Double Transition Metal Carbides MXenes (D-MXenes) as Promising Electrocatalysts for Hydrogen Reduction Reaction: Ab Initio Calculations

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ABSTRACT: Double-transition-metal MXenes (D-MXenes) have been widely pursued in the advancement of the renewable energy storage technology in recent years. In this work, the hydrogen evolution reaction (HER) catalytic mechanism of several oxygen-terminated D-MXenes with the chemical formula of $M'^2M''C_2O_2$ ($M' = Mo, Cr; M'' = Ti, V, Nb, Ta$) is theoretically studied. For comparison, the corresponding monometallic MXenes (M-MXenes, $M'C_2O_2$) are fairly compared by means of the density functional theory calculations. Based on our theoretical results, the HER performance of M-MXenes can be improved by constructing a "sandwich-like" ordered D-MXene configuration. Moreover, the HER performance of Mo-based D-MXenes ($Mo_2M''C_2O_2$) is superior to that of Cr-based D-MXenes ($Cr_2M''C_2O_2$), which highlights that the HER activity of $Mo_2V_2C_2O_2$ and $Mo_2NbC_2O_2$ is better than that of $Pt(111)$. This work not only unravels the HER mechanism of D-MXenes ($M'_2M''C_2O_2$) but also paves the way in designing emergent MXene-based HER electrocatalysts with high efficiency.

INTRODUCTION

In recent decades, the long-standing issues to attain a sustainable future on a clean and renewable energy resource have remained elusive. A potential candidate has gained a favor in terms of the energy field research, such as hydrogen energy, as it offers a high energy density and a green energy source. It has been considered that this effort to utilize hydrogen as a storage material could be a promising alternative to reduce the global fossil consumption. The electrocatalytic hydrogen evolution reaction (HER) plays an increasingly important role to enhance the development of hydrogen energy economy.\cite{1,2} Recently, several emerging MXenes have garnered increasing attention within the communities owing to their excellent structural and chemical characteristics, such as high metal conductivity, a large specific surface area, an adjustable molecular structure, and diverse chemical compositions.\cite{3-5}

The MXene fabrication is commonly obtained by etching A-layer atoms in the MAX ceramic phase in which the general chemical formula is stated as $M_{n+1}X_nT_x$, where $M$ refers to early transition-metal elements; $X$ refers to carbon and/or nitrogen; $n = 1, 2, 3$; and $T_x$ stands for surface termination. MXenes have been widely used as the active materials for the electrochemical energy storage,\cite{6} nanodevices,\cite{7} electrocatalysts,\cite{8} and other fields.\cite{6} It is worth noting that the MXenes can also be used as the electrocatalysts for water splitting via HER.\cite{9} Currently, there are more than 20 types of MXenes that have been successfully synthesized through experiments and theoretical calculations. There is a prediction that a large number of monometallic MXenes (M-MXenes) can be theoretically feasible to be synthesized.\cite{10,11} These materials have shown promising HER performance with a simplified design of MXenes.\cite{12,13}

In addition, when the transition-metal (M) component of MXenes is replaced with two different metal elements, then the structures can be defined as double-transition-metal MXenes (D-MXenes) with the chemical formula of $(M'M'')_{n1}X_nT_x$ ($M'$ and $M''$ refer to different metal elements). D-MXenes are divided into two types, solid-solution-type D-MXenes and ordered-type D-MXenes, which can be differentiated from different metal atom arrangements within the MXene lattices. The former case has two metal elements that are randomly arranged in the M layer without a well-defined stoichiometric

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constant, while the latter case comprises the alteration between two distinct metal layers and non-metal atomic layers that are stacked under the lowest energy state composition. Anasori et al. used density functional theory (DFT) calculations to compare the characteristics of two different types of D-MXenes. The calculated results suggest that when similar transition-metal elements are included for the MXene structure, the ordered-type D-MXenes are thermodynamically more stable than the solid-solution-type D-MXenes. Through high-throughput screening, they have discovered that 10 D-MXenes' structures can form complete ordered “sandwich-like” MXenes.

