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Review

Recent Progress on Molybdenum Carbide-Based Catalysts for Hydrogen Evolution: A Review

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Abstract: Hydrogen is an ideal alternative energy for fossil fuels to solve aggravating environmental and energy problems. Electrocatalytic hydrogen evolution reaction (HER) driven by renewable electricity (sunlight, wind, tide, etc.) is considered to be one of the most promising approaches for hydrogen production. However, its large-scale applications are greatly limited by the use of noble platinum (Pt) group electrocatalysts. As an earth-abundant/non-noble HER catalyst, molybdenum carbide (Mo_xC: MoC or Mo_2C) has attracted extensive attention in the field of sustainable hydrogen production due to its excellent Pt-like catalytic activity, low cost, high chemical stability, and natural abundance. In this review, the progress on the strategies for optimizing the catalytic activity of Mo_xC is summarized, including optimization of synthesis methods, composites with carbon material, non-precious metal doping, transition metal doping, construction of the heterogeneous structure, etc. Among them, the importance of sulphur-doping, Ni-doping, and heterophase structure on molybdenum carbide-based catalysts for enhancement of HER activity has been highlighted. In addition, molybdenum carbide-based bi-functional catalysts are presented for the application in full water splitting. Finally, several effective strategies for molybdenum carbide-based catalyst design are concluded, and challenges remained in electrocatalytic water splitting are raised. Future development trends and perspectives for this promising material are also discussed.

Keywords: molybdenum carbide; hydrogen evolution reaction; electrolysis

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1. Introduction

With the rapid development of society, fossil energy and other non-renewable energy are increasingly exhausted [1]. Meanwhile, the massive use of fossil fuels has also led to worsening environmental problems [2]. To solve this problem, sustainable and green energy sources need to be developed. Nowadays, large-scale renewable clean energy includes hydrogen energy, solar energy, wind energy, etc. [3]. Among them, hydrogen has the advantages of being clean, non-polluting, having a high energy density, and having excellent combustion performance, which has been proven to be a new efficient clean energy [4,5]. Due to its small molecular weight, hydrogen can be present in gaseous [6], liquid [7] or solid metal [8] hydride form to meet the requirements of different applications, storage, and transport environments [9,10]. In addition, the energy density of hydrogen is 142 $MJ \cdot kg^{-1}$, more than three times that of petrol, and the energy conversion efficiency of a hydrogen fuel cell with an electric motor system is so high that 1 kg of hydrogen can run a car for 100 km, which is unmatched by other fossil fuels and biofuels. Therefore, hydrogen has great potential as a kind of clean energy, which has attracted the attention of many researchers [11,12].

Hydrogen evolution reaction (HER) through water splitting (Figure 1a) is considered the most promising technology because of its sustainability and environmental friendliness for hydrogen production. Pt/C is currently the best electrocatalyst for HER because of its unique electronic structure and high stability [13]. However, its small reserves and high price limit its large-scale use [14]. Non-precious metal molybdenum-based electrocatalysts (such as molybdenum oxide, molybdenum phosphide, molybdenum nitride, molybdenum sulfide, and molybdenum carbide, etc.) have attracted a lot of attention because of their abundance and low cost [15–17]. Among them, molybdenum carbide has a D-orbital electronic structure similar to Pt, which has better HER activity and excellent stability [18]. However, the traditional synthesis methods of molybdenum carbide usually require high temperatures and complex processes, and the prepared molybdenum carbide has a large particle size and poor conductivity. In addition, the adsorption and desorption processes of proton H on the Mo active site usually receive numerous limitations [19] (slower adsorption processes for MoC and slower desorption processes for Mo_2C). Therefore, it is important to find a simple synthesis of molybdenum carbide materials and to balance the free energy of proton H at the Mo active site.

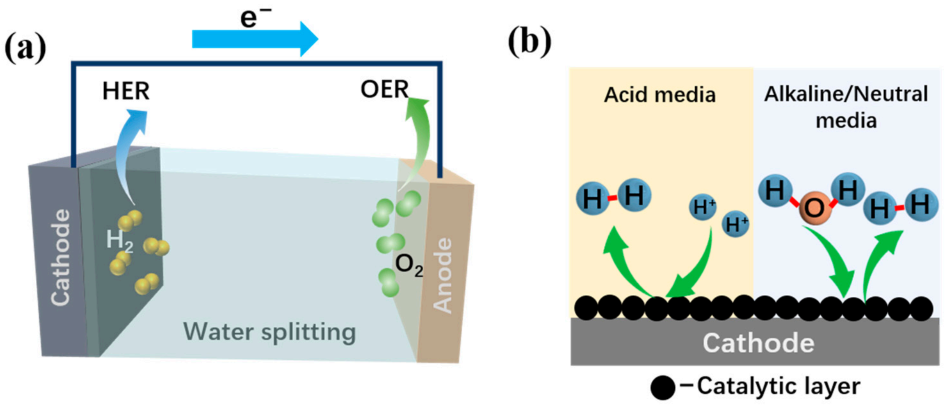

Figure 1. Diagram of the (**a**) water splitting and (**b**) HER reaction in different media.

Nowadays, many methods have been proposed, such as optimization of synthesis methods [20], composites with carbon material [21], non-precious metal doping [22], transition metal doping [23], construction of heterogeneous structures [24], etc. Among them, the importance of sulphur-doping, Ni-doping, and heterophase structure on molybdenum carbide-based catalysts for enhancement of activity in acidic and basic media has been highlighted in this review. These methods can either increase the conductivity of the surface active sites and composites or use phase engineering and doping to modulate the intrinsic catalytic activity of the material and optimize the Mo–H bond to enhance HER performance [25]. Therefore, this article briefly describes the mechanism of electrochemical water splitting and the characteristics of molybdenum carbide materials, details the methods by which the activity of molybdenum carbide can be improved, and gives an outlook on future research directions.

2. Mechanism of Hydrogen Evolution Reaction

The water splitting consists of two half-reactions, including the hydrogen evolution reaction (HER) at the cathode and the oxygen evolution reaction (OER) at the anode [26]. As a half-reaction of water splitting, the hydrogen evolution reaction (HER) is a two-electron-proton coupling reaction that takes place on the surface of the cathode catalyst [27,28]. In acidic media, the hydrogen evolution reaction is generally considered to consist of two basic steps (Figure 2a). In the first step (Equation (1)), hydrogen ions near the electrode surface (H^+) get electrons (e^-) and undergo a reduction reaction to become absorbed. H_{ads} on the electrode surface are then desorbed in two ways [29]. The first step is that when the coverage of H_{ads} on the electrode surface is high, two H_{ads} combine to form H_2

and are removed from the electrode surface (Equation (2), Volmer-Tafel mechanism) [30]. The second step is that when the coverage of H_{ads} on the electrode surface is low. H_{ads} continues to react with H^+ and e^- to form H_2 and is removed from the electrode surface (Equation (3), Volmer–Heyrosky mechanism) [31,32]. These two mechanisms correspond to the reaction equations:

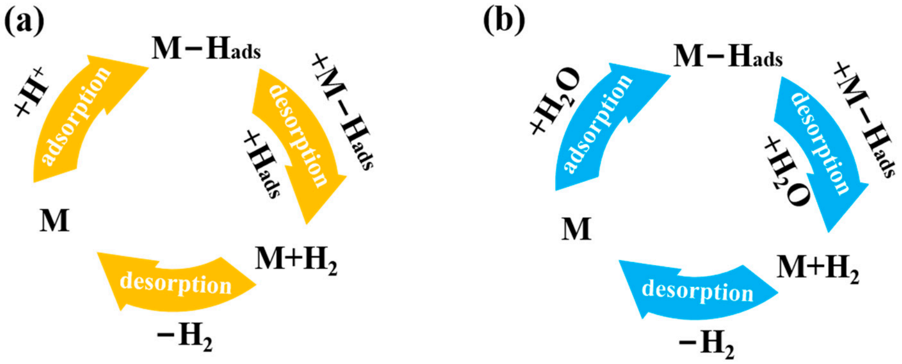

Figure 2. The Volmer–Tafel–Heyrovsky HER mechanism on the electrode surface in (**a**) acidic media, (**b**) alkaline or neutral media [29–32].

