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Review

Progress of electrochemical CO₂ reduction reactions over polyoxometalate-based materials

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ABSTRACT

Electrochemical CO₂ reduction to value-added fuels and chemicals is recognized as a promising strategy to alleviate energy shortages and global warming owing to its high efficiency and economic feasibility. Recently, understanding the activity origin, selectivity regulation, and reaction mechanisms of CO₂ reduction reactions (CO₂RRs) has become the focus of efficient electrocatalyst design. Polyoxometalates (POMs), a unique class of nanosized metal-oxo clusters, are promising candidates for the development of efficient CO₂RR electrocatalysts and, owing to their well-defined structure, remarkable electron/proton storage and transfer ability, and capacities for adsorption and activation of CO₂, are ideal models for investigating the activity origin and reaction mechanisms of CO₂RR electrocatalysts. In this review, we focus on the activity origin and mechanism of CO₂RRs and survey recent advances that were achieved by employing POMs in electrocatalytic CO₂RRs. We highlight the significant roles of POMs in the electrocatalytic CO₂RR process and the main factors influencing selectivity regulation and catalytic CO₂RR performance, including the electrolyte, electron-transfer process, and surface characteristics. Finally, we offer a perspective of the advantages and future challenges of POM-based materials in electrocatalytic CO₂ reduction that could inform new advancements in this promising research field.

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1. Introduction

With the continuous growth of the global population and industrial development, the demand for fossil fuels increases daily, exacerbating the energy shortage while the significant carbon dioxide (CO₂) emissions accompanying the use of fossil fuels adversely affects the global environment [1]. The concentration of CO₂ in the atmosphere has risen from 0.028% before the industrial revolution to over 0.041% in 2020 and continues to increase at a rate of 2.1×10^{-6} per year [2,3]. Such high concentrations of CO₂ cause a series of environmental problems such as global warming [4], increased desertification [5], seawater acidification [6], and the extinction of species [7]. Conversely, the CO₂ in the atmosphere is an indispensable C1 resource for plant growth and various industrial process. Thus, the reasonable utilization and conversion of CO₂ into high value-added chemicals presents a promising, clean, and carbon-neutral strategy to alleviate CO₂-induced environmental problems and meet future energy demands.

Structurally, a CO₂ molecule is linear and centrosymmetric, which endows it with exceptional stability, intrinsic chemical inertia, low electron affinity, and a large energy gap (13.7 eV) [8]. These features make the transformation of CO₂ a challenging process that requires a substantial input of energy that can only proceed under harsh reaction conditions. Moreover, the practical application of CO₂ conversion and concomitant product utilization are hampered by the high energy requirements of CO₂ conversion, insufficient socio-economic motivation, and a lack of industry commitment to promote CO₂-related chemicals [9–11]. Despite the *status quo*, diverse routes to convert CO₂ into carbon-based chemicals and fuels have been developed, which include chemical reforming [12], mineralization [13], biochemical [14], photochemical [15], thermochemical [16], and electrochemical reactions [17–20]. Among these approaches, the photochemical or electrochemical CO₂ reduction technologies, driven by clean and renewable energy, have attracted enormous attention and display huge potential for future industrial applications owing to their environmental compatibility and operation under ambient temperature and pressure. In particular, electrocatalytic CO₂ reduction reactions (CO₂RRs) present a promising alternative approach offering various advantages, including controllable applied voltages and reaction temperatures, recyclable supporting electrolytes, sustainable input energy sources, and easy to scale up application [21–23]. However, researchers in the field of electrocatalytic reduction of CO₂ still face the challenges of large overpotentials, slow electron transfer kinetics, unsatisfactory selectivity, and low energy efficiency due to accompanying solvent decomposition reactions [24–26]. Electrocatalysts have been recognized as the key to improving CO₂ electroreduction performance.

In the electroreduction process of CO₂, the C=O bonds are broken by high-energy electrons and protons to selectively produce small carbonaceous molecules with high energy densities, such as formic acid (HCOOH, 2e/2H reduction), carbon monoxide (CO, 2e/2H reduction), and methanol (CH₃OH, 6e/6H reduction), methane (CH₄, 8e/8H reduction), or some C2 products such as ethylene (C₂H₄), ethane (C₂H₆), and ethanol

(CH₃CH₂OH) via C–C coupling [23]. However, the desired selectivity and optimum purity of target products depend on the selection of CO₂RR electrocatalysts. Accordingly, various electrocatalysts have been developed, such as molecular electrocatalysts (e.g., metal carbonyl [25–29], macrocyclic [30–33], covalent organic framework [34–36], and metal-organic framework [37–39]), single-atom catalysts [40–42], metal [43–45] and metal alloy [46–48], oxide [49–50], sulfide [51], and carbon-based materials [52,53]. Despite the realization of electrocatalysts with high CO₂RR activity and selectivity, in-depth studies of the activity origin and selectivity regulation of electrocatalysts along with their reaction mechanisms and CO₂RR processes are still required.

Polyoxometalates (POMs), an extraordinary class of nanoscale metal-oxo clusters constructed with *d*⁰ or *d*¹ metal ions (M = W, Mo, Nb, V, etc.) bridged *via* shared oxygen atoms, have attracted attention in various fields, such as catalysis [54–56], medicine [57], material [58] and energy [59], owing to their well-defined structures and fascinating physical and chemical properties. The application of POMs in electrocatalytic CO₂RRs is growing rapidly. In 2002, Kozik *et al.* [60] reported the first investigation into electrocatalytic CO₂ reduction using a homogeneous transition metal (TM)-substituted POM catalyst. Recent years have seen a rapid increase in the number reports featuring POM-based CO₂RR electrocatalysts, which mainly concern the well-defined adjustable structure, unique electrochemical redox properties, and flexible modifiability of POMs. The adjustable structure and composition of POMs can accommodate more than one kind of TM atom allowing the precision construction of TM-substituted POMs with metalloporphyrin-like properties, which are ideal models for understanding the interaction between metal atoms and ligands in molecular catalysis. Moreover, POMs, as a class of uniformly nanosized metal-oxo clusters, possess the characteristics of both molecules and nanoclusters, and also display surface features similar to TM oxides [61] and sulfides [62,63], offering an important platform for the in-depth investigation of nano-catalyst surface chemistry and adsorption processes. Furthermore,

Scheme 1. The various features of POMs including an adjustable structure, modifiability, electrochemical redox properties, and catalytic activity.

POMs can serve as flexible scaffolds that can be assembled via organic modification [64], electrostatic/hydrogen bonding interaction, or host–guest interactions to form POM-based composite materials [65]. In these POM-based composite materials, POMs can undergo reversible multivalent reductions/oxidations to form mixed-valence species while retaining their structural integrity. The outstanding electron/proton storage and transport capacities of POMs also provide a convenient model for studying the redox reactions and electron/proton coupling transfer behaviors of multicomponent catalysts in the electrochemical process [66]. Therefore, POMs play an indispensable and irreplaceable role in multiscale electrocatalysis (Scheme 1). They can bridge molecular- (homogeneous catalysis) and nano-electrocatalysts (heterogeneous catalysis), to offer an ideal catalyst model for the in-depth understanding of CO₂RR mechanisms and the structure–activity relationships in complicated electrocatalyst systems.

In the past few years, POMs have been widely used in the field of CO₂ conversion and chemical fixation, and several impressive reviews have been published that mainly focus on thermal and photocatalytic CO₂ conversion. He et al. [67] and Hu et al. [68] reviewed the use of POMs in CO₂ cycloaddition reactions and speculated on the adsorption process and reaction mechanism of CO₂ on POM surfaces. With the rapid development of POMs in electrocatalysis, several reviews on POM-based electrocatalysts have also been published. He and co-workers [69] summarized the application of POMs in CO₂-involved photo/electrocatalysis and carbonylation, while Lan et al. [70] discussed the application of POM-based materials in various energy-related reactions, some of which involved POM-based CO₂RR electrocatalysts. The limited review papers available on electrocatalytic CO₂RRs over POMs mainly summarize catalyst types and catalytic performance. Whereas, a systematic and comprehensive review on the application of POMs in electrocatalytic CO₂RRs is not available. The urgent need for a deeper understanding of the activity origin, selectivity regulation, and reaction mechanism of CO₂RRs over POMs prompted us to systematically review the latest progress in POM-involved electrocatalytic CO₂ reduction.

In this review, we focus on the mechanisms and the major advances involving POMs and electrocatalytic CO₂RRs, and highlight the significant roles of POMs in such electrocatalytic processes. Particular attention is paid to the catalytic activity origin of electrocatalytic CO₂RRs over POMs, the main principles of selectivity regulation and factors influencing catalytic CO₂RR performance, including the electrolyte, electron transfer process, and surface characteristics. Finally, we briefly discuss the challenges and perspectives of electrocatalytic CO₂ reduction over POM-based materials, and speculate on possible future directions for the development of efficient and controllable CO₂RR electrocatalysts.

