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Historical perspective

Sustainable hydrogen production by molybdenum carbide-based efficient photocatalysts: From properties to mechanism



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ABSTRACT

Hydrogen is considered to be a promising energy carrier to solve the issue of energy crisis. Molybdenum carbide (Mo_xC) is the typical material, which has similar properties of Pt and thought to be an attractive alternative to noble metals for H₂ evolution. The study of Mo_xC as alternative catalyst for H₂ production is almost focused on electrocatalytic field, while the application of Mo_xC as a co-catalyst in photocatalytic H₂ evolution has received in-depth research in recent years. Particularly, Mo_xC exhibits significant enhancement in the H₂ production performance of semiconductors under visible light irradiation. However, a review discussing Mo_xC serving as a co-catalysts in the photocatalytic H₂ evolution is still absent. Herein, the recent progress of Mo_xC on photocatalytic H₂ evolution is reviewed. Firstly, the preparation methods including chemical vapor deposition, temperature programming, and organic-inorganic hybridization are detailly summarized. Then, the fundamental structure, electronic properties, and specific conductance of Mo_xC are illustrated to illuminate the advantages of Mo_xC and other semiconductors for enhancing the photocatalytic performance are emphasized. Finally, perspectives regarding the current challenges and the future research directions on the improvement of catalytic performance of Mo_xC-based photocatalysts are also presented.

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1. Introduction

Energy crisis and environmental pollution issues are becoming serious threats to the whole world [1–3]. Solar energy is a sustainable and clean energy, which is thought to be a promising way to solve these problems. At the beginning of 1972, Fujishima and Honda used solar energy to decompose water into H_2 by using TiO₂ as photoanode [4]. Hydrogen is considered to be an energy carrier that could address the upcoming energy crisis. As a safe, economic, clean and renewable technology, photocatalysis has been widely applied in a variety of different areas, such as water splitting, pollutants degradation, CO₂ reduction, bacteria disinfection, and selective organic synthesis [5–7]. Among them, solar-driven hydrogen evolution reactions (HER) have attracted great interest.

Nevertheless, most photocatalysts suffer from relatively high recombination of photo-induced charge carriers and low solar-energy utilization efficiency [8,9]. Loading of proper co-catalyst is a major strategy to form an efficient and stable photocatalytic H₂ evolution system [10-14]. It has been demonstrated that co-catalysts undergo multiple functions in the photocatalytic processes, such as facilitating the separation of photo-induced charges, reducing the activation energy barrier of H₂ evolution, and forming heterojunction with semiconductor to inhibit the recombination of charge carriers [15,16]. Meanwhile, an ideal cocatalyst may also serve as the active sites for proton reduction [17,18]. Unfortunately, the co-catalysts for photocatalytic H₂ evolution are mainly composed of noble metals, including rhodium (Rh), ruthenium (Ru), palladium (Pd), and platinum (Pt) [11,19–21]. Among them, Pt is the most efficient catalyst due to its high conductivity [22,23]. However, the noble metals are unsuitable for large-scale applications because of their low abundance and high-cost [24,25]. Hence, developing highly efficient non-noble metal co-catalysts, which are earthabundant and economical materials still remains in great demand.

Interest in transition metal carbides (TMCs) has been aroused because they show promising catalytic properties, making them alternative candidates for noble metals in various catalytic reactions. Prof. Oyama introduced the properties and applications of TMCs [26,27]. The materials have interesting physical characteristics and electronic properties. These properties give them varied applications on optical, electronic, magnetic, and catalytic field. As an important member of TMCs, molybdenum carbide (Mo_xC) catalysts exhibited excellent catalytic activity in some reactions and have been intensively investigated recently [28]. Density functional theory (DFT) calculations of Mo_xC reveal that the hybridization between p- and s-orbitals of carbon and d-orbital of metal molybdenum results in the broadening of d-band structure of MoxC. Therefore, MoxC possesses similar d-band electronic structure to the noble metals [29] and its characteristics are comparable to those of Pt-group metals. In addition, Mo_xC is low-cost, raw material abundant, and easy to fabricate, which indicates promising application prospect. In addition to the above merits, Mo_xC is also stable and refractory even in the presence of substances which are poisonous for noble-metal catalysts, such as S or CO [30,31]. Nevertheless, the types of non-precious metal catalysts reported are mainly sulfides, which are relatively rare. Compared with the transition metal sulfides, such as MoS₂ [32,33], Ni₃S₂ [34], WS₂ [35,36] and CoS₂ [37], Mo_xC is less toxic and displays excellent physicochemical properties, such as high adsorption capacity, melting point, electrical conductivity, thermal stability, and hardness [38,39]. Mo_xC has received in-depth research and extensive attention as evidenced from the growing number of papers on indexed journals concerning the keyword "molybdenum carbide" over the past decades (Fig. 1). The study of Mo_xC as alternative catalyst for H₂ production is almost focused on electrocatalytic field while the related investigation of Mo_xC as a co-catalyst in the photocatalytic hydrogen evolution reaction (PHER) is currently undergoing exciting development. Several excellent reviews discussed the recent development of Mo_xC-based electrocatalysts for HER [16,21,31]. However, the review focused on the Mo_xC serving as co-catalysts in photocatalytic system is still absent.

Mo_xC as a co-catalyst exhibits significant enhancement in the H₂ production performance of semiconductors under visible light irradiation. Mo_xC has been reported to serve as electron mediator and facilitate the charge transfer in heterojunctions formed between Mo_xC and other semiconductors. Benefiting from all these merits, the excellent Mo_xC would be able to act as a co-catalyst to increase the H₂ production rate remarkably. Thus, we believe this review will bring comprehensive insight for the development of MoxC-based photocatalysts. This review introduces the fabrication methods including chemical vapor deposition, temperature programming and organic-inorganic hybridization. A fundamental understanding of its physical and chemical factors which enables further insights into photocatalytic enhancement mechanisms. Moreover, this review highlights the roles and performance of Mo_xC during the photocatalytic progress. The strategies for constructing Mo_xC-based photocatalysts are also emphasized. Finally, unresolved challenges and prospects for the application of MoxC-based photocatalysts are proposed.

2. Synthesis of molybdenum carbides

Different synthesis methods can prepare Mo_xC catalysts with varied properties and applications. Suitable carbon precursors and carburization temperature is the key to prepare Mo_xC nanoparticles [40]. The developed synthesis methods can be divided into three main categories: chemical vapor deposition method, temperature-programed reduction method, and organic-inorganic hybrid method. The typical synthetic methods of Mo_xC are summarized in Table 1.

2.1. Chemical vapor deposition method

As a member of the MXene (a new family of transition metal carbides/nitrides), two-dimensional (2D) Mo_2C has attracted considerable interest for energy storage and catalysis. Chemical vapor deposition (CVD) method offers the possibility to prepare 2D vertical heterostructures materials for the study of proximity effects and charge transfer. This method is widely used for growing 2D ultrathin Mo_2C with uniform thicknesses and large crystal sizes. For example, Geng



Fig. 1. Representation of the number of publications containing the keyword "molybdenum carbide" published from 2001 to February 2020. The data are obtained from "Web of Science".

et al. [41] prepared high-quality and large-area 2D Mo₂C film grown on graphene via molten copper-catalyzed CVD method. H₂ was used as reducing gas, CH₄ was the carbon precursor, and liquid Cu supported on Mo substrate was served as catalyst at the growth temperature of 1100 °C. On the surface of graphene, uniform large area centimeterscale Mo₂C films can be seen. Fig. 2 schematically shown the growth process. The morphology and growth kinetics were influenced by the CH₄ flow rate. At low CH₄ flux, the growth of Mo₂C was inhomogeneous with respect to thickness and morphology. The thickness was in range of several hundred nanometers and there was wide distribution of fragments with various shapes. If increased the flow rate of CH₄ to reach surface saturation limit, large hexagonal-shaped Mo₂C crystals grown rapidly. Compared to Mo₂C-only catalyst. The Mo₂C-on-graphene heterostructure exhibited significant enhancement of catalytic activity in HER due to the efficient interfacial charge-transfer kinetics. Xu et al. [42] synthesized 2D ultrathin α -Mo₂C crystals with large-area via CVD method. The high temperature made Cu melted and formed Mo-Cu alloys at the liquid Cu/Mo interface. Mo, diffused from the interface to the surface of liquid Cu, and formed a Mo₂C crystal by reacting with carbon atoms decomposed by methane. The crystal was nanometer in thickness with the size over 100 µm and was very stable under ambient conditions. By changing the experimental condition, the thickness and size of Mo₂C crystals can be easily tuned. The 2D α -Mo₂C crystals exhibited characteristics of superconducting transitions and strong anisotropy with magnetic field orientation. Such high-quality 2D superconducting crystals not only offer new platforms to study 2D superconductor materials, but also provide ideal blocks assembled with other 2D crystals in a hybrid material construction. The CVD growth method develops a versatile strategy for fabricating high quality 2D ultrathin crystals with no disorder or defects being observed. These 2D ultrathin crystals provide further possibilities for the investigation of many exciting properties and intriguing applications that are complementary to those of existing 2D crystals.

2.2. Temperature-programed reduction method

Generally, Mo_xC is synthesized by temperature-programmed reduction (TPR) method which uses molybdenum oxides as precursor, mixture H₂ gas as reduction agent and carbon-containing gases as carbon source, such as methane or aromatic compounds [43]. For example, Ma et al. [44] synthesized nickel (Ni) doped Mo_2C by using ammonium molybdate tetrahydrate (AMT) and nickel nitrate as reactant. Carburization of Ni-MoO₃ was carried out in microreactor under the CH₄/H₂ atmosphere. After a successive temperature-programmed process, the Ni-MoO₃ was annealed from room temperature to 300 °C at a rate of 2 °C/min and then increased to 700 °C at a rate of 1 °C/min, and maintained at 700 $^{\circ}$ C for 2 h, then the Ni – MoO₃ powders were transferred to Ni-Mo₂C. The surface area of Mo₂C catalysts is relatively low and may greatly influence the catalytic performance. This may be caused by the excessive carbon deposition generated from the pyrolysis of carbon containing gases in the interfacial reaction between gas and solid. Xu et al. [30] prepared contorted cuboid Mo₂C and CdS was deposited on the surface of Mo₂C. The Mo species are affected greatly by the carbonization temperatures, as can be seen in the XRD patterns. At a lower temperature, such as below 600 °C, the components of MoO₂ and MoO₃ can be observed. At 600 °C, the XRD patterns are mainly due to MoO₂. At 700 °C, pure Mo₂C formed. With increased temperature, the Mo species transformed from MoO₃ to MoO₂ and last to Mo₂C.

During the TPR process, the flammable gases are employed, and such environmental-unfriendly gases are potentially dangerous during the operation process. In addition, the significant differences between surface and bulk phase of gas-solid interfaces result in excessive carbon deposition and incomplete transformation of the reactants. These polymeric carbon species would block the active sites on the catalyst surface, causing the decrease in catalyst activity. Additionally, the composition and crystallographic structure of resultant products by TPR method are difficult to control, and generally, bulk structure with low specific surface area. Besides, the strict and complex manipulation conditions limit the large-scale preparation and further application. Therefore, the emergence of ameliorating TPR method to synthesize Mo_xC with novel morphologies and structures under mild condition is significant. Dong et al. [45] synthesized cost effective Mo rich Mo₂C (Mo-Mo₂C) catalyst without using any dangerous gases. The synthesis process is shown in Fig. 3a. (NH₄)₆Mo₇O₂₄·4H₂O and aniline were used as raw material to obtain precursor. Then the precursor was annealed from room temperature to 775 °C at a heating rate of 2 °C/min and maintained at 775 °C for 2 h. After naturally cooling to ambient temperature, the Mo-Mo₂C sample was obtained. The elemental mapping images of Mo, O and C atoms show the homogeneous distribution of these elements over Mo-Mo₂C. Yue et al. [46] developed a new synthetic method for the design and construction of one-dimensional (1D) SrTiO₃@Mo₂C core-shell nanostructure. The SrTiO₃ nanofibers (NFs) were synthesized through a single spinneret electrospinning process (Fig. 3b). The synthesis route of SrTiO₃@

Table 1 Typical synthetic methods of Mo_xC.

