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Structure-activity correlation of Ti_2CT_2 MXenes for C–H activation

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Abstract

As a burgeoning class of 2D materials, MXenes have recently attracted significant attention within heterogeneous catalysis for promoting reactions such as hydrogen evolution and C–H activation. However, the catalytic activity of MXenes is highly dependent on the structural configuration including termination groups and their distribution. Therefore, understanding the relation between the structure and the activity is desired for the rational design of MXenes as high-efficient catalysts. Here, we present that the correlation between the structure and activity of Ti_2CT_2 (T is a combination of O, OH and/or F) MXenes for C–H activation can be linked by a quantitative descriptor: the hydrogen affinity (E_H). A linear correlation is observed between the mean hydrogen affinity and the overall ratio of O terminations (x_O) in Ti_2CT_2 MXenes, in which hydrogen affinity increases as the x_O decreases, regardless to the species of termination groups. In addition, the hydrogen affinity is more sensitive to the presence of OH termination than F terminations. Moreover, the linear correlation between the hydrogen affinity and the activity of Ti_2CT_2 MXenes for C–H activation of both $-\text{CH}_3$ and $-\text{CH}_2-$ groups can be extended to be valid for all three possible termination groups. Such a correlation provides fast prediction of the activity of general Ti_2CT_2 MXenes, avoiding tedious activation energy calculations. We anticipate that the findings have the potential to accelerate the development of MXenes for heterogeneous catalysis applications.

Keywords: MXenes, heterogeneous catalysis, hydrogen affinity, dehydrogenation, C–H activation

Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

Introduction

In the chemical industry, light olefins (C_1 to C_6) are considered as important building blocks for the synthesis of organic components [1]. Recently, such building blocks have

registered a rapid growth on the global trade market due to the wide applications in further polymerization and functionalization [2]. Conventionally, the most common approaches for commercially producing industrial olefins are steam cracking of naphtha and fluid catalytic cracking of heavy oil [3, 4]. Although the recovery rate of light olefins (especially for propylene) from a fluid catalytic cracking unit has increased by 29% in the past decades, the commercial methods for the synthesis of propylene are still not capable for closing the increasing ‘propylene gap’ [5, 6]. Alternatively, a primary route for

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the synthesis of light olefins is via the direct C–H activation of natural abundant paraffin that can be easily obtained from shale gas deposits [7, 8]. Generally, the C–H activations for saturated alkanes proceed with the presence of catalysts such as Pt and CrO_x [9–12]. Nevertheless, the dehydrogenation is thermodynamically restricted to rather high temperatures (770 K for 20% conversion of propane) due to the chemical stability of the C–H bond [13]. Such high temperatures and its endothermic nature make the reaction energy-inefficient. Moreover, these catalysts still suffer from limitations including high costs, poor chemoselectivity and toxicity of active centers [14, 15].

In the past decades, various strategies have been employed to improve the catalytic performance of catalysts towards dehydrogenation of alkanes. For example, the selectivity towards propylene can be effectively promoted by alloying another metal (e.g. Sn) into Pt catalysts in the propane dehydrogenation [16]. The underlying mechanism can be ascribed to a geometric effect, in which introduced metal would help generate dispersed Pt active sites [17]. Taking into account that the C–H cleavage would take place on every surface Pt atom, the catalytic performance of the Pt-metal alloy catalysts is still highly structure-sensitive [18]. On the other hand, metal-oxides catalyze the C–H bond activation via the so-called radical-like pathway, in which the M–O sites serve as the active sites [19]. However, due to the structural complexity, the mechanism of M–O sites for C–H activations are elusive [20]. For instance, the activity of the V–O and Cr–O sites are highly sensitive to the bonding nature between the metal ions and O sites [15, 21]. Such diversity of active sites hinders the generation of uniformly dispersed M–O sites with high catalytic activity towards C–H activations [18]. Therefore, it has been long desired to obtain catalysts with uniformly-dispersed active sites and high catalytic performance towards the dehydrogenation of light alkanes.