2. Fundamental understanding of electrocatalytic CO₂ reduction reactions

Understanding the mechanisms of CO₂RRs is crucial to improving product selectivity and efficiency. CO₂ molecules have

Table 1

Electrochemical potentials of reactions that may occur during electrocatalytic CO₂ reduction in aqueous solutions.

Possible half-reactions in electrochemical CO ₂ RRs	Electrode potentials (V vs. SHE)
CO ₂ (g) + e [−] → *COO [−]	−1.90
CO ₂ (g) + 2H ⁺ + 2e [−] → CO (g) + H ₂ O (l)	−0.52
CO ₂ (g) + 8H ⁺ + 8e [−] → CH ₄ (g) + 2H ₂ O (l)	−0.24
2CO ₂ (g) + 12H ⁺ + 12e [−] → C ₂ H ₄ (g) + 4H ₂ O (l)	−0.34
CO ₂ (g) + 2H ⁺ + 2e [−] → HCOOH (l)	−0.61
CO ₂ (g) + 4H ⁺ + 4e [−] → HCHO (l) + H ₂ O (l)	−0.51
CO ₂ (g) + 6H ⁺ + 6e [−] → CH ₃ OH (l) + H ₂ O (l)	−0.38
2H ⁺ + 2e [−] → H ₂ (g)	−0.42

two vertical conjugated π bonds, which induce a high bond energy, high chemical stability, and chemical inertia [71]. It is, therefore, necessary to design and develop highly efficient electrocatalysts to promote electrocatalytic CO₂RRs. Since the first report of metal electrode-driven electrocatalytic CO₂ reduction in the 1980s, a large number of electrocatalysts have been developed [45]. However, the limited activity and product selectivity of electrocatalysts are still key weaknesses that hinder their practical application. The investigation into the electrochemical pathway of CO₂RRs reported by Hori and co-workers [72] proposed that CO₂ in an aqueous electrolyte is initially adsorbed on the electrode surface to form a CO₂*[−] radical, which is an important intermediate for the subsequent product selectivity of the CO₂RR [71]. This step requires a significant amount energy (−1.9 V vs. SHE) to rearrange the linear CO₂ molecule into a curved free radical anion (however, the role and reaction pathway of the intermediate in this step are still controversial) [72,73], which is the main reason for low CO₂RR activity. Thus, a clear active center that easily activates CO₂ molecules is the primary feature required of CO₂RR electrocatalysts.

Once the CO₂*[−] intermediate is formed in the CO₂RR process, a series of proton-coupled electron transfer processes can occur efficiently. However, due to the small potential differences between the possible products (Table 1), product selectivity is

Fig. 1. Kinetic volcano plot for CO evolution at a 0.35 V overpotential from the (211) step of TMs. The TMs fall along a trendline that does not pass over the top of the volcano. However, the noble metals occupy near-optimum positions along this trend line. The specific CO evolution current for the ChCODH II and MbCODH enzyme models is comparable or better than those of the noble metals. Reprinted with the permission of Ref. [75]. Copyright 2013, American Chemical Society.

challenging in electrocatalytic CO₂RRs and usually depends largely on the adsorption characteristics of the catalyst surfaces or active sites. When the oxygen atom of the *COO[−] intermediate is protonated to form a *COOH intermediate, the CO₂ reduction product tends to be CO, whereas when the nucleophilic carbon atom in the CO₂[−] intermediate is protonated to form the HCOO* intermediate, the catalytic product is mainly formic acid [74]. Key to the regulation of CO₂RR product selectivity is the optimization of intermediate adsorption energy on the surface of electrocatalysts. Nørskov and co-workers [75] established a kinetic volcano diagram of the adsorption energies of two intermediates (ΔE_{COOH} and ΔE_{CO}) by using density functional theory (DFT) to describe the catalytic activity trend of CO₂ reduction to CO (Fig. 1), and found that the ideal electrocatalyst for CO₂ reduction to CO should demonstrate suitable binding energy toward the key intermediates, *COOH and *CO. As illustrated in Fig. 1, the surfaces of metals (Au and Ag) have weak binding energies toward *CO but strong binding energies toward *COOH, limiting the activation of CO₂. In the cases of Pd, Ni, Pt, and Ru, CO₂ activation and conversion to adsorbed CO is facile but the strong binding of *CO limits the desorption of CO. Moreover, the adsorption energies of different intermediates on a single TM surface are linearly correlated, that is, it is impossible to simultaneously enhance *COOH binding and decrease *CO binding at a single active site. A number of strategies have been developed to overcome the linear relationship between the binding energies of key intermediates, such as *COOH and *CO. For example, adjusting the composition of alloy catalysts [17], the modification of ligands [76,77], the application of an electric field [78–80], surface engineering [81], and electron/proton transfer processes [82] can selectively stabilize the adsorbed intermediates. A doping strategy can also optimize the adsorption energies of intermediates, for example, increasing the content of subsurface oxygen in copper oxide enhances the binding of *CO [83]. In addition, DFT calculations predict that MoS₂ and MoSe₂ can break the linear relationship between the binding energies of *CO, *COOH, and *CHO [84]. Besides the above thermodynamic characteristics, a series of kinetic characteristics, including the concentration of the electrolyte [85], the gas diffusion [86], and the presence of active sites on the catalyst surface [87], also affect the activity and selectivity of CO₂RRs.

Therefore, ideal CO₂RR electrocatalysts should have clear active centers that can easily adsorb and activate CO₂ molecules, and suitable binding energies toward specific intermediates. Moreover, considering the complicated multi-proton/electron-coupled process involved in CO₂RRs, a distinct proton/electron transfer pathway is useful in understanding the selectivity regulation of electrocatalytic CO₂RRs. The high dispersion of catalytically active centers and appropriate electrolyte solutions are also important factors in promoting the high activity and selectivity of electrocatalytic CO₂RRs.

3. Advantages of polyoxometalates in electrocatalytic CO₂RRs

POMs with their unique electrochemical redox properties

and outstanding electron/proton storage and transport capacities, display enormous potential as electrocatalysts. Since the first POM was reported by Berzelius in 1826, numerous POM structures have been revealed that promote the development of POM chemistry in energy-related fields [70]. In recent years, the application of POMs in electrocatalytic CO₂RRs has grown rapidly, and is closely related to the POM properties. The oxygen-enriched surfaces of POMs offer Lewis base sites, endowing POMs with the ability to couple and activate CO₂ molecules. In 1998, Kozik *et al.* [88] reported the interaction between CO₂ and nonreduced heteropolyanions $[\alpha\text{-SiW}_{11}\text{O}_{39}\text{Co}(\text{L})]^{6-}$ in a nonpolar solvent, and demonstrated the η^1 metal-carbon bond and hydro-bonding interaction in CO₂-POM adducts through a series of spectral characterizations. Ten years later, Xu *et al.* [89] demonstrated the successful covalent bonding of CO₂ molecules with polyoxoanions by slightly bending the O–C–O angles from 180° to ca. 158.7°, to realize the fixation and activation of CO₂. It should be noted that POMs can adopt various clear coordination modes to combine and activate CO₂ molecules, which makes POMs the most structurally functional model for studying different adsorption and activation modes of CO₂.

Moreover, POMs possess the features of both molecules and highly dispersed nanoclusters, in which the size of nanoclusters can be adjusted from 1 to 100 nm [90]. The surfaces of POMs are also ideal models for understanding the surfaces of nanosized metal oxides, sulfides, and nitrides. Since Caughlan *et al.* [91] determined the molecular structure of titanyl clusters in 1967, titanium-oxo clusters have become the most effective molecular model of the properties of nanosized TiO₂, and have turned into a unique bridge between theoretical modeling, crystallography, and spectroscopy [61]. Subsequently, Wright and co-workers [92] prepared a series of cobalt (II) doped titanium oxide clusters, which were used as regulation models to study the effect of metal doping on the band gap of TiO₂. Owing to the development of POM chemistry over the past two hundred years, besides the titanium-oxo clusters, the constituent elements of POMs are becoming more and more abundant. Some novel palladium-oxo clusters [93] and molybdenum sulfur clusters [63] have been discovered. These POMs provide the most accurate molecular models for understanding the effect of O- and S-doping on the adsorption process of key intermediates during electrocatalytic CO₂RRs. Therefore, POMs provide a molecular-scale perspective for understanding the electrocatalytic CO₂RR process and are expected to present accurate models for understanding and regulating the activity and selectivity of CO₂RRs.

The TM atoms in POMs typically have d^0 or d^1 electronic configurations, implying that POMs have electron/proton storage and transport capacities and can undergo reversible multi-valent reductions/oxidations to form mixed-valence species while retaining their structural integrity [94]. The reduced POMs generally demonstrate good solubility and solvent compatibility, and in an electron/proton buffer solution can reveal the effect of the redox behavior of the electrolyte on mass transfer and electron transfer during electrocatalytic CO₂RRs [95]. The stored electrons or protons in reduced POMs can

Scheme 2. The fascinating properties of POMs informing the potential application of POM-based materials in electrochemical CO₂ reduction reactions.

specifically transfer to the reaction substrate through direct electron transfer or proton-coupled electron transfer mechanisms [96], which is expected to optimize the proton-coupled electron transfer process in electrocatalytic CO₂RRs, and regulate the selectivity of CO₂RRs.

