Interface engineering in transition metal carbides for electrocatalytic hydrogen generation and nitrogen fixation

Kuang, Min; Huang, Wenjing; Hegde, Chidanand; Fang, Wei; Tan, Xianyi; Liu, Chuntai; Ma, Jianming; Yan, Qingyu

2019

Kuang, M., Huang, W., Hegde, C., Fang, W., Tan, X., Liu, C., . . . Yan, Q. (2020). Interface engineering in transition metal carbides for electrocatalytic hydrogen generation and nitrogen fixation. *Materials Horizons*, 7(1), 32-53. doi:10.1039/C9MH01094G

<https://hdl.handle.net/10356/139588>

<https://doi.org/10.1039/C9MH01094G>

© 2020 The Royal Society of Chemistry. All rights reserved. This paper was published in *Materials Horizons* and is made available with permission of The Royal Society of Chemistry.

Downloaded on 26 Apr 2023 22:20:42 SGT

REVIEW

Interface engineering in transition metal carbides for electrocatalytic hydrogen generation and nitrogen fixation

Q2

Cite this: DOI: 10.1039/c9mh01094g

Min Kuang,^{†a} Wenjing Huang,^{†a} Chidanand Hegde,^a Wei Fang,^{IDa} Xianyi Tan,^{IDa} Chuntai Liu,^b Jianming Ma^{ID*cb} and Qingyu Yan^{ID*a}

With an increasing energy consumption rate and rising global population, constructing sustainable energy technologies has become one of the major scientific challenges. Therefore, the development of electrocatalytic conversion technologies that can convert renewable resources, such as water and nitrogen, into value-added chemicals or fuels (e.g., hydrogen and ammonia) can be crucial. A number of transition metal carbides (TMCs) have been investigated over the past few years as effective electrocatalysts for various reactions. This is mainly owing to their unique electronic structures, which leads to high electrical conductivity and chemical stability. Moreover, the reactivity of TMC-based electrocatalysts is highly dependent on their surface and interfacial properties. This review focuses on tuning nanostructures and interfaces to enhance the electrocatalytic activity of TMC-based materials for hydrogen production and nitrogen fixation. The mechanisms behind the surface and interface engineering are discussed, including the synergy effects, facet binding energy, active defects, and low-coordinated sites. In particular, studies on activity enhancement through design of the interfacial phase, composition, and structure in TMC-based electrocatalysts are highlighted. The effective tuning strategies might pave the way for future development of highly active TMC-based electrocatalysts for sustainable energy-related conversion.

Received 14th July 2019,
Accepted 17th September 2019

DOI: 10.1039/c9mh01094g

rsc.li/materials-horizons

^a School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore. E-mail: alexyan@ntu.edu.sg

^b Key Laboratory of Materials Processing and Mold, Ministry of Education, Zhengzhou University, Zhengzhou 450002, China

^c School of Physics and Electronics, Hunan University, Changsha 138634, China. E-mail: nanoelechem@hnu.edu.cn

[†] These authors contributed equally to this work.

Min Kuang

Min Kuang received her PhD degree (2018) in the Laboratory of Advanced Materials at Fudan University in China, under the supervision of Prof. Gengfeng Zheng. She is currently a postdoctoral fellow in School of Materials Science and Engineering at Nanyang Technological University in Singapore, under the supervision of Prof. Qingyu Yan. Her research focuses on the development of hybrid earth-abundant

Wenjing Huang

Wenjing Huang received her PhD Chemistry from Soochow University in 2018. Now she works as a research fellow under the supervision of Prof. Qingyu Yan in MSE at Nanyang Technological University. Her current research focuses on application of nanostructured materials in electrocatalysis.

nanostructured electrocatalysts for clean and renewable energy-related reactions, including water splitting, fuel cells, electrochemical CO₂ reduction and nitrogen fixation.

1. Introduction

Electrochemical conversion of renewable resources to valuable chemicals and fuels is regarded as one of the sustainable strategies to meet the rising global energy demands in an environmentally benign approach.^{1–4} Hydrogen (H_2) is one of the prime clean energy carriers and ammonia (NH_3) is drawing increasing attention as a promising chemical intermediate.^{5,6} While hydrogen can be produced by the electrolysis of water, electrochemical nitrogen fixation is a promising route to ammonia synthesis.^{7,8} However, the electrochemical generation of H_2 and NH_3 using renewable energy resources (solar, hydropower or wind energy) is still not in industrial practice, owing in part to the high cost of these electrochemically generated products relative to their conventionally produced counterparts.^{9,10} Most importantly, these electrocatalytic reactions highly dependent on the development of new electrocatalysts with excellent reactivity and stability.^{11–14} Furthermore, the majority of the active and stable catalysts for these processes are well known to be precious metals, whose low-abundance and high cost limit their large scale industrial application.¹⁵ Therefore, this presents an urgent demand for scalable synthesis of earth-abundant electrocatalytic materials that are highly active and stable.

Transition metal carbides (TMCs), with structures consisting of carbon (C) atoms occupying the interstitial sites of their parent metals, have sparked increasing attention as efficient electrocatalysts toward several electrochemical reactions, such as the hydrogen evolution reaction (HER),¹⁶ oxygen evolution reaction (OER),¹⁷ nitrogen reduction reaction (NRR),¹⁸ and oxygen reduction reaction (ORR).¹⁹ TMC-based electrocatalysts, as a class of special “interstitial alloys”, are interesting because of their advantageous physical and chemical properties, including their precious-metal-like electronic structures, high electrical conductivities, excellent stabilities, and good corrosion

Fig. 1 (a) Typical transition metals in the TMC compounds. Reproduced with permission from ref. 22. Copyright 2013, Elsevier Ltd. (b) Common crystal structure in TMC compounds. The blue points represent the metal atoms and the brown points represent the carbon atoms. Reproduced with permission from ref. 23. Copyright 2016, John Wiley and Sons, Inc.

resistance.²⁰ The precious-metal-like electronic structures render TMCs effective to adsorb and activate hydrogen, thus exhibiting intrinsic activities like Pt-based electrocatalysts.²¹ In addition, most transition metals, with the Pt-group metals as exceptional examples, are intensively capable of forming TMCs with significant variations in their crystal structures. Fig. 1a exhibits the Group 4–10 metals and their stable carbides.²² As we can see from Fig. 1a, the transition metals on the left and center can alloy with the C atoms to form carbides generally with the formulas of MC and M_2C respectively. On the other hand, for the transition metals on the right, metal-rich stoichiometries of M_3C and M_4C are more prevalent. It is worth noting that the bonding arises from the interaction

Jianmin Ma

Jianmin Ma is an Associate Professor in Hunan University, China. He received his BSc degree in Chemistry from Shanxi Normal University in 2003 and his PhD degree in Materials Physics and Chemistry from Nankai University in 2011. During 2011–2015, he also conducted research in several overseas universities as a postdoctoral research associate. His research interests are focused on energy storage and conversion, green catalytic technologies, and theoretic calculations.

Qingyu Yan

Qingyu Yan is currently a professor in School of Materials Science and Engineering in Nanyang Technology University. He obtained his BS in Materials Science and Engineering, Nanjing University. He finished his PhD from Materials Science and Engineering Department of State University of New York at Stony Brook. After that, He joined the Materials Science and Engineering Department of Rensselaer Polytechnic Institute as a postdoctoral research associate. He joined School of Materials Science and Engineering of Nanyang Technological University as an assistant professor in early 2008 and became a Professor in 2018.

of 2s and 2p orbitals of the C atoms with the d orbital of the transition metals. Thus, with rising sp electrons, the parent metal structure progressively transitions from body-centered cubic (bcc) to hexagonal close-packed (hcp) to face-centered cubic (fcc) (Fig. 1b).^{23,24} Likewise, elements in Group 4 and 5 prefer the bcc structure owing to their partially-filled bands capable of accommodating large amounts of sp-C orbitals, while Group 6 elements adopt the hcp structure and other elements in Groups 7 and 8 favor the fcc structure.^{23,25} Moreover, it has been demonstrated that the broadening of the parent metal d-band, due to the introduction of C atoms, would raise the density of states (DOS) at the Fermi level, hence resulting in high electrocatalytic activities.²⁶

Unfortunately, many of the reported TMCs suffer from limited specific surface areas, which hinders their widespread applications in the field of electrocatalysis.²⁷ Furthermore, during the carbide synthesis process, the generation of surface contaminants blocks the active sites and cavities, resulting in the degradation of electrocatalytic activities.²⁸ In general, carbides are typically prepared by solid-solid or gas-solid reactions to achieve high surface area, namely, direct pyrolysis of metal carbonyl compounds, or reaction of metal/metal oxides with a C source.²² Consequently, the aggregation and/or excessive growth of TMCs during pyrolysis at relatively high temperatures leads to a reduction in the active sites and electrocatalytic activities for electrochemical reactions.²⁹ Up until now, significant efforts have been dedicated to enhancing electrocatalytic activities *via* the engineering of structures and interfaces, including nanostructuring,³⁰ heteroatom doping,³¹ morphology control,³² and introduction of various carbon-based materials.^{33,34} Furthermore, the problem of char contamination has also been studied.^{35–37} One of the effective solutions is the strategy of carburizing the metal precursor using compounds such as $g\text{-C}_3\text{N}_4$,³⁸ carbon nanotubes (CNT),^{39,40} graphene,^{16,41–43} and other inorganic carbon sources.⁴⁴ Compared with their organic counterparts (like aniline, dopamine, and melamine), the diffusion speed of C atoms away from the inorganic compounds is slower, thereby avoiding the char contamination.⁴⁵ More specially, oxygen (O_2) plasma treatment is also demonstrated to be an effective method to eliminate the surface contamination with minimal effect on the carbide structure.⁴⁶ Based on the discussion above, rational design and controllable preparation of TMCs with the utmost exposure of active sites is very important to realize efficient electrochemical reactions.

The Pt-like electrocatalytic behavior of TMCs can be traced back to the pioneering investigations by R. B. Levy and M. Boudart in 1973.⁴⁷ They reported that carbon sp electrons enhanced the apparent electron to atom ratio, thereby forming a more Pt-like electronic configuration. A series of TMC-based electrocatalysts were subsequently reported, such as molybdenum carbides, tungsten carbides, titanium carbides, *etc.*, which exhibited high activity in various electrocatalytic technologies.^{48,49} With the development of advanced characterization techniques, novel preparation strategies and theoretical methods, the mechanisms behind the electrocatalytic activities of TMCs have been widely explored. For instance, Jingguang Chen and co-workers⁴⁸ reported that the d-band center of both Mo- and C-terminated $\beta\text{-Mo}_2\text{C}$ surfaces could be broadened *via* the hybridization between d-orbitals of Mo and s/p-orbitals of C,

thereby resulting in the enhancement of electrocatalytic activities toward the HER. Shuit Tong Lee and co-workers⁴⁵ reported the preparation of phase-pure and ultrasmall W_2C nanoparticles *via* an improved carburization strategy. Kian Ping Loh and co-workers⁵⁰ reported the synthesis of edge segregated Mo_2C electrocatalysts consisting of conventional AA-stacked T-phase Mo_2C and Bernal-stacked (AB-stacked) Mo_2C crystals using the diffusion-mediated method. The density functional theory (DFT)-based calculations demonstrated that the AB-stacked Mo_2C crystals possessed a d-band closer to the Fermi energy compared to the AA-stacked Mo_2C crystals, resulting in the improvement of electrocatalytic activities toward the HER. R. R. Adzic and co-workers⁴⁰ demonstrated that the inlaid structure coupled with the electronic modification could facilitate the electrocatalytic activity of carbides, as exemplified by Mo_2C and CNT (covalent binding). The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) results suggested that this unique anchored structure induced a charge-transfer from Mo to C, which could further downshift the d-band center of Mo, and thus formed a moderate hydrogen binding energy. Most recently, by utilizing first-principles DFT, Q. Jiang *et al.*⁵¹ investigated cobweb-like MoC_6 electrocatalysts and they claimed that the d orbitals of Mo atoms could be strongly hybridized with the orbitals of graphyne, leading to strong interactions between the Mo atom and graphyne. The as-prepared MoC_6 exhibited high activity and selectivity toward the NRR at low potential and ambient conditions, which was mainly ascribed to the selective stabilization of N_2H^* species and destabilization of the NH_2^* species.

Research on TMC-based materials is an emerging field. Further developments can expand the widespread application of TMCs in electrochemical technologies (involving hydrogen generation and nitrogen fixation) to potentially substitute the noble-metal catalysts. In addition, TMCs can be surface decorated with active materials or chemically doped with metal/non-metal atoms or heterostructures to direct the desired electrocatalysis of energy-related reactions, and such surface/interface modifications can be used to tune multiple electrocatalytic steps. In this review, we summarize recent advances in hydrogen generation and nitrogen fixation *via* the HER and NRR using TMC-based materials. Emphasis is given to discussions on the relationship between surface/interface engineering and electrocatalytic activity, and mechanisms for the increasing electrocatalytic performance. The important strategies of surface/interface engineering such as control of nanocrystal shape, size, crystallographic orientation, doping, chemical state, support material, and composition are described. Finally, an outlook of future prospects for hydrogen generation and nitrogen fixation by TMC-based electrocatalysts is described.

2. Fundamentals of electrochemical HER and NRR

2.1 HER

The HER is the cathodic half reaction of a water electrolyzer, which involves distinct mechanisms for acidic and basic

Table 1 Reaction steps for the HER in acidic, neutral, and basic electrolytes

Reactions	Reaction steps	Equations	Tafel slope (mV dec ⁻¹)
Acidic solution: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	Volmer	$\text{H}^+ + \text{e}^- \rightarrow \text{H}^*$	$b = 2.3RT/\alpha F = 120$
	Heyrovsky	$\text{H}^* + \text{H}^+ + \text{e}^- \leftrightarrow \text{H}_2$	$b = 2.3RT/2F = 30$
	Tafel	$\text{H}^* + \text{H}^* \leftrightarrow \text{H}_2$	$b = 2.3RT/(1 + \alpha)F = 40$
Alkaline/neutral solution: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$	Volmer	$\text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{H}^* + \text{OH}^-$	
	Heyrovsky	$\text{H}_2\text{O} + \text{e}^- \leftrightarrow \text{H}_2 + \text{OH}^-$	
	Tafel	$\text{H}^* + \text{H}^* \leftrightarrow \text{H}_2$	

media.⁵² The reaction proceeds through three possible sub-reaction steps (as illustrated by Table 1).⁵ For instance, in acidic media, the first step is the hydrogen adsorption step, namely, the as-called Volmer reaction. In this step, an electron combines with a proton to generate an adsorbed H atom (H_{ads}) intermediate on the surface of the electrode. After the formation of H_{ads} , the HER can either proceed by the Heyrovsky reaction or Tafel reaction or both (Fig. 2).⁵³ From the perspective of HER mechanism, the generation of H_{ads} and its binding energy play an essential role in the process of HER. Therefore, the free energy of hydrogen adsorption (ΔG_{H}) is extensively used as an activity descriptor to rationally design active HER electrocatalysts. If the ΔG_{H} is negative, the intermediate has a strong bonding with the surface of the electrode, favoring the Volmer reaction, while suppressing the Heyrovsky or Tafel reaction; in contrast, if the ΔG_{H} is positive, the intermediate is bound weakly to the surface of the electrode, leading to a slower Volmer reaction that hinders the overall turnover rate.