The ordered D-MXenes can exist in two different forms: (a) o-MXenes, where one transition metal occupies the perimeter layers and the other metal occupies the central M layers, and (b) i-MXenes, where one transition metal forms a honeycomb pattern and the other metal occupies the center of the honeycomb. Compared with M-MXenes, the ordered D-MXenes have unique physical and chemical properties. On the basis of theoretical investigation for the past few years, the fabrication of the “sandwich-like” structure is an effective way to promote the catalytic performance of 2D layered materials.

In this work, the structural models of eight ordered D-MXenes (M′,M′′C2O2) are constructed and their catalytic mechanism in relation to the HER is investigated using ab initio calculations. By comparing the HER activity of D-MXenes and the M-MXene counterparts, we shed light into the role of the “sandwich” configuration of MXenes on their HER catalytic performance. In addition, we found that Mo-based D-MXenes (Mo2M′′C2O2) promote higher HER performance than the Cr-based D-MXenes. Moreover, we also discussed the effects of the oxygen terminal adsorption site and hydrogen coverage on the HER catalytic performance of ordered D-MXenes.

COMPUTATIONAL DETAILS

The ab initio thermodynamic method allows a rapid screening of the parameter space to determine material properties with a reasonable accuracy, and it has a low computational cost compared with the kinetic aspects of the reaction. The ab initio thermodynamics is also often used to understand the activity and mechanism of electrochemical reactions. Therefore, we used the ab initio approach in our work. The theoretical calculations were carried out using the Vienna ab initio simulation package (VASP 5.3.5) under the framework of well-defined DFT. The interaction between the ion real and valence electron was described using the projector augmented wave method, and the Perdew–Burke–Ernzerhof functional with the generalized gradient approximation was used to describe the exchange–correlation interactions of electrons. The cutoff energy was set to 450 eV, and the tolerance of energy precision of 10−5 eV and a force convergence of 0.02 eV Å−1 were employed to determine the structural geometric optimization. The Monkhorst–Pack method was used to sample the Brillouin region. The k-points of 7 × 7 × 1 and 1 × 1 × 1 were used for structure geometric optimization and the zero-point energy (ZPE) calculations. ZPE is calculated by frequency calculations. The van der Waals forces in the MXene structure were modified effectively by Grimme’s DFT-D3 method. The 2 × 2 × 1 supercells were selected for the DFT calculations, following the examples of similar studies in the literature. A vacuum layer of 15 Å was introduced along the Z-axis direction of the reported MXene structural models in this study.

Generally, there are two mechanisms in the HER response, namely, the Volmer–Tafel and Volmer–Heyrovsky mechanisms. However, the energy barrier of the Volmer–Tafel mechanism is too high for computation work; therefore, the Volmer–Heyrovsky mechanism is used in our calculations. The
Gibbs free energy of hydrogen adsorption (Δ\(G^*_H\)) is used to evaluate the HER activity of materials, and it can be defined as eq 1:

\[
\Delta G^*_H = \Delta E^*_H + \Delta ZPE^*_H - T\Delta S^*_H
\]

where \(\Delta E^*_H\) stands for the adsorption energy of H-atoms on the surface of MXenes, \(\Delta ZPE^*_H\) is the corrective value taking into account different phase states of hydrogen atoms, and \(\Delta S^*_H\) is approximately equal to half of the entropy of gas-phase H\(_2\) under standard conditions. The entropy of gas-phase H\(_2\) under standard conditions is a constant and can be obtained directly from the literature. \(\Delta E^*_H\) was computed by eq 2:

\[
\Delta E^*_H = E(\text{MXene} + (n + 1)H) - 1/2E(H_2) - E(\text{MXene} + nH)
\]

where \(E(\text{MXene} + (n + 1)H)\) and \(E(\text{MXene} + nH)\) refer to the total energies of MXenes with \(n + 1\) and \(n\) adsorbed hydrogen atoms, respectively. \(E(H_2)\) stands for the energy of H\(_2\) in the gas phase. The \(\Delta ZPE^*_H\) was obtained by eq 3:

\[
\Delta ZPE^*_H = ZPE(\text{MXene} + (n + 1)H) - 1/2ZPE(H_2) - ZPE(\text{MXene} + nH)
\]

where \(ZPE(\text{MXene} + (n + 1)H)\) and \(ZPE(\text{MXene} + nH)\) represent the zero-point energy of adsorbed \(n + 1\) and \(n\) hydrogen atoms on the MXenes, respectively. \(ZPE(H_2)\) stands for the zero-point energy of H\(_2\) under gas conditions.

