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REVIEW ARTICLE

Research progress of polyoxometalates photocatalyst for degradation of organic wastewater

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ABSTRACT

Polyoxometalate (POM) is an eco-friendly solid acid. It is a polyatomic anion containing transition metal (group V or group VI) oxyanions, which are connected by common oxygen atoms. In addition to the advantages of other photocatalysts, such as non-toxic, no secondary pollution, convenient, fast and efficient, it also has the characteristics of high oxygen rich surface, and because there are a large number of metal centers in its structure, it can show rapid reversible and multi electron redox transformation. Its band gap is narrow, and the spectral response range is wide. It has excellent photocatalytic degradation performance, and has been widely used in photocatalytic degradation of wastewater containing organic pollutants. In this paper, the types of polyoxometalates photocatalysts, the modification methods of polyoxometalates and the application of polyoxometalates and its compounds in the degradation of organic pollutants are reviewed. The prominent problems and corresponding solutions of polyoxometalates photocatalytic degradation technology at present are pointed out, and its future development direction is prospected.

Keywords: Photocatalysis; Wastewater; Degradation; Catalyst; Environment; Polyoxometalates

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1. Introduction

The organic pollutants contained in water are easy to induce human beings to produce carcinogenic, teratogenic, mutagenic and other adverse effects. The original conventional physical, chemical and biological treatment methods are inefficient, and easy to lead to secondary pollution or pollutant transfer. It is difficult to make the treated wastewater meet the requirements of relevant laws and regulations. Therefore, the development of new and efficient wastewater treatment technology has become a research hotspot in the field of environment[1,2]. Photocatalytic degradation can overcome the shortcomings of the above treatment methods, and it is a new and effective organic wastewater treatment technology. Photocatalytic degradation technology has many advantages, such as complete degradation of pollutants, elimination of secondary pollution, fast reaction speed, strong degradation ability, energy conservation and efficiency, low cost, in line with environmental protection requirements, and can operate under mild conditions, which has aroused the widespread interest of researchers[3,4], and has become a research hotspot in the treatment of refractory organic pollutants in recent years, and has been widely used in the treatment of organic wastewater in different fields. Among them, photocatalyst plays a central role in the degradation process, and its catalytic performance directly affects the effect of degradation treatment. At present, the commonly used photocatalysts include TiO_2, semiconductor oxide, polyoxometalates (POM), CdS, graphite phase carbon nitride (g-C_3N_4) and MOF materials emerging in recent years, but the advantages and disadvantages of various photocatalysts are different, such as light response, preparation process, light stability, economic cost and so on. In addition to the advantages of other photocatalysts, such as no secondary pollution, convenience, rapidity and efficiency, POM also has a series of excellent characteristics such as high oxygen enriched surface and strong redox ability, which has been widely used[5–8]. However, there are few reviews on the photocatalytic effect of POM at present. In order to better promote the treatment of organic wastewater containing refractory pollutants, it is very necessary to review the performance and application characteristics of efficient POM photocatalysts.

In this paper, the types of polyoxometalates photocatalysts, the modification methods of polyoxometalates and the application of polyoxometalates and its compounds in the degradation of organic pollutants are reviewed, the prominent problems and corresponding solutions of polyoxometalates photocatalysts and photocatalytic degradation technology at present are pointed out, and its future development direction and application prospects are prospected.

2. The introduction of polyoxometalates photocatalyst

Polyoxometalate (POM) is an eco-friendly solid acid. It is a polyatomic anion containing transition metal oxyanions, which are connected by shared oxygen atoms. The metal atoms are usually transition elements of the V or VI sub groups, which are in their high oxidation state (as shown in **Figure 1**). The electron distribution of transition metals such as molybdenum (Mo), vanadium (V), tantalum (Ta), niobium (Nb) and tungsten (W) is d^0 or d^1, so that POM can surround one or more heteroatoms such as phosphorus or silicon. For example, the phosphotungstate anion ($[PW_{12}O_{40}]^{3-}$) is composed of 12 octahedral tungsten polyoxyanion frameworks surrounding a central phosphate group.

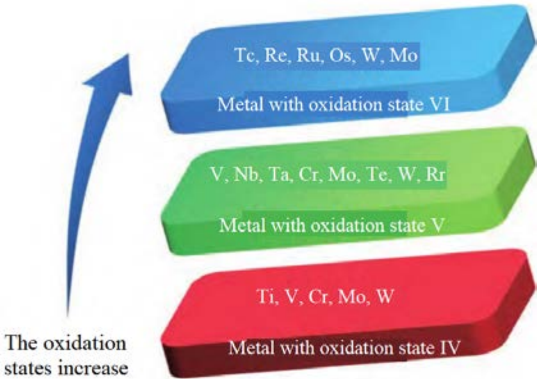

Figure 1. Oxidation states of heteroatoms in POMs.

POM photocatalyst not only integrates the advantages of traditional photocatalysts, but also has excellent characteristics such as dissolving polar molecules, easily tunable electronic properties, high oxygen rich surface, strong oxidation ability, etc., its unique metal oxygen-containing cluster structure makes it similar to semiconductors. In addition, POM has obvious physical adsorption on most organic dyes such as methylene blue, methyl orange, Congo red, etc., which can better remove organic pollutants through the dual effects of photocatalytic degradation and adsorption, so that it has been widely used as a photocatalyst in the photocatalytic degradation of organic pollutants.

3. Classification of polyoxometalates photocatalysts

POM can be mainly divided into two categories, namely homopolyanion polyoxometalates and heteropolyanion polyoxometalates[9]. The general structural formula of the same polyanion is $[M_mO_o]^{-p}$, which is composed of d^0 group metal cations and oxygen-containing anions or paragroup metals and oxygen. By polymerization in acid solution, the coordination number of accessory metals with oxygen can be changed between 4–6, and has a high positive charge. Heteropolyanions are composed of heteroatoms, d^0 group metal cations and oxygen-containing anions. Its general structural formula is $[X_xM_mO_0]^{-q}$, M is a metal cation, and X can be Si(V), P(IV), B(III), etc. Heteropolyanions are formed by acidifying the solution to make MO_x(x = 4–7) gather around heteropolyanions. In this case, various elements with different coordination numbers can participate in the reaction to form different polyoxometalates. PO_4^{3-}, SiO_4^{4-}, and AsO_4^{3-} in Keggin type and wells-Dawson type polyoxometalates is 4 (tetrahedron); $Al(OH)_6^{3-}$ and TeO_6^{6-} in the structure of Anderson Evans polyoxometalates, the coordination number is 6 (octahedron); the coordination number of $[(UO_{12})Mo_{12}O_{30}]^{8-}$ is 12 (Silverton polyoxometalates). Homopolyanionic polyoxometalates are only composed of metal and oxygen atoms, which can be divided into different categories according to the type of heteroatoms. Molybdate, tungstate, vanadate, niobate and tantalate are the most important types.