To evaluate the electrocatalytic activity of target HER electrocatalysts, several crucial parameters such as the total electrode activity, Tafel slope, exchange current density (j_0), faradaic efficiency (FE), stability and turnover frequency (TOF) are essential to be measured/calculated carefully.^{52,54,55} In general, linear sweep voltammetry (LSV) is performed to estimate the total electrode activity, in which low sweep rates (e.g., 2 or 5 mV s⁻¹) are commonly applied to minimize the non-faradaic capacitive current. Based on the LSV curves, two

important parameters for the HER can be evaluated; namely, the onset potential and the overpotential (η). Onset overpotential is the excess potential at which the current density starts to enhance significantly. Furthermore, the overpotential (η), which is the excess potential to reach the current density of 10 mA cm⁻² is generally regarded as the benchmark to compare the HER activity of as-prepared electrocatalysts, corresponding to photoelectrochemical hydrogen generation efficiency of 12.3%.^{56–58} In addition, the Tafel slope and j_0 are two essential parameters which can be determined from the Tafel equation ($\eta = a + b \log j$), where j is the current density and b is the Tafel slope. Tafel slope is commonly correlated with the electrocatalytic mechanism of the HER (Table 1) and j_0 reflects the rate of electron transfer under equilibrium conditions. A promising electrocatalyst should offer a low Tafel slope and high j_0 simultaneously during the HER process. FE, also called coulombic efficiency, is the ratio of the experimental to the theoretical H_2 generation. Thereinto, the theoretically produced H_2 can be calculated by estimating the total charge transfer from potentiostatic or galvanostatic electrolysis plots and the experimental H_2 production can be measured by gas chromatography (GC). In general, the FE is less than 100% owing to the existence of side reactions in the HER process. Furthermore, in order to realize the largescale application of the catalysts, the long-term stability is another important parameter, which can be measured by two methods: CV and galvanostatic/potentiostatic electrolysis. Finally, the TOF, which is a measure of the intrinsic activity of each electrocatalytic site, is defined as the number of reactants that an electrocatalyst can convert to a desired product at each electrocatalytic site per unit time. But, it is still a challenge to precisely measure the TOF due to the heterogeneous catalytic reaction often occurring on the electrode surface.⁵² Despite the fact that the measured TOF is relatively imprecise, it may still give insights into the comparative catalytic activity or efficiency of two or more materials if carefully executed. In conclusion, promising HER electrocatalysts should possess a low overpotential, small Tafel slope, high j_0 , large TOF, and long-term stability.

However, accurately measuring and evaluating the activity of various electrocatalysts is difficult owing to the various measurement methods/conditions, such as electrolyte compositions, deposited substrates, and pH values. Therefore, standard electrocatalytic measurements are of great value. As a successful example, Thomas F. Jaramillo and co-workers⁵⁹ proposed a benchmark to explore various HER electrocatalysts (Fig. 3), which may be greatly significant for the development of

Fig. 2 (a) The Volmer–Heyrovsky and (b) the Volmer–Tafel mechanism of the HER. Reproduced with permission from ref. 53. Copyright 2018, Nature Publishing Group.

Fig. 3 Suggested protocol for benchmarking the performance of electrocatalysts for the HER. Reproduced with permission from ref. 59. Copyright 2015, American Chemical Society.

standard measure techniques. Aiming toward higher accuracy of reported results, we need to pay special attention to the following points:^{60,61} First, the electrode setup should well define the overpotential of the working electrode. Second, if the researchers use the manual iR drop compensation at the benchmark current densities, they should exhibit a detailed iR compensated method, and especially the percentage of iR drop compensation should be cited in reports. Third, in order to ensure the accuracy of the activities, researchers should choose a suitable reference electrode and calibrate it experimentally.

2.2 NRR

The electroreduction of N_2 is another crucial energy conversion reaction to obtain a useful chemical intermediate, namely, NH_3 .^{10,62} It is worth noting that the HER is the major side reaction during the electrochemical NRR process, owing to its lower kinetic barrier and comparable thermodynamic potential. In contrast to the HER, the NRR involves a variety of proton–electron conversion processes in aqueous solution, including multiple surface-bound reaction intermediates.^{63,64} Until now, the reaction mechanisms of the electrochemical NRR on the heterogeneous materials have been classified into two types, *viz.* associative and dissociative mechanisms (Fig. 4a).⁶⁵ In the dissociative pathway, the $N\equiv N$ bonds are firstly cleaved, and subsequently, the two N-atoms undergo hydrogenation processes independently. On the other hand, in the associative pathway, the N_2 is firstly adsorbed on the

Fig. 4 (a) Possible mechanisms for NRR on heterogeneous catalysts. Reproduced with permission from ref. 65. Copyright 2017, Elsevier Ltd. (b) Dissociative (solid lines) and associative (dashed lines) mechanisms, with (dotted lines) and without (solid lines) H-bonds effect on both stepped (red line) and flat (black line) metal surfaces. Reproduced with permission from Ref. 66. Copyright 2012, Royal Society of Chemistry.

electrocatalyst surface and subsequently undergoes a hydrogenation process with two N-atoms binding to each other. Moreover, the associative mechanism can be further classified into the alternating and distal pathway based on the different hydrogenation sequences. In the alternating pathway, the two N atoms are simultaneously hydrogenated, whereas, in the distal pathway, the N atom far away from the electrode surface is hydrogenated first and released as the NH_3 molecule, while the adsorbed N atom is hydrogenated subsequently to form NH_3 .

Similar to the electrochemical HER, the free energies of N_2 ad molecules and N adatoms are also regarded as an important descriptor to tune the activity and selectivity of an electroreduction nitrogen reaction. For instance, Nørskov and co-workers⁶⁶ calculated the free energy profiles for the NH_3 generation on both the flat and steeped surface using DFT, demonstrating the correlation between the adsorbed N intermediates and the selectivity of the NRR. Fig. 4b displays a volcano diagram for flat (black line) and stepped (red line) electrode surfaces for the NRR, containing associative (dotted lines) and dissociative (solid lines) mechanisms, with (dashed lines) and without (solid lines) H-bonds.⁶⁶ As we can see from Fig. 4b, the most active metal surfaces for NH_3 generation are Mo and Fe. However, these metal surfaces are evaluated to be more active for the HER instead of the NRR. In particular, most of the flat metal surfaces studied in this work, such as Co, Ni, Rh, Ir, and Pt, are predicted to be covered by H adatoms rather than N adatoms, resulting in low selectivity for the NRR. Note that several early transition metals (*e.g.*, Zr, Ti, Y, and Sc) exhibit stronger N adatom binding energy compared to H adatoms. Thus higher selectivity to the NRR than the HER can be expected on these electrodes. Most recently, Nørskov and co-workers⁶⁷ further reported a promising strategy to increase NRR selectivity by limiting the proton and electron supply, by numerous strategies such as increasing the barrier for proton transfer to the electrode surface, lowering the concentration of protons in the electrolyte, preventing the electron thermalization, and supplying a slow stream of electrons. Therefore, the theoretical investigations provide a good indicator to better understand the trend for electroreduction of N_2 to NH_3 .

The NRR process severely suffers from poor reliability and reproducibility because of the low production rates of the NRR

Fig. 5 Protocol for the benchmarking of electrocatalysts for the NRR. Reproduced with permission from Ref 69. Copyright 2019, Nature Publishing Group.

and ubiquitous contaminants.⁶⁸ Similar to HER study, standard protocols for measuring the NRR are of fundamental importance for the NRR. In this regard, Chorkendorff and co-workers⁶⁹ proposed a rigorous protocol to quantify the electrochemical reduction of N_2 to ammonia (Fig. 5). A set of rigorous control experiments under an Ar, N_2 , and $^{15}N_2$ atmosphere for each electrocatalyst should be performed to exclude ammonia contamination. Moreover, it is recommended that at least two testing methods be used to quantify the amount of ammonia, and an average of the two detection methods taken.⁷⁰

3. Surface structure engineering for the HER

3.1 Doping with heteroatoms

In the context of an electrocatalytic reaction, tuning the surface active sites and adsorption energy of reactants can be achieved via engineering the composition and nanostructure of electrocatalysts. Doping with heterogeneous atoms is a viable alternative to increase the number of active sites and optimize the kinetic process, and modulate the electronic structure and adsorption free energy of electrocatalysts synergistically.

Apart from this, as demonstrated by previous studies, early-transition-metal carbides possess strong H-binding, which prejudices against gaseous H_2 release.⁷¹ Taking Mo_2C for example, there are high d-orbital vacancies around the E_F which impede HER kinetics.⁷¹ TMC electrocatalyst doping with rich electrons elements reduces the vacancies effectively. The optimization of the H binding energy of TMC materials enhanced the kinetic reaction of the HER effectively.^{36,72,73} Rich electron dopants including metal atoms such as Fe, Ni, Co, Pt, and Pd,^{74–80} and non-metal atoms such as B, N, P, and S,^{30,81–85} show positive effects on modulating the surface composition and the internal electronic structure of the electrocatalysts. To cite N-doped Mo_2C nanosheets as an example, the 1.0 nm

Fig. 6 (a) HRTEM image of N- Mo_2C NS. (b) Polarization curves of MoO_2 NSs, Mo_2C NSs, N- Mo_2C nanoparticles, N- Mo_2C NSs, and 20 wt% Pt/C on the GC electrode at 5 mV s^{-1} in $0.5\text{ M H}_2\text{SO}_4$. (c) Polarization curves of N- Mo_2C NSs with different content of N. (d) ΔG_{H^*} values of Mo and C atoms in MoC and Mo_2C . Insets are the corresponding theoretical structural models. Reproduced with permission from ref. 30. Copyright 2017, American Chemical Society.

ultrathin structures were constructed by transformation of the crystal phase and the surface atomic structure between MoO_2 NSs and N- Mo_2C NSs.³⁰ Highly crystalline and porous structures were confirmed by HR-TEM (Fig. 6a). Besides, DFT calculations demonstrated that after N doping, new active sites associated with the N atom and Mo-3-T atom on the surface were introduced and with low $|\Delta G_{H^*}|$ values of 0.07 and 0.3 eV, respectively. The overpotential ($\eta = 10\text{ mA cm}^{-2}$) of N-doped Mo_2C nanosheets was only 99 mV owing to the robust sheet structure and N doping reduced the energy input for activating the HER (Fig. 6b). The morphology, phase transformation and composition of the N doped Mo_2C NSs was affected by the amount of dicyandiamide and calcination temperature obviously. The authors also verified that the larger amount of dicyandiamide increased disordered carbon on the surface of the nanosheets during the calcining process. Besides, the more dicyandiamide led to phase transformation from Mo_2C to MoC, and produced an excess amount of carbon coating the surface active sites of the Mo_2C nanosheets resulting in poor HER activity (Fig. 6c). DFT calculations further verified that MoC possessed weaker HER activity than that of Mo_2C (Fig. 6d). Hence, N doped Mo_2C NS electrocatalysts with the appropriate amount of dicyandiamide possessed the best HER performance. Carbide electrocatalysts doped with transition metals which are rich in electrons such as group VIII metals can effectively reduce the unoccupied d orbitals of metal atoms in carbides.^{86,87} Wei and co-workers⁸⁸ introduced a study about Ni-doped Mo_2C supported on Ni foam, which showed excellent HER activity in alkaline solution. In another work, Yan and his colleagues reported a Fe-doped Ni_3C electrocatalyst with remarkable water splitting performance in both acid and alkaline solutions.⁷⁴ Thus, carbides doped with heterogeneous metal atoms (e.g. Fe, Ni, Co) exhibit remarkable enhancement

in activity for the electrocatalytic hydrogen evolution reaction.⁸⁰ To cite Co-doped Mo₂C nanowires as an example, Gao and his co-workers⁷⁵ reported a series of Co-doped Mo₂C nanowire electrocatalysts, synthesized by means of a simple process of annealing Co-modified Mo₃O₁₀(C₆H₅NH₃)₂·2H₂O precursors in an inert atmosphere. Nanowire structures provided abundant active sites in the radial direction for H₂ generation and bubble release, while facilitating charge transfer in the axial dimension. After Co-doping into Mo₂C, the electronic density around the Fermi level (E_F) in Mo₂C significantly increased which led to declination of the Mo–H bond toward optimized HER kinetics. XRD patterns undoubtedly confirmed that β -Mo₂C was successfully prepared (Fig. 7a). On increasing the Co doping, the lattice parameter, a/b in β -Mo₂C decreased resulting in a positive shift in the peaks of (100), (002) and (101) to higher angles (Fig. 7b and c). Analogous peak shifting was observed in electrocatalysts of Fe-doped Mo₂C as reported by Leonard and his co-workers.⁸⁹ Furthermore, the Mo₂C unit cell shrunk on account of the replacement of some Mo atoms with the smaller Co in the lattice. On increasing the content of Co, the peak intensity of Co 2p_{3/2} and Co 2p_{1/2} in Co-Mo₂C increased gradually. The peak position at 780.6 eV and 778.3 eV corresponded to metal Co and the peak position at 781.3 eV corresponded to oxidized Co, which was attributed to the interaction in the Mo₂C lattice (Fig. 7d). The electronic feature of Mo in Mo₂C varied after Co-doping, and there were three states (+2, +4 and +6) for Mo on the surface of the electrocatalysts. Mo⁴⁺ and Mo⁶⁺ were due to the inactive MoO₂ and MoO₃ as the carbides were exposed to air. Plenty of foregoing studies consider that Mo²⁺ species are the active centers for electrocatalytic HER. The Mo²⁺ signals were visibly red-shifted in Co-Mo₂C (Fig. 7e), with increased Co-doping, which led to the lower binding energy. The shifting indicates that there are enriched electrons around Mo because

of Co-doping. Besides, the Mo 3d peaks shifted to lower binding energy were reasonable on account of electron transfer from Co to Mo. The higher electronegativity of Mo (2.16) *versus* Co (1.88), and partially oxidized Co in Mo₂C were the main contributing factors for electron transfer. Valence band (VB) study exhibited that a new peak at 3.45 eV arose with increasing amount of Co on account of more electrons around its Fermi level (Fig. 7f).

The optimal Co-doping with the Co/Mo ratio of 0.020, guaranteed abundant Mo²⁺ species in Co doped β -Mo₂C. Thus, Co- β -Mo₂C nanowires acquired increased electron density by Co doping, which is in favor of its remarkable HER activity in both acid and alkaline solutions.

Co-doping of organic–inorganic heteroatoms is recently reported as an effective way to increase the active sites of the catalyst. Recently, Lin and his co-workers⁹⁰ reported porous MoC nanosheets co-doped with Zn, N metal–nonmetal atoms which demonstrated the advantages of metal/non-metallic heteroatom doping. A low melting point transition metal Zn acting as a dopant has attracted more attention in recent years due to the low electron negativity and divalent state of Zn.^{91–94} Besides, Chen and his co-workers⁹¹ confirmed that Zn was an efficient promoter for improving the HER catalytic activity of CoP. The bi-metal oxide precursor of ZnMoO₄ acted as a template and a Zn doping source simultaneously. The porous Zn–N MoC nanosheets exhibited enhanced HER activity and remarkable long-time stability owing to the optimized Mo–H bonding as a result of the Zn, N co-doping and the large electrochemical surface area of the porous nanosheet structures. DFT calculations confirmed that the faster HER kinetics were achieved by Zn, N co-doping, on account of weakening the strong bond of Mo–H and facilitate the desorption of the absorbed hydrogen atom (H_{ads}).

Fig. 7 (a) XRD patterns of different phase Mo₂C. (b) Corresponding zoomed-in regions showing evolution with Co-doping. (c) TEM image of Co-Mo₂C-0.020. (d) XPS patterns of Co 2p and (e) Mo 3d in (I) Mo₂C, (II) Co-Mo₂C-0.012, (III) Co-Mo₂C-0.020, (IV) Co-Mo₂C-0.035, and (V) Co-Mo₂C-0.049, and (f) their UPS spectra of the valence band. Ref. 75. Copyright 2016, John Wiley and Sons, Inc.