Two-dimensional materials have been considered as promising catalysts towards various heterogeneous catalysis due to unsaturated and uniformly-distributed active sites [22, 23]. MXenes, with the general formula of $\text{M}_{n+1}\text{X}_n\text{T}_z$, have attracted tremendous interests in many different fields due to the tunable electronic structure and good thermal stability [24, 25]. Moreover, the O termination groups of MXenes may serve as the active sites for various heterogeneous catalysis [26]. For instance, Jiang *et al* have reported that the $\text{Ti}_3\text{C}_2\text{O}_x$ exhibits high catalytic activity towards hydrogen evolution reaction, which is attributed to the highly-active O-sites on the basal plane [27]. Of importance, Diao *et al* have shown that the $\text{Ti}_3\text{C}_2\text{O}_2$ MXenes possess remarkable catalytic activity towards the ethylbenzene dehydrogenation [28]. Theoretical calculations reveal that the O termination groups are considered to account for the good catalytic performance. Nevertheless, three possible termination groups (O, OH and F) can be experimentally observed in the MXenes synthesized by HF etching [29]. Previous studies have shown that the co-existence of multiple termination groups are commonly observed via experimental characterization for different MXenes [30, 31]. In addition, properties of MXenes such as electronic properties and catalytic activity are highly dependent on the

surface chemistry [32]. For instance, the O termination always increases the work function while the OH termination would decrease it [33]. Furthermore, the configuration and defects of termination groups including O-vacancy not only tune the electronic structure but also enhance the catalytic activity [34]. Therefore, it is crucial to study how termination groups influence the property of MXenes as well as to explore the correlation between the termination configuration and the catalytic performance of the catalyst. Previous studies have shown that the catalytic performance of MXenes is closely related to the ratio of O terminations, in which more O terminations would lead to better catalytic activity [35]. Our preceding study has shown how the hydrogen affinity (E_H)—the ability of an O active site to abstract a H atom—could be used to characterize the termination configurations of Ti_2CT_2 MXenes and the activity towards C–H activations [36]. For the O/OH terminated Ti_2C MXenes, the mean hydrogen affinity is linear to the overall ratio of O terminations. Moreover, the hydrogen affinity exhibits linear correlations with respect to the activation energies for C–H cleavage at both $-\text{CH}_3$ and $-\text{CH}_2-$ sites of propane. Note that the dehydrogenation at $-\text{CH}_2-$ site is energetically favorable, indicating high selectivity of the $\text{Ti}_2\text{CO}_z(\text{OH})_{2-z}$ MXenes towards propane dehydrogenation [36]. However, the influence of F terminations on the catalytic activity and selectivity is yet to be addressed, to obtain a complete understanding of the correlation between the termination configurations and the catalytic activity, including O, OH and F terminations.

The main purpose of the present study is to obtain a more complete understanding of the influence of the termination groups on the catalytic activity for the Ti_2CT_2 MXene; in particular how the F terminations affect the hydrogen affinity of the MXenes, and whether or not the linear correlation between the hydrogen affinity and the catalytic activity is valid for generalized Ti_2CT_2 MXenes. By performing first-principles calculations, we show that the mean hydrogen affinity of the Ti_2CT_2 ($\text{T} = \text{O}, \text{OH}$ and F) MXene is linear to the ratio of the O terminations to all terminations present on the surface. The influence of the F termination on the hydrogen affinity is weaker than that of OH termination, i.e. with the same O ratio, the O and F terminated Ti_2C possesses lower hydrogen affinity compared to O and OH terminated ones. Furthermore, the catalytic activity of the Ti_2CT_2 MXene towards C–H activations of propane is investigated. It is found that the validity of probing activity by hydrogen affinity can be extended to all three possible termination groups. Of importance, a universal linear correlation can be found between the activation energies of C–H bond at the $-\text{CH}_2-$ site and the hydrogen affinity, indicating that the catalytic activity can be solely characterized by the hydrogen affinity.

