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Review

Research advances of light-driven hydrogen evolution using polyoxometalate-based catalysts

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ABSTRACT

With the increasing concerns to energy shortage and environmental problems in modern society, the development of cheap, clean, and sustainable energy alternatives has been attracting tremendous attention globally. Among various strategies of renewable energy exploration, solar-driven water splitting into its compositional elements H_2 and O_2 is an ideal approach to convert and store renewable solar energy into chemical bonds. In recent few decades, as an emerging new type of catalysts, polyoxometalates (POMs) have been widely utilized for water splitting due to their versatile synthetic methodology and highly tunable physicochemical and photochemical properties. This critical review addresses the research advances of light-driven hydrogen evolution using polyoxometalate-based catalysts, including plenary POMs, transition-metal-substituted POMs, POM@MOF composites, and POM-semiconductor hybrids, under UV, near UV and visible light irradiation. In addition, the catalytic mechanism for each reaction system has been thoroughly discussed and summarized. Finally, a comprehensive outlook of this research area is also prospected.

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1. Introduction

Energy shortage and environmental pollutant have been regarded as two very serious issues facing mankind in the 21st century. On one hand, the global energy demand towards limited traditional fossil fuels (e.g. coal, oil, and natural gas) has been increasing rapidly. On the other hand, CO_2 , SO_2 , NO_x and other VOCs released by the combustion of traditional fossil fuels will cause many environmental problems [1–5]. In this regard, in order to realize the sustainable development of societal activity, it is urgent to seek safe, clean, and renewable energy alternatives that could replace traditional fossil fuels. Among various renewable energy sources (e.g. solar, wind, tide, hydroelectric, geothermal energy, etc.), solar energy remains

the most promising one because the sunlight energy received by the earth surface per hour is sufficient for mankind consumption per year. As a consequence, most aspects of solar energy utilization have been an increasing concern recently because technical institutions as well as government divisions realize both the significant demand and the attracting opportunity that exists in the pursuit of green and sustainable energy sources. For example, researches towards photovoltaic (PV) devices (e.g. Si-based solar cells, dye-sensitized solar cells, and widely studied perovskite-based solar cells) have been increasingly active and competitive with respect to efficiency, production costs, and operating lifetime. However, due to the lower energy density (both weight and molar energy density) of most current batteries, the PV technology is largely limited to

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production and storage of electrical energy [6–8]. Therefore, ever more research attention has been focused on the direct production of fuel by utilizing sunlight energy. In nature, the process that achieves production of “solar fuel” by harvesting sunlight energy is photosynthesis. However, such photosynthetic process, even optimized over billions of years, is less than 1% efficient for most terrestrial plants. These facts define not only a pressing need for “solar fuels” but also a major opportunity for scientific researchers in this burgeoning area. Inspired by this remarkable natural photosystem, tremendous efforts have been made to develop efficient and robust artificial photosynthetic (AP) systems. As one of the widely studied forms among various artificial photosynthetic systems, solar-driven water splitting into its compositional elements H_2 and O_2 is an ideal approach to convert and store solar energy into renewable chemical bonds (Fig. 1), and at the same time the utilization of H_2 and O_2 in the form of either combustion or fuel cells will release energy and generate clean water as the sole side product, thereby accomplishing a perfect sustainable energy cycle [9,10].

The solar-driven water splitting reaction can be dated back to Honda and Fujishima’s report that the total water splitting into H_2 and O_2 was achieved using TiO_2 -based photoelectrodes [11]. Given the complexity of total water splitting (four electron and four proton processes), solar-driven water splitting is usually studied in two half reactions: hydrogen evolution reaction (HER) [12] and oxygen evolution reaction (OER) [13] where the reduction of protons to H_2 is a two-electron process and the oxidation of H_2O to O_2 is a four-electron process, respectively. The major problem that has been faced for a long time in these reactions is the sluggish kinetics of the two half reactions especially the OER process which usually need to overcome high energy barriers, leading to a low overall energy conversion efficiency. Therefore, the development of efficient, robust, inexpensive, selective, and environmentally-benign catalysts for each half reaction or total water splitting has been attracting tremendous research efforts to reduce the energy barriers of both HER and OER processes and to achieve high solar to chemical energy conversion efficiency [14–17]. Therein, both water reduction catalysts (WRCs) and water oxidation catalysts (WOCs) should be capable of reducing/oxidizing water at a potential minimally above the thermodynamic value reductively/oxidatively, while in the meanwhile being hydrolytically and thermally stable under operating conditions; and critically fast enough to achieve high turnover numbers (TONs) or turn-

over frequency (TOF). Traditional noble metal (such as Pt, Rh, and Ir, etc.) [18–20] and noble metal oxides (such as IrO_2 and RuO_2 , etc.) catalysts, to some extent, meet these criteria usually exhibiting high HER and OER catalytic activity, but the scarcity and high cost greatly limit their large-scale applications [21].

In the process of developing targeted WRCs, researchers have reported a variety of viable, efficient, and inexpensive transition metals-based catalysts including Ni, Fe, Mo, and Co-based organometallic complexes, and their corresponding metal oxides/hydroxides/nitrides/phosphides/sulfides [22–29]. Generally, these WRCs can be categorized into two types: homogeneous catalysts and heterogeneous catalysts. These two types of catalysts exhibit specifically their own advantages and disadvantages. For homogeneous catalysts, basically every catalytic active center of the catalyst can participate in the reaction process, therefore they usually show high TONs, TOF, and selectivity. As molecular catalysts, their compositional and electronic structures are highly controllable and adjustable, also the mechanism of catalytic reaction can be thoroughly explored using various spectroscopic, crystallographic approaches and theoretical calculations. Such detailed molecular-level information could benefit to a more rational optimization of catalytic efficiency, interface chemistry with light absorbers/photosensitizers, and system robustness. However, in addition to these advantages, some appreciable disadvantages of homogeneous WRCs cannot be ignored, namely poor stability. For example, organometallic complexes may undergo ligand dissociation, decomposition as well as hydrogenation or carboxylation under strongly reducing catalytic conditions, resulting in the deactivation of the catalysts [30]. In contrast, heterogeneous catalysts usually have the advantages of cost-effectiveness, availability, and high stability, but they also show the disadvantages of being easily poisoned/deactivated on the surface and forming agglomerated particles. Also, it is usually difficult to study and optimize the catalytic mechanism at the molecular level. More importantly, the catalysis using heterogeneous catalysts usually involves only a few catalytically active sites over the catalyst surface, resulting in lower TONs and TOF values. In this regard, the development of viable water reduction catalysts that combine the advantages of heterogeneous metal oxide catalysts (typically stability and durability) and those of homogeneous catalysts (usually high activity, selectivity, and tunability) is of scientific significance and very challenging. As an emerging type of catalysts, polyoxometalate-based WRCs seem to be an effective, rational choice because they not only have comparable catalytic activity to organometallic-based homogeneous catalysts in most cases, but also are based on earth-abundant elements stabilized by all-inorganic lacunary polyoxometalate ligands. Their unique structures could bridge the gap between homogeneous molecular compounds and heterogeneous metal oxides, thereby offering them special properties that could combine the advantages of homogeneous molecular catalysts and heterogeneous metal oxide catalysts. Also, during the catalytic processes, the lacunary POM ligands of TMSPOMs could work as electron storage sponges and in the meanwhile transition metal atoms work as catalytic active sites, some special combination

Fig. 1. A schematic illustration for artificial photosynthesis: an antenna light-absorption and charge separating structure interfaced with catalysts.

could greatly enhance the catalytic activity in terms of high turnover number (TON) and turnover frequency (TOF) comparing to other catalysts such as metal sulfides and oxides.

Polyoxometalates (POMs) are early transition metal oxygen anion clusters with precise chemical composition and geometric structures formed by corner-, edge- and face-sharing of the MO_6 ($M = \text{Mo}, \text{W}, \text{V}, \text{Nb}$, and Ta in high oxidation states) octahedral building blocks [31,32]. The versatile synthetic methodology and the highly tunable physicochemical properties of POMs make them show wide potential applications in various areas including medicine, magnetism, functional materials, catalysis, energy storage, and others (Fig. 2). Based on the geometrical structures of POMs, two major structural families of plenary polytungstates that have been well documented in the field of catalysis mainly include Keggin structure $[\text{XW}_{12}\text{O}_{40}]^{n-}$, $X = \text{P}, \text{Si}$, and Ge , etc.) and Wells-Dawson structure $[(\alpha\text{-X}_2\text{W}_{18}\text{O}_{62})^{n-}$, $X = \text{P}$ in most common case) [33]. The traditional plenary Keggin or Wells-Dawson POMs are sensitive to pH so that one or several terminals $[\text{W}=\text{O}]^{n+}$ building blocks can be removed *via* base hydrolysis under appropriate conditions (pH, temperature, ionic strength, etc), resulting in the formation of defect or “lacunary” POMs. These lacunary POMs are diamagnetic, multidentate O-donor ligands that can incorporate various mono- or multinuclear d- and f-block transition metals including those with appended organic groups, thus leading to the generation of various transition-metal-substituted POMs (TMSPOMs). Those TMSPOMs exhibit unique structure bridging the gap between a homogeneous molecular compound and a heterogeneous metal oxide, thereby offering them special properties that could combine the advantages of homogeneous molecular catalysts and heterogeneous metal oxide catalysts [34]. In addition, their highly controllable composition, electronic structures, and rich redox chemistry make them very promising candidate for multi-electron-transfer catalysis.