3.2 Creating surface porosity

As discussed above, electric conductivity, reactivity and the number of active sites are three key parameters, which affect the electrocatalytic activity of the catalysts. In terms of electrocatalysis process, exposure of more active sites is critical for the adsorption of intermediates in aqueous electrocatalytic reactions. Surface topography engineering is widely prevalent in the field of electrochemical energy conversion devices to enhance the adsorption of intermediates by the exposure of unique active sites. Transition metal carbide nanostructures with various dimensions and morphologies, such as nanodots, nanowires, nanobelts, nanorods, nanosheets, and 3D nanoframes,^{95–103} are theoretically and experimentally proved to exhibit marvelous HER and NRR electrocatalytic properties.^{71,95,104–106} Among them, carbides with porous structures were extensively studied because of excellent tunability of the pore size and shape in porous materials.¹⁰⁴ It is understood that porous materials provide abundant active sites both on their surface and within their porous frameworks, which plays a pivotal role in the enhanced adsorption of reactants and intermediates.

Metal–organic framework (MOF) materials to prepare mesoporous TMC materials have attracted much attention due to their unique structural characteristics in recent years.^{107,108} Continuous pore structures greatly facilitate electron transport and mass transfer during electrocatalytic reactions.^{109–112} MOF materials are extensively used in gas storage and separation, sensors, catalysts, and any other related fields.^{108–114} MOFs are materials of a porous coordination network formed by the interaction between metals and organic ligands, with a record surface area that exceeds that of activated carbon and zeolites. A large number of studies confirm that the introduction of MOFs into the catalyst plays an important role in promoting the electrocatalytic process. Huang *et al.*⁹⁹ reported a porous Mo₂C

electrocatalyst with controlled compositions (doping) and morphologies (1D nanowires or 2D nanosheets) synthesized *via* carburizing cobalt or zinc-based zeolite-type MOF (ZIF-67 or ZIF-8) and cladding MoO₃ nanosheets or nanowires under high temperature. A porous Mo₂C electrocatalyst emerged with excellent electrocatalytic performance owing to unique pore structures. In this work, MOFs only acted as a precursor. However, the traditional method of preparing carbides relies on high temperature pyrolysis. Carbides with bulk structures form easily under high temperature conditions, resulting in loss of large number of active sites of the electrocatalysts.¹⁰⁸ Recently, Lou *et al.*¹⁰⁴ reported nano-octahedron MoC_x electrocatalysts synthesized by a metal–organic framework (MOF)-assisted strategy, that exhibited excellent HER activity. Using the MOF-assisted strategy as a template to prepare porous transition metal carbides can effectively avoid diffusion/agglomeration during the pyrolysis process. And the porous structures remained intact even at higher temperatures. After preparing [Cu₂(BTC)_{4/3}(H₂O)₂]₆[H₃PMo₁₂O₄₀] (BTC = benzene-1,3,5-tricarboxylate) nano-octahedron structures, highly porous texture MoC_x octahedral nanoparticles were finally obtained through a successive process of annealing and Fe³⁺ etching to remove Cu (Fig. 8a). The polycrystalline structure was confirmed by a selected-area electron diffraction (SAED) pattern (Fig. 8b). Some large particles formed at the corners of octahedral particles because of higher surface activity and stress, which was caused by collapse of MOFs, and MoC_x nanocrystallites grew subsequently during high-temperature reaction. A number of MoC_x clusters with a size of 5 nm anchored on the surface of amorphous carbon (Fig. 8c). The interplanar distance of 0.24 nm was consistent with (006) planes of η-MoC. Owing to the large electrochemical active surface of the unique nanostructures, porous MoC_x nanooctahedrons showed excellent HER activity both in acid and alkaline media. The overpotentials at

Fig. 8 (a) Schematic illustration of the synthesis procedure for porous MoC_x nano-octahedrons. (b) TEM images of MoC_x nano-octahedrons; inset is the SAED pattern. (c) Magnified TEM image of MoC_x nano-octahedrons. (d) Polarization curve at 2 mV s⁻¹ and (e) Tafel plots in 0.5 M H₂SO₄. (f) Polarization curve at 2 mV s⁻¹ and (g) Tafel plots in 1 M KOH. Ref. 104. Copyright 2015, Nature Publishing Group.

10 mA cm⁻² were 142 mV and 151 mV in acid and alkaline media respectively (Fig. 8d–f). And the electrocatalysts presented a small Tafel slope in both acid and alkaline media.

3.3 Tailoring crystal facets

The electrochemical performance of nanostructures predominantly depends on the nature of their surface/interface properties.¹¹⁵ Tailoring high-index crystal facets is an effective method to enhance the surface energy of nanocrystals. Nanostructures with at least one miller index larger than 1 are considered high-index crystal faces.^{116,117} Surface structures with high surface energy tend to have high density of atoms with low-coordination numbers and kink atoms which greatly contribute to the catalyst performance of nanomaterials. Manufacturing high-index crystal facets to improve electrocatalytic activity of the catalysts is commonly found in the noble metal based electrocatalysts, such as Pt, Pd, and Au,^{118–123} which are usually applied for the reactions of fuel cells. However, structural instability of high index crystal facets for electrocatalytic reactions is the main problem to be solved. Mu and co-workers developed a subtle Cl₂-assisted “micro-cutting-fragmentation” method to obtain carbon-cohered high-index (222) faceted tantalum carbide nanocrystals (TaC NCs@C) derived from TaC blocks.¹²⁴ Low-index facets have a tendency to transform into high-index facets during high temperature processes.¹²⁵ In this work, a series of experimental results demonstrated that the higher temperature favors fragmentation of the crystal into smaller nanocrystals by Cl₂ gas.

The chlorination temperature played a vital role in nanocrystal size and HER performance. Higher temperatures favored the formation of nanocrystals with a small size which

was further confirmed by theoretical calculations based on the reactive kinetics of chlorination.¹²⁶ Furthermore, carbide-derived carbon (CDC) growth on the surface of carbide blocks,^{127,128} can be understood as a diffusion-controlled mechanism based on linear-parabolic Deal-and Grove-like growth kinetics. The transition belts produced during the preparation process between high-index (222) facets of TaC NCs and *in situ* amorphous carbon layers prevented structural collapse during high temperature preparation and electrocatalytic processes. The challenge of structural instability of high crystal face index materials obtains a satisfactory solution.

Furthermore, DFT calculations uncovered the high-index (222) faceted TaC with no band gap as the crossover of the Dirac cone at the G point. In other words, a TaC electrocatalyst with high-index (222) had a fast electron transfer during an electrocatalytic hydrogen reduction process. Partial density of states verified that the Fermi level of all facets crosses the conduction band. Hence, the influence of electron mobility on different facets is insignificant, which is beneficial for the HER electrocatalysis. As we all know, Pt is the best electrocatalyst for the HER with a very low ΔG_{H^+} value of -0.09 eV.^{129–133} In comparison, the ΔG_{H^+} values of low-index (311), (220), (200) and (111) facets of the TaC electrocatalyst were -0.53 eV, -0.56 eV, -0.73 eV and -0.67 eV respectively. The TaC electrocatalyst with high-index (222) facets showed a least negative ΔG_{H^+} value of -0.23 eV. From the thermodynamic point of view, high-index (222) facets of TaC have the best electrocatalytic hydrogen evolution ability relative to other low-index crystal faces. The ultra-fine structure of carbon-cohered high-index (222) faceted tantalum carbide nanocrystals (TaC NCs@C) was obtained *via* using Cl₂ to cut TaC blocks into TaC NCs at high temperature (Fig. 9a).¹²⁴

Fig. 9 (a) Schematic formation of TaC NCs@C by a subtle chlorine-assisted micro-cutting fragmentation strategy. (II) Pristine TaC blocks; (III) intermediate state of the reaction; (IV) final product TaC NCs@C; (V) side-view model of the product. (b and c) High magnification TEM images of TaC NCs@C, presenting exposed high-index (222) facets on the surface of TaC NCs. (d) Powder XRD pattern of bulk TaC and TaC NCs@C. (e) Polarization curves and (f) Tafel plots (b) of commercial 20% Pt/C, TaC NCs@C and bulk TaC. (g) Volcano plots of j^0 as a function of the ΔG_{H^+} for newly developed high-index (222) faceted TaC (red pentacle), common metal catalysts, molybdenum carbide and carbon hybrid catalyst, typical nanostructured MoS₂ and WS₂ catalyst as well as metal-free C₃N₄@N-doped graphene catalyst. Reproduced with permission from ref. 124. Copyright 2017, Elsevier Ltd.

The transition belts would be produced between high-index (222) facets of TaC NCs and *in situ* formed amorphous carbon layers which prevented conversion of high-index crystal facets. The high activity and stability of high-index (222) facets of TaC NC electrocatalysts was attributed to these unique structures. The authors maintained that Cl₂ molecules preferentially reacted with Ta atoms located at small cracks existing in TaC blocks (Fig. 9b). This is the main reason for disorderly piled residue surface C atoms turning into amorphous carbon. The average size of TaC NCs was about 12.5 nm which uniformly encapsulated in the *in situ* formed carbon blocks during high-temperature reaction. The interplanar spacing of TaC NCs was 1.3 Å corresponding to high-index (222) facets (Fig. 9c). A weak carbon peak was exhibited in the XRD patterns (Fig. 9d). The authors considered that the cohered carbon was beneficial to maintain high-index faceted structures and exceptional dispersivity of nanostructured TaC NCs. The overpotential of high-index (222) facet carbon-cohered TaC NCs (146 mA cm⁻²) was substantially lower than that of the bulk TaC electrocatalyst (Fig. 9e). High-index facets of TaC NCs also showed an excellent Tafel slope of 143 mV dec⁻¹, where the Tafel slope of bulk TaC was 232 mV dec⁻¹ (Fig. 9f). The theoretical free energy of the hydrogen adsorption on different HER electrocatalysts indicated that the position of the *j*₀ and Δ*G*_H^{*} values was closer to the peak (Fig. 9g), indicating a better HER activity.

Another study on high-index facets was reported recently. Ma *et al.*¹³⁴ prepared high-index {120} faceted dendritic hexagonal NiC_x nanosheets on a Ni/CF substrate by a mild electrodeposition approach. The obtained dendritic NiC_{0.2}NS/Ni/CF showed remarkable activity and stability of water splitting.

The overpotential at 10 mA cm⁻² was 121 mV, and the corresponding Tafel slope was 51 mV dec⁻¹ in an alkaline medium. Furthermore, a dendritic NiC_{0.2}NS/Ni/CF electrocatalyst offered superior catalytic stability of more than 100 h. Excellent electrocatalytic performance of NiC_{0.2}NS/Ni/CF electrocatalysts was ascribed to several factors. The dendritic nanosheet morphology contributed abundant active sites for catalysis in NiC_{0.2}NS/Ni/CF electrocatalysts. Besides, the enhanced electron transport characteristic between NiC_{0.2} nanosheets and the conductive substrate and the optimal carbon content also contributed to excellent HER performance. High-index crystal plane regulation improved the performance of electrocatalysts effectively. However, it is difficult to attain the best performance of electrocatalysts only by crystal plane regulation. Therefore, when considering the electrocatalyst design, it is quite essential to combine other techniques such as impurities doping, morphology modulation, electronic effects, interface engineering, *etc.*

3.4 Forming defects

Defects play a pivotal role in an electrocatalytic process because they can change the interaction between the surface and the target reactant molecule and reaction intermediate molecule. This can lower the reaction activation energy and consequently even change the reaction pathway. To improve the exposure of the surface active sites, defect engineering is regarded as a

promising strategy and is often applied in the synthesis of nano-sized electrocatalysts. Defect-rich MoS₂ was prepared through a reaction of a high concentration of precursors and excess thiourea.¹³⁵ Thiourea performed the dual function as a reductant for conversion of Mo(vi) to Mo(iv) and as a morphological stabilizer.¹³⁶ During the preparation of defective MoS₂, the thiourea adsorbed on the surface of primary nanocrystals hindered the oriented crystal growth. Owing to a defective structure, the MoS₂ nanosheets have a small overpotential of 120 mV at a current density of 10 mA cm⁻² and the Tafel slope of 50 mV dec⁻¹. Thus, for transition metal carbides, defect engineering regulation plays an important role in the electrocatalytic process. Recently, Li *et al.*¹⁰⁶ prepared macroporous inverse opal-like Mo_xC electrocatalysts with a prolific number of defects *via* a hard-template method. SiO₂ spheres were mixed with dicyandiamide and Mo precursors before the carbonization process. In the following step, the SiO₂ template was removed completely with HF (Fig. 10a).

Macroporous inverse opal-like (IOL) Mo_xC structures with a number of defects were formed finally (Fig. 10b). Mo_xC IOL structures with different pore sizes were prepared for evaluating electrocatalytic performance. A pore size of 380 nm demonstrated the best hydrogen evolution performance among all pore sizes as the macroporous structures provided more convenient mass transport channels than mesoporous structures. Furthermore, Mo_xC nanoparticles existed in the IOL structure with a size of 2.5–3 nm (Fig. 10c). Mo_xC-IOL showed superior intrinsic electrocatalytic activity in both acid and alkaline media. The overpotentials at 10 mA cm⁻² in acid and alkaline solution were 117 mV and 82 mV respectively (Fig. 10d and e). Besides, Mo_xC-IOL also exhibited large exchange current densities of 0.18 mA cm⁻² and 0.5 mA cm⁻² in both acid and alkaline media, respectively. The authors attributed the excellent performance of an electrocatalyst to the abundant defects generated from a myriad of Mo⁺ species introduced in the Mo_xC IOL structure.

DFT calculations provided a fundamental understanding of the remarkable electrocatalytic activity of Mo_xC-IOL at the atomic level. Metal–hydrogen (M–H) bond strength was calculated on the surface of Mo²⁺, Mo³⁺ and Mo²⁺/Mo³⁺ (Fig. 10f). In the acidic solution, the binding energy for the Mo_xC-IOL was only 0.07 eV smaller than Pt (Fig. 10g). Such hydrogen binding energy was beneficial for proton adsorption, reduction, and H₂ release in the acidic solution.¹³⁷ On the other hand in the alkaline medium, H₂O molecules are the reactant to release H₂. H₂O is first absorbed on the surface of catalysts, followed by subsequent reactions to produce H₂. The H₂O binding energies of Pt and Mo_xC-IOL are 0.12 and 1.12 eV, respectively. Higher binding energy of H₂O favors capture of more H₂O molecules. Hence, the Mo_xC-IOL electrocatalysts showed significantly enhanced HER performance in alkaline solution.

