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Computational screening study of double transition metal carbonitrides $M'_2M''CNO_2$ -MXene as catalysts for hydrogen evolution reaction

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Two-dimensional (2D) transition metal carbonitrides (MXene) have attracted growing interest in electrocatalytic hydrogen production due to its structural and electronic properties. In this work, the hydrogen evolution reaction (HER) activity of all 64 O-terminated ordered double transition metal carbonitrides in the form of $M'_2M''CNO_2$ ($M' = \text{Ti, V, Cr, Zr, Nb, Mo, Hf, Ta}$; $M'' = \text{Ti, V, Cr, Zr, Nb, Mo, Hf, Ta}$) has been investigated by well-defined density functional theory (DFT) calculations. The results indicate that there are 11 $M'_2M''CNO_2$ -MXene candidates whose HER performance is superior to that of Pt. Moreover, according to the stability screening, it is proved that Ti_2NbCNO_2 , Mo_2TiCNO_2 , and Ti_2VCNO_2 are more stable than other candidates. Especially, Ti_2NbCNO_2 have the potential to be perfect HER catalyst with the small Gibbs free energies of hydrogen adsorption (ΔG_H) value of 0.02 eV, abundant catalytic sites on the C-side, and better stability. This work paves the way on designing excellent HER catalyst candidates based on $M'_2M''CNO_2$ -MXenes.

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INTRODUCTION

Electrochemical water splitting through hydrogen evolution reaction (HER) associated with catalysis is an attractive method for hydrogen production^{1,2}, but it is still challenging due to the lack of effective and low-cost HER catalyst. Noble metals such as platinum (Pt) have been verified as excellent HER catalysts, but the corresponding scarcity and high price limit its large-scale applications. Therefore, finding a cost-effective alternative to platinum is crucial. Computational screening is an effective method for exploring catalysts. First-principles calculations can be used to evaluate the performance of a mass of potential candidates before selecting catalysts suitable for experimental synthesis. In comparison to traditional materials, two-dimensional (2D) materials have more superiorities as HER catalysts. The large specific surface area of 2D materials can provide abundant active sites, and its diverse chemical properties also supply convenience for adjusting its catalytic performance. In recent years, some efficient and 2D HER catalysts, including MoS_2 ^{3–5}, metal phosphides⁶, $g-C_3N_4$ ^{7–9}, and chalcogenides¹⁰, have been extensively studied. However, the poor charge transfer performance³ and restricted active sites^{4,11} are major defects of these catalysts. Wherefore, it is still necessary to search efficient and economical 2D HER catalysts.

In recent years, 2D materials involving transition metal carbides, nitrides, and carbonitrides known as MXene have been widely studied in both experiment^{12–16} and theory^{17–20}. MXenes usually have a general formula $M_{n+1}X_nT_x$, where M denotes the early transition metals, X represents C and/or N, T_x represents surface functional groups (O, OH, or F), and n takes values from 1 to 3. Owing to its electronic properties, excellent stability, hydrophilicity, extensive chemical and structural adjustments, MXenes have possessed broad application prospects in nanodevices^{21,22},

hydrogen storage^{23,24}, supercapacitors²⁵, photolytic or electric catalysis^{26,27} and other fields. At the same time, MXenes are also effective HER catalysts, and have recently received extensive attention in electrocatalytic water splitting to produce hydrogen. Huang et al.²⁸ have systematically evaluated the HER activity of transition metal carbonitrides M_3CN ($M = \text{Ti, V, Cr, Zr, Nb, Mo, Hf, Ta}$) by first-principles calculations. Based on the calculation results, they found that only Ti_3CNO_2 and Nb_3CNO_2 have potential HER catalytic activity, where the ΔG_H value of C-side for Ti_3CNO_2 is -0.122 eV, while the ΔG_H values of C- and N-side for Nb_3CNO_2 are -0.117 and -0.097 eV, respectively. For the other transition metal carbonitrides M_3CN , the HER activity is not good. Anasori et al.¹⁷ discovered more than 20 double transition metal MXenes $M'_2M''C_2$ and $M'_2M''_2C_2$ by experimental methods and density functional theory calculations. The result showed that the ordered double MXenes were thermodynamically more stable than the solid solution MXenes. Their work is significant to the development of MXene-based catalysts, and provides a constructive method to regulate the HER performance of MXene by constructing 2D “sandwich” structure. Jin et al. have investigated the HER activity of 24 different ordered double transition metal carbide MXenes by DFT calculations. Among them, 18 different carbides have been predicted to be active HER electrocatalyst candidates²⁹. Therefore, we tried to construct “sandwich” structure of transition metal carbonitrides M_3CN , that is, double transition metal carbonitrides $M'_2M''CNO_2$ -MXene to improve its HER activity.

