Progress in the study of heteropolyacid-based-nanocomposite photocatalytic materials

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Abstract. As a kind of mild green photocatalysts, Heteropoly acid have a good prospect in photocatalysis due to its high activity, good selectivity and non-toxicity and possess photochemical characteristics similar to those of the semiconductor photocatalysts. Heteropoly acid (HPA), which are very soluble in water and polar solvents, these compounds are activated only by UV light, which restricts the practical application of HPA. Dispersing HPA onto nanoparticle supports with high surface area is useful to increase their specific surface area and hence (photo)catalytic activity. In this paper, the application of HPA-nanoparticles composites such as HPA/TiO$_2$ nanoparticles composites, HPA/SiO$_2$ nanoparticles composites, HPA/ZrO$_2$ nanoparticles composites and so on, in photocatalytic degradation of printing and dyeing wastewater, and the future research direction is prospected.

1. Introduction

With the development of the printing and dyeing industry, a large amount of printing and dyeing wastewater seriously threatens the ecological, environmental systems and human health, and it is urgent to develop a simple and efficient treatment technology for printing and dyeing wastewater [1], [2]. Semiconductor photocatalysis, using sunlight as the light source and inexpensive semiconductor materials as the medium, has the advantages of mild reaction conditions, low cost and no pollution, which is an ideal treatment technology for printing and dyeing wastewater [3]. In recent years, researchers have developed a wide variety of semiconductor photocatalytic materials, such as metal oxides (such as TiO$_2$, ZnO, SnO$_2$), metal sulphides (such as CdS, MoS$_2$, WS$_2$), inorganic non-metals (such as graphene, graphene oxide, g-C$_3$N$_4$), etc. [4]-[6]. Traditional semiconductor photocatalytic materials still have some drawbacks in use: (1) low visible light utilization, (2) high photogenerated electron-hole complexation rate, (3) low quantum efficiency, which makes it difficult to treat large amounts of printing and dyeing wastewater. Therefore, the solution of the above scientific problems is currently a hot research topic in the field of semiconductor photocatalysis.

Heteropolyacids (HPA), a semiconductor-like material, have properties similar to those of semiconductors [7]. HPA, as a class of excellent electron acceptors, can effectively promote photogenerated electron-hole separation and fast electron transport, with the advantages of good selectivity, high catalytic activity and no pollution [8]. However, the light-responsive absorption region of HPA is mainly concentrated in the UV region, with low utilization of visible light sources; HPA also has the disadvantages of low porosity, lack of active sites on the surface, low specific surface area (5-8 m$^2$/g), and easy solubility in polar solvents causing secondary pollution, which limits the further application of HPA [9]. To overcome this drawback, HPA-based nanocomposites are often prepared by loading HPA onto nanomaterials using methods such as impregnation, adsorption and hybridization [10]. HPA-based nanocomposites have been widely used in electrocatalysis,
photocatalysis and biocatalysis because of their properties such as high charge density, diverse size and multifunctional structure, as well as the optical and mechanical properties of nanoparticles [11], [12]. In this paper, we will focus on the application of HPA-based nanocomposites in photocatalytic degradation of printing and dyeing wastewater, and look into future research directions.

2. HPA/TiO₂ nanocomposites

Titanium dioxide (TiO₂) nanoparticles are widely used for their non-toxicity, photostability, unique photochemical properties and high chemical stability [13]. However, the photocatalytic efficiency of TiO₂ is limited due to the rapid complexation of light-induced electron-hole pairs. Therefore, the use of different electron acceptors to retard the electron-hole complexation reaction can help to improve the photocatalytic efficiency [13]. As mentioned above, HPA/TiO₂ nanocomposites, which can increase the specific surface area, increase the active sites and thus improve the photocatalytic activity, have a synergistic enhancement effect and are gaining increasing attention.