3.5 Nano-size effect

Electrocatalysts with a nano-structure are one of the most common and popular means to boost electrocatalytic activity.^{138–140} In view of the significance of exposure of more

Fig. 10 (a) Synthesis of inverse opal-like Mo_2C without SiO_2 spheres and formation of a rich density of defects. (b) Low-resolution TEM images of Mo_2C -IOL. (c) Magnified TEM image of Mo_2C -IOL. Inset is the corresponding particle size distribution of Mo_2C in Mo_2C -IOL. (d) Overpotentials@10 mA cm^{-2} of Mo_2C -NP, Mo_2C -IOL and Pt wire (left) and corresponding exchange current densities (right) in 0.5 M H_2SO_4 . (e) Overpotentials@10 mA cm^{-2} of Mo_2C -NP, Mo_2C -IOL, and Pt wire (left) and corresponding exchange current densities (right) in 1 M KOH, Scan rate: 5 mV s^{-1} . (f) Hydrogen adsorption configuration on the Mo_2C surfaces with $\text{Mo}^{2+}/\text{Mo}^{3+} = 0/1$ (I), 0.4/0.6 (II), 1/0 (III). (g) Corresponding H binding energies. Ref 106. Copyright 2017, American Chemical Society.

surface active sites for an electrochemical reaction, a series of electrocatalysts with nano-size were fabricated and exhibited enhanced electrocatalytic activity *via* experiments and DFT calculations in recent studies.^{33,104,141–143} Lee and his co-workers⁷⁵ prepared B and N co-doped Mo_2C nanoparticles imbedded in a BCN network *via* a novel Mo-imidazole complex route. B, N-doping decreased the crystal size of Mo_2C NPs from 29.1 nm (pure $\text{Mo}_2\text{C}@C$) to 17.6 nm ($\text{N}:\text{Mo}_2\text{C}@NC$) and 8.6 nm for $\text{B,N}:\text{Mo}_2\text{C}@BCN$. In alkaline solution, the corresponding overpotentials at 10 mA cm^{-2} were 270 mV, 150 mV and 100 mV, respectively. Excellent electrocatalytic properties of Mo_2C were attributed to both the nano-size effect and co-doped with B and N. In another work, Qu *et al.*³³ prepared 1 nm Mo_2C nanoparticles supported on N-doped carbon ($\text{Mo}_2\text{C}@NC$) nanomesh which exhibited remarkable HER activity with an overpotential of 36 mV at 10 mA cm^{-2} in 0.5 M H_2SO_4 solution. In general, the nano-size effect is important to enhance the electrocatalytic performance of the catalyst. However, in practical applications, the size effect often combines with other methods to achieve the optimal electrocatalytic performance, such as doping, morphology, interface engineering, *etc.*

3.6 Surface phase modulation

Tuning a specific phase of a homogeneous catalyst is an effective method to improve the catalytic activity for electrocatalysis. The specific facet, the corner site exposed in a crystal and the surface electronic configuration all depend on the crystalline phase. These parameters identify the adsorption energy of the reaction intermediate on the catalyst surface, in turn controlling the reaction rate. Different phases of Mo-C, including $\alpha\text{-MoC}_{1-x}$, $\beta\text{-Mo}_2\text{C}$, $\eta\text{-MoC}$, and $\gamma\text{-MoC}$, were

successfully prepared *via* a unique amine-metal oxide composite material by the Lenard research group.¹⁴⁴ All these four phases exhibited similar hexagonal crystal structures and different stacking sequences (Fig. 11a). High temperature treatment with appropriate atomic ratios of precursor at different dwelling times is an effective method to obtain carbide ceramic materials with different phases.^{145,146} The morphology and size of four phases of molybdenum carbide were quite different due to the high temperature processing conditions. The miniature size of carbides contributed to the enhanced surface area. $\beta\text{-Mo}_2\text{C}$ has the smallest size among four phases of molybdenum carbide and the BET was about 90 $\text{m}^2 \text{g}^{-1}$, while the BET of $\gamma\text{-MoC}$ was about 25 $\text{m}^2 \text{g}^{-1}$. The large surface area of $\beta\text{-Mo}_2\text{C}$ was beneficial for impressive HER activity. $\beta\text{-Mo}_2\text{C}$ exhibited the best HER activity among the four phases of molybdenum carbide (Fig. 11b). $\gamma\text{-MoC}$ also had similar catalytic activity for the HER owing to the similar valence band shape of $\beta\text{-Mo}_2\text{C}$ and $\gamma\text{-MoC}$ electrocatalysts to that of Pt. The excellent HER

Fig. 11 (a) X-ray diffraction (XRD) patterns of different phase MoC. The insets show the corresponding crystal structures. (b) Polarization curves for four phases of molybdenum carbide, Pt on a carbon support, and multiwall carbon nanotubes (MWCNTs) in 0.1 M HClO_4 . (c) The corresponding Tafel plots for $\beta\text{-MoC}$ and $\gamma\text{-Mo}_2\text{C}$. The catalyst loading for all samples is 0.28 mg cm^{-2} and the scan rate is 2 mV s^{-1} . Ref. 144. Copyright 2014, John Wiley and Sons, Inc.

Table 2 A summary of HER performance of TMCs in both acid and alkaline solutions

	Electrocatalyst	Catalyst loading (mg cm ⁻²)	Electrolyte	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	Ref.	
5	β -Mo ₂ C/N-doped carbon	0.35	0.5 M H ₂ SO ₄	119	72	<i>J. Mater. Chem. A</i> , 2018, 6 , 6054	5
	2D WC@graphene	0.00222	0.5 M H ₂ SO ₄	120	38	<i>Nano Energy</i> , 2017, 33 , 356	
	Nanoporous Mo ₂ C NMs	0.21	0.5 M H ₂ SO ₄	120	53	<i>Energy Environ. Sci.</i> , 2014, 7 , 387	
	V ₈ C ₇ networks	NA	0.5 M H ₂ SO ₄	38	34.5	<i>Adv. Energy Mater.</i> , 2018, 8 , 1800575	
			1 M KOH	47	44		
	Mo ₂ C@NC nanomesh	0.5	0.5 M H ₂ SO ₄	36	33.7	<i>Adv. Funct. Mater.</i> , 2018, 28 , 1705967	
	Ni ₃ Mo ₃ C@NPC NWs	0.285	0.5 M H ₂ SO ₄	161@ η_{100}	74.8	<i>ChemSusChem</i> , 2018, 11 , 2717	
10	B,N:Mo ₂ C@BCN	1	1 M KOH	360@ η_{100}	62	<i>ACS Catal.</i> , 2018, 8 , 8296	10
	Co ₄ Mo ₂ @NC	0.35	1 M KOH	218	73.5	<i>J. Mater. Chem. A</i> , 2017, 5 , 16929	
	Co-Mo ₂ C nanowires	0.14	0.5 M H ₂ SO ₄	140	39	<i>Adv. Funct. Mater.</i> , 2016, 26 , 5590	
			1 M KOH	118	44		
	Mo ₂ C@NPC/N,P-doped RGO	0.14	0.5 M H ₂ SO ₄	34	33.4	<i>Nat. Commun.</i> 2016, 7 , 11204	
	Mo ₂ C@NC	0.28	0.5 M H ₂ SO ₄	124	60	<i>Angew. Chem., Int. Ed.</i> , 2015, 54 , 10752	
	α -Mo ₂ C	0.102	0.5 M H ₂ SO ₄	198	56	<i>J. Mater. Chem. A</i> , 2015, 3 , 8361	
15			1 M KOH	176	58		15
	NiMo ₂ C@C	0.531	0.5 M H ₂ SO ₄	72	65.8	<i>Nanoscale</i> , 2018, 10 , 6080	
	Nanoporous Mo carbide	NA	0.5 M H ₂ SO ₄	229	100.7	<i>Adv. Sci.</i> , 2018, 5 , 1700601	
	Fe-Ni ₃ C-2%	0.15	0.5 M H ₂ SO ₄	178	36.5	<i>Angew. Chem., Int. Ed.</i> , 2017, 56 , 12566	
			1 M KOH	292	41.3		
	N@Mo ₂ C-3/CFP	2	0.5 M H ₂ SO ₄	56	49	<i>Adv. Energy Mater.</i> , 2018, 8 , 1800789	
			1 M KOH	66	51		
20	Mo ₂ CNWAs/CFP	20	0.5 M H ₂ SO ₄	56	68	<i>Adv. Funct. Mater.</i> , 2018, 28 , 1804600	20
			1 M KOH	52	72		
	Mo ₂ C	1.5	0.5 M H ₂ SO ₄	140	124	<i>J. Mater. Chem. A</i> , 2015, 3 , 16320	
	Co/ β -Mo ₂ C@N-CNTs	0.014	1 M KOH	170	92	<i>Angew. Chem., Int. Ed.</i> 2019, 58 , 1	
	β -Mo ₂ C nanotubes	0.75	0.5 M H ₂ SO ₄	172	62	<i>Angew. Chem., Int. Ed.</i> , 2015, 54 , 15395	
			0.1 M KOH	112	55		
25	Ni/WC hybrid	0.7	0.5 M H ₂ SO ₄	53	43.5	<i>Energy Environ. Sci.</i> , 2018, 11 , 2114	25
	Mo ₂ C	1	0.5 M H ₂ SO ₄	35	25	<i>Adv. Energy Mater.</i> , 2018, 8 , 1801461	
	Mo ₂ C-N, P-rGO	0.24	0.5 M H ₂ SO ₄	95	60	<i>ChemCatChem</i> , 2018, 10 , 2300	
			1 M KOH	71	49		
	Mo ₂ N-Mo ₂ C	0.337	0.5 M H ₂ SO ₄	157	55	<i>Adv. Mater.</i> , 2018, 30 , 1704156	
			1 M KOH	154	68		
	Mo ₂ C/N-doped graphene	0.25	1 M KOH	142	101.8	<i>Electrochim. Acta</i> , 2019, 299 , 627	
30	Mo/Mo ₂ C heteronanosheets	0.285	0.5 M H ₂ SO ₄	89	70.7	<i>ACS Energy Lett.</i> , 2018, 3 , 341	30
	Fe ₃ C-Mo ₂ C/NC	0.14	0.5 M H ₂ SO ₄	116	43	<i>ChemSusChem</i> , 2017, 10 , 2597	
	W _x C@WS ₂	0.3	0.5 M H ₂ SO ₄	146	61	<i>Adv. Funct. Mater.</i> , 2017, 27 , 1605802	
	Inverse opal-like Mo ₂ C	2.22	0.5 M H ₂ SO ₄	117	60	<i>ACS Nano</i> , 2017, 11 , 7527	
			0.1 M KOH	82	56		
	Co-NC@Mo ₂ C	0.83	0.5 M H ₂ SO ₄	143	60	<i>Nano Energy</i> , 2019, 57 , 746	
			1 M KOH	173	65		
35	Mo ₂ C/GCSs hybrids	0.36	0.5 M H ₂ SO ₄	120	62.6	<i>ACS Catal.</i> , 2014, 4 , 2658	35
	Mo ₂ C nanoparticles	0.28	0.5 M H ₂ SO ₄	144	55	<i>ACS Nano</i> , 2016, 10 , 11337	
			1 M KOH	100	65		
	Mo ₂ C	0.57	0.5 M H ₂ SO ₄	70	39	<i>Adv. Sci.</i> , 2018, 5 , 1700733	
			1 M KOH	66	37		
	Mo ₂ C-RGO hybrid	0.285	0.5 M H ₂ SO ₄	70	54	<i>Chem. Commun.</i> , 2014, 50 , 13135	
40	MoC _x -DecoratedCo@N-C	0.7	0.5 M H ₂ SO ₄	187	82	<i>Small</i> , 2018, 14 , 1704227	40
			1 M KOH	157	148		
	Mo _x C-Ni@NCV	1.1	0.5 M H ₂ SO ₄	75	45	<i>J. Am. Chem. Soc.</i> , 2015, 137 , 15753	
	MoP/Mo ₂ C@C	0.453	0.5 M H ₂ SO ₄	89	45	<i>ACS Appl. Mater. Interfaces</i> , 2017, 9 , 16270	
			1 M KOH	75	58		
	MoC _x @C	0.354	0.5 M H ₂ SO ₄	79	56	<i>J. Mater. Chem. A</i> , 2016, 4 , 3947	
45	Mo ₂ C nanobelts	0.5	0.5 M H ₂ SO ₄	140	51.3	<i>Appl. Catal., B</i> , 2018, 224 , 533	45
			1 M KOH	110	49.7		
	Ni/Mo ₂ C-NCNFs	1.4	1 M KOH	143	57.8	<i>Adv. Energy Mater.</i> , 2019, 1803185.	
	Porous N@MoPC hybrid	0.14	0.5 M H ₂ SO ₄	139	69.4	<i>Adv. Energy Mater.</i> , 2018, 8 , 1701601	
	Mo ₂ C	0.255	0.5 M H ₂ SO ₄	160	66	<i>Electrochim. Acta</i> , 2018, 274 , 23	
			1 M KOH	92	63		
	N,P-Doped Mo ₂ C@C	0.9	0.5 M H ₂ SO ₄	56	56	<i>ACS Nano</i> , 2016, 10 , 8851	
			1 M KOH	47	71		
50	MoC _x	0.8	0.5 M H ₂ SO ₄	142	53	<i>Nat. Commun.</i> , 2015, 6 , 6512	50
			1 M KOH	151	59		
	Mo ₂ C/C	0.3	0.5 M H ₂ SO ₄	145	60.6	<i>ChemCatChem</i> , 2017, 9 , 1588	
	Ni-Mo ₂ C/C composite	1	1 M KOH	99	73	<i>Chem. – Eur. J.</i> , 2017, 23 , 4644	
	MoS _x @Mo ₂ C	0.213	0.5 M H ₂ SO ₄	178	44	<i>ACS Catal.</i> , 2015, 5 , 6956	
	Mo ₂ C-G	0.8	0.5 M H ₂ SO ₄	150	57	<i>Chem. Commun.</i> , 2015, 51 , 8323	

Table 2 (continued)

Electrocatalyst	Catalyst loading (mg cm ⁻²)	Electrolyte	η_{10} (mV)	Tafel slope (mV dec ⁻¹)	Ref.
Zn-N porous MoC NSs	0.357	0.5 M H ₂ SO ₄	128	52.1	<i>Nanoscale</i> , 2019, 11 , 1700
Mo ₂ C NPs	0.25	0.5 M H ₂ SO ₄	78	41	<i>Angew. Chem., Int. Ed.</i> , 2015, 127 , 14936
Vanadium carbide nanoparticles	0.28	0.5 M H ₂ SO ₄	98	56	<i>Nano Energy</i> , 2016, 26 , 603
MoS ₂ /Mo ₂ C NSs	1.67	0.5 M H ₂ SO ₄	63	53	<i>ACS Catal.</i> , 2017, 7 , 7312
VC@NCNT	0.9	0.5 M H ₂ SO ₄	161	95	<i>Nanoscale</i> , 2018, 10 , 14272
		1 M KOH	159	125	

performance of β -Mo₂C and γ -MoC may be due to their Pt-like Fermi level energy. However, there is no detailed research to confirm the trends in activity. Additionally, density around the Fermi level of β -Mo₂C is higher than γ -MoC. This is the main reason that β -Mo₂C exhibits less stability compared to γ -MoC. The Tafel slope of β -Mo₂C was 120 mV dec⁻¹ (Fig. 11c) which was marginally lower than that of γ -MoC (121.6 mV dec⁻¹). The exchange current density of β -Mo₂C was 17.29 μ A cm⁻², which was substantially higher than that of γ -MoC (3.2 μ A cm⁻²). Although the HER performance of β -Mo₂C is much better than γ -MoC, substantial improvement is needed in comparison with existing carbide catalysts. The hydrogen evolution performance of representative carbides in the past five years is summarized in Table 2.

4. Interface engineering for the HER

As discussed in the previous section, most TMCs are inert for the electrochemical reactions owing to their limited number of active sites, weak adsorption energy, and low surface area.¹⁴⁷ Interface engineering, especially integrating different types of materials into a single nanostructure, is a promising strategy to improve the electrocatalytic performances.¹⁴⁸ Interface engineering can facilitate the formation of strong chemical bonds and synergistic interaction between the various components, which may change the electronic DOS and the positions of the valence and conduction bands of the as-prepared electrocatalysts.^{149,150} Until now, carbon-based materials (such as CNTs, graphene, reduced graphene oxide, and mesoporous carbon),^{32,151,152} metals,^{153,154} and metal compounds^{98,155,156} have been introduced into the TMCs to form hybrid materials with unique physical/chemical properties. The incorporation of other materials not only enhances the electrical conductivity, but also introduces additional active sites.

4.1 TMC/carbon-based materials

Owing to the large specific surface, high charge mobility, and good durability, CNTs are usually used as support materials in electrochemistry.^{157,158} By introducing these materials, the electronic structure of TMCs can be tuned. In particular, the CNTs are reactive C sources for forming nanosized TMCs. For instance, Adzic and co-workers⁴⁰ synthesized Mo₂C/CNTs by *in situ* carburization of ammonium molybdate on CNTs without using any gaseous carbon source. The XANES results

demonstrated that, in the Mo₂C/CNTs, there is charge transfer from Mo to C, which downshifts the d-band center of Mo and thus weakens its H-binding energy. This results in the improved HER activity. Recently, the confinement preparation of TMCs on the surface of CNTs was investigated by Lee and co-workers.⁴⁵ They synthesized ultrasmall and phase-pure W₂C nanoparticles, which have higher activity and stability for electrochemical HER than that of conventional WC owing to the greater electronic DOS close to the Fermi level. The authors proposed that the gaseous C sources (*e.g.*, CH₄) and the non-volatile solid C sources (*e.g.*, Multi-walled carbon nanotubes (MWCNTs)) might have different effects on the chemical composition and nanostructure of the carburized materials. As displayed in Fig. 12a,⁴⁵ conventional strategies using CH₄ as the C precursors were unable to obtain the highly active W₂C owing to the lack of control over the ratio between C atoms and

Fig. 12 (a) Schematic illustration exhibiting the effect of different carbon precursors. (b) TEM image of W₂C/MWNT. (c) W 4f XPS spectrum, (d) W L₃-edge XANES spectrum and (e) Fourier transform EXAFS spectrum and associated fitting curve of W₂C/MWNT at the W L₃-edge. Reproduced with permission from ref. 45. Copyright 2016, Nature Publishing Group.