In acidic media:

$$M + H^+ + e^- \rightarrow M\text{-}H_{ads} \text{ Volmer reaction} \tag{1}$$

$$M\text{-}H_{ads} + M\text{-}H_{ads} \rightarrow H_2 + 2\,M \text{ Tafel reaction} \tag{2}$$

$$M\text{-}H_{ads} + H^+ + e^- \rightarrow H_2 + M \text{ Heyrovsky reaction} \tag{3}$$

The reaction pathway of HER is similar to that of an acidic environment (Figure 2b), but since a hydrolysis step is required to form H_{ads} intermediates of basic HER (Equation (4)), followed by the Tafel (Equation (5)) and Heyrosky (Equation (6)) reactions.

In alkaline or neutral media:

$$M + H_2O + e^- \rightarrow M\text{-}H_{ads} + OH^- \text{ Volmer reaction} \tag{4}$$

$$M\text{-}H_{ads} + M\text{-}H_{ads} \rightarrow H_2 + 2\,M \text{ Tafel reaction} \tag{5}$$

$$M\text{-}H_{ads} + H_2O + e^- \rightarrow H_2 + M + OH^- \text{ Heyrovsky reaction} \tag{6}$$

These two steps are hydrogen adsorption and hydrogen desorption in the HER, and the rate of hydrogen adsorption and hydrogen desorption directly affects the whole hydrogen precipitation reaction [33]. Usually, the materials used for electrocatalytic hydrogen evolution are directly affected by these two steps, which reflect the different performances of catalytic hydrogen evolution [34,35].

3. Characteristic of Molybdenum Carbide Materials

Molybdenum-based carbides are considered to be a class of intermetallic compounds and have metallic conductivity and mechanical strength [36]. During the formation of molybdenum carbide, carbon atoms with smaller atomic radii enter the lattice interstices of molybdenum metal by infiltration, and the amount of infiltrable carbon atoms is a variable interval [37]. Therefore, the synthesis of molybdenum carbides with different crystal types (MoC, Mo_2C) can be regulated by modulating the reaction conditions (Figure 3), and Mo_2C exhibits superior activity to MoC due to its strong adsorption for proton H [38]. The infiltration of carbon atoms leads to the expansion of the metal lattice and the widening of the spacing between the metal atoms, which leads to the shift of the metal d-band and the increase of valence electrons. This modification causes a change in the adsorption energy of the hydrogen atoms [39] and enables molybdenum carbide to produce electrochemical catalytic performances in comparison with those of noble metals (such as Pt), which is one of the reasons why molybdenum carbide exhibits excellent electrochemical activity.

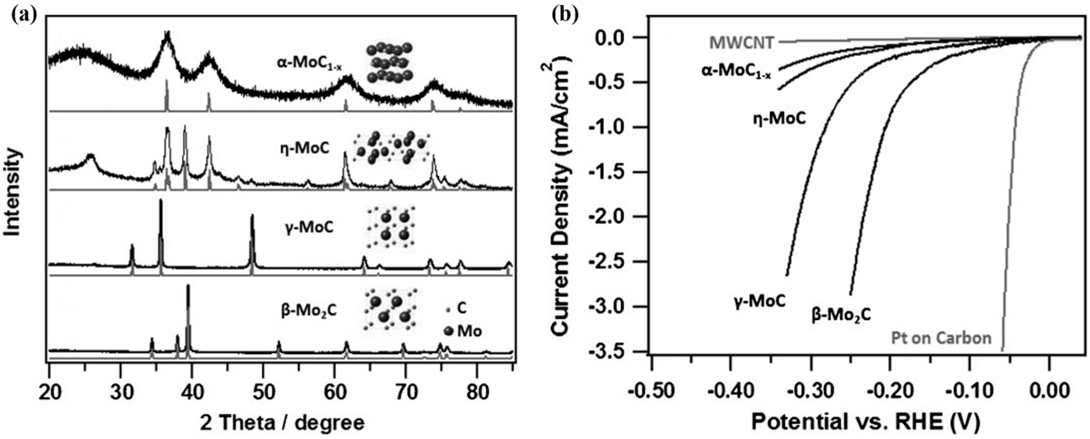

Figure 3. X-ray diffraction (XRD) patterns (**a**) and LSV curves (**b**) of different crystal types of molybdenum carbide (reaction conditions: α-MoC_{1-x} (heat at 750 °C for 12 h), β-Mo_2C (heat at 850 °C for 12 h), γ-MoC (heat at 850 °C for 24 h), η-MoC (heat at 1050 °C)), adapted with permission from Ref. [38] ©2014 Wiley-VCH.

DFT calculations have demonstrated that the overlap between the d-orbital of the Mo atom and the p-orbital of the C atom broadens the d-orbital structure of Mo (Figure 4), giving molybdenum carbide a Pt-like electronic structure [40], which has good hydrogen evolution activity, excellent stability, and performs well among all types of molybdenum-based electrocatalysts. Because commercial Pt/C is very expensive, using molybdenum carbide-based catalysts instead of Pt/C can reduce the cost of hydrogen fuel production during the hydrogen evolution reaction. Mo_2C has a large exchange current density, but due to the strong hydrogen binding energy, the Mo–H bond is too strong for the desorption of proton H, blocking the further enhancement of LSV activity [41]. To improve the activity of molybdenum-based carbides, researchers have them it to enhance their HER activity by various methods, such as optimizing the synthetic pathway [42], elemental doping [43,44] and heterophase engineering [45].

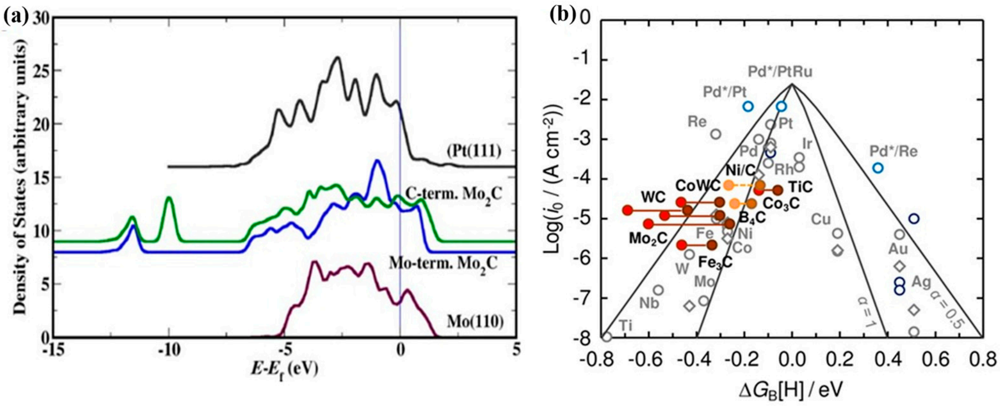

Figure 4. (**a**) The d-band electronic structures of Pt (111), β-Mo_2C (001) surface and Mo (110). (**b**) Volcano plots of exchange current density and hydrogen binding energy of HER electrocatalysts, adapted with permission from Ref. [40] ©2017 Wiley-VCH.

4. Different Synthesis Methods of Molybdenum Carbide Materials

Conventional synthesis methods for molybdenum carbide are based on a gas-solid phase reaction with high-temperature carbonization (≥800 °C) of MoO_3 in a CH_4/H_2 atmosphere [46,47]. However, the high-temperature carbonization of MoO_3 in a CH_4/H_2 atmosphere is poorly controllable, and the molybdenum carbides obtained have a large particle size, which inevitably leads to the agglomeration of Mo_xC nanoparticles and limits the HER activity. Currently, high-temperature carbonization and precipitation–calcination are commonly used methods for the synthesis of molybdenum carbide (Figure 5).