Construction methods	Precursor	Reaction condition	Crystal phase	Structure	Reference	Advantages	Disadvantages
CVD method	methane, liquid Cu, Mo substrate	Liquid Cu on the supporting Mo foil is used as the catalyst, methane (CH ₄) is the carbon precursor, and hydrogen (H ₂) is used as the reducing and carrier gas at the growth temperature of 1100 °C.	α-Mo ₂ C	uniform Mo ₂ C film	[41]	The thickness and size of Mo_xC crystals can be easily tuned; Benefit to synthesize ultrathin crystals with no disorder or defects.	Multistep procedures; Require special instruments
	Methane, Cu foil, Mo foil	Methane as the carbon source and a Cu foil sitting on a Mo foil as the substrate at a temperature above 1085 °C.	α-Mo ₂ C	2D ultrathin crystals	[42]		
Temperature-programed reduction method	molybdic acid; aqueous ammonia	Heating from room temperature to 400 °C at a rate of 5 °C/min, then a heating rate of 2 °C/min was employed to the target temperature and maintained for 5 h under a flowing mixed gas of H_2 and CH ₄ .	β- Mo ₂ C	small particle size of 10 nm	[30]	Solution processable; Large scale	Flammable gases; Carbon deposition
	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O, Ni$ $(NO_3)_2 \cdot 6H_2O$	The carburgation temperature was raised from room temperature to 300 °C at a rate of 5 °C/min, then a heating rate of 1 °C/min was employed to 700 °C and maintained for 2 h under a flowing mixed gas of H ₂ and CH ₄ .	β-Mo ₂ C	bulk structure	[44]		
Organic-inorganic hybrid method	${\rm MoO_x/pphenylenediamine}$	calcinated at 750 °C for 5 h in an Ar flow.	β -Mo ₂ C	nanowires and nanosheets	[50]	Benefiting for the synthesis of	Energy-intensive; Complex
	ammonium heptamolybdate, aniline, (NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O, melamine, oxalic acid dibudrato	calcinated at 725 °C for 5 h in argon flow calcined at 900 °C for 2 h in N ₂ flow	β-Mo ₂ C γ-MoC, β-Mo ₂ C	nanoMo ₂ C/RGO rod-like structure	[77] [66]	Mo _x C-based materials with controllable morphology and innovative structure.	processes.
	cetyltrimethyl ammonium bromide, sodium molybdate	heated to 600 °C under flowing nitrogen for 240 min, then heated to 900 °C and maintained for 120 min	β -Mo ₂ C	nanosheets	[75]		
Mechanochemical synthesis	MoO ₃	Commercial MoO ₃ and graphite powders were ball milled using a planetary ball mill with stainless steel vials and balls under areon atmosphere	β- Mo ₂ C	bulk structure	[82]	Simplicity of operation.	Limited physiochemical properties of the products.
In situ O ₂ emission-assisted synthesis method	Polyaniline, phosphomolybdic acid, H ₂ O ₂	Firstly, preparation of a nanosized polymeric hybrid of phosphomolybdate anions doped polyaniline with H ₂ O ₂ as the polymerization oxidant. Then, the hybrid was pyrolysised at 900 °C under an argon atmosphere.	γ-ΜοC, β-Μο ₂ C	porous and loose morphologies	[85]	The prepared Mo _x C nanoparticles with high effective surface area and dense active site.	Manipulation complexity.
Template-assisted method	ammonium molybdate, nitrogen-doped carbon framework (PNDCF)	Firstly, preparation of PNDCF on a mixture of sodium and pyridine as precursor. Then, the PNDCF were mixed together with aqueous Mo supply to obtain Mo-PNDCF hybrids. Finally, Mo-PNDCF hybrids were carburized at 700 °C under H ₂ /Ar gas flow.	β-Mo ₂ C	3D hierarchical porous Mo ₂ C	[87]	Controllable morphology, Stable structure.	Complex processes

 Mo_2C was as follows: SrTiO₃ NFs, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and dicyandiamide were conducted as mixture aqueous solution; after the mixed solution was ultrasonically uniformed, the sample was dried at an oven; at last, these obtained powers were heated from room temperature to 800 °C at a ramp rate of 5 °C/min in Ar atmosphere and maintained for 3 h. The 1D SrTiO₃@Mo₂C core-shell nano-structure catalysts exhibited highly active and stable properties for H₂ production under visible light irradiation. The thin nanolayer of Mo₂C provides channels for electronic transmission and could be the origin for excellent H₂ production capacity.

2.3. Organic-inorganic hybrid method

With the deeper understanding of organic materials, synthesis of functional materials from organic species has attracted increasing interest. Generally, traditional methods used inorganic materials to prepare Mo_xC. These methods exist disadvantages such as the aggregation, uncontrollable morphology, and small specific surface area. The periodic porous and stable structure of organic species provides unique benefits for the synthesis of molybdenum-based materials with innovative nanostructure. In recent years, there are considerable progresses in



Fig. 2. Schematic showing the growth of Mo₂C crystals under low and high flow rates of CH₄. Thick Mo₂C crystals with different shapes are randomly distributed on the Cu surface at low CH₄ concentration, whereas at higher CH₄ concentration, the growth of predominantly hexagonal-shaped, thin Mo₂C flakes on graphene is seen. Reproduced with permission from ref. [41]. Copyright 2017 Wiley.

the synthesis of novel Mo_xC nanostructures by heterozygous organic components in more versatile approaches. Organic-inorganic hybrid method is a new approach based on the simple pyrolysis of organic species and Mo precursor [28]. These as-prepared products are of significant tunable periodic structures and various functional properties. Wang et al. [47] successfully synthesized a novel Mo_xC nanobelt

containing high valence state Mo via the one-pot pyrolysis method (Fig. 4a). The molybdenum carbide-ethylenediamine (Mo_x C-EDA) hybrids were obtained through the pyrolysis of MoO₃-EDA inorganic/organic hybrid precursors in inert atmosphere. The 1D structure of MoO₃-EDA hybrid precursors were formed via solvothermal reaction and the MoO₃-EDA precursors were with an average length of 15–20



Fig. 3. (a) Schematic illustration of Mo–Mo₂C-n synthesis via a facile two-step synthetic method and hydrogen evolution reaction. $2H_2O = O_2(g) + 4H^+(aq) + 4e^-, 4H^+(aq) + 4e^- = 2H_2(g)$. Reproduced with permission from ref. [45]. Copyright 2018 Royal Society of Chemistry. (b) Schematic illustration of the fabrication of the SrTiO₃@ Mo₂C hybrid NFs. Reproduced with permission from ref. [46]. Copyright 2018 Elsevier.



Fig. 4. (a) Schematic illustration of the formation procedure of the Mo_xC with high-valence state Mo nanobelts. (b) SEM, (c) TEM images of the MoO₃-EDA. Reproduced with permission from ref. [47]. Copyright 2017 Elsevier.

mm and diameters of 500–700 nm (Fig. 4b-c). Subsequently, the MoO₃-EDA precursors were heated from room temperature to 600 °C with a constant heating rate of 1 °C/min and maintained for 5 h. Finally, the black Mo_xC nanobelts containing high valence state Mo were obtained. Gao et al. [48] prepared a series of nanowires of MoO_x-based organicinorganic hybrids, and the results showed that 1D growth of Mo_xC was related to the chain-like structure of $Mo_3O_{10}^{2-}$ anions. After pyrolysis treatment at 600 °C, the MoO₃-EDA converted into Mo_xC nanobelt, and the resulting Mo_xC still preserved the 1D structure of its precursor. This might be attributed to their sub-nanometer-contacting between organic and inorganic components in the precursors. Such hybrids can provide uniform quasi-homogeneous reaction environment and could successfully avoid the disadvantages of interface reactions during material preparations process [49]. Ge et al. [50] synthesized shapecontrollable Mo₂C nanosheets (NSs) and nanowires (NWs) through the pyrolysis of MoO_x/pphenylenediamine (PPD) hybrid precursors. PPD and molybdate tetrahydrate served as C and Mo sources, respectively. The obtained MoO_x/PPD hybrid precursors were heated at 750 °C for 5 h under argon atmosphere. Then, the black product of Mo₂C NWs and Mo₂C NSs were obtained. This organic component greatly facilitates the formation of nanostructured Mo₂C. By simply varying the proportion of reactants, the shape of the precursors can be adjusted. The high-magnification SEM image revealed the formation of a large number of uniform nanowires, when the MoO_x/PPD hybrid precursor obtained at a molar ratio of 1:18. Adjust the molar ratio to 1:9 while other conditions remain unchanged, the MoO_x/PPD hybrid nanosheets can be clearly seen from the SEM image. The electromagnetic attraction interaction between the negatively charged molybdate tetrahydrate and the positively charged PPD drives them into supramolecular MoO_x/PPD hybrids. This nanostructured Mo_xC catalyst was further used for HER and exhibited good activity and stability. The molar ratio of the reactants greatly affects the morphology and activity of the catalyst. It was found that the nanowires have superior activity and durability to the nanosheets.

As a new class of special porous materials, metal-organic frameworks (MOFs) are currently widely used in the synthesis of functional materials [51]. Over the past decade, more than 20,000 different MOFs have been reported and researched [52,53]. These MOFs have huge surface area from 1000 to 10,000 m²/g, far more than the traditional porous materials such as carbon and zeolites [54–57]. The hybrid structure and periodically porous property of MOFs provide unique benefits for constructing nanostructured carbon and metal-based materials. The homogeneous confined carburization process of transition metal carbides can be achieved in MOFs materials with tunable composition and structure, thus producing small carbide nanocrystallites. In addition, the carburization process within MOFs would prevent the coalescence and agglomeration of in situ-generated carbide nano-crystallites effectively. Zhang et al. [58] prepared a new hybrid catalyst by incorporating Mo_xC nanoparticles into a nitrogen-implanted three-dimensional carbon matrix (MoCN-3D). They used zeolitic imidazolate skeleton (ZIF) as a robust tool to obtain MoxC nanoparticles with interconnected hierarchically micro/mesoporous structure (Fig. 5a-c). Experimental observations and theory calculations demonstrated that the synergistic effects between the carbon layers, Mo₂C nanoparticles, and N hybrid coordination, could effectively reduce the Gibbs free energy value of HER and change the charge density of the final hybrid (Fig. 5d-e). Qamar and his colleagues demonstrated a two-step synthesis approach to prepare β -Mo₂C, which was embedded into porous and rigid carbon matrix [59]. A microporous matrix (namely MIL-53(Al)) was used to guide the nucleation and confined growth of Mo₂C nanocrystallites. Restricted space in the porous frameworks of MIL 53(Al) appeared to preclude the coalescence and agglomeration of Mo₂C, resulted in enriched porosity. Shi and his co-workers [60] prepared highly dispersed nanostructured MoC encapsulated in graphite shell (nanoMoC@GS) via in situ carburization of Mo-based MOF. This work demonstrated a feasible strategy to convert "atomic contact" hybrid structures (e.g., MOFs) for designing high-performance catalysts. Merits were reflected in the ultrathin and fluffy graphitized carbon shell (1-3 layers) and ultrafine MoC nanocrystallites (3 nm).

