Preparation of the floating HGMs-Ag₃PO₄ composites and the visible-light photocatalytic properties

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Abstract

The hollow glass microspheres (HGMs) with low density were used as the support to obtain the floating visible-light photocatalysts (HGMs–Ag₃PO₄) composites, in which silver orthophosphate (Ag₃PO₄) was dispersed on the surface of HGMs via silane coupling agents. The morphology, crystal structure and optical property of the HGMs–Ag₃PO₄ composites were characterized and the contents of Ag₃PO₄ dispersed on the surface of HGMs were quantified by atomic absorption spectrometry (AAS). Methylene blue (MB) was selected as the typical organic pollutants to evaluate the photocatalytic activity of HGMs–Ag₃PO₄ composite photocatalysts. The photo-catalytic rate of the floating composites was larger than the sinking composites and even pure Ag₃PO₄. Ag₃PO₄ particles could be dispersed well on the HGMs. The floating composites has a larger light contact area and the increased photo-catalytic activity sites even at the low Ag₃PO₄ loading. This work may open up a new insight for the floating photocatalyst to degrade organic dye on account of the low density and high visible-light responsiveness.

1. Introduction

In recent years, the experts and scholars have paid a wide range attention on environmental and energy issues such as non-compliance emissions of various textile industry dyestuffs, excessive consumption of traditional fossil fuels, and so on, which have threatened human health and ecosystem stability [1]. Because semiconductor photocatalysts can utilize solar energy to oxidize organic pollutants into carbon dioxide, water and other harmless substances [2], they are applied on environmental pollution remediation and solar energy conversion in an environmental friendly method.

As one of the most effective photo-catalysts, TiO₂ composites [3] have been widely used in the photodegradation of organic dye pollutants due to its low cost, stability, anti-corrosion non-toxic and energy saving. However, TiO₂ exhibits low quantum efficiency and low utilization of solar energy, for TiO₂ can only absorb the UV light (λ < 380 nm) making up for only 4% of the sunlight and has a relatively wide band gap of 3.2 eV [4–6]. Hence, it is very necessary to have a research on efficient visible-light photo-catalysts with relatively narrow band gap. Yi [7] reported Ag₃PO₄ had excellent performance on the evolution of O₂ from water splitting and remove of organic dyes under the visible-light exposure due to the capability to effectively separate photoexcited electrons and holes with suitable band gap of 2.45 eV, achieving a quantum yield of up to 90% (λ > 420 nm), thus extending a new application of Ag₃PO₄ in the field of photo-catalysis. The visible-light photo-catalytic degradation properties of Ag₃PO₄ can be further enhanced by controlling its morphology [8], feature size [9], surface area [10] and low-index facets [11], by assembling with other semiconductors such as TiO₂ [6, 12, 13], Fe₂O₃ [14], AgX (X = Cl, Br, I) [15–17], Int(OH)₃ [18], BiVO₄ [19], MOF [20], MoSe₂ [21], CeO₂ [22].
Table 1. The photocatalytic activities parameters of Ag₃PO₄ composites.