In summary, POMs possess well-defined structures and the capacities for the adsorption and activation of CO₂, satisfying the requirements for electrocatalytic CO₂RR catalysts. Moreover, POMs can serve as a functional platform to understand key steps of the electrocatalytic CO₂RR process on a molecular scale, but also as a mechanism model for understanding the effect of the properties of TM oxides and sulfides on CO₂RRs (Scheme 2). Therefore, investigating the electrocatalytic CO₂RRs over POMs can provide an in-depth understanding of the structure-activity relationship during electrocatalytic CO₂RRs and lay the foundation for the design of efficient CO₂RR electrocatalysts with high selectivity and designability for practical application.

4. Research progress of electrocatalytic CO₂RRs over POMs

4.1. POM-based molecular electrocatalysts for CO₂RRs

POMs are considered promising homogeneous molecular catalysts for electrocatalytic CO₂RRs due to their well-defined structures, and good solubility and stability in aqueous or non-polar solvents. Polyoxoanions can undergo one or more electron(s)/proton(s) coupled redox processes in solution, and their redox activities can be regulated by introducing suitable TM cations or small organic molecules. In the 1990s, there were a series of studies on TM-substituted polyoxoanions for the activation of CO₂ molecules [88]. Kozik et al. [88] systematically studied the interaction of CO₂ and TM-substituted POMs in nonpolar solvents and used spectroscopic evidence to prove the formation of a POM-CO₂ complex. As shown in Fig. 2, a series of UV-Vis absorption, infrared (IR), and ¹³C NMR spectra were used to prove the coordination of POMs and CO₂ molecules in nonpolar solutions. The coordination mode of TM-substituted POMs is easy to observe based on the color changes of the solution. When the α-[SiW₁₁O₃₉Co(OH₂)]⁶⁻ (SiW₁₁Co(H₂O)) is coordinated with water, the solution appears orange-red (Fig. 1(a), Curve I), the “dry” SiW₁₁Co() appears green (Fig. 1(a), Curve II), and the CO₂ coordinated SiW₁₁Co(CO₂) is burgundy red (Fig. 1(a), Curve II). At the same time, the IR spectrum (Figs. 1(b)–(c)) indicates two vibrations at 1675 and 1350 cm⁻¹, which are assigned to the interactions between POMs and CO₂. The ¹³C NMR spectra was also used to confirm the formation of a TM-substituted POM-CO₂ complex. As shown as Fig. 2(d), two clear signals are attributed to the carbon atoms in a paramagnetic environment, and the complex

Fig. 2. (a) Visible spectra of tetraheptylammonium salts of (I) α-[SiW₁₁O₃₉Co(OH₂)]⁶⁻, (II) α-[SiW₁₁O₃₉Co()]⁶⁻, and (III) α-[SiW₁₁O₃₉Co(CO₂)]⁶⁻ in toluene. (b) Infrared spectrum of the tetraheptylammonium salt of α-[SiW₁₁O₃₉Co(CO₂)]⁶⁻ in CCl₄. The two peaks marked with arrows appear after the CO₂ is bubbled, and are assigned to vibrations of CO₂ complexed to cobalt. (c) Difference spectrum between α-[SiW₁₁O₃₉Co(CO₂)]⁶⁻ and α-[SiW₁₁O₃₉Co()]⁶⁻. The peak at 2335 cm⁻¹ originates from the CO₂ gas dissolved in the solvent. (d) ¹³C NMR spectra of 0.1 M α-[SiW₁₁O₃₉Co(CO₂)]⁶⁻ in toluene at temperatures from -40 °C to +35 °C. (e–h) Proposed hypothetical bonding modes for CO₂ with cobalt in α-[SiW₁₁O₃₉Co(CO₂)]⁶⁻, stabilized by hydrogen bonding utilizing both hydrogen atoms from water. Reprinted with the permission of Ref. [88]. Copyright 1998, American Chemical Society (ACS).

is stable up to 35 °C. Based on the spectroscopic characterization, the structures of four possible, water-molecule stabilized, POM-CO₂ complexes have been deduced (Figs. 2(e)–(h)). This work demonstrated for the first time the formation of complexes between TM-substituted POMs and CO₂ molecules in nonpolar solutions, which provided a basis for understanding the activation of CO₂ molecules and for future electrocatalytic CO₂ reduction research involving POMs.

Based on this work, Kozik *et al.* [60] continued to study the electrochemical behavior of TM-substituted POM-CO₂ complexes and reported the first TM Co-substituted polyoxoanions α -[SiW₁₁O₃₉Co]⁶⁻ (SiW₁₁Co) for electrocatalytic CO₂RRs in nonpolar solvents. Compared to the cyclic voltammetry (CV) curve of SiW₁₁Co in a dichloromethane (CH₂Cl₂) electrolyte without CO₂, the CV curve of SiW₁₁Co in a CH₂Cl₂ electrolyte bubbled with CO₂ achieved a higher reduction current signal, which indicated that SiW₁₁Co has electrocatalytic CO₂RR activity. For polyoxoanions α -[P₂W₁₈O₆₂]⁶⁻ (P₂W₁₈) without TM substitution, the cyclic voltammetry curve in the CH₂Cl₂ electrolyte before and after CO₂ bubbling did not change significantly, suggesting the important role of TM substituted polyoxoanions in electrocatalytic CO₂RR activity. However, the CV curve of the CO₂ reduction by SiW₁₁Co in CH₂Cl₂ showed an irreversible redox current peak, which may have been caused by the lack of protons in the electrolyte, indicating that SiW₁₁Co cannot stably support electrocatalytic CO₂RRs. In the presence of a proton source (such as H₂O), the vacant Co sites of SiW₁₁Co will coordinate with water molecules and lose catalytic CO₂RR activity. If SiW₁₁Co is first reduced in an aqueous electrolyte and then transferred to toluene via tetraheptylammonium bromide (THABr), electrons and protons can be stored in SiW₁₁Co while preventing H₂O molecules from occupying the active Co sites of SiW₁₁Co, to achieve stable electrocatalytic CO₂RRs driven by SiW₁₁Co in toluene. This work was the first to use TM-substituted polyoxoanions for electrocatalytic CO₂RRs, the electron/proton storage characteristics of the reduced POMs made it possible to achieve stable electrocatalytic CO₂RRs with the active Co sites of polyoxoanions in a nonpolar electrolyte. This work studied the effect of the electrolyte on the activity of metal-substituted polyoxoanions in terms of electron/proton transfer and coordination chemistry, providing some insights for understanding and illustrating the working conditions of metal-complexed molecular electrocatalysts in CO₂RRs. However, the nature of the products or the electrocatalytic selectivity of the reaction were not reported in this work.

Proust *et al.* [97] investigated the interaction of POMs with CO₂ in acetonitrile. The electrolysis of a CO₂-saturated, (TOA)₆[α -SiW₁₁O₃₉Co(–)] (TOA = tetraoctyl ammonium) dichloromethane solution, at –1.5 V vs. Hg₂Cl₂/Hg (1 M LiCl) on a Hg working electrode, revealed that CO₂ could be reduced to CO with a low faradaic yield of 18% and no H₂ by-product. The introduction of an extra proton source (TBAHSO₄) into this electrolysis system, resulted in the detection of a 4e[–]/4H reduction product, formaldehyde, along with CO. The faradaic efficiency for this reaction reached up to 25% while the turnover number (TON) was 1.75. Interestingly, the authors found that a trace amount of formaldehyde was detected after electrolysis

of a (TOA)₆[SiW₁₁O₃₉Co(–)] solution under argon; the likely source of carbon in this case was the solvent, CH₂Cl₂. This illustrated the important role of isotope-labeled CO₂ in determining the carbon source of the electrocatalytic CO₂RR products. Although the efficiency of this system was low, the relatively systematic investigation process demonstrated the working conditions of polyoxoanions in electrocatalytic CO₂RRs, explored the reaction efficiency and the product species, and illustrated the important role of the proton source (in the electrolyte) in electrocatalytic CO₂ reduction over polyoxoanions. It is worth noting that the electrocatalytic reduction of CO₂ to formaldehyde over (TOA)₆[SiW₁₁O₃₉Co(–)] is very rare. A promising research avenue is the further exploration of different types of POMs and TM substitutes to achieve the highly selective reduction of CO₂ to formaldehyde.

These works demonstrate the metalloporphyrin-like reactivity of POMs in nonpolar electrolytes and explain the activation pathways of CO₂ molecules and the reason for the loss of activity over TM-substituted POMs in aqueous electrolytes. Accordingly, the development of metalloporphyrin-like POMs with heterogeneous, stable active sites in aqueous electrolytes is essential to achieving highly efficient, highly selective, POM-based electrocatalytic CO₂ reduction in the future. Using TM-substituted POMs to understand the process of CO₂ reduction activated by TM complexes may also provide design and guiding principles for the development of new heterogeneous metalloporphyrin electrocatalysts and metalloporphyrin-like, single-atom electrocatalysts.

