

Mo₂Ti₂C₃T_x as an electrocatalyst for the hydrogen evolution reaction

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Abstract

Recently, MXene has an increasingly wide range of applications in energy conversion and storage. The Mo₂Ti₂C₃T_x was well prepared and further explored in the hydrogen evolution reaction (HER). Although Ti was introduced in Mo₂Ti₂C₃T_x to easily prepare the Mo-based MXene, the results of theoretical calculations showed that the introduction of Ti changed the electronic structure characteristics of MXene. Mo₂Ti₂C₃T_x have a stronger H adsorption energy, which limiting the desorption process of H and making the HER activity of Mo₂Ti₂C₃T_x weaker, as shown in the experimental results. Considering the multi-component is the unique property of MXene materials, this work provides a new idea for the design and research of HER electrocatalysts.

Keywords

MXene, hydrogen evolution reaction, electrocatalysis.

1. Introduction

In the traditional electrocatalysis process, hydrogen is generated by electrochemical reduction reaction on the cathode in water splitting, mainly driven by nanostructured Pt or other platinum group metals (PGM). In general, electrochemical energy storage and conversion technologies, particularly the commercialization of fuel cells and water splitting, rely on the development of new electrocatalytic materials to reduce reaction overpotential, and the cost of catalysts can also be reduced by replacing the use of PGMs. Therefore, many researchers have concentrated on the development of non-PGM HER electrocatalysts, which are currently known to include sulfides, nitrides, carbides, phosphides, and the like having a range of stoichiometry and morphology[1, 2]. However, the durability of these materials is still problematic at present, and it is needed to further increase the reaction activity.

MXenes are a family of materials, and more than 70 kinds of MXene have been reported[2]. They are mainly made by selectively etching away the "A" in the precursor of the MAX phase (a layered ceramic material). Wherein, the MAX phase is usually expressed as M_{n+1}AX_n(M represents an early transition metal, A is a Group IIIA or IVA element, and X is a C and/or N element). After the layer A element is removed, the M_{n+1}X_n structure is obtained. It can be seen that MXene have a combination of various components, and it is possible to obtain materials with unique electronic properties by designing the components. In addition, many active surface functional groups would be produced after removal of the "A" atom, which makes the MXenes have good hydrophilicity and electronegativity. The unique properties of MXene make it as an attractive electrocatalytic material. Recent computational and experimental analysis of Mo-based MXene have demonstrated their potential applications exist as an efficient catalyst HER[3]. The adsorption of HER active intermediates of Mo₂CT_x single-layer materials was predicted by density functional theory (DFT). The near-thermal neutral free energy adsorption H(ΔG_{ad}) in a wide range of H surface coverage shows that Mo₂CT_x is at the top of the reactive volcano map, indicating its efficient potential for HER. In this work, Mo-based MXene, Mo₂Ti₂C₃T_x, was prepared and applied to the HER reaction..

2. Experimental

2.1 Synthesis of catalysts.

The precursor MAX phase of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$, $\text{Mo}_2\text{Ti}_2\text{AlC}_3$, can be prepared by solid phase reaction[4]. The synthesis process of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ is as follows:

First, 1.0 g of $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ powder was slowly added in a high density polyethylene beaker with hydrofluoric acid solution. The beaker was placed in an oil bath held at 55 °C and kept stirring for 90 hours. After completion of the reaction, the mixture was subjected to centrifugal washing using dehydrated with Ar degassed water until the pH of the supernatant reached 6 to 7. The solid were then obtained by vacuum filtration and dried under vacuum at room temperature.

Finally, a stripping operation was carried out using tetramethylammonium hydroxide (TMAOH) as an intercalation molecule. The thin $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ powder can be obtained by freeze drying.

2.2 Characterization of catalyst.

The XRD patterns were collected by X-ray diffractometer (Rigaku D/max-2400, Tokyo, Japan) using $\text{Cu K}\alpha$ ($\lambda = 1.54 \text{ \AA}$) radiation. The morphology and microstructure of samples were separately analyzed by scanning electron microscope (SEM, KYKY-EM8000F, China) and Transmission electron microscopy (TEM, JEM-2100, Japan).