| Photocatalysts | Ratio | Organic Pollution | C<sub>catalyst</sub> (g l<sup>−1</sup>) | k (min<sup>−1</sup>) | Time | References |
|---------------|-------|-------------------|-------------------------------|-----------------|-----|------------|
| Ag₃PO₄       | 1.00:0(n) | 10 mg l<sup>−1</sup> MB          | 0.83                          | 0.152           | 30 min 100% | [6]        |
| Ag₃PO₄/TiO₂  | —     | 10 mg l<sup>−1</sup> RhB         | 1.00                          | 0.023           | 25 min 100% | [1,2]      |
| Ag₃PO₄/Fe₂O₃ | —     | 2 mg l<sup>−1</sup> imidacloprid | 0.50                          | 0.014           | 90 min 73%  | [1,4]      |
| Ag₃PO₄/AgCl  | —     | 20 mg l<sup>−1</sup> methylparaben | 0.50                        | 0.090           | 40 min 100% | [16]       |
| Ag₃PO₄/In(OH)₃ | 1.65:1.00(n) | 8 mg l<sup>−1</sup> RhB      | 2.00                          | 1.71            | 1.5 min 98% | [18]       |
| Ag₃PO₄/BiVO₄ | 0.60:1.00(n) | 10 mg l<sup>−1</sup> RhB   | 0.50                          | 0.034           | 90 min 95%  | [19]       |
| Ag₃PO₄/MOF   | 95:5(m) | 40 mg L<sup>−1</sup> phenol   | 1.00                          | —               | 14 min 99%  | [20]       |
| Ag₃PO₄/CeO₂  | 1:2.5(n) | 10 mg l<sup>−1</sup> MO       | 1.50                          | 0.077           | 60 min 91%  | [22]       |
| Ag₃PO₄/g-C₃N₄ | 95:5(m) | 10 mg l<sup>−1</sup> MB       | 0.50                          | 0.074           | 40 min 90%  | [24]       |
| Ag₃PO₄/polyaniline | 97.3(m) | 25 mg l<sup>−1</sup> phenol   | 0.50                          | 0.160           | 20 min 98%  | [25]       |
| Ag₃PO₄/N-GR/g-C₃N₄ | —     | 20 mg l<sup>−1</sup> tetracycline | 1.00                        | 0.020           | 90 min 94%  | [26]       |
| Ag₃PO₄/RGO   | —     | 20 mg L<sup>−1</sup> phenol   | 0.20                          | —               | 60 min 94%  | [28]       |
| Ag₃PO₄/QCDs  | 97:3(m) | 10 mg l<sup>−1</sup> MO       | 0.25                          | —               | 40 min 80%  | [29]       |
| Ag₃PO₄/CNTs  | 98:2(m) | 6.7 × 10<sup>−5</sup> mol l<sup>−1</sup> MB | —                            | 0.480           | 10 min 98%  | [30]       |
| HGMs-TiO₂/Ag₃PO₄ | —     | 5 mg L<sup>−1</sup> MB      | 2.00                          | 0.029           | 90 min 96%  | [13]       |
| HGMs- Ag₃PO₄ | 8:92(m) | 5 mg L<sup>−1</sup> MB      | 5.00                          | 0.044           | 60 min 96%  | This work  |

* In the Ratio column, n represents a molar ratio, and m represents a mass ratio.

N-Sr₂Nb₂O₇ [23], g-C₃N₄ [24], polyaniline [25] and carbon based materials including graphene (GR) [26], graphene oxide (GO) [27], reduced graphene oxide (RGO) [28], carbon quantum dots (CQDs) [29] and carbon nanotubes (CNTs) [30] to construct a surface heterojunction, and the doping of atomic impurities [31]. The photo-catalytic activity performance of Ag₃PO₄-composites has been summarized in table 1. There are many typical organic pollutants to evaluate the photocatalytic activity of Ag₃PO₄-composites photocatalysts, such as using organic dyes (methylene blue-MB [8, 13, 24, 30], rhodamine B-RhB [12, 18, 19], methyl orange-MO [22, 29], etc), preservatives (methylparaben [16], phenol [20, 25, 28], etc), insecticides (imidacloprid [14], etc), antibiotic (tetracycline [26], etc). Compared with pure Ag₃PO₄ photocatalyst, the Ag₃PO₄-composites have a certain degree of improvement in the photocatalytic activity on different organic pollutants. Nevertheless, in order to achieve high photocatalytic performance, Ag₃PO₄ needs to account for a large proportion even in the Ag₃PO₄ composite photocatalyst [20, 24, 25, 30]. The high cost of raw materials AgNO₃ and the difficulty of separating as well as recovering Ag₃PO₄-based photo-catalysts from the reaction suspension limit the large-scale practical application of the photo-catalysts [32]. Therefore, the fabrication of high-cost-performance Ag₃PO₄-based composites reducing the dosage of AgNO₃ and being recovered easily is of great significance.