Recently, MOFs incorporating polyoxometallates (POMs) have emerged as promising precursors, where the POMs are uniformly distributed in the ordered carbon-containing host matrix [61]. POMs are a subset of early transition metal oxyanion clusters. In terms of catalysis, POMs have a good prospect since the electronic and physical properties of POMs can be adjusted by changing constituent elements. Owing to the rich structural versatilities and adjustable compositions of POMbased MOFs, they have attracted considerable attention for preparing diverse nanomaterials by rationally designing synthetic systems [61]. The choice of POM-MOF nanocomposites as precursors to synthesis Mo_xC is quite general, such as NENU-5 ([Cu₂(BTC)₄/3(H₂O)₂]₆ $[H_3PMo_{12}O_{40}]$, BTC = benzene-1,3,5-tricarboxylate) [62], PECP-1 ([Zn $(bimbp)_2$]3[PMo₁₂O₄₀]₂·2H₂O, bimbp = 4,4'-bis(imidazolyl)biphenyl) [63], and POM@MIL-100 (Fe) [64]. Wu et al. [62] first reported the preparation of porous Mo_xC nano-octahedron consisting of ultrafine nanocrystals by using MOFs-assisted strategy. The presented synthesis strategy used unique POM-MOF nanocomposites (NENU-5) as the precursors, to achieve confined and uniform carburization reaction between the organic matrix and POM. This confined carburization process was effective in preventing the aggregation and coalescence of carbide nanocrystallites generated in situ. In addition, copper-based



Fig. 5. (a) Scanning electron microscopy images of HZIF-Mo crystals in different magnification. (b) N_2 adsorption-desorption isotherms for MoCN-3D and MoCN-2D. (c) Schematic illustration for the construction of MoCN-3D for a highly efficient hydrogen evolution reaction. (d) Three-dimensional charge density difference for Mo₂C-CN composite with an isovalue of 0.0006 e A^{-3} . Yellow and blue isosurfaces represent charge accumulation and depletion in the space with respect to isolated Mo₂C and C layer. (e) Gibbs free energy (ΔG) profile of the HER on various catalysts. Reproduced with permission from ref. [58]. Copyright 2016 Macmillan Publishers Limited. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

metal ions were introduced in the MOFs-assisted method. The synthesis of early transition metal carbides was made easier by introducing guest metal species into the MOF hosts as co-precursors, which was difficult to obtain from a single MOF source. The synthesis route is shown in Fig. 6a. The prepared Mo_xC nanooctahedron was composed of ultrafine primary nanocrystallites (Fig. 6b-d). Benefiting from these characteristics, this nanooctahedron exhibited remarkable catalytic activity under both acidic and basic conditions. Xu et al. [65] prepared carbon-coated nickel-decorative MoxC hollow sphere by combining Mo-based POM and MOFs (Fig. 7a-d). Ascribed to the unique composition of the hollow structure, it exhibited significant properties and stability for HER. Mo-based POM-anion-incorporated Ni-MOF hollow structure was prepared by using hexaammonium molybdate as Mo source, 1,3,5-benzenetricarboxylic acid (H₃BTC) as organic linkers, nickel ions as metallic nodes and N, N-dimethylformamide (DMF) as solvent. Then, carbon film was coated on the surface of the precursor with hollow structure. The carbon layer can improve the mechanical strength of the hollow structure precursor and avoid the aggregation and collapse of the hollow structure during the calcination process. The transition ions in MOF converted to transition metal ion oxides after pyrolysis, which also served as active sites and created synergistic effects for HERs [66]. Li et al. [64] conceived a novel approach to synthesis Fe₃C/Mo₂C containing N, P co-doped graphitic carbon (Fe₃C/Mo₂C@NPGC). As shown in SEM and HRTEM images, the hierarchically porous carbon structure was obtained after carbonization (Fig. 7e-g) and the existence of Fe in MIL-100 (Fe) contributed to the formation of highly graphitized carbon. As expected, the Fe₃C/Mo₂C@NPGC showed excellent activity and stability in acidic media. Yang et al. [63] prepared N-doped graphene-coated molybdenum carbide nanoparticles (MoC_x@C), which obtained from polyoxometalate-encapsulated coordination polymer (PECP-1) through the etching and annealing processes. The synergistic effects among graphene shells, highly dispersive nanoscale MoC_x cores and the N dopants maybe the origin for the highly efficient HER activity.

The methods of synthesizing Mo_xC nanostructures with enriched active-sites generally involve the preparation of molybdenum and carbon-based materials. Using nanocarbon supports or coating with carbon materials can significantly improve the catalytic activity of Mo_xC. Firstly, the framework structure of carbon materials could avoid the aggregation of Mo_xC during the pyrolysis process, ensuring the sufficient accessible active sites for catalytic reaction. Secondly, carbon supports play a critical role of boosting the electrical conductivity of Mo-carbon hybrid catalysts. Thus, it promotes the rapid diffusion and transfer of electrons. Thirdly, the carbon substrates provide numerous exposed edge sites and greater surface area by controlling the morphology of carbon nanostructures. Fourthly, the nanocarbon shells could stabilize Mo₂C cores and protect them from liquid corrosion, enhancing the durability of catalysts. Fifthly, the improved catalytic performance of heteroatom doping on nano-carbon materials has been verified. For example, the catalytic performance of Mo2C/N-doped nano-carbon materials exhibited significant enhancement [67]. The nitrogen possessed a higher electronegativity than carbon and it interacted strongly with H⁺. The electronic structures of adjacent C and Mo were modified by the doped-N, affecting the H⁺ adsorption and desorption of Mo-H bond. Various carbon-based materials have been devoted to this purpose, including carbon black [68], carbon nanotubes [69,70], graphene [69], N-doped carbon nanotubes [71], N-rich carbon nanolayers [72], N-doped graphene [63], etc. Graphene is an effective substrate for growing active nanomaterials due to its high charge mobility, good stability, and large specific surface. Wei et al. [73] provided a facile, scalable and low-cost method to fabricate Mo₂C-based catalysts (Fig. 8a). The ultrafine Mo₂C nanoparticles were uniformly embedded into graphene wrapping N-doped porous carbon microspheres. The introduction of graphene not only improved electrical conductivity of the hybrids, but



Fig. 6. (a) Schematic illustration of the synthesis procedure for porous MoC_x nano-octahedrons. (b) FESEM image (inset: digital photo) of porous MoC_x nano-octahedrons; scale bar, 2 mm. (c) XRD patterns and (d) EDX spectrums of MoC_x-Cu and MoC_x nano-octahedrons. Reproduced with permission from ref. [62]. Copyright 2015 Macmillan Publishers Limited.

also served as framework to support Mo_2C , thus effectively reducing its aggregation at high temperatures. In this method, the low-cost ammonium heptamolybdate (AHM) and chitosan were regarded as molybdenum and carbon source, respectively. Due to the electrostatic interaction of $Mo_7O_{24}^-$ with the NH_3^+ group derived from the long chain chitosan molecule in the acid medium, uniform hybrid of Mo and carbon sources was achieved, thereby ensuring that ultrafine Mo₂C was embedded into the N-doped carbon nanostructures. Wang et al. [66] prepared molybdenum-carbide modified Ni-encapsulated carbon vesicle material with uniform N atom doping (Mo_xC-Ni@NCV). Water-insoluble melamine-related oxalate and molybdate complexes (Ni@MOM-com) were used as precursors for solid state thermal decomposition. Quantum chemical calculations showed that N-doped carbon-supported Mo₂C can further reduce the Gibbs free energy of



Fig. 7. (a) Schematic of carbon-coated Ni-decorated molybdenum carbide hollow spheres (HC-T). (b) TEM (c, d) HRTEM images of HC-800. Reproduced with permission from ref. [65]. Copyright 2016 American Chemical Society. (e) Preparation of the Fe₃C/Mo₂C@NPGC nanocomposite derived from POM-based MOFs. (f) SEM (g) HRTEM images of Fe₃C/Mo₂C@NPGC. Reproduced with permission from ref. [64]. Copyright 2016 Royal Society of Chemistry.





Fig. 8. (a) Schematic illustration of the procedure for preparing Mo₂C/G-NCS. Reproduced with permission from ref. [73]. Copyright 2018 Wiley. (b) Schematic illustration for the fabrication of nanoMo₂C/RGO structure. Reproduced with permission from ref. [77]. Copyright 2016 Wiley. (c) The synthetic process of the Mo₂C/CTSS nanohybrids [81]. Copyright 2018 Royal Society of Chemistry.

H₂ adsorption and promote the initial H* adsorption, enhancing HER activity compared to carbon-supported Mo₂C [72,74]. And the significant HER activity can be achieved by combining N-rich carbon with small Mo_xC nanoparticles, due to the superactive nonmetallic catalytic sites generated in the materials [72,75]. Zhang et al. [76] prepared a new composite catalyst consisting of Mo₂C and MoP nanoparticles coated by few-layer N-doped graphitic carbon shells. This new combination mode was achieved by a one-step annealing route using a mixture of a Mo/P-based POM and dicyandiamide. The synergistic effects among graphitic carbon shells, N-dopants, and highly dispersive nanoscale MoP/Mo₂C nanoparticles resulted in the high catalytic activity and durability of the composite catalyst over the entire pH values. Moreover, preparing Mo_xC encapsulated in graphene carbon shell has been reported. Wang et al. [77] completed the synthesis of highly-dispersed nanosized Mo₂C/RGO for the first time, via simply calcinating the MoO_x/amine hybrid precursors (Fig. 8b). Hydrophilic functional groups on the surface of

GO have been shown to effectively improve their dispersibility in aqueous solutions, and more importantly, enhance their interaction with organic-inorganic precursors to form highly dispersed carbide nanoparticles during subsequent calcination. The remarkable structure and characteristics of Mo₂C/RGO have proven to be the determinants of accelerated interfacial catalytic reactions with high interfacial capacitance and low charge transfer resistance. Pan et al. [78] developed a two-step process for the preparation of carbon layer stabilized molybdenum carbide nanoparticles (Mo₂C–RGO composites). The presence of GO led to the reduction of particle size of the Mo₂C nanoparticles and a significant acceleration of the carbonization reaction. The Mo₂C-RGO hybrids exhibited excellent performance due to the close interaction between Mo₂C and graphene. Pu et al. [74] prepared Mo₂C quantum dot (QD) catalyst supported on chitosan-derived N-doped carbon layer. Chitosan may self-organize carbon materials into graphene-like carbon layer during the carbonization process [79,80]. Chitosan was chosen as the N

sources because it was a renewable biopolymer rich in nitrogencontaining groups. In addition, Xu et al. [81] prepared a carbon tubesheet superstructure Mo₂C/C hierarchical nanocomposite (MO₂C/CTSS) with controllable carbon nanosheet array by assembly-carburizationleaching strategy (Fig. 8c). For this purpose, nickel molybdate/polyimide (PI) was first carbonized and subsequently leached with polyamic acid. The hierarchical nanohybrids of MO₂C/CTSS manifested outstanding HER performance. It was found that carbon nanosheets array in MO₂C/CTSS could affect the catalytic activity, and periodic alignment exhibited better catalytic performances than random alignment.

2.4. Other methods

In the previous reports, various traditional methods such as annealing mechanochemical synthesis [82], microwave-assisted method [83], and sonochemical method [84] have also been used to fabricate Mo_xC nanomaterials. However, deficiencies of manipulation complexity and limited physiochemical properties of the products exist in these methods. Fortunately, new and facile synthetic strategies have been developed in recent years to modulate the structure and properties of the catalyst.

Various novel methods provide new approach to construct Mo_xC nanocomposite with controllable morphology and structure. Ji et al. [85] prepared Mo_xC nanoparticles with highly effective surface area and dense active site by using a unique in situ O₂ emission-assisted synthesis method. In the early years, Zhao et al. [86] synthesized nanosized molybdenum carbon nitride (MoCN) by pyrolysis of polymeric hybrid precursor of polydiaminopyridine and Na₂MoO₄, via CO₂ emission assisting strategy. Wang et al. [87] showed the preparation of 3D layered porous Mo₂C framework by template-assisted method. Zheng and his colleagues [88] showed a scalable and facile salt template method for preparing Mo₂C with 3D hierarchically porous architecture (3DHP-Mo₂C). It was worth noting that the clear and abundant hierarchical macro-meso-micropores of 3DHP-Mo₂C not only significantly increased the specific surface area, but also significantly decreased the relevant transfer resistance, thereby effectively improving the catalyst performance of nanomaterials.