According to the type of heteroatom, heteropolyanion heteropolyacid can be divided into two categories, central heteropolyanion heteropolyacid and cortical heteropolyanion heteropolyacid. The structure of central heteropolyacid requires a heteroatom to complete and maintain its family structure. The heteroatom in this kind of heteropolyacid cannot move without destroying its structure. Cortical heteropolyacid has a secondary heteroatom, and the loss of this heteroatom will not affect its structure and stability.

Due to the special structure of polyoxometalates photocatalyst, its absorption peak is located in the ultraviolet region, and its tail band can extend to 350–400 nm. By changing the composition of polyoxometalates, its spectral properties can be effectively adjusted to overcome the characteristics of titanium dioxide with wide band gap, narrow spectral response range and absorption wavelength mainly concentrated in the ultraviolet region.

4. Modification of polyoxometalates photocatalyst and its application in degradation of organic pollutants

Polyoxometalates photocatalysts are used for homogeneous photocatalytic degradation of organic pollutants. The ·OH radical produced by the reaction of photon excited POM with water plays a key role in the degradation process. The photocatalytic degradation ability of POM has been proved in the degradation of various organic pollutants, including dyes, phenol, chlorophenol, chloroacetic acid and pesticides. The results show that these organic molecules are completely degraded into carbon dioxide, water and corresponding inorganic anions, and these organic pollutants can be removed from wastewater through a simple one pot process[10].

Among the classical structures of polyoxometalates (POM), Keggin type polyoxometalates are most widely used in photocatalytic degradation of organic wastewater. Although the classical polyoxometalates have good photocatalytic performance, their specific surface area is small and their thermal stability is poor. At the same time, most of the polyoxometalates are water-soluble substances, which are easy to cause secondary pollution and the wastewater is difficult to be further treated. In order to overcome the shortcomings of classical polyoxometalates, polyoxometalates salts containing Keggin skeleton structure are prepared. These polyoxometalates salts can not only maintain the excellent catalytic performance of polyoxometalates, but also insoluble in water, and can be recycled, easy to separate solid and liquid. They are environmental-friendly products for the degradation and treatment of organic wastewater. At present, the widely accepted photocatalysis mechanism of polyoxometalates is: the ground state electrons in POM obtain energy under UV irradiation, and the transition of O→M (oxygen bridge transition to metal) metal ligands occurs[11], followed by the formation of hole centers and electron capture centers, which is similar to the separation of photogenerated electrons and photogenerated holes (e^- and h^+) in semiconductors; then, active ·OH radicals are generated by “spin trapping reaction” with absorbed oxygen, and finally organic molecules are oxidized and decomposed by ·OH[12].

The proposed heterogeneous photocatalytic degradation mechanism of dyes can be expressed as follows:

$$POM + hv \rightarrow POM\left(h_{VB}^{+} + e_{CB}^{-}\right) \tag{1}$$

$$POM(e_{CB}^{-}) + O_2 \rightarrow POM + O_2^{-} \tag{2}$$

$$O_2^{-} + H^{+} \rightarrow HO_2^{-} \tag{3}$$

$$HO_2^- + O_2^- + H^+ \rightarrow H_2O_2 + O_2 \tag{4}$$

$$2HO_2 \rightarrow H_2O_2 + O_2 \tag{5}$$

$$HO_2^{\cdot} + H^+ + POM\left(e_{CB}^-\right) \rightarrow POM + H_2O_2 \tag{6}$$

$$HO_2^{\cdot} + O_2^- \rightarrow OH + OH^- + O_2 \tag{7}$$

$$H_2O_2 + POM\left(e_{CB}^-\right) \rightarrow POM + OH^- + OH^- \tag{8}$$

$$H_2O + POM\left(h_{VB}^+\right) \rightarrow POM + OH^- + H^+ \tag{9}$$

$$OH^- + POM\left(h_{VB}^+\right) \rightarrow POM + OH^- \tag{10}$$

$$\text{dye} + OH \rightarrow \text{degradationproduct} \tag{11}$$

$$\text{dye} + POM\left(h_{VB}^+\right) \rightarrow \text{oxidation product} \tag{12}$$

$$\text{dye} + POM\left(e_{CB}^-\right) \rightarrow \text{reduction product} \tag{13}$$

$$H_2O_2 + hv \rightarrow 2OH^- \tag{14}$$

Table 1. Forbidden band width, valence band, and absorption boundary of common POM (V *vs*.NHE, pH = 7)

Common POM	Band gap	Valence band/eV	Conduction band/eV	Solution absorption boundary/nm
$H_3PW_{12}O_{40}$	3.344	3.31	−0.034	372
$H_3PMo_{12}O_{40}$	2.65	2.21	−0.44	468
$H_4SiW_{12}O_{40}$	3.00	2.63	−0.37	430
$H_5BW_{12}O_{40}$	3.46			359
$H_6CoW_{12}O_{40}$	3.34			372
$H_3AsMo_{12}O_{40}$	2.9			428
$H_3PMo_9W_3O_{40}$	2.73			454
$H_3PMo_6W_6O_{40}$	2.93			425
$H_3PMo_3W_9O_{40}$	3.02			411
$H_3PMo_1W_{11}O_{40}$	3.1			400
$H_4PW_{11}V_1O_{40}$	2.56			485
$H_5PW_{10}V_2O_{40}$	2.37			524
$H_6PW_9V_3O_{40}$	2.32			534
$H_4PMo_{11}V_1O_{40}$	2.36			526
$H_5PMo_{10}V_2O_{40}$	2.33			532
$H_6PMo_9V_3O_{40}$	2.31			536

Although polyoxometalates have many advantages, their high solubility in water limits the further expansion of their application fields. Therefore, it is necessary to develop heterogeneous POM photocatalysts that are efficient, easy to recover and reusable. In order to achieve this goal, researchers have carried out various work. For example, POM is fixed on montmorillonite, activated carbon, functional polymers, resins and oxides. Some researchers also solidified LbL compounds such as polymers and layered double hydroxides by embedding them[14]. Another obvious disadvantage of POM as a photocatalyst is that it has no catalytic activity under visible light, which is caused by the high band gap between the highest occupied molecular orbital (HOMO) and the lowest occupied molecular orbital (LUMO) (3.34 eV for $PW_{12}O_{40}^{3-}$), so they can only be used as photocatalysts under ultraviolet light[15]. Ultraviolet light accounts for only 4% of the total sunlight, which seriously limits the application of POM in the real world. **Table 1** summarizes the band gap widths, valence conduction bands, and their absorption boundaries of common POMs.