W atoms. Furthermore, the diffusion rate of C atoms from CH₄ to W lattice took place too fast to allow for phase tuning. When the MWCNTs were selected as the solid C sources, the C diffusion through the solid–solid interface slowed down owing to their chemical inertness, resulting in the formation of coking-free, nanosized, and phase-pure W₂C. The high-resolution transmission electron microscopy (HR-TEM) image demonstrated that the size of the as-prepared W₂C nanoparticles ranged between 2 and 5 nm and few smaller clusters had size in the sub-nanometer range (Fig. 12b). Moreover, the XPS and EXAFS spectrum (Fig. 12c–e) indicated that the ultra-small size and defect-rich structure of the as-obtained W₂C could decrease the coordination number of W–C and W–W. When evaluating their performance for the HER, they found that, compared to WC/MWNTs, W₂C/MWNTs exhibited better activity with a low onset overpotential of ~ 50 mV and a small Tafel slope of 45 mV dec^{−1} (Fig. 12f and g).

Analogously, graphene-based materials, e.g., graphene oxide (GO),^{159,160} reduced graphene oxide (rGO),^{41,43} and graphene nanoribbons (GNRs),¹⁶¹ are another class of materials widely applied as the supports to synthesize TMCs. Yang and co-workers⁴² prepared Mo₂C nanoparticles stabilized by a carbon layer on rGO using a general two-step strategy. They found that the outer protection by the carbon layer could increase the stability of the as-prepared materials. Moreover, the synergistic interaction/intimate contact between Mo₂C and rGO as well as the carbon layer was the main reason for the improved HER activity. A similar phenomenon has also been reported by Lan and co-workers.⁴³ They fabricated a 2D coupled hybrid consisting of Mo₂C nanoparticles encapsulated by N, P-codoped carbon layer and rGO (marked as Mo₂C@NPC/NPRGO) with efficient HER activity. They proposed that the improved HER performance is mainly attributed to the small size of Mo₂C nanoparticles, the enhanced interaction with H⁺, the robust conjugation between Mo₂C and NPC/NPRGO, and the enhanced electron penetration from Mo₂C to rGO. Other hybrid materials such as Fe₃C/rGO,⁴¹ Fe₃C/GRNs,¹⁶¹ and Mo₂C/graphene foam¹⁶² have been fabricated using a similar principle.

In addition to the aforementioned as-formed carbon-based materials, there are other carbon supports which can be/are *in situ* formed during the carburization process. In the past, low-cost polymers (including polydopamine (PDA)¹⁶³ and PANI¹⁶⁰) and renewable biomass (including chitosan¹⁶⁴ and glucose¹⁶²) have been widely used to rationally design efficient TMCs/carbon hybrids. Li and coworkers¹⁶⁵ reported a simple two-step method to fabricate Mo₂C nanoparticles (~3 nm) uniformly dispersed on N-doped carbon microflowers (denoted as Mo₂C/NCF) using the self-polymerization of dopamine. The as-prepared Mo₂C/NCF exhibited excellent HER performance with small onset overpotential, low Tafel slopes, and superior durability both in acidic and basic solution. Most recently, ultra-small 1 nm Mo₂C nanoparticles confined in mesh-like N-doped C (denoted as Mo₂C@NC) were fabricated using dicyandiamide as a C precursor (Fig. 13a).³⁴ As displayed in the HR-TEM image (Fig. 13b), the Mo₂C@NC had a fine pore size between 2 and 15 nm, and the corresponding lattice fringes

Fig. 13 (a) Schematic illustration of the synthesis procedure for the as-prepared Mo₂C@NC nanomesh. (b) HRTEM image of the Mo₂C@NC nanomesh and corresponding crystal lattice fringes of the Mo₂C nanoparticle and N-doped carbon. (c) Polarization curves of the Mo₂C@NC nanomesh in comparison with Mo₂C@NC sheet and Pt/C. (d) TOF plots of Mo₂C@NC nanomesh in comparison with Mo₂C@NC sheet, Pt/C, and other reported noble-metal free catalyst. (e) Theoretical calculations of the free adsorption energy of the sites of the catalyst (the * represents the H atoms adsorption site). Reproduced with permission from ref. 34. Copyright 2018, John Wiley and Sons, Inc.

(~0.32 nm) on the carbon nanolayers around the Mo₂C corresponds to the (004) graphene crystal plane. Furthermore, the as-prepared Mo₂C@NC offered exceptional HER activity with a low overpotential of 36 mV at the current density of −10 mA cm^{−2} and a high TOF of 0.046 H₂ s^{−1} at the overpotential of 40 mV (Fig. 13c and d). DFT calculations further demonstrated that the N dopants in the carbon layers close to an Mo atom could withdraw an electron and introduce a fast electron-transfer process, which contributes to the enhanced performance of the HER (Fig. 13e). Mu and co-workers¹⁶⁶ developed a novel colloid-confinement method for the preparation of ultra-fine Mo₂C nanoparticles with sub-2 nm size assembled in the *in situ* formed amorphous carbon foams (denoted as uf-Mo₂C/CF). Uniformly sized SiO₂ nanospheres and glucose were chosen as the template and C precursors, respectively. The as-obtained uf-Mo₂C/CF exhibited excellent and stable activity for the HER in the whole pH range due to the 3D hierarchical architecture, synergistic effects of ultrasmall size, and low valence states of the Mo atoms on the surface. This work might provide some new insights into the fabrication of ultrafine nanocrystals assembled in the 3D porous frameworks as a class of highly active electrocatalysts.

4.2 TMCs/other metal compounds

Apart from the hybridization with carbon-based materials, other metal or metal compounds have also been regarded as a promising alternative to tune the interface of the as-prepared nanocomposites.^{34,167} Moreover, regulating the chemical composition is a promising method to tune the adsorption/desorption energy of intermediates for the design of highly efficient electrocatalysts.⁹⁶ In addition, the incorporation of multiple components is also expected to induce strong synergistic effects, such as electronic structure modulation, atomic

arrangement, and interfacial stabilization, which are beneficial for the improvement in the electrocatalytic performance.⁷⁹ For instance, Dai and co-workers¹⁵⁶ prepared Mo₂C/MoO₂ heteronanorods *via* manipulating the pyrolysis temperature, which displayed high HER activity in the whole pH range. The excellent electrocatalytic performances were mostly contributed by the synergistic effects of the heterointerfaces between MoO₂ and Mo₂C. Wang and co-workers¹⁵⁵ reported the sulfur (S) decoration of Mo₂C, which exhibited a great enhancement in the final HER activity due to the synergistic effect between MoS_x and Mo₂C. Similarly, Xin Wang and co-workers⁹⁶ prepared a novel Mo₂C/WC catalyst with a well-defined and highly robust 1D structure. They demonstrated that the Mo atoms were dissolved into the WC lattice during the carburization process improving the structural stability. Bao and co-workers¹⁶⁸ synthesized free-standing vertically aligned MoS₂/Mo₂C nanosheets by integrating a hydrothermal method with gas-phase carburization (Fig. 14a and b). This MoS₂/Mo₂C electrocatalyst exhibited excellent activity for the HER, achieving a low overpotential of 63 mV at the current density of 10 mA cm⁻² and a small Tafel slope of 48 mV dec⁻¹ (Fig. 14c). DFT calculations demonstrated that the excellent HER activity of the MoS₂/Mo₂C electrocatalyst was a consequence of enhanced number and activity of Mo-S-C sites formed during the carburization process. Similarly, Tang and co-workers¹⁶⁹ developed MoC–Mo₂C heteronanowires (denoted as MoC–Mo₂C-*x*, where *x* refers to the MoC weight percentage) as high performance HER electrocatalysts using MoO_x-amine as the precursor and investigated the role of MoC nanocrystals. The interfaces between MoC and Mo₂C were visible in the TEM image with clear lattice fringes (Fig. 14d). It is worth noting that the HER activities of the MoC_x-based electrocatalysts (such as MoC, MoC–Mo₂C-31.4, MoC–Mo₂C-68.1, and Mo₂C) were highly dependent on the Mo³⁺/Mo²⁺ ratio (*n*_{3+/2+}), evident from the

current density at *j*₀ (*η* = 0 mV) and *j*₁₅₀ (*η* = 150 mV). As displayed in Fig. 14e and f, the MoC–Mo₂C-31.4 (*n*_{3+/2+} = 3) exhibited higher HER activities compared to Mo₂C (*n*_{3+/2+} = 0.4), MoC–Mo₂C-68.1 MoC (*n*_{3+/2+} = 7.2), and MoC (*n*_{3+/2+} = 10.9), owing to the optimized H-binding of the MoC/Mo₂C interfaces by virtue of the optimized MoC–Mo₂C ratio.

Most recently, MOFs have been widely used as both the precursor and template to construct highly active multiple interfaces due to their well-defined nanostructure, high surface area, and uniformly dispersed metal ions.^{170–172} In this regard, Luo and co-workers¹⁷³ fabricated a CoP–Mo₂C heterojunction using the Co-based ZIF-67 and an Mo-based compound as the precursor. The as-prepared CoP/Mo₂C–NC hybrid catalyst exhibited a significantly improved HER activity over the whole pH range with a small overpotential of ~55.7 mV at the current density of 10 mA cm⁻². The XPS analysis confirmed that the electron could transfer from Co to Mo through the Co–P–Mo bond, leading to the generation of a higher Co valence and lower Mo valences, which could effectively optimize the H binding energy during the electrochemical HER process. In addition, Arne Thomas and co-workers⁴⁴ developed a metal-organic coordination-precursor assisted method to prepare mesoporous Mo-based carbon catalysts (denoted as mC–Mo) consisting of uniformly distributed Mo₂C–Mo₂N heterojunctions. As shown in Fig. 15a, distinct from other investigations on Mo-based precursors *via* MOF precursors, this novel strategy was a fast and controlled aqueous self-assembly process based on dopamine (DA) hydrochloride and sodium molybdate. The introduced Si nanoparticles not only acted as a template but also played a crucial role in stabilizing the formed

Fig. 14 (a) Schematic illustration of the steps for preparation of vertically aligned MoS₂/Mo₂C nanosheets. (b) SEM image of the MoS₂/Mo₂C hybrid nanosheets. (c) LSV curves of vertically aligned MoS₂/Mo₂C nanosheets and the 5, 15, 25, and 60 min (Mo₂C) samples. Reproduced with permission from ref. 182. Copyright 2017, American Chemical Society. (d) HRTEM image of the as-prepared MoC–Mo₂C–31.4 heterojunction nanowires. (e) *j*₀ (current density at *η* = 0 mV) and *j*₁₅₀ (current density at *η* = 150 mV) for Mo₂C, MoC–Mo₂C–31.4, MoC–Mo₂C–68.1, and MoC as a function of Mo³⁺/Mo²⁺ ratio in 0.5 M H₂SO₄. (f) Schematic illustration of the HER activity depending on the electron density of Mo in Mo₂C, MoC–Mo₂C–31.4, MoC–Mo₂C–68.1, and MoC electrocatalysts. Reproduced with permission from ref. 168. Copyright 2017, American Chemical Society.

Fig. 15 (a) Schematic illustration of the synthesis procedure of Mo₂C/Mo₂N-doped mesoporous carbon spheres. (b) TEM and (c) HRTEM images of the as-prepared hybrid. (d) Polarization curves of mC–Mo–750, mC–Mo–850, mC–Mo–950, and Pt/C in 1 M KOH. (e) Long-term stability of the mC–Mo–850 and Pt/C electrocatalysts under the various current densities of 10, 50, and 100 mA cm⁻², and the inset image exhibits the LSV curves of mC–Mo–850 electrocatalyst before and after stability tests. Reproduced with permission from ref. 44. Copyright 2019, John Wiley and Sons, Inc.

microspheres, thus resulting in the homogeneous assembly of isolated organic–inorganic microspheres. The TEM image demonstrated that the as-prepared mC-Mo exhibited a uniform spherical morphology (Fig. 15b). As shown in Fig. 15c, a large amount of ultrasmall overlapping crystals of Mo₂C or Mo₂N were formed in the boundary regions between Mo₂C and Mo₂N, thus indicating the *in situ* generation of heterojunctions in the electrocatalysts. Benefiting from the Mo₂C/Mo₂N heterojunctions and the mesoporous structure, the as-prepared mC-Mo electrocatalysts exhibited an impressive HER activity with a low overpotential of ~173 mV at the current density of 10 mA cm⁻² and excellent stability (Fig. 15d and e). Other efforts have been devoted to constructing an efficient interface between the metal and metal carbides. For example, Yangguang Li and co-workers⁷⁹ reported multi-interfacial Ni/WC hybrid nanoparticles anchored on N-doped carbon sheets (denoted as Ni/WC@NC) using a two-step strategy as shown in Fig. 16a. Polyoxometalate (POM) molecular cages [Ni(en)₂(H₂O)₂]₆{Ni₆(Tris)(en)₃(BTC)_{1.5}(B-αPW₉O₃₄)₈·12en·54H₂O} (denoted as Ni₅₄W₇₂) were chosen as the metal source as the Ni and W elements in this POM cluster were naturally intimately linked with each other, which might facilitate the *in situ* formation of a Ni/WC interwoven architecture with multiple interfaces. Moreover, the introduced rGO not only favored the good dispersion of POM clusters but also promoted the deoxygenation and collapse of Ni₅₄W₇₂. The TEM image confirmed that the Ni/WC hybrid nanoparticles had a fine size between 4 and 14 nm and intimately anchored in the N-doped carbon sheets (Fig. 16b and c). The HRTEM image of one Ni/WC nanoparticle

confirmed the formation of multiple interfaces between Ni and WC (Fig. 16d), which might benefit the mass and charge transfer of the hybrid. Furthermore, the loose N-doped carbon sheets around Ni/WC nanoparticles not only offered rich defect sites but also stabilized the Ni/WC during the electrochemical process. The as-prepared Ni/WC@NC exhibited an excellent HER activity in the acidic electrolyte (0.5 M H₂SO₄) with a low overpotential of 53 and 125 mV to reach 10 and 50 mA cm⁻², respectively, which is very close to that of commercial Pt/C (Fig. 16e). The DFT calculations demonstrated that the Ni/WC@NC had a weaker Δ*G*_{H*} than either of the parent surfaces (Fig. 16f), confirming optimized electronic interaction between Ni and WC. Importantly, the *in situ* X-ray adsorption spectroscopy (XAS) further verified a conceivable electron transfer process (from WC to Ni) and a synergistic mass transport process occurring in Ni/WC@NC during the electrocatalytic HER process. Analogously, a similar improvement mechanism whereby multiple interfaces could facilitate the electrochemical activity was also verified in the Mo/Mo₂C heteronanosheets.¹⁷⁴ Xiaofeng Lu and co-workers¹⁸³ synthesized N-doped carbon nanofibers integrated with Ni and Mo₂C nanocrystals (denoted as Ni/Mo₂C-NCNFs) and investigated the relationship between the interfaces and the improved electrocatalytic activity. They proposed that the close interaction of Ni (weak H binding energy) with Mo₂C (strong H binding energy), could form a moderate metal–H binding energy, which would benefit the adsorption and desorption of H_{ads}. Most importantly, Ni/Mo₂C-NCNFs possessed a higher Ni valence and lower Mo valence caused by the electron transfer from Ni to Mo₂C in their interfaces, which could further facilitate the electrocatalytic activity. Their study further confirmed that constructing hetero-interfaces is an effective method to increase the active sites of the as-prepared hybrids and thus enhance their electrocatalytic performances.