Besides TM-substituted POMs, metal-organic complexes with CO₂RR activity can also be introduced into the structure of POMs. Inspired by this idea, Proust's team grafted [Cp*^{III}Rh(bpy)Cl]⁺ (Cp* = pentamethylcyclopentadienyl anion, bpy = 2,2'-bipyridine) with CO₂RR activity to vacant α -H₂PW₁₁O₃₉ polyoxoanions to construct a (TBA)₃[H₂PW₁₁O₃₉{Rh^{III}Cp*(OH₂)}] catalyst for electrocatalytic CO₂RR in an acetonitrile solution (Fig. 3) [98]. [H₂PW₁₁O₃₉{Rh^{III}Cp*(OH₂)}]^{3–} exhibited poorer electrocatalytic CO₂RR activity than that of the parent [Cp*^{III}Rh(bpy)Cl]⁺ catalyst, and the Faraday efficiency (FE) for the CO₂RR product, HCOOH, was only 4.5%. However, the FE for the by-product H₂ was as high as 68%. Under the same conditions, the FE for CO₂ reduction to HCOOH on [Cp*^{III}Rh(bpy)Cl]⁺ was 60% while that of the by-product, H₂, was only 30%. This result suggests that the strategy of replacing the bpy group with polyoxoanions adversely affects the electrocatalytic CO₂RRs. The low FE of the electrocatalytic CO₂RRs may result from the reduction of the

Fig. 3. Synthesis of the organometallic derivative [α-H₂PW₁₁O₃₉{Rh^{III}Cp*(OH₂)}]^{3–} (the POM skeleton is displayed in polyhedral representation). Reprinted with the permission of Ref. [98]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

polyoxoanions themselves and the protons stored by the reduced POMs. This work provides some guidelines for the reasonable ligand-modification of bipyridyl-based molecular catalysts.

The above facts indicate that substituted polyoxoanions can, to a certain extent, perform electrocatalytic CO₂RRs. These substituted polyoxoanions can be used as homogeneous catalysts in organic electrolytes for electrocatalytic CO₂RRs; despite the reaction efficiency, the selectivity and FE is very poor. These works achieved limited success in the application of polyoxoanions in electrocatalytic CO₂RRs but, considering the well-defined structures, adjustable composition and redox properties, could inform the design and optimization principles of molecular electrocatalysts for CO₂RRs. Therefore, polyoxoanions can be used to elucidate the electron transfer process and the activity origin in electrocatalytic CO₂RR processes at a molecular level, and potentially regulate the selectivity and activity of molecular catalysts.

4.2. POM-based organic-inorganic hybrids for electrocatalytic CO₂RRs

Due to the high solubility of polyoxoanions in aqueous solutions, the design of insoluble POM-based heterogeneous catalysts is considered another feasible approach to promoting its application in electrocatalytic CO₂RR. The use of POMs to construct organic-inorganic hybrids can not only significantly reduce the solubility of POMs, but also integrate the functional characteristics of organic molecular catalysts for CO₂RRs into polyoxoanions, which presents an ideal strategy for designing POM-based hybrid materials for electrocatalytic CO₂RRs [99].

Metalloporphyrin compounds are a typical kind of catalyst for electrocatalytic CO₂RRs often used for electrocatalytic CO₂ reduction in organic solvents. Isaacs *et al.* [100] modified an indium tin oxide (ITO) electrode with M- μ -(*meso*-5,10,15,20-tetra(pyril)porphyrin)tetrakis{bis(bip

Fig. 4. (a) Structural representation of Mn(III), Ni(II), and Zn(II) μ -(*meso*-5,10,15,20-tetra(pyril)porphyrin)tetrakis{bis(bipyridine)chloride ruthenium(II)}; Linear sweep voltammogram of bare ITO electrode (b), [Mn^{III}TRP]⁵⁻/[SiW₁₂O₄₀]⁴⁻ multilayer modified electrode (c) [Zn^{II}TRP]⁴⁺/[SiW₁₂O₄₀]⁴⁻ multilayer modified electrode (d) and [Ni^{II}TRP]⁴⁺/[SiW₁₂O₄₀]⁴⁻ multilayer modified electrode (e) in the presence (solid line) and absence (dash line) of CO₂ and 0.1 M NaClO₄ solution at 5 mV s⁻¹ (e). Reprinted with the permission of Ref. [100]. Copyright 2013 Elsevier Ltd.

Table 2

Electrocatalytic CO₂RR activity and products of [MTRP]/[SiW₁₂O₄₀]/ITO electrodes.

Electrode	Products and TOF (s ⁻¹)		
	CO	HCOOH	CH ₃ OH
[Mn ^{III} TRP] ⁵⁻ /[SiW ₁₂ O ₄₀] ⁴⁻ /ITO	N.D. ^a	0.48 ^b	0.023
[Zn ^{II} TRP] ⁵⁻ /[SiW ₁₂ O ₄₀] ⁴⁻ /ITO	0.0037	N.D. ^a	8.2
[Ni ^{II} TRP] ⁵⁻ /[SiW ₁₂ O ₄₀] ⁴⁻ /ITO	0.24	0.083	N.D. ^a

^a means that no product was detected; ^b the values in red are the main products.

yrindine)chloride ruthenium(II)} (MTRP, M = Mn, Zn, Ni, Fig. 4(a)) and [SiW₁₂O₄₀]⁴⁻ polyoxoanions using a layer-by-layer method (LBL), and studied the electrocatalytic CO₂RR activities of the modified electrodes in a NaClO₄ electrolyte.

The TM cation in the metalloporphyrin complex can significantly affect the species and selectivity of the electrocatalytic CO₂RR product (Fig. 4(b)–(e)), as shown in Table 2. [Mn^{III}TRP]⁵⁻/[SiW₁₂O₄₀]⁴⁻/ITO induces electrocatalytic CO₂ reduction to formic acid and methanol at a potential of −0.8 V vs. Ag/AgCl (and turnover frequency (TOF) of 0.48 and 0.023 s⁻¹ respectively), no CO is produced. The main electrocatalytic CO₂RR product using [Zn^{II}TRP]⁵⁻/[SiW₁₂O₄₀]⁴⁻/ITO is methanol (TOF = 8.2 s⁻¹), while the TOF of CO is only 0.0037 s⁻¹ and the formation of formic acid is not detected.

The use of [Ni^{II}TRP]⁵⁻/[SiW₁₂O₄₀]⁴⁻/ITO in electrocatalytic CO₂RRs primarily produces CO (TOF = 0.24 s⁻¹), while only a small amount of formic acid is produced (TOF = 0.083 s⁻¹) and no methanol is detected. Interestingly, under light irradiation, [Mn^{III}TRP]⁵⁻/[SiW₁₂O₄₀]⁴⁻/ITO can reduce CO₂ to formaldehyde at a potential of −0.65 V vs. Ag/AgCl (TOF = 16.7 s⁻¹). The above results indicate that photo-generated electrons can improve the electron transfer process of the catalyst and change the electrocatalytic CO₂RR products from CO (a 2-electron reduced product) to formaldehyde (a 4-electron reduced product), possibly the result of the electron transfer from the Ru(bipy)₂Cl⁺ component to the metalloporphyrin component. These results demonstrate that the central cations of metalloporphyrin complexes can regulate the electrocatalytic CO₂RR product and selectivity; moreover, the deep reduction of CO₂ and the acceleration of the reaction rate can be achieved under light conditions. The improved electron transfer in the electrocatalytic CO₂ reduction process under light conditions may be related to the electron storage characteristics of POMs. It appears that photoelectric CO₂ reduction uses electrons efficiently and can achieve deep reduction of CO₂. However, this hypothesis requires evidence showing the electron transfer process from the POMs to CO₂ molecules, and the Faraday efficiency of the electrocatalysis in this system needs clarification.

On this basis, Lan's group [37] prepared a series of stable polyoxometalate-metalloporphyrin organic framework (PMOF) materials consisting of Zn- ϵ -Keggin POM (ϵ -PMo₈VMo₄VO₄₀Zn₄) and M-tetrakis[4-carboxyphenyl]-porphyrin (M-TCPP, M=Co, Fe, Ni) *via* a hydrothermal method for electrocatalytic CO₂RRs in aqueous electrolyte solutions (KHCO₃, Fig. 5(a)). The researchers found that the TMs in the PMOFs significantly influence the catalysts' performances in

Fig. 5. (a) Schematic illustration of the structures of M-PMOFs (M = Co, Fe, Ni, Zn). M-PMOFs consist of 4-connection TCPP linkers and zigzag POM chains; (b) Linear sweep voltammetry (LSV) curves of M-PMOFs; (c) Faradaic efficiencies for CO; (d) Durability test of Co-PMOF at a potential of -0.8 V vs. RHE. Reprinted with the permission of Ref. [37]. Copyright 2018, Springer Nature.

electrocatalytic CO₂RRs (Figs. 5(b)–(c)). The Co-modified PMOF achieved the highest CO₂RR activity, reducing CO₂ to CO at a potential of -0.8 V vs. RHE and showing excellent stability over 36 hours (Fig. 5(d)). The FE for CO was 99% and the TOF was 1656 h⁻¹. DFT calculations have also been used to investigate the increased activity of Co-PMOFs, refer to Section 4.5. This work demonstrated for the first time that POM-based materials can achieve highly efficient electrocatalytic CO₂RRs in aqueous electrolytes, and the use of isotope-labeled ¹³CO₂ proved that the carbon source of the reduction product was CO₂ molecules. These results may provide new perspectives on the regulation of electrocatalytic performance of metalloporphyrin molecular

catalysts in aqueous electrolytes. Since the electrocatalytic CO₂RR activity of this series of PMOFs originates from the M-TCPP component, the regulatory effects of the different POMs in these composite systems require further research.