To solve this problem, researchers synthesized a series of POM-based compounds and used them for the degradation of various organic pollutants. According to the current research results, in order to overcome the above shortcomings of traditional polyoxometalates, the modification methods of polyoxometalates mainly include Substituted Polyoxometalates, modified anti charged ion polyoxometalates, organic-inorganic modification methods, and polyoxometalates loading methods. Among them, the combination of loading method and the previous modification methods is the most commonly used method at present.

4.1 Substituted Polyoxometalates and their application in the degradation of organic pollutants

Taking the common Keggin type 12-phosphotungstic acid ($H_3PW_{12}O_{40}$) as an example, the missing phosphotungstic acid (P-W-O) can be synthesized first, and then a variety of transition metals (Mo, V, etc.) can be inserted into the vacancy to form transition metal substituted phosphotungstic acid, so as to enhance its oxidation-reduction ability, improve thermal stability and expand the scope of application[16]. Hori *et al.*[17] showed that using $H_4SiW_{12}O_{40}$ as photocatalyst can realize the decomposition of hydrofluoric acid and other bioaccumulative surfactants. In the absence of $H_4SiW_{12}O_{40}$, the pollutant will not decompose under UV visible light irradiation (>290 nm), but when $H_4SiW_{12}O_{40}$ and UV visible light irradiation exist at the same time, the pollutant can be effectively decomposed into fluorine ions and carbon dioxide. The reaction mechanism of this process can be explained by the following process: the activated catalyst will remove hydrogen ions from hydrofluoric acid ω-H atom is removed and perfluorocarboxylic acid is produced. In pulp bleaching, POM and its complex can make the pulp look brighter and remove lignin by removing chromophores. If the pulp bleaching wastewater is not treated, the chromophore and residual lignin will produce chlorinated aromatic hydrocarbons and dioxin compounds, which will pose a serious threat to human health and the environment. In recent years, heteropoly acid salts and oxygen have been used to bleach pulp in the paper industry. According to the research results of Qian *et al.*[18], $H_5PMoV_2O_{40}$ is a suitable photocatalyst suitable for degrading chromophores and residual lignin.

Hu *et al.*[19] studied the effectiveness of several Keggin type polyoxometalates as photocatalysts in the degradation of organic pollutants (condition: irradiation with ultraviolet light in water with pH = 10). These polyoxometalates include $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4GeW_{12}O_{40}$, $H_3PMo_{12}O_{40}$. The relative activity order of these polyoxometalates is $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_4GeW_{12}O_{40} > H_3PMo_{12}O_{40}$. The removal efficiency of pollutants depends on the pH value of the solution, light intensity and the amount of catalyst, but it is not significantly related to the concentration of dissolved oxygen in the wastewater. The mechanism study shows that hydroxyl radicals participate in the degradation process. Ji *et al.*[20] prepared a series of phosphorus tungsten vanadium polyoxometalates salt (MPWV) photocatalysts and studied their performance in the degradation of phenol containing wastewater. It was found that, using 2 $\mu mol\cdot L^{-1}$ $Fe_5(PW_{10}V_2O_{40})_3$ and 4 $\mu mol\cdot L^{-1}$ hydrogen peroxide as photocatalysts, under the irradiation of a 10 W mercury lamp, 50 $mg\cdot L^{-1}$ containing 50 $mg\cdot L^{-1}$ could be obtained within 60 min. The degradation rate of phenol in the phenol solution reaches more than 96%, and the photocatalyst effect is excellent. It was found that the order of photocatalytic degradation effect was FePWV > ALPWV > CuPWV > HPWV. It shows that this kind of photocatalyst has a very broad application prospect in the degradation of phenol containing wastewater.

Although substitution modification can reduce the photodegradation cost of polyoxometalates and improve the water solubility problem, the photocatalytic degradation efficiency will also be reduced. At the same time, when the dye concentration in the wastewater is too high, it will also hinder the light absorption of the catalyst, thereby reducing the efficiency of the catalyst. Therefore, in the future, we should mainly focus on how to improve the applicability and application range of the catalyst.