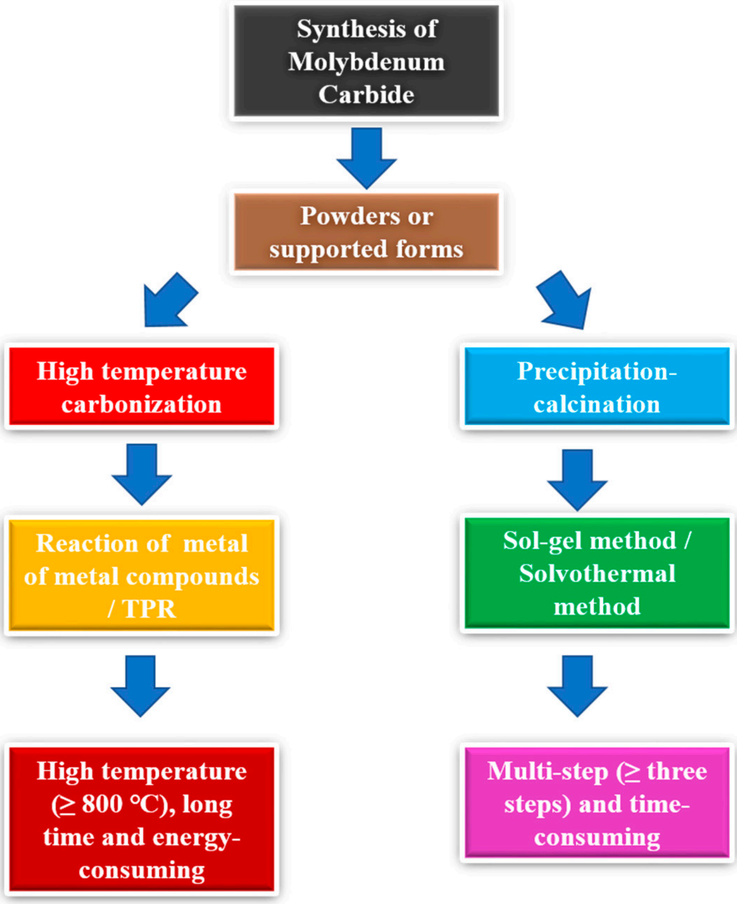

Figure 5. Traditional synthesis methods of molybdenum carbide [46,47].

Ma et al. [48] used $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and dicyanamide as precursors to produce Mo_2C by high-temperature carbonization in N_2 at 800 °C for 6 h, which showed good activity in 0.5 M H_2SO_4 (10 mA/cm^2 is 205 mV). Lv et al. [49] used a two-step precipitation–calcination method using glucose, NaCl, and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ as precursors, which were first preroasted at 800 °C under N_2 and then reacted at 850 °C for 2 h under a 5% H_2/95% N_2 gas mixture to obtain Mo_2C. The overpotential at 10 mA/cm^2 is 430 mV in 1 M KOH media. Wu et al. [50] produced Mo_2C-C by a multi-step precipitation–calcination method using $(NH_4)_6Mo_7O_{24}\cdot 6H_2O$, glucose, and ethylene glycol as precursors at 900 °C under 8% H_2/Ar, showing good activity under alkaline conditions (10 mA/cm^2 is 149 mV). Du et al. [51] also used the precipitation–calcination method to react sodium molybdate and cetyltrimethylammonium bromide as precursors in N_2 at 900 °C to produce Mo_2C-NS, which showed good activity in alkaline media (10 mA/cm^2 is 205 mV). The results of other research on traditional synthesis methods are listed in Table 1, and they all have disadvantages such as long synthesis processes/time, high temperatures, and energy consumption.

Table 1. Traditional synthesis methods of molybdenum carbide-based catalysts.

Sample	Synthetic Method	Precursors	Synthetic Conditions	Electrolyte	η_{10}	Ref
Mo_2C	High-temperature carbonization	$(NH_4)_6Mo_7O_{24}·4H_2O$, dicyanamide	Step 1: calcination at 400 °C for 30 min; step 2: 800 °C in N_2 for 6 h	0.5 M H_2SO_4	205 mV	[48]
Mo_2C	Precipitation–calcination	Glucose, NaCl and $(NH_4)_6Mo_7O_{24}·4H_2O$	Step 1: stir and preheating at 800 °C in N_2; step 2: calcination at 850 °C in 5% H_2/95% N_2 for 2 h	1 M KOH	430 mV	[49]
Mo_2C-C	Precipitation–calcination	$(NH_4)_6Mo_7O_{24}·6H_2O$, glucose and ethylene glycol	Step 1: stir for 30 min; step 2: heating at 200 °C for 10 h; step 3: calcination at 900 °C in 8%H_2/Ar for 2 h	1 M KOH	149 mV	[50]
Mo_2C NS	Precipitation–calcination	Sodium molybdate, cetyltrimethylammonium bromide	Step 1: stir for 2.5 h; calcination at 600 °C for 4 h in N_2; step 2: calcination at 900 °C for 2 h in N_2	1 M KOH	205 mV	[51]
Mo_2C	High-temperature carbonization	MoO_3 and SiO_2/Si	Step 1: chemical vapor deposition in Ar; step 2: carbonization under CH_4 and H_2; step 3: heated at 800 °C	1 M KOH	168 mV	[52]
Ni–Mo_2C–PC	Precipitation–calcination	$Ni(NO_3)_2·6H_2O$, $Na_2MoO_4·2H_2O$ and dopamine hydrochloride	Step 1: hydrothermal treatment at 150 °C for 6 h; step 2: stir for 24 h at room temperature; step 3: calcination at 800 °C for 2 h in Ar	1 M KOH	179 mV	[53]
MoC_x	High-temperature carbonization	NENU-5	Step 1: calcination at 800 °C in Ar for 6 h;step 2: etch with Fe^{3+} for 2 h	1 M KOH	151 mV	[54]
				0.5 M H_2SO_4	142 mV	
Mo_2C	High-temperature carbonization	$MoCl_5$ and urea	Step 1: calcination at 800 °C in N_2 for 3 h	0.5 M H_2SO_4	198 mV	[55]
N-doped Mo_2C	High-temperature carbonization	MoO_3	Step 1: calcination at 900 °C in Ar/H_2 for 1 h; step 2: 700 °C in $C_2H_4N_4$ for 2 h	0.5 M H_2SO_4	319 mV	[56]
Mo_2C nanoparticles	High-temperature carbonization	$MoCl_5$, ethanol, and urea	Step 1: irradiation at 50 °C for 10 min; step 2: calcination at 800 °C in N_2 for 3 h	0.5 M H_2SO_4	220 mV	[57]

To overcome these drawbacks, many attempts have been made by scholars to synthesize molybdenum carbide. Tang et al. [58] obtained a highly dispersed organic-inorganic hybrid precursor containing molybdenum by hydrothermal method and then carbonized it at high temperature (725 °C) for 5 h to obtain a molybdenum carbide catalyst with good LSV activity in 0.5 M H_2SO_4. Upadhyay et al. [59] discovered a one-step high-temperature carburization–reduction route for the synthesis of molybdenum carbide by using ammonium molybdenum tetrahydrate (AHM) and hexamethylenetetramine (HMT) as precursors and Mg as a reducing agent at high temperatures ($\geq$700 °C, $\geq$6 h). Wang et al. [60] obtained Mo_2C nanoparticle layers by homogeneously coating MoS_2 on carbon cloth (CC). Mo_2C nanoparticle layers were obtained by electrochemical reduction in molten NaCl-KCl, which exhibited a low overpotential of 134.4 mV at 10 mA cm^{-2} in acidic media. Zhou et al. [61] developed a one-step synthesis of C_{60}-MoC nanocomposites in Li_2CO_3-K_2CO_3 molten salts using carbon dioxide and ammonium molybdate as the carbon and molybdenum sources, respectively. As is shown in Figure 6, the C_{60}-MoC material was obtained in a reaction at 600 °C for 2 h for the HER reaction and achieved good activity (η_{10} is 142 mV) with industrial current density stability (220 mA/cm^2 for 10 h) in alkaline media. In addition, the particle size of the C_{60}-MoC material decreases significantly when the reaction temperature is less than or equal to 600 °C. At the same time, the specific surface area increases significantly, providing sufficient electrochemical active sites.