3. Properties of molybdenum carbides

3.1. Structural properties

The structural diversity of Mo_xC particles is due to their complex nature and metastable/stable phases. A carbon atom with small radius is inserted into the gap of Mo atom, causing the expansion of its original metal lattice. The spacing of the Mo atom also increases. The insertion of carbon atoms changes the original d-band structure and subsequently the Fermi level and state density changed. Thus, the Mo_xC exits a series of new properties different from its parent metal. There are mainly five different crystal structures of molybdenum carbides, α -MoC_{1-x}, α -Mo₂C, β -Mo₂C, γ -MoC and η -MoC [39,89]. The crystallographic structure is shown as Fig. 9a. The variant stacking sequences of metal Mo atoms and non-metallic carbon atoms in the structure affect the electrochemical properties. The crystal structure of α -MoC_{1-x} is face-centered cubic (fcc) [89]. The other molybdenum carbides such as γ -MoC and η -MoC possess the same hexagonal crystal structure but different stacking sequences [89,90]. While the α -Mo₂C presents hexagonal close packed (hcp) structure in which the Mo and C layers are alternately arranged [91]. The β -Mo₂C phase has an orthorhombic crystal structure [92]. Since the molybdenum atoms are only slightly distorted from the position in closed packed plane and the carbon atoms occupy the octahedral gap sites in an orderly manner, the crystal structure of β -Mo₂C can usually be loosely described as a hexagonal-closed packed (hcp) structure [92,93]. Discrepant crystallographic structure of Mo_xC exhibits different catalytic performance.

The properties of Mo_xC are closely related to its structure, which is mainly caused by its variant surface atom stacking sequences and different lattice structures. Experimental phase diagrams show that the stoichiometric ratio of Mo:C with 1:1 and 2:1 are the most stable ones. Among all the Mo_xC structure, the β-Mo₂C contributes mostly to the activity and stability [28,94]. In the case of β -Mo₂C, a relatively small cleavage energy indicates that the surface is fairly easy to form and highly stable. And the work function of nonpolar (011) surface is only 3.4 eV, which is smaller than the other phases. The low work function can facilitate the transfer of surface adsorption electrons in the catalytic process [91]. The density functional theory (DFT) calculation reveals that β -Mo₂C possesses stronger metallic character, compare to the other polymorphs [91]. Based on Perdew-Burke-Ernzerhof (RPBE) and DFT, the lattice constant of bulk α -MoC_{1-x} is 4.36 Å [95], which is almost similar to the experimental value of 4.33 Å [96]. The lattice constants of β -Mo₂C are as follows: a = 4.819 Å, b = 6.012 Å, and c = 5.150 Å [95]. For α -Mo₂C, the lattice constants are a = b = 6.118 Å, and c = 5.150 Å [97]. Operating conditions also affect the phase of molybdenum carbide. For example, Wan et al. [90] synthesized four different phases of Mo_xC with AMT and 4-Cl-o-phenylenediamine (4Cl-oPDA) as raw materials. When amine-metal oxide hybrid was heated at 750 °C for 12 h, the α -MoC_{1-x} formed. While for β -Mo₂C, the carbonization temperature should be raised to 850 °C. As for γ -MoC, the carbonization time must be extended to 24 h. n-MoC was produced at 1050 °C with zero dwell time. The low Miller-index surfaces of Mo_xC is shown as Fig. 9b. The MoC_{1-x}, have C- and Mo- terminated (111) polar surfaces and (001), (011) polar surfaces. Researches confirmed the (001) surface as the most stable one and (011) surface as the most unstable one. And the simple hexagonal phase possesses C- and Mo- terminated polar surfaces ((001) and (100)) [98]. Concerning the α -Mo₂C and β -Mo₂C, both them have polar surface ((001) and (111)) and non-polar surface ((100), (011) and (101)).

3.2. Electronic properties

The electronic properties of hexagonal and orthorhombic Mo₂C were investigated using first principles calculations based on DFT. Compare to that of Mo₂C with orthorhombic structure, the formation enthalpy of hexagonal Mo₂C shows a higher value. The formation enthalpy of Mo_xC suggests that orthorhombic-Mo₂C is easier to form than hexagonal Mo₂C [99]. The electronic structure of traditional metal carbides is analyzed by calculating the density of state (DOS) and energy band structure in their stable phase. These band structures are closely related to each other. The minimum value of the valence band is at the G (Gamma) point under normal pressure [100]. By studying the total and partial DOS for cubic α -MoC, hexagonal β -MoC and γ -MoC at equilibrium lattice constants, it can be found that the total DOS was primary constituted by molybdenum d and carbon s states [99]. The non-zero values of DOS near the Fermi level indicates the well metallic nature for the three structures. In addition, the DOS curves for the three structures can be divided into three main areas: (I) the valence band extending from -63 eV to -61 eV is mainly the contribution of s orbitals of Mo; (II) -37.5 eV to -35 eV is mainly the p orbitals of Mo; (III) -15eV to 15 eV is mainly metal Mo d states hybridizing carbon p states [101]. The strong hybridization between the carbon and metal atoms means the bonds of these materials are covalent. In order to describe the bonding properties and the charge transfer process of MoC more clearly, the total charge density is calculated. The electron density increases at the C atom, but decreases in the interstitial region between the metal atoms. This change of charge density distribution indicates the transfer of charge from metal Mo atoms to carbon atoms. Besides, charge transfer with ionic components between metal and carbon atoms is also observed. Thus, it can be clearly seen that the coexistence of covalent, ionic and metallic bonds in molybdenum carbide. Jalil et al. [102] studied the electronic properties of single-walled 2D graphite phase Mo₂C nanotube. The results showed that the versatile electronic



Fig. 9. (a) Bulk crystallographic structures of fcc δ-MoC, hcp α-MoC, and orthorhombic β-Mo₂C. Turquoise and magenta spheres denote C and Mo atoms, respectively. (b) Top (left panels) and side views (right or middle panels) of the studied δ-MoC, α-MoC, and β-Mo₂C surfaces. In the δ-MoC (111) surfaces three panels are shown, being Mo- (left panel) and C-terminations (right panel). On β-Mo₂C polar surfaces-(111) and (001) left and right panels belong to C- and Mo-terminations, while the middle panel is a top view. Surface unit cells are displayed with red lines. Reproduced with permission from ref. [91]. Copyright 2013 Royal Society of Chemistry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and magnetic properties were derived from the metal and ions bonds in Mo_2C nanotubes and the delocalized electrons around Mo atoms. These properties of Mo_xC endow them potential applications in electronics and catalysts. It has been theoretically demonstrated that the most stable form is the H-type graphene-like Mo_2C monolayer and it could possess tunable superconductivity through chemical functionalization, similar to the structure of transition metal dichalcogenides reported in the previous literatures [103,104].

3.3. High specific conductance and capacitance

Mo₂C has recently drawn much attention for the potential application in energy conversion and storage due to its high specific conductance and capacitance [105,106]. Mo₂C exhibits ultrahigh electrical conductivity of 1.02×10^2 S cm⁻¹ and the capacitance of 600–1000 mA h g^{-1} , far exceeding that of amorphous carbon [107]. The high specific conductance of Mo₂C minimizes the charge transport resistance, resulting in better electronic conductivity [108]. Mo₂C is used to modify the electrodes of high performance lithium ion batteries and demonstrates enhanced energy storage behavior [109]. The electrochemical inactive and highly conductive of Mo₂C enhance the structural stability of electrodes and decrease the resistance of electrons transport. By hybridization with appropriate amount of Mo₂C, the Li-ion battery electrode exhibits high rate capability and superior cycling stability. Shi et al. [110] uniformly encapsulated high-conductivity Mo₂C nanofibers into lamellar manganese dioxide (MnO₂) as electrodes for high-performance capacitor. Nanostructured Mo₂C with superior electrochemical properties is an ideal material for high-performance energy-storage. The inner layer of Mo₂C nanofibers served as conducting support due to its desirable electronic conductivity. It provided efficient and abundant pathways for rapid charge transport and ionic diffusion. In addition, Mo₂C can provide high capacity and improve the conductivity of composites after hybridization with other materials. Yang et al. [107] fabricated hierarchical MoO₂/Mo₂C/C hybrid nanowires. Compared with bulk MoO₂, MoO₂/Mo₂C heteronanotubes exhibited larger specific capacitance of 950 mA h g^{-1} . Incorporation with Mo₂C could largely improve the conductivity of the MoO₂/Mo₂C/C hybrid nanowires, thus effectively facilitating the electron transfer. Tiwari et al. [111] developed a highly active, stable (MoS₂)Mo₂C core-shell electrocatalyst for oxygen evolution and oxygen reduction reaction. MoS₂ have been investigated for HER processes both in photocatalytic and electrocatalytic field. However, basal plane inactivity such as low conductivity restricts its practical applications [112]. Mo₂C has ultrahigh electrical conductivity and exhibits excellent performance for HER. Hybrid structures of MoS₂ and Mo₂C may overcome these issues. The Mo₂C core served as electron conductor to form oxygen radicals, which migrated to the catalytic sites of MoS₂ subsequently. According to the Nyquist plot of the impedance spectrum, the electron transfer resistance of pristine MoS₂ and core-shell structured $(MoS_2)Mo_2C$ can be known. The $(MoS_2)_{0.125}Mo_2C$ sample has the electron transfer resistance of 148 Ω , which was 10 times lower than that of pristine MoS₂. The lowest among the reported MoS₂ hybrid structures with metal carbides. These results indicated that Mo₂C provided a lower resistance connection for the transport of electrons.

4. Role of molybdenum carbide in photocatalytic hydrogen production

The properties of Mo_xC are virtually analogous to the noble metal such as Pt and Mo_xC is a promising co-catalyst for photocatalytic H_2 production, which plays significant roles in the H_2 production under visible light irradiation.

4.1. Facilitating the separation of photo-induced charges

The intimate conjugation interface between Mo₂C and semiconductor facilitates the separation and migration of photo-induced charges, thereby inhibiting the recombination of electron-hole pairs. This interfacial effects between two semiconductors cause changes in electron distribution and lead to excellent catalytic performance. For example, there are rich coupling interfaces between SrTiO₃ and Mo₂C. This interfacial effect between SrTiO₃ and Mo₂C promotes the charge exchange and transfer for high separation of photo-generated charge carriers [46]. Mo₂C can significantly improve the interfacial conductivity. In the SrTiO₃@Mo₂C hybrid system, Mo₂C was used as an electron trap, and electrons generated in SrTiO₃ were rapidly shuttle into the surface active sites, achieving more efficient charge separation and photocatalytic H₂ production. In addition, a type-I S–S junction was formed between the semiconductor Mo₂C and SrTiO₃, in which the conduction band and valence band positions of SrTiO₃ straddle those of Mo₂C. The formed heterostructure realized effective spatial separation of electron-hole pairs, and prolonged the lifetime of photogenerated electrons. Besides, the intimate interface between Mo₂C and SrTiO₃ promoted strong electronic interaction, which was vital to the electrons transport, eventually resulting in high apparent quantum efficiency during photocatalytic water reduction process.

Benefiting from the d-state density around Fermi level and unique Mo-C chemical bonding, Mo₂C exhibits well metallic nature [110]. The metallic character of Mo ensures good electronic conduction, which is an essential factor in determining electrochemical performance [87]. Mo₂C has extremely high electronic conductivity, which minimizing charge transfer resistance, facilitating the transfer of electrons. Remarkably, the highly conductive Mo₂C acts as "transport superhighway" to rapidly transport electrons to the active catalytic sites. Mo₂C with abundant active area and large specific capacitance benefits to the accumulation of effective electric charge. Electrons generated in the semiconductor under visible light irradiation are continuously delivered to the surface of Mo₂C, and Mo₂C acts as a reservoir to accept these electrons. In addition, in the Mo₂C based photocatalytic system, Mo species with different valence states provide a large number of active sites, which account for the excellent performance of molybdenum carbide-based photocatalysts. Besides, Mo₂C demonstrates strong photo-absorption over the ultraviolet-visible range of 200-800 nm. When Mo₂C is combined with other semiconductors, the light absorption capability of the semiconductor photocatalyst in the whole spectrum can be significantly improved, indicating the efficient sensitization effect of Mo₂C [35,100].