4.2 Changing the anti-charged ionic polyoxometalates and its application in the degradation of organic pollutants

Using monovalent cations such as K$^+$, Cs$^+$, NH$_4^+$, etc., to form insoluble salts with POM is a classical method to overcome the solubility defects of POM. By changing the counter charged ions, POM can not only have a larger specific surface area, but also provide more acidic sites. Chen *et al.*[21] prepared microporous solid $K_3PW_{12}O_{40}$ with phosphotungstic acid and potassium ion as raw materials. The material is used as photocatalyst and irradiated with visible light ($\lambda > 420$ nm) and hydrogen peroxide effectively degraded a series of dye pollutants such as rhodamine B. The photocatalyst was characterized by scanning electron microscope, BET specific surface area, infrared spectrum and X-ray diffraction. The photocatalyst has a large specific surface area, and the Keggin type structure of phosphotungstate radical is complete during precipitation and calcination. The degradation kinetics, TOC changes, degradation products, ESR detection of reactive oxygen species and the role of free radical scavengers were studied, and the degradation process and reaction pathway were clarified. Dyes can be easily bleached and mineralized (TOC removal rate of RHB is about 40%). In addition to CO_2, the main degradation products of RHB are small molecular organic acids. They are released from the catalyst surface to the bulk solution in the process of dye degradation, avoiding the toxicity of intermediates to photocatalysts. Reactive oxygen species, such as $O^{2-}\cdot/HO_2\cdot$ and $\cdot OH$, were detected in the process of dye degradation, which were the main reasons for dye degradation. $K_3PW_{12}O_{40}$ catalyst is very stable and can be easily separated from the reaction system for reuse. Ghalebi *et al.*[22] prepared cesium phosphomolybdate ($Cs_3PMo_{12}O_{40}$) by solid-state method and used it as a photocatalyst to degrade basic red 46 (BR46) dye. Cesium phosphomolybdate is a porous material with Keggin type structure. $Cs_3PMo_{12}O_{40}$ has a higher specific surface area and a narrower band gap than the original Keggin type heteropoly acid $H_3PMo_{12}O_{40}$. Its forbidden band width was determined to be 2.35 eV by UV-Vis diffuse reflectance spectroscopy. Under simulated sunlight (xenon lamp), $Cs_3PMo_{12}O_{40}$ nanoclusters showed high photocatalytic degradation activity for Basic Red 46 dye. The results show that the hydroxyl radicals and electron hole pairs produced by photocatalysis are the main reasons for the photodegradation of BR46. The presence of hydrogen peroxide significantly improved the photocatalytic activity of cesium phosphomolybdate. At the same time, cesium phosphomolybdate catalyst is very stable and easy to separate from the reaction system for reuse. Yue *et al.*[23] prepared a new $(NH_4)_3PW_{11}O_{39}Sn/TiO_2$ composite photocatalyst by impregnation method, characterized the prepared catalyst by XRD, SEM, XPS and DRS, and used it for the degradation of acid red 3R (AR3R) dye. The results show that $(NH_4)_3PW_{11}O_{39}Sn/TiO_2$ has good visible light response ability, and AR3R can reach 100% degradation after 30min under visible light irradiation. The results of scavenging experiments show that holes and ·Oh play a crucial role in the photocatalytic process, while $\cdot O_2$ plays a very small role. Wang et al.[24] prepared a new visible light active composite material $Cs_3PMo_{12}O_{40}/Bi_2O_3$($CsPMo/Bi_2O_3$) by a simple solution precipitation method. The samples were characterized by XRD, XPS, FT-IR, SEM, UV-Vis-DRS, N_2 adsorption desorption isotherms and electrochemical analysis. The results show that Bi_2O_3 has been successfully modified by trace cspmo. After adding $H_3PMO_{12}O_{40}$ (HPMo), the surface of Bi_2O_3 can be roughened. Meanwhile, the presence of Cs_2CO_3 can neutralize the protons of HPMo and form cspmo precipitation on Bi_2O_3. Compared with Bi_2O_3 and CsPMo alone, binary composites show many beneficial characteristics in charge generation and separation, such as the formation of p-n heterojunction, the reduction of band gap, the enhancement of photocurrent response and the significant reduction of charge transfer resistance. The photocatalytic activity of the samples was evaluated by degrading phenol under visible light. The pseudo-first-order rate constants for the degradation of phenol are 2.7 and 14.8 times higher than those of Bi_2O_3 and CsPMo, respectively. The $CsPMo/Bi_2O_3$ composite with the best ratio (2.5% wt CsPMo) can significantly improve the photocatalytic performance. The activities of the main active substances involved in the degradation process are superoxide radical ($O_2^{\cdot-}$) > hydroxyl radical (·OH) > hole (h^+). The charge separation mechanism of CsPMo/Bi_2O_3 composite under visible light is shown in **Figure 2**. In addition, CsPMo/Bi_2O_3 composites also showed good stability in cyclic experiments. For the anti-charge ion modified polyoxometalates, future research should focus on the low-cost and excellent anti-charge ions, including K^+, Rb^+, Cs^+, NH_4^+, etc.

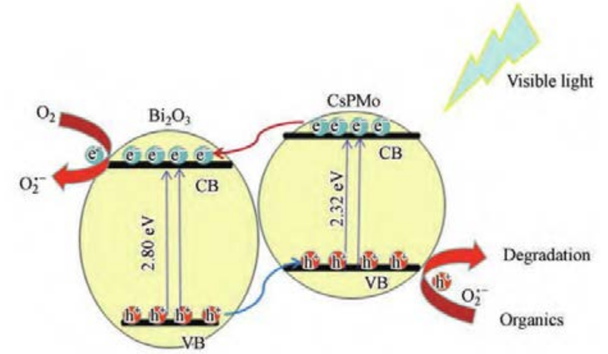

Figure 2. Proposed mechanism for charge separation in CsPMo/Bi_2O_3 composite under visible light irradiation.

4.3 Organic inorganic modification of polyoxometalates and their application in the degradation of organic pollutants

The organic-inorganic hybrid materials based on Polyoxometalates have the advantages of high stability of inorganic components and high flexibility of organic components. At present, the common methods of hybrid method include (1) constructing organic polymer material carrier[25], using the advantages of polymer such as high corrosion resistance and high functionality to cooperate with POM to realize selective catalysis, but the cost of organic polymer is high and the cost performance ratio is low; (2) to construct metal organic framework materials (MOFs)[25], POM can be combined with organic framework as inorganic node by covalent bond, which has higher stability than simple loading method, and can significantly improve the problem of POM catalyst stripping.

Liu *et al.*[26,27] synthesized a metal organic skeleton ($Cu_3(BTC)_2$，BTC = 1,3,5-benzoic acid) composite based on Polyoxometalate ($H_6P_2W_{18}O_{62}$) by a simple one pot solvothermal method, and used it as an adsorbent to remove methylene blue (MB) from aqueous solution. The chemical structure, morphology and thermal stability of the composites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric analysis (TG) and N_2 adsorption isotherm. The removal rate of the composite $H_6P_2W_{18}O_{62}@Cu_3(BTC)_2$ was higher than that of pure $Cu_3(BTC)_2$, especially at higher initial concentrations, indicating that the modified $H_6P_2W_{18}O_{62}$ could improve the adsorption performance of porous $Cu_3(BTC)_2$. At the same time, the effects of initial concentration, contact time, initial solution pH value and temperature on the adsorption of MB on the composites were systematically studied. The experimental isotherm data were in good agreement with the Freundlich model, and the adsorption process of MB on H6P2W18O62@Cu3(BTC)$_2$ is governed by a pseudo-second-order kinetic model. Thermodynamic parameters suggest that the adsorption is a spontaneous exothermic process. These results suggest that designing metal-organic framework composites is a very promising strategy to realize extreme applications of metal-organic frameworks. Liu *et al.*[28] firstly used a new type of linker TTPB-4 and the self-assembly behavior of CdI_2 to construct metal-organic framework compounds, and then used Keggin-type heteropolyacid $H_3PMo_{12}O_{40}$(POM) as a template to prepare by hydrothermal method. POM-based metal organic framework material $[Cd(TTPB\text{-}4)(DMF)_3]_4[PMo_{12}O_{40}]_2[HPMo_{12}O_{40}]$. 6DMF·4$H_2O$(POM-MOF) using IR, XRD, TGA, UV-Vis and fluorescence spectroscopy prepared photocatalysts were characterized, and the photocatalytic degradation performance of the prepared catalysts on dyes such as crystal violet and basic red 2 was studied. The results showed that the prepared POM-MOF had strong chemical stability and could withstand pH. At the same time, compared with pure heteropolyacids, POM-MOF has higher photocatalytic degradation activity towards crystal violet and basic red 2 in solutions of various pH values, and has better recyclability.