The idea of using POMs as potential water/proton reduction catalysts can be dated back to 1960s, when Pope and Papaconstantinou reported a series of systematical research on electronic, spectroscopic and magnetic properties of reduced heteropolytungstates and heteropolymolybdates (also known as “heteropoly blues (HPB)”) [35–38]. Later on, researchers have

discovered that heteropoly blues can efficiently generate hydrogen in the presence of noble metal cocatalysts (e.g. Pt) [39–42]. However, in all of these studies, either Pt or other noble water reduction catalysts were used and most of these works were done under UV light irradiation that has very low match with the solar spectrum [43–45]. Although many recent works still focused on hydrogen production in the presence of Pt noble catalyst under UV light irradiation, the development of more viable, more efficient, and noble-metal-free POM-based WRCs which works under visible light illumination remains a substantial challenge. After years of efforts, Lv *et al.* [46–50] firstly proposed the idea of using lacunary POM ligands as electron storage sponges and transition metal atoms as catalytic active sites, respectively, these catalytic systems coupled with visible-light-absorbing photosensitizers and sacrificial reagents have greatly improved the efficiency of HER. Those pioneering works greatly stimulated research interests to develop a series of earth-abundant transition-metal-substituted POM-based WRCs. The research timeline revealing the representative breakthroughs of the POM-based catalysts for light-driven hydrogen evolution is shown in Scheme 1.

To date, the synthetic approaches for plenary POMs or TMSPOMs includes the conventional solution-based pathway and the hydrothermal/solvothermal pathway. The conventional solution synthesis represents the most common and effective method for the preparation of soluble POMs, especially the TMSPOMs, which exhibit some intrinsic advantages including the relatively easy operation, mild reaction conditions, high controllability, and the simple post-synthetic purification and characterization, etc [51–54]. It's noted that the POMs of W or Mo are usually assembled at acidic conditions, while the polyoxoniobates (PONbs) or polyoxotantalates (POTas) are prepared in alkaline conditions [55]. With respect to the synthesis of inorganic-organic hybrid POMs, it is generally difficult to develop suitable reaction system which could effectively dissolve a mixture of organic ligands, lacunary POM precursors, and transition metals at the same time under conventional solution synthetic conditions. In this case, the hydrothermal or solvothermal synthetic approach has been proven to be very effective way to overcome these problems because the subcritical and supercritical hydrothermal conditions (usually at high pressure and temperature) can greatly increase the solubility of the starting reagents to form new stable or metastable phases of inorganic-organic hybrid POMs [56]. In addition to the syntheses of inorganic-organic hybrid POMs, the hydrothermal or solvothermal approach has also been used for the synthesis of other POM-based materials, such as POM@MOF composites

Fig. 2. Various potential applications of polyoxometalates.

Scheme 1. Timeline of representative breakthroughs of POM-based photocatalysts for light-driven hydrogen evolution reaction.

and POM-Semiconductor hybrids. Specially, there are three common way for the synthesis of POM@MOF composites: (1) *in situ* one-pot synthetic method: this method is basically easy to handle and widely used for the preparation of POM@MOF with small main windows and cavities, but it is only applicable for polyacids with high stability due to its harsh reaction conditions; (2) the impregnation method: this method usually requires very mild conditions, but it is only suitable for MOFs with larger pores or cavities to incorporate appropriate POMs; (3) the mechanical grinding synthetic method: this method is green, energy-saving, simple, and efficient; however, it is only suitable for the synthesis of MOFs with low formation energy, and the yield and crystallinity of the product are not very satisfactory [57]. Overall, these above-mentioned synthetic approaches basically meet requirements of the preparation of POMs and POM-based materials.

This comprehensive review focuses on the POM-based catalysts especially developed after 1980s for photocatalytic hydrogen production under both UV and visible light irradiation. The structures of different POM-based catalysts, hydrogen-evolving activity, and catalytic mechanism of some representative research works have been summarized and discussed in detail. Finally, the outlook of future development in this area is prospected. All the related POM-based WRCs characterized by X-ray crystallography are summarized in Fig. 3.

2. Overview of POM-based WRCs

2.1. Catalytic H_2 production using POM photocatalysts under UV or near UV light

Photocatalytic water splitting using semiconductive photocatalysts generally includes three stages (Fig. 4): (1) absorption of appropriate sunlight by photocatalyst and photogeneration of electron and hole pairs; (2) migration of photogenerated charge carriers to the catalyst surface; (3) photogenerated carriers undergo a redox reaction with H^+ , OH^- , or H_2O species to produce hydrogen and oxygen gases. As one type of well-defined soluble metal oxides, POMs are also a special type of semiconductor [58,59]. Therefore, POMs could be used as both light-absorbers and catalysts in photocatalytic hydrogen production systems. Upon UV light irradiation, the intramolecular oxygen-to-metal charge-transfer (e.g. $O_{2p} \rightarrow W_{5d}$) happens

Fig. 3. X-ray crystal structures of polyoxometalates in combined ball-and-stick and polyhedral representations. blue: W; green: Nb; yellow: Ta; orange: V; light blue: transition metals; Pink: P; grey: K; Red: O.

Fig. 4. The mechanistic illustration of hydrogen production using semiconductor photocatalyst.

in the POM frameworks, where the electrons from a spin-paired, highest occupied molecular orbital (HOMO) will be promoted to and delocalized over the lowest unoccupied molecular orbital (LUMO). The generated holes in the O_{2p} orbitals are highly oxidizing for organic substrate oxidation (also known as sacrificial reagents) [60,61], finally leading to reduced POMs. Such reduced POMs exhibit a deep blue color with absorption in the range of 600 to 1000 nm due to the broad d-d and intervalence charge transfer absorptions [62–65]. Since the POMs or reduced POMs are highly negatively charged, they can store many protons at the same time. Then, as mentioned above, the reduced POMs can catalyze proton reduction to hydrogen gas, and this process will be greatly speeded up in the presence of noble metal cocatalysts (e.g. Pt). In 1985, Ioannidis *et al.* [66] first reported about 1:12 heteropolytungstates with the Keggin structures $[XW_{12}O_{40}]^{n-}$ ($X=P, Si, Fe, H$) in 0.1 M $HClO_4$ solvent, isopropanol as sacrificial electron donor, Pt as cocatalyst, in UV light achieved hydrogen production.

Hydrogen production studies. The photocatalytic hydrogen evolution studies by POM-based WRCs under UV light irradiation after 1980s have been summarized in Table 1.

Following the early pioneering works, Wang's group has achieved great breakthrough in 2012 [67]. In that work, Pt nanoparticles were used as co-catalysts to promote the photocatalytic H_2 evolution using a series of transition-metal substituted Keggin-type POMs, $K_6SiW_{11}O_{39}M(H_2O) \cdot nH_2O$ $\{MSiW_{11}\}$ ($M = Co, Ni, Cu$ and Zn). While using Zn powder as sacrificial electron donor, the H_2 evolution rates reached 150, 98, 65 and 48 $\mu mol\ g^{-1}\ h^{-1}$ for $SiW_{11}Cu$, $SiW_{11}Ni$, $SiW_{11}Co$ and $SiW_{11}Zn$, respectively. Then, Zhang's group reported the photocatalytic hydrogen evolution using transition-metal substituted Keggin-type titano-tungstates $(Na_{5(6)}[MTiW_{11}O_{39}] \cdot xH_2O)$ ($M = Fe, Co, Zn$, $\{MTiW_{11}\}$) as photocatalyst and polyvinyl alcohol as electron donor [68]. Upon irradiation by simulated solar light, such homogeneous reaction system showed good photocatalytic activity toward H_2 evolution. Fig. 5 shows a schematic diagram of photocatalytic H_2 evolution by $\{MTiW_{11}\}$ under simulated sunlight. Regarding the high activity of this system, the authors claimed an analogous “Z-scheme” mechanism that both pristine $\{MTiW_{11}\}$ complexes and photogenerated HPB are active species towards catalytic hydrogen production, where pristine $\{MTiW_{11}\}$ complexes and photogenerated HPB absorb UV-light (350–400 nm) *via* oxygen to metal charge

Table 1Summary of catalytic H₂ production using POM photocatalysts under UV or near UV light.

Catalyst	Light source	Photosensitizer	Sacrificial agent	Cocatalyst	Activity ($\mu\text{mol h}^{-1} \text{g}^{-1}$)	Ref.
{MSiW ₁₁ } (M=Ni, Cu, Co, Zn)	500 W Xe lamp	None	Zn powder	Pt	150, 98, 65, 48	[67]
{MTiW ₁₁ } (M = Fe, Co, Zn)	simulated solar light (350–760 nm)	None	polyvinyl alcohol	None	500, 484, 294	[68]
{Ta ₁₂ }	(250 W Hg) ultraviolet irradiation	None	CH ₃ OH	Pt	1250	[75]
{Ta ₁₆ }	(250 W Hg) ultraviolet irradiation	None	CH ₃ OH	Pt	803	[75]
{Ta ₁₈ P ₁₂ W ₉₀ }	(500 W Hg) ultraviolet irradiation	None	CH ₃ OH	None	8301.32	[76]
{Yb ₂ Ta ₁₈ P ₁₂ W ₉₀ }	(500 W Hg) ultraviolet irradiation	None	CH ₃ OH	None	6494.4	[76]
{CrTa ₆ Si ₂ W ₁₈ }	(500 W Hg) ultraviolet irradiation	None	CH ₃ OH	None	1001.7	[77]
{FeTa ₆ Si ₂ W ₁₈ }	(300 W Hg) ultraviolet irradiation	None	CH ₃ OH	None	743.8	[77]
{Cr ₃ [Ta ₃ P ₂ W ₁₅] ₂ }	(500 W Xe)	None	CH ₃ OH	H ₂ PtCl ₆	198.3	[78]
{Cr ₄ [Ta ₃ P ₂ W ₁₅] ₄ }	(500 W Xe)	None	CH ₃ OH	H ₂ PtCl ₆	89.2	[78]
{[Nb ₂ O ₂][SiNb ₁₂]}	300 W Xe lamp	None	CH ₃ OH	Pt	2100	[81]
{Nb ₂₄ }	(500 W Hg) ultraviolet irradiation	None	TEOA	Cobaloximes	5193.87	[82]
{Nb ₃₂ }	(500 W Hg) ultraviolet irradiation	None	TEOA	Cobaloximes	5056.43	[82]
{Nb ₉₆ }	(500 W Hg) ultraviolet irradiation	None	TEOA	Cobaloximes	4714.7	[82]
{Nb ₄₈ }	300 W Xe lamp	None	TEA	Cobaloximes	13.9	[83]
{PNb ₁₂ V ₆ -1}	300 W Xe lamp	None	CH ₃ OH	0.75% Pt	10.31	[84]
{PNb ₁₂ V ₆ -2}	300 W Xe lamp	None	CH ₃ OH	0.75% Pt	10.45	[84]
{Nb ₄ O ₆ (SiW ₉ Nb ₃) ₄ }	150 W Hg ultraviolet irradiation	None	CH ₃ OH	Pt	1284.12	[87]
{TeNb ₅ }	300 W Xe lamp	None	CH ₃ OH	Te	776	[88]
{Sn ₄ Si ₂ W ₁₈ }	300 W Xe > 420 nm	None	CH ₃ OH	H ₂ PtCl ₆	4.62	[90]
{Fe ₆ Se ₆ W ₃₄ }	500 W Hg lamp	None	CH ₃ OH	None	1422.5	[91]
{Fe ₁₀ Se ₈ W ₆₂ }	500 W Hg lamp	None	CH ₃ OH	None	900.8	[91]

transfer and visible light (400–760 nm) *via* d–d and/or inter-valence charge transfer band excitation, respectively.