2.3 Electrochemical Measurements of HER.

5 mg of the powder sample was weighed into a 2 ml sample vial, 400 μL of water and 600 μL of isopropanol were taken with a pipette, and finally 10 μL of Nafion solution was added as a binder, to get the ink. After ultrasonic dispersion in an ice water bath for one hour, 5 μL of the ink was used to drip onto a polished glassy carbon electrode (7 mm in diameter), and naturally dried at room temperature as a working electrode. The electrolyte for the test was 0.5 M H_2SO_4 . A conventional three-electrode system was used, with a saturated calomel electrode as the reference electrode, and a carbon rod for the counter electrode. The electrochemical measurements were conducted by the CHI 760e workstation (CH Instruments, China).

3. Results and Discussion

The XRD patterns of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ and their corresponding MAX phases by X-ray diffraction analysis are shown in Figure 1. For $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$, it could be seen that compared to its precursor, its (0002) peak was shifted to the lower angles and widened after etching, which suggested the increase in the c lattice parameter and the loosely packed $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$. On the one hand, the strongest diffraction peak disappeared and the interlayer structure appeared after the removal of the Al atom layer. it is inevitable that water molecules and the like will be introduced into the layers, and similar phenomena exist in other MXenes such as Nb_2CT_x [2].

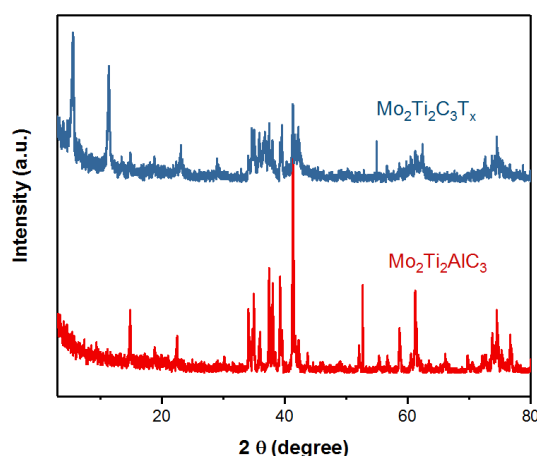


Fig. 1 The XRD patterns of $\text{Mo}_2\text{Ti}_2\text{AlC}_3$; $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$

SEM is a common means of observing the fine structure of materials. Obtaining the topographical characteristics of the material contributes to the research and performance improvement of the material properties. $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ after hydrofluoric acid etching was shown in Fig. 2(a). The SEM results showed that the interlayer structure could be clearly found. During the etching process, the hydrogen product escaped, so that the interlayer distance increased. Further, through the intercalation of TMAOH and ultrasonic assisted stripping, the thin layer of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ was successfully obtained, as shown in Fig.2(b). $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ was visually more thin and had SEM characteristics of graphene-like. To further explore the microstructure of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$, TEM analysis was performed, shown in Fig.2(c). It could be seen that the prepared $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ was thin layer two-dimensional materials and had a thin layer structure similar to graphene.

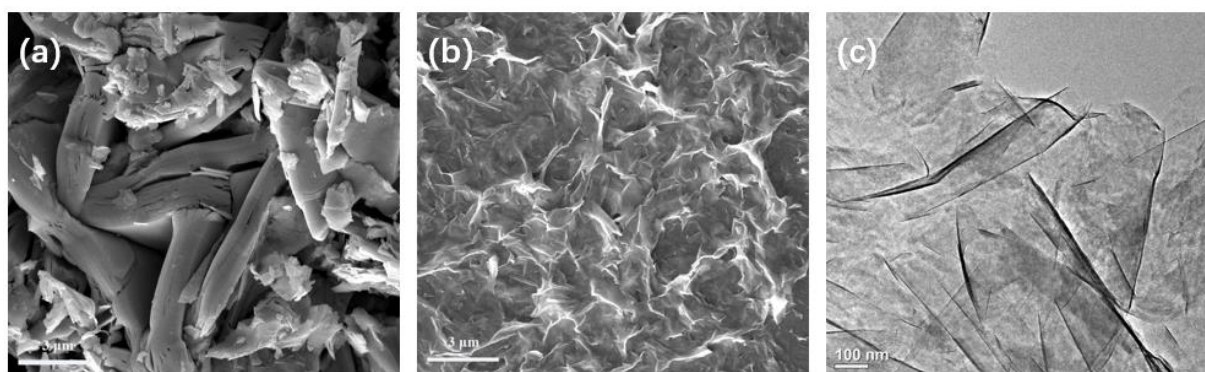


Fig. 2 The SEM images of $\text{Mo}_2\text{Ti}_2\text{AlC}_3$ (a) and $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ (b); TEM image of thin layer of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ (c)