In this work, theory studies based on well-defined DFT calculations were used to systematically investigate the HER activity and geometric structure of the O-terminated double transition metal carbonitrides $M'_2M''CNO_2$ -MXene ($M' = \text{Ti, V, Cr, Zr, Nb, Mo, Hf, Ta}$; $M'' = \text{Ti, V, Cr, Zr, Nb, Mo, Hf, Ta}$), as well as the stability of some selected MXene candidates. By high-throughput

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computational screening, 11 $M'_2M''\text{CNO}_2$ -MXene candidates whose HER performance is even better than that of Pt were found. Further, the catalytic active sites and stability of the selected candidates were taken into consideration. Ultimately, $\text{Ti}_2\text{NbCNO}_2$, $\text{Mo}_2\text{TiCNO}_2$, and Ti_2VCNO_2 were identified as highly efficient and more stable HER catalysts, among which $\text{Ti}_2\text{NbCNO}_2$ with the ΔG_{H} value of 0.02 eV and a great deal of catalytic sites on the C-side is the most ideal HER catalyst candidate.

RESULTS AND DISCUSSION

The bare structure of ordered double transition metal carbonitrides

Figure 1a shows the geometric structure of the studied bare ordered double transition metal carbonitrides. The M' layers are located in the outermost layer of the MXenes monolayer, and M'' layer fills the middle layer of MXenes, and the carbon layer and nitrogen layer are distributed on both sides of M'' layer. In other expression, the atomic layer of another type of transition metal element was used to replace the original intermediate layer of the M_3CN MXenes²⁸. Due to the high chemical activity of the bare MXenes monolayer surface, the generated MXenes are easily functionalized by surface terminal groups (O, OH, and F)³⁰. The bare MXenes have been proved to be thermodynamically prone

to be functionalized with oxygen terminals³¹. Therefore, we only focus on the properties of O-terminated MXenes in the subsequent researches.

The O-terminated structure of ordered $M'_2M''\text{CNO}_2$ -MXenes

For O-terminated MXenes, in order to maximize the coordination number of the outermost transition metals, the oxygen groups are normally located in the hollow position of the outermost layers. The basal planes of bare MXenes have two different hollow sites, denoted as fcc and hcp (Fig. 1b). Therefore, there are four different structures for $M'_2M''\text{CNO}_2$ -MXene (Fig. 1c), marked as fcc-fcc, fcc-hcp, hcp-fcc, and hcp-hcp. Based on the calculation results, we selected the configurations of $M'_2M''\text{CNO}_2$ with the lowest energy as the most stable structures for further research, as shown in Fig. 2. When the outermost transition metals are d^2 group elements ($M' = \text{Ti, Zr, Hf}$), all of the most stable configurations of $M'_2M''\text{CNO}_2$ are fcc-fcc type, where the atomic number of the outermost transition metals M' and the type of the intermediate transition metals M'' have little effect on the most stable configurations of $M'_2M''\text{CNO}_2$.

Specially, there are two different most stable configurations of $M'_2M''\text{CNO}_2$, when the outermost transition metals are $d3$ group elements. The most stable configurations of $M'_2M''\text{CNO}_2$ are still fcc-fcc type when $M' = \text{V}$ with smaller atomic number, while $M' =$

Fig. 1 Top and side views of crystal structure. **a** Top views and side views of ordered bare double transition metal carbonitrides. **b** Top views and side views of ordered O-terminated double transition metal carbonitrides. **c** Side views of four different configurations of $M'_2M''\text{CNO}_2$ -MXenes.