Jin Hongxiao et al [14] prepared several XW₁₂/TiO₂ (X = P, Si, Ge) nanocomposites by the sol-gel method, and the visible light degradation of the textile dye X-3B revealed that the photocatalytic activity of XW₁₂/TiO₂ nanocomposites was significantly higher than that of HPA and TiO₂ alone. Different heteropolyacids had a significant effect on the photocatalytic activity of XW₁₂/TiO₂ nanocomposites. The order of photocatalytic activity of HPA-based nanocomposites was as follows: phosphotungstic acid (PW₁₂)/TiO₂ > silicotungstic acid (SiW₁₂)/TiO₂ > germanium tungstic acid (GeW₁₂)/TiO₂. Shahram et al [15] prepared a Na₅[PV₂Mo₁₀O₄₀]/TiO₂ nanocomposite composite. Photocatalytic degradation experiments showed that Na₅[PV₂Mo₁₀O₄₀]/TiO₂ could photocatalyze the degradation of nine organic dyes such as bromothymol blue and congo red. The degradation of methyl orange, congo red and methylene blue by the nanocomposite Na₅[PV₂Mo₁₀O₄₀]/TiO₂ was above 90% under ultrasound-assisted visible light irradiation for 20 min. Yang Changjun et al [16] prepared a novel polyvinyl chloride (PVC)/PW₁₂/TiO₂ nanocomposite film and photodegradation behavior was investigated. The results of rhodamine B photocatalytic degradation showed that the photocatalytic activity of PVC/ PW₁₂/TiO₂ with a HPA loading of 2 wt. % was 1.5 times higher than that of PVC/TiO₂. Shi Huixian et al [17] used a sol-gel method to prepare nanoscale TiO₂ photocatalysts co-doped with rare-earth ions (La³⁺, Ce³⁺) and HPA Ce/ La-PW₁₂/TiO₂ nanocomposites. The photocatalytic degradation of methyl blue was found to be 98% and 96% for Ce-PW₁₂/TiO₂ and La-PW₁₂/TiO₂, respectively, with significantly higher photocatalytic degradation activities than Ce-TiO₂, La-TiO₂, PW₁₂/TiO₂ and PW₁₂/TiO₂ for 100 min of light exposure. The photocatalytic mechanism study showed that there is a synergistic effect between rare earth ions and heteropolyacids as well as TiO₂, which can increase the light adsorption and inhibit the compounding of photogenerated electron-hole pairs. Therefore, improving the synergistic effect of the multi-component is one of the ideal methods to overcome the disadvantages of low quantum efficiency and high electron-hole complexation rate of photocatalytic materials. Various HPA/TiO₂ nanocomposites for organic dye degradation are listed in Table 1.

| Photocatalyst               | Synthesis method | Contaminants       | Degradation efficiency | Reference |
|-----------------------------|------------------|--------------------|------------------------|-----------|
| PW₁₂/TiO₂                   | sol–gel method   | X-3B               | ~89% in 50min          | [14]      |
|                             |                  | bromothymol blue   | ~90% in 30min          |           |
| Na₅[PV₂Mo₁₀O₄₀]/TiO₂         | Solvothermal     | Congo Red          | ~90% in 30min          | [15]      |
|                             |                  | Rhodamine B        | ~90% in 30min          |           |
| PVC/ PW₁₂/TiO₂              | Solvothermal     | Rhodamine B        | ~18% in 60min          | [16]      |
| Ce-PW₁₂/TiO₂                | Sol-gel method   | Rhodamine B        | 98% in 100min          | [17]      |

Compared with HPA and TiO₂ monomers, the photocatalytic activity of HPA/TiO₂ nanocomposites has been greatly improved, but there are still drawbacks such as not easy separation and poor reusability in practical applications. In the future, the preparation of composite photocatalytic
materials with high photocatalytic activity, good selectivity and easy separation and recycling will be an important direction for research.

3. HPA/SiO₂ nanocomposites

Although silicon dioxide (SiO₂) has no obvious photocatalytic activity, the encapsulation of photocatalytically active materials in mesoporous or microporous SiO₂ matrices is currently a hot topic of research in the field of photocatalysis. Furthermore, due to the unique physicochemical properties and unusual internal structure of the SiO₂ matrix, it is easy to separate and recover from the reaction environment while enhancing the catalytic activity of the photoactive material [18], [19]. Therefore, HPA/SiO₂ nanocomposites have been used as multiphase photocatalysts for various organic pollutants. Tao Shengyang et al [20] prepared PW₁₂/SiO₂ by grafting method and photocatalytic degradation experiments showed that PW₁₂/SiO₂ achieved 97.8% removal of basic magenta by 80 min of light. Besides, the PW₁₂/SiO₂ catalyst prepared by graded porous SiO₂ as a carrier was very stable and easily recovered from the reaction solution for reuse. Hou Yang et al [21] prepared a series of Fe₃O₄/SiO₂/PW₁₂ core-shell nanoparticles by the impregnation method, and the degradation experiments of rhodamine B showed that the UV light irradiation for 60 min, the ratio of PW₁₂ 0.4% of Fe₃O₄/SiO₂/PW₁₂ showed the best photocatalytic activity (99.3%). The separation of rhodamine B solution from Fe₃O₄/SiO₂/PW₁₂ photocatalytic material was achieved in 30 s under the action of an external magnetic field, which provides a new idea for the construction of a new HPA-type photocatalyst that can be separated rapidly.