Hollow glass microspheres (HGMs) are the hollow powdery borosilicate with a particle size of 10–100 μm with wall thickness of 1–2 μm. HGMs can be separated from the coal fly ash to make use of waste resources [33]. Due to the unique properties of low density, large surface areas, light-trapping effects, low thermal conductivity, high strength, non-toxic, non-combustible, thermal and sound insulating, high dispersion and good chemical stability, HGMs are widely applied in the synthesis of microwave absorbing materials [34], hydrogen storage materials [35], low density foams [36], deep sea buoyancy materials [37], catalyst carriers [13, 38], biomaterial defect fillers [39] and so on.

The preparation of new photo-catalytic Ag₃PO₄-based composites using HGMs as the photo-catalyst carriers can compensate the limitations of Ag₃PO₄. On the one hand, Ag₃PO₄ dispersed on the floating micron-sized HGMs not only can be easily separated from the treatment solution, but also can improve the light contact chance and the photo-catalytic activity due to its floating property at the surface of the effluent. On the other hand, the surface of the HGMs loaded with a small amount of Ag₃PO₄, significantly reducing the dosage of raw materials AgNO₃, can achieve a certain photo-catalytic performance because only the outer layer of photocatalyst could absorb visible-light in the practical application.

In this work, the floating visible-light-responsive HGMs-Ag₃PO₄ composites were prepared by a facile ion exchange method using HGMs as a floating photo-catalyst carrier with a silane coupling agent as a bridge. The visible-light catalytic activities of the floating HGMs-Ag₃PO₄ composites was investigated by the MB photodegradation efficiency under visible-light irradiation in contrast with pure Ag₃PO₄ and the sinking HGMs-Ag₃PO₄ composites. Furthermore, the possible photo-degradation mechanism of floating HGMs-Ag₃PO₄ composites was proposed.
2. Experimental

2.1. Materials
Hollow glass microspheres (HGMs) were provided by Zhengzhou Hollowlite Corp (Henan, China). Silane coupling agent 3-triethoxysilyl-1-propanamine (KH550) were obtained from Aladdin Chemistry Corp (Shanghai, China). All of the other reagents purchased from Tianjin Chemical Company (Tianjin, China) were analytical grade and were used directly without further purification.

2.2. The preparation of HGMs-Ag3PO4 composites
The surface pretreatment of HGMs: 0.1 μl of silane coupling agent KH550 was dissolved in 12.5 ml of distilled water in a beaker, then 2.5 g HGMs were dispersed to the above solution under vigorous stirring. After magnetic stirring for 30 min, the mixture was vacuum filtered, then washed several times with deionized water and absolute ethanol. The floating products were dried at 60 °C for 8 h. The pretreatment products were marked as HGMs-KH550.

HGMs-Ag3PO4 powders were prepared by the simple ion-exchange method. 2.0 g HGMs-KH550 was added to 100 ml of AgNO3 aqueous solution with magnetic stirring at 280 r min−1 for 1.5 h. 100 ml Na2HPO4 aqueous solution was added dropwise to the mixture slowly with magnetic stirring for 1 h. After the completion of the dropwise addition, the mixture was steadily stirred for 0.5 h and washed with distilled water to move any unreacted raw material. Last, the final product was vacuum filtered and dried at 60 °C for 8 h. The HGMs-Ag3PO4 composites with different Ag3PO4 loadings were synthesized with adjusting the concentrations of AgNO3, Na2HPO4 solutions. The AgNO3 and Na2HPO4 solutions with the same concentrations (0.0215, 0.0430, 0.0645 and 0.0860 mmol l−1) were used to fabricate the HGMs-Ag3PO4 composites with different Ag3PO4 theoretical loadings (0.045, 0.090, 0.135 and 0.180 g g−1), which were marked as HGMs0, HGMs1, HGMs2, HGMs3 and HGMs4, respectively. HGMs1, HGMs2 and HGMs3 float in water, while HGMs4 deposited in water. Pure Ag3PO4 was prepared in the same method without adding HGMs-KH550. HGMs0 was prepared as the same method as HGMs3 without amino modification.