Considering the similarity of the composition and surface structure of POM with metal oxide semiconductors (such as WO₃, MoO₃, TiO₂, Ta₂O₅, Nb₂O₅, etc.), similar electronic and light-absorption characteristics would be expected. Therefore, polyoxoniobates (PONbs) and polyoxotantalates (POTas), as important subjects of POMs, have also attracted increasing attention because of their interesting properties and potential applications in photocatalytic hydrogen production.

Early works have investigated the H₂ evolution activity of tantalum oxides [69–71] and tantalates [72–74]; however, the use of POTas for catalyzed hydrogen production was not reported until 2012. In this work, Li and co-workers reported the use of K₉Na₈H₄[P₈W₆₀Ta₁₂(H₂O)₄(OH)₈O₂₃₆]₄·42H₂O {Ta₁₂}, and Cs_{10.5}K₄H_{5.5}[Ta₄O₆(SiW₉Ta₃O₄₀)₄]₃·30H₂O {Ta₁₆}-substituted heteropolytungstates (Fig. 3(a)) and cocatalyst H₂PtCl₆ to successfully catalyze efficient hydrogen production under the irradiation of a mercury lamp, the proposed mechanism is shown in Fig. 6 [75]. At the same time, the control experiment using K₆[P₂W₁₈O₆₂]₁₄H₂O (abbreviated as {P₂W₁₈}) yields very low hydrogen production activity; in contrast, the H₂ evolution rate of {Ta₁₂}-catalyzed reaction system reaches as high as 1250 $\mu\text{mol g}^{-1} \text{h}^{-1}$. Such significantly enhanced performance of {Ta₁₂} catalyst against the control {P₂W₁₈} catalyst can be ascribed to the modulation of the electronic structures of these POMs through Ta metal incorporation.

Subsequently, Su's group synthesized some Ta/W mixed-addendum POMs, such as Cs₁₆K₁₆Na₄[Ta₁₈P₁₂W₉₀(OH)₆(H₂O)₂O₃₆₀]₂₄H₂O {Ta₁₈P₁₂W₉₀}, Cs₂₆K₂H₂[Yb₂Ta₁₈P₁₂W₉₀(OH)₆(H₂O)₁₆O₃₆₀]₅₂H₂O {Yb₂Ta₁₈P₁₂W₉₀}, Cs₅K₂[(Si₂W₁₈Ta₆O₇₈)Cr(H₂O)₄]₈H₂O {CrTa₆Si₂W₁₈}, and Cs₃K₄H₂[(Si₂W₁₈Ta₆O₇₈)FeCl₂(H₂O)₂]₁₅H₂O {FeTa₆Si₂W₁₈} [76,77]. Figs. 3(b) and 3(c) shows the X-ray crystal structures of {Ta₁₈P₁₂W₉₀} and {CrTa₆Si₂W₁₈}. Photocatalytic experiments revealed that all four compounds exhibited significant photocatalytic water splitting activity under UV light illumination.

Fig. 5. Schematic diagram and time courses of photocatalytic H₂ evolution by {MTiW₁₁} (M = Fe, Co, Zn) under simulated sunlight. Adapted with permission from Ref. [68]. Copyright 2014 Royal Society of Chemistry.

Fig. 6. X-ray crystal structures of {Ta₁₂} and {Ta₁₆} and the schematic mechanism of photocatalytic hydrogen production. Adapted with permission from Ref. [75]. Copyright 2012 American Chemical Society.

tion. In the optimal photocatalytic system, the use of titled four complexes as catalysts and methanol as the sacrificial electron donor could obtain the average hydrogen evolution rates in three circulations of 8301.32, 6494.4, 1001.7, and 743.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. In 2017, the same research group synthesized two nanoscale polytantalotungstates (POTTs), $\text{Cs}_5\text{K}_4\{\text{Cr}_3[\text{Ta}_3\text{P}_2\text{W}_{15}\text{O}_{62}]_2(\text{H}_2\text{O})_{12}\} \cdot 15\text{H}_2\text{O}$ $\{\text{Cr}_3[\text{Ta}_3\text{P}_2\text{W}_{15}]_2\}$, and $\text{Cs}_{8.5}\text{K}_8\text{Na}_2\text{H}_{5.5}\{\text{Cr}_4[\text{Ta}_3\text{P}_2\text{W}_{15}\text{O}_{62}]_4(\text{H}_2\text{O})_{12}\} \cdot 53\text{H}_2\text{O}$ $\{\text{Cr}_4[\text{Ta}_3\text{P}_2\text{W}_{15}]_4\}$ (Fig. 3(d) and 3(e)), under hydrothermal synthetic conditions [78]. In the photocatalytic systems, the compounds $\{\text{Cr}_3[\text{Ta}_3\text{P}_2\text{W}_{15}]_2\}$ and $\{\text{Cr}_4[\text{Ta}_3\text{P}_2\text{W}_{15}]_4\}$ were used as photocatalysts, Pt as H_2 -evolving cocatalyst, and CH_3OH as sacrificial electron donors. Experimental results revealed that POTTs exhibit significant activity towards photocatalytic water splitting, the H_2 evolution rate of $\{\text{Cr}_3[\text{Ta}_3\text{P}_2\text{W}_{15}]_2\}$ and $\{\text{Cr}_4[\text{Ta}_3\text{P}_2\text{W}_{15}]_4\}$ reaches 198.3 h^{-1} and 89.2 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. This work has made great contributions to the exploration of POTTs and their applications in the field of photocatalysis. The discovery of these new POTTs offers new opportunities for designing highly efficient POM-based photocatalysts and enriching the POTTs chemistry.

Similar to POTTs, polyoxoniobates (PONbs) have been also prepared under hydrothermal conditions bearing the properties of narrow reaction pH range and insufficient precursor solubility [79,80]. For a long period of time, the PONbs chemistry is growing relatively very slow, great breakthrough has been achieved since the first discovery of the heteropolyoniobate $\text{K}_{12}[\text{Ti}_2\text{O}_2][\text{SiNb}_{12}\text{O}_{40}] \cdot 16\text{H}_2\text{O}$ $\{\text{Ti}_2\text{O}_2\}[\text{SiNb}_{12}]$ by Nyman *et al.* [59] in 2002, leading to a fast development of this area. In 2011, Feng's group [81] reported the photocatalytic H_2 production activity using heteropolyoxoniobate $\text{K}_{10}[\text{Nb}_2\text{O}_2(\text{H}_2\text{O})_2][\text{SiNb}_{12}\text{O}_{40}] \cdot 12\text{H}_2\text{O}$ (Fig. 3(f), $\{\text{Nb}_2\text{O}_2\}[\text{SiNb}_{12}]$) as photocatalyst and Pt as cocatalyst. Under appropriate conditions, both H_2 and O_2 evolved from catalytic water splitting while using NiO-loaded $\{\text{Nb}_2\text{O}_2\}[\text{SiNb}_{12}]$ as photocatalyst under UV irradiation (Fig. 7), proving the feasibility of using $\{\text{Nb}_2\text{O}_2\}[\text{SiNb}_{12}]$ photocatalyst for photocatalytic overall water-splitting reactions.