In addition to metalloporphyrin compounds, manganese carbonyl compounds are also typical catalysts for electrocatalytic CO₂RRs, however, they can only function as homogeneous catalysts in organic electrolytes. Recently, our group selected a carbonyl manganese bipyridine complex ([Mn^I(bipyridyl)(CO)₃Br], *abbr.* MnL) and POMs to prepare three POM-MnL composite electrocatalysts (SiW₁₂-MnL, PW₁₂-MnL, and SiW₁₂-MnL, Fig. 6(a)) [101]. By combining

Fig. 6. (a) Schematic diagram of the reaction mechanism induced by POM-MnL; (b) TEM image of SiW₁₂-MnL/KB (inset: HR-TEM image of SiW₁₂-MnL/KB, scale bar: 5 nm); (c) The CV curves for MnL/KB, CsSiW₁₂/KB, and SiW₁₂-MnL/KB in 0.5 mol L⁻¹ N₂-saturated KHCO₃ at a 0.05 V s⁻¹ scan rate; (d) The LSV curves of SiW₁₂-MnL/KB and MnL/KB in 0.5 M N₂-saturated KHCO₃ (black curve) or CO₂-saturated KHCO₃ (red curve); (e) The FE for CO at different potentials for MnL/KB and SiW₁₂-MnL/KB (the line is drawn only to guide the eye); (f) The FEs for CO and H₂ at the overpotential of the highest FE for CO of MnL/KB and POM-MnL/KB. Reprinted with the permission of Ref. [101]. Copyright 2020, Royal Society of Chemistry (RSC).

POM-MnL with Ketjen Black (KB), the conductivity of POM-MnL can be increased for use in electrocatalytic CO₂ reduction (Fig. 6(b)). This POM-MnL composite catalyst system demonstrated electron storage ability (Fig. 6(c)) and low solubility in aqueous electrolytes; it was, therefore, expected to function as a heterogeneous catalyst for electrocatalytic CO₂RRs. In the KHCO₃ electrolyte, SiW₁₂-MnL achieves the best electrocatalytic CO₂RR activity. SiW₁₂-MnL achieves a significantly improved FE for CO (at -0.72 V vs. RHE potential) of 95% (compared to the 65% achieved by the parent MnL) and a reduced FE for H₂ (Figs. 6(d)–(f)). Conversely, PMo₁₂-MnL exhibits poor electrocatalytic CO₂RR activity, in which the hydrogen evolution reactions (HERs) and the CO₂RRs occur simultaneously. The FE for CO is approximately 65%, while the FE of H₂ is 12% (Fig. 6(f)). In addition, SiW₁₂-MnL functions stably for 12 h in a 0.5 M KHCO₃ electrolyte, and the FE for CO remained stable above 95%. A series of electrochemical experiments, DFT calculations (discussed in detail in Section 4.5), and transient spectroscopy characterization confirmed that the electron transfer processes between POMs and MnL units differ, depending on the type of POM, and that a highly efficient electron transfer process from POM to MnL increases the FE for CO and reduces the FE for H₂. This work not only realized heterogeneous MnL, which allows the MnL to achieve efficient electrocatalytic CO₂RRs in aqueous electrolytes, but also confirmed the effect of the electron transfer process between POMs and MnL components on electrocatalytic CO₂RRs, providing several insights into the synergistic effect of multi-component molecular electrocatalysts in terms of electron transfer. However, this work did not provide *in-situ* experimental characterization to prove the reaction process of

POM and MnL during electrochemical CO₂RRs and was unable to achieve the deep reduction of CO₂ to multielectron products using the electron-storage capability of POMs.

The above studies demonstrated series of POM-based organic-inorganic molecular hybrid catalysts used in electrocatalytic CO₂RRs. The combination of POMs and organic molecular catalysts with CO₂RR activity via electrostatic, covalent, or coordination interaction, can significantly reduce the solubility of POMs and organic molecular catalysts in the electrolyte and achieve heterogeneous POM-organic molecular catalysts. Moreover, the POMs can drive electron transfer to the organic molecular components during electrocatalytic CO₂RRs, to assist the organic molecular catalyst in catalyzing the CO₂RRs in the aqueous electrolyte, significantly improving electrocatalytic CO₂RR selectivity, and suppressing side reactions. These works offer some explanations of the activity origin of multi-component, multi-center composite electrocatalysts, reveal several factors that affect their electrocatalytic performance in CO₂RRs on a molecular scale, and finally provide a deeper understanding of the electron transfer process during electrocatalytic CO₂ reduction. Nevertheless, the electron transfer processes of POMs cannot change the type of CO₂RR products catalyzed by the organic molecular catalyst to realize the deep reduction of CO₂ to high-value, multielectron products.

4.3. POMs as electrolytes for electrocatalytic CO₂RR

POMs are considered good electron/proton carriers due to their good solubility and adjustable redox activity in solvents, which can be employed as electron/proton buffer solutions.

Fig. 7. Square reaction scheme representing the interaction between the reduced forms of $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ and CO_2 during electrochemical reduction. $[\alpha\text{-SiW}_{12}\text{O}_{40}]^{4-}$ is represented as SiW^{4-} for convenience. Reprinted with the permission of Ref. [102]. Copyright 2016 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Accordingly, POMs are regarded as a new kind of electrolyte with electronic regulation effects. As explained in Section 4.1, the activity of TM-substituted POMs in nonpolar solutions is owed to the coordinated unsaturated substitute metal atoms. When TM-substituted POMs are present in an aqueous electrolyte, the water molecules will preferentially coordinate with the TM active sites of the TM-substituted POMs, inhibiting the electrocatalytic CO_2 reduction activity of the TM atoms. Saturated POMs are similar to the oxides of Mo or W, which do not have electrocatalytic CO_2RR activity. Therefore, unlike the POM-based homogeneous molecular electrocatalysts used for electrocatalytic CO_2RR , POMs serving as electrolytes often have no electrocatalytic CO_2RR activity in the electrolyte, but can significantly increase the CO_2RR activity of other catalysts.

Given the good solvent compatibility, favorable structural stability, and redox activity (in a certain pH range) of POMs, Zhang *et al.* [102] first studied the electrocatalytic CO_2RR activity of Ag nanoparticles stabilized with bovine serum albumin

(AgNC@BSA) in $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ containing dimethylformamide (DMF) electrolyte. As shown in Fig. 7, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ anions as electron transfer medium strongly interacts with CO_2 molecules, promoting electron transfer between the electrode and AgNC@BSA. This process is similar to the reduction processes of the redox enzyme in nature. Finally, the AgNC@BSA efficiently catalyzes the reduction of CO_2 to CO. The study recorded a FE for CO up to 75.6%. The AgNC@BSA demonstrated good stability, a slight decrease of approximately 20% in the current magnitude was observed over a period of 20000 s. In general, this study employed electrochemical CV to analyze the role of POMs as electron transfer media in detail, which has recently been confirmed to be consistent with their role in other CO_2RR electrolytes. Therefore, using POMs with different structures and compositions as a model facilitates the systematic study of the effects of electrolytes on electrocatalytic CO_2RR s. However, the electron transfer process from SiW_{12} to AgNC@BSA during the electrocatalytic CO_2 reduction process requires further *in-situ* characterization to prove.