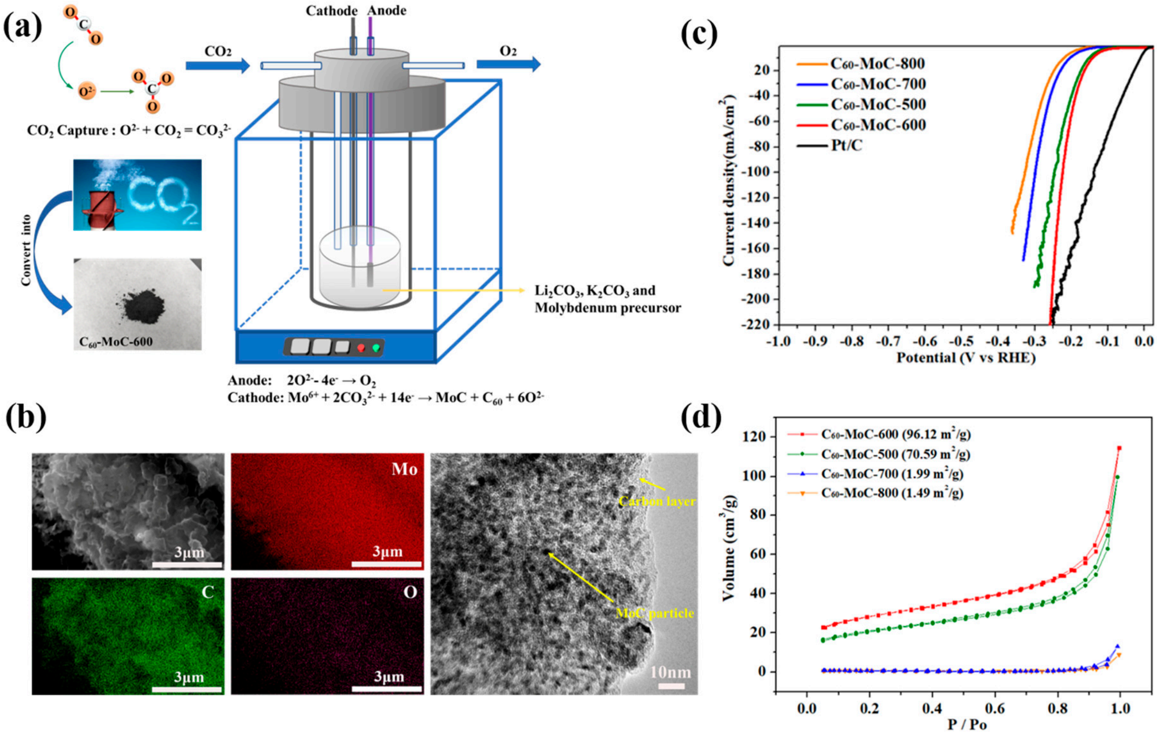

Figure 6. (**a**) Synthesis of molten salt in one-step process of C_{60}-MoC-600. (**b**) SEM, mapping, and TEM of C_{60}-MoC-600. (**c**) LSV curves and (**d**) BET results of C_{60}-MoC under different synthesis temperature, adapted with permission from Ref. [61] ©2023 Electrochemical Society.

The optimization of the molybdenum carbide synthesis method (reduction of synthesis steps and lower synthesis temperature) helps to reduce energy consumption during the synthesis of molybdenum carbide materials, while controlling the synthesis temperature to 600 °C helps to refine the particles, increase the specific surface area, and increase the active site of the HER reaction.

5. The Activity Enhancement of Molybdenum Carbide by Compositing with Carbon Materials

Poor electrical conductivity is one of the reasons for the low activity of molybdenum carbide materials [62,63]. Nowadays, many researchers find that the conductivity of the molybdenum carbide material and the hydrogen evolution capacity can be improved by compounding molybdenum carbide with carbon materials or doped carbon materials.

Yang et al. [64] obtained homogeneous dispersion of Mo_2C nanoparticles on carbon micron flowers by self-polymerization of dopamine. Among them, the strong chelation of $MoO_4{}^{2-}$ with dopamine plays an important role in the morphology regulation process, and the obtained composites have a large surface area while avoiding the agglomeration of Mo_2C nanoparticles caused by high temperatures. Wang et al. [65] obtained Mo_2C nanoparticles and carbon flakes strongly coupled by annealing at 1000 °C for 3 h under an Ar atmosphere with ammonium molybdate tetrahydrate and glucose in a certain mass ratio for the electrolytic water reaction, which facilitated the charge interconnection. Then the MoO_2 spheres were thermally reduced with carbon to obtain Mo_2C hollow spheres with good thermal stability and hydrogen precipitation activity. Arka et al. [66] obtained MoO_2 spheres with uniformly dispersed optimal carbon content by using hexadecyltrimethylammonium bromide as a soft template, carbon source, and ammonium heptamolybdate as a metal source, followed by carbon thermal reduction to obtain β-Mo_2C hollow spheres with composite carbon, which have good thermal stability and HER activity. Zhu et al. [67] converted phosphomolybdic acid in the template SBA-15 to MoO_2, which was then converted in situ to Mo_2C nanowires with abundant surface defects. After the removal of the template, Mo_2C@GC core–shell layer nanowire arrays with a rough Mo_2C nanowire core and a thin shell layer were obtained. The former provided a large number of active sites, while the latter provided short and continuous electron transfer pathways, thus exhibiting excellent performance. Huo et al. [68] synthesized 2D layered composites of mesoporous Mo_2C and graphene using glucose as the carbon source and in situ assembled mesoporous materials as templates (m-Mo_2C/G). Their good mesoporous structure exposed more active sites, while the high conductivity of graphene allowed the m-Mo_2C/G to have high catalytic activity and excellent HER durability over a wide pH range (Figure 7). Li et al. [69] reported the Mo_2C composite Mo_2C@NPC/NPRGO based on reduced graphene oxide (RGO), which showed excellent HER performance under both acid and alkaline media. Under alkaline media, the Tafel slope of Mo_2C@NPC/NPRGO is even smaller than that of Pt/C.

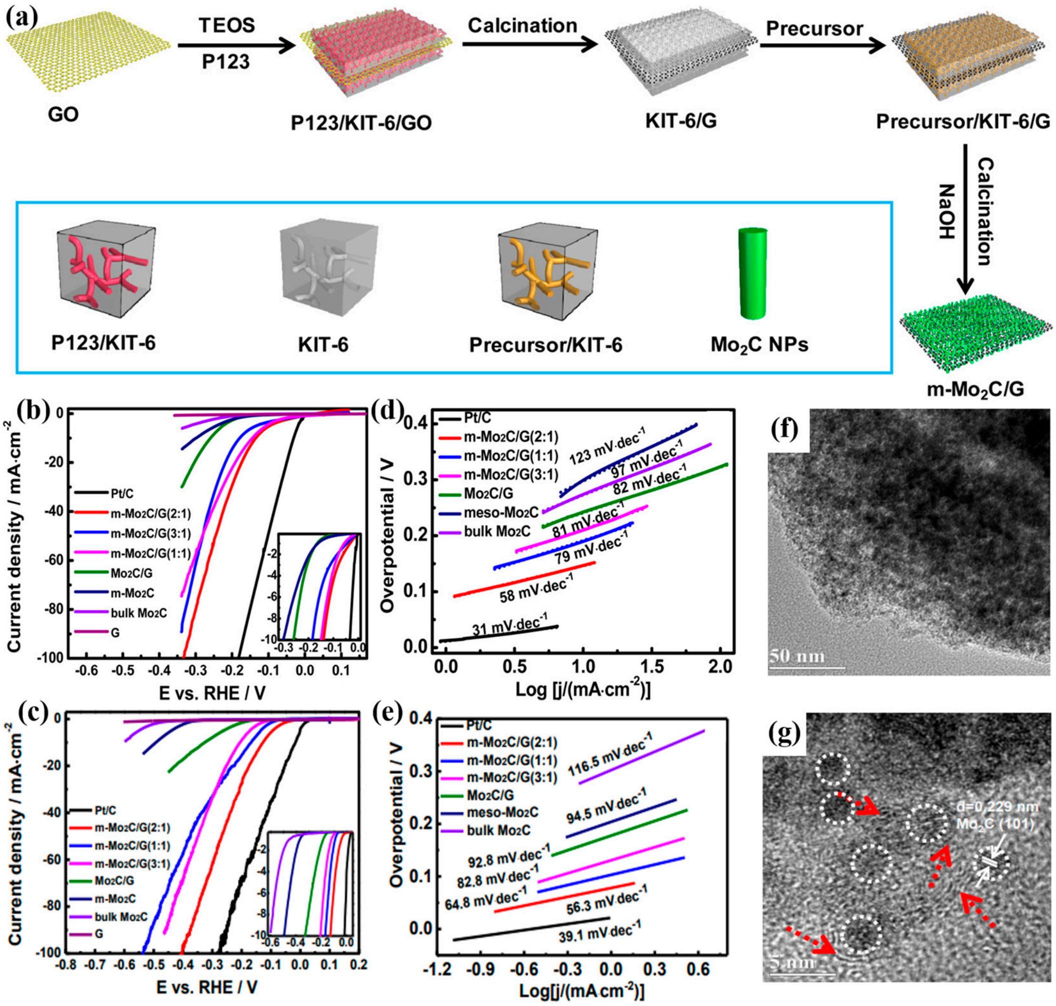

Figure 7. (**a**) Synthesis process of m-Mo_2C/G. (**b**) LSV and (**d**) Tafel results in 0.5 M H_2SO_4. (**c**) LSV and (**e**) Tafel results in 1 M KOH. (**f**) TEM and (**g**) HRTEM images of m-Mo_2C/G electrocatalyst, adapted with permission from Ref. [68] ©2016 American Chemical Society.