1. Methods

All density functional theory (DFT) calculations were performed by the Vienna *ab initio* simulation package together with the atomic simulation environment [37, 38]. The projected augmented wave potentials were employed for describing electron–ion interactions [39]. The exchange–correlation

Scheme 1. Top and side views of example structures of Ti_2CT_2 MXenes, with different mixtures of the terminations T. (a) $T = \text{O/F}$, (b) $T = \text{O/OH}$ and (c) $T = \text{O, OH and F}$. The Ti, O, F, C and H atoms are represented by silver, red, green, brown and white circles, respectively.

interactions were treated by van der Waals density functional (vdWDF) with the version of rev-vdWDF2 proposed by Hamada [40]. The energy cutoff for the plane wave was set as 400 eV. A 20 Å vacuum layer was adopted to prevent the periodic image interactions. A combined method of climb-image nudged elastic band (CI-NEB) and dimer method was employed for the search of transition states [41–43]. Firstly, 20 images were generated between the initial and final state. Secondly, the central image was used as the input for the further dimer method in order to obtain the transition state. The structure of local minima and saddle point were optimized until the average atomic force was lower than $0.02 \text{ eV } \text{\AA}^{-1}$. As illustrated in [scheme 1](#), three types of $p(4 \times 4)$ supercells of Ti_2CT_2 were employed as catalysts: (a) O/F terminated, (b) O/OH terminated, and (c) a mixture of all three terminations. The calculation of the hydrogen affinity and the dehydrogenations were performed on the top side of the Ti_2CT_2 MXenes (upper panel of [scheme 1](#)), while the bottom surface remained unchanged in order to be consistent with our preceding investigation [35]. The Brillouin zone was modelled by gamma-center Monkhorst–Pack scheme, in which the Γ point and $4 \times 4 \times 1$ grid were adopted for geometry optimization and electronic structure calculations, respectively [44].

2. Results and discussion

2.1. Hydrogen affinity for the O and F terminated Ti_2C MXenes

As suggested by our preceding study, the hydrogen affinity (E_{H}) can be considered as a function of the termination configuration for O/OH terminated Ti_2C . Herein, the validity of the correlation between the E_{H} and termination configurations is extended by including F terminations. The hydrogen affinity is defined as the ability of O termination on the top surface for abstracting one H atom from the molecule:

$$E_{\text{H}} = E(\text{M}_m\text{O}_x\text{F}_y\text{H}_{z+1}) - E(\text{M}_m\text{O}_x\text{F}_y\text{H}_z) + \frac{1}{4}E(\text{O}_2) - \frac{1}{2}E(\text{H}_2\text{O}) \quad (1)$$

in which the $E(\text{M}_m\text{O}_x\text{F}_y\text{H}_{z+1})$, $E(\text{M}_m\text{O}_x\text{F}_y\text{H}_z)$, $E(\text{H}_2\text{O})$ and $E(\text{O}_2)$ are referred to the potential energy of the catalyst with an extra H atom, the original catalyst, a water molecule and an oxygen molecule, respectively [36, 45]. Such descriptor is expected to be related to the termination configuration of the Ti_2C MXenes that can be characterized by the ratio of O terminations to all terminations present on the surface:

$$x_{\text{O}} = N_{\text{O}} / (N_{\text{O}} + N_{\text{OH}} + N_{\text{F}}) \quad (2)$$