4.2. Mass transfer enhancement

The surface chemistry properties play an important role on water dissociation kinetics. Due to the formation of hydrogen bonds between water molecules and its surface groups, β -Mo₂C exhibits strong affinity to water [113]. The strong affinity is benefit to the interaction between catalysts and hydrogen bubbles, thus obtaining high gas and liquid transfer. After cycling for HER, the surface of β -Mo₂C is modified by surface oxygen groups, such as Mo_2CO_x (-O terminated), $Mo_2C(OH)_x$ (-OH terminated), Mo₂C(OH)_x-H₂O (-OH terminated) [114]. The surface oxygen groups on Mo₂C resulted in the enhanced transfer of hydrogen bubbles and reactants, and fast reaction kinetics. The modified Mo₂C particles act as a water dissociation promoter, greatly improving the HER catalytic performance. New species might be formed at the surface of Mo₂C, avoiding direct contact between the co-catalyst and the aqueous solution. The direct contact would lead to reversible H₂ production (water formation from O₂ and H₂), limiting the activity of co-catalyst for water dissociation [115]. In addition, the surface modification by these new species is benefit to the improvement of catalytic activity. For example, the formation of molybdenum oxide is inevitable due to the passivation reaction, which can protect and keep stability of Mo₂C. CdMoO₄ can be found in Mo₂C/CdS photocatalysts which connects Mo₂C and CdS closely to bridge the electron transport, leading to more convenient electron transport and suppressed recombination of electron-hole pairs [30].

4.3. Reducing the activation energy barrier of H₂ evolution

The theoretical calculations based on DFT are performed to investigate the adsorption energy of hydrogen and the energy barrier of decomposed water. For example, Luo et al. [114] calculated the adsorption energies for disassociated H_2O (OH and H) on the surface of β -Mo₂C as function of the number of adsorbed H_2O molecules. A small energy barrier for water dissociation and hydrogen free energy are achieved on the surface of β -Mo₂C, corresponding to the rapid H* absorption/desorption and water splitting kinetics. The adsorption and desorption of hydrogen atoms on the catalyst surface is natural and it is essentially a pair of competitive reaction. For an ideal catalyst for HER, it should own the strong functions to activate and cleave O-H bonds of water molecules to form H atoms, and it should adsorb H atoms suitably. The formation of adsorbed hydrogen intermediates (Hads) is crucial to the water dissociation. According to the Sabatier principle [116], an excellent HER catalyst should show ideal trade-off between release and binding of Hads intermediates. Hads intermediate should be easily adsorbed but cannot be securely immobilized on the surface of HER catalysts. Unfortunately, the energetics between the Hads intermediate and the HER rate are difficult to evaluate, because the values of Hads bonding energy cannot be direct measured. The calculated Gibbs free energy of hydrogen adsorption (ΔG_{H^*}) can be used as an important parameter for evaluating the catalysts. The optimal ΔG_{H^*} should approach to thermoneutral, e.g. $\Delta G_{H^*} = 0$ [117]. Pt is supposed as the most efficient catalyst for HER, the $|\Delta G_{H^*}|$ value of Pt is very close to thermoneutral, nearly 0.09 eV [118]. As a member of transition metal carbide, the $|\Delta G_{H^*}|$ value of Mo_xC is considered to be very close to Pt. Zhang et al. [119] demonstrated the binding energy of adsorbed H* on the surface of Mo_xC was comparable to that of noble metals. They evaluated the ΔG_{H^*} value of the adsorbed H^* on Mo_xC surface, where the Mo-C ratios ranging from 1:1 to 2:1. In other words, the models used different mole ratio of α -MoC_{1-x}/ β -Mo₂C. In DFT calculations, the binding energy of adsorbed H^* on $Mo_{48}C_{24}$ (β -Mo₂C) was strong and the binding energy of adsorbed H^{*} on Mo₄₈C₄₈ (α -MoC_{1-x}) was weak. As the β -Mo₂C content increased, the positive ΔG_{H^*} value decreased close to zero, indicating the binding energy of adsorbed H* was enhanced. With excessive β -Mo₂C, the ΔG_{H^*} value turned to be negative, suggesting the binding energy of adsorbed H* was too strong and inhibited H desorption in turn. Among the constructed models, the ΔG_{H^*} value of the adsorbed H^{*} on the surface of the optimized Mo_xC (α -MoC_{1-x}/ β - $Mo_2C = 0.56/0.44$) was comparable with the Pt surface (0.08 eV vs. 0.04 eV). Such appropriate composite between β -Mo₂C and α -MoC_{1-x} produces strong synergistic effects, thus improving the intrinsic catalytic activity. Wang et al. [120] revealed that the catalytic performance of Mo₂C was related to N doping concentrations. Nitrogen saturated Mo₂C exhibited the best catalytic performance for hydrogen production. Theoretical calculation results indicated that the doped-N atoms contributed to weaken the binding energy of adsorbed H^{*} and brought more active sites. The ΔG_{H^*} values of three possible H adsorption sites on perfect Mo₂C (001) are explored: C-T (Top), H-1 (HCP), and F-1 (FCC) are -0.57, -0.18 and -0.13 eV, respectively. When one C atom was substituted by an N atom in the top layer, the $|\Delta G_{H^*}|$ on F-2 and N-T site is about 0.03 and 0.36 eV smaller than that on the corresponding sites on Mo₂C (001). When N atoms substituted half of the C in top layer of Mo₂C (001), the $|\Delta G_{H^*}|$ decreases about 0.06, 0.05, and 0.03 eV than that of the first three sites. The change of $|\Delta G_{H^*}|$ at a given site is closely related to the electronic properties of the top layer of Mo₂C (001). Further research found that the doped N atoms modified the d- or p-band center of the atoms in the top layer, resulting the weakened hydrogen adsorption ability and enhanced HER performance.

Table 2

Hydrogen evolution of Mo_xC-based photocatalysts.

Name	Synthetic method	Morphology	Sacrificial reagent	Optimal hydrogen evolution (μ mol h ⁻¹ g ⁻¹)	Enhancement factor	Quantum efficiency (%)	Reference
MoC-QDs/C/ZnIn ₂ S ₄	in situ induced growth	flower-like morphology	lactic acid	1131.9	$48(ZnIn_2S_4)$	-	[127]
Mo ₂ C-Erythrosin B	temperature programmed reduction	rod-like morphology	triethanolamine (TEOA)	524.9	-	29.7@480 nm, 18@520 nm	[176]
CdS/Mo ₂ C@C	hydrothermal	nanospheres	lactic acid	554.3	2(CdS/Pt)	33.4@460 nm	[154]
Mo ₂ N/Mo ₂ C/GR/CdS	deposition	nanosheet morphology	lactic acid	4520	18(CdS/Pt) 3.6(Pt/CdS)	-	[172]
Mo-Mo ₂ C/g-C ₃ N ₄	ultrasound assisted deposition method	nanobelt structure	triethanolamine (TEOA)	219.7	$440(g-C_3N_4)$	8.3@420 nm	[164]
Co (Mo-Mo ₂ C)/g-C ₃ N ₄	ultrasound assisted deposition method	nanobelt structure	triethanolamine (TEOA)	11,291	$1.4(Pt/g-C_3N_4)$	6.7@420 nm	[165]
SrTiO ₃ @Mo ₂ C	electrospinning method	core-shell nanofibers	triethanolamine (TEOA)	7930	14.93(SrTiO ₃)	29.3@313 nm	[46]
$g-C_3N_4/Mo_2C$	deposition	rod-like morphology	triethanolamine (TEOA)	507	9.8(g-C ₃ N ₄)	3.74@420 nm	[162]
CdS/Pt/Mo ₂ C	chemical bath deposition	particles	Na ₂ S/Na ₂ SO ₃	1828.82	8.6(CdS), 16.2 (CdS/Mo ₂ C)	9.39@400 nm	[173]
Mo ₂ C/CdS	precipitation method	particles	Na ₂ S/Na ₂ SO ₃	161	2.3(Pt/CdS)	3.41@420 nm	[30]
Mo ₂ C/CdS	liquid-phase ultrasonic exfoliation	nanosheets	lactic acid	7700	6(bulkMo ₂ C/CdS); 16(pure CdS); 4(Pt/CdS)	86@460 nm	[155]
Mo ₂ C@C/2D g-C ₃ N ₄	self-assembly method	nanoparticle morphology	triethanolamine (TEOA)	2269.47	$850(g-C_3N_4)$	9.07@405 nm	[170]
CdS@Mo ₂ C-C	Solvothermal/hydrothermal	core-shell nanorods	Na ₂ S/Na ₂ SO ₃	17,240	42(CdS)	-	[157]
Mo ₂ C/TiO ₂	Solvothermal/hydrothermal	Dandelion like morphology	triethanolamine (TEOA)	39,400	25(TiO ₂)	12.1@365 nm	[122]
$Mo_2C@C/g-C_3N_4$	Solvothermal	nanosheet	triethanolamine (TEOA)	52.1	$260(g-C_3N_4)$	-	[171]
Mo ₂ C/TiO ₂	Temperature programmed reaction	particles	phenol	52.5	15(TiO2) 1.28(Pd/TiO2)	-	[150]
Mo ₂ C/CdMoO ₄ /CdS	Annealing-hydrothermal method	nanosphere	Na ₂ S/Na ₂ SO ₃	1843	50(pure CdS)	-	[175]

4.4. Morphology and structure controlling of Mo₂C-based photocatalysts

It is generally believed that morphology and structure have significant impact on the photoelectrical properties and catalytic performance of photocatalysts [121–123]. Therefore, the researchers designed various semiconductor catalysts with controlled morphology and structure to support Mo_xC. Table 2 summarizes Mo_xC-based photocatalysts with different morphology and their photocatalytic performance.

The Mo_xC has multiple crystal structures with variable compositions in nature. The different crystal structures will greatly affect its electrochemical performance [89]. Mo_xC with different crystal structure and morphology can be obtained by tuning the chemical components of precursors and synthesis conditions [124]. Various well-defined Mo_xC nanostructures are usually designed to expose more active sites, such as 1D nanotubes [125], 2D nanosheets [126]. For example, Gao et al. [127] designed a 2D layered flower-like co-catalyst (Fig. 10a), in which MoC quantum dots are anchored on the thin carbon film (MoC-QDs/C). QDs represent all 3D ultrasmall dot-like nanocrystals in several nanometers. Due to the quantum effects, MoC QDs possess unique size-dependent optical properties. With the introduction of MoC-QDs/C, the obtained MoC-QDs/C/ZnIn₂S₄ composite shows a significant improvement in the photocatalytic H₂ evolution performance (Fig. 10b). MoC quantum dots provide lots of active sites for HER, which can promote efficient separation of photogenerated electron-hole pairs in ZnIn₂S₄. Besides, there may be synergistic effect between the carbon films and highly dispersing MoC quantum dots. As a 2D matrix, the carbon film can avoid excessive aggregation of MoC-QDs, exposing rich catalytic active sites, and the large contact area between the carbon film and ZnIn₂S₄ ensures more electron transport channels from ZnIn₂S₄ to MoC. In brief, the introduction of MoC-QDs/C and the close contact between MoC-QDs/C and ZnIn₂S₄ improved the transport rate and separation ability of the charge carriers, resulting in the enhancement of photocatalytic performance of MoC-QDs/C/ZnIn₂S₄ composites (Fig. 10c).

Monodisperse inverse opal like Mo_xC nanospheres with superior HER performance were synthesized via a facile strategy [119]. The Mo_xC inverse opal-like structure exhibited significantly structural advantages, including large exposed surface, appropriate hydrogen binding energy, fast mass/charge transport [128]. β -Mo₂C possessed strong hydrogen-binding energy but restricted desorption step [69]. The inefficient H^{*} adsorption and weak Mo–H bonds restricted MoC HER activity [129]. The optimized atomic structure of Mo_xC was achieved through tuning ratio between the two extreme cases. The enhancement of HER activity should be ascribed to the robust inverse opal-like structure and synergistic effect between β -Mo₂C and MoC.