Compared to HPA homogeneous catalysts, HPA/SiO₂ nanocomposites possess different sized pore-like structures, have higher photocatalytic activity and are easy to recycle, but the biggest drawback is the low response to visible light. Li Hongfang et al [22] deposited (phosphotungstic acid-sulphur cordial, PW₁₂-TH)n polymers onto Fe₃O₄@SiO₂ magnetic microspheres by a layer-by-layer autoloading method. SiO₂ magnetic microspheres to produce Fe₃O₄@SiO₂ (PW₁₂-TH)n nanocomposites. The visible light irradiation for 4 h resulted in a degradation rate of methyl orange of about 90% and a significantly higher catalytic activity than Fe₃O₄@SiO₂. Besides, the use of magnetic materials ensured a convenient, clean, fast and efficient separation of the composites and allowed a high photocatalytic activity even after multiple reuses. Various HPA/SiO₂ nanocomposites for organic dye degradation are listed in Table 2.

| Photocatalyst | Synthetic method | Contaminants     | Degradation efficiency | Reference |
|--------------|------------------|------------------|------------------------|-----------|
| PW₁₂/SiO₂    | grafting method  | Fuchsin basic    | 98% in 80min            | [20]      |
| Fe₃O₄/SiO₂/PW₁₂ | impregnation      | Rhodamine B      | 99% in 60min            | [21]      |
| Fe₃O₄@SiO₂@(PW₁₂-TH)n | impregnation method | methyl orange | 90% in 240min          | [22]      |

SiO₂ itself does not have photocatalytic activity, but as a carrier for HPA it has the following advantages: it improves the adsorption of pollutants and improves photocatalytic activity; it increases the specific surface area of the composite, and it improves the physicochemical properties of HPA. Currently, HPA/SiO₂ nanocomposites are in urgent need of solutions to increase the response to visible light and improve photocatalytic activity.

4. HPA/ZrO₂ nanocomposites

Compared to TiO₂, ZrO₂ has a wider band gap (5.0 eV) and much lower photocatalytic performance. However, Devassy Biju et al [23] made HPA/ZrO₂ nanocomposites using ZrO₂ as a carrier for the catalytic synthesis of alkylbenzenes, and the results showed that the catalytic activity was enhanced by loading HPA onto ZrO₂.

Jiang Chunjie et al [24] loaded Ti-substituted Keggin-type HPA (Li₃PW₁₂TiO₄₀, K₇PW₁₀(Ti₃O₄₀) onto ZrO₂ to produce a series of HPA/ZrO₂ nanocomposites. The photocatalytic degradation of naphthol
blue-black was found that the photocatalytic activity of the HPA/ZrO₂ nanocomposites was significantly higher than that of the monomeric HPA, and the high specific surface area of the composites and the electron transfer to Keggin-type HPA were the main reasons for the increased photocatalytic activity. Qu Xuesong et al [25] prepared a PW₁₂/ZrO₂ nanocomposite, and photocatalytic degradation experiments showed that the PW₁₂/ZrO₂ nanocomposite could effectively degrade methylene blue under UV irradiation, and the degradation rate of methylene blue reached over 90% in 90 min. Farhadi Saeid et al [26] prepared a series of PW₁₂/ZrO₂ nanocomposites with different loadings (5%-20%) by the impregnation method. The photocatalytic degradation experiments of 4-nitrophenol and methylene blue showed that the photocatalytic activity of 15% PW₁₂/ZrO₂ nanocomposites was significantly higher than that of HPA and ZrO₂ alone. Salavati Hossein et al [27] investigated the degradation of methylene blue, rhodamine B, Congo red, bromothymol blue, alizarin GG, etc. by HPA/ZrO₂ nanocomposites in an aqueous solution. The photocatalytic activity of the organic dye pollutants was investigated. The experimental results showed that the HPA/ZrO₂ nanocomposites had higher photocatalytic performance compared with pure HPA or pure ZrO₂. The photocatalytic mechanism was found that: the specific surface area of HPA/ZrO₂ nanocomposites was higher than that of HPA or ZrO₂; electron transfer from ZrO₂ to HPA delayed the photogenerated hole-electron complex. Therefore, the photocatalytic activity of HPA/ZrO₂ nanocomposites is significantly higher than that of HPA or ZrO₂. HPA and ZrO₂ are compounded together mainly through electrostatic interaction and hydrogen bonding, avoiding secondary pollution of the environment by HPA. HPA loading on ZrO₂ causes a red shift in the absorption spectrum of the composite, which in turn reduces the band gap of the composite and improves the utilization of visible light. Various HPA/ZrO₂ nanocomposites for organic dye degradation are listed in Table 3.