2.3. Characterization
The morphology of the as-prepared photocatalysts were characterized by using a field emission scanning electron microscope (SEM, S-4800). The crystal phases of HGMs-Ag3PO4 composites were determined by x-ray diffraction (XRD, D/MAX-2500) with CuKα radiation (λ = 1.54 Å) in the range of 15–75° (2θ) with a scanning rate of 4° min−1. The valence and content of silver were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250 with monochromatized Mg KR x-ray as the source). The resulting binding energies were calibrated to the C 1 s (284.6 eV) peak. The specific surface area of HGMs, HGMs3, and Ag3PO4 were measured with an Autosorb-1 specific surface area analyzer (Quantachrome Instruments, USA) using the BET method on the base of N2 adsorption data. FT-IR spectra were measured on an Excalibur 3100 infrared spectrophotometer from KBr pellets as the sample matrix. The ultraviolet-visible diffuse reflectance spectra (UV−vis DRS) were recorded with a UV−2450 spectrophotometer using BaSO4 as the reference of diffuse reflectance and converted to absorption spectra by the standard Kubelka-Munk method. UV−Vis absorption spectra was measured at room temperature on a UV−1800 (Mapada) spectrometer. When Ag3PO4 on HGMs-Ag3PO4 composites was dissolved with 1:499 (v/v) dilute HNO3 solution, the Ag3PO4 loading percentage of as-prepared composites was estimated by measuring Ag⁺ contents with Atomic absorption spectroscopy (AAS, Thermo Scientific iCE3000).

2.4. Evaluation of photocatalytic properties
The visual-light catalytic activity of HGMs-Ag3PO4 composites was evaluated by the photodegradation of MB organic dye pollutants under the simulated sunlight irradiation. In all catalytic activity of experiments, the as-obtained samples (0.3 g) were put into MB solution (60 ml, 5 mg l−1), which was placed for 60 min in the dark to achieve adsorption-desorption equilibrium before the lamp turned on and then irradiated vertically by a 300W Xe arc lamp equipped with an ultraviolet cutoff filter (λ ≥ 420 nm) to provide visible light without magnetically stirring to imitate the photodegradation of organic effluent at the natural environmental conditions. In the photo-catalytic testing, the liquid level of MB dye solution was 95 mm from the Xe arc lamp. With a 5-min interval, 3 ml suspension of MB was sampled, then filtered by a 0.22 μm Millipore filter to remove the residual catalysts. The concentration of MB was analyzed by UV−1800 at the wavelength of 663 nm.

To assess the stability of the HGMs-Ag3PO4 composites, cycling runs of MB photodegradation were conducted. The floating composites were scooped out and dried at 60 °C for 4 h at the end of each circle. The photo-degradation rate of MB dye is fit from the line ln(C/C0) = −t. C is the concentration of MB at time t and C0 is the initial MB concentration. On the basis of Beer-Lambert Law, C/C0 is the ratio of the MB absorbance at
time $t$ to the initial absorbance. The concentrations of MB at time $t$ were calculated by testing the maximum absorption intensity of the UV-visible spectrum at 663 nm.

