO-$Ti_3C_2T_x$	1.06	23.04	70	17.09
HO-$Ti_3C_2T_x$	1.06	22.18	66	15.52
HO-$Ti_3C_2T_x$@ $Ti_3C_2T_x$	1.07	23.11	74	18.29
TiO_2	1.03	20.61	70	14.86

Figure 7. Calculated state densities and cell energy levels of $Ti_3C_2T_x$ materials with different oxidation levels [12].

5. Conclusion

The preparation of MXenes materials via Chemical Vapor Deposition (CVD) method presents a new avenue based on the traditional methods of preparing MAX phases. MXenes synthesized directly on substrates through this method exhibit high ion intercalation energy storage characteristics, which not only improve production efficiency and reduce production costs but also help mitigate the irreversible environmental damage caused by traditional production methods. It enables the rapid acquisition of large-scale, high-quality, defect-free MXenes materials, significantly fostering exploration and development of their performance applications. To date, our development and utilization of MXenes materials only represent a small fraction of their potential. By controlling their oxidation level, combining them with different two-dimensional materials, or adjusting their chemical compositions, it's possible to achieve transitions in chemical properties from metallic to semiconducting to topological insulators, controllable interlayer structures, and high compatibility with other materials, all highlighting their broad application potential. However, to truly advantage MXenes materials over other two-dimensional nanomaterials like graphene in practical applications, numerous challenges and difficulties remain. For instance, although most theoretical studies confirm the chemical stability of MXenes materials, actual production has been limited to a few common materials, such as Ti3C2Tx and Mo2C. How to enhance their oxidation resistance in water and air, as well as precise control over their compositional structure, are fundamental issues that are key to whether MXenes can be applied on a commercial scale.

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