Based on above-mentioned works, it is found that the development of photocatalytic hydrogen production using high-nuclear PONbs catalysts still remains largely unexplored. Then, focusing on this topic, Wang's group has made great contributions to the synthesis and photocatalytic studies of high-nuclear PONbs. For instance, Wang's group [82] reported three novel polyoxoniobates, namely $\text{KNa}_2[\text{Nb}_{24}\text{O}_{72}\text{H}_{21}] \cdot 38\text{H}_2\text{O}$ $\{\text{Nb}_{24}\}$, $\text{K}_2\text{Na}_2[\text{Nb}_{32}\text{O}_{96}\text{H}_{28}] \cdot 80\text{H}_2\text{O}$ $\{\text{Nb}_{32}\}$, and $\text{K}_{12}[\text{Nb}_{24}\text{O}_{72}\text{H}_{21}]_4 \cdot 107\text{H}_2\text{O}$ $\{\text{Nb}_{96}\}$ (Figs. 3(g), 3(h), and 3(i))

Fig. 7. Schematic diagram of photocatalytic H_2 and O_2 evolution by photocatalyst $\{\text{Nb}_2\text{O}_2\}[\text{SiNb}_{12}]$ under UV irradiation. Adapted with permission from Ref. [81]. Copyright 2011 American Chemical Society.

bearing triangular, rectangular, and cuboctahedral molecular cage geometries, respectively, these three PONbs were successfully synthesized using conventional aqueous methods. UV-light-driven photocatalytic H_2 evolution was observed for these compounds using noble-metal-free $\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}$ (dmgH = dimethylglyoxime, py = pyridine) as a cocatalyst and triethylamine (TEA) as a sacrificial electron donor. For compounds $\{\text{Nb}_{24}\}$, $\{\text{Nb}_{32}\}$, and $\{\text{Nb}_{96}\}$, the H_2 evolution rates reached 5198.87, 5056.43, and 4714.4 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively. Subsequently, a new dimer polyoxoniobate $[\text{Cu}(\text{en})_2]_{11}\text{K}_4\text{Na}_2[\text{KNb}_{24}\text{O}_{72}\text{H}_9]_2 \cdot 120\text{H}_2\text{O}$ has been synthesized and systematically characterized [83]. Under similar catalytic conditions, $[\text{Cu}(\text{en})_2]_{11}\text{K}_4\text{Na}_2[\text{KNb}_{24}\text{O}_{72}\text{H}_9]_2$ $\{\text{Nb}_{48}\}$ exhibits photocatalytic H_2 evolution activity using $[\text{Co}^{\text{III}}(\text{dmgH})_2\text{pyCl}]$ as co-catalyst and TEA as sacrificial reagent upon irradiation by 500 W Xe lamp with a 400 nm cut-off filter. The H_2 evolution rates in five successive runs reached 14.0, 14.8, 13.6, 13.9 and 13.2 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively. Therein, organic ligand modification has offered PONbs the possibility of catalyzing hydrogen evolution under visible-light irradiation. This work provided some insights for the development of PONbs in the field of visible-light-driven photocatalysis. Afterwards, the group firstly constructed two PONb-based 3D frameworks using hexa-capped Keggin phosphoniobates $[\text{PNb}_{12}\text{O}_{40}(\text{VO})_6]^{3-}$ and copper cations, and investigated their photocatalytic hydrogen evolution activity [84]. Since vanadium cations are alkali-soluble ions and have higher reactivity than niobium, transition metal vanadium is an excellent candidate to construct heteropolyoxoniobate complexes [85,86]. In this work, two 3D heteropolyoxoniobate-based frameworks $[\text{Cu}(\text{en})_2]_4[\text{PNb}_{12}\text{O}_{40}(\text{VO})_6](\text{OH})_5 \cdot 8\text{H}_2\text{O}$ $\{\text{PNb}_{12}\text{V}_6\text{-1}\}$ and $[\text{Cu}(\text{enMe})_2]_4[\text{PNb}_{12}\text{O}_{40}(\text{VO})_6](\text{OH})_5 \cdot 6\text{H}_2\text{O}$ $\{\text{PNb}_{12}\text{V}_6\text{-2}\}$ were obtained by the reaction of $\text{K}_7\text{HNB}_6\text{O}_{19} \cdot 13\text{H}_2\text{O}$, H_3PO_4 and NaVO_3 with the assistance of Cu^{2+} cations under hydrothermal conditions. Single-crystal X-ray diffraction analyses revealed that compounds $\{\text{PNb}_{12}\text{V}_6\text{-1}\}$ and $\{\text{PNb}_{12}\text{V}_6\text{-2}\}$ were isostructural (Fig. 3(j)). The photocatalytic hydrogen evolution activity of these two compounds was investigated using 0.75 wt% Pt as cocatalyst in CH_3OH aqueous solution under 300 W Xe lamp irradiation, and H_2 evolution rates reached 10.31 and 10.45 $\mu\text{mol h}^{-1} \text{g}^{-1}$, respectively. As shown in Fig. 8, the solid-state emission spectra and the XRD patterns of $\{\text{PNb}_{12}\text{V}_6\text{-1}\}$ and $\{\text{PNb}_{12}\text{V}_6\text{-2}\}$ were tested, revealing the structural stability of these photocatalysts after photocatalytic experiments. The discovery of these new type PONbs clusters afford new opportunities for developing PONb chemistry and exploring efficient PONb-based photocatalysts.

Subsequently, Zhao and Su's group [87] synthesized a tetrameric polyoxometalate $\text{Cs}_{19}\text{K}_2[\text{Nb}_4\text{O}_6(\text{SiW}_9\text{Nb}_3\text{O}_{40})_4]\text{Cl} \cdot 27\text{H}_2\text{O}$ $\{\text{Nb}_4\text{O}_6(\text{SiW}_9\text{Nb}_3)_4\}$ (Fig. 3(g)) through the self-assembly of W/Nb mixed-addendum $[\text{SiW}_9(\text{NbO}_2)_3\text{O}_{37}]^{7-}$ under hydrothermal conditions. Complex $\{\text{Nb}_4\text{O}_6(\text{SiW}_9\text{Nb}_3)_4\}$ could be perceived as four $\{\text{SiW}_9\text{O}_{34}\}$ units linked together by a $\{\text{Nb}_{16}\text{O}_{30}\}$ cluster. The photocatalytic activity of complex $\{\text{Nb}_4\text{O}_6(\text{SiW}_9\text{Nb}_3)_4\}$ for H_2 evolution from water was observed under UV irradiation (Fig. 9). The photocatalytic H_2 production experiments of complex $\{\text{Nb}_4\text{O}_6(\text{SiW}_9\text{Nb}_3)_4\}$ were conducted

Fig. 8. The solid-state emission spectra of {PNb₁₂V₆-1} (a) and {PNb₁₂V₆-2} (b) at room temperature; the experimental (red) and simulated (black) PXRD patterns of {PNb₁₂V₆-1} (c) and {PNb₁₂V₆-2} (d); XRD patterns of photocatalysts {PNb₁₂V₆-1} (c) and {PNb₁₂V₆-2} (d) after photocatalytic water splitting reaction under 125 W Hg lamp (green) and 300 W Xe lamp (blue) irradiation. Adapted with permission from Ref. [84]. Copyright 2014 Royal Society of Chemistry.

in a sealed circulation system using methanol as a sacrificial electron donor and H₂PtCl₆ as cocatalyst, obtaining the H₂ evolution rates in three runs of 1389.54, 1313.08, and 1151.84 μmol h⁻¹ g⁻¹, respectively.

As another important POM type, the Lindqvist {Nb₆} has been well known for a long time; however, its application to the field of photocatalytic hydrogen production is rarely reported. In 2014, a new tellurium-substituted Lindqvist-type polyoxoniobate TMA₅[H₂TeNb₅O₁₉]₂·20H₂O {TeNb₅} was synthesized as a tetramethylammonium salt by Son and co-workers [88]. Upon irradiation with a Xe lamp, mixed water-methanol solution containing {TeNb₅} cluster showed exceptionally high H₂-production activity at a rate of 776 μmol h⁻¹ g⁻¹, which is 70 times higher than that of {Nb₆} (11 μmol h⁻¹ g⁻¹). Experimental results proved that the TMA salt of the {TeNb₅} cluster reported herein exhibits a similar pH stability range and solid-state structure comparing to complex {Nb₆}; however, complex {TeNb₅} demonstrated much higher H₂-evolution activity *via* a photo-decomposition route to form {Nb₆} and Te⁰ nanowires as more active species. In the same year, the research group also reported synthesis and characterization of tetramethylammonium (TMA) salts of Cr-, Mn- and Co-substituted decaniobates, TMA₆[H₂Cr^{III}Nb₉O₂₈]₂·14H₂O {CrNb₉}, TMA₈[Mn^{III}Nb₉O₂₈]₂·29H₂O {MnNb₉}, and TMA₇[H₂Co^{III}Nb₉O₂₈]₂·25H₂O {CoNb₉} [89]. Among the TM-substituted decaniobates, {CoNb₉} and {NiNb₉} exhibited a higher photocatalytic H₂ evolution activity in methanol-water mixtures than that of others (Fig. 10).

Fig. 9. X-ray crystal structure of {Nb₄O₆(SiW₉Nb₃)₄} and the schematic mechanism of photocatalytic hydrogen production. Adapted with permission from Ref. [87]. Copyright 2014 Elsevier.

In addition to those above-mentioned works, some other type transition-metal-containing POMs were also studied as catalysts in photocatalytic hydrogen evolution reactions. For example, Feng's group [90] reported a Tin(II)-containing tungstosilicate derivative, K₁₁H[Sn₄(SiW₉O₃₄)₂]₂·25H₂O {Sn₄Si₂W₁₈}, with four Sn²⁺ cations sandwiched by two [SiW₉O₃₄] POM ligands. Visible-light photocatalytic H₂ evolution activity was achieved using Pt nanoparticles as cocatalyst and methanol as sacrificial agent under a 300 W Xe lamp (400 nm cut-off filter). The H₂ evolution rates in five successive runs were 4.2, 4.9, 4.1, 4.8, and 5.1 μmol h⁻¹ g⁻¹, respectively. This work provides a new research platform using main-group metal-containing POMs in photocatalysis.

Later on, Wang's group [91] reported two Fe-substituted Dawson-type nanoscale selenotungstates clusters, (C₂H₈N)₄Na₁₄[Fe₆Se₆W₃₄O₁₂₄(OH)₁₆]₂·44H₂O {Fe₆Se₆W₃₄} and (NH₄)₉Na₁₉[Fe₁₀Se₈W₆₂O₂₂₂(OH)₁₈(H₂O)₄]₂·42H₂O {Fe₁₀Se₈W₆₂} (Fig. 11), which exhibited high photocatalytic H₂ evolution activity. Herein, using CH₃OH as sacrificial electron donor and the source of the electrons, the H₂ evolution rates in three runs reached 1447.5, 1445.0 and 1375.0 μmol h⁻¹ g⁻¹ for catalyst {Fe₆Se₆W₃₄} and 925.0, 897.5 and 880.0 μmol h⁻¹ g⁻¹ for catalyst {Fe₁₀Se₈W₆₂}, respectively.