**RESULTS AND DISCUSSION**

**Geometric Structure of Ordered D-MXenes.** Here in our study, the ordered D-MXene structure model is constructed by replacing the inner metallic layer with the other atoms such as Ti, V, Nb, and Ta, taking into account the crystal structures of the M-MXenes (Mo\(_3\)C\(_2\) and Cr\(_3\)C\(_2\)) as references. Figure 1a–d shows the geometric structures of the “sandwich-like” ordered D-MXenes (\(M'_{2}M''C_2\)) where \(M'\) stands for Mo and Cr and \(M''\) represents four transition-metal elements such as Ti, V, Nb, and Ta, and X refers to C. The 2D MXene surface formed by HF etching is highly chemically active and therefore easily passivated by functional groups (−O, −OH, or −F). To understand how the surface terminations of D-MXenes change as a function of applied potential and pH values, the surface Pourbaix diagram of Mo\(_2\)NbC\(_2\) is constructed, as shown in Figure S1. In addition, the recent theoretical studies show that the surface functional groups of MXenes can be completely transformed into a full decoration of O-functional groups after heating treatment. Based on these previous works, we investigate the catalytic performance of O-terminal MXenes in this study. In order to simplify the theoretical variables, we consider that the O-functional groups decorated in the upper and lower surfaces of MXenes are fully adsorbed (the coverage

| \(M'_{2}M''C_2\) | \(a\) (Å) | thickness (Å) | \(M'_{2}M''C_2O_2\) | \(a\) (Å) | thickness (Å) | O adsorption site |
|-----------------|-------|-------------|-----------------|-------|-------------|-----------------|
| Cr\(_2\)C\(_2\) | 2.82  | 4.46        | Cr\(_2\)C\(_2O_2\) | 2.76  | 7.15        | HCP             |
| Cr\(_2\)TiC\(_2\) | 2.89  | 4.65        | Cr\(_2\)TiC\(_2O_2\) | 2.81  | 7.25        | HCP             |
| Cr\(_2\)VC\(_2\) | 2.84  | 4.55        | Cr\(_2\)VC\(_2O_2\) | 2.79  | 7.17        | HCP             |
| Cr\(_2\)NbC\(_2\) | 2.96  | 4.74        | Cr\(_2\)NbC\(_2O_2\) | 2.96  | 6.91        | FCC             |
| Cr\(_2\)TaC\(_2\) | 2.94  | 4.75        | Cr\(_2\)TaC\(_2O_2\) | 2.97  | 6.86        | FCC             |
| Mo\(_2\)C\(_2\) | 3.01  | 4.87        | Mo\(_2\)C\(_2O_2\) | 2.92  | 7.79        | HCP             |
| Mo\(_2\)TiC\(_2\) | 2.97  | 4.98        | Mo\(_2\)TiC\(_2O_2\) | 2.91  | 7.60        | HCP             |
| Mo\(_2\)VC\(_2\) | 2.94  | 4.81        | Mo\(_2\)VC\(_2O_2\) | 2.91  | 7.48        | HCP             |
| Mo\(_2\)NbC\(_2\) | 3.04  | 5.00        | Mo\(_2\)NbC\(_2O_2\) | 2.98  | 7.77        | HCP             |
| Mo\(_2\)TaC\(_2\) | 3.02  | 4.99        | Mo\(_2\)TaC\(_2O_2\) | 2.96  | 7.77        | HCP             |
rate is 100%). As shown in Figure 1a, b, there are three available adsorption sites for the O-functional groups on the MXene surface, namely, TOP sites, FCC sites, and HCP sites. The TOP sites indicate that the O-functional groups are adsorbed on top of the outermost metal atom of MXenes. The FCC sites indicate that the O-functional group adsorption position is directly above the metal atomic layer of the innermost layer of MXenes, and the HCP sites refer to the O-functional groups that are adsorbed directly above the C-atom at the outmost layer of the MXene structure as shown in Figure S2. We consider that the adsorption sites of O-functional groups adsorbed on the upper and lower surfaces of MXenes are invariant.

