Electro catalytic Performance of bimetallic LDH on Mxene Adsorbed Nickle Foam

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Abstract. Mxene is a typical two-dimension material which have widely applied in many fields. Following the design strategy of electrostatic adsorption, coupled with bimetallic LDH, the layered Mxene is successfully used in electrochemical system. A large number of negative groups on the surface of Mxene are used to let Mxene monolayer adsorb on self-supporting materials. The comparison of the electrocatalytic performance before and after the adsorption of Mxene showed that a small amount of absorbed Mxene did have the effect on the reaction activity. The different bimetallic LDH synthesised by hydrothermal method was supported on this new material NF@Mxene. After exploring various combinations, the NF@Mxene with NiFe LDH was proved to be the best OER catalyst. This strategy will provide possibilities for subsequent Mxene electrocatalytic applications.

1. Introduction
The depletion of traditional fossil fuels and serious environmental problems have led to the need of a new renewable energy source. In this situation, hydrogen is considered to be one of the promising candidates for solving these problems1-4. Based on this fact, researchers have made great efforts to find sustainable and efficient hydrogen production methods. Among them, water electrolysis is the most promising methods. At the material design level, the conductivity, the reactivity and the number of active sites are the crucial points affecting the performance of the electrochemical water splitting catalyst. Experimental studies have found that transition metal carbonatites (Ti2C, Ti2N, Ti3C2, Ti4C3, V2C, Nb2C, etc.) can form stable two-dimensional structures with only 3-7 layers of atomic thickness, called Mxene5. The chemical formula of Mxene is M n+1Xn (n=1, 2, 3; X=C, N; M= transition metal). The two-dimensional Mxene structure can be obtained by immersing the ternary layered structure M n+1AXn (A=Al, Si, etc.) in hydrofluoric acid. The preparation processes allow the Mxene surface to be widely covered with O, F, and OH groups. After chemical etching, MXene still maintains the high conductivity of the original sample, and its ultra-thin property shows the vigorous catalytic active site density. It is well known that transition metal layered double hydroxides exhibit the ultra-high activity in various fields of electro catalysis, especially HER and OER1, 6-7. The combination of high specific surface of Mxene and the excellent properties of LDH is a great material design strategy. Thus, because of the large number of anionic groups on the Mxene layer surface, it has strong electrostatic adsorption. This trait can be used to absorb metal ions on two-dimensional Mxene surface. The prepared transition metal layered double hydroxides supported on Mxene were formed by hydrothermal method. The obtained
material, NF@Mxene with NiFe LDH, showed the excellent performance in OER, compared with other transition metal layered double hydroxides supported on NF@Mxene. This strategy is a new way to obtain excellent OER catalysts based on Mxene.

2. Experiment section

2.1. Material preparation

Ti$_3$C$_2$Tx was prepared by HF treatment. Firstly, Ti$_3$AlC$_2$ powders were added into the polytetrafluoroethylene beaker with HF solution to kept 24 h with magnetic stirring. After that, the black solid was collected. After the intercalation of DMSO and the ultrasonic stripping operation, multilayer Ti$_3$C$_2$Tx can change into monolayer Ti$_3$C$_2$Tx.

The Ni foam was kept in the solution with above monolayer Ti$_3$C$_2$Tx overnight to obtain NF@Mxene. In typical synthesis of NF@Mxene with NiFe LDH, the Ni$^{2+}$ and Fe$^{2+}$ (3:1) was dissolved in ultrapure water, the NF@Mxene was changed into NF@Mxene with NiFe LDH with 8h hydrothermal treatment. In synthesis of other metal-based materials, total concentration of metal precursor remained unchanged, other processes and equipment were all the same as above.

2.2. Electrochemical measurement

CHI 660 electrochemical station was used for electrochemical measurements. The electrochemical measurements were performed under a three-electrode system at a scan rate of 1 mV/s. The as-synthesized materials were directly used as the working electrode, carbon rod was used as the counter electrode, and the Hg/HgO electrode was used as the reference electrode.

3. Result and discussion

Mxene is a general term for a series of material which can be etched into layer structure. Among these materials, Ti$_3$C$_2$Tx can be perfectly etched and the rear layer is obtained as a single layer Ti$_3$C$_2$Tx.

The morphology of the multilayer and monolayer Ti$_3$C$_2$Tx were characterized by SEM, as shown in Figure 1. The multilayered Ti$_3$C$_2$Tx after acid etching exhibits an accordion-like layered structure. The interlayer gap is clearly visible, while the thickness of a single layer is approximately 100 nm. It can be seen that after the intercalation of DMSO and the ultrasonic stripping operation, the obtained monolayer Ti$_3$C$_2$Tx has a similar graphene-like two-dimensional material morphology and exhibits a high specific surface area. Its unique layered structure has great application potential in supercapacitors and catalysis field.