M''\M'	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	
Ti	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	hcp-fcc	hcp-hcp	fcc-hcp
Zr	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	hcp-fcc	hcp-hcp	fcc-hcp
Hf	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	hcp-fcc	hcp-fcc	fcc-hcp
V	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	hcp-fcc	hcp-hcp	hcp-fcc
Nb	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	fcc-fcc	fcc-hcp	hcp-hcp
Ta	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	fcc-fcc	hcp-fcc	hcp-hcp
Cr	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	fcc-fcc	--	
Mo	fcc-fcc	fcc-fcc	fcc-fcc	fcc-fcc	fcc-hcp	fcc-hcp	--	fcc-fcc	

Fig. 2 The most stable configurations of $M'_2M''\text{CNO}_2$ -MXenes after geometric optimization. The order of the outermost metal M' from left to right is d^2 to d^4 , and the order of the intermediate metal M'' from top to bottom is d^2 to d^4 .

Nb or Ta become fcc-hcp type. When the outermost transition metals are d^4 group elements ($M' = \text{Cr}, \text{Mo}$), the most stable configurations of $M'_2M''\text{CNO}_2$ are irregular and diverse. In addition, the lattice parameters of $M'_2M''\text{CN}$ and $M'_2M''\text{CNO}_2$ are shown in Supplementary Table 1; the data are in good agreement with the previous results²⁸.

HER activity screening of $M'_2M''\text{CNO}_2$

Figure 3 represents the flow chart for selecting the most ideal HER catalyst from all 64 $M'_2M''\text{CNO}_2$ -MXenes. As we know, the Gibbs free energy of hydrogen adsorption is usually used as the indicator of the HER activity³² and defined as

$$\Delta G_{\text{H}} = \Delta E_{\text{H}} + \Delta E_{\text{ZPE}} - T\Delta S_{\text{H}} \quad (1)$$

where ΔE_{H} represents the adsorption energy of hydrogen, ΔE_{ZPE} and ΔS_{H} are the difference in zero point energy (ZPE) and the entropy between the hydrogen adsorbed state and gas phase, respectively. The ΔE_{H} is defined as

$$\Delta E_{\text{H}} = E(\text{MXene} + n\text{H}) - E(\text{MXene} + (n-1)\text{H}) - 1/2E(\text{H}_2) \quad (2)$$

where $E(\text{MXene} + n\text{H})$ denotes the energy of MXene with n adsorbed hydrogen atoms, and $E(\text{MXene} + (n-1)\text{H})$ represents the energy of MXene with $n-1$ adsorbed hydrogen atoms. $E(\text{H}_2)$ is energy of H_2 in the gas phase. The ΔE_{ZPE} is computed by

$$\Delta E_{\text{ZPE}} = E_{\text{ZPE}}(n\text{H}) - E_{\text{ZPE}}((n-1)\text{H}) - 1/2E_{\text{ZPE}}(\text{H}_2) \quad (3)$$

where $E_{\text{ZPE}}(n\text{H})$ and $E_{\text{ZPE}}((n-1)\text{H})$ denote the zero point energy of MXene with n and $n-1$ adsorbed hydrogen atoms, respectively. $E_{\text{ZPE}}(\text{H}_2)$ represents the zero point energy of H_2 in gas conditions. ΔS_{H} is approximately equal to the entropy of gas phase H_2 under standard conditions. Generally speaking, catalysts with $|\Delta G_{\text{H}}|$ lower than 0.2 eV are identified to have HER activity (the closer the value of $|\Delta G_{\text{H}}|$ to zero, the higher is the HER activity). ΔG_{H} with high positive value denotes strong hindrance for the electrochemical reduction reaction; on the contrary, ΔG_{H} with more negative value indicates that the detachment of protons from the catalyst surface will become more difficult. Since the chemical environment for both sides of $M'_2M''\text{CNO}_2$ is different, ΔG_{H} is calculated on both C- and N-side of all 64 $M'_2M''\text{CNO}_2$ -MXenes in our study, as shown in Supplementary Tables 2 and 3. The diagonal of the heat map is

Fig. 3 Screening work flow. The screening process of HER catalysts from 64 $M'_2M''\text{CNO}_2$ -MXenes.