5. Surface and interface structure engineering for the NRR

It is well known that theoretical studies and computational modelling are regarded as an effective strategy to predict promising electrocatalysts, including catalysts for the NRR. Furthermore, theoretical investigations might provide a fundamental insight into the experimental rational design of active TMC-based electrocatalysts toward the NRR. For example, Sun and his co-workers¹⁷⁵ investigated N₂ capture capability of d² (M = Ti, Zr, and Hf), d³ (M = V, Nb, and Ta), and d⁴ (M = Cr and Mo) MXenes, considering that TMC materials with predominant capability of N₂ capture are in favor of activation for electrochemical conversion into ammonia. Calculation results confirmed that the bonding energy between d² MXenes and CO₂ was much higher than that of N₂ and H₂O. However, the chemical adsorption capacity of d³ and d⁴ MXenes to N₂ was higher than that of CO₂ and H₂O. Videlicet, d³ and d⁴ MXenes displayed favorable selectivity to N₂-philicity, which encouraged their applications for electrocatalytic NRR under ambient conditions. Similarly, Garzon and co-workers¹⁷⁶ demonstrated that

Fig. 16 (a) Schematic illustration of the preparation of a Ni/WC@NC catalyst. (b) TEM image and (c and d) HRTEM images of Ni/WC@NC. (e) Polarization curve of Ni/WC@NC, Ni@NC, WC@NC, N-doped C and Pt/C in a 0.5 M H₂SO₄ electrolyte. (f) Gibbs free energy diagram of the HER on different surfaces. Reproduced with permission from ref. 79. Copyright 2017, Royal Society of Chemistry.

higher index surfaces and defects could render the MoC with the capability of driving the NRR in an aqueous or humid environment using DFT calculations. The comparison between the adsorption energies of N-adatoms and H-adatoms exhibited that MoC(111) is the only surface at which the HER process might be suppressed at low potentials. According to the free energy diagrams for electrocatalytic N₂ to ammonia on the surface of MoC(111), a low cell potential of −0.3 V relative to the standard hydrogen electrode (SHE) was required to catalyse the NRR process. Furthermore, the introduction of C vacancies, namely increasing the ratio of Mo to C atoms, could mitigate the HER and thus enhance the affinity of the active surface for both N₂ and N-adatoms. Recently, Sun and his colleagues¹⁷⁷ proposed that H-terminated molybdenum carbides were potential catalysts for electrocatalytic nitrogen reduction. They demonstrated that doping highly electronegative atoms at pre-defined locations is a unique approach to design non-metal terminated carbides with tailored N₂ adsorption energy suitable for NH₃ release. DFT calculations confirmed that the interaction between Mo sites and N₂ molecules weakened in the H terminated Mo₂C(100) surface, which further promoted NH₃ release during an NRR process. As mentioned above, the same electrocatalyst would often have active sites for NRR and HER. Therefore, selectivity should be considered. When considering the electrocatalyst design, an effective NRR catalyst should have desired surface characteristics, textural structure, and crystal structure which enhance the strong binding with N-adatoms rather than H-adatoms.^{178,179}

From such a perspective, Wang *et al.*¹⁰² prepared Mo₂C nanodots embedded on ultrathin carbon nanosheets (Mo₂C/C) and explored their nitrogen reduction performance (Fig. 17a). The Mo₂C nanodots with a size of 3.5 nm anchored on the ultra-thin carbon (Fig. 17b–d). The inlaid structure of Mo₂C dots could availably reduce the coverage of H spillover on the electrocatalyst surface, thus offering more chance for N₂ diffusion and adsorption on the surface of the electrocatalyst. As a result, the as-synthesized Mo₂C/C exhibited superior electrocatalytic performances with a maximum NH₃ yield rate of 11.3 μg h^{−1} mg^{−1} at an applied voltage of −0.3 V vs. RHE (Fig. 17e) and the highest faradaic efficiency of 1.6% occurred at −0.2 V vs. RHE (Fig. 17f). Meanwhile, Mo₂C/C also displayed the good NRR electrocatalytic stability owing to its excellent structural stability (Fig. 17g). Beyond the regulation of dimension tuning, research indicated that carbides with a porous structure are potential nitrogen reduction catalysts. For instance, Sun and his co-workers reported that porous Mo₂C nanorods displayed excellent NRR performance.¹⁰³ It provided important experimental evidence of the applications of TMC materials for electrocatalytic NRR. The yield of NH₃ was 95.1 μg h^{−1} mg_{cat}^{−1} at −0.3 V in 0.1 M HCl and the faradaic efficiency was up to 8.13%. In addition, porous Mo₂C nanorods exhibited remarkable long-term stability and good selectivity of NH₃. Thus, experimental and theoretical calculation results indicated that porous carbide structures are promising electrocatalysts for nitrogen fixation under mild conditions. Up to now, only a few TMC-based electrocatalysts can catalyse N₂

Fig. 17 (a) Illustration of the molten salt synthesis route for Mo₂C/C nanosheets. (b) AFM images of the Mo₂C/C nanosheets. (c) TEM images of the Mo₂C/C nanosheets. (d) HRTEM image of the Mo₂C/C nanosheets, the inset in (d) is the corresponding fast-Fourier-transform (FFT) pattern. (e) NH₃ synthesis yield rate. (f) Corresponding faradaic efficiency. (g) NH₃ synthesis yield rate and faradaic efficiency of each cycle at −0.3 V versus RHE. Ref. 102. Copyright 2018, John Wiley and Sons, Inc.

reduction, although, there is still much space for improvement of underexplored reactions.

6. Conclusions and outlook

Electrochemical energy-related technologies, such as water splitting, the nitrogen cycle, and the carbon cycle, play an important role in next-generation clean energy devices. TMC materials due to their appealing properties of high conductivity, high chemical stability and thermal stability have been highly explored in electrocatalytic hydrogen evolution reaction and nitrogen reduction reaction.¹⁸⁰ In this review, we summarize the effects of surface engineering and interface engineering on the electrocatalytic performance of the HER and NRR of carbides from theoretical calculations and experiments. Surface and interface engineering strategies are beneficial for adjusting the unique physical/chemical properties of TMCs, such as phase modulation, constructing porous structures with different morphology, preparing nano-sized catalysts, tailoring high index crystal facets, doping with heteroatoms, fabricating surface defects, and forming interfaces between carbides and carbon materials, metals, and metal compounds. The surface and interface engineering strategies mentioned in this review provide an important guiding principle for the design and preparation of HER and NRR electrocatalysts in the future, to a certain degree. However, challenges prevail for the design of highly active catalysts due to lack of in-depth understanding of the reaction process and mechanism of the HER and NRR. In view of the electrocatalytic HER, carbides exhibit splendid catalytic activity and stability under both acid and basic conditions. Their overpotential at 10 mA cm^{−2} (η_{10}) was only tens to hundreds of millivolts. Some of them were comparable to the performance of precious metal electrocatalysts. The electrocatalytic HER performance of TMC electrocatalysts is summarized in Table 2. It is worth mentioning here that η_{10} cannot serve as

Table 3 A summary of NRR performance of recent electrocatalysts in an aqueous electrolyte

	Electrocatalyst	Electrolyte	FE (%)	Yield rate	Ref.
5	Carbides				
	Mo ₂ C/C	0.5 M Li ₂ SO ₄	7.80	11.30 $\mu\text{g h}^{-1} \text{mg}_{\text{Mo}_2\text{C}}^{-1}$	<i>Adv. Mater.</i> , 2018, 30 , 1803694
	Mo ₂ C nanorod	0.1 M HCl	8.13	95.10 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>ACS Cent. Sci.</i> , 2019, 5 , 116
10	MXene (Ti ₃ C ₂ T _x) nanosheets	0.01 M HCl	5.78	4.72 $\mu\text{g h}^{-1} \text{mg}^{-1}$	<i>Joule</i> , 2019, 3 , 279
	Metal				
	THH Au NRs	0.1 M KOH	4	1.648 $\mu\text{g h}^{-1} \text{cm}^{-2}$	<i>Adv. Mater.</i> , 2017, 29 , 1604799
15	Bi nanocrystals	0.5 M K ₂ SO ₄	66	200 $\text{mmol g}^{-1} \text{h}^{-1}$	<i>Nat. Catal.</i> , 2019, 2 , 448
	Mo catalysts	0.1 M KOH	14.60 $\pm$ 1.60	34.0 $\pm$ 3.6 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>Angew. Chem., Int. Ed.</i> , 2019, 58 , 2321
	Ru SAC@ZrO ₂ /NC	0.1 M HCl	21	3.665 $\text{mg h}^{-1} \text{mg}_{\text{Ru}}^{-1}$	<i>Chem</i> , 2019, 5 , 204
20	Fe/NC	0.1 M PBS	18.60 $\pm$ 0.80	62.9 $\pm$ 2.7 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>Nano Energy</i> , 2019, 61 , 420
	Ag triangular nanoplates	0.5 M K ₂ SO ₄	25	58.5 $\text{mg g}_{\text{Ag}}^{-1} \text{h}^{-1}$	<i>Chem. Commun.</i> , 2019
25	Sulfide				
	MoS ₂	0.1 M Na ₂ SO ₄	1.17	8.08 $\times 10^{-11} \text{mol s}^{-1} \text{cm}^{-1}$	<i>Adv. Mater.</i> , 2018, 30 , 1800191
	Sn/SnS ₂	0.1 M PBS	6.50	23.8 $\mu\text{g h}^{-1} \text{mg}^{-1}$	<i>Small</i> , 2019, 1902535
30	Oxide				
	MoO ₃ nanosheets	0.1 M HCl	1.90	29.43 $\text{mg h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>J. Mater. Chem. A</i> , 2018, 6 , 12974
	MoO ₂	0.1 M HCl	8.20	12.20 $\mu\text{g h}^{-1} \text{mg}^{-1}$	<i>Nano Energy</i> , 2019, 59 , 10.
35	Nb ₂ O ₅ nanofiber	0.1 M HCl	9.26	43.6 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>Nano Energy</i> , 2018, 52 , 264
	Nitride				
	Mo ₂ N nanorod	0.1 M HCl	4.50	78.4 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>Chem. Commun.</i> , 2018, 54 , 8474
40	VN nanowire	0.1 M HCl	3.58	2.48 $\times 10^{-10} \text{mol}^{-1} \text{s}^{-1} \text{cm}^{-2}$	<i>Chem. Commun.</i> , 2018, 54 , 5323
	Non-metallic material				
	Polymeric carbon nitride	pH = 1 HCl	11.59	8.09 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>Angew. Chem., Int. Ed.</i> , 2018, 57 , 10246
45	Nitrogen-doped porous carbon	0.1 M HCl	1.45	15.7 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>J. Mater. Chem. A</i> , 2018, 6 , 7762
	N,P co-doped carbon	0.1 M HCl	4.20	0.97 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>Chem. Commun.</i> , 2019, 55 , 687
50	Other				
	Bi ₄ V ₂ O ₁₁ /CeO ₂ hybrid	pH = 1 HCl	10.16	23.21 $\mu\text{g h}^{-1} \text{mg}_{\text{cat}}^{-1}$	<i>Angew. Chem., Int. Ed.</i> , 2018, 57 , 6073
	Zr ⁴⁺ -doped anatase TiO ₂	0.1 M KOH	17.30	8.90 $\mu\text{g h}^{-1} \text{cm}^{-2}$	<i>Nat. Commun.</i> , 2019, 10 , 2877
	SeO/Te nanrod	0.1 M HCl	24.56	21.54 $\mu\text{g h}^{-1} \text{mg}^{-1}$	<i>Adv. Sci.</i> , 2019, 1901627

a sole criterion for judging the HER performance of the catalysts, as η_{10} is greatly affected by the testing setup, electrocatalysts loading, and the choice of counter electrode.^{181,182}

Judging the hydrogen evolution performance based on Tafel slope and exchange current density along with η_{10} is particularly important. Furthermore, Pt contamination is worth paying more attention. The use of an ion exchange membrane to separate the working electrode and Pt counter electrode or using carbon rod to replace Pt is recommended. Highly dispersed and nano-sized carbide materials facilitate their use in electrochemically related reactions due to the easy availability of bulk materials for carbides at increased temperatures.

Low activity and poor selectivity are the primary challenges for nitrogen reduction reactions. In the last few years, metals,¹⁸³ metal oxides,¹⁸⁴ sulphides,¹⁸⁵ carbides,¹⁰² nitrides,¹⁸⁶ non-metallic materials,¹⁸⁷ etc. have been used for the electrocatalytic nitrogen reduction reaction, and the corresponding Faraday efficiency for producing ammonia is not more than 15%. The electrochemical performance properties of some typical nitrogen reduction electrocatalysts in an aqueous electrolyte are shown in Table 3. The ammonia yield of the existing nitrogen reduction electrocatalysts is extremely low, and ammonia is ubiquitous in a laboratory environment. Thus, ammonia contamination should be taken very seriously.¹⁵N isotope labeling experiments should be carefully performed to confirm that the ammonia is only derived from nitrogen.¹⁸⁸ Besides, more accurate product detection methods such as ion chromatography and nuclear magnetic resonance spectroscopy should be greatly recommended in electrocatalytic nitrogen reduction reactions.

At present, the investigation of the HER and NRR is still in the laboratory stage. Information on the reaction rate descriptor, reactive active sites and reaction mechanisms is urgently needed to guide design of the electrocatalyst. Hence, we propose that the following potential research opportunities need to be addressed in the field of carbide applications of the HER and NRR. First of all, the importance of the catalyst–electrolyte interface in addition to the electrocatalysts, which can be explored in-depth by many *in situ* or in operando analytical methods and optimized by surface modification of electrocatalysts, regulation of electrolyte composition, etc. Combination of experimental and theoretical calculations to probe into the electrocatalytic hydrogen evolution and nitrogen reduction mechanism and confirm the reactive sites is of great importance for the design of electrocatalysts. Next, the above-mentioned surface and interface engineering have not been widely used in carbide electrocatalysts. Thus, designing an ideal structure that can overcome the drawbacks of carbides to provide desired electro-chemical performance is very attractive and important for next-generation clean energy devices.

Conflicts of interest

The authors declare no conflict of interests.

Acknowledgements

The authors gratefully acknowledge the financial support from Singapore MOE AcRF Tier 1 under grant No. RG119/16 and

2017-T1-002-009, Singapore MOE AcRF Tier 2 under Grant No. 2017-T2-2-069 and 2018-T2-01-010, and Guoxuan-NTU joint lab.