With the in-depth study of polyoxometalates and MOF composites, a variety of smart and flexible framework materials have emerged, broadening the catalytic application of POM. However, this method has the disadvantages of high cost and low selectivity, which is an urgent problem to be solved in the development of such materials in the future. In the future, organic-inorganic modified polyoxometalates may be improved mainly in the direction of low cost, high environmental protection, high applicability and high selectivity.

4.4 Modified polyoxometalates by loading method and its application in degradation of organic pollutants

The main reason for the reduction of the catalytic capacity of polyoxometalates photocatalyst is the leaching of active components. In addition, the limitation of mass transfer resistance and diffusion on the active site of catalytic reaction also highlights the disadvantage that POM is easily soluble in polar solvents. In order to overcome such defects, loading POM on different carriers can improve its solubility and increase its specific surface area. High specific surface area is not only conducive to the contact between catalyst and dye, but also can increase the acidic sites on the surface of catalyst, so as to improve the catalytic efficiency. At present, the carriers carrying POM mainly include titanium dioxide, magnetic materials, silicate, molecular sieve, bismuth oxide (bismuth salt), etc.

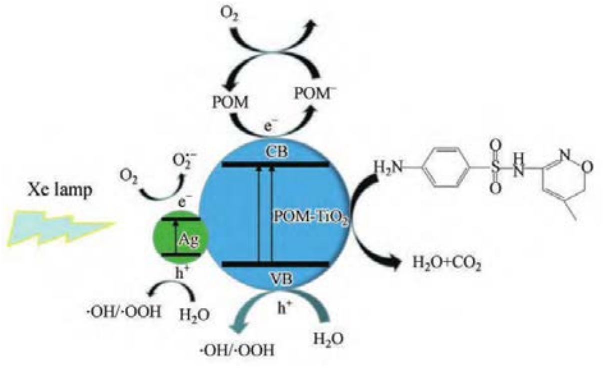

Figure 3. SMZ degradation process over the Xe lamp irradiation of the $H_3PW_{12}O_{40}/Ag\text{-}TiO_2$ material.

At present, the research on Polyoxometalates-supported on titanium dioxide is relatively most and mature. In this composite system, because the reduction potential of heteropolyanions is higher than that of titanium dioxide, when the excited electrons transition from the conduction band of titanium dioxide, the composite system will release more electronegative heteropolyanions, thus having stronger photocatalytic performance[29]. Xu *et al.*[30] synthesized Keggin pom/metallic silver/titanium dioxide ($H_3PW_{12}O_{40}/Ag\text{-}TiO_2$) by sol-gel hydrothermal method. The catalyst has photocatalytic activity under both UV and visible light. The improvement of photocatalytic activity of titanium dioxide depends on its size reduction and the good dispersion of Keggin clusters and metallic silver in the composite matrix. When using the catalyst, it can be irradiated by xenon lamp (320 nm < λ < 680 nm) to remove drug pollutants such as sulfamethoxazole (SMZ) from wastewater. Many research results have proved that the combination of $H_3PW_{12}O_{40}$ and TiO_2 can enhance the photocatalytic effect of titanium dioxide, because there is synergy between them and the strong electron acceptance ability of Keggin clusters, which leads to the transfer of electrons from Keggin clusters to oxygen atoms in the reaction medium[31]. The photocatalytic mechanism process of the complex is shown in **Figure 3**. After 120 minutes of visible light irradiation, using $Ag\text{-}TiO_2$ and $H_3PW_{12}O_{40}/Ag\text{-}TiO_2$ as photocatalysts, the degradation rate of SMZ ($40 mg\cdot L^{-1}$) respectively reached 35.7% and 51.3%. The high photocatalytic degradation efficiency of $H_3PW_{12}O_{40}/Ag\text{-}TiO_2$ may be due to the following reasons. First, compared with the photocatalytic system of $H_3PW_{12}O_{40}/Ag\text{-}TiO_2$ without metallic silver, using $H_3PW_{12}O_{40}/Ag\text{-}TiO_2$ can produce more h_{VB}^+ and e_{CB}^- to participate in the photocatalytic reaction. Second, due to the strong electron acceptance ability of POM and metallic silver, the recombination of h_{VB}^+ and e_{CB}^- is delayed, thereby enhancing the quantum efficiency of $H_3PW_{12}O_{40}/Ag\text{-}TiO_2$. The initial acidity of the reaction medium, the initial concentration of SMZ and the amount of photocatalyst all affect the removal efficiency of pollutants. The photocatalytic activity of the photocatalyst did not decrease significantly after repeated use.