ΔG_{H} of $M_3\text{CNO}_2$ ($M' = M''$), and only a few MXenes (Ti_3CNO_2 , Nb_3CNO_2) have ideal HER activity (Fig. 4).

Notably, when the second transition metal element is introduced to form $M'_2M''\text{CNO}_2$, the HER activity of MXenes will be greatly improved. Obviously, the M' compared with M'' have a greater impact on the HER activity. The outermost transition metal M' is Ti or Nb, most of $M'_2M''\text{CNO}_2$ -MXenes exhibit desired HER activity on the C-side, while the M' is Ta, the HER activity is better on the N-side. Overall, the number of shadow region of the C-side is more than that of N-side, indicating that the C-side of $M'_2M''\text{CNO}_2$ -MXenes is more active for HER. It is well known that ΔG_{H} is connected with the bonding energy between H atoms and the surface of MXenes. The bonding energy is relevant to the electronegativity of all atoms of MXenes (such as M' , M'' , C, and N atoms), which results in different electronic structure for the C- and N-side of $M'_2M''\text{CNO}_2$. Therefore, it is hard to summarize the regularity of HER activity for whole $M'_2M''\text{CNO}_2$ -MXenes.

The volcano curve can be used to intuitively characterize the HER activity of electrocatalysts. The abscissa of the volcano curve is the ΔG_{H} while the ordinate is the overpotential ($\eta_r = \pm \Delta G_{\text{H}}/e^-$). The closer the coordinate is to the top of the volcano, the more perfect HER performance of the catalyst. We divide the volcano curve into two branches, the points on the left branch represent the strong adsorption between H atom and the catalyst, while the

Fig. 4 The Gibbs free energy of hydrogen adsorption for all 64 $M'_2M''\text{CNO}_2$ -MXenes. **a** The ΔG_H for the C-side of $M'_2M''\text{CNO}_2$ -MXenes. **b** The ΔG_H for the N-side of $M'_2M''\text{CNO}_2$ -MXenes. The abscissa and ordinate of each square of the heat map correspond M' and M'' of $M'_2M''\text{CNO}_2$, respectively. The color corresponds to the value of ΔG_H for MXenes. The square passed by the diagonal dashed line corresponds to the $M_3\text{CNO}_2$. The shadow regions represent MXenes with $|\Delta G_H| < 0.2$ eV.

Fig. 5 The volcano plotted for all 64 $M'_2M''\text{CNO}_2$ -MXenes. **a** The volcano plotted for the C-side of $M'_2M''\text{CNO}_2$ -MXenes. **b** The volcano plotted for the N-side of $M'_2M''\text{CNO}_2$ -MXenes. **c** The corresponding enlarged view of the area near the volcano apex of C-side. **d** The corresponding enlarged view of the area near the volcano apex of N-side. The different shapes represent different M' , and different colors represent different M'' (red, orange, yellow, green, cyan, blue, purple, and pink represent Ti, V, Cr, Zr, Nb, Mo, Hf, and Ta, respectively).

right branch is the opposite. Moreover, the volcano diagram is employed to characterize the HER activity of the C- and N-side of all 64 $M'_2M''\text{CNO}_2$ -MXenes, as shown in Fig. 5a, b. Here some representative HER catalysts are marked in Fig. 5c, d, such as Pt³³, MoS₂ (ref. ³⁴), WS₂ (ref. ³⁵), C₃N₄ (ref. ³⁶). The profiles indicate that there are 11 $M'_2M''\text{CNO}_2$ -MXenes on the C- or N-side have the better electrocatalytic HER activity than Pt, for the C-side such as Ti₂NbCNO₂, Ti₂VCNO₂, Ti₂HfCNO₂, Mo₂TiCNO₂, Ti₂ZrCNO₂, Ti₂TaCNO₂, and Nb₂TaCNO₂, and for the N-side such as Ta₂NbCNO₂, Ta₂TiCNO₂, Ta₂ZrCNO₂, and Zr₂CrCNO₂. The calculated $|\Delta G_H|$ ranges from 0.071 to 0.003 eV at 1/4 coverage.