5. Photocatalytic hydrogen production

Accompanying the tremendous growth of photocatalysts in the past decade [130–134], visible-light-driven water splitting for H_2 evolution has witnessed explosive advances. For the typical HER on the photocatalysts, there are three main processes: (I) photon absorption by the semiconductor upon irradiation by light source and excitons generation (i.e. electron-hole pairs); (II) the separation and migration of electron-hole pairs; (III) photocatalytic redox reactions for H_2 production to maintain equilibrium [135], which leads to the low-efficiency of photocatalysts. Loading of co-catalysts on the semiconductor is a promising strategy to restrict the recombination, leading to the adaptation of heterojunction. These junctions allow electrons to be effectively separated from the holes, mimicking the electron paths in natural photosynthesis. Non-precious metal co-catalyst has been a hot research issue in photocatalytic H_2 production due to their low cost and the potential to



Fig. 10. (a) SEM image of the MoC-QDs/C hybrid. (b) Photocatalytic activities of MoC-QDs/C/ZIS with different loading amounts of MoC-QDs/C. (c) The proposed mechanism of photocatalytic reaction using the MoC-QDs/C/ZIS composite under visible light irradiation. Reproduced with permission from ref. [127]. Copyright 2018 Royal Society of Chemistry.

replace expensive precious metal co-catalysts. Mo_xC is an attractive cocatalyst for the replacement of noble metals and has been applied in many cases to enhance the performance of photocatalysts.

5.1. Binary structure

By constructing a heterojunction, it is possible to suppress electronhole pair recombination and accelerate the surface reaction of H_2 generation [136–138]. This strategy offers opportunities to greatly improve solar-hydrogen conversion efficiency. Therefore, many groups constructed heterojunctions between Mo_xC and other semiconductors to elevate its H_2 evolution ability.

5.1.1. Mo₂C/SrTiO₃ heterostructure

Among all the variety of developed photocatalysts, SrTiO₃ as the representative perovskite metal oxide has been widely investigated due to its chemical stability, non-toxicity, low cost, and high catalytic efficiency [139]. SrTiO₃ is promising in the field of photocatalytic H₂ production. The valence band of $SrTiO_3$ at the level is lower than the O_2/H_2O potential and the conduction band is higher than H^+/H_2 potential, thereby making it able to split water thermodynamically [140]. The features of photocorrosion resistance and good photocatalytic activity are the reasons for the application in photocatalysis. However, SrTiO₃ has a wide band gap of 3.4 eV, indicating it is active only under ultraviolet radiation [141]. Besides, the high recombination rate of photogenerated electronhole pairs also limits its usage for further photocatalytic applications. Several strategies have been adopted to improve the performance of SrTiO₃ photocatalyst [142–144], most notably is coupling with other semiconductors in an S-S junction [145]. The use of Mo₂C as an electron acceptor to form heterojunctions for water splitting has been widely employed. But its coupling with SrTiO₃ has been rarely reported. In fact, Mo₂C is an efficient co-catalyst that not only resists the recombination of charge carriers but also enhances the light harvesting efficiency of SrTiO₃. For example, Yue et al. [46] constructed 1D Mo₂C/SrTiO₃ S–S heterojunction with excellent H₂ evolution performance under solar light irradiation. The H₂ generation rate of Mo₂C/SrTiO₃ was up to 7.93 mmol h^{-1} g⁻¹, which was 15 times higher than that of the pure SrTiO₃. The unique S–S junction could achieve light absorption over a wide spectral range, improve charge carrier separation efficiency and prolong their life time [146]. This well-defined heterostructure significantly enhanced the light absorption ability, improved the interfacial conductivity, and accelerated the separation and transport of photoinduced charge carriers. Besides, the introduction of appropriate Mo₂C was of great significance for H₂ generation. Because Mo₂C could effectively suppress the recombination of electron-holes and prolong the lifetime of charge carriers, and Mo₂C is the main active center of H₂ production. A series of photoelectrochemical analyses were used to study the H₂ production process of SrTiO₃@Mo₂C heterostructures. The transient photovoltage (TPV) and surface photovoltage (SPV) spectra are shown in Fig. 11a and b. The remarkable SPV signal of SrTiO₃@2Mo₂C demonstrated that the separation of photogenerated charge carriers was greatly improved. The slow component peak of SrTiO₃@2Mo₂C shown in TPV spectra indicated the extended life time of charge carriers. The current density curve clearly showed that the cathode current of SrTiO₃@Mo₂C was improved due to the good conductivity of Mo₂C (Fig. 11c). The results showed that the improvement in photocatalytic H₂ production ability of the composite catalyst mainly due to the excellent electrochemical properties of Mo₂C. The surface recombination process of photogenerated carriers on SrTiO₃@2Mo₂C electrodes was investigated by using open circuit potential (OCP) response (Fig. 11d). Obviously, the OCP decay over SrTiO₃@2Mo₂C was slower than that of bare SrTiO₃, indicating the effective suppression of surface



Fig. 11. (a) The SPV of SrTiO₃, Mo₂C and SrTiO₃@Mo₂C specimens. And (b) the TPV of SrTiO₃ and SrTiO₃@Mo₂C specimens. Inset: schematic setup for the SPV and TPV transient measurements. (c) The current density curves as a function of the applied potential of SrTiO₃, Mo₂C and SrTiO₃@2Mo₂C specimens. (d) The normalized OCP decay curves at the transient when illumination is turned off of SrTiO₃ and SrTiO₃@2Mo₂C specimens. (e) SrTiO₃@Mo₂C specimens in cross-section and vertical views. Reproduced with permission from ref. [46].Copyright 2018 Elsevier.

recombination. The above results demonstrated that Mo_2C could greatly affect the migration behavior of carriers in $SrTiO_3$ and play an important role in photocatalytic H_2 production. The proposed charge transfer process is shown in Fig. 11e.

5.1.2. Mo₂C/TiO₂ heterostructure

Owing to its chemical stability, resistance toward corrosion, and low production cost, TiO₂ is the most widely used among all the photocatalysts [147]. Nevertheless, for such TiO₂ system, the higher photon-generated carrier recombination and lower solar utilization would always be the most formidable issues [148]. The well-designed heterojunction would be deemed as an effective way to enhance the photocatalytic performance of TiO₂. Previous researches have shown that the low weight percentages of noble metal can significantly enhance the photocatalytic activity of TiO₂ [149] And Mo₂C possesses the properties virtually analogous to noble metals. Based on the above considerations, researchers demonstrated that Mo₂C coupling with nanoanatase TiO₂ is an ideal system to achieve high photocatalytic activity. Li et al. [150] synthesized Mo₂C/TiO₂ catalysts with different amounts of Mo₂C, and investigated the effect of Mo₂C content on the performance of the catalyst. The higher photocatalytic H₂ production rate was achieved by adding only 0.54 wt% Mo₂C, compared to either Pd/TiO₂ catalyst or pure anatase TiO₂. Besides, the Mo₂C/TiO₂ photocatalysts presented higher resistance to sulfur poisoning. Under the illumination of visible light, the electrons were excited to the conductive band of TiO₂ and then trapped by Mo₂C particles, thereby producing a 'charge separation effect' and extending the lifetime of electron-hole pairs. The heterostructure of Mo₂C/TiO₂ ameliorated the high recombination of photo-induced carriers. In addition, Mo₂C content also exerted effects on the activity of photocatalyst. At the beginning, with the increasing of Mo₂C content, the photocurrent density and photocatalytic activity increased gradually. This could be understood by the following reasons. Firstly, Mo₂C enhanced the light absorption capacity of the Mo₂C/TiO₂ composite catalyst and then achieved a high photocatalytic activity. Secondly, the increased of Mo₂C content led to the decrease of the band gap energy of Mo₂C/TiO₂, which effectively enhanced the excitation of electrons from valence band to conduction band. When the Mo₂C content was higher than 0.54%, the photocurrent density decreased. This may be due to the shielding effect of the catalyst affecting the light absorption efficiency. And excessive Mo₂C could form defect sites or recombination centers to reduce quantum efficiency. Yue et al. [122] constructed Mo₂C/TiO₂ heterojunction photocatalysts with novel 3D architecture. This heterostructure achieved the highest H_2 production rate of 39.4 mmol h^{-1} g⁻¹, which

was almost 25 times as much as that of pristine TiO₂. The strong conjugation of this heterostructure between the TiO₂ supports and anchored Mo₂C nanoparticles efficiently inhibited the aggregation of Mo₂C nanoparticles. In addition, as demonstrated by the results of photoelectrochemical measurements, this novel structure endowed it with favorable charge carrier dynamics. The separation, transfer, and recombination processes of electron-hole pairs together with the role that Mo₂C played in the photocatalytic process were characterized by the photoluminescence (PL) and time-resolved photoluminescence (TRPL) decay spectra. Generally, a lower PL intensity suggests a higher charge separation efficiency. As described in Fig. 12a, the intensity of the PL spectrum peak of Mo₂C/TiO₂ composite was much weaker than that of pure TiO₂, indicating the charge separation efficiency was enhanced and the recombination of electron-hole pairs was retarded. TRPL decay behavior of photocatalyst was deemed as a vital parameter for evaluating the catalytic performance. More described in Fig. 12b, the Mo₂C/TiO₂ sample possessed longer average decay time than that of pure TiO₂, suggesting that the introduction of Mo₂C effectively depressed the charge recombination and speeded up the photogenerated charge transfer. This dandelion-shaped structure brings great benefits to electron transmission. The electrons was first excited under solar light irradiation and then transferred along the TiO₂ branches as a stream of meteor showers, advantageously reaching the surface of Mo₂C for proton reduction. This type of photocatalytic structure was capable of exposing dense reaction sites on its surface, accelerating the rate of H₂ production. As a result, the novel architecture of 3D dandelion-like TiO₂ loaded with Mo₂C exhibited high performance photocatalytic H₂ production and excellent long-term durability. Wang et al. [119] synthesized hierarchical porous TiO₂/C nanocomposites and loaded Mo₂C as cocatalysts for H₂ evolution. The excellent photocatalytic performances were ascribed to its unique hierarchical pore

structure. The synergistic effect of ternary interconnected pore structure improved gas/fluid exchange efficiency in diffusion-limited photochemical processes. The hierarchical pore structure guaranteed sufficient activity sites and accessible electrons transfer channels for photochemical reactions.

5.1.3. Mo₂C/CdS heterostructure

CdS has two structural polytypes, zinc blende and wurtzite structures. The calculated values of band energy for cubic zinc blende and hexagonal wurtzite type CdS are approximately 2.3 eV and 2.4 eV, respectively [151]. For wide-gap semiconductors, including KTaO₃, ZnS, ZrO₂, TiO₂, KTaO₃, SrTiO₃, SiC and ZnO, the narrow range of spectral response is one of the biggest obstacles to photocatalytic efficiency. In possessing the narrow band-gap, CdS is thought to be a highly responsive visible-light driven photocatalyst. Compare to the above mentioned wide-gap semiconductors, CdS has stronger photoabsorption capacity in the visible light region, resulting in higher solar energy conversion efficiency. In addition, CdS possesses other advantages for photocatalytic water splitting, such as relatively high stability, excellent reactivity and low cost [152,153]. While pristine CdS exhibited poor photocatalytic activity, loading co-catalysts on the surface of CdS is thought to be an efficient approach to improve its photocatalytic performance.

Several literatures reported that loading Mo_2C as a co-catalyst can significantly improve the photocatalytic performance of pristine CdS. For the first time, Ma and his group [30] reported the synthesis of Mo_2C/CdS composite catalyst for photocatalytic H₂ evolution. The presence of Mo_2C co-catalyst significantly enhanced the activity of CdS. Compared with CdS alone, the H₂ evolution rate of optimized Mo_2C/CdS increased by 10 times. Intimate contact between co-catalyst Mo_2C and CdS accelerated the electron transfer and inhibited charge



Fig. 12. (a) PL, and (b) TRPL decay spectra of TiO₂ and 1 wt% Mo₂C/TiO₂ hybrid. (c) Schematic illustration of the mechanism for the photocatalytic activity of the Mo₂C/TiO₂ heteronanostructure. Reproduced with permission from ref. [122]. Copyright 2017 Royal Society of Chemistry.