Wang *et al.*[32] prepared a composite photocatalyst ($HPW\text{-}Y\text{-}TiO_2$) by loading phosphotungstic acid (HPW) in yttrium doped titanium dioxide by sol-gel method and impregnation method, and studied its ultraviolet radiation (λ ≥ 365 nm). The results showed that when $HPW\text{-}Y\text{-}TiO_2$ was used as photocatalyst to degrade methyl orange in wastewater, the inorganic anions such as Cl^-, SO_4^{2-},CO_3^{2-},NO_3^- etc., in wastewater had an adverse effect on the degradation efficiency. The addition of hydrogen peroxide and ethanol can significantly improve the degradation efficiency of methyl orange. Yang *et al.*[33] first combined sol-gel technology with programming, designed and prepared uniformly dispersed polyoxytungstate ($H_3PW_{12}O_{40}$) nanoparticles at a low temperature (200 °C), and combined them with nano porous anatase TiO_2 crystal particles to obtain $H_3PW_{12}O_{40}/TiO_2$. The materials were characterized by UV diffuse reflectance spectroscopy, XRD, ^{31}P MAS NMR, TEM and nitrogen adsorption. This new photocatalyst can degrade 10 kinds of organic dyes in water by changing their chemical structure under visible light catalysis. The intermediate and final products of degradation were detected by electrospray spray mass spectrometry (ES-MS) and ion chromatography (IC). The results showed that the prepared material had high photocatalytic activity for the degradation of dyes under visible light irradiation, and the recyclable catalyst was separated after the reaction. After the catalyst was recycled for 3 times, almost the same dye conversion was obtained, which showed that the photocatalytic activity of the composite was very stable under visible light irradiation. Rafiee *et al.*[34] prepared $[(C_4H_9)_4N]_5PW_{11}Co\text{-}O_{39}(CoW)@TiO_2$ composite photocatalyst by sol-gel hydrothermal method, and studied its photocatalytic degradation effect on methyl orange (MO). The results showed that the composite photocatalyst with 10% wt of CoW loading had the best photocatalytic degradation effect. When the initial dye concentration is 1.0 $g \cdot L^{-1}$, the loading amount of cow is 10% wt, the initial pH value of the solution is 5, and the catalyst concentration is 3 $g \cdot L^{-1}$, the degradation rate of MO can reach 98.058%. At the same time, the composite photocatalyst has a good recycling effect, and the photocatalytic activity basically does not decrease after recycling for more than 4 times. Shi *et al.*[35] prepared a polyoxometalates salt titanium dioxide composite photocatalyst ($PMo_{12}O_{40}(PMo_{12})/\text{-}TiO_2/Ag$) supported on silver nanoparticles. The photocatalytic degradation experiment showed that under visible light irradiation ($\lambda > 420$ nm), $PMo_{12}/TiO_2/Ag$ has high photocatalytic degradation effect on methyl orange (MO), and has strong sustainability of activity. In the range of silver nanoparticles loading studied, when the loading amount of silver is 5. The photocatalytic activity of the composite photocatalyst prepared at 41% wt was the highest, and the methyl orange with a concentration of 20 $mg \cdot L^{-1}$ could be completely degraded in 120 min. The photocatalysis mechanism shows that both silver and PMo_{12} can be excited under visible light irradiation, which can significantly improve the visible light absorption capacity of the prepared composite photocatalyst. In addition, the introduction of POM can not only improve the light absorption capacity and redox capacity of titanium dioxide, but also improve the photochemical stability of the composite photocatalyst, because the band gap of POM is relatively narrow and the reversible redox potential of polyoxyanion is low.

However, the light response range of titanium dioxide and polyoxometalates (POM) are concentrated in the ultraviolet region, which makes its application range narrow. Therefore, researchers try to composite POM with silicate, molecular sieve, bismuth semiconductor materials, graphene, magnetic materials and other carriers to broaden the light response range of photocatalysts and expand their application fields. The synergistic effect of Lewis acid of some silicates and Bronsted acid of POM to enhance the degradation activity is the unique advantage of polyoxometalates modified by silicate loading method. Yahya *et al.*[36] successfully prepared mesoporous silica aerosol/polyoxometalates salt $H_3PW_{12}O_{40}$ composite photocatalyst under mild conditions. The prepared catalyst was characterized by FTIR, TGA, XRD, UV-Vis, AAS, BET, SEM and EDX. Under UV irradiation, Rhodamine B and methylene blue were used as model dyes to study its photocatalytic degradation performance. The results showed that the prepared composite photocatalyst had a good photocatalytic degradation effect on Rhodamine B and methylene blue. Under UV irradiation, the degradation rates of methylene blue and Rhodamine B reached 81%–98% and 55%–90% within 120 min. UV-Vis method was used to track the intermediate products formed in the degradation process. The results showed that the photocatalytic degradation process could be completed in a short time of 5 min.

Molecular sieves have the characteristics of large specific surface area and uniform pore structure. Loading POMs on molecular sieves can narrow the energy band gap and expand the light response range to the direction of visible light, which can effectively improve its catalytic effect. Dubey *et al.*[37] incorporated transition metal TiO_2 and heteropoly acid (HPA) into the zeolite structure to prepare a new photocatalytic material, which was characterized by XRD, UV visible diffuse reflectance spectroscopy and elemental analysis. In the presence of 1:40 ethanol water mixed solvent, the photocatalytic activity of the material for the photoreductive degradation of methyl orange under visible light was studied. Compared with Zeo-Y/TiO_2/HPA, the photocatalytic activity of Zeo-Y/TiO_2/Co^{2+}/HPA for methyl orange was as high as 4.11 $mg \cdot g^{-1}$, indicating the role of transition metal ions. The interaction of transition metal ions and HPA can improve the visible light catalytic performance, and these components and molecular sieve framework may also help to delay charge recombination.

In recent years, it has been found that the band gap of graphene oxide (GO) can be increased by sp^3 hybridization of carbon on the surface[38], so that graphene oxide becomes a hole rich, multi electronegative oxygen atom semiconductor. By introducing guest into the main body of graphene, a stable and efficient photogenerated charge system can be established to further strengthen the photocatalytic performance[39], so researchers began to use graphene oxide in the preparation of photocatalysts. Fakhri *et al.*[40] prepared a series of polyoxometalates based functionalized graphene oxide complexes $H_3PMo_2W_{10}O_{40}$@ ethylenediamine functionalized graphene oxide with ethylenediamine as crosslinking agent (Mo_2W_{10}@EDMG) and $H_3PMo_4W_8O_{40}$@ ethylenediamine functionalized graphene oxide (Mo_4W_8@EDMG), characterized by XRD, TEM and FT-IR. The photocatalytic degradation performance of these two composite photocatalysts was studied by using methylene blue as a model dye under visible light irradiation. The results show that the prepared photocatalyst has excellent photocatalytic degradation performance, 20% Mo_4W_8@EDMG Methylene blue can be degraded 100% in 50 min. Mechanism studies show that amine functionalization can produce crosslinked porous networks and positively charged quaternary nitrogen atoms to load POM anion guest, and the coated polyoxometalates can optimize the electron transport of the system. At the same time, the presence of POM guest can enhance the stability of photogenerated electrons. In addition, polyoxometalates can be used as electron acceptors to absorb photogenerated electrons from functionalized graphene oxide. However, the main problem of this method is that the production cost of graphene oxide is too high, which is not conducive to large-scale industrial application, which is an urgent problem to be solved in the follow-up research.