Further, we compare the adsorption energy of the three adsorption sites of O-functional groups on the surface of MXenes. The adsorption site with the lowest energy is proposed as the optimum site of O-functional groups on the surface of MXenes. The calculated lattice parameters and the adsorption sites of O-groups on the surface of the optimized ordered D-MXenes and the two corresponding M-MXenes are shown in Table 1. The lattice constants of Mo$_3$C$_2$ and Cr$_3$C$_2$ are 3.01 and 2.82 Å, respectively, which indicate that a strong interaction is realized between the O-groups and the absorbed H* on the MXene surface. In terms of the other Cr$_3$M$^*$C$_2$O$_2$, such as Cr$_3$TiC$_2$O$_2$, Cr$_3$VC$_2$O$_2$, and Cr$_3$CrC$_2$O$_2$, we found that the values of $|\Delta G_{\text{HH}}|$ are less than 1.0 eV, indicating that their HER performance is higher than those of Cr$_3$NbC$_2$O$_2$ and Cr$_3$TaC$_2$O$_2$. To illustrate the description, we find that the O-groups in Cr$_3$NbC$_2$O$_2$ and Cr$_3$TaC$_2$O$_2$ tend to adsorb at the FCC sites, while in the other type of Cr$_3$M$^*$C$_2$O$_2$, the O-groups are adsorbed on the HCP sites. We denote that the O-groups located at the FCC sites have a higher adsorption energy between the O-groups and absorbed H*, and consequently, the absorbed H-atoms are tightly bound, which create a low HER activity. However, MXenes whose O-groups are located at the HCP sites demonstrate a promising HER activity.

Let us consider the case of D-MXenes where M$^*$ = Mo; the $|\Delta G_{\text{HH}}|$ values of Mo$_3$M$^*$C$_2$O$_2$ and Mo$_3$O$_2$ are less than 0.3 eV. The $\Delta G_{\text{HH}}$ values of Mo$_3$VC$_2$O$_2$, Mo$_3$NbC$_2$O$_2$, and Mo$_3$TaC$_2$O$_2$ are $-0.078$, $-0.005$, and $0.095$ eV, respectively, which are comparable to those of the reference materials such as Pt(111).$^{24}$ The results suggest that Mo-based ordered D-MXenes exhibit excellent HER activity and these materials can be considered as the promising HER catalysts. In addition, it is worth noting that the O-functional groups of the Mo-based ordered D-MXenes tend to be adsorbed on the HCP site. This further supports our hypothesis that the O-functional-group-decorated MXenes that adsorbed on the HCP sites have better HER catalytic performance than the FCC counterparts. Overall, based on the calculation results of the $\Delta G_{\text{HH}}$, the Mo-based MXenes have a better HER activity than the Cr-based MXenes. By comparing the HER activity of the ordered D-MXenes with the corresponding M-MXenes, we found that the $|\Delta G_{\text{HH}}|$ value of the latter is larger than the corresponding ordered D-MXenes (except for Cr$_3$NbC$_2$O$_2$ and Cr$_3$TaC$_2$O$_2$). According to the calculation results, we postulate that the “sandwich-like” structure of MXenes can be useful for improving their HER activity by the internal metal layer incorporation with other transition-metal atoms.

