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 $M'_2M''CNO_2$ ($M' = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta$; $M'' = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta$) 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$_2$NbCNO$_2$, Mo$_2$TiCNO$_2$, and Ti$_2$VCNO$_2$ are more stable than other candidates. Especially, Ti$_2$NbCNO$_2$ have the potential to be perfect HER catalyst with the small Gibbs free energies of hydrogen adsorption ($\Delta G_h$) 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.

**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$$^{3-5}$, metal phosphides$^{6}$, g-C$_3$N$_4$$^{6-9}$, and chalcogenides$^{10}$, have been extensively studied. However, the poor charge transfer performance$^8$ and restricted active sites$^{1,11}$ 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 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$^{23,24}$, supercapacitors$^{25}$, 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 $M_2CN$ ($M = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta$) by first-principles calculations. Based on the calculation results, they found that only Ti$_2$CNO$_2$ and Nb$_2$CNO$_2$ have potential HER catalytic activity, where the $\Delta G_h$ value of C-side for Ti$_2$CNO$_2$ is $-0.122$ eV, while the $\Delta G_h$ values of C- and N-side for Nb$_2$CNO$_2$ are $-0.117$ and $-0.097$ eV, respectively. For the other transition metal carbonitrides $M_2CN$, the HER activity is not good. Anasori et al.$^{17}$ discovered more than 20 double transition metal carbonitrides $M'_2M''CNO_2$ 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 candidates$^{29}$. Therefore, we tried to construct "sandwich" structure of transition metal carbonitrides $M_2CN$, 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 ($M' = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta$; $M'' = Ti, V, Cr, Zr, Nb, Mo, Hf, Ta$), as well as the stability of some selected MXene candidates. By high-throughput
computational screening, 11 $M'_2M''CNO_2$-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, Ti$_2$NbCNO$_2$, Mo$_2$TiCNO$_2$, and Ti$_2$VCNO$_2$ were identified as highly efficient and more stable HER catalysts, among which Ti$_2$NbCNO$_2$ with the $\Delta G_H$ 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 $M_3CN$ MXenes$^{28}$. 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 terminals$^{31}$. Therefore, we only focus on the properties of O-terminated MXenes in the subsequent researches.

The O-terminated structure of ordered $M'_2M''CNO_2$-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 $M'_2M''CNO_2$-MXene (Fig. 1c), marked as fcc–fcc, fcc–hcp, hcp–fcc, and hcp–hcp. Based on the calculation results, we selected the configurations of $M'_2M''CNO_2$ 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 ($M' = Ti, Zr, Hf$), all of the most stable configurations of $M'_2M''CNO_2$ 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 $M'_2M''CNO_2$.

Specially, there are two different most stable configurations of $M'_2M''CNO_2$ when the outermost transition metals are $d^3$ group elements. The most stable configurations of $M'_2M''CNO_2$ are still fcc–fcc type when $M' = V$ with smaller atomic number, while $M' =
adsorbed hydrogen atoms, and the energy of MXene with \( \Delta E \) under standard conditions. Generally speaking, catalysts with \( |\Delta G| \) lower than 0.2 eV are identified to have HER activity (the closer the value of \( |\Delta G| \) to zero, the higher is the HER activity). \( \Delta G \) with high positive value denotes strong hindrance for the electrochemical reduction reaction; on the contrary, \( \Delta G \) 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 \( \text{M}'\text{M}''\text{CNO}_2 \) is different, \( \Delta G \) is calculated on both C- and N-side of all 64 \( \text{M}'\text{M}''\text{CNO}_2 \)-MXenes in our study, as shown in Supplementary Tables 2 and 3. The diagonal of the heat map is chosen to reflect the strong adsorption between H atom and the catalyst, while the Nb or Ta become fcc–hcp type. When the outermost transition metals are \( d^0 \) group elements (\( M' = \text{Cr}, \text{Mo} \)), the most stable configurations of \( \text{M}_2\text{M}'\text{CNO}_2 \) are irregular and diverse. In addition, the lattice parameters of \( \text{M}_2\text{M}''\text{CNO}_2 \) are shown in Supplementary Table 1; the data are in good agreement with the previous results.**