Composites with carbon materials to improve the hydrogen evolution capacity of electrocatalysts have been a research topic in recent years [70]. Molybdenum carbide combine with carbon materials in various forms (e.g., non-metal-doped graphene, porous carbon, or carbon nanotubes) not only prevents corrosion of the catalyst surface but also increases the active sites and improves the hydrogen evolution capacity. It also improves the reaction efficiency of the catalyst due to its good conductivity [71].

6. Metal doping of Molybdenum Carbide Materials

6.1. Non-Precious Metal Doping of Molybdenum Carbide Materials

Non-precious metal doping is another way to optimize the activity of molybdenum carbide materials. The catalytic activity of molybdenum carbide can be improved by the introduction of other elements, which may adjust the electron sites in a rational way [72]. The introduction of non-metal elements such as nitrogen (N), phosphorus (P), and sulfur (S) into the carbon matrix in order to improve charge transfer rates and active sites increases the activity of HER [73–75].

Lv et al. [76] have synthesized N- and P-doped molybdenum carbide nanofibers for efficient electrochemical hydrogen precipitation. They concluded that the introduction of an appropriate amount of electron-rich (N, P) doping into the lattice reduces the d-band orbital density of the Mo_2C hollow. In addition, the formation of N–Mo and P–Mo bonds weakened the Mo–H bonds of the Mo_2C site intermediates, promoting H desorption and improving electrochemical hydrogen precipitation performance. Zhou et al. [77] have synthesized an N-doped Mo_2C derived from giant poly molybdate clusters. The formation of N–Mo bonds in this material inhibited the aggregation of Mo_2C nanoparticles during high-temperature annealing, while N was also doped into the graphene, significantly increasing its activity. Zhang et al. [78] formed SS-MoC by doping MoC with a small amount of S. As shown in Figure 8, the addition of a small amount of S can greatly increase the number of active sites and intrinsic activity, optimize the electronic structure of MoC, and improve the electron transfer efficiency, resulting in excellent HER activity and a small Tafel slope (48 mV dec^{-1}) in 0.5 M H_2SO_4 media. Meanwhile, theoretical studies have shown that terminal S plays a key role in promoting a near-zero hydrogen adsorption energy (ΔG_H*) and a lower hydrogen release potential. Zhu et al. [79] synthesized S-doped α-MoC in molten carbonate in a one-step method by introducing Li_2SO_4 into the electrolyte using CO_2 and MoO_3 as precursors. DFT calculations showed that the ΔG_H* of S-doped α-MoC (-0.32 eV) was closer to zero than that of α-MoC (-0.70 eV), which promotes water adsorption and dissociation, weakens the Mo–H bond energy, and promotes the formation of H_2 in 1 M KOH media.

As one of the main modification means for electrocatalysts, non-metallic doping has a good development prospect [80]. The doping of non-metallic elements with strong electronegativity into molybdenum carbide catalysts changes the composition and electronic structure of the materials, provides more active sites or optimizes the activity of the active sites, and shows a feasible method for the modification of molybdenum carbide-based catalysts [81]. In particular, the S-doped balances the bonding energy of Mo–H bonds under both acidic and basic conditions and promotes the formation of H_2.

6.2. Transition Metal Doping of Molybdenum Carbide Materials

In recent years, researchers have been able to optimize the electronic structure of molybdenum carbide and improve HER activity by doping with transition metal elements (Fe, Co, Ni, and Cr) [82]. Yu et al. [83] explored the activity of Mo_2C doped with different transition metals (Figure 9). Both the DFT calculations and the electrocatalytic experiments show that transition metal doping has a significant effect on both the hydrogen binding energy (ΔG_H*) and the catalytic activity of Mo_2C. The order of HER activity is as follows: Ni–Mo_2C > Co–Mo_2C > Fe–Mo_2C > Cr–Mo_2C. As a result, Ni–Mo_2C@C has the best LSV performance, requiring an overpotential of 72 mV at a current density of 10 mA/cm^2 in 0.5 M H_2SO_4.

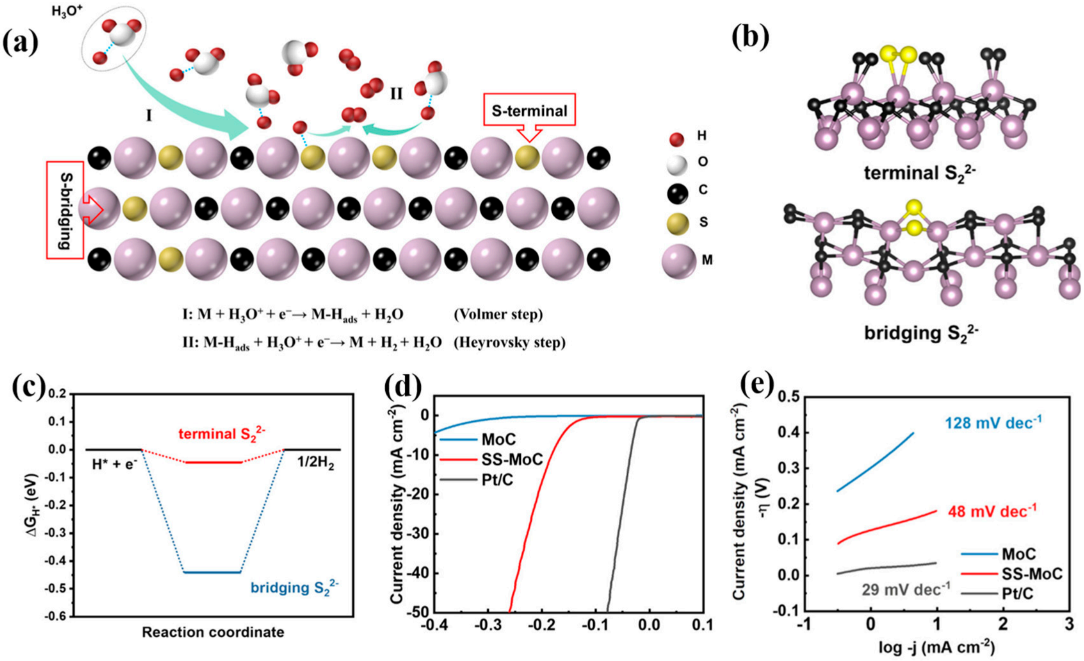

Figure 8. (**a**) Schematic illustration of the HER mechanism for SS-MoC. DFT calculations of SS-MoC. (**b**) Atomic structure of SS-MoC with terminal S_2^{2-} and bridging S_2^{2-} (**c**) $\triangle G_H$* diagrams of adsorbed *H on terminal S_2^{2-} and bridging S_2^{2-}; (**d**) LSV; and (**e**) Tafel results of all the samples in 0.5 M H_2SO_4, adapted with permission from Ref. [78] ©2021 American Chemical Society.