The HER activity of the catalysts can be presented by means of the volcano map as shown in Figure 3. The absissa represents the $\Delta G_{\text{HH}}$, and the ordinate represents the overpotential ($\eta = \pm \Delta G_{\text{HH}}/e_0$). Here, we denote that the data points located on the left and right branches of the volcano map of Cr$_2$M$^*$C$_2$O$_2$...
represent the strong and weak adsorption sites of H-atoms, respectively, depicted in Figure 3a. One can also find that Mo-based MXenes (the filled red dot) have better HER activity than Cr-based MXenes (the filled purple dot). Figure 3b shows an enlarged detail at the vicinity of the volcano peak. For comparison, we included several representative HER catalysts, including Pt,32 MoS2,33 and WS2.34 Similarly, the coordinate positions of the ordered D-MXenes are closer to the peak than that of the M-MXenes, which strengthen our hypothesis where the “sandwich-like” MXenes effectively improve the HER activity. It can be seen that two M-MXenes and the most ordered D-MXenes are located on the left side of the volcano map, which suggests strong interactions between the O-groups and H*. For D-MXenes such as Mo2VC2O2, Mo2NbC2O2, and Mo2TaC2O2, we found that their relative positions with respect to the volcano peak are closer than Pt, indicating that the required overpotential to facilitate the catalytic HER is negligible, exhibiting a superior HER activity. In addition, the coordinate position of Mo2TiC2O2 is close to WS2, which indicates its good prospect for the HER catalyst applications.

We further discuss the effect of H-coverage on the HER performance of MXenes outlined in Figure 4. We note that 2 × 2 × 1 MXene monolayers have four sites occupied by O-atoms, and this can be used for the hydrogen adsorption sites. As shown in Figure 4a–d, the H-coverages (θ) of ordered D-MXenes vary from 1/4, 1/2, 3/4, and 1, respectively. The calculation results of the ΔG_H* are taken into account for different H-coverages outlined in Figure 5.

The catalytic active site represents the site on the surface of MXenes where HER can be carried out. Therefore, the more active sites the catalyst has, the stronger its catalytic performance will be. The points in the shadow region (|ΔG_H*| < 0.2 eV) stand for the MXenes with an outstanding HER activity under suitable H-coverage. Under different H-coverages, the more the points in the shadow, the more the active sites of the MXene for HER catalysis. The value of ΔG_H* shows an upward trend as a function of the H-atom coverages. In the case of Mo-based MXenes, when the H-coverages reach 1/4 from the total surface area, consequently, the MXenes are expected to show a promising HER activity. On the contrary, the H-coverage requirement is 1/2 for the case of Cr-based MXenes. The Mo-based M-MXene (Mo3C2) has no HER activity at any H-coverage within the boundary theoretical limit, while the Mo-based D-MXenes (Mo2VC2O2, Mo2NbC2O2, and Mo2TaC2O2) showed an ideal HER activity at a 1/4 H-coverage, indicating that Mo-based D-MXenes have more active sites than the monometallic ones. Thus, we hypothesize that the presence of the “sandwich-like” configuration increases the available catalyst active sites; thereby, this tunable effort would increase the HER activity of MXenes significantly.

■ CONCLUSIONS

In summary, the HER activities of eight ordered D-MXenes and two corresponding M-MXenes are investigated by means of DFT calculations. Under the geometric structural optimizations, we found that the Gibbs free energy of hydrogen adsorptions and H-coverages display an intimate relationship to the HER activity of MXenes. The results infer that the “sandwich-like” ordered D-MXenes effectively promote the HER performance of M-MXenes. The ΔG_H* values of Mo-based MXenes, such as Mo2VC2O2, Mo2NbC2O2, and Mo2TaC2O2, are closer to 0 eV (the ideal value) than those of the Cr-based MXene, indicating that Mo-based MXenes have a better HER activity than the Cr-based MXenes. In addition, the adsorption sites of O-functional
groups of D-MXenes greatly affect the HER activity. Moreover, our theoretical study implies that the O-functional groups occupying the HCP sites facilitate an improved HER catalytic performance than the FCC sites. We also have demonstrated that the HER activity of D-MXenes is tunable by modulating the H-coverages. This effect provides a promising theoretical guidance for the experimentalist toward the utilization of HERs with high efficiency to come.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c00870.

Calculated surface Pourbaix diagrams of Mo$_2$NbC$_2$ showing the most stable terminations on the surface at specific potentials and pH values and side view of FCC and HCP sites for O-terminal double MXenes (M’;M’C$_2$O$_y$) (PDF)

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Notes
The authors declare no competing financial interest.