Zirconia (ZrO_2) is an n-type semiconductor material with high mechanical strength, thermal stability and redox ability[41]. Zirconia is very stable even under light. Therefore, using zirconia as a carrier can overcome the disadvantage that titanium dioxide is easy to be reduced under reducing atmosphere or negative pressure. Zirconia can fix POM anions through relatively strong chemical bonds. These interactions can avoid the leaching of POM in liquid phase reaction and maintain the main POM structure. Sampurnam *et al.*[42] prepared different proportions of Keggin type polyoxometalates 12 phosphotungstic acid (PTA)-supported ZrO_2 composite photocatalysts by impregnation method. The phase structure, chemical composition and oxidation state of tungsten and zirconium were characterized by XRD and XPS, and the functional groups and light absorption properties were characterized by FT-IR, Raman spectroscopy and ultraviolet visible diffuse reflectance (DRS-UV-VIS). The photocatalytic degradation effects of the photocatalyst on methylene blue (MB), methyl orange (MO), Rhodamine B (Rh-B), crystal violet (CV), bromocresol green (BCG) dye, 4-nitrophenol and 2,4-dichlorophenoxyacetic acid under UV irradiation were studied. The results showed that in order to achieve effective degradation within a given time, the composite ratio required for each dye was different. For MB, when the composite ratio of PTA and ZrO_2 is 3:1, the photocatalyst prepared shows the maximum photocatalyst activity; for RHB, MO, CV and BCG dyes, when the composite ratio of PTA and ZrO_2 is 1:3, the photocatalyst prepared shows the maximum photocatalyst activity; when the composite ratio of PTA and ZrO_2 is 3:1, the photocatalyst can also effectively degrade 4-nitrophenol, 2,4-dichlorophenoxyacetic acid and other organic pollutants.

Due to the narrow light response range of POM, some researchers have used the corresponding bismuth-based semiconductor materials to load POM under visible light, which can broaden the light response range of POM, and the introduction of POM can overcome the defect of faster electron hole recombination rate of bismuth-based semiconductor materials, so the catalytic effect of composite photocatalyst can be significantly improved[43]. Liu *et al.*[44] used Keggin type polyoxometalates salt $H_3PW_{12}O_{40}$(PW_{12}) as substrate to prepare a new PW_{12}/Bi_2WO_6 composite photocatalyst by an effective method. The prepared photocatalyst was characterized by IR, XRD, SEM and photoelectrochemical measurements. The photocatalytic activity of PW_{12}/Bi_2WO_6 was evaluated by using the model reaction of visible photocatalytic degradation of Rhodamine B (RHB). Under visible light irradiation, PW_{12}/Bi_2WO_6 can significantly improve the photocatalytic degradation effect of RhB compared with Bi2WO6 alone. PW_{12}/Bi_2WO_6 can make the degradation rate of RhB reach more than 99% within 4h, almost twice that of Bi_2WO_6 alone. The mechanism study shows (**Figure 4**) that the introduction of PW_{12} increases the charge separation efficiency in Bi_2WO_6 and limits the rapid electron hole recombination, which can effectively enhance the photocatalytic activity of Bi_2WO_6.

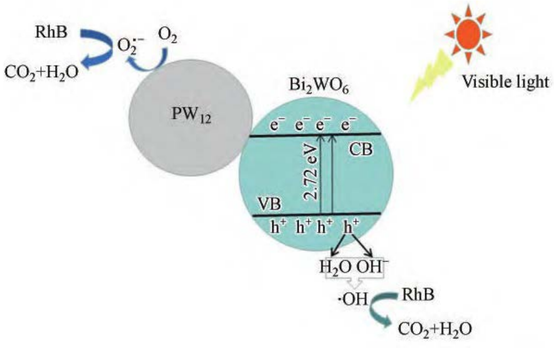

Figure 4. Schematic diagram of electron-hole pair separation and the possible photocatalytic reaction mechanism over the PW_{12}/Bi_2WO_6 composite photocatalyst.

In order to promote the separation of POM and enhance its reusability, many researchers loaded homogeneous POM on various carriers. The carriers include titanium dioxide and various polymers, which can be recovered by mechanical methods. Although the method of mechanical separation is very useful, it is time-consuming in many cases. In order to overcome this shortcoming, it is a good choice to use magnetic materials such as Fe_3O_4 and $NiFeO_4$ as carriers[45]. The design and synthesis of composite photocatalysts based on magnetic POM have attracted extensive attention of researchers. Shi *et al.*[46] grafted phosphotungstic acid anion ($PW_{12}O_{40}^{3-}$) onto Fe_3O_4 magnetic nanoparticles through a layer of silver to prepare a POM containing magnetic photocatalyst. The silver layer was used as an intermediate bond to connect the POM anion to the magnetic particles. The photocatalytic degradation performance of the composite photocatalyst was studied by degrading rhodamine B. The results showed that the composite photocatalyst had higher degradation efficiency than pure titanium dioxide and pure POM. Due to the presence of magnetic particles in the composite structure, the photocatalyst can be easily recovered by using the external magnetic field, which simplifies the separation and recovery of nanocomposite photocatalyst and improves its reusability. The prepared photocatalyst has good photocatalytic activity and certain magnetism, which provides a reasonable method for the degradation of organic pollutants and makes the catalyst have good reusability. Mahmoodi *et al.*[47] first synthesized iron cobaltate (CF) nanoparticles and modified the prepared iron cobaltate with (3-aminopropyl) trimethoxysilane. Then, Keggin type polyoxometalates $H_3PW_{12}O_{40}$ was immobilized on modified iron cobaltate nanoparticles (MCF), and a new magnetic polyoxometalates salt composite photocatalyst (IPMCF) was prepared. The prepared ipmcf was characterized by FTIR, SEM, AFM and XRD. The photocatalytic properties of IPMCF were studied by using acid orange 95, acid red 18 and direct red 81 as model dyes. The effects of catalyst dosage, dye concentration and salt in the solution on the degradation of dyes were investigated. The results showed that the prepared catalyst IPMCF had a good photocatalytic degradation effect on the above dyes, and the degradation