Geng et al. [84] coupling MoC NPs with Ni-NPs onto CC (NiMoC@NCNT/CC) using alkaline etching introduce Ni into the Mo precursor NW/CC, which is then subjected to high-temperature pyrolysis. The catalytic activity of the self-supported electrode can be optimized by simply adjusting the molar ratio of Mo to Ni. The optimized self-supported electrode exhibited excellent catalytic performance with overpotentials of 70 mV for HER in a 1 M KOH solution. Zhou et al. [85] report a new method for the synthesis of MoC_x catalysts at lower temperatures for the hydrogen evolution reaction in acidic solutions of Ni^{2+}, $MoO_4{}^{2-}$, and 2-methylimidazole in an aqueous solution that produces Mo–Ni–imidazole complexes as precursors by room-temperature co-precipitation reactions. Mo_xC/Ni-650 was obtained by carbonization in the Ar atmosphere at 650 °C. The coexistence of the MoC and Mo_2C phases promoted an electrochemical hydrogen evolution reaction, the MoC_x/Ni-650 exhibits a rather low overpotential (172 mV) at 20 mA cm^{-2}. This high performance results from the synergistic effect between MoC_x and the Ni–Mo alloy, the high Mo^{3+}/Mo^{2+} ratio, as well as the high electrochemically active surface area and low charge transfer resistance. Hu et al. [86] formed a nanostructured layer of Ni–Mo_2C/CCB with a thickness of 20–30 nm by introducing molybdenum powder, nickel powder, and carbon black (CB) to cover the surface of carbon fiber paper (Ni–Mo_2C/CCB/CFP). The doping of Ni reduces the content of high-valence Mo^{6+} and Mo^{4+} and increases the content of low-valence Mo^{2+}, which is the main catalytic active site. The synergistic effect of CB and Ni improves the HER performance, resulting in an overpotential at 10 mA/cm^2 of 121.4 mV for Ni–Mo_2/CCB/CFP in 0.5 M H_2SO_4. Ouyang et al. [87] reported a method for loading dispersed Ni atoms in β-Mo_2C electrocatalysts, Ni/β-Mo_2C obtained by synthesizing NiMo/MOM using bpe, $MoO_4{}^{2-}$, and $NiCl_2{\cdot}6H_2O$ at 25 °C, followed by carbonizing at 800 °C under N_2. The Ni/β-Mo_2C shows good HER activity at all pHs (η_{10} of 155 mV in 0.5 M H_2SO_4 and η_{10} of 157 mV in 1 M KOH). The Ni–Mo bonding promotes the formation of the Ni/β-Mo_2C structure, which results in excellent all-HER activity due to the porous structure and interatomic synergistic interactions of Ni/β-Mo_2C.

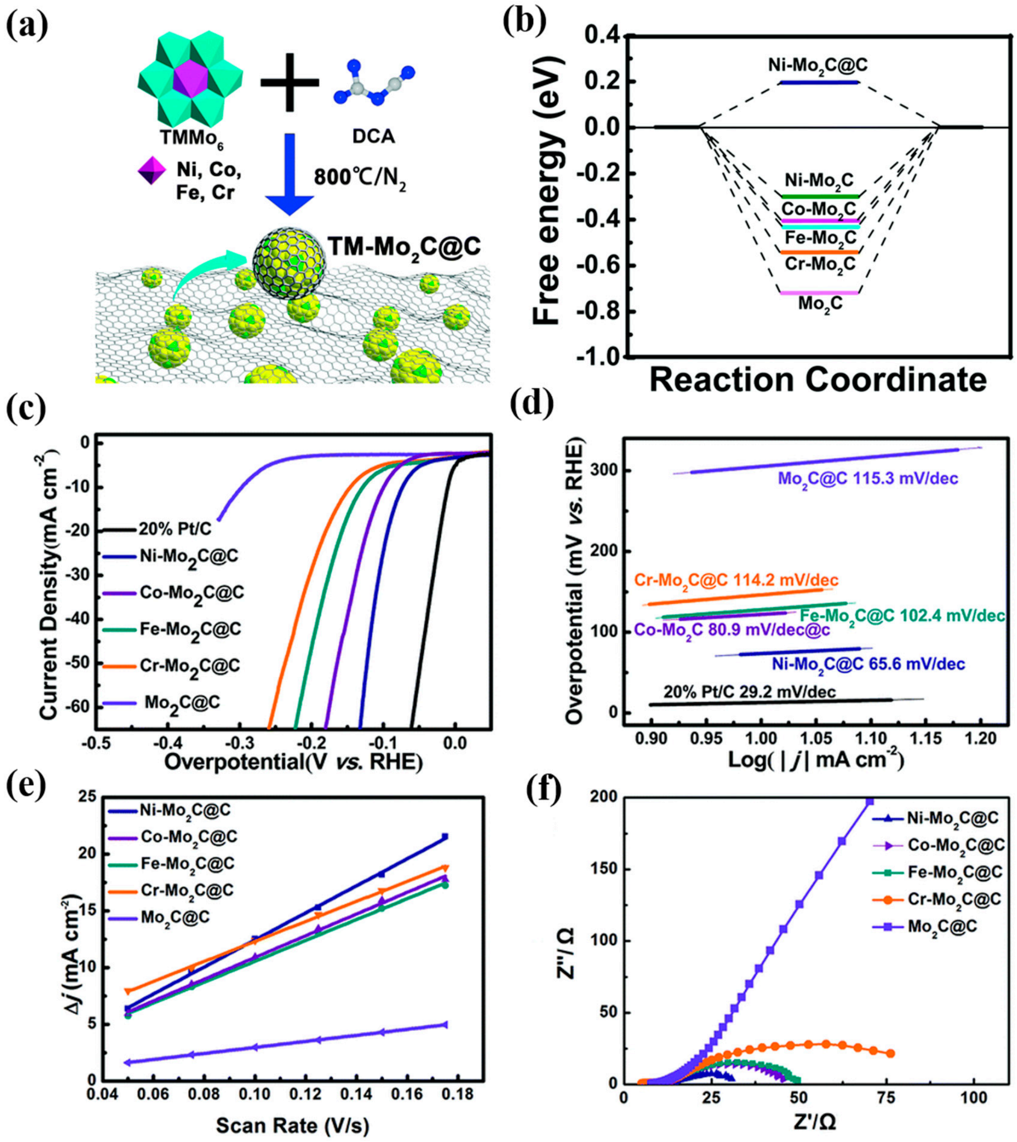

Figure 9. (**a**) Diagram of the synthesis of TM–Mo_2C@C. (**b**) Free–energy diagram of all the catalysts. (**c**) LSV curves for all the catalysts in 0.5 M H_2SO_4. (**d**) Tafel plots of all the catalysts in 0.5 M H_2SO_4. (**e**) Capacitive current of all the catalysts in 0.5 M H_2SO_4. (**f**) Electrochemical impedance spectra (EIS) of all the catalysts in 0.5 M H_2SO_4, adapted with permission from Ref. [83] ©2018 Royal Society of Chemistry.

Metal doping, like non-metal doping, is one of the main modification methods for electrocatalysts [88]. Transition metals (Fe, Co, Ni, and Cr) with high catalytic activity are doped by hydrothermal and annealing methods. Among them, Ni-doping usually shows the best effect. The Ni–Mo bond formed by Ni-doping well balances the adsorption and desorption of proton H on the active sites, and new active sites can be added to improve the hydrogen evolution performance of the electrocatalysts.

7. Heterophase Structure of Molybdenum Carbide Materials

Among the many molybdenum carbide crystalline forms, Mo_2C has the best HER activity due to its strong Mo–H bond that facilitates the adsorption of proton H (Volmer reaction). However, the excessively strong Mo–H bond blocks the release of proton H (Heyrovsky reaction) [89]. Therefore, balancing the Mo–H bond can help optimize the electronic structure of Mo_2C and further enhance LSV activity. Currently, heterophase electrocatalytic catalysts are more widely used in HER. Due to the unique structure and synergistic effect between different phases [90], the heterogeneous interface of heterophase catalysts provides a large number of catalytically active sites, which accelerates electron transport and compensates for the disadvantages of single-phase catalysts, promoting efficient hydrogen production. For molybdenum carbide, MoC-Mo_2C composite catalysts with heterophase structures have been widely studied.