Furthermore, the coordinate for the N-side of Ta₂NbCNO₂ with the ΔG_H value of 0.003 eV is very close to the peak of the volcano, meaning that very little overvoltage is required by this material during the HER electrochemical reaction, which indicates its excellent HER activity. Of course, the rest of $M'_2M''\text{CNO}_2$ appeared in Fig. 5c, d also have quite good prospects as HER catalysts, but we will not do much research on them in the follow-up work.

Furthermore, for these 11 $M'_2M''\text{CNO}_2$ -MXenes we preliminary screened, the effect of H coverage on the HER activity is investigated. The C- or N-side of the $2 \times 2 \times 1$ $M'_2M''\text{CNO}_2$ monolayer has four O atoms that can be used as hydrogen

Fig. 6 Top view of the H coverage and the ΔG_H with different H coverage for 11 $M'_2M''CNO_2$ -MXenes. **a** Top view of the H coverage for the C-side of Ti_2ZrCNO_2 . **b** The calculated ΔG_H with different H coverage for the C- or N-side of 11 $M'_2M''CNO_2$ -MXenes.

Table 1. The thermodynamic competitors for 11 candidates selected from the material project database⁴³, and the corresponding formation energy we calculated.

$M'_2M''CNO_2$ -MXenes	Competitors	$E_{\text{formation}}$ (eV/atom)
Mo_2TiCNO_2	MoO_2 , MoN, TiC	-1.934
Nb_2TaCNO_2	NbO_2 , NbN, TaC	1.223
Ti_2NbCNO_2	TiO_2 , TiC, NbN	-0.723
Ti_2HfCNO_2	TiO_2 , TiN, HfC	0.167
Ti_2VCNO_2	TiO_2 , TiC, VN	-0.368
Ti_2TaCNO_2	TiO_2 , TiN, TaC	0.366
Ti_2ZrCNO_2	TiO_2 , TiN, ZrC	0.190
Ta_2NbCNO_2	TaO_2 , TaC, NbN	1.230
Ta_2ZrCNO_2	TaO_2 , TaN, ZrC	0.827
Ta_2TiCNO_2	TaO_2 , TaC, TiN	0.267
Zr_2CrCNO_2	ZrO_2 , ZrC, CrN	1.775

The $M'_2M''CNO_2$ -MXenes with negative formation energy have been highlighted in bold font.

adsorption sites. As shown in Fig. 6a, taking the C-side of Ti_2ZrCNO_2 as an example, the H coverage (θ) of the C-side of Ti_2ZrCNO_2 is 1/4, 1/2, 3/4, and 1, respectively. The relationship between the ΔG_H and H coverage for the 11 $M'_2M''CNO_2$ -MXenes has been shown in Fig. 6b. ΔG_H presents an overall upward tendency with the increase of H coverage. The points in the shadow ($|\Delta G_H| < 0.2$ eV) stand for the MXenes with fit coverage considering to have outstanding HER activity. It can also be understood as the HER active sites of MXenes. Most of the $M'_2M''CNO_2$ -MXenes we screened show HER activity only when the H

coverage is 1/4. It is worth noting that the C-side of Ti_2NbCNO_2 and Ti_2ZrCNO_2 still have HER activity when the H coverage is 2/4, which indicates that there are more HER active sites for them.

Thermodynamic and dynamic stability of $M'_2M''CNO_2$ -MXenes

The stability of the materials is the prerequisite for its synthesis and application. Therefore, the stability of 11 $M'_2M''CNO_2$ -MXenes we have screened is investigated in order to prove that our research objects can be synthesized experimentally. Firstly, the formation energy ($E_{\text{formation}}$) of 11 $M'_2M''CNO_2$ -MXenes is calculated, which could be obtained by subtracting the energy of the 2D MXene from the energy of the most stable competitors with the same number of atoms and stoichiometry³⁷.

As shown in Table 1, there are 3 $M'_2M''CNO_2$ -MXenes with negative formation energy, namely Ti_2NbCNO_2 , Ti_2VCNO_2 , and Mo_2TiCNO_2 , which indicates that these candidates are thermodynamically stable. Furthermore, to check the dynamic stability of the aforementioned 3 $M'_2M''CNO_2$ -MXenes, the canonical ensemble (NVT) ab initio molecular dynamics (AIMD) simulation is performed at 300K for 10 ps, as shown in Fig. 7. The energy of the MXenes fluctuate slightly above and below the average value, and the crystal structures have no obvious deformation (Fig. 7d), indicating the prominent dynamic stability of them. Therefore, we believe that these 3 $M'_2M''CNO_2$ -MXenes are stable and can be synthesized experimentally.