Simultaneously, a tetranuclear cerium-containing polyoxometalate, TBA₆[{Ce(H₂O)}₂{Ce(CH₃CN)}₂(μ₄-O)(γ-SiW₁₀O₃₆)₂], was reported by Mizuno's group [92] in 2014, this complex exhibited an unique intramolecular multiple electron transfer (Ce³⁺-to-POM(W⁶⁺)) upon irradiation by visible light (λ > 400 nm). Catalytic hydrogen evolution proceeded under visible light irradiation (λ > 400 nm) in the presence of H₂[PtCl₆] as the cocatalyst, 4-methoxybenzyl alcohol as the electron donor, and *N,N'*-dimethylacetamide as the reaction solvent. Under experimental conditions, the total amount of hydrogen produced after 10 h reached 249 μmol, corresponding to a TON of 249. This works provided the possibility of using metal-to-POM charge transfer to drive photocatalytic reactions.

Possible catalytic mechanism. It is known that most of POMs absorb strongly in the UV light region *via* ligand-to-metal charge transfer (O_{2p} to POM (W⁶⁺, Mo⁶⁺, etc.)). In these

Fig. 10. Polyhedral model of {CrNb₉}, {MnNb₉}, and {CoNb₉} clusters, and H₂-evolution upon Xe-lamp irradiation of 0.2 g of TM-substituted decaniobate TMA salts in 50 mL MeOH-H₂O solution (20% v/v). Adapted with permission from Ref. [89]. Copyright 2014 Royal Society of Chemistry.

Fig. 11. Polyhedral model of $\{\text{Fe}_6\text{Se}_6\text{W}_{34}\}$, $\{\text{Fe}_{10}\text{Se}_8\text{W}_{62}\}$ clusters, and the time course of H_2 evolution from 100 mg of photocatalysts (a) $\{\text{Se}_4\text{W}_{36}\}$, (b) $\{\text{Fe}_6\text{Se}_6\text{W}_{34}\}$, and (c) $\{\text{Fe}_{10}\text{Se}_8\text{W}_{62}\}$ under 500 W mercury lamp irradiation in methanol/ H_2O (1/5, v/v). Adapted with permission from Ref. [91]. Copyright 2014 Royal Society of Chemistry.

above-mentioned studies, POM-based complexes were used directly as photosensitizers to absorb UV light to further drive photocatalytic hydrogen production reactions. Upon UV light irradiation, POMs will be photoexcited to the excited states that could be further quenched by sacrificial electron donors (such as CH_3OH , triethanolamine and triethylamine) leading to the formation of reduced POMs (HPB). In these reactions, noble metal cocatalyst (e.g. Pt) will be frequently used to decrease the overpotential for H^+ reduction to H_2 gas (Scheme 2). In some cases, the cocatalyst is not required where POMs play the dual roles of photosensitizer and catalyst at the same time. For example, Su's group synthesized $\{\text{Ta}_{18}\text{P}_{12}\text{W}_{90}\}$ and $\{\text{Yb}_2\text{Ta}_{18}\text{P}_{12}\text{W}_{90}\}$ and adjusted the electronic structures of these complexes by using different transition metal ions in the substitution. The connection of some H_2O ligands and $\mu_2\text{-OH}$ to the Ta atoms of $\{\text{Ta}_{18}\text{P}_{12}\text{W}_{90}\}$ cluster could enhance the transportation of charge carriers and the subsequent proton reduction to H_2 [76].

The other proposed mechanism mentioned in above works

Scheme 2. Schematic diagram of photocatalytic H_2 evolution using POM-based photocatalyst under UV-light irradiation.

belongs to a “Z scheme” mechanism that is often used in heterojunction nanostructured photocatalysts for photocatalytic H_2 evolution (Scheme 3) [93]. In this case, the pristine POM-based photocatalysts are firstly excited under UV light (350–400 nm) to produce “heteropoly blue (HPB)” in the presence of sacrificial organic substrates as electron donors. The resulting HPB species absorb strongly in the visible light region (400–760 nm) through d-d and/or intervalence charge-transfer band excitation to further drive H^+ reduction to H_2 , thereby leading to better hydrogen production activity [68].

2.2. Visible-light-driven catalytic H_2 evolution by POM-based catalysts

In the previous section, the photocatalytic hydrogen evolution studies were usually conducted by directly photoexciting POM-based photocatalysts with UV light and at the same time noble metal cocatalyst (usually Pt or H_2PtCl_6) will be used to facilitate the proton reduction. Therein, there are two obvious disadvantages in this system: (1) the scarcity and high cost of

Scheme 3. Schematic “Z scheme” mechanism of photocatalytic H_2 evolution using POM-based photocatalysts under simulated solar light irradiation. D means electron donor.

Table 2

Overview of POM-catalyzed water reduction reactions under visible light.

Catalyst	Photosensitizer	Sacrificial agent	Co-catalyst	TON/TOF (s ⁻¹)	Time (h)	Ref.
{ AlSiW ₁₁ }	Eosin Y	TEOA	Pt	12.5/7	20	[94]
{ CoCoW ₁₁ }	Eosin Y	TEOA	Pt	100/7×10 ⁻⁶	2.3	[95]
{ Ds[Ir] }	None	NEt ₃	None	41/69.4×10 ⁻⁶	168	[96]
{ Mn₄V ₂ }	[Ru(bpy) ₃] ²⁺	TEOA	None	42/—	5.5	[46]
{ Ni₄P ₂ }	[Ir(ppy) ₂ (dtbbpy)] ⁺	TEOA	None	290/—	2.5	[47]
{ Ni₁₆As₄P ₄ }	[Ir(ppy) ₂ (dtbbpy)] ⁺	TEOA	None	360/—	5	[48]
{ Cu₄P ₂ }	[Ir(ppy) ₂ (dtbbpy)] ⁺	TEOA	None	1270/—	5	[49]
{ Co₆P ₃ }	Eosin Y	TEOA	None	—	—	[97]
{ NiGeW ₁₁ }	[Ru(bpy) ₃] ²⁺	Ascorbic acid	None	36.8/9×10 ⁻³	15	[98]
{ [Ni₁₆(B-PW₉O₃₄)₄] }	[Ir(ppy) ₂ (dtbbpy)] ⁺	TEOA	None	931.1/—	12	[99]
{ Ni₁₄SiW ₉ }	[Ir(ppy) ₂ (dtbbpy)] ⁺	TEOA	None	256/2.7×10 ⁻²	4	[100]
{ Cu₅Si ₂ }	[Ir(ppy) ₂ (dtbbpy)] ⁺	TEOA	None	718.9/134.8	6	[101]
{ P₂W₁₈@UiO (Ru-derived) }	None	TEOA	None	79/—	14	[109]
{ Ni₄P₂@MOF-1 (Ir derived-UiO) }	None	CH ₃ OH	None	1476/—	72	[110]
{ WD-POM@SMOF-1 }	[Ru(bpy) ₃] ²⁺	TEOA	None	392/—	12	[111]
{ P₂W₁₅V₃@MIL-101 }	[Ru(bpy) ₃] ²⁺	TEOA	None	56/—	8	[112]
{ Cu₂₄-Based POM@ZZULI-1 }	Fluorescein	TEOA	None	—	—	[113]
{ Ta₆-3/CZS }	None	S ²⁻ /SO ₃ ²⁻	None	—	—	[121]

using noble metal cocatalyst could greatly limit their large-scale applications; (2) the direct photoexcitation of POMs with UV light leads to very low efficiency of solar energy utilization due to the mismatch of UV light with solar spectrum. In this context, the development of Pt-free photocatalytic systems using visible-light-responsive photosensitizers has been attracting tremendous research interests in recent years. Table 2 summarizes an overview of photocatalytic hydrogen evolution systems using POM-based catalysts and visible light irradiation, which can be classified as three categories according to the type of light-absorbers using the system, namely molecular photosensitizer, light-responsive metal-organic-frameworks (MOFs), and the semiconductive nanocrystals.

2.2.1. Photocatalysis using molecular photosensitizers

Hydrogen production studies. In 2012, Li's group [94] reported the first study of dye-sensitized POM for the visible-light hydrogen evolution. In this work, Eosin Y (EY)-sensitized α -[AlSiW₁₁(H₂O)₃₉]⁵⁻ {**AlSiW**₁₁} (Fig. 3(k)) was used for photocatalytic hydrogen production under visible light in the presence of TEOA as electron donor and Pt as cocatalyst. A TON of 473 was achieved under the optimal reaction conditions. Later on, Ding's group [95] reported the synthesis of a molecular Keggin polyoxometalate catalyst K₇[Co^{III}Co^{II}(H₂O)W₁₁O₃₉] {**CoCoW**₁₁} and its application to catalyze hydrogen evolution. The photocatalytic activity of catalyst {**CoCoW**₁₁} was evaluated under visible light irradiation using TEOA, EY, and Pt as sacrificial donor, photosensitizer and co-catalyst, respectively. The schematic illustration of the proposed photocatalytic mechanism is shown in Fig. 12. This catalytic system showed a remarkable activity at a hydrogen production rate of 13395 $\mu\text{mol h}^{-1} \text{g}^{-1}$, belonging to the highest value at that time. However, both two studies have used noble metal Pt as cocatalyst, although the presence of Eosin Y photosensitizer has moved the light absorption to visible light region.

The first example of Pt-free photocatalytic system using POM catalyst was reported by Matt and co-workers [96]. In this work, a covalently linked Ir(III)-photosensitized POM dyad ({**Ds[Ir]**}) was isolated as a tetrabutylammonium salt, which contains two heteroleptic cyclometalated iridium(III) units anchored to the mono-lacunary site of the Dawson-type α_2 -[P₂W₁₇O₆₁]¹⁰⁻ through a Si–O–Si linkage (Fig. 13). This work provided the best compromise between efficient charge separation and long-life charge separation states. In the presence of TEA as sacrificial electron donor, a very efficient photoreduction of the POM unit was achieved to further catalyze H₂ production with a TON of 41 after 7 d of visible light irradiation.