Subsequently, Li's group [103,104] studied the electrocatalytic CO_2RR activity of the In electrode in aqueous solutions containing SiW_9V_3 and SiW_{11}Mn POMs as electrolytes. In the POM electrolyte, the In electrode not only induces the electrocatalytic reduction of CO_2 to C1 compounds such as CO and formic acid, but the C2 product, acetic acid, is also detected. As shown in Fig. 8(a), in the SiW_9V_3 electrolyte, the In electrode induces electrocatalytic CO_2RR s at a potential of -0.71 V vs. RHE (pH 4.07) and the FE for the product acetic acid reaches 96.5%. Whereas in the SiW_{11}Mn electrolyte, the In electrode induces the electrocatalytic reduction of CO_2 to acetic acid at a

Fig. 8. The Faradaic efficiencies of products of In cathode in SiW_9V_3 (a) and SiW_{11}Mn (b) electrolyte. (c) XPS spectra of In 3d for the indium electrode before and after electrolysis with 1 and 12 h. (d) XPS spectra of W 4f for the indium electrode after 1 h electrolysis. (e) The FTIR spectroscopy characterization for the 2 mM SiW_9V_3 -0.1 M Na_2SO_4 electrolyte during electrolysis, in which the peak at 2071 cm^{-1} corresponds to the adsorbed CO^* . (f) Current density with electrolysis time at different potential for 1 h; The inset is the current density with electrolysis time at -1.15 V vs. Ag/AgCl for 12 h. Reprinted with the permission of Refs. [103,104]. Copyright 2020 Elsevier Ltd.

potential of -0.55 V vs. RHE (pH 4.07) and the FE for acetic acid reaches 72.1% (Fig. 8(b)). X-ray photoelectron spectroscopy (XPS) and *in-situ* IR spectroscopy were used to study the reaction of the In electrode surface during the electrocatalytic CO_2 reduction process in order to infer the possible reaction mechanism. As shown in Figs. 8(c)–(d), after the electrocatalytic CO_2 reduction reaction, the concentration of the oxide species on the surface of the In electrode has decreased, while the W^{6+} species has formed on the electrode surface. The formation of In-CO_2^* intermediates was detected through *in-situ* IR spectroscopy (Fig. 8(e)), indicating that the In electrode is at the center of activated CO_2 . Based on the electrochemical CV, XPS, and IR spectroscopy results, it was inferred that the reduction process of W in POMs improves the selectivity of the In electrode in catalyzing the reduction of CO_2 to acetic acid through the electron transfer path in the electrolyte. In addition, the POM-assisted, In-electrode catalyzed CO_2 reduction is stable for at least 12 h (Fig. 8(f)). This investigation proves the electron transfer process between the POM solution and the metal electrode, and achieved the deep reduction of CO_2 on an In electrode, thus increasing the selectivity of the C2 product. This work provides a new way to optimize the product selectivity of electrocatalytic CO_2 RRs, in terms of electrolyte solutions, and offers some guidance for designing electrolytes that can be used for the deep reduction of CO_2 based on *in-situ* experiments and mechanism research.

4.4. POM-involved nanocomposite electrocatalysts for CO_2 RRs

In addition to their excellent electrochemical activity and redox properties, POMs have also attracted great attention in the field of materials chemistry due to their rich structures and composition characteristics. The elements found in POMs include not only the aforementioned TMs, but also metals in the *d* block, *ds* block, *f* block, and even the *p* block. The molecular scale of POMs can be adjusted from sub-nanometer to hundreds of nanometers. In addition, POMs are widely recognized as a reducing agent and stabilizer for the preparation of nanomaterials. These characteristics of POMs make them ideal precursors for the preparation of efficient CO_2 RR nano-electrocatalysts.

Zhang's group [105] used $\text{PMo}_{12}\text{O}_{40}^{3-}$ as a stabilizer and prepared a $\text{Ag}[\text{PMo}_{12}\text{O}_{40}]^n-$ (Ag-PMo) nanocomposite through electrochemical deposition. As shown in Figs. 9(a) and (b), Ag-PMo forms a dendritic structure of nano-silver, PMo_{12} polyoxoanions can be adsorbed onto the surface of the nano-silver to reduce the adsorption energy and further stabilize the structure of nano-Ag. The porous 3D structure of Ag-PMo promotes access to the catalytic active center, enhancing the catalytic performance during CO_2 RRs (Fig. 9(c)). In a DMF electrolyte, Ag-PMo nanocomposites induced highly selective electrocatalytic CO_2 RRs. The onset potential of the Ag-PMo nanocomposite electrode during CO_2 RRs was found to be more positive than that of an Ag polycrystalline electrode (about 700 mV), and Ag-PMo reduced CO_2 to CO with a FE of about 90% over a wide potential range. The mechanism study showed that PMo_{12} promotes the adsorption and stabilization of CO_2 intermedi-

Fig. 9. (a) SEM images of Ag-PMo nanocomposite-modified ITO glasses; (b) TEM images of Ag-PMo nanocomposites, inset: Schematic diagram of Ag-PMo catalytic CO_2 reduction; (c) Comparison of cyclic voltammograms obtained at an Ag-PMo nanocomposite-modified GC electrode in DMF (0.1 M $[\text{n-Bu}_4\text{N}]\text{PF}_6$) with 0.5% (v/v) added H_2O under a CO_2 (black line) or a N_2 (red line) atmosphere (Scan rate: 100 mV s^{-1}); (d) Potentiostatic *i-t* curves obtained at an Ag-PMo nanocomposite modified GC electrode in DMF (0.1 M $[\text{n-Bu}_4\text{N}]\text{PF}_6$) with 0.5% (v/v) added water under CO_2 or N_2 atmospheres. Applied potential: -1.9 V vs. $\text{Fc}^{0/+}$. Reprinted with the permission of Ref. [105]. Copyright 2018, American Chemical Society.

ates, which decrease the overpotential, suppress the occurrence of side reactions, and improve the electrocatalytic CO_2 RR activity. The POM-modified Ag nanoparticles remained stable for more than three hours (Fig. 9(d)). This work illustrates the role of POMs in POM-involved nanocomposites for electrocatalytic CO_2 RRs, that is, POMs serve as Lewis bases to interact with CO_2 molecules in a Lewis acid-base interaction, which stabilizes the key intermediates in the CO_2 RRs, and promotes the activity of Ag toward electrocatalytic CO_2 RRs. However, the introduction of POMs still cannot deepen the reduction of CO_2 induced by the Ag catalyst, the main product is still 2-electron reduced CO.

Subsequently, Zhang and co-workers [106] used PMo_{12} as a protective agent in the production of ultra-thin Bi nanosheets under electrodeposition conditions. The obtained nanocomposite was used for the electrocatalytic reduction of CO_2 to formic acid in aqueous electrolytes. Using bipotential electrodeposition, the PMo_{12} polyoxoanions in the electrolyte interact with the Bi^{3+} cations through electrostatic interaction to promote the electroreduction of Bi^{3+} to form an ultra-thin (4 nm) porous 3D structure (Bi-PMo, Figs. 10(a) and (b)). In the absence of PMo_{12} , Bi^{3+} can only form a nano-dendritic structure under electrochemical reduction conditions. Raman spectroscopy (Fig. 10(c)) show that Bi-PMo nanosheets do not produce the characteristic peak of PMo_{12} , suggesting that during the preparation of the Bi-PMo nanosheets, the POMs may have decomposed. XPS spectra (Figs. 10(d) and (e)) indicate that the Mo in Bi-PMo exists in the form of MoO_x species. CV experiments (Fig.

Fig. 10. (a) SEM image of the film deposited on an FTO electrode in aqueous 0.25 M HNO_3 solutions containing 1.0 mM $\text{Bi}(\text{NO}_3)_3$; (b) Atomic force microscopy (AFM) image and height profile of Bi-PMo nanosheets; (c) Raman spectra of Bi-PMo nanosheets before (black) and after electrolysis (red), and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ (blue); (d,e) High-resolution XPS spectra recorded for Mo 3d and Bi 4f regions of the Bi-PMo nanosheets; (f) Cyclic voltammograms obtained for Bi-PMo nanosheet (solid lines) and Bi nano-dendrite (dash lines) modified GC electrodes in CO_2 - (black) or N_2 - (red) saturated 0.5 M NaHCO_3 aqueous solutions, scan rate: 0.1 V s^{-1} ; (g) Faradaic efficiencies for formate produced on Bi-PMo nanosheets (black) and Bi nano-dendrites (red) at various applied potentials in CO_2 -saturated 0.5 M NaHCO_3 solutions; (h) Long term stability study of Bi-PMo nanosheets during controlled potential electrolysis at -0.86 V vs. RHE in a CO_2 -saturated 0.5 M NaHCO_3 solution; (i) Tafel plots obtained for Bi-PMo nanosheets (black) and Bi nano-dendrites (red). Reprinted with the permission of Ref. [106]. Copyright 2019 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

10(f)) show that both Bi nanomaterials demonstrate CO_2 reduction activity. As shown in Fig. 10(g), in aqueous electrolyte solution (0.5 M KHCO_3), the ultra-thin Bi nanosheets selectively reduce CO_2 to formic acid with a FE of 93% at a potential of -0.86 V vs. RHE. Compared with the performances of Bi nano-dendrites, the overpotential of ultra-thin Bi nanosheets is 300 mV less, the FE for formic acid is 10% greater, and the FE for H_2 (resulting from side reactions) is suppressed. The catalytic activity of Bi-PMo is maintained for at least 10 h (Fig. 10(h)). The mechanism study (Tafel curve; Fig. 10(i)) found that the rate-limiting step of the process on ultra-thin Bi nanosheets is the protonation of the CO^* intermediate, while the rate-limiting step of the process on Bi nano-dendrites is the formation of CO^{*+} . The geometry of the ultra-thin Bi nanosheets, provides more reaction sites for the adsorption of CO_2 , which promotes the formation of CO^* intermediates, reduces the overpotential, and increases the FE for formic acid. Although the PMo_{12} decomposed during the electrocatalytic CO_2RRs , the electron transfer process and the electrostatic interaction between PMo_{12} and Bi^{3+} ensured the formation of Bi nanosheets, which provides new avenues for the design and synthesis of

POM-derived electrocatalysts. This work demonstrates a new approach to the preparation of electrocatalytic CO_2 reduction catalysts, with unique morphologies, using POMs. The performances of the reported POM-based electrocatalysts are compared with those of state-of-the-art electrocatalytic CO_2 reduction systems in Table 3.