References

- 1 J. Liu, D. Zhu, Y. Zheng, A. Vasileff and S. Z. Qiao, *ACS Catal.*, 2018, **8**, 6707.
- 2 M. Kuang and G. Zheng, *Small*, 2016, **12**, 5656.
- 3 Q. Lu and F. Jiao, *Nano Energy*, 2016, **29**, 439.
- 4 Y. Liu, Y. Li, H. Kang, T. Jin and L. Jiao, *Mater. Horiz.*, 2016, **3**, 402.
- 5 K.-H. Liu, H.-X. Zhong, S.-J. Li, Y.-X. Duan, M.-M. Shi, X.-B. Zhang, J.-M. Yan and Q. Jiang, *Prog. Mater. Sci.*, 2018, **92**, 64.
- 6 L. Tao, M. Qiao, R. Jin, Y. Li, Z. Xiao, Y. Wang, N. Zhang, C. Xie, Q. He, D. Jiang, G. Yu and S. Wang, *Angew. Chem., Int. Ed.*, 2019, **58**, 1019.
- 7 N. Cao and G. Zheng, *Nano Res.*, 2018, **11**, 2992.
- 8 Z.-L. Wang, K. Sun, J. Henzie, X. Hao, Y. Ide, T. Takei, Y. Bando and Y. Yamauchi, *Mater. Horiz.*, 2018, **5**, 1194.
- 9 P. Du and R. Eisenberg, *Energy Environ. Sci.*, 2012, **5**, 6012.
- 10 C. Guo, J. Ran, A. Vasileff and S. Z. Qiao, *Energy Environ. Sci.*, 2018, **11**, 45.
- 11 M. Kuang, P. Han, L. Huang, N. Cao, L. Qian and G. Zheng, *Adv. Funct. Mater.*, 2018, **28**, 1804886.
- 12 C.-S. Li, Y. Sun, W.-H. Lai, J.-Z. Wang and S.-L. Chou, *ACS Appl. Mater. Interfaces*, 2016, **8**, 27710.
- 13 S. Laha, Y. Lee, F. Podjaski, D. Weber, V. Duppel, L. M. Schoop, F. Pielnhofer, C. Scheurer, K. Müller and U. Starke, *Adv. Energy Mater.*, 2019, 1803795.
- 14 M. Wu, Q. Wei, G. Zhang, J. Qiao, M. Wu, J. Zhang, Q. Gong and S. Sun, *Adv. Energy Mater.*, 2018, **8**, 1801836.
- 15 J. Wang, W. Cui, Q. Liu, Z. Xing, A. M. Asiri and X. Sun, *Adv. Mater.*, 2016, **28**, 215.
- 16 M. Zeng, Y. Chen, J. Li, H. Xue, R. G. Mendes, J. Liu, T. Zhang, M. H. Ruemmel and L. Fu, *Nano Energy*, 2017, **33**, 356.
- 17 T. Ouyang, Y. Q. Ye, C. Y. Wu, K. Xiao and Z. Q. Liu, *Angew. Chem., Int. Ed.*, 2019, **58**, 4923.
- 18 Y. Luo, G.-F. Chen, L. Ding, X. Chen, L.-X. Ding and H. Wang, *Joule*, 2019, **3**, 279.
- 19 Y. Hu, J. O. Jensen, W. Zhang, L. N. Cleemann, W. Xing, N. J. Bjerrum and Q. Li, *Angew. Chem., Int. Ed.*, 2014, **53**, 3675.
- 20 P. Yu, F. Wang, T. A. Shifa, X. Zhan, X. Lou, F. Xia and J. He, *Nano Energy*, 2019, **58**, 244.
- 21 J. Pang, J. Sun, M. Zheng, H. Li, Y. Wang and T. Zhang, *Appl. Catal., B*, 2019, **254**, 510.
- 22 Y. Liu, T. G. Kelly, J. G. Chen and W. E. Mustain, *ACS Catal.*, 2013, **3**, 1184.
- 23 Y. Zhong, X. Xia, F. Shi, J. Zhan, J. Tu and H. J. Fan, *Adv. Sci.*, 2016, **3**, 1500286.
- 24 L. S. Macedo, R. R. Oliveira Jr, T. van Haasterecht, V. T. da Silva and H. Bitter, *Appl. Catal., B*, 2019, **241**, 81.
- 25 C. Wan, Y. N. Regmi and B. M. Leonard, *Angew. Chem., Int. Ed.*, 2014, **53**, 6407.
- 26 M. Miao, J. Pan, T. He, Y. Yan, B. Y. Xia and X. Wang, *Chem. – Eur. J.*, 2017, **23**, 10947.
- 27 X. Zang, W. Chen, X. Zou, J. N. Hohman, L. Yang, B. Li, M. Wei, C. Zhu, J. Liang and M. Sanghadasa, *Adv. Mater.*, 2018, **30**, 1805188.
- 28 K. Zhang, G. Zhang, J. Qu and H. Liu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 2451.
- 29 S. Y. Bae, I. Y. Jeon, J. Mahmood and J. B. Baek, *Chem. – Eur. J.*, 2018, **24**, 18158.
- 30 J. Jia, T. Xiong, L. Zhao, F. Wang, H. Liu, R. Hu, J. Zhou, W. Zhou and S. Chen, *ACS Nano*, 2017, **11**, 12509.
- 31 A. M. Gómez-Marín and E. A. Ticianelli, *Appl. Catal., B*, 2017, **209**, 600.
- 32 W. Yuan, Q. Huang, X. Yang, Z. Cui, S. Zhu, Z. Li, S. Du, N. Qiu and Y. Liang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 40500.
- 33 J. Guo, Z. Mao, X. Yan, R. Su, P. Guan, B. Xu, X. Zhang, G. Qin and S. J. Pennycook, *Nano Energy*, 2016, **28**, 261.
- 34 Z. Cheng, Q. Fu, Q. Han, Y. Xiao, Y. Liang, Y. Zhao and L. Qu, *Adv. Funct. Mater.*, 2018, **28**, 1705967.
- 35 H. Lin, N. Liu, Z. Shi, Y. Guo, Y. Tang and Q. Gao, *Adv. Funct. Mater.*, 2016, **26**, 5590.
- 36 S. Wang, J. Wang, M. Zhu, X. Bao, B. Xiao, D. Su, H. Li and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 15753.
- 37 H. Jin, J. Chen, S. Mao and Y. Wang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 22094.
- 38 L. Zhang, H. Yang, D. K. Wanigarathna and B. Liu, *Small Methods*, 2018, **2**, 1700353.
- 39 Y. Hu, B. Yu, W. Li, M. Ramadoss and Y. Chen, *Nanoscale*, 2019, **11**, 4876.
- 40 W.-F. Chen, C.-H. Wang, K. Sasaki, N. Marinkovic, W. Xu, J. Muckerman, Y. Zhu and R. Adzic, *Energy Environ. Sci.*, 2013, **6**, 943.
- 41 S. K. Kim, Y. Qiu, Y.-J. Zhang, R. Hurt and A. Peterson, *Appl. Catal., B*, 2018, **235**, 36.
- 42 L. F. Pan, Y. H. Li, S. Yang, P. F. Liu, M. Q. Yu and H. G. Yang, *Chem. Commun.*, 2014, **50**, 13135.
- 43 J.-S. Li, Y. Wang, C.-H. Liu, S.-L. Li, Y.-G. Wang, L.-Z. Dong, Z.-H. Dai, Y.-F. Li and Y.-Q. Lan, *Nat. Commun.*, 2016, **7**, 11204.
- 44 S. Li, C. Cheng, A. Sagaltchik, P. Pachfule, C. Zhao and A. Thomas, *Adv. Funct. Mater.*, 2019, **29**, 1807419.
- 45 Q. Gong, Y. Wang, Q. Hu, J. Zhou, R. Feng, P. N. Duchesne, P. Zhang, F. Chen, N. Han, Y. Li, C. H. Jin, Y. G. Li and S.-T. Lee, *Nat. Commun.*, 2016, **7**, 13216.
- 46 X. Yang, Y. C. Kimmel, J. Fu, B. E. Koel and J. G. Chen, *ACS Catal.*, 2012, **2**, 765.
- 47 R. Levy and M. Boudart, *Science*, 1973, **181**, 547.
- 48 Q. Zhang, Z. Jiang, B. M. Tackett, S. R. Denny, B. Tian, X. Chen, B. Wang and J. G. Chen, *ACS Catal.*, 2019, **9**, 2415.
- 49 L. Peng, J. Shen, L. Zhang, Y. Wang, R. Xiang, J. Li, L. Li and Z. Wei, *J. Mater. Chem. A*, 2017, **5**, 23028.
- 50 X. Zhao, W. Sun, D. Geng, W. Fu, J. Dan, Y. Xie, P. R. Kent, W. Zhou, S. J. Pennycook and K. P. Loh, *Adv. Mater.*, 2019, **31**, 1808343.
- 51 Z. Chen, X. Lang and Q. Jiang, *J. Mater. Chem. A*, 2018, **6**, 9623.

- 1 52 C. G. Morales-Guio, L.-A. Stern and X. Hu, *Chem. Soc. Rev.*, 2014, **43**, 6555.
- 53 D. Voiry, H. S. Shin, K. P. Loh and M. Chhowalla, *Nat. Rev. Chem.*, 2018, **2**, 0105.
- 5 54 P. Xiao, W. Chen and X. Wang, *Adv. Energy Mater.*, 2015, **5**, 1.
- 55 M. Zeng and Y. Li, *J. Mater. Chem. A*, 2015, **3**, 14942.
- 56 J. Li and G. Zheng, *Adv. Sci.*, 2017, **4**, 1600380.
- 57 M. Kuang, P. Han, Q. Wang, J. Li and G. Zheng, *Adv. Funct. Mater.*, 2016, **26**, 8555.
- 10 58 M. Kuang, Q. Wang, P. Han and G. Zheng, *Adv. Energy Mater.*, 2017, **7**, 1700193.
- 59 S. BibliographyC., C. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2015, **137**, 4347.
- 15 60 C. Wei, R. R. Rao, J. Peng, B. Huang, I. E. Stephens, M. Risch, Z. J. Xu and Y. Shao-Horn, *Adv. Mater.*, 2019, **31**, 1806296.
- 61 S. Anantharaj, S. Ede, K. Karthick, S. S. Sankar, K. Sangeetha, P. Karthik and S. Kundu, *Energy Environ. Sci.*, 2018, **11**, 744.
- 20 62 G. F. Chen, S. Ren, L. Zhang, H. Cheng, Y. Luo, K. Zhu, L. X. Ding and H. Wang, *Small Methods*, 2018, 1800337.
- 63 X. Guo, H. Du, F. Qu and J. Li, *J. Mater. Chem. A*, 2019, **7**, 3531.
- 25 64 B. Hu, M. Hu, L. C. Seefeldt and T. L. Liu, *ACS Energy Lett.*, 2019, **4**, 1053.
- 65 M. A. Shipman and M. D. Symes, *Catal. Today*, 2017, **286**, 57.
- 30 66 E. Skulason, T. Bligaard, S. Gudmundsdóttir, F. Studt, J. Rossmeisl, F. Abild-Pedersen, T. Vegge, H. Jonsson and J. K. Nørskov, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1235.
- 67 A. R. Singh, B. A. Rohr, J. A. Schwalbe, M. Cargnello, K. Chan, T. F. Jaramillo, I. Chorkendorff and J. K. Nørskov, *ACS Catal.*, 2017, **7**, 706.
- 35 68 G. F. Chen, S. Ren, L. Zhang, H. Cheng, Y. Luo, K. Zhu, L. X. Ding and H. Wang, *Small Methods*, 2019, **3**, 1800337.
- 69 S. Z. Andersen, V. Čolić, S. Yang, J. A. Schwalbe, A. C. Nielander, J. M. McEnaney, K. Enemark-Rasmussen, J. G. Baker, A. R. Singh and B. A. Rohr, *Nature*, 2019, **570**, 504.
- 40 70 C. Tang and S.-Z. Qiao, *Chem. Soc. Rev.*, 2019, **48**, 3166.
- 71 J. Halim, S. Kota, M. R. Lukatskaya, M. Naguib, M.-Q. Zhao, E. J. Moon, J. Pitock, J. Nanda, S. J. May, Y. Gogotsi and M. W. Barsoum, *Adv. Funct. Mater.*, 2016, **26**, 3118.
- 45 72 W.-F. Chen, S. Iyer, S. Iyer, K. Sasaki, C.-H. Wang, Y. Zhu, J. T. Muckerman and E. Fujita, *Energy Environ. Sci.*, 2013, **6**, 1818.
- 73 Y. Zhao, K. Kamiya, K. Hashimoto and S. Nakanishi, *J. Am. Chem. Soc.*, 2015, **137**, 110.
- 50 74 H. Fan, H. Yu, Y. Zhang, Y. Zheng, Y. Luo, Z. Dai, B. Li, Y. Zong and Q. Yan, *Angew. Chem., Int. Ed.*, 2017, **56**, 12566.
- 75 H. Lin, N. Liu, Z. Shi, Y. Guo, Y. Tang and Q. Gao, *Adv. Funct. Mater.*, 2016, **26**, 5590.
- 55 76 S. T. Hunt, M. Milina, Z. Wang and Y. Román-Leshkov, *Energy Environ. Sci.*, 2016, **9**, 3290.
- 77 T. G. Kelly, S. T. Hunt, D. V. Esposito and J. G. Chen, *Int. J. Hydrogen Energy*, 2013, **38**, 5638.
- 78 F. Yu, Y. Gao, Z. Lang, Y. Ma, L. Yin, J. Du, H. Tan, Y. Wang and Y. Li, *Nanoscale*, 2018, **10**, 6080.
- 79 Y.-Y. Ma, Z.-L. Lang, L.-K. Yan, Y.-H. Wang, H.-Q. Tan, K. Feng, Y.-J. Xia, J. Zhong, Y. Liu, Z.-H. Kang and Y.-G. Li, *Energy Environ. Sci.*, 2018, **11**, 2114.
- 80 Y. Ma, G. Guan, C. Shi, A. Zhu, X. Hao, Z. Wang, K. Kusakabe and A. Abudula, *Int. J. Hydrogen Energy*, 2014, **39**, 258.
- 10 81 M. A. R. Anjum, M. H. Lee and J. S. Lee, *ACS Catal.*, 2018, **8**, 8296.
- 82 L. Ji, J. Wang, X. Teng, H. Dong, X. He and Z. Chen, *ACS Appl. Mater. Interfaces*, 2018, **10**, 14632.
- 83 Z. Shi, K. Nie, Z.-J. Shao, B. Gao, H. Lin, H. Zhang, B. Liu, Y. Wang, Y. Zhang, X. Sun, X.-M. Cao, P. Hu, Q. Gao and Y. Tang, *Energy Environ. Sci.*, 2017, **10**, 1262.
- 84 Y.-Y. Chen, Y. Zhang, W.-J. Jiang, X. Zhang, Z. Dai, L.-J. Wan and J.-S. Hu, *ACS Nano*, 2016, **10**, 8851.
- 85 H. Ang, H. T. Tan, Z. M. Luo, Y. Zhang, Y. Y. Guo, G. Guo, H. Zhang and Q. Yan, *Small*, 2015, **11**, 6278.
- 20 86 R. Michalsky, Y.-J. Zhang and A. A. Peterson, *ACS Catal.*, 2014, **4**, 1274.
- 87 J. Greeley, T. F. Jaramillo, J. Bonde, I. Chorkendorff and J. K. Nørskov, *Nat. Mater.*, 2006, **5**, 909.
- 25 88 K. Xiong, L. Li, L. Zhang, W. Ding, L. Peng, Y. Wang, S. Chen, S. Tan and Z. Wei, *J. Mater. Chem. A*, 2015, **3**, 1863.
- 89 C. Wan and B. M. Leonard, *Chem. Mater.*, 2015, **27**, 4281.
- 90 Q. Cao, L. Zhao, A. Wang, L. Yang, L. Lai, Z.-L. Wang, J. Kim, W. Zhou, Y. Yamauchi and J. Lin, *Nanoscale*, 2019, **11**, 1700.
- 30 91 T. Liu, D. Liu, F. Qu, D. Wang, L. Zhang, R. Ge, S. Hao, Y. Ma, G. Du, A. M. Asiri, L. Chen and X. Sun, *Adv. Energy Mater.*, 2017, **7**, 1700020.
- 92 Y. Shi, Y. Zhou, D.-R. Yang, W.-X. Xu, C. Wang, F.-B. Wang, J.-J. Xu, X.-H. Xia and H.-Y. Chen, *J. Am. Chem. Soc.*, 2017, **139**, 15479.
- 35 93 X. Wang, R. Su, H. Aslan, J. Kibsgaard, S. Wendt, L. Meng, M. Dong, Y. Huang and F. Besenbacher, *Nano Energy*, 2015, **12**, 9.
- 40 94 H. Zhang, X. Huang, O. Noonan, L. Zhou and C. Yu, *Adv. Funct. Mater.*, 2017, **27**, 1606023.
- 95 L. Liao, S. Wang, J. Xiao, X. Bian, Y. Zhang, M. D. Scanlon, X. Hu, Y. Tang, B. Liu and H. H. Girault, *Energy Environ. Sci.*, 2014, **7**, 387.
- 45 96 P. Xiao, X. Ge, H. Wang, Z. Liu, A. Fisher and X. Wang, *Adv. Funct. Mater.*, 2015, **25**, 1520.
- 97 S. Jing, L. Zhang, L. Luo, J. Lu, S. Yin, P. K. Shen and P. Tsiakaras, *Appl. Catal., B*, 2018, **224**, 533.
- 98 P. Xiao, Y. Yan, X. Ge, Z. Liu, J.-Y. Wang and X. Wang, *Appl. Catal., B*, 2014, **154**, 232.
- 50 99 J. Wan, J. Wu, X. Gao, T. Li, Z. Hu, H. Yu and L. Huang, *Adv. Funct. Mater.*, 2017, **27**, 1703933.
- 100 G. Humagain, K. MacDougall, J. MacInnis, J. M. Lowe, R. H. Coridan, S. MacQuarrie and M. Dasog, *Adv. Energy Mater.*, 2018, **8**, 1801461.