3. Results and discussion

3.1. Characterization of the composites

In figure 1, the preparation of HGMs-Ag$_3$PO$_4$ powders were depicted. HGMs were modified by the silane coupling agent KH550 to introduce -NH$_2$ groups on HGMs. The valence electron orbit of the Ag$^+$ ion is 4d$^{10}$5s$^0$5p$^0$, the sp-hybrid orbit of which can accept the lone pair electrons of -NH$_2$ from the silane coupling agent to form a complex. As a bridge, the silane coupling agent KH550 connects HGM surface and Ag$^+$. PO$_4^{3-}$ from the hydrolysis of HPO$_4^{2-}$ reacts with Ag$^+$ to generate Ag$_3$PO$_4$ on the surface of HGMs-KH550. As the reaction proceeded, the color of the floating HGMs-KH550 gradually varied from the initial white to yellow, illustrating the formation of Ag$_3$PO$_4$ on the surface of HGMs-KH550. The actual Ag$_3$PO$_4$ loading on HGMs0, HGMs1, HGMs2, HGMs3 and HGMs4, were measured by AAS, which were listed in table 2. The only difference between HGMs0 and HGMs3 in the preparation process is that HGMs0 is not modified by amination. From table 2, we can see that only 0.4 wt% of the silane coupling agent can increase the catalyst loading rate by 52%. The results illustrated that trace KH550 had a significant effect on the loading of Ag$_3$PO$_4$ and played a vital role as a bridge between Ag$_3$PO$_4$ and HGMs. The measured Ag$_3$PO$_4$ loading increased in the order of HGMs1, HGMs2, HGMs3 and HGMs4 with the increasing of the reactants. However, the actual Ag$_3$PO$_4$ percent conversions decreased by HGMs1, HGMs2 and HGMs3, because the more Ag$^+$ could connect with NH$_2$ groups on HGMs and the HGMs-KH550 had limited NH$_2$- active sites to absorb Ag$^+$, resulting in the direct deposition of partial Ag$_3$PO$_4$ at the bottom of the reaction vessel, rather than the attachments on HGMs. In addition, the actual Ag$_3$PO$_4$ loading percentage of HGMs3 had dropped to 56.9%. If the more input of AgNO$_3$ and Na$_2$HPO$_4$, the loading percentage of Ag$_3$PO$_4$ on floating HGMs-Ag$_3$PO$_4$ composites will drop even lower and will generate more Ag$_3$PO$_4$ deposition rather than loaded on HGMs. But for the deposited HGMs4, which is a sinking-type material including unloaded pure Ag$_3$PO$_4$ and Ag$_3$PO$_4$ loaded by hollow glass microspheres, the loading percentage of Ag$_3$PO$_4$ increased with the increasing of the reactants, because Ag$_3$PO$_4$ is already saturated with loads on HGMs-KH550 so that HGMs4 sinks and unloaded Ag$_3$PO$_4$ sinks. This was very different from the floating HGMs1, 2 and 3.

Figure 2 shows the SEM images of the morphologies of HGMs-KH550, HGMs1, HGMs2, HGMs3, HGMs4 and pure Ag$_3$PO$_4$. HGMs-KH550 (figure 2(a)) has a smooth surface with a diameter of about 20 μm. With the increasing of AgNO$_3$ loading from figures 2(b) to (e), more Ag$_3$PO$_4$ particles were formed on the surface of HGMs, and the color changes from pale yellow to deep yellow. The size of the Ag$_3$PO$_4$ particles on HGMs were uniform, and the loaded Ag$_3$PO$_4$ on HGMs3 (figure 2(d)) with the mean size of 400–500 nm exhibited the morphology of regular rhombic dodecahedrons. For HGMs4 (figure 2(e)), the excessive Ag$_3$PO$_4$ loading resulted in the aggregation of Ag$_3$PO$_4$ particles and the deposition of HGMs because of the high density.
6.37 g cm$^{-3}$ of Ag$_3$PO$_4$. The morphology of pure Ag$_3$PO$_4$ (dark yellow) presented irregular sphere and rhombic dodecahedrons in figure 2.