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**REFERENCES**

1. Rather, R. A.; Singh, S.; Pal, B. Visible and direct sunlight induced H$_2$ production from water by plasmonic Ag-TiO$_2$ nanorods hybrid interface. *Sol. Energy Mater. Sol. Cells* **2017**, *160*, 463–469.

2. Prakash, A.; Dan, M.; Yu, S.; Wei, S.; Li, Y.; Wang, F.; Zhou, Y. In$_{S_x}$Cu$_{S_{1-x}}$ nanocomposite: an excellent visible light photocatalyst for H$_2$ production from H$_2$S. *Sol. Energy Mater. Sol. Cells* **2018**, *180*, 205–212.

3. Naguib, M.; Mashtalir, O.; Carle, J.; Presser, V.; Lu, J.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. Two-dimensional transition metal carbides. *ACS Nano* **2012**, *6*, 1322–1331.

4. Halim, J.; Lukatskaya, M. R.; Cook, K. M.; Lu, J.; Smith, C. R.; Näslund, L.-Å.; May, S. J.; Hultman, L.; Gogotsi, Y.; Eklund, P.; Barsoum, M. W. Transparent conductive twodimensional titanium carbide epitaxial thin films. *Chem. Mater.* **2014**, *26*, 2374–2381.

5. Xu, Q.; Ding, L.; Wen, Y.; Yang, W.; Zhou, H.; Chen, X.; Street, J.; Zhou, A.; Ong, W.-J.; Li, N. High photoluminescence quantum yield of 18.7% by using nitrogen-doped Ti$_2$C$_2$ MXene quantum dots. *J. Mater. Chem. C* **2018**, *6*, 6360–6369.

6. Naguib, M.; Halim, J.; Lu, J.; Cook, K. M.; Hultman, L.; Gogotsi, Y.; Barsoum, M. W. New two-dimensional niobium and vanadium carbides as promising materials for Li-ion batteries. *J. Am. Chem. Soc.* **2013**, *135*, 15966–15969.

7. Chen, J.; Chen, K.; Tong, D.; Huang, Y.; Zhang, J.; Xue, J.; Huang, Q.; Chen, T. CO$_2$ and temperature dual responsive “Smart” MXene phases. *Chem. Commun.* **2015**, *51*, 314–317.

8. Ling, C.; Shi, L.; Ouyang, Y.; Wang, J. Searching for highly active catalysts for hydrogen evolution reaction based on O-terminated MXenes through a simple descriptor. *Chem. Mater.* **2016**, *28*, 9026–9032.

9. Peng, J.; Chen, X.; Ong, W.-J.; Zhao, X.; Li, N. Surface and heterointerface engineering of 2D MXenes and their nanocomposites: insights into electro-and photocatalysis. *Chem. 2019*, *5*, 18–50.

10. Ding, B.; Ong, W.-J.; Jiang, J.; Chen, X.; Li, N. Uncovering the electrochemical mechanisms for hydrogen evolution reaction of heteroatom doped M,C MXene (M = Ti, Mo). *Appl. Surf. Sci.* **2020**, *500*, 143987.

11. Anasori, B.; Lukatskaya, M. R.; Gogotsi, Y. 2D metal carbides and nitrides (MXenes) for energy storage. *Nat. Rev. Mater.* **2017**, *2*, 16098.

12. Seh, Z. W.; Fredrickson, K. D.; Anasori, B.; Kibsgaard, J.; Strickler, A. L.; Lukatskaya, M. R.; Gogotsi, Y.; Jaramillo, T. F.; Vojvodic, A. Two-dimensional molybdenum carbide (MXene) as an efficient electrocatalyst for hydrogen evolution. *ACS Energy Lett.* **2016**, *1*, 589–594.
Dimensional transition-metal carbonitrides (MXenes). Electrochemical hydrogen evolution reaction mechanism on two- and theoretical trends. Metal phosphide catalyst for hydrogen evolution using experimental Abild-Pedersen, F.; Jaramillo, T. F. Designing an improved transition hydrogen evolution. Anniversary article: MXenes: a new family of two-dimensional materials. Allwood, D. A. Sulfur-depleted monolayered molybdenum disulfide edges for superior hydrogen-evolution electrocatalysis. Two-dimensional Mo1.33C MXene with divacancy ordering prepared from parent 3D laminate with in-plane chemical ordering.