in which N_{O} , N_{OH} and N_{F} denote the number of O, OH and F terminations, respectively ($N_{\text{OH}} = 0$ for O/F terminated Ti_2C). It should be noted that the same x_{O} may lead to different combination of $x_{\text{O-top}}$ (the ratio of O terminations to all terminations on the top surface) and $x_{\text{O-bottom}}$ (the ratio of O terminations to all terminations on the bottom surface). Therefore, five different configurations are considered in order to eliminate the influence of the termination distribution for each combination of $x_{\text{O-top}}$ and $x_{\text{O-bottom}}$. Our calculations show that the influence of the termination configuration on the hydrogen affinity is limited, in which the variance is smaller than 0.01 eV for MXenes with the same combination of $x_{\text{O-top}}$ and $x_{\text{O-bottom}}$ [as listed in table S1 (<https://stacks.iop.org/JPCM/33/235201/mmedia>)]. As seen in [figure 1](#), the mean hydrogen affinity is linear to the ratio of O groups x_{O} for both O/OH terminated Ti_2C and O/F terminated Ti_2C , in which the higher O ratio leads to lower hydrogen affinity, agreeing well to our previous study [36]. Of importance, the F termination exhibits weaker influence on the hydrogen affinity compared to OH groups. As seen, the distribution of E_{H} for the O/F terminated Ti_2C (blue triangles) is lower than that of O/OH terminated Ti_2C (pink triangles). In particular, the mean E_{H} for O/F terminated Ti_2C is lower than that of O/OH terminated Ti_2C at the same x_{O} , indicating that the influence of the F terminations on the hydrogen affinity is not as significant as the OH terminations. Furthermore, the discrepancy between E_{H} for O/F terminated Ti_2C and O/OH terminated Ti_2C is increasing as the decreasing of the x_{O} . Such results indicate that the ability of O terminations to abstract H atoms is more sensitive to the ratio of OH terminations.

Figure 1. The correlation between the hydrogen affinity (E_H) and the ratio of the O termination groups of Ti_2CT_2 . The blue and red triangles refer to the hydrogen affinity of $\text{Ti}_2\text{CO}_2\text{F}_{2-z}$ and the $\text{Ti}_2\text{CO}_2(\text{OH})_{2-z}$ ($0 \leq z \leq 2$), in which the blue dots and the red circles represent the mean affinity, respectively. The blue and red lines are the corresponding linear regression of mean E_H with respect to the ratio of O termination.

Figure 2. The linear correlation of E_H with respect to the ratio of the O termination in the Ti_2CT_2 MXenes. The red and blue points represent the MXenes in which the ratio of F and OH termination is fixed to 50%, respectively.

2.2. The hydrogen affinity for MXenes with mixture of terminations

The co-existence of all possible termination groups is commonly observed in experiments [46]. Therefore, our subsequent analysis is focused on the hydrogen affinity for Ti_2C MXenes with O, OH and F terminations. In addition, the termination groups are randomly distributed on the top and bottom surfaces of Ti_2C MXenes, and their structure exhibits high degree of freedom including the ratio of termination groups as well as their distribution on both top and bottom side [47]. Thus, it is difficult to obtain every possible structure for Ti_2CT_2 MXenes. To begin with, the relation between the hydrogen affinity and the termination configurations is investigated by fixing the ratio of one termination group (F or OH) to 50%. As

seen, the mean E_H is linear to the ratio of the O termination in the Ti_2CT_2 (figure 2). The hydrogen affinity is more sensitive to the ratio of OH terminations, in which the range of the mean E_H for Ti_2CT_2 with the F terminations fixed to 50% is significantly larger than that of Ti_2CT_2 with 50% of OH terminations. Further calculations have shown that the change of E_H is solely determined by variation of ratio of O termination when $x_F < 50\%$. The scaling relations for Ti_2CT_2 MXenes with $x_F < 50\%$ are parallel to each other, in which the slopes of the linear regressions are almost the same (figure S1). Such results agree to our discussion above where effect of the F termination on the hydrogen affinity is less significant. Furthermore, it has been reported that the hydrogen affinity can be employed for probing the catalytic activity, in which the low E_H leads to high activity [45]. Therefore, the Ti_2C MXenes with F termination may possess high catalytic activity towards C–H activation.