In the process of improving the photocatalytic efficiency, Hill's group reported a series of TMSPOMs catalysts for efficient photocatalytic hydrogen evolution. The first example reported a tetramanganese-containing POM, [Mn₄(H₂O)₂(VW₉O₃₄)₂]¹⁰⁻ {**Mn₄V**₂} (Fig. 3(l)), that catalyzes hydrogen evolution from water obtaining a TON of 42 after 5.5 h visible light irradiation [46]. Although the efficiency of this system is higher than that of the {**Ds[Ir]**} dyad system, there is still large room for improvement. Following above work, a tetranickel-containing polyoxotungstate, Na₆K₄[Ni₄(H₂O)₂(PW₉O₃₄)₂·32H₂O] {**Ni₄P**₂} (Fig. 3(l)), has been synthesized in high yield and systematically characterized [47]. The visible-light-driven catalytic activity of

Fig. 12. Schematic illustration of photocatalytic hydrogen evolution by catalyst K₇[Co^{III}Co^{II}(H₂O)W₁₁O₃₉]. Adapted with permission from Ref. [95]. Copyright 2014 Elsevier.

Fig. 13. Molecular representation of different $\{Dsi[Ir]\}$ dyads described in this study. Color code: WO_6 octahedra, blue; PO_4 tetrahedra, green. Adapted with permission from Ref. [96]. Copyright 2013 Royal Society of Chemistry.

$\{Ni_4P_2\}$ was carried out by using $[Ir(ppy)_2(dtbbpy)]^+$ (4,4'-di-tert-butyl-2,2'-dipyridyl)-bis(2-phenylpyridine(1*H*))-iridium(III)) as photosensitizer, TEOA as sacrificial electron donor, and $\{Ni_4P_2\}$ as catalyst. Under minimally optimized conditions, catalyst $\{Ni_4P_2\}$ catalyzes H_2 production over 1 week without obvious loss of activity, achieving a TON of as high as 6500 (Fig. 14). Then, a new polyoxometalate structural family $[Ni_4(OH)_3AsO_4]_4(B-\alpha-PW_9O_{34})_4]^{28-}$ ($\{Ni_{16}As_4P_4\}$, Fig. 3(o)) was reported for catalytic hydrogen evolution in 2015 [48]. When coupling TEA as sacrificial electron donor and $[Ir(ppy)_2(dtbbpy)]^+$ as photosensitizer, the highest TON of $\{Ni_{16}As_4P_4\}$ reached approximately 580, corresponding to a quantum yield of approximate 4.07%, after 5 h visible light irradiation. In 2016, this group [49] further reported a Cu-based polyoxometalate catalyst for efficient catalytic hydrogen production, where tetra-copper-containing polyoxotungstate, $Na_3K_7[Cu_4(H_2O)_2(B-\alpha-PW_9O_{34})_2] \cdot 30H_2O$ ($\{Cu_4P_2\}$) was synthesized and used as a water-compatible catalyst for efficient hydrogen evolution in the presence of $[Ir(ppy)_2(dtbbpy)]^+$ photosensitizer and TEOA under visible light irradiation. Under minimally optimized conditions, a TON of 1270 per $\{Cu_4P_2\}$ catalyst was achieved after 5 h irradiation. Hill group has conducted extensive research in the field of photocatalytic hydrogen production using POMs catalysts containing Mn, Ni, and Cu transition metals ranging from catalyst design, photosensitizer selection to mechanistic studies [46–49]. These pioneering works have provided insightful guidelines for the subsequent work of exploring efficient photocatalytic systems using noble-metal-free POM catalysts and visible-light-responsive photosensitizers.

Fig. 14. (a) Proposed mechanism for visible-light-driven hydrogen evolution catalyzed by catalyst $\{Ni_4P_2\}$; (b) Long-term photocatalytic H_2 evolution using $\{Ni_4P_2\}$ catalyst. Adapted with permission from Ref. [47]. Copyright 2014 American Chemical Society.

In recent years, more works have been reported by combining POMs catalyst and molecular photosensitizers for photocatalytic hydrogen production. For example, Lu and co-workers [97] synthesized a cobalt-based polyoxometalate, $Na_7H_{10}[Co_6(H_2O)_2(PW_9O_{34})_2(PW_6O_{26})] \cdot 30H_2O$ (Fig. 3(m), $\{Co_6P_3\}$), and used it as catalyst to drive visible-light-driven H_2 evolution using Eosin Y as photosensitizer and TEOA as electron donor. The initial rate of the H_2 evolution reached $141 \mu mol h^{-1}$, which was higher than that of Co^{2+} -catalyzed system of $55 \mu mol h^{-1}$. In 2015, Patzke's group [98] reported the nickel-substituted Keggin-type POMs, $[Ni(H_2O)PW_{11}O_{39}]^{5-}$ ($\{NiPW_{11}\}$), $[Ni(H_2O)GeW_{11}O_{39}]^{6-}$ ($\{NiGeW_{11}\}$), and $[Ni(H_2O)SiW_{11}O_{39}]^{6-}$ ($\{NiSiW_{11}\}$), and investigated their water reduction activity with $[Ru(bpy)_3]^{2+}$ as a photosensitizer in aqueous media, where complex $\{NiGeW_{11}\}$ displayed the highest TON of 37.1 ± 0.4 among all three catalysts. Then, by artificially mimicking the natural $[FeFe]$ -hydrogenases, a series of high-nuclearity Ni-containing polyoxometalate clusters with varying numbers of $\{Ni_4O_4\}$ cubane core (Fig. 15), $K_{1.5}Na_{26.5}[(Ni_4(OH)_3(PO_4))_4(A-PW_9O_{34})_4] \cdot 62H_2O$ ($\{Ni_{16}(A-PW_9O_{34})_4\}$), $Na_{28}[(Ni_4(OH)_3(PO_4))_4(A-PW_9O_{34})_2(B-PW_9O_{34})_2] \cdot 102H_2O$ ($\{Ni_{16}(A-PW_9O_{34})_2(B-PW_9O_{34})_2\}$), and $Na_{28}[(Ni_4(OH)_3(VO_4))_4(B-PW_9O_{34})_4] \cdot 74H_2O$ ($\{Ni_{16}(B-PW_9O_{34})_4\}$), were synthesized by Wang's group [99] and used as homogeneous catalysts in a $[Ir(ppy)_2(dtbbpy)]^+$ /visible-light illumination/TEOA system. All three complexes showed high photocatalytic performance with TONs of 578.8, 679.1, and 931.1, respectively, and the catalytic performance was proportional to the increasing number of $\{Ni_4O_4\}$ cubanes. This study demonstrated the optimal transition metal in the cubane core and revealed the relationship between the numbers of cubane core and catalytic performance. Then, the Mialane's group reported an unprecedented and stable POM $\{Ni_{14}SiW_9\}$, which is composed of nickel clusters stabilized by $\{SiW_9\}$ units with tetradecyl binuclear bisphosphonate capping ligand [100]. This stable compound exhibits a high photocatalytic activity for hydrogen evolution under visible light irradiation, obtaining the highest TON value of 256 after 4 h photocatalysis. The organic/inorganic hybrid nature of this POM provides new opportunity to the elaboration of a rich family of TMSPOMs derivatives.

Very recently, to promote the development of Cu-based molecular catalysts for energy conversion, Ding's group [101] reported an earth-abundant Cu-containing POM cluster,

Fig. 15. X-ray crystal structures of $\{Ni_{16}(A-PW_9O_{34})_4\}$, $\{Ni_{16}(A-PW_9O_{34})_2(B-PW_9O_{34})_2\}$, and $\{Ni_{16}(B-PW_9O_{34})_4\}$, and the schematic diagram of photocatalytic hydrogen production. Adapted with permission from Ref. [99]. Copyright 2017 Elsevier.

Fig. 16. (a) Polyhedral and ball-and-stick representation of the structure of compound $\{Cu_5Si_2\}$ and $\{Ni_5Si_2\}$; (b) Visible light-driven HER kinetics of different control experiments. Adapted with permission from Ref. [101]. Copyright 2020 Royal Society of Chemistry.

$[Cu_5(OH)_4(H_2O)_2(A-\alpha-SiW_9O_{33})_2]^{10-}$, (Fig. 3(n), $\{Cu_5Si_2\}$) for visible-light-driven H_2 evolution in a system containing $[Ir(ppy)_2(dtbbpy)]^+[PF_6]^-$ and TEOA under white LED light irradiation. A TON of 718.9 was achieved in the photocatalytic reaction, which is superior to its isostructural analogue of Ni-containing POM (Fig. 16).

Proposed catalytic mechanism. In these above-reported studies, the catalytic mechanism of reaction systems using Pt as cocatalyst could be proposed as shown in Scheme 4 [94,95]. Upon visible light irradiation, photosensitizer EY is excited by absorbing light energy to generate photoexcited state, which will further be oxidatively quenched by POM catalyst to produce reduced POM $^-$. Then, the generated EY $^+$ can be recovered to ground state EY by obtaining electrons from TEOA sacrificial electron donor. And the Pt nanoparticles could be generated through reduction of $PtCl_6^{2-}$ by reduced POM $^-$ following the equation of $4POM^- + [PtCl_6]^{2-} \rightarrow 4POM + Pt + 6Cl^-$, which further works as hydrogen-evolving center to reduce H^+ to H_2 gas.