4.5. DFT calculations of POM-based electrocatalysts for CO_2RRs

DFT is a powerful tool used to reveal key information of electrocatalytic CO_2RRs , including the geometric structures, electronic structures, adsorption characteristics, and electron transfer processes, which can well reveal the reactivity and mechanisms of CO_2RRs .

Lan *et al.* [37] used DFT calculations to illustrate the catalytic activity of different TM-modified PMOFs in terms of the adsorption free energy of key steps in the electrocatalytic CO_2RRs . During the assembly of Zn- ϵ -Keggin and Co-TCPP, the Co-PMOF exhibits remarkably lower ΔG_1 and ΔG_2 (Figs. 11(a) and (b)), which is consistent with the electroreduction activity and selectivity tendency of this PMOF. The reaction mechanism, based

Table 3Performance of major POM-based electrocatalysts and other representative electrocatalysts used in electrocatalytic CO₂RRs.

Electrocatalyst	Electrolyte	Potential	Principal product	FE (%)	TON	Ref.
(TOA) ₆ [α-SiW ₁₁ O ₃₉ Co(…)]	CH ₂ Cl ₂	–1.5 V vs. Hg ₂ Cl ₂ /Hg	CO	18	—	[97]
(TBA) ₃ [H ₂ PW ₁₁ O ₃₉ (Rh ^{III} Cp* (OH ₂))]	CH ₃ CN	–1.8 V vs. Hg ₂ Cl ₂ /Hg	HCOOH	4.5	0.8	[98]
[Cp*Rh ^{III} (bpy)Cl] ⁺	CH ₃ CN	–1.8 V vs. Hg ₂ Cl ₂ /Hg	HCOOH	60	18	[98]
[Mn(III)TRP] ⁵⁺ /[SiW ₁₂ O ₄₀] ⁴⁻ /ITO	0.1 M NaClO ₄	–0.8 V vs. Ag/AgCl	HCOOH	—	1.06 × 10 ⁴	[100]
[Zn(II)TRP] ⁴⁺ /[SiW ₁₂ O ₄₀] ⁴⁻ /ITO	0.1 M NaClO ₄	–0.8 V vs. Ag/AgCl	Methanol	—	1.76 × 10 ⁵	[100]
[Ni(II)TRP] ⁵⁺ /[SiW ₁₂ O ₄₀] ⁴⁻ /ITO	0.1 M NaClO ₄	–0.8 V vs. Ag/AgCl	CO	—	3.85 × 10 ³	[100]
[Ni(II)TRP] ⁵⁺	DMF	–0.8 V vs. SHE	CO	—	—	[107]
Co-PMOF	0.5 M KHCO ₃	–0.8 V vs. RHE	CO	98.7	7693	[37]
Fe-PMOF	0.5 M KHCO ₃	–0.8 V vs. RHE	CO	28.8	—	[37]
Ni-PMOF	0.5 M KHCO ₃	–0.8 V vs. RHE	CO	18.5	—	[37]
Zn-PMOF	0.5 M KHCO ₃	–0.8 V vs. RHE	CO	0.95	—	[37]
Co-TMCP	0.5 M KHCO ₃	–0.9 V vs. RHE	CO	~50	—	[37]
MOF-525(Co)	0.5 M KHCO ₃	–0.8 V vs. RHE	CO	47.9	—	[37]
CoPPC/CNT	0.5 M KHCO ₃	–0.58 V vs. RHE	CO	~90	—	[108]
SiW ₁₂ -MnL/KB	0.5 M KHCO ₃	–0.72 V vs. RHE	CO	95	—	[101]
PW ₁₂ -MnL/KB	0.5 M KHCO ₃	–0.72 V vs. RHE	CO	80	—	[101]
PMo ₁₂ -MnL/KB	0.5 M KHCO ₃	–0.52 V vs. RHE	CO	65	—	[101]
MnL/KB	0.5 M KHCO ₃	–0.72 V vs. RHE	CO	65	—	[101]
[Mn(L)(CO) ₃ Br (MnL)]	CH ₃ CN	–1.7 V vs. Ag/Ag ⁺	CO	85	34	[109]
AgNC@BSA	1 mM [Bu ₄ N] ₄ [α-SiW ₁₂ O ₄₀] in DMF	–2.32 V vs. Fc ^{0/+}	CO	75.6	—	[102]
Ag-PMo	DMF	–1.9 vs. Fc ^{0/+}	CO	90 ± 5	—	[105]
Ag/N-doped graphene/carbon foam	0.1 M KHCO ₃	–0.6 V vs. RHE	Ethanol	85.2	—	[110]
Ag QDDCs	0.5 M KHCO ₃	–0.3 V vs. RHE	CO	95	—	[111]
Indium sheet	2 mM SiW ₉ V ₃ + 0.1 M Na ₂ SO ₄	–1.15 vs. Ag/AgCl	CH ₃ COOH	96.5	—	[103]
Indium sheet	2 mM SiW ₁₁ Mn + 0.1 M Na ₂ SO ₄	–1.0 V vs. RHE	CH ₃ COOH	72.1	—	[104]
In ₂ O ₃ -rGO	0.1 M KHCO ₃	–1.2 V vs. RHE	HCOOH	84.6	—	[112]
Sulfur-doped indium	0.5 M KHCO ₃	–0.98 V vs. RHE	HCOOH	93	—	[113]
Bi-PMo nanosheets	0.5 M KHCO ₃	–0.86 V vs. RHE	CH ₃ COOH	93	—	[105]
Bi nano-dendrites	0.5 M KHCO ₃	–0.96 V vs. RHE	CH ₃ COOH	81	—	[105]
Bi nanoflakes	0.1 M KHCO ₃	–0.6 V vs. RHE	HCOOH	~100	—	[114]

— indicates that the data is not given.

on the DFT calculations, suggest that the POM components first accept electrons in the electrochemical process of CO₂RR (Fig. 11(c) and (d)), these electrons then transfer to the Co-TCPP units, which promotes the electrocatalytic CO₂RR activity on TCPP, therefore, the Co-PMOF shows higher catalytic activity than the parent Co-TCPP. This work uses DFT calculations to reveal the electrocatalytic CO₂ reduction activity of PMOFs modified with different metals in terms of the free energy of the electron/proton transfer step, which agree well with the experimental results. These DFT calculations provide a theoretical basis for revealing the regulation of catalyst activity during CO₂RRs.

Since electrocatalytic CO₂ reduction involves a complex electron transfer process, and the electron transfer process during electrocatalysis is very rapid and involves multiple time scales, DFT is an effective tool for studying the electron transfer processes in electrocatalytic CO₂RRs. Our research group and collaborators used DFT, in combination with transient spectroscopy experiments, to study the electron transfer process of different types of POMs and manganese carbonyl compounds (MnL), which revealed the reason for the synergistic effect of the electrocatalytic CO₂ reduction activity over POM-MnL. As shown in Fig. 12(a), analysis of the molecular orbital energy of

POM-MnL revealed that after POM is introduced into MnL, the lowest unoccupied molecular orbital (LUMO) of POM-MnL has complete participation of the W(4d) and O(2p) orbitals from the POM, which indicates that during electrocatalytic CO₂RRs, the POM units preferentially accept electrons, and only once the LUMO of the POM is filled does the MnL center undergo electrochemical reduction. This process has been confirmed through electrochemical CV, refer to Section 4.2, Fig. 6(c) for details. In order to reveal the electron transfer process between POM and MnL, the electronic structures of POM-MnL with different degrees of reduction were calculated. As shown in Fig. 12(b), when POM-MnL undergoes 4-electron reduction, the electrons stored on the POMs spontaneously transfer to the MnL component. Electron transfer to the MnL component occurs most easily in SiW₁₂ POM and least easily in PMo₁₂ POM. This electron transfer process is also captured by a transient photovoltage spectrum (Fig. 12(b)). In terms of energy, the SiW₁₂ POM has the lowest activation energy toward electrocatalytic CO₂RRs (Fig. 12(d)). This work reveals in detail the reduction process and electron transfer process of the multi-component electrocatalysts for electrocatalytic CO₂ reduction through DFT and experimental spectroscopy characterization and provides new insights for understanding the synergistic

Fig. 11. The DFT calculation and proposed reaction mechanism. (a) The free energy diagrams of CO₂ reduction to CO for POM (orange), Co-TCPP (green), and Co-PMOF (pink). The rate-determining step and the corresponding free energy of each material are indicated (Note that an asterisk represents a surface-active site for reaction); (b) Comparison of the free energy of each elementary reaction (ΔG_1 , ΔG_2 , and ΔG_3 represent the free energy of *COOH formation, *CO formation, and CO desorption, respectively) during CO₂RRs for Co-PMOF, Fe-PMOF, Ni-PMOF, and Zn-PMOF, respectively; (c,d) Proposed mechanism scheme for the CO₂RRs on Co-PMOF (POMs as electron-donors, porphyrins as charge transfer ligands, and TMs as electron-acceptors). Reprinted with the permission of Ref. [37]. Copyright 2018, Springer Nature.

effect of multi-component electrocatalysts and the electron transfer process of POM-based electrocatalysts.