HER activity screening of \( \text{M}_2\text{M}'\text{CNO}_2 \)

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

\[
\Delta G = \Delta E + \Delta E_{ZPE} - T \Delta S
\]

where \( \Delta E \) represents the adsorption energy of hydrogen, \( \Delta E_{ZPE} \) and \( \Delta S \) are the difference in zero point energy (ZPE) and the entropy between the hydrogen adsorbed state and gas phase, respectively. The \( \Delta E_{ZPE} \) is defined as

\[
\Delta E_{ZPE} = E_{ZPE}(nH) - E_{ZPE}((n-1)H) - 1/2E_{ZPE}(H_2)
\]

where \( E_{ZPE}(nH) \) and \( E_{ZPE}((n-1)H) \) denote the zero point energy of MXene with \( n \) and \( n-1 \) adsorbed hydrogen atoms, respectively. \( E_{ZPE}(H_2) \) represents the zero point energy of H2 in gas conditions. \( \Delta S \) is approximately equal to the entropy of gas phase H2 under standard conditions. Generally speaking, catalysts with \( |\Delta G| \) lower than 0.2 eV are identified to have HER activity (the closer the value of \( |\Delta G| \) to zero, the higher is the HER activity). \( \Delta G \) with high positive value denotes strong hindrance for the electrochemical reduction reaction; on the contrary, \( \Delta G \) 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 \( \text{M}_2\text{M}'\text{CNO}_2 \) is different, \( \Delta G \) is calculated on both C- and N-side of all 64 \( \text{M}_2\text{M}'\text{CNO}_2 \)-MXenes in our study, as shown in Supplementary Tables 2 and 3. The diagonal of the heat map is chosen to reflect the strong adsorption between H atom and the catalyst, while the
The 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 $M'_2M''_2CNO_2$-MXenes, as shown in Fig. 5a, b. Here some representative HER catalysts are marked in Fig. 5c, d, such as Pt, MoS$_2$ (ref. 34), WS$_2$ (ref. 35), C$_3$N$_4$ (ref. 36). The profiles indicate that there are 11 $M'_2M''_2CNO_2$-MXenes on the C- or N-side have the better electrocatalytic HER activity than Pt, for the C-side such as Ti$_2$NbCNO$_2$, Ti$_2$VCNO$_2$, Ti$_2$HfCNO$_2$, Mo$_2$TiCNO$_2$, Ti$_2$ZrCNO$_2$, Ti$_2$TaCNO$_2$, and Nb$_2$TaCNO$_2$, and for the N-side such as Ta$_2$NbCNO$_2$, Ta$_2$TiCNO$_2$, Ta$_2$ZrCNO$_2$, and Zr$_2$CrCNO$_2$. 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 Ta$_2$NbCNO$_2$ with the $\Delta G_H$ 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 $M'_2M''_2CNO_2$ 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 $M'_2M''_2CNO_2$-MXenes we preliminary screened, the effect of H coverage on the HER activity is investigated. The C- or N-side of the $2 \times 2 \times 1$ $M'_2M''_2CNO_2$ monolayer has four O atoms that can be used as hydrogen donors.
adsorption sites. As shown in Fig. 6a, taking the C-side of Ti₂ZrCNO₂ as an example, the H coverage (θ) of the C-side of Ti₂ZrCNO₂ is 1/4, 1/2, 3/4, and 1, respectively. The relationship between the ΔG_θ and H coverage for the 11 M′₂M″CNO₂-MXenes has been shown in Fig. 6b. ΔG_θ presents an overall upward tendency with the increase of H coverage. The points in the shadow (|ΔG_θ| < 0.2 eV) stand for the MXenes with fitting coverage considering to have outstanding HER activity. It can also be understood as the HER active sites of MXenes. Most of the M′₂M″CNO₂-MXenes we screened show HER activity only when the H coverage is 1/4. It is worth noting that the C-side of Ti₂NbCNO₂ and Ti₂ZrCNO₂ 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″CNO₂-MXenes