In another scenario of Pt-free catalytic systems, transition-metal-containing POMs worked as both electron storage sponge and catalytic active site for H_2 evolution. After excitation of the photosensitizer, there are two possible pathways to quench the excited state photosensitizer: (1) only oxidative quenching by POM catalysts, (2) both oxidative quenching by POM catalysts and reductively quenching by sacrificial electron donor. As shown in Scheme 5, when using $[Ru(bpy)_3]^{2+}$ as photosensitizer and TEOA as electron donor, the catalytic system only undergo oxidative quenching of the excited state $[Ru(bpy)_3]^{2+*}$ by POM. The resulting $[Ru(bpy)_3]^{3+}$ is rapidly reduced back to $[Ru(bpy)_3]^{2+}$ by TEOA [46]. In the other case of using $[Ir(ppy)_2(dtbbpy)]^+$ as photosensitizer and TEA/TEOA as electron donor, the excited state $[Ir(ppy)_2(dtbbpy)]^{+*}$ can be

Scheme 4. Schematic illustration of photocatalytic hydrogen evolution by EY-sensitized POM.

Scheme 5. Schematic illustration of visible-light-induced H_2 evolution using $[Ru(bpy)_3]^{2+}$ photosensitizer and POM catalyst.

either oxidatively quenched by POM catalysts or reductively quenched by TEA/TEOA to generate reduced POM or one-electron-reduced $[Ir(ppy)_2(dtbbpy)]^-$ (Fig. 14). In both quenching pathways, the final reduced POM will react with proton to produce H_2 gas [47–49].

2.2.2. Catalytic H_2 production by photosensitizing POM@MOF composites

POM@MOF composites belong to a new type of multifunctional materials with great potential in solar energy conversion. Such composite integrates both the excellent physicochemical properties of POMs and the structural diversity and adjustability of MOFs [102]. On one hand, some modified MOFs can strongly absorb visible light and exhibit semiconductive property which can be coupled with external catalysts to drive catalytic renewable energy utilization (e.g. water splitting, CO_2 reduction, etc.). On the other hand, encapsulation of POMs into the pores of MOFs will not only facilitate the recyclability and dispersity of POM catalysts, but also promote the charge separation and transportation of photogenerated electrons and holes upon light excitation of MOFs [103–106].

In this context, Hill's group [107] reported a hybrid material through self-assembly of Keggin-type POM ($\{PW_{12}\}$), Pt nanoparticles (NPs), and NH_2 -MIL-53 MOF in 2016, such hybrid material exhibits synergistic activity for visible-light-driven catalytic hydrogen evolution. And, this approach greatly increased photocatalytic H_2 evolution relative to that of each separate component alone. The $\{PW_{12}\}$ POM has four targeted functions in such hybrid material including the reduction of H_2PtCl_6 to Pt NPs, stabilization of the Pt NPs, enhancement of the electrostatic association of the negatively charged Pt NPs with the protonated NH_2 -MIL-53 sites, and the facilitation of catalytic reduction reaction. In the same year, Wang's group studied the photocatalytic hydrogen production performance of POM-based framework material $(TBA)_2[Cu^{II}(BBTZ)_2(x-Mo_8O_{26})]$ ($x = \beta$ for 1, $x = \alpha$ for 2 and 3, Fig. 17) under UV excitation, exhibiting an average hydrogen production rate of $0.78 \mu mol h^{-1}$. The blank control experiments and the use of $(TBA)_4(Mo_8O_{26})$ alone as a catalyst do not produce hydrogen gas, proving the catalytic activity of the synthesized POMs@MOFs materials for hydrogen production [108].

Later on, Lin's group [109] developed a method to encapsulate a Dawson-type POM ($\{P_2W_{18}\}$) into a porous and phosphorescent MOF constructed from $[Ru(bpy)_3]^{2+}$ -derived dicarbox-

Fig. 17. (a) A ball-and-stick representation of **1**, highlighting the three directional channels in the 3D framework. The three different colored tubes represent the different channels in **1**. (b) A topological representation of **2**. The channels within which are shown in blue tubes. (c) Channel and ball-and-stick representations of **3**. In the pictures, the polyanions are shown in sticks. Adapted with permission from Ref. [108]. Copyright 2012 Wiley.

ylate ligands and $\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ secondary building units (Fig. 18). In this work, hierarchical organization of photosensitizing and catalytic components in such POM@MOF assembly promotes fast multielectron injection from the photoactive framework to the encapsulated redox-active POMs upon illumination, finally leading to an efficient visible-light-driven hydrogen production. The TON of this system for hydrogen production reached 307 after 14 h illumination when coupling with TEOA as the sacrificial electron donor in mixed DMF/ CH_3CN solution. The synthetic strategy presented in this work is highly tunable for the future design of multifunctional MOF materials for other applications.

Considering the relative low TONs obtained using sole Dawson type POM, the same group further reported the design of a highly efficient photocatalytic HER system by encapsulating Ni-containing POM $[\text{Ni}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ $\{\text{Ni}_4\text{P}_2\}$ into two highly stable and porous phosphorescent MOFs (Fig. 19) in 2016 [110]. The close interaction between Ni_4P_2 and photosensitizers in such Ni_4P_2 @MOF composite benefits to facile multi-electron transfer to enable efficient visible-light-driven hydrogen evolution reaction with TON as high as 1476. After-

Fig. 18. One-pot synthesis of the POM@UiO system via charge assisted self-assembly. $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$, purple polyhedra; Zr, cyan; Ru, gold; N, blue; O, red; C, light gray. Adapted with permission from Ref. [109]. Copyright 2015 American Chemical Society.

Fig. 19. Structural model of Ni_4P_2 @MOF and the schematic diagram of photocatalytic hydrogen production. Adapted with permission from Ref [110]. Copyright 2016 Wiley.

wards, Tian and co-workers reported the construction of WD-POM@SMOF-1 hybrid assemblies by using cationic SMOF-1 to adsorb anionic Wells-Dawson-type polyoxometalates (WD-POMs) [111]. Upon visible-light illumination, such hybrids enable effective multi-electron injection from the light-absorbing $[\text{Ru}(\text{bpy})_3]^{2+}$ units to the redox-active WD-POM units, leading to efficient hydrogen production in both aqueous and organic media. Using TEOA as the sacrificial electron donor, the TON of this catalytic system could reach 1820 after 14 h irradiation. Such strategy provides new avenues for the development of other types of liquid-phase and solid-phase ordered porous materials.

Very recently, Zhang *et al.* further reported a series of POM@MOF composite materials by immobilizing several transition metal-substituted Wells-Dawson-type polyoxometalates $[\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}]^{9-}$ $\{\text{P}_2\text{W}_{15}\text{V}_3\}$, $[\text{P}_2\text{W}_{17}(\text{NiOH}_2)\text{O}_{61}]^{8-}$ $\{\text{P}_2\text{W}_{17}\text{Ni}\}$, $[\text{P}_2\text{W}_{17}(\text{CoOH}_2)\text{O}_{61}]^{8-}$ $\{\text{P}_2\text{W}_{17}\text{Co}\}$ into a Cr-MOF of the MIL-101 structure. The resulting composite materials all catalyzed visible-light-driven water reduction reaction with the TONs of these three catalytic systems reaching 56, 50, and 49, respectively after 8 h irradiation [112]. Up to now, although POM@MOF composites were extensively used for photocatalytic hydrogen production, there is only one reported POM@MOF photocatalytic system that could promote either water reduction or water oxidation in different catalytic systems. Shi *et al.* [113] reported a high-nuclear $\{\text{Cu}^{124}(\mu_3\text{-Cl})_8(\mu_4\text{-Cl})_6\}$ -based POM@MOF, which is rationally designed to work as a robust dual-functional photocatalyst (Scheme 6). The authors claimed that the mixed Keggin- and Lindqvist-type POMs may serve as oxidizing catalysts to produce O_2 , whereas the $\{\text{Cu}^{124}(\mu_3\text{-Cl})_8(\mu_4\text{-Cl})_6\}$ clusters of the cationic framework can work as photoelectron generators to produce hydrogen. While using TEOA as sacrificial electron donor and fluorescein as the photosensitizer, the reported POM@MOF composite could catalytic hydrogen production in the mixed solvents of $\text{H}_2\text{O}/\text{CH}_3\text{CH}_2\text{OH}$ with the H_2 evolution rate reaching $6614 \mu\text{mol h}^{-1} \text{g}^{-1}$, providing new possibility for the development of cost-effective high-nuclear cluster-based POM@MOFs in solar-to-fuel conversion area.

General catalytic mechanism. The general photocatalytic mechanism of these above-mentioned POM@MOF-based cata-

Scheme 6. Dual-functionalized mixed Keggin- and Lindqvist-type $\{Cu_{124}(\mu_3-Cl)_8(\mu_4-Cl)_6\}$ -based POM@ MOFs as photocatalysts for both H_2 and O_2 evolution. Adapted with permission from Ref. [113]. Copyright 2019 American Chemical Society.

lytic system could be summarized as shown in Scheme 7. Herein, taking $[Ir(ppy)_2(bpy)]^+$ -derived MOFs as an example, the photosensitizing unit of $[Ir(ppy)_2(bpy)]^+$ in the MOF structures will be photoexcited to the $[Ir(ppy)_2(bpy)]^{*+}$ excited state under visible light irradiation. Such excited-state $[Ir(ppy)_2(bpy)]^{*+}$ further transfers electron to the POM, forming reduced POM and oxidized $[Ir(ppy)_2(bpy)]^{2+}$. After receiving successive electrons during this process, the highly reduced POM will reduce proton to generate H_2 . In the meanwhile, the $[Ir(ppy)_2(bpy)]^{2+}$ species can be reduced back to the ground state $[Ir(ppy)_2(bpy)]^+$ by receiving electron from the sacrificial donor to complete the catalytic cycle [110].

2.2.3. Catalytic H_2 production by POM-semiconductor hybrids

In the previous section of using POM@MOF composites for photocatalytic hydrogen production, the organometallic photosensitizers containing precious metals (such as $[Ir(ppy)_2(dtbbpy)]^+$, $[Ru(bpy)_3]^{2+}$, and their derivatives) were usually used to harvest light energy. However, these types of photosensitizers have the obvious disadvantages of high cost and poor photostability towards degradation or ligand dissociation during the photocatalytic reaction, finally leading to the termination of the reaction as well as low TONs or TOF. Therefore, reasonable development of new type visible-light-responsive photosensitizers with low cost, high stability, and high tunability remains a big challenge in solar energy conversion area.