2.3. The correlation between catalytic activity and hydrogen affinity

The hydrogen affinity is an intrinsic property for not only characterizing the termination configuration, but also probing the catalytic activity towards the C–H activations of propane [36]. We begin by studying the thermodynamics of the C–H activations on Ti_2CT_2 MXenes. Based on the Brønsted–Evans–Polanyi relation, the energy of transition states (E_a) is proportional to the reaction energies (ΔE) of the chemical reactions [48–50]. Herein, catalytic activity of 24 O/OH terminated Ti_2C and 16 O/F terminated Ti_2C is investigated by calculating the reaction energies. As shown in figure 3, the thermodynamics of the C–H activations on Ti_2CT_2 MXenes can be lumped into a simple linear correlation, in which the reaction energy increases as the hydrogen affinity increases for both $-\text{CH}_3$ and $-\text{CH}_2-$ sites. Note that the hydrogen affinity exhibits different scaling relations with the reaction energy at the $-\text{CH}_3$ site (figure 3(a)). Such discrepancy may be related to the steric hindrance of final states of C–H cleavage. The Ti_2C MXenes with low O termination exhibit larger strain, in which the formation of the C–O bond would elongate the Ti–O bonds, resulting in higher potential energy (see figure S2). Such distortion of the final states would decrease the accuracy of the linear regression, leading to different scaling relations with respect to different termination configurations. As seen in figure 3(b), however, the O/OH terminated Ti_2C and O/F terminated Ti_2C can be grouped into one linear regression for the $-\text{CH}_2-$ site (black line). Such result indicates that the catalytic activity of the terminated Ti_2C MXenes can be accurately predicted by the hydrogen affinity. In addition, six Ti_2C MXenes with all three possible termination groups are selected to evaluate the accuracy of the prediction (squares in figure 3, data in tables S1–S3). The mean absolute errors (MAE) for the $-\text{CH}_3$ and $-\text{CH}_2-$ sites are 0.19 and 0.12, respectively. Such small MAE indicates that the hydrogen affinity exhibits high accuracy in the prediction the reaction energy for both $-\text{CH}_3$ and $-\text{CH}_2-$ sites.

Furthermore, DFT calculations have shown that the hydrogen affinity can be utilized as a quantitative descriptor for probing the activity of Ti_2CT_2 MXenes towards the propane dehydrogenation regardless to the termination configuration.

Figure 3. The linear correlations of the reaction energies (ΔE) with respect to the hydrogen affinity (E_H) at (a) $-\text{CH}_3$ and (b) $-\text{CH}_2-$ site. The circles, triangles and squares represent the $\text{Ti}_2\text{CO}_2(\text{OH})_{2-z}$, $\text{Ti}_2\text{CO}_2(\text{F})_{2-z}$, and Ti_2CT_2 ($T = \text{O}, \text{OH}$ and F , $0 \leq z \leq 2$), respectively. The color bar from blue to green corresponds to the ratio of O terminations in Ti_2CT_2 from fully OH and/or F termination (0%) to Ti_2CO_2 .

Figure 4. The scaling relations between the activation energy and the hydrogen affinity at (a) $-\text{CH}_3$ and (b) $-\text{CH}_2-$ in the propane on the $\text{Ti}_2\text{CO}_2(\text{OH})_{2-z}$ (circles) and $\text{Ti}_2\text{CO}_2\text{F}_{2-z}$ (triangles). The color bar from blue to green corresponds to the ratio of O groups in Ti_2CT_2 from fully OH and F termination (0%) to Ti_2CO_2 .

Note that the C–H activation exhibits similar reaction pathways on Ti_2CT_2 MXenes independent of the termination stoichiometry, in which the reaction initiates at the physisorption of the propane and finalizes at the co-adsorption of the radical and H atom (exemplified in figure S3). Figure 4 summarizes the activation energies for C–H cleavage on 24 O/OH terminated Ti_2C and 8 O/F terminated Ti_2C MXenes with respect to E_H . As seen, there is no significant difference between the linear regression for the O/OH terminated Ti_2C and O/F terminated Ti_2C MXenes, indicating that the termination configuration would not affect the scaling relation between the catalytic activity and the hydrogen affinity. Moreover, the validity of such scaling correlation can be extended to both $-\text{CH}_3$

and $-\text{CH}_2-$ site, suggesting that the hydrogen affinity is an intrinsic property of Ti_2CT_2 MXenes. To this end, it is reasonable to extend the application of the hydrogen affinity to the general Ti_2CT_2 MXenes ($T = \text{O}, \text{OH}$ and F).