Lin et al. [91] synthesized MoC-Mo_2C composite nanowires for efficient hydrogen production. Mo_2C has a strong adsorption capacity for proton H but limits the desorption of proton H. The MoC-Mo_2C heterogeneous structure optimizes the adsorption and desorption of proton H and enhances its HER performance. As shown in Figure 10, MoC-Mo_2C-31.4 shows the best LSV activity in both acidic and alkaline media.

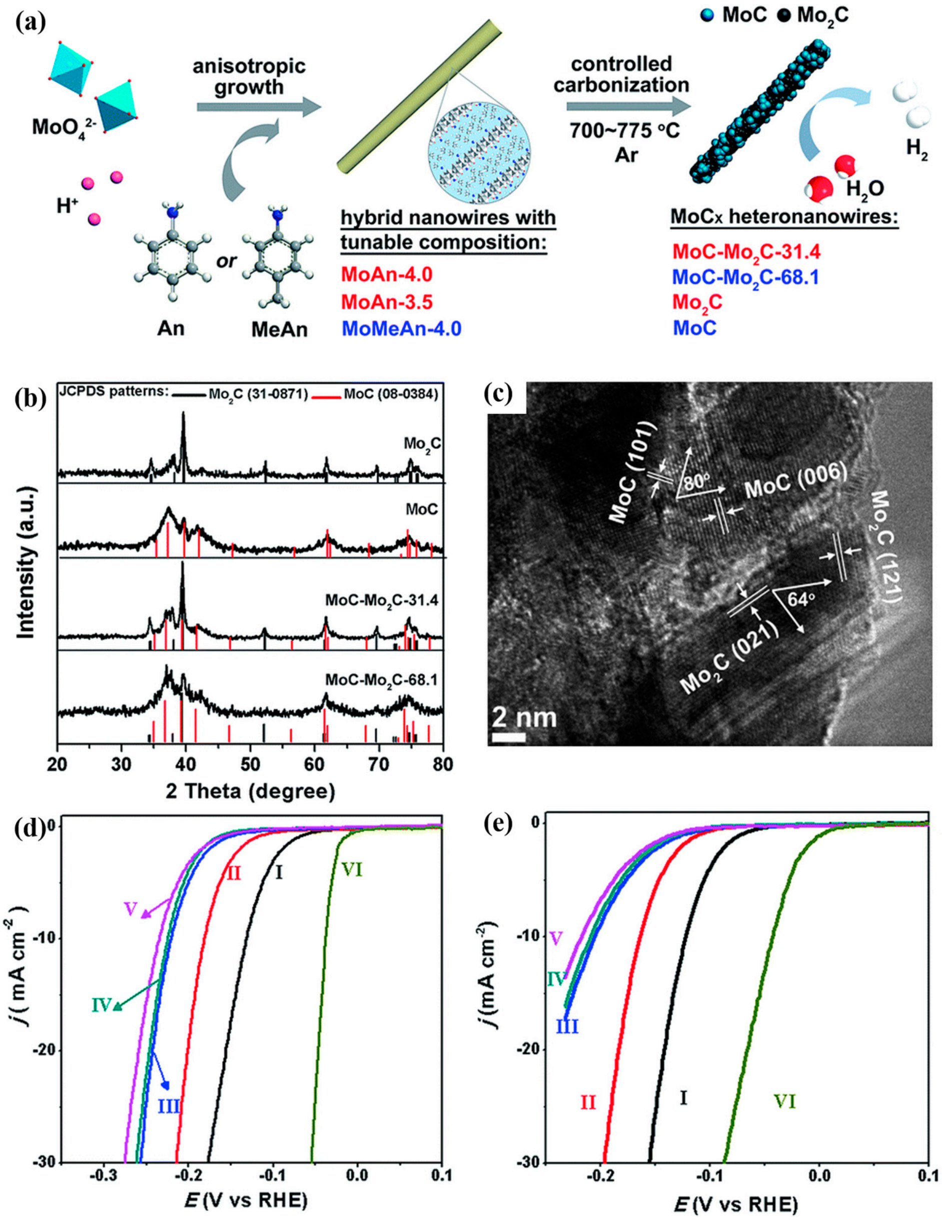

Figure 10. (**a**) Diagram of the synthesis of heterophase MoC-Mo_2C. (**b**) XRD patterns of all the catalysts. (**c**) HRTEM of MoC-Mo_2C-31.4. LSV curves of all the samples (I) MoC-Mo_2C-31.4, (II) Mo_2C, (III) MoC-Mo_2C-68.1, (IV) MoC-Mo_2C-30 (mixed), (V) MoC, and (VI) commercial Pt/C in (**d**) 0.5 M H_2SO_4 and (**e**) 1 M KOH, adapted with permission from Ref. [91] ©2016 Royal Society of Chemistry.

Liu et al. [92] constructed Mo_2C/MoO_2 composite nanorods with ultra-small nanostructures and tunable compositions by self-templated carbon thermal reduction of poly molybdic acid-melamine precursors. Due to the unique interface and compositional controllability of Mo_2C and MoO_2, the Mo_2C/MoO_2-650 nanorods exhibited excellent hydrogen evolution activity. Chen et al. [93] prepared heterophase MoC-Mo_2C nanosheets using a molten salt method. In this process, carbon dioxide is reduced to carbon, which reacts with molybdenum in situ to form molybdenum carbide nanosheets. The composition of the molybdenum carbide could also be adjusted according to the electrolytic conditions, and the results show that the heterophase structure of MoC-Mo_2C facilitates the activity enhancement of the catalyst in acidic media. Liu et al. [94] prepared self-supporting sparse porous MoC-Mo_2C heterojunction catalytic layers on Mo sheets in molten carbonate. The prepared MoC-Mo_2C heterojunction layers showed good activity in both acidic (overpotential of 114 mV at 10 mA/cm^2 and 183 mV at 100 mA/cm^2) and alkaline (overpotential of 98.2 mV at 10 mA/cm^2 and 292 mV at 500 mA/cm^2) solutions. There is good stability at an industrial operating temperature of ~70 °C. At the same time, it has good hydrophilicity, which contributes to the release of hydrogen gas bubbles. It indicates that MoC-Mo_2C heterojunction is a promising low-cost catalyst for hydrogen production under simulated industrial operating conditions.

Most of the activity enhancement of heterogeneous catalysts is attributed to the synergistic effect of multiphase [95]. For example, the formation of a MoC-Mo_2C heterostructure enhances electrical conductivity because MoC has more C content than Mo_2C. Meanwhile, the introduction of MoC also helps to balance the free energy of proton H in the active site of the catalyst [96], which promotes the release of proton hydrogen to form H_2.

8. Molybdenum Carbide-Based Catalysts for Full Water Splitting

Electrochemical water splitting is a viable method of producing high-purity hydrogen fuel in an environmentally friendly manner, which is recognized as a core clean energy technology essential to the hydrogen economy [97,98]. Full water splitting is an important parameter for evaluating the catalytic performance of electrolytic water catalysts. High voltages (typically > 1.8 V) are required to overcome the activation barriers of the reaction. Large overpotentials arise from the two half-reactions: Anodic OER and cathodic HER [99]. To minimize the overvoltage of the full water splitting and increase the efficiency of the energy conversion, it is necessary to make use of high-performance electrocatalysts. Nowadays, some molybdenum carbide-based bi-functional electrocatalysts with excellent HER activity and OER activity are applied to full water splitting reactions.