Comparing to traditional organometallic or pure organic

Scheme 7. Proposed catalytic cycle for visible-light-driven hydrogen evolution catalyzed by POM@MOF composites.

molecular photosensitizers, colloidal semiconductor nanocrystals materials have received extensive attention in recent years for solar energy harvesting. Due to the quantum confinement effect, the electronic properties (e.g. light absorption, redox potential, charge separation or recombination, etc.) of these materials can be precisely adjusted by controlling their particle sizes. More importantly, the semiconductor nanocrystals-based photosensitizers usually exhibit ultrahigh photostability and wide visible light absorption property. As one of the widely studied semiconductor nanocrystals, cadmium sulfide quantum dots (CdS QDs) have attracted broad and interdisciplinary attention given their excellent light absorption properties and suitable band gap (2.3 eV) alignment with H_2O/H_2 redox potentials [113–119]. In 2013, Zhang's group [120] successfully prepared the molecular self-assembled CdS QDs-POM-Au nanohybrids. Interestingly, the prepared tricomponent nanohybrids exhibited both photocatalytic activity for hydrogen evolution through water splitting and degradation of organic dyes by visible light irradiation. Then, Zhou *et al.* [121] demonstrated the combination of polyoxotantalates with metal sulfides to form binary composite photocatalysts $Na_8Ta_6O_{19}/Cd_{0.7}Zn_{0.3}S$ {**Ta₆/CZS**} for catalyzing efficient water splitting under visible light (Fig. 20). The $Na_8Ta_6O_{19}/Cd_xZn_{(1-x)}S$ composite worked for catalytic hydrogen production in the absence of cocatalyst with the maximum H_2 -evolution rate of $43050 \mu mol h^{-1} g^{-1}$ (based on 10 mg catalyst). The work provided new strategy to develop highly efficient photocatalyst composite for the sustainable utilization of solar energy by combining POM chemistry with semiconductor nanomaterials.

As another widely studied semiconductor photocatalyst, TiO_2 has been extensively used in the field of photocatalysis, but the rapid recombination of photogenerated charge carriers and the mismatch of its light absorption with solar spectrum greatly remain the major disadvantages of this material [122–132]. With respect to the combination of TiO_2 with POMs, Gao *et al.* [133] very recently designed a Pt-substituted polyoxometalate, $[(CH_3)_4N]_3[PW_{11}O_{39}\{cis-Pt(NH_3)_2\}_2] \cdot 10H_2O$ {**PW₁₁Pt₂**}, that was firstly modified onto the surface of commercially-available TiO_2 to prepare novel heterogeneous catalyst $TiO_2-SiNH_2-PW_{11}Pt_2$. Under photocatalytic conditions, the hydrogen production rate reached $5.6 mmol h^{-1} g^{-1}$ and remained stable at $4.5 mmol h^{-1} g^{-1}$ after the continuous catalytic process, although the content of Pt^0 in the nanocomposite is

Fig. 20. Proposed schematic mechanism of catalytic reaction using {**Ta₆/CZS**} composite. Adapted with permission from Ref. [121]. Copyright 2019 Elsevier.

only 0.6%. A series of studies revealed that the synergistic effect of TiO_2 , $\{\text{PW}_{11}\text{Pt}_2\}$, and Pt nanoparticles greatly improved the photocatalytic hydrogen production efficiency (Fig. 21).

General catalytic mechanism. Generally speaking, the mechanism of the light-driven hydrogen evolution using POM-Semiconductor hybrids can be interpreted as following: upon visible light illumination, the electrons located on the valence band (VB) of the semiconductor will be promoted to the conduction band (CB), generating the electron-hole pair charge separation state. Then the CB electrons could be transferred to the POM catalyst or Pt cocatalyst in some catalytic systems, where the H^+ will be reduced to H_2 gas. The photo-generated holes located in the VB of the semiconductor will be scavenged by sacrificial reagents in the reaction system to accomplish a catalytic cycle.

3. Conclusions and outlook

To summarize, in this critical review we have addressed the importance and necessity of exploring cheap, clean, and sustainable energy alternatives in the form of solar-driven water reduction into H_2 . Given the versatile synthetic methodology and highly tunable physicochemical and photochemical properties of polyoxometalates (POMs), they have been widely applied as emerging new type of catalysts for catalyzing solar-driven hydrogen production. The applications of polyoxometalate-based catalysts in solar-driven hydrogen production have been thoroughly discussed and reviewed. Some representative works include the catalytic reaction systems using plenary POMs, transition-metal-substituted POMs, POM@MOF composites, and POM-Semiconductor hybrids as catalysts under UV, near UV light, and visible light irradiation; at the same time the catalytic mechanism for each specific reaction system has been thoroughly discussed and summarized.

Although there are so far many research works reported in this area, the room for improvement still remains substantial. To date, the main problems of the light-driven water reduction

systems catalyzed by POM-based catalysts can be summarized as: (1) many reaction systems still require UV or near UV light irradiation and the use of noble metal cocatalyst; (2) noble-metal-containing organometallic photosensitizers (e.g. $[\text{Ru}(\text{bpy})_3]^{2+}$, $[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]^+$, and their derivatives in the case of POM@MOF composites) are utilized for light energy harvesting; (3) most transition-metal-substitute POMs contain only single type of catalytic active site; (4) the long-term stability of the catalytic system should be assured for possible practical applications. Therefore, we prospect that the future development of this area should focus on solving above-mentioned problems through the development of cost-effective, visible-light-responsive, and photostable light-absorbers, novel earth-abundant TMSPOMs with multiple different catalytic active sites, as well as more robust and recyclable catalytic systems for practical applications. In addition, the exploration of new catalytic properties of TMSPOMs could also become an active research area in the near future. For example, researchers have already investigated the application of POM-based catalysts for photocatalytic/electrochemical carbon dioxide reduction to CO , HCOO^- , and other carbon-base fuels. Also, the host-guest chemistry between POMs and MOFs, COFs, and other macrocyclic molecules would also attract increasing attention with the development of these important research areas. Finally, we hope this critical review and our personal thoughts could provide some insightful guidelines for the better development of POM Chemistry and the related interdisciplinary research areas.

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Fig. 21. (a) The PL emission spectra of TiO_2 , $\text{TiO}_2\text{-SiNH}_2$, $\text{TiO}_2\text{-Pt}$ and $\text{TiO}_2\text{-SiNH}_2\text{-PW}_{11}\text{Pt}_2$; The LSV graph (b), EIS spectra (c) and transient photocurrent responses (d) of TiO_2 , $\text{TiO}_2\text{-SiNH}_2$ and $\text{TiO}_2\text{-SiNH}_2\text{-PW}_{11}\text{Pt}_2$. Adapted with permission from Ref. [133]. Copyright 2020 Royal Society of Chemistry.

Graphical Abstract

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Research advances of light-driven hydrogen evolution using polyoxometalate-based catalysts

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This critical review addresses the research advances of light-driven hydrogen evolution using polyoxometalate-based catalysts (including plenary POMs, transition-metal-substituted POMs, POM@MOF composites, and POM-Semiconductor hybrids) under UV, near UV, and visible light irradiation.

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基于多金属氧酸盐催化剂的光驱动产氢研究进展

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摘要: 能源和环境问题是21世纪人类面临的两个巨大挑战。鉴于此, 为了实现人类社会的可持续发展, 寻求能够替代化石能源的安全无污染可再生能源已迫在眉睫。太阳光驱动水分解是实现太阳能转化生产清洁可再生氢能的理想方法, 其分解产物氢气和氧气在燃烧释放能量的同时生成洁净无污染的可饮用水, 实现了完美的可持续能量循环, 对于解决当今全球面临的能源危机与环境污染问题具有巨大的应用价值。然而, 长期以来光驱动水分解所面临的巨大难题是半反应动力学非常缓慢, 通常需要克服较高的能量势垒, 导致整体能量转化效率低。利用非贵金属制备高催化效能、低成本的水分解催化材料成为该领域的研究热点和难点。目前, 已报道的光驱动产氢催化剂可以被归纳为两大类: 均相催化剂和异相催化剂。均相催化剂通常具备高催化活性、高选择性以及易于进行机理研究等优点, 而异相催化剂则具备廉价、易得和高稳定性等优点; 然而它们也存在一些不容忽视的问题, 如均相催化剂的低稳定性、易分解失活, 异相催化剂表面易被毒化失活、低催化转化数及转化频率等。如何设计合成兼具二者优点的产氢催化剂吸引了领域内研究者的广泛关注。作为一类新兴的多电子转移催化剂, 多金属氧酸盐因其丰富多样的合成策略以及高度可调的物理化学及光化学性质, 已被广泛用于催化水分解制氢气研究。该类多金属氧酸盐催化剂具备了介于均相分子化合物和异相金属氧化物之间的结构, 这种独特的结构赋予它们同时具备均相分子催化剂的高活性、高选择性、高可控性、易于进行机理性研究等优点, 又具备异相金属氧化物催化剂的廉价易得及稳定性高等优势。随着研究的开展, 基于多金属氧酸盐的光催化产氢体系已由当初的贵金属辅助逐渐转变为丰产元素参与, 光源的选择方面也从与太阳光谱匹配度低的紫外光转变为可见光。本文对30多年来基于多金属氧酸盐催化剂的光驱动产氢成果进行了综述, 主要包括有/无贵金属辅助的多金属氧酸盐, 多酸@金属有机框架复合物, 多酸-半导体复合材料在紫外光或可见光条件下的光催化产氢研究; 同时讨论总结了不同类型催化体系的反应机理; 并对该领域的未来发展趋势及研究方向进行了展望。

关键词: 多金属氧酸盐; 光驱动产氢; 多酸@金属有机框架复合物; 多酸-半导体复合材料; 催化反应机理

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