3. Conclusions

In conclusion, the termination configuration and the catalytic activity of the Ti_2CT_2 ($T = \text{O}, \text{OH}$ and F) MXenes are investigated by DFT calculations. The termination configuration of the Ti_2CT_2 MXenes can be characterized by a quantitative descriptor, hydrogen affinity (E_H), which is defined as the ability for an O active site to abstract a H atom from the propane.

Our calculations show that the mean hydrogen affinity is linear to the overall O ratio of the Ti_2C MXenes, in which high O ratio leads to E_{H} . By considering either O/OH or O/F terminated Ti_2C MXenes, the E_{H} is more sensitive to the OH termination groups, while the influence of the F termination groups on the E_{H} is less significant. Such result can be further demonstrated by the E_{H} of Ti_2CT_2 ($T = \text{O}, \text{OH}$ and F). For the Ti_2C MXenes with low F terminations ($x_{\text{F}} < 50\%$), the scaling relations between the hydrogen affinity and the O ratio are parallel, indicating that the effect of F termination can be considered as a constant. Of importance, the linear correlation between the hydrogen affinity and the catalytic activity can be extended to the general Ti_2CT_2 MXenes, in which the low activation energy and/or reaction energy of C–H activations at both $-\text{CH}_3$ and $-\text{CH}_2-$ site of the propane can be found on the surface with low hydrogen affinity.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