5. Conclusions and prospects

Owing to the substantial overlap of polyoxometalate chemistry with material chemistry and catalytic chemistry, the application of polyoxometalates in the field of energy conversion field increasing, especially in electrocatalysis [115–118]. Informing the rapid development of POMs in electrocatalytic carbon dioxide reduction, are their ability to serve as models used to facilitate the understanding of key adsorption and activation processes of CO₂ reduction, the involved important intermediates, and the electron/proton transfer pathways, which provides important guidelines for the design of efficient and highly selective electrocatalysts for electrocatalytic CO₂RRs.

In this review, we highlight the advances in POM-based electrocatalysts for electrocatalytic CO₂ reduction and illustrate the key roles played by POMs in electrocatalytic CO₂RRs, providing insights into understanding the mechanism regulating electrocatalytic CO₂RR activity and selectivity. Despite the enormous progress that has been made in the development of POM-based electrocatalysts for CO₂ reduction, as outlined in this review, the important roles of POMs in the electrocatalytic process and the key steps involved in the electrocatalytic CO₂RRs over POMs require further clarification. Several challenges must be overcome in order to scale-up POM electrocatalysts for industrial application.

(1) Although the adsorption sites and activation modes of

CO₂ molecules on POM molecules are relatively clear, the adsorption-activation pathway of CO₂ as well as the rate-determining step on POM-based nanomaterials and nanoclusters require elucidation.

(2) While POMs are known to exhibit reversible electron storage and transfer behavior, owing to the rapid electron transfer kinetics of electrocatalytic reactions, the direct observation and capture of these processes are very difficult using conventional characterization methods [119,120]. Moreover, the electron transfer processes in electrocatalytic reactions are very complicated, involving intra-molecular, intermolecular, interfacial, and catalyst-reaction substrate electron transfer. Clarifying the mechanisms of these electron transfer processes is not only of scientific significance but can also offer rational guidance to optimizing and improving the reaction efficiency towards specific products of electrocatalytic CO₂RRs.

(3) The good solubility of POMs is an advantage in homogeneous catalysis but a disadvantage in composite heterogeneous electrocatalysts, since the dissolution of POM species during electrocatalysis deactivates the electrocatalysts. The stabilization of POM molecular structures requires specific conditions; some POMs are only stable in acidic environments, and decompose under neutral or alkaline conditions. However, due to the weak acidity of CO₂, the electrolyte used for CO₂ reduction is often neutral or alkaline, which benefits to the dissolution of CO₂ molecules. The development of polyoxometalates that are stable under electrocatalytic carbon dioxide reduction is a pressing challenge.

We speculate on possible solutions to these challenges and

Fig. 12. (a) Computed frontier orbitals (compositions and energies) for MnL, SiW₁₂-MnL, PW₁₂-MnL, and PMo₁₂-MnL (the green lines represent the unoccupied molecular orbitals (MO) contributed by MnL in POM-MnL); (b) The electronic configurations for the different reduction degree states of SiW₁₂-MnL, PW₁₂-MnL, and PMo₁₂-MnL; (c) The transient photovoltage curves of powder POM-MnL and MnL; (d) Potential energy surfaces for H⁺ and CO₂ addition to the respective active CO₂ and H adducts. Reprinted with the permission of Ref. [101]. Copyright 2020, Royal Society of Chemistry (RSC).

suggest development directions that should be focused on. By taking full advantage of the POM model to inform an in-depth understanding of the key influencing factors of electrocatalytic CO₂RRs, a blueprint for the design of efficient and highly selective CO₂RR electrocatalyst can be derived.

(1) CO₂ adsorption and activation are the most important factors affecting the activity and selectivity of electrocatalytic CO₂RRs, however, it is very difficult to observe these adsorption intermediate states. On the one hand, POMs can be used to clarify the characteristics of molecular structures, which, combined with computational chemistry, can be used to establish a scientific theoretical model for theoretical research. On the other hand, *in-situ*, time-resolved characterization techniques such as *in-situ* XPS, *in-situ* IR spectroscopy, and *in-situ* Raman spectroscopy can be developed to directly observe the intermediate states and adsorption sites during the reaction process.

(2) Electrocatalytic CO₂RRs involve complex proton/electron transfer processes, that occur at different time scales. The use of a combination of suitable time-resolved spectroscopies, such as time-resolved fluorescence spectroscopy, transient absorption spectroscopy, and transient photovoltage spectroscopy, is expected to offer insights into the electron transfer processes between different surface interfaces and components.

(3) Classic POMs tend to show good stability in acidic environments, while their stability is poor at higher pH values. Given their adjustable negative charges and abundant surface reaction sites, POM immobilization and encapsulation can be achieved through host-guest chemistry, coordination polymers or organic functional group modification to promote their electrochemical stability. Moreover, considering the rich elemental

composition of the POM family, POMs containing Nb, Pd, and Ti can be developed for electrocatalytic CO₂RRs, and used as a nanocluster models for the investigation of the active components in electrocatalytic CO₂RRs and broadening the stability of POMs to neutral or even alkaline conditions.

In summary, although our understanding of the critical role of POMs in electrocatalytic CO₂ reduction is still limited, there remains great potential for developing promising POM-based electrocatalysts. By exploiting the model role of POM-based electrocatalysts in electrocatalytic CO₂RRs to develop a deeper understanding of the activation, adsorption, and electron transfer processes during CO₂RR, it should be possible to control the product selectivity and reduction depth of CO₂RRs in order to convert CO₂ into the energy and chemicals on which humanity depends.

Author contributions

J. Du, H. Q. Tan, Z. H. Kang and Y. G. Li conceived the idea. J. Du. and Y. Y. Ma surveyed and summarized the literatures. All the authors discussed and wrote the manuscript.

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Graphical Abstract

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Progress of electrochemical CO₂ reduction reactions over polyoxometalate-based materials

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Recent progress in the field of electrochemical CO₂ reduction reactions over polyoxometalate (POM)-based materials have been summarized and critically reviewed, highlighting the activity origin and reaction mechanisms of POM-based materials.

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多金属氧酸盐材料在二氧化碳电催化还原领域中的研究进展

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摘要: 随着工业发展和全球人口的持续增长, 人类对化石燃料的消耗日益增加, 从而导致大气中二氧化碳含量的显著增加以及与之相伴的一系列环境问题。电化学还原二氧化碳制备高附加值的燃料和化学品具有稳定的效率和较高的经济可行性等特点, 目前已成为一种有前景的策略来缓解当前全球面临的能源短缺和气候变暖问题。然而, 电催化二氧化碳还原过程存在反应能垒高和复杂的多电子/质子耦合过程等不足, 因此, 合理有效的电催化剂设计成为该领域的关键问题。近年, 理解和明确电化学二氧化碳还原反应过程的活性起源、选择性调控机制和催化反应机理已成为高效电催化剂设计过程中的重要指导原则。作为一类独特的纳米尺度的金属氧簇, 多金属氧酸盐(多酸)已成为二氧化碳还原领域的热点材料。尤其是, 多酸明确的结构、优越的电子/质子存储转移能力和二氧化碳吸附活化能力有助于探究二氧化碳还原反应过程中的活性起源和构效机制。因此, 利用多酸阐明电化学二氧化碳还原反应中的这些关键问题对于开发高效、可实用化的电催化剂意义重大。

本文综述了近年多酸在电催化二氧化碳还原反应中取得的进展, 重点介绍了多酸阴离子均相分子催化剂、多酸基无机-有机杂化材料催化剂、多酸电解质溶液、多酸-纳米复合材料在电催化二氧化碳还原反应中的应用。利用密度泛函理论结合原位实验证据推测了可能的反应机理, 探讨了多酸对电催化活性和产物选择性的影响, 揭示了电子/质子存储-转移过程和多酸表面修饰工程在电催化二氧化碳还原过程中的重要作用。最后, 本文还分析了多酸基材料存在的问题与面临的挑战, 并对多酸基材料在二氧化碳还原领域的未来发展进行了展望, 这对理解电催化二氧化碳还原反应中的关键步骤和开发新型高效的电催化二氧化碳还原电催化剂具有启发意义。

关键词: 多金属氧酸盐; 电催化; 二氧化碳还原; 电子转移; 机理

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