Fig. 13. (a) Illustration of the structure and mechanism of Mo₂C/CdS composite for enhanced photocatalytic H₂ production. (b) Photocatalytic activities of CdS loaded with different cocatalysts. The amount of noble metal is 1.0% whereas the amount of Mo₂C is 2.0%. Reproduced with permission from ref. [30]. Copyright 2016 Wiley. (c) Mechanism for the visiblelight-driven photocatalytic H₂ evolution from water on CdS/Mo₂C@C. (d) SEM and (e) TEM images of Mo₂C@C. Reproduced with permission from ref. [154]. Copyright 2017 American Chemical Society.

recombination, effectively improving photocatalytic activity (shown as Fig. 13a). The authors investigated the photocatalytic activities of the Mo₂C-based catalysts and compared with other precious metal-based catalysts (Fig. 13b). Among all catalysts, the H₂ evolution rate of Mo₂C/CdS was the highest, even slightly more than that of Pd/CdS. In addition, Mo₂C/CdS composite catalyst remained stable after 50 h of illumination. The protection of CdMoO₄ and molybdenum oxide covering the surface of Mo₂C may be the reason for the good stability of the catalyst. The stability of the composite catalyst may bring potential commercial applications. Pan et al. [154] synthesized CdS/Mo₂C@C nanosphere photocatalyst. CdS nanoparticles were supported on the nanospheres, which consisting of Mo₂C and carbon (Fig. 13c-e). Benefiting from the intensified charge transfer and exciton dissociation, the asobtained CdS/Mo₂C@C hybrid exhibited superior visible-light-driven H₂ evolution ability. The H₂ evolution rate reached to 554.3 μ mol h⁻¹ g⁻¹, which was two times higher than that of CdS/Pt under the same conditions. The ability of CdS/Mo₂C@C to separate photo-induced electrons-hole pairs has been studied. Photoluminescence spectrum and photocurrent analysis demonstrated that the separation efficiency of photogenerated electron-hole pairs on CdS/Mo₂C@C was higher than that of CdS. This may be attributed to the strong interfacial interaction between CdS nanoparticle and Mo₂C@C nanosphere. The introduction of the carbon film enlarged the surface area, and facilitated the interaction between H₂O molecules and photocatalysts, resulting in a higher H₂ precipitation rate. The bond between Mo₂C and carbon formed during calcination and hydrothermal processes, therefore the interaction between carbon and Mo₂C was more intimate than physical bonding. Besides, nanoscale pores existed in Mo₂C@C nanospheres, causing confinement effects and also contributing to the improvement of electron separation efficiency. For the first time, Ruan et al. [155] obtained Mo₂C nanosheets with thickness of 20 nm by liquid phase ultrasonic exfoliation. Exfoliation has been recognized as an efficient method to prepare materials with a monolayer or few-layers structure providing more edge sites and active sites for reactions [156]. Liquid phase ultrasonic exfoliation is an efficient and practical method to prepare materials with few-layers or even a monolayer structure. Thus, this method was used for preparing Mo₂C with 2D layered structure. The highly exfoliated Mo₂C nanosheets were hybridized on CdS and Mo₂C/CdS composite exhibited remarkable H₂ production rate, about 16-folds as high as that of pure CdS. The apparent quantum efficiency of 3 wt% Mo₂C/CdS reached to 86% at 460 nm. The 2D nanosheet structure exposed more active sites and the photogenerated charge carriers could easily transfer to the surface-active sites. Mo₂C nanosheets with large planar area and low thickness can facilitate charge transfer in a shortened distance, leading to an efficient photocatalytic HER.

Yi et al. [157] constructed 1D CdS@Mo₂C-C core-shell nanorods (Fig. 14a). The unique morphology of core-shell nanorods photocatalyst demonstrated its superior photocatalytic H₂ generation performance (17.24 mmol h^{-1} g⁻¹). CdS@Mo₂C-C even showed H₂ evolution rate higher than that of Pt/CdS, suggesting the excellent co-catalytic properties of Mo₂C. Mo₂C played an important role in the enhancement of photocatalytic activity, providing trapping sites for photo-induced charges and accelerating the separation of electron-hole pairs. As shown in the curves of transient photocurrent responses (Fig. 14b), CdS@Mo₂C-C obtained much higher rapid photocurrent response, demonstrating a significant suppression of charge recombination, which can attribute to the heterojunction formed between CdS nanorods and Mo₂C-C nanolayers. The advantages of CdS@Mo₂C-C in photogenerated electron transport process were demonstrated by the electrochemical impedance spectroscopy (EIS) Nyquist plots. (Fig. 14c). As mentioned in section 3, the Mo₂C has high electrical conductivity which can facilitate charge carrier



Fig. 14. (a) Schematic illustration of the charge transfer and separation in the CdS@Mo₂C-C core-shell NRs. (b) Transient photocurrent responses at 0 V vs. Ag/AgCl over CdS and CdS@ $1Mo_2$ C-C under visible light irradiation ($\lambda > 420$ nm). (c) EIS Nyquist plots of CdS and CdS@ $1Mo_2$ C-C in the dark and under visible light irradiation ($\lambda > 420$ nm), inset: enlarged view of the specified position. Reproduced with permission from ref. [157]. Copyright 2017 Royal Society of Chemistry.

transport. The semicircle diameter of Mo_2C/TiO_2 was much smaller than that of pure TiO₂, indicating the transport resistance of $Mo_2C/$ TiO₂ composites was reduced upon the loading of Mo_2C and thus facilitated the charge transfer. A significant increase in the efficiency of charge transfer and migration was realized by the introduction of Mo_2C-C nanolayer. It worth to note that the as-prepared core-shell structure greatly improved the photocatalytic H₂ production performance and photoelectric stability. The Mo_2C-C shell provided perfect photochemical protection for internal CdS core. Photogenerated holes could be effectively transferred from CdS to carbon layer, avoiding photo-oxidation of CdS and enhancing the stability of CdS. In addition, a large number of capture sites on the surface of Mo_2C led to the improvement of photoelectron capture efficiency and the innovative core-shell heterojunction inhibited the recombination of electron-holes.

5.1.4. Mo₂C/g-C₃N₄ heterostructure

Among the as reported numerous photocatalysts, $g-C_3N_4$, as a novel metal-free visible-light driven photocatalyst, has attracted intensive attention owning to its attractive electronic band structures and remarkable physicochemical stability [158–160]. For the first time, Wang and his group found the ability of $g-C_3N_4$ to produce H_2 under visible light irradiation [161]. But pristine $g-C_3N_4$ exhibited

low level of photocatalytic activity due to the rapid recombination of photo-generated charge carriers, insufficient solar light absorption and relatively low electrical conductivity. Aim to elevate the performance of H_2 production of g-C₃N₄, loading non-precious metal cocatalysts such as molybdenum carbide is one of the promising strategies.

For example, Zhang and his colleagues obtained g-C₃N₄/Mo₂C hybrid photocatalyst by a facile two step processing [162]. The photocatalytic H₂ production rate of $g-C_3N_4/Mo_2C$ reached to 507 μ mol·h⁻¹ g⁻¹, which was about 9.8 times higher than the sole g-C₃N₄. Due to the high conductivity, high capacitance of Mo₂C, and relative low conduction band (CB) potentials of Mo₂C, the electrons generated in the g-C₃N₄ conduction band were rapidly transferred to the conduction band of molybdenum carbide. Then the electrons activated by visible light participated in the H₂ generation reaction. In the g-C₃N₄/Mo₂C heterostructure system, Mo₂C acted as a co-catalyst to facilitate the generation of photogenerated electrons, accelerate the separation of electron-hole pairs, and contribute to the efficient photocatalytic H₂ generation from water splitting. The heterostructure could rapidly pull the generation of photogenerated electrons in g-C₃N₄ rods. In addition, the designed heterostructure material not only enhanced the light adsorption efficiency of g-C₃N₄, but also exhibited high stability over extended periods of application.



Fig. 15. (a) Schematic illustration of the synthesis procedures of Mo-Mo₂C/g-C₃N₄ photocatalyst. (b) Specific photocatalytic H₂ evolution rates of 2.0 wt% Mo₂C₂-C₃N₄, 2.0 wt% Mo/g-C₃N₄, 2.0 wt% Mo/g-C₃N₄, 2.0 wt% Mo/g-C₃N₄, 2.0 wt% Mo/Mo₂C/g-C₃N₄ and g-C₃N₄ under visible-light irradiation. Schematic diagrams of electron transfer in (c) Mo-Mo₂C/g-C₃N₄ and (d) Mo₂C/g-C₃N₄ system. Reproduced with permission from ref. [164]. Copyright 2019 Elsevier.

Adding additional metal particles to the semiconductor can significantly improve the catalytic performance of the photocatalyst [163]. Therefore, Dong and co-workers [164] prepared Mo-Mo₂C/g-C₃N₄ composite photocatalyst via a temperature-programmed reaction. The molybdenum rich molybdenum carbide (Mo-Mo₂C) nanoparticles were supported on the surface of g-C₃N₄ by ultrasound assisted deposition method (Fig. 15a). The Mo-Mo₂C/g-C₃N₄ nanocomposites demonstrated excellent photocatalytic performance with H₂ production rate of 219.7 μ mol h⁻¹ g⁻¹, which was approximately 440 times higher than g-C₃N₄ alone (Fig. 15b). And the apparent quantum efficiency of Mo-Mo₂C/g-C₃N₄ composite reached to 8.3%. It was demonstrated that there were strong synergy effects between the Mo and Mo₂C particles. The doping of metallic Mo particles can improve the conductivity of molybdenum carbide. Compared to pristine $g-C_3N_4$, the light absorption ability of Mo-Mo₂C/g-C₃N₄ was significantly improved, owning to the strong photo-absorption capacity of Mo-Mo₂C nanoparticles. This may be one of the reasons for the higher solar energy conversion efficiency of Mo-Mo₂C/g-C₃N₄ photocatalysts. The tight contact between the two semiconductors enhanced the stability of photocatalysts and facilitated the separation and transfer of photoinduced electrons between Mo-Mo₂C and g-C₃N₄. In addition, Dong and his group proposed the photocatalytic mechanism of Mo-Mo₂C/ g-C₃N₄ system, which can achieve higher electron transfer efficiency than Mo₂C/g-C₃N₄ system (Fig. 15c and d). Metal Mo particle acted as electron mediator, and g-C₃N₄ as a conjugated host scaffold which combined with Mo₂C to form solid-state Z-scheme system. The metallic Mo particle served as a relay to accept electrons from conduction band of g-C₃N₄ and hole pairs from valence band of Mo₂C. The electrons in the Mo₂C conduction band participated in proton reduction reaction for H₂ production, while the holes in the g-C₃N₄ valence band undergone the oxidation reaction of triethanolamine. Comparing with $Mo_2C/g-C_3N_4$, this scheme of charge transfer achieved higher H_2 production activity. The metal Mo particle was of great significance in the Mo-Mo₂C/g-C₃N₄ composite photocatalyst. Aim to further improve the H₂ production ability of Mo₂C/g-C₃N₄, the Group VIII metals (such as Fe, Ni, or Co) were doped into the system. Dong and co-workers [165] further reported highly active cobalt (Co) doped Mo-Mo₂C as cocatalyst loaded on g-C₃N₄ for photocatalytic hydrogen production. The hydrogen production rate of optimal 2.0 wt% Co(Mo-Mo₂C)/g-C₃N₄ can be as high as 11,291 µmol h⁻¹ g⁻¹. The apparent quantum efficiency of optimal photocatalyst reached to 6.7% at 420 nm. Co-doped Mo₂C can improve the hydrogen evolution performance of Mo₂C [166]. The rich electrons for metal Co particles occupied the orbitals of Mo atoms, effectively reduced the unoccupied d-orbitals, resulting in the enhanced catalytic activity of HER for Co-doped Mo₂C.