Table 2. Application of POMs and their composites in photocatalytic processes

Organic pollutants	**POM or POM composites**	**References**
Bioaccumulative pollutants including hydrofluoric acid	$H_4SiW_{12}O_{40}$	[17]
Chromophore (in pulp bleaching)	$H_5PMoV_2O_{40}$	[18]
Textile dye X3B	$H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_4GeW_{12}O_{40}$, $H_3PMo_{12}O_{40}$	[19]
phenol	Phosphotungstavanadate (MPWV)	[20]
Rhodamine B	$K_3PW_{12}O_{40}$	[21]
Alkaline Red 46	Cesium phosphomolybdate ($Cs_3PMo_{12}O_{40}$)	[22]
Acid red 3R (AR3R)	$(NH_4)_3PW_{11}O_{39}Sn/TiO_2$	[23]
Methylene blue (MB)	$H_6P_2W_{18}O_{62}@Cu_3(BTC)_2$	[26,27]
Crystal violet, alkaline red 2	$[Cd(TTPB\text{-}_4)(DMF)_3]_4[PMo_{12}O_{40}]_2[HPMo_{12}O_{40}]\cdot 6DMF\cdot 4H_2O$	[28]
Sulfamethoxazole (sulfamethoxazole, SMZ)	$H_3PW_{12}O_{40}/Ag\text{-}TiO_2$	[30]
Methyl orange	Phosphotungstic acid/yttrium doped TiO_2 (HPW-γ-TiO_2）	[32]
Various organic dyes	$H_3PW_{12}O_{40}/TiO_2$	[33]
Methyl orange (MO)	$[(C_4H_9)_4N]_5PW_{11}CoO_{39}(CoW)@TiO_2$	[33]
Methyl orange (MO)	$PMo_{12}O_{40}(PMo_{12})/TiO_2/Ag$	[34]
Rhodamine B, methylene blue	Mesoporous SiO_2 aerosol/$\backslash H_3PW_{12}O_{40}$	[36]
Methyl orange	Zeo-Y/TiO_2/Co^{2+}/HPA	[37]
Methylene blue	$H_3PMo_2W_{10}O_{40}$@ ethylenediamine functionalized graphene oxide (Mo_2W_{10}@EDMG) and $H_3PMo_4W_8O_{40}$@ ethylenediamine functionalized graphene oxide (Mo_4W_8@EDMG)	[40]
Methylene blue (MB), methyl orange (MO), Rhodamine B (Rh-B), crystal violet (CV), bromocresol green (BCG) dye, 4-nitrophenol and 2,4-dichlorophenoxyacetic acid	Phosphotungstic acid (PTA)-supported ZrO_2	[41]
Rhodamine B (RhB)	$H_3PW_{12}O_{40}(PW_{12})/Bi_2WO_6$	[44]
Rhodamine B	$PW_{12}O_{40}^{3-}/Fe_3O_4$	[46]
Organic dyes such as acid orange 95, acid red 18 and direct red 81	$H_3PW_{12}O_{40}$/(3-aminopropyl) trimethoxysilane modified iron cobaltate	[47]
Methylene blue (MB)	$Fe_3O_4/Ag/[Cu(C_6H_6N_2O)_2(H_2O)]$ $H_2[Cu(C_6H_6N_2O)_2(P_2Mo_5O_{23})]\cdot 4H_2O$	[48]

rate of dyes increased with the increase of the amount of catalyst. At the same time, the mechanism study shows that the decolorization process of the solution conforms to the zero-order kinetic model. Zhan *et al.*[48] coated polyoxometalates salt $[Cu(C_6H_6N_2O)_2(H_2O)]H_2[Cu(C_6H_6N_2O)_2(P_2Mo_5O_{23})]\cdot 4H_2O$(POM) on Fe_3O_4/Ag nanoparticles with core-shell structure to prepare ternary nanocomposite photocatalyst Fe_3O_4/Ag/POM. The structure of the prepared photocatalyst was characterized by HR-TEM, XRD and UV-Vis. The photocatalytic degradation performance of Fe_3O_4/Ag/POM was studied using methylene blue (MB) as a model dye. Under room temperature and visible light irradiation, MB can be quickly removed by adsorption and photocatalytic degradation, and the removal rate reaches 98.7%. Even if the prepared photocatalyst is reused for 6 times after magnetic separation, the removal rate of MB can still reach 97.5%, indicating that the prepared nanocomposite photocatalyst Fe_3O_4/Ag/POM has good reusability and high stability, and is very promising to be used as functional materials in wastewater treatment in the future.

Table 2 lists the application examples of some polyoxometalates and their complexes in photocatalytic degradation of organic pollutants.

5. Conclusion and prospects

Photocatalytic degradation technology can completely convert organic pollutants in wastewater into inorganic substances such as carbon dioxide and water. It has a good prospect of industrial development and has been widely used in the degradation of wastewater containing organic pollutants. Among them, the performance of photocatalyst plays an important role in the photocatalytic degradation effect.

Polyoxometalates (POM) is a photocatalyst widely used in the degradation of wastewater containing organic pollutants. In recent years, POM has shown broad application prospects in the photocatalytic degradation of dioxin, 2,4-dichlorophenol and other refractory organic pollutants, whether as the main body of the catalyst or as a catalytic promoter. However, at present, the research on Polyoxometalates photocatalyst mostly takes several specific anionic/cationic dyes as the catalytic model, and there is little research on the selectivity of photocatalytic degradation and the main catalytic mechanism of POM. At the same time, polyoxometalates photocatalysts also face a series of problems, such as low conversion efficiency, less use of visible light, long reaction time required for catalytic degradation alone, etc., in addition, semiconductor carriers with good catalytic effect in the study of polyoxometalates loading have higher costs, and there are many factors affecting the efficiency of catalysts in the process of catalyst preparation, which are not conducive to practical application, and further research may be needed to realize industrial application. Therefore, the main research directions in the future can mainly include the following aspects: (1) improving the visible light catalytic efficiency of polyoxometalates photocatalysts; (2) reduce the recombination of photogenerated electron hole pairs; (3) developing polyoxometalates salts for selective photocatalytic degradation of dyes or other pollutants; (4) focus on the further modification of POM and explore the appropriate ratio to improve the application range of polyoxometalates photocatalyst; (5) from the point of view of practical use, we should find a cheap and excellent carrier, and prepare efficient supported polyoxometalates photocatalyst through a simple and easy method. In addition, from the perspective of environmental protection, the recovery, regeneration and reuse of polyoxometalates photocatalysts after organic wastewater treatment are the key issues to be considered in later research. With the continuous research, polyoxometalates photocatalyst will show a good industrial application prospect in the treatment of organic wastewater containing refractory pollutants.

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Conflict of interest

The authors declared no conflict of interest.

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