In summary, the HER activity of all 64 $M'_2M''CNO_2$ -MXenes has been performed by well-defined density functional theory calculations. The crystal structure, Gibbs free energy of hydrogen adsorption, and the stability of several MXene candidates are systematically investigated. According to the calculated ΔG_H , the outermost transition metal M' is Ti or Nb, the C-side for most of $M'_2M''CNO_2$ -MXenes exhibit the desired HER activity while the M' is Ta showing better HER activity on the N-side. In addition, the

Fig. 7 **Vibration of energy against time and side view of $\text{Ti}_2\text{NbCNO}_2$.** **a** Vibration of energy against time in AIMD simulation of the $\text{Ti}_2\text{NbCNO}_2$ under 300 K with the time step of 2 fs. **b** Vibration of energy against time in AIMD simulation of the Ti_2VCNO_2 . **c** Vibration of energy against time in AIMD simulation of the $\text{Mo}_2\text{TiCNO}_2$. **d** Side view of $\text{Ti}_2\text{NbCNO}_2$ monolayer after the AIMD simulation.

HER performance of the C- or N-side for 11 $\text{M}'_2\text{M}''\text{CNO}_2\text{-MXenes}$ is even better than that of Pt. More active sites in $\text{Ti}_2\text{NbCNO}_2$ and $\text{Ti}_2\text{ZrCNO}_2$ than that of other candidates result in their excellent HER performance. Moreover, $\text{Ti}_2\text{NbCNO}_2$, $\text{Mo}_2\text{TiCNO}_2$, and Ti_2VCNO_2 are stable HER catalysts proven by examining the thermodynamic and dynamic stability of the candidates. Especially, $\text{Ti}_2\text{NbCNO}_2$ with a small ΔG_{H} value of 0.02 eV, more catalytic sites on the C-side, and better stability can be regarded as the most ideal HER catalyst. In addition, to verify the stability of $\text{Ti}_2\text{NbCNO}_2$ in an acidic environment, the NVT ensemble AIMD simulation is performed at 300 K for 4 ps. The energy oscillate slightly near the equilibrium configuration, and no notable geometric deformation is found (Supplementary Fig. 1), suggesting the excellent stability of $\text{Ti}_2\text{NbCNO}_2$ in an acidic environment.

METHODS

Computational details

All calculations were carried out by employing the Vienna Ab initio Simulation Package (VASP)³⁸. The projector augmented wave (PAW)³⁹ method was employed to explain the interaction between ions and valence electrons, and the exchange-correlation interaction of electrons was handled by the generalized gradient approximation⁴⁰ with Perdew-Burke-Ernzerhof⁴¹ potential. All calculation parameters were selected after the convergence test of the total energy of the system. The cut-off energy of plane wave was set to be 520 eV, the energy and force convergence were selected as 10^{-5} eV and -0.01 eV/Å, respectively. The Grimme's DFT-D3 (ref. ⁴²) method was exerted to effectively rectify the van der Waals interactions. The Brillouin zone of $5 \times 5 \times 1$ k -points mesh created by Monkhorst Pack Scheme were used for the structural optimization, and the Gamma point ($1 \times 1 \times 1$) was employed for the calculation of the zero point energy and AIMD simulations. The $2 \times 2 \times 1$ supercell was applied in computation screening research of HER activity for all MXenes monolayers, and the $4 \times 4 \times 1$ supercell was taken for the AIMD

simulations. In order to avoid interference between MXenes monolayers, at least 15 Å vacuum layer was required in the z -axis direction of all MXenes structural models.

DATA AVAILABILITY

Data will be available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

The initial idea was developed by N.L., Z.Z. and X.C. did the simulation under N.L. supervision. The implementation was discussed with Y.W., K.W., P.Z., and J.J. All authors participated in the data analysis and writing and reading of the paper. N.L. managed the project.

COMPETING INTERESTS

The authors declare no competing interests.

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