In previous researches, Mo₂C was easily supported on a range of carbon materials, including carbon sheets [167], carbon fibers [168], and graphene [169], resulting in high electrical conductivity and large surface area. Herein, Mo₂C@C/2D g-C₃N₄ heterostructure photocatalyst was successfully prepared by Song and his group [170]. The addition of carbon material can inhibit the aggregation of Mo₂C during pyrolysis at high temperature, thereby exposing more sufficient active sites on the surface. In addition, the intimate conjugation between Mo₂C and carbon can further improve the electrical conductivity of Mo₂C, which is benefit for the electrons transfer in photocatalysis. On the other hand, the 2D g- C_3N_4 structure has many advantages such as large specific surface areas, sufficient absorption sites, and the minimum distance that the photo-carriers transport to the contact interface. For the reasons described above, the problem of rapid recombination of photogenerated carriers in g-C₃N₄ can be effectively solved, thus resulting in the high H₂ production rate of Mo₂C@C/2D g-C₃N₄. The role of carbon nanosheet in Mo₂C/g-C₃N₄ photocatalytic system was further proved by Zou and his colleagues [171]. In their work, a well-designed nonprecious metal Mo₂C@C/g-C₃N₄ heterostructure was constructed. The

intercalated carbon nanosheets were used as binders to form an excellent contact interface between g-C₃N₄ and Mo₂C. And it was found that a large number of carbon quantum dots embedded in the carbon nanosheets homogeneously. Embedding carbon nanosheets into the interfaces of two semiconductors led to smooth flow of electrons from g-C₃N₄ to Mo₂C. The conductive nanosheet was served as efficient electron mediator between g-C₃N₄ and Mo₂C to achieve fast charge migration and separation. The quantum dots embedded in carbon nanosheet can improve solar-to-chemical energy conversion efficiency. The photocatalytic mechanism was explained as shown as Fig. 16. After the analysis of band structure, the heterojunction of type-I was formed between g-C₃N₄ and Mo₂C. Due to the presence of ultrathin carbon film, CB-electrons of g-C₃N₄ can migrate from the inner part to the conductive band of Mo₂C, shortening the distance between g-C₃N₄ and Mo₂C. The in-plane micro pores in the carbon film provided excellent pathway for electrons.

5.2. Ternary structure

In addition to constructing heterojunctions between two different semiconductors, multicomponent composite photocatalysts have also been investigated.

5.2.1. Mo₂N/Mo₂C/GR ternary co-catalyst

Ma and his group formed Mo₂N/Mo₂C/graphene ternary co-catalyst to enhance the H₂ production capacity of CdS [172]. The junction structure formed between the metal free co-catalysts produced a synergistic effect. It was beneficial to photoexcitation electron transfer and separation, thus improving H₂ production activity. The H₂ production rate of the Mo₂N/Mo₂C/GR/CdS catalyst reached to 4520 μ mol h⁻¹ g⁻¹, indicating the ultra-efficiency of the Mo₂N/Mo₂C/GR ternary co-catalyst. According to the characterization analysis, the ultra-efficiency of Mo₂N/ Mo₂C/GR may be closely related to its structure. The XRD image of the Mo₂N/Mo₂C composite was different from Mo₂N and Mo₂C alone, meaning that a new interface or a material with new structure may be formed during the reaction. The HRTEM image showed that the special structure existed between the Mo₂N and Mo₂C interface. Besides, graphene has excellent electron mobility, high specific surface area and excellent electroconductivity. Therefore, the combination of graphene and Mo₂N/Mo₂C co-catalyst can result in easily transfer of the photo-induced electrons. In short, Mo₂N/Mo₂C/graphene ternary

heterostructure co-catalyst significantly enhanced the photocatalytic H₂ production performance of CdS and provided new ideas for constructing and fabricating composite photocatalysts.

5.2.2. CdS/Pt/Mo₂C heterostructure

Jing et al. [173] constructed a novel CdS/Pt/Mo₂C heterostructure to enhance the separation of photocarriers. The photocatalytic H₂ evolution rate up to 1828.82 μ mol h⁻¹ g⁻¹, which was higher than both pristine CdS and CdS/Mo₂C. Due to the introduction of Pt nanoparticles and Mo₂C, the excellent separation efficiency of photogenerated electron holes and narrow band gap energy was generated, thus effectively increasing the H₂ production activity of CdS/Pt/Mo₂C. Ammonium molybdate and powder active charcoal were used as the molybdenum and charcoal source to synthesize tubular Mo₂C. The triphase heterojunction structure of CdS/Pt/Mo₂C caused changes in the band structures, compared with those of CdS. Comparing the potentials of CdS and CdS/Pt/ Mo₂C-0.5, the valence band position increased from 1.25 eV to 1.8 eV and the conduction band position shifted from 0.63 eV to 0.07 eV. The construction of the heterostructure system improved the reducing ability of photogenerated electrons effectively, thereby leading to the improvement of photocatalytic activity of CdS.

5.2.3. MoS₂/Mo₂C/CdS heterostructure

Shao et al. [174] presented a ternary composite photocatalyst with unique morphology which containing leaf-like CdS and nanosheet-like MoS_2/Mo_2C . The $MoS_2/Mo_2C/CdS$ exhibited outstanding photocatalytic performance and excellent apparent quantum efficiency. Theoretical calculations clearly demonstrated that the MoS_2/Mo_2C possessed suitable Gibbs free energy of H₂ adsorption. The unique morphology endowed catalysts with larger specific surface area than pristine CdS, indicating more active sites. Photoinduced electrons accumulated on these sites to achieve fast H₂ evolution reaction. Molybdenum-based catalysts with highly hydrogen evolution activity could be obtained by morphology and surface chemical engineering [106].

5.2.4. Mo₂C/CdMoO₄/CdS heterostructure

Wang et al. [175] synthesized Mo₂C/CdS hollow core-shell composite with CdMoO₄ transition layer. The non-noble metal co-catalyst Mo₂C exhibited a remarkable enhancement for photocatalytic H₂ evolution. The H₂ evolution of the as-prepared Mo₂C/CdMoO₄/CdS composite was 1843 µmol h⁻¹ g⁻¹, about 50 folds higher than that of pure CdS



Fig. 16. Schematic illustration of charge transfer processes over Mo₂C/CN (a) and Mo₂C@C/CN (b); (c) Proposed photocatalytic mechanism in Mo₂C@C/CN under visible-light irradiation ($\lambda \ge 420$ nm) and the band positions together with H⁺/H₂ and OH/H₂O redox potentials. Reproduced with permission from ref. [171]. Copyright 2019 Elsevier.

(36 µmol h⁻¹ g⁻¹). The composite photocatalysts exhibited decent photocatalytic stability, the H₂ evolution maintained a decent average of about 1818 µmol h⁻¹ g⁻¹ during the 24 h photocatalytic H₂ evolution process. Pt-behavior like Mo₂C, with lower Fermi level, can quickly capture diffused photoelectrons and act as an ideal diffused electrons accepter. With the CdMoO₄ transition layer, the photogenerated electron could easily transfer from CdS to Mo₂C. The CdMoO₄ transition layer bridged the band structure between CdS and Mo₂C to promote charge carriers transport. 3D hollow core-shell structure with double walls, decreased the photo-corrosion and increased the specific surface areas. The hollow core-shell structure maintained the multiple diffuse reflection, and greatly improved the solar energy utilization efficiency.

6. Conclusions and perspectives

Mo_xC is non-precious transition mental carbide with similar properties to noble metals and can be used as an alternative for platinum-based precious metals. Mo_xC-based photocatalysts have recently attracted increasing research interests due to its excellent performance for H₂ production. In the photocatalytic system, Mo_xC plays a crucial role as a co-catalyst, which is usually used to accelerate the separation and migration efficiency of photoinduced charge carriers. Due to its outstanding properties, easy to fabricate and environmentally friendly, Mo_xC has great research value in photocatalytic applications. Various methods provide new ideas for constructing Mo_xC-based components with novel structure. For example, the organic-inorganic hybrids method is a new approach based on simple pyrolysis of organic matters and Mo precursor. Due to the in-depth understanding of organic matter in recent years, this method has been widely used. MOFs is a new class of porous materials, which can be used to prepare Mo_xC with favorite structure. With the assistance of MOFs, the problem of coalescence and aggregation of Mo_xC nanoparticles in the process of high temperature pyrolysis can be effectively prevented. Mo_xC-based materials have shown excellent performance for H₂ production under visible light irradiation. Mo_xC exhibits co-catalytic properties comparable to or even higher than precious metals. However, the research on the role of Mo_xC as a co-catalyst for photocatalytic H₂ production is still in its early stage. This review is focused specifically on latest advances of Mo_xC-based photocatalysts and the role of Mo_xC in the photocatalytic system. Compare to the pristine semiconductor, the Mo_xCbased composite photocatalysts exhibit higher efficiency of H₂ evolution. Mo_xC plays a vital role in accelerating the industrial development of photocatalytic H₂ production technology. From the series of Mo_xC-based photocatalysts reported in previous literatures, the excellent physical and chemical properties of the Mo_xC are closely related to the photocatalytic performance of the photocatalysts. The role of co-catalysts can be summarized as follows: Firstly, the strong interaction between Mo_xC and semiconductor results in rich conjugation interface with special structure. This facilitates convenient electron transfer and migration and effectively suppresses the recombination of electronhole pairs excited in the surface of semiconductor. Secondly, the heterojunction formed between Mo_xC and semiconductor allows efficient separation of electrons and holes. This charge separation strategy provides opportunities for more efficient photocatalysis. Thirdly, Mo_xC demonstrates strong photo-absorption under a wider spectrum of solar irradiation. This is beneficial for intensifying the solar energy utilization. In addition, the strong electrical conductivity of Mo_xC minimizes the charge transport resistance and leads to rapid transfer of electrons. Fourthly, the surface chemistry properties play an important role on water dissociation kinetics. Theoretical calculations demonstrate that Mo_xC displays proper Gibbs free energy of H-adsorption. Summarily, Mo_xCbased photocatalysts with superior properties will occupy an

important position in H_2 energy production in the near future. Despite the bright future of Mo_x C-based photocatalysts, several issues still need to be further developed:

- I. Carbon deposition during preparation. During calcination process, carbon is easily deposited on the surface of Mo_xC , when using gaseous carbon sources or carbon-containing material as reactants. On the one hand, carbon materials may boost the electrical conductivity of catalysts and facilitate the transfer of electrons. On the other hand, excessive carbon deposition may block the active sites of Mo_xC , thus decrease the catalytic efficiency. Therefore, the carbon deposition mechanism needs to be investigated in detail. Based on the better understanding of how carbon species absorb and dissociate on the surface, the surface properties of Mo_xC catalyst may be tunable.
- II. More efforts are required to synthesis Mo_xC-based catalyst with controllable nanostructure and excellent performance. Recently, MOFs-assisted strategies have attracted great interest and the as-prepared product was of significant tunable periodic structures and various functional properties. Nevertheless, most of the synthesis strategies involve multistep procedures as well as expensive instruments. Producing catalysts with well-engineered interface to meet requirements for further industrial applications is still challenging. Systematic controlled-synthesis methods are urged to be developed in order to control the size, surface and morphology of Mo_xC.
- III. Further investigation of the structure-performance relationship in Mo_xC materials, including surface termination, crystal structure, metal/carbon ratio, etc., is significant. The structure variation of Mo_xC would significantly change the catalytic activity. It is necessary to investigate the intrinsic structure which influences the catalytic behavior and the surface chemistry. Understanding the structure-performance relationship enables further optimization of Mo_xC, as well as the modulation of active site on molecule/atom phaselevel.
- IV. Surface/interface engineering can be achieved by constructing porous and hierarchical structure, decreasing particle size, and introducing hetero-component, which can enhance the photocatalytic performance of the nanomaterials. Enormous efforts for designing scalable and simple methods for surface/interface engineering of Mo_xC-based materials are still required to promote the practical application and future development. Advanced nanoscience and nanotechnology may offer solutions for constructing highly efficient photocatalysts in the practical application.
- V. Theoretical calculation of Mo_xC-based materials. Owing to the distinctive properties, the Mo_xC played significant roles in photocatalytic H₂ production. More detailed experimental and theoretical investigations are necessary to understand the inherent mechanism as co-catalysts. We need to improve the existing characterization techniques including imaging, diffraction, spectroscopic and time-resolved in situ characterization techniques to analysis the structure and mechanism of the photocatalysts. These works are expected to definitely illustrate the relationship between properties and intrinsic structure to enhance hydrogen evolution. And all these efforts will bestow experimentalists with better capability to design Mo_xC-based photocatalysts with sufficient performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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