- 101 C. He and J. Tao, *J. Catal.*, 2017, **347**, 63.
- 102 H. Cheng, L. X. Ding, G. F. Chen, L. Zhang, J. Xue and H. Wang, *Adv. Mater.*, 2018, **30**, 1803694.
- 103 X. Ren, J. Zhao, Q. Wei, Y. Ma, H. Guo, Q. Liu, Y. Wang, G. Cui, A. M. Asiri, B. Li, B. Tang and X. P. Sun, *ACS Cent. Sci.*, 2018, **5**, 116.
- 104 H. B. Wu, B. Y. Xia, L. Yu, X.-Y. Yu and X. W. D. Lou, *Nat. Commun.*, 2015, **6**, 6512.
- 105 S. Li, C. Cheng, A. Sagaltchik, P. Pachfule, C. Zhao and A. Thomas, *Adv. Funct. Mater.*, 2019, **29**, 1807419.
- 106 F. Li, X. Zhao, J. Mahmood, M. S. Okyay, S.-M. Jung, I. Ahmad, S.-J. Kim, G.-F. Han, N. Park and J.-B. Baek, *ACS Nano*, 2017, **11**, 7527.
- 107 A. Mahmood, W. Guo, H. Tabassum and R. Zou, *Adv. Energy Mater.*, 2016, **6**, 1600423.
- 108 S. L. James, *Chem. Soc. Rev.*, 2003, **32**, 276.
- 109 J. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.
- 110 A. Corma, H. García and F. X. Llabrés i Xamena, *Chem. Rev.*, 2010, **110**, 4606.
- 111 J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011.
- 112 H. Furukawa, K. E. Cordova, M. O'Keeffe and O. M. Yaghi, *Science*, 2013, **341**, 1230444.
- 113 J.-R. Li, J. Sculley and H.-C. Zhou, *Chem. Rev.*, 2012, **112**, 869.
- 114 Z. Hu, B. J. Deibert and J. Li, *Chem. Soc. Rev.*, 2014, **43**, 5815.
- 115 P. Chen, Y. Tong, C. Wu and Y. Xie, *Acc. Chem. Res.*, 2018, **51**, 2857.
- 116 Z. L. Wang, *J. Phys. Chem. B*, 2000, **140**, 1153.
- 117 Y.-N. Wen and J.-M. Zhang, *Solid State Commun.*, 2007, **144**, 163.
- 118 P. Swetha and S.-P. Feng, *Electrochem. Commun.*, 2018, **94**, 64.
- 119 N. Tian, Z.-Y. Zhou, N.-F. Yu, L.-Y. Wang and S.-G. Sun, *J. Am. Chem. Soc.*, 2010, **132**, 7580.
- 120 N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding and Z. L. Wang, *Science*, 2007, **316**, 732.
- 121 Z. Quan, Y. Wang and J. Fang, *Acc. Chem. Res.*, 2013, **46**, 191.
- 122 N. Zhang, L. Bu, S. Guo, J. Guo and X. Huang, *Nano Lett.*, 2016, **16**, 5037.
- 123 S. Luo and P. K. Shen, *ACS Nano*, 2017, **11**, 11946.
- 124 Z. Kou, K. Xi, Z. Pu and S. Mu, *Nano Energy*, 2017, **36**, 374.
- 125 K. Hata, T. Ikoma, K. Hirakawa, T. Okano, A. Kawazu, T. Ueda and M. Akiyama, *J. Appl. Phys.*, 1994, **76**, 5601.
- 126 D. A. Ersoy, M. J. McNallan and Y. Gogotsi, *Mater. Res. Innovations*, 2001, **5**, 55.
- 127 L. Chen, G. Behlau, Y. Gogotsi and M. McNallan, John Wiley & Sons, 2003, vol. 4.
- 128 A. N. Zelikman and L. M. Leonova, *Tsvetn. Met.*, 1978, **19**, 54.
- 129 H. Yin, S. Zhao, K. Zhao, A. Muqsit, H. Tang, L. Chang, H. Zhao, Y. Gao and Z. Tang, *Nat. Commun.*, 2015, **6**, 6430.
- 130 R. Subbaraman, D. Tripkovic, D. Strmcenik, K.-C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic and N. M. Markovic, *Science*, 2011, **334**, 1256.
- 131 N. Cheng, S. Stambula, D. Wang, M. N. Banis, J. Liu, A. Riese, B. Xiao, R. Li, T.-K. Sham, L.-M. Liu, G. A. Botton and X. Sun, *Nat. Commun.*, 2016, **7**, 13638.
- 132 M. Li, Q. Ma, W. Zi, X. Liu, X. Zhu and S. Liu, *Sci. Adv.*, 2015, **1**, e1400268.
- 133 J. K. Nørskov, T. Bligaard, A. Logadottir, J. Kitchin, J. G. Chen, S. Pandelov and U. Stimming, *J. Electrochem. Soc.*, 2005, **152**, J23.
- 134 H. Yang, S. Luo, X. Li, S. Li, J. Jin and J. Ma, *J. Mater. Chem. A*, 2016, **4**, 18499.
- 135 J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. Lou and Y. Xie, *Adv. Mater.*, 2013, **25**, 5807.
- 136 L. Yang, S. Wang, J. Mao, J. Deng, Q. Gao, Y. Tang and O. G. Schmidt, *Adv. Mater.*, 2013, **25**, 1180.
- 137 J. Mahmood, F. Li, S.-M. Jung, M. S. Okyay, I. Ahmad, S.-J. Kim, N. Park, H. Y. Jeong and J.-B. Baek, *Nat. Nanotechnol.*, 2017, **12**, 441.
- 138 H. Mistry, A. S. Varela, S. Kuehl, P. Strasser and B. R. Cuenya, *Nat. Rev. Mater.*, 2016, **1**, 16009.
- 139 S. Cao, F. F. Tao, Y. Tang, Y. Li and J. Yu, *Chem. Soc. Rev.*, 2016, **45**, 4747.
- 140 B. E. Hayden, *Acc. Chem. Res.*, 2013, **46**, 1858.
- 141 W. Han, L. Chen, B. Ma, J. Wang, W. Song, X. Fan, Y. Li, F. Zhang and W. Peng, *J. Mater. Chem. A*, 2019, **7**, 4734.
- 142 S. T. Hunt, T. Nimmanwudipong and Y. Román-Leshkov, *Angew. Chem., Int. Ed.*, 2014, **53**, 5131.
- 143 Y. Hu, B. Yu, W. Li, M. Ramadoss and Y. Chen, *Nanoscale*, 2019, **11**, 4876.
- 144 C. Wan, Y. N. Regmi and B. M. Leonard, *Angew. Chem., Int. Ed.*, 2014, **53**, 6407.
- 145 K. Hackett, S. Verhoef, R. A. Cutler and D. K. Shetty, *J. Am. Ceram. Soc.*, 2009, **92**, 2404.
- 146 L. Limeng, Y. Feng, Z. Yu and Z. Zhiguo, *J. Am. Ceram. Soc.*, 2010, **93**, 2945.
- 147 L. Yang, X. Li, Y. Ouyang, Q. Gao, L. Ouyang, R. Hu, J. Liu and M. Zhu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 19987.
- 148 M. Kuang, Q. Wang, H. Ge, P. Han, Z. Gu, A. M. Al-Enizi and G. Zheng, *ACS Energy Lett.*, 2017, **2**, 2498.
- 149 J. Hou, Y. Wu, B. Zhang, S. Cao, Z. Li and L. Sun, *Adv. Funct. Mater.*, 2019, **19**, 1808367.
- 150 K. X. Wang, X. H. Li and J. S. Chen, *Adv. Mater.*, 2015, **27**, 527.
- 151 R. Ma, Y. Zhou, Y. Chen, P. Li, Q. Liu and J. Wang, *Angew. Chem., Int. Ed.*, 2015, **54**, 14723.
- 152 J. Jia, W. Zhou, Z. Wei, T. Xiong, G. Li, L. Zhao, X. Zhang, H. Liu, J. Zhou and S. Chen, *Nano Energy*, 2017, **41**, 749.
- 153 C. Wu, D. Liu, H. Li and J. Li, *Small*, 2018, **14**, 1704227.
- 154 X. Xu, F. Nosheen and X. Wang, *Chem. Mater.*, 2016, **28**, 6313.
- 155 C. Tang, W. Wang, A. Sun, C. Qi, D. Zhang, Z. Wu and D. Wang, *ACS Catal.*, 2015, **5**, 6956.
- 156 M. Liu, Y. Yang, X. Luan, X. Dai, X. Zhang, J. Yong, H. Qiao, H. Zhao, W. Song and X. Huang, *ACS Sustainable Chem. Eng.*, 2018, **6**, 14356.
- 157 S. Iijima and T. Ichihashi, *Nature*, 1993, **363**, 603.
- 158 J. W. Wilder, L. C. Venema, A. G. Rinzler, R. E. Smalley and C. Dekker, *Nature*, 1998, **391**, 59.

- 1 159 H. Wei, Q. Xi, X. A. Chen, D. Guo, F. Ding, Z. Yang, S. Wang, J. Li and S. Huang, *Adv. Sci.*, 2018, **5**, 1700733.
- 160 C. Lu, D. Tranca, J. Zhang, F. N. R. Hernández, Y. Su, X. Zhuang, F. Zhang, G. Seifert and X. Feng, *ACS Nano*, 2017, **11**, 3933.
- 5 161 X. Fan, Z. Peng, R. Ye, H. Zhou and X. Guo, *ACS Nano*, 2015, **9**, 7407.
- 162 J. Wang, H. Xia, Z. Peng, C. Lv, L. Jin, Y. Zhao, Z. Huang and C. Zhang, *ChemSusChem*, 2016, **9**, 855.
- 10 163 F. X. Ma, H. B. Wu, B. Y. Xia, C. Y. Xu and X. W. Lou, *Angew. Chem., Int. Ed.*, 2015, **54**, 15395.
- 164 Z. Pu, M. Wang, Z. Kou, I. S. Amiinu and S. Mu, *Chem. Commun.*, 2016, **52**, 12753.
- 15 165 Y. Huang, Q. Gong, X. Song, K. Feng, K. Nie, F. Zhao, Y. Wang, M. Zeng, J. Zhong and Y. Li, *ACS Nano*, 2016, **10**, 11337.
- 166 Z. Kou, T. Wang, Y. Cai, C. Guan, Z. Pu, C. Zhu, Y. Hu, A. M. Elshahawy, J. Wang and S. Mu, *Small Methods*, 2018, **2**, 1700396.
- 20 167 L. Huo, B. Liu, Z. Gao and J. Zhang, *J. Mater. Chem. A*, 2017, **5**, 18494.
- 168 Z. Zhao, F. Qin, S. Kasiraju, L. Xie, M. K. Alam, S. Chen, D. Wang, Z. Ren, Z. Wang, L. C. Grabow and J. M. Bao, *ACS Catal.*, 2017, **7**, 7312.
- 25 169 H. Lin, Z. Shi, S. He, X. Yu, S. Wang, Q. Gao and Y. Tang, *Chem. Sci.*, 2016, **7**, 3399.
- 170 Z. Liang, C. Qu, W. Guo, R. Zou and Q. Xu, *Adv. Mater.*, 2018, **30**, 1702891.
- 30 171 J. Yang, F. Zhang, H. Lu, X. Hong, H. Jiang, Y. Wu and Y. Li, *Angew. Chem., Int. Ed.*, 2015, **54**, 10889.
- Q8 172 R. Wang, X. Y. Dong, J. Du, J. Y. Zhao and S. Q. Zang, *Adv. Mater.*, 2017.
- 35 173 X. Luo, Q. Zhou, S. Du, J. Li, L. Zhang, K. Lin, H. Li, B. Chen, T. Wu, D. Chen, M. L. Chang and Y. L. Liu, *ACS Appl. Mater. Interfaces*, 2018, **10**, 42335.
- 174 J. Xiong, J. Li, J. Shi, X. Zhang, N.-T. Suen, Z. Liu, Y. Huang, G. Xu, W. Cai and X. Lei, *ACS Energy Lett.*, 2018, **3**, 341.
- 175 L. M. Azofra, N. Li, D. R. MacFarlane and C. Sun, *Energy Environ. Sci.*, 2016, **9**, 2545.
- 176 I. Matanovic and F. H. Garzon, *Phys. Chem. Chem. Phys.*, 2018, **20**, 14679.
- 177 Q. Li, S. Qiu, L. He, X. Zhang and C. Sun, *Phys. Chem. Chem. Phys.*, 2018, **20**, 23338.
- 178 F. Zhou, L. M. Azofra, M. Ali, M. Kar, A. N. Simonov, C. McDonnell-Worth, C. Sun, X. Zhang and D. R. MacFarlane, *Energy Environ. Sci.*, 2017, **10**, 2516.
- 179 A. R. Singh, B. A. Rohr, J. A. Schwalbe, M. Cargnello, K. Chan, T. F. Jaramillo, I. Chorkendorff and J. K. Nørskov, *ACS Catal.*, 2017, **7**, 706.
- 180 R. Wang, X. Y. Dong, J. Du, J. Y. Zhao and S. Q. Zang, *Adv. Mater.*, 2018, **30**, 1703711.
- 181 J. D. Benck, T. R. Hellstern, J. Kibsgaard, P. Chakthranont and T. F. Jaramillo, *ACS Catal.*, 2014, **4**, 3957.
- 182 R. Wei, M. Fang, G. Dong and J. C. Ho, *Sci. Bull.*, 2017, **62**, 971.
- 20 183 L. Han, X. Liu, J. Chen, R. Lin, H. Liu, F. Lü, S. Bak, Z. Liang, S. Zhao and E. Stavitski, *Angew. Chem., Int. Ed.*, 2019, **58**, 2321.
- 184 G. Zhang, Q. Ji, K. Zhang, Y. Chen, Z. Li, H. Liu, J. Li and J. Qu, *Nano Energy*, 2019, **59**, 10.
- 25 185 L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang and X. Sun, *Adv. Mater.*, 2018, **30**, 1800191.
- 186 X. Zhang, R.-M. Kong, H. Du, L. Xia and F. Qu, *Chem. Commun.*, 2018, **54**, 5323.
- 30 187 C. Lv, Y. Qian, C. Yan, Y. Ding, Y. Liu, G. Chen and G. Yu, *Angew. Chem., Int. Ed.*, 2018, **57**, 10246.
- 188 X. Yang, J. Nash, J. Anibal, M. Dunwell, S. Kattel, E. Stavitski, K. Attenkofer, J. G. Chen, Y. Yan and B. Xu, *J. Am. Chem. Soc.*, 2018, **140**, 13387.