The stability of the materials is the prerequisite for its synthesis and application. Therefore, the stability of 11 M′₂M″CNO₂-MXenes we have screened is investigated in order to prove that our research objects can be synthesized experimentally. Firstly, the formation energy (E_{formation}) of 11 M′₂M″CNO₂-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 stoichiometry^{37}.

| M′₂M″CNO₂-MXenes | Competitors | E_{formation} (eV/atom) |
|-------------------|-------------|-------------------------|
| Mo₂TiCNO₂         | MoO₂, MoN, TiC | −1.934                  |
| Nb₂TaCNO₂         | NbO₂, NbN, TaC | 1.223                   |
| TiₙNbCNO₂         | TiO₂, TiC, NbN | −0.723                  |
| TiₙHfCNO₂         | TiO₂, TiN, HfC | 0.167                   |
| TiₙVCNO₂          | TiO₂, TiC, VN  | −0.368                  |
| Ta₂TaCNO₂         | TaO₂, TaC, NbN | 1.230                   |
| Ta₂ZrCNO₂         | TaO₂, TaN, ZrC | 0.827                   |
| Zr₂CrCNO₂         | ZrO₂, ZrC, CrN | 0.267                   |

The M′₂M″CNO₂-MXenes with negative formation energy have been highlighted in bold font.

As shown in Table 1, there are 3 M′₂M″CNO₂-MXenes with negative formation energy, namely Ti₂NbCNO₂, Ti₂VCNO₂, and Mo₂TiCNO₂, which indicates that these candidates are thermodynamically stable. Furthermore, to check the dynamic stability of the aforementioned 3 M′₂M″CNO₂-MXenes, the canonical ensemble (NVT) ab initio molecular dynamics (AIMD) simulation is performed at 300 K 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″CNO₂-MXenes are stable and can be synthesized experimentally.

In summary, the HER activity of all 64 M′₂M″CNO₂-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_θ, the outermost transition metal M′ is Ti or Nb, the C-side for most of M′₂M″CNO₂-MXenes exhibit the desired HER activity while the M′ is Ta showing better HER activity on the N-side. In addition, the
HER performance of the C- or N-side for 11 M″M′CNO2-MXenes is even better than that of Pt. More active sites in Ti2NbCNO2 and Ti2ZrCNO2 than that of other candidates result in their excellent HER performance. Moreover, Ti2NbCNO2, Mo2TiCNO2, and Ti2VCNO2 are stable HER catalysts proven by examining the thermodynamic and dynamic stability of the candidates. Especially, Ti2NbCNO2 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 Ti2NbCNO2 in an acidic environment, the NVT ensemble AIMD simulation is performed at 300 K for 4 ps. The energy oscillates slightly near the equilibrium configuration, and no notable geometric deformation is found (Supplementary Fig. 1), suggesting the excellent stability of Ti2NbCNO2 in an acidic environment.

METHODS
Computational details
All calculations were carried out by employing the Vienna Ab initio Simulation Package (VASP). The projector augmented wave (PAW) 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 approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) 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 method was exerted to effectively rectify the van der Waals interactions. The Brillouin zone of 5 × 5 × 1 k-points mesh created by Monkhorst Pack Scheme were used for the structural optimization, and the Gamma point (1 × 1 × 1) was employed for the calculation of the zero point energy and AIMD simulations. The 2 × 2 × 1 supercell was applied in computation screening research of HER activity for all MXenes monolayers, and the 4 × 4 × 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.

ADDITIONAL INFORMATION

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