The LSV test was performed first with a scan rate of 5 mV/s. The result was shown in Figure 3(a). All the potentials were calibrated with respect to a RHE. For further comparison of performance, Mo_2CT_x was chose as another Mo-based MXene. It could be seen that the two MXenes had a certain hydrogen production activity of water electrolysis. Specifically, the overpotential of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ was 318 mV at a current density of 10 mA/cm^2 . In contrast, the HER activity of these two Mo-based MXenes do not match the phosphide and other catalysts already reported[5], but it is worth noting that MXenes are a series of materials with multi-component properties and have the unique nature of two-dimensional materials, there are still a lot of room for choices, and can also be further improved by means of modification. In short, this work provides a new idea for the study of HER electrocatalyst. Compared with Mo_2CT_x , the thin layer $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ is easier to prepare, but the HER performance of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ is significantly weaker than Mo_2CT_x , the possible reasons for analysis are as follows:

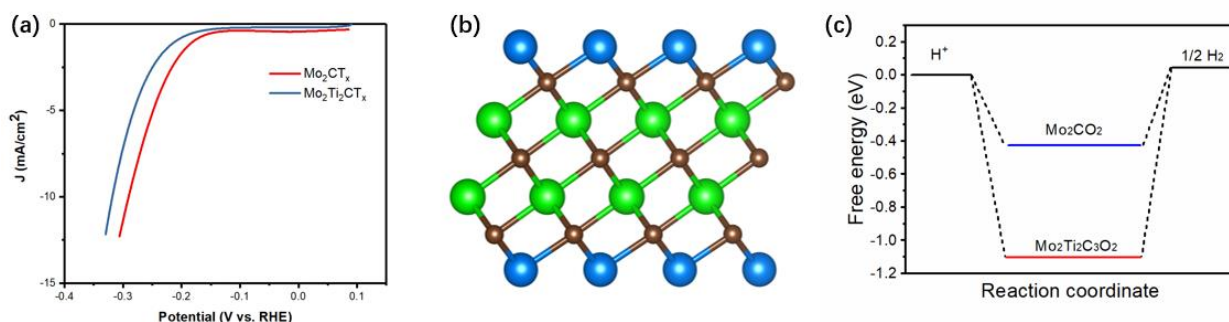


Fig.3 LSV curves of Mo-based MXene (a); atomic structure of bare $\text{Mo}_2\text{Ti}_2\text{C}_3$ (b) and the calculated free-energy diagram (c)

Due to the MXene structure, like $\text{Mo}_4\text{C}_3\text{T}_x$, is unstable[4], the Ti layer atom is introduced to stably synthesize the MAX phase $\text{Mo}_2\text{Ti}_2\text{AlC}_3$, which is easier to be etched. So the MXene with bimetal, $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$, is constructed and can be more easily prepared. On the other hand, since the Ti element itself does not have a significant advantage in the electrolysis of hydrogen production applications. For example, $\text{Ti}_3\text{C}_2\text{T}_x$ has almost no HER activity[3], so performance cannot be improved. In order

to further confirm, the theoretical simulation calculation of hydrogen adsorption energy was done, shown in Figure 3(c). It was found that Mo_2CT_x energy was changed to -368.7eV from -363.3eV after adsorption of a hydrogen, and hydrogen adsorption energy was -2.1eV . Correspondingly, the energy of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ was became -345.8eV from -332.5eV , so the hydrogen adsorption energy is -9.5eV , which meant there was a stronger H adsorption energy. It could be found that the structure of the material had not been changed even with the introduction of titanium atoms, but the adsorption capacity for hydrogen atoms was strengthened. It is not conducive to release hydrogen in the electrocatalytic process, so the $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ showed a relatively general electrocatalytic hydrogen evolution.

4. Conclusion

In summary, The main work is to complete the preparation of Mo-based MXene, and further explore its partial electrocatalytic performance. In electrocatalytic hydrogen production, it can be seen that $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ do have certain HER activity. With the introduction of Ti to stably synthesize the precursor MAX phase, it is easier to prepare Mo-based MXene. The theoretical calculations showed that the introduction of Ti changed the electronic structure of Mo-based MXene, and made $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ having a stronger H adsorption energy. so the HER activity of $\text{Mo}_2\text{Ti}_2\text{C}_3\text{T}_x$ was weaker than Mo_2CT_x . Considering the multi-component is the unique property of MXene materials, this work provides a new idea for the design and research of subsequent electrocatalysts.

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