Yu et al. [53] reported a novel porous carbon-supported Ni/Mo_2C (Ni/Mo_2C-PC) composite catalyst obtained by heat treatment of nickel molybdate nanorods coated with dopamine, which is capable of highly efficient and robust HER and OER reactions in alkaline electrolytes with remarkable kinetic indices. The catalyst provides small overpotentials (179 mV for HER and 368 mV for OER) at a current density of 10 mA cm^{-2}. These results are superior to those of Mo_2C–PC, Ni–PC, and most other documented nickel- and molybdenum-based catalysts. The high activity of Ni/Mo_2C–PC may be attributed to the transfer of electrons from Ni to Mo_2C resulting in a higher valence number of Ni and a lower valence number of Mo in the Ni/Mo_2C–PC catalysts, which are HER- and OER-active species and therefore responsible for the enhanced activity. It is noteworthy that a homemade alkaline electrolyzer assembled with Ni/Mo_2C-PC as a bi-functional catalyst achieved a water separation current density of 10 mA cm^{-2} at a low cell voltage of 1.66 V. Gong et al. [100] designed an efficient molybdenum carbide-based self-supported bi-functional catalyst (Figure 11). Nanoscale hybridized Mo_2C–CoO encapsulated in N-doped carbon nanofibers (Mo_2C–CoO@NCNFs). DFT calculation and electrochemical tests showed that the synergistic effect of Mo/Co bimetallic accelerated the kinetic process of the hydrogen evolution reaction (HER), resulting in better hydrogen adsorption/desorption capacity and lowering the energy barrier of the oxygen evolution reaction (OER). Due to their structural and compositional advantages, Mo_2C–CoO@N–CNFs as a bi-functional catalysts exhibit remarkable catalytic activity in both HER and OER reactions, which show excellent electrocatalytic performance in alkaline electrolytes, providing low overpotentials of 115 mV and 222 mV at 10 mA cm^{-2} for HER and OER, respectively. When used for alkaline full water splitting, a current density of 10 mA cm^{-2} can be generated at a voltage of 1.56 V.

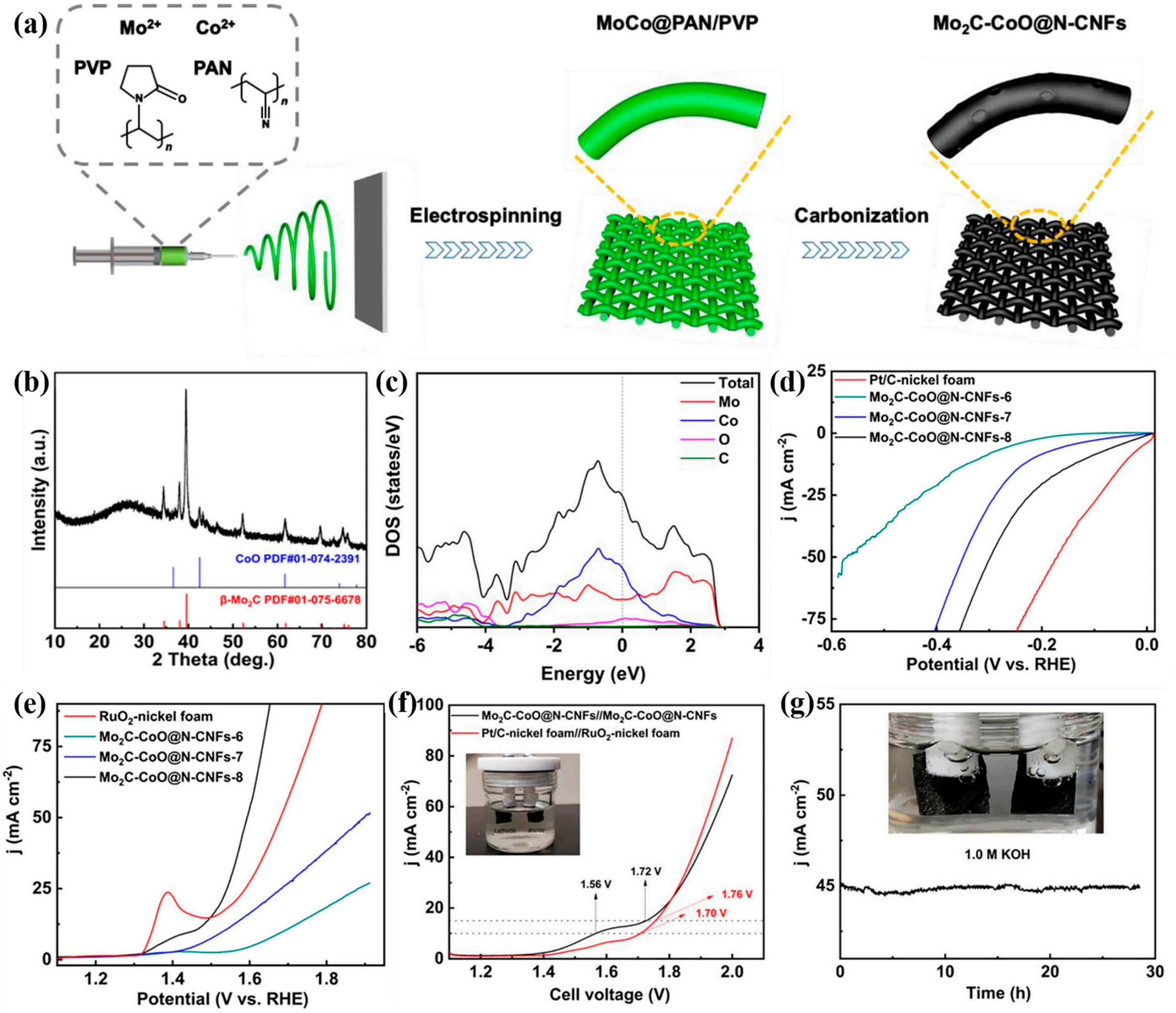

Figure 11. (**a**) Diagram of the synthesis of heterophase Mo_2C-CoO@NCNFs. (**b**) XRD pattern of Mo_2C-CoO@NCNFs catalysts. (**c**) Density of state of Mo_2C-CoO@NCNFs. (**d**) HER curves and (**e**) OER curves in 1 M KOH. (**f**) LSV curves of Pt/C-nickel foam//RuO_2-nickel foam and Mo_2C-CoO@N-CNFs//Mo_2C-CoO@N-CNFs for full water splitting. (**g**) chronoamperometry curve of the Mo_2C-CoO@N-CNFs//Mo_2C-CoO@N-CNFs cell in 1 M KOH, adapted with permission from Ref. [100] ©2023 Elsevier Ltd.

Efficient full-water splitting electrocatalysts require both intrinsic activity determined by electronic structure and superior mass transfer ability [101,102]. Molybdenum carbide-based catalyst is a promising bi-functional full-water splitting catalyst because of its noble metal-like electronic structure, high conductivity, excellent catalytic activity, and stability [103]. These design concepts provide insights for the rational construction of low-cost and high-activity full-water splitting catalysts in the future.

9. Conclusions and Prospects

In summary, several ways were summarized to enhance the HER activity of molybdenum carbide: (1) Optimizing the synthesis method, modulating the morphology, increasing the specific surface area, and exposing more active sites. (2) Compounding with carbon materials, which can disperse molybdenum carbide particles and effectively avoid their agglomeration, in addition to the good electrical conductivity of carbon materials, can provide a channel for electron transfer. (3) Atomic doping, which improves the internal electronic structure of the material, modulates the catalytic activity of the catalytic sites, or generates new active sites for hydrogen precipitation. (4) Optimization of the phase structure of molybdenum carbide by modulating the synthesis conditions to form multiphase structures or heterojunctions for optimization of properties.

Several of the above approaches to modifying molybdenum carbide electrocatalysts can improve the HER performance of the material. The first two methods enhance the performance by increasing the surface active sites and the conductivity of the composites [104], while the latter two methods use phase engineering and doping to modulate the intrinsic catalytic activity of the material [105], which is more conducive to exploring the mechanism of catalytic activity and facilitating in-depth research on molybdenum carbide electrocatalysis. In addition, molybdenum carbide-based bi-functional catalysts are presented for application in full water splitting. However, there are still some gaps compared to Pt/C. While great efforts have been made to improve the catalytic activity of molybdenum carbide for HER, there is still a long way to go before it can be used in electrolytic hydrogen production. Firstly, there is still not enough research on the catalytic mechanism of molybdenum carbide materials, particularly in terms of in situ characterization tools and techniques for rapid signal capture [106]. Secondly, there is still a lack of in-depth research about the structure of molybdenum carbide, and the difficulty lies in identifying the active center of the material. There is a need to further identify the site and physicochemical properties of the catalytic active center by combining computational [107] and experimental methods [108]. For example, the relationship between energy band structure, density of electronic states, and catalytic activity can guide more effective modulation of the activity of the catalytic site [109]. Finally, there is still a need to continue to explore effective methods to improve the performance of non-precious metal electrocatalysts in the hope of outperforming and replacing Pt/C.

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