Screening study. Catalysts for electrochemical hydrogen evolution: A computational approach. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54, 11169.

(17) Exner, K. S.; Over, H. Kinetics of electrocatalytic reactions from first-principles: a critical comparison with the ab initio thermodynamics approach. Acc. Chem. Res. 2017, 50, 1240–1247.

(18) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 1758.

(20) Blochl, P. E. Projector augmented-wave method. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953.

(21) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation. Phys. Rev. B: Condens. Matter Mater. Phys. 1992, 46, 6671.

(22) Perdew, J. P.; Wang, Y. Accurate and simple analytic representation of the electron gas correlation energy. Phys. Rev. B: Condens. Matter Mater. Phys. 1992, 45, 12443.

(23) Grimme, S. Semiempirical GGA-type density functional constructed with a longrange dispersion correction. J. Comput. Chem. 2006, 27, 1787–1799.

(24) Gao, G.; O’Mullane, A. P.; Du, A. 2D MXenes: a new family of promising catalysts for the hydrogen evolution reaction. ACS Catal. 2017, 7, 494–500.

(25) Jin, D.; Johnson, L. R.; Raman, A. S.; Ming, X.; Gao, Y.; Du, F.; Wei, Y.; Chen, G.; Vojvodic, A.; Gogotsi, Y.; Meng, X. Computational Screening of 2D Ordered Double Transition-Metal Caricides (MXenes) as Electrocatalysts for Hydrogen Evolution Reaction. J. Phys. Chem. C 2020, 124, 10584–10592.

(26) Huang, Z.; Luo, W.; Ma, L.; Yu, M.; Ren, X.; He, M.; Polen, S.; Click, K.; Garrett, B.; Lu, J.; Amine, K.; Hadad, C.; Chen, W.; Asthagiri, A.; Yu, Y. Dimeric [Mo2S12]2− cluster: a molecular analogue of MoS2 edges for superior hydrogen-evolution electrocatalysis. Angew. Chem., Int. Ed. 2015, 54, 15181–15185.

(27) Kibsgaard, J.; Tsai, C.; Chan, K.; Benck, J. D.; Nørskov, J. K.; Abild-Pedersen, F.; Jaramillo, T. F. Designing an improved transition metal phosphide catalyst for hydrogen evolution using experimental and theoretical trends. Energy Environ. Sci. 2015, 8, 3022–3029.

(28) Huang, B.; Zhou, N.; Chen, X.; Ong, W. J.; Li, N. Insights into the electrocatalytic hydrogen evolution reaction mechanism on twodimensional transition-metal carbonitrides (MXene). Chem.—Eur. J. 2018, 24, 18479–18486.

(29) Naguib, M.; Mochalin, V. N.; Barsoum, M. W.; Gogotsi, Y. 25th anniversary article: MXenes: a new family of two-dimensional materials. Adv. Mater. 2014, 26, 992–1005.

(30) Pandey, M.; Thygesen, K. S. Two-dimensional MXenes as catalysts for electrochemical hydrogen evolution: A computational screening study. J. Phys. Chem. C 2017, 121, 13593–13598.

(31) Azoﬁa, L. M.; Li, N.; MacFarlane, D. R.; Sun, C. Promising prospects for 2D d0−d1 M3C2 transition metal carbides (MXenes) in N2 capture and conversion into ammonia. Energy Environ. Sci. 2016, 9, 2545–2549.

(32) Nørskov, J. K.; Bligaard, T.; Logadottir, A.; Kitchin, J.; Chen, J. G.; Pandelov, S.; Stimming, U. Trends in the exchange current for hydrogen evolution. J. Electrochem. Soc. 2005, 152, J23–J26.

(33) Lin, L.; Miao, N.; Wen, Y.; Zhang, S.; Ghosez, P.; Sun, Z.; Allwood, D. A. Sulfur-depleted monolayered molybdenum disulfide nanocrystals for superelectrochemical hydrogen evolution reaction. ACS Nano 2016, 10, 8929–8937.