| Photocatalyst          | Synthetic method | Contaminants                | Degradation efficiency | Reference |
|------------------------|------------------|----------------------------|------------------------|-----------|
| K₄PW₁₀Ti₂O₄/ZrO₂       | Sol-gel method   | Naphthol Blue Black        | -90% in 60min          | [24]      |
| PW₁₂/ZrO₂              | Impregnation method | Methylene Blue              | -90% in 90min          | [25]      |
| PW₁₂/ZrO₂              | Impregnation method | Methylene Blue              | -90% in 120min         | [26]      |
| PW₁₂/ZrO₂              | Sol-gel method   | Methylen Blue Congo red    | 99% in 50min           | [27]      |
|                        |                  | Rhodamin B Bromothymol Blue| 97% in 50min           |           |

5. HPA/Ta₂O₅ nanocomposites

Ta₂O₅ has a band gap of 3.9 eV and exhibits some photocatalytic activity only under UV irradiation. Jiang Shujuan et al [28] produced HPA/Ta₂O₅ (HPA= H₃PW₁₂O₄₀ and H₃P₂W₁₈O₆₂) nanocomposites with different loadings of HPA (5.6-15.3%) by hydrolyzing TaCl₅, which exhibited high photocatalytic activity under visible light. The HPA/Ta₂O₅ (HPA=H₃PW₁₂O₄₀ and H₃P₂W₁₈O₆₂) nanocomposites were effective in degrading salicylic acid and rhodamine B under visible light irradiation and still had high photocatalytic activity after three reuses. The structural analysis showed that HPA was uniformly dispersed within the Ta₂O₅ skeleton, effectively reducing the band gap and improving the photocatalytic activity. Currently, HPA/Ta₂O₅ nanomaterials have been widely used in organic synthesis and biodegradation, but little research has been reported in the field of photocatalytic degradation of wastewater.

6. HPA/ CNTs nanocomposites

Carbon nanotubes (CNTs) have been widely used in the field of electrochemistry due to their excellent heat transfer performance, special electrical and optical properties. CNTs can adsorb HPA on the surface of CNTs through chemical adsorption, and produce a synergistic effect, thus enhancing the
electrocatalytic performance of HPA/CNTs nanocomposites, which has attracted extensive attention [29]. However, HPA is the only photocatalytic material in HPA/CNTs nanocomposites, so the application of HPA/CNTs nanocomposites in the field of photocatalysis has received little attention. Lisw et al. [30] prepared three-component Au/HPA/CNTs nanocomposites with visible light photocatalytic activity by using Keggin type PW$_{12}$ as a reducing and bridging molecule between Au metal nanoparticles and carbon nanotubes. It was found that the degradation rate of Rhodamine B by Au/HPA/CNTs nanocomposites was about 91% after 2 h visible light irradiation, while the degradation rate of Au/HPA was only 45%. The photocatalytic degradation activity of three-component Au/HPA/CNTs nanocomposites was significantly higher than that of a single component or two-component photocatalysts.

7. HPA/ CdS nanocomposites
As one of the semiconductor materials, CdS has a band gap of about 2.42 eV, which can absorb less than 520 nm light and has a wide response range to visible light. However, in practical applications, CdS has the disadvantages of easy recombination of photogenerated carriers and poor photochemical stability, which leads to low photocatalytic quantum efficiency [31]. Xing et al. [32] prepared CdS-PW$_{12}$-Au ternary nanocomposites by molecular self-loading method. It was found that the photocatalytic degradation of Rhodamine B by CdS-PW$_{12}$-Au could reach 90% under the condition of 0.6% Au nanoparticles loading and 2 h illumination. Besides, HPA can be used not only as reducing, encapsulating, and bridging molecules but also as cocatalyst in photocatalysis.

8. Conclusion and outlook
The synergistic interaction between HPA and nanoparticle carriers can improve the physicochemical properties of HPA/nanocomplexes, such as high specific surface area, more active sites, lower photogenerated electron-hole complexation rate, etc., which in turn significantly enhance the photocatalytic performance of HPA-based nanocomplexes. However, there are still many problems to be solved and further researched in terms of theoretical and practical applications: (1) the preparation method of HPA-based nanocomplexes needs to be further improved, which in turn leads to uniform-sized nanoparticles and improved photocatalytic activity; (2) the construction of multifaceted HPA-based nanocomplexes and the improvement of the stability of HPA-based nanocomplexes to avoid the leaching of HPA, which leads to secondary pollution; (3) the HPA-based nanocomplexes for photocatalytic degradation of printing and dyeing wastewater, most of which choose dyes as the target molecules for degradation. To further determine the photocatalytic performance of HPA-based nanocomplexes, difficult pollutants can be used as degradation or reaction substrates; (4) At present, the photocatalytic research of HPA-based nanocomplexes mostly stays in the laboratory stage, and the technology should be further optimized in the future in terms of preparation methods and recycling, to truly realize the industrialization of nanotechnology.

9. Acknowledgments
This work was supported by the Science and Technology Research Program of Chongqing Municipal Education Commission (grant No. KJQN 201804501).

10. References
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