The XRD patterns are displayed in figure 3. For the diffraction pattern of HGMs-KH550 (figure 3(a)), the curve is broad and weak from 15° to 40° without characteristic diffraction peaks. For HGMs3, HGM4 and pure Ag$_3$PO$_4$ (figures 3(b)–(d)), the diffraction peaks of Ag$_3$PO$_4$ were readily matched to the body-centered cubic phase structure of Ag$_3$PO$_4$ single crystal (JCPDS NO.06-0505). The XRD patterns of HGMs3 and HGMs4 exhibited a coexistence of both HGMs-KH550 and Ag$_3$PO$_4$ diffraction phases, indicating the formation of HGMs-Ag$_3$PO$_4$ composites. The mixed diffraction pattern included no other peaks, illustrating that the combination of HGMs-KH550 and Ag$_3$PO$_4$ had no effect on the crystal structure of Ag$_3$PO$_4$. With the increasing of Ag$_3$PO$_4$ loading in the order of HGMs3, HGMs4 and pure Ag$_3$PO$_4$, the intensities of the characteristic peaks of Ag$_3$PO$_4$ enhanced (figures 3(b)–(d)). In addition, HGMs3 were treated for MB photo-degradation under the visible-light irradiation for an hour. This used HGMs3 (figure 3(e)) had a new obvious diffraction peak at 38.07° compared with the fresh HGMs3, which can be well-assigned to the (111) crystal face of metallic Ag (JCPDS NO. 04-0783), suggesting that a certain amount of Ag$_3$PO$_4$ loaded on HGMs3 was reduced to Ag after treating MB photo-degradation [40]. And the color of HGMs3 become pale after being used for MB photo-degradation.

Figure 2. SEM images of (a) HGMs-KH550, (b) HGMs1, (c) HGMs2, (d) HGMs3, (e) HGMs4 and (f) pure Ag$_3$PO$_4$. The illustrations on the upper right corner of each image are the respective digital pictures of the samples. The inset on the bottom right corner of (d): Ag$_3$PO$_4$ particles on HGMs3 (the red bar is 500 nm).
under the visible-light irradiation. This point can also be proved by x-ray photoelectron spectroscopy (XPS) shown as figure 4. It is found that the peaks of Ag 3d 5/2 and Ag 3d 3/2 are located at ~368 and ~374 eV both in figures 4(a) and (b), respectively. In figure 4(a), the XPS pattern of HGMs3 without the first photodegradation displays that the peaks of Ag 3d 5/2 and Ag 3d 3/2 were fitted at 373.98 and 368.07 eV, which can be attributed to Ag\(^+\) ions in Ag\(_3\)PO\(_4\) [41]. And these peaks cannot continue to be divided and exhibited the smallest value of residual STD which degree of fitting was optimal. In other words, the silver elements in HGMs3 before the first photodegradation all existed in the form of Ag\(^+\). However, the Ag 3d 3/2 and Ag 3d 5/2 peaks of HGMs3 after the first photodegradation can be further divided into two different peaks at 375.14, 374.09 eV and 368.89, 368.02 eV in figure 4(b), respectively. According to the results reported by Zhang et al [41], the peaks at 374.09 and 368.02 eV can be attributed to Ag\(^+\) ions in Ag\(_3\)PO\(_4\), whereas the peaks at 375.14 and 368.89 eV are attributed to Ag\(^0\). The calculated contents of Ag\(^0\) and Ag\(^+\) are 13.07 mol% and 86.93 mol% by integrating peak area, respectively. This also means that 13% of Ag\(^+\) is transformed into Ag\(^0\) after one photodegradation of HGMs3.