- [1] Sun K et al 2018 *J. Am. Chem. Soc.* **140** 4820
- [2] Yang M-L, Zhu Y-A, Fan C, Sui Z-J, Chen D and Zhou X-G 2011 *Phys. Chem. Chem. Phys.* **13** 3257
- [3] Zhao Z-J, Chiu C-c and Gong J 2015 *Chem. Sci.* **6** 4403
- [4] Baek J, Yun H J, Yun D, Choi Y and Yi J 2012 *ACS Catal.* **2** 1893
- [5] Gomez E, Kattel S, Yan B, Yao S, Liu P and Chen J 2018 *Nat. Commun.* **9** 1398
- [6] Sattler J J H B, Ruiz-Martinez J, Santillan-Jimenez E and Weckhuysen B M 2014 *Chem. Rev.* **114** 10613
- [7] McFarland E 2012 *Science* **338** 340
- [8] Chowdhury A D, Weding N, Julis J, Franke R, Jackstell R and Beller M 2014 *Angew. Chem., Int. Ed.* **53** 6477
- [9] Hakuli A, Kytökiivi A and Krause A O I 2000 *Appl. Catal. A* **190** 219
- [10] Creaser D, Andersson B, Hudgins R R and Silveston P L 1999 *Appl. Catal. A* **187** 147
- [11] Bariás O A, Holmen A and Blekkan E A 1996 *J. Catal.* **158** 1
- [12] Valcarcel A, Ricart J, Clotet A, Illas F, Markovits A and Minot C 2006 *J. Catal.* **241** 115
- [13] Xie Q, Zhang H, Kang J, Cheng J, Zhang Q and Wang Y 2018 *ACS Catal.* **8** 4902
- [14] Niu K, Qi Z, Li Y, Lin H and Chi L 2019 *J. Phys. Chem. C* **123** 4969
- [15] Zhao Z-J, Wu T, Xiong C, Sun G, Mu R, Zeng L and Gong J 2018 *Angew. Chem., Int. Ed.* **57** 6791
- [16] Zhu H et al 2014 *J. Catal.* **320** 52
- [17] Yang M-L, Zhu Y-A, Zhou X-G, Sui Z-J and Chen D 2012 *ACS Catal.* **2** 1247
- [18] Chen S, Pei C, Sun G, Zhao Z-J and Gong J 2020 *Acc. Mater. Res.* **1** 30
- [19] Latimer A A, Aljama H, Kakekhani A, Yoo J S, Kulkarni A, Tsai C, Garcia-Melchor M, Abild-Pedersen F and Nørskov J K 2017 *Phys. Chem. Chem. Phys.* **19** 3575
- [20] Liu G, Zhao Z-J, Wu T, Zeng L and Gong J 2016 *ACS Catal.* **6** 5207
- [21] Kumar M, Hammer N, Ronning M, Holmen A, Chen D, Walmesley J and Oye G 2009 *J. Catal.* **261** 116
- [22] Besenbacher F, Chorkendorff I, Clausen B, Hammer B, Molenbroek A, Nørskov J and Stensgaard I 1998 *Science* **279** 1913
- [23] Gai L, To C T and Chan K S 2014 *Tetrahedron Lett.* **55** 6373
- [24] Li Z and Wu Y 2019 *Small* **15** e1804736
- [25] Naguib M, Kurtoglu M, Presser V, Lu J, Niu J, Heon M, Hultman L, Gogotsi Y and Barsoum M W 2011 *Adv. Mater.* **23** 4248
- [26] Seh Z W, Fredrickson K D, Anasori B, Kibsgaard J, Strickler A L, Lukatskaya M R, Gogotsi Y, Jaramillo T F and Vojvodica A 2016 *ACS Energy Lett.* **1** 589
- [27] Jiang Y, Sun T, Xie X, Jiang W, Li J, Tian B and Su C 2019 *ChemSusChem* **12** 1368
- [28] Diao J et al 2018 *ACS Catal.* **8** 10051
- [29] Hu T, Li Z, Hu M, Wang J, Hu Q, Li Q and Wang X 2017 *J. Phys. Chem. C* **121** 19254
- [30] Harris K J, Bugnet M, Naguib M, Barsoum M W and Goward G R 2015 *J. Phys. Chem. C* **119** 13713
- [31] Magne D, Mauchamp V, Célérier S, Chartier P and Cabioch T 2016 *Phys. Chem. Chem. Phys.* **18** 30946
- [32] Wen Y, Rufford T E, Chen X, Li N, Lyu M, Dai L and Wang L 2017 *Nano Energy* **38** 368
- [33] Liu Y, Xiao H and Goddard W A 2016 *J. Am. Chem. Soc.* **138** 15853
- [34] Bafekry A, Nguyen C V, Stampfl C, Akgec B and Ghergherehchi M 2020 *Phys. Status Solidi** **257** 2000343
- [35] Gao G, O'Mullane A P and Du A 2016 *ACS Catal.* **7** 494
- [36] Niu K, Chi L, Rosen J and Björk J 2020 *Phys. Chem. Chem. Phys.* **22** 18622
- [37] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
- [38] Larsen A H et al 2017 *J. Phys.: Condens. Matter* **29** 273002
- [39] Blöchl P E 1994 *Phys. Rev. B* **50** 17953
- [40] Hamada I 2014 *Phys. Rev. B* **89** 121103
- [41] Henkelman G and Jónsson H 1999 *J. Chem. Phys.* **111** 7010
- [42] Heyden A, Bell A T and Keil F J 2005 *J. Chem. Phys.* **123** 224101
- [43] Henkelman G, Uberuaga B P and Jónsson H 2000 *J. Chem. Phys.* **113** 9901
- [44] Monkhorst H J and Pack J D 1976 *Phys. Rev. B* **13** 5188
- [45] Latimer A A, Kulkarni A R, Aljama H, Montoya J H, Yoo J S, Tsai C, Abild-Pedersen F, Studt F and Nørskov J K 2017 *Nat. Mater.* **16** 225
- [46] Agresti A et al 2019 *Nat. Mater.* **18** 1228

- [47] Naguib M, Mochalin V N, Barsoum M W and Gogotsi Y 2014 *Adv. Mater.* **26** 992
- [48] Bligaard T, Nørskov J K, Dahl S, Matthiesen J, Christensen C H and Sehested J 2004 *J. Catal.* **224** 206
- [49] Cheng J, Hu P, Ellis P, French S, Kelly G and Lok C M 2008 *J. Phys. Chem. C* **112** 1308
- [50] Viñes F, Vojvodic A, Abild-Pedersen F and Illas F 2013 *J. Phys. Chem. C* **117** 4168