![Figure 1. SEM images of multilayer Ti$_3$C$_2$Tx (a, b), monolayer Ti$_3$C$_2$Tx (c).](image-url)
and negative ions, this method can effectively disperse and uniformly adsorb Mxene sheet on Ni foam skeleton.

![Figure 2. SEM images of Ni foam (a, b) and Ni foam with absorbed monolayer Ti$_3$C$_2$Tx (NF@Mxene) (c, d)](image)

The LSV tests were performed at a scan rate of 1 mV/s, shown in Figure 3. In Figure 3a, it can be seen that the NF@Mxene has a lower alkaline oxygen evolution activity than the pure NF. This may be due to the poor conductivity of Ti$_2$C$_3$Tx. Specifically, at the current density of 10 mA cm$^{-2}$, the overpotential drops by about 20 mV after Mxene absorbed on Ni foam surface. The NF@Mxene has an enhancement in hydrogen evolution reaction activity compared to the pure NF. Specifically, at a current density of 100 mA cm$^{-2}$, the overpotential of NF@Mxene increased 20 mV. In contrast, the HER activity of these materials is indeed not comparable to the reported catalysts such as phosphides, but it is worth noting that MXene is a series of materials with multi-component properties and two-dimensional materials. The performance of Mxene based catalysts can also be further improved by means of modification. In short, it provides a new idea for the study of electro catalyst.

![Figure 3. a) LSV of Ni Foam and NF@Mxene in OER; b) LSV of Ni Foam and NF@Mxene in HER.](image)

Scanning electron microscopy (SEM) images (Fig.4) show the morphology of the two magnifications. The independent Ni Foam skeleton can be observed on the 30 μm scale. The stereoscopic three-dimensional structure of the skeleton surface can be seen on the 7 μm scale. Figure. 4-2a, d show the morphology of NF@Mxene-Ni (OH)$_2$. Compared to Figure 3, there is a distinct layer structure on the skeleton. Figure 4-2b, e show NF@Mxene-NiCo LDH with a large amount of filamentous material on
its surface. Figure 4-2c, f are morphologies images of NF@Mxene-NiFe LDH. At high magnification, there is a layer structure material covered on NF skeleton.

**Figure 4.** SEM images of NF@Mxene with Ni hydroxide (a, d); NF@Mxene with NiCo LDH (b, e) and NF@Mxene with NiFe LDH (c, f)

Aiming at investigating the role of Mxene in this system, we tested OER performance of various bimetallic hydroxide loaded on NF@Mxene, such as NF@Mxene with NiCu LDH, NF@Mxene with NiZn LDH, NF@Mxene with NiFe LDH and NF@Mxene with NiCo LDH. After screening and comparing the properties of these materials, the OER performance of NF@Mxene with NiFe LDH is significantly better than other metal combinations.

**Figure 5.** LSV of Ni Foam, NF@Mxene, NF@Mxene with Ni (OH)$_2$, NF@Mxene with Ni Cu LDH, NF@Mxene with NiZn LDH, NF@Mxene with NiFe LDH and NF@Mxene with NiCo LDH in OER

Different bimetallic LDH supported on NF@Mxene exhibit different electro catalytic activities. In the OER reaction, Ti$_3$C$_2$T$_x$ has low conductivity resulting in worse performance of NF@Mxene. However, bimetallic LDH, especially NiFe LDH, NiCo LDH, can undoubtedly greatly increase the electro catalytic OER activity.
4. Conclusion
In this work, we use the multilayer Ti$_3$C$_2$Tx or monolayer Ti$_3$C$_2$Tx as the base material for electrochemical activity testing. Mxene, as we all know, is a new type of ultra-thin two-dimensional material. Among many transition metal carbides in Mxene series, only Ti$_3$C$_2$Tx can be etched to prepare monolayer Ti$_3$C$_2$Tx. During the acid etching process, the resulting layer Ti$_3$C$_2$Tx surface contained a large number of negative groups. Thus, these negative groups make monolayer Ti$_3$C$_2$Tx easily adsorbed on the self-supporting metal supporter. By comparing the NF@Mxene to blank Ni foam, we demonstrated that the poor conductivity of Ti$_3$C$_2$Tx limits its application in electro catalysis. Thus, we combined double metal hydroxides with NF@Mxene and hydrothermally prepared a variety of different materials, such as NF@Mxene with Ni (OH)$_2$, NF@Mxene with NiCu LDH, NF@Mxene with NiZn LDH, NF@Mxene with NiFe LDH and NF@Mxene with NiCo LDH. In alkaline electrolytes, OER activity of these materials was tested using the electrochemical workstation. NF@Mxene-NiFe LDH has proven to be the best performing material in this system. In addition, several materials, such as NF@Mxene with NiCo LDH, also exhibit certain enhancements in OER activity.

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