Further evidence for successful loading of Ag\(_3\)PO\(_4\) comes from FT-IR. As can be seen from figures 5(a), (b), the difference in infrared spectra between the amino-modified and unmodified hollow glass microspheres is not
obvious. This may be due to the small amount of KH550 added, which is only 0.4% of the hollow glass microspheres mass fraction. $1065 \text{ cm}^{-1}$, $794 \text{ cm}^{-1}$ and $463 \text{ cm}^{-1}$ are Si-O symmetry stretching vibration, asymmetric stretching vibration and bending vibration absorption peak, respectively $[42]$. In figure 5(d), the broad absorption at around 3000–3500 cm$^{-1}$ and 1646 cm$^{-1}$ are attributed to O–H stretching vibrations, and the band at 1400 cm$^{-1}$ is related to the H–O–H bending band of the adsorbed H$_2$O molecules on the surface of the Ag$_3$PO$_4$. $966 \text{ cm}^{-1}$ and $552 \text{ cm}^{-1}$ are all ascribed to P–O stretching vibrations of PO$_4$$^-$$^43$. We can see from figure 5(c) that HGMs3 has a more absorption peak than HGMs at 552 cm$^{-1}$, which is P–O stretching vibrations, proving that Ag$_3$PO$_4$ exists on HGMs.

The optical absorption (figure 6(a)) of HGMs-KH550, HGMs-Ag$_3$PO$_4$ and pure Ag$_3$PO$_4$ were determined with the ultraviolet-visible diffuse reflectance spectrum (UV-vis DRS). HGMs-KH550 had a certain absorption shorter than 400 nm and almost no absorption in the visible wavelength range. The band gaps of the as-prepared samples were estimated from the intercept of the tangent at the x-axis of the Tauc plot, which was $(A\nu)^2 = h\nu - E_g$ $(A$: absorbance; $h$: Planck constant; $\nu$: light frequency; $E_g$: band gap energy) $[25, 26]$. As shown in the inset image of figure 6(b), the $E_g$ of HGMs-KH550 was 4.59eV, which was an insulator, not a semiconductor. Pure Ag$_3$PO$_4$ showed broad absorption of visible light at a wavelength less than 530 nm and the $E_g$ of Ag$_3$PO$_4$ was estimated to be 2.36eV, consistent with the previous reported results $[7, 25]$. At a wavelength $< 530$ nm, the intensity order of visible light absorption is as follows: HGMs-KH550 $<$ HGMs1 $<$ HGMs2 $<$ Ag$_3$PO$_4$ $<$ HGMs4 $<$ HGMs3. HGMs3 had an absorption edge at

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**Figure 5.** FT-IR of (a) HGMs, (b) HGMs-KH550, (c) HGMs3 and (d) pure Ag$_3$PO$_4$.

**Figure 6.** UV-vis diffuse reflectance spectra (a) and the corresponding band gap energy diagram (b) of HGMs-KH550, HGMs1, HGMs2, HGMs3, HGMs4 and pure Ag$_3$PO$_4$. 
about 540 nm, slightly wider than the range of pure Ag₃PO₄. The crystal form of Ag₃PO₄ loaded on microspheres is rhombic dodecahedrons, and the HGMs-Ag₃PO₄ composites containing a certain amount of Ag₃PO₄ could allow more multiple scattering of light [10]. The results also suggested HGMs3 might effectively utilize sunlight and enhance photocatalytic properties under visible light irritation. The band gaps of HGMs1, HGMs2, HGMs3, and HGMs4 are 2.28 eV, 2.29 eV, 2.37 eV and 2.35 eV, respectively. Especially, the Eg of HGMs3 and HGMs4 were similar to Ag₃PO₄, which meant the HGMs-Ag₃PO₄ composites showcased high optical responses under visible light irradiation, thus could be applied as a visible light active photocatalyst.

3.2. Photocatalytic properties

The effects of the Ag₃PO₄ loading on photocatalytic properties were evaluated by determining the MB photo-degradation rate under the irradiation of simulated visible light. The MB photo-degradation as a function of time was shown in figure 7(a). Prior to light irradiation, the MB solutions containing HGMs-KH550, the HGMs-Ag₃PO₄ composites or pure Ag₃PO₄ were placed in the dark for 60 min to achieve the adsorption-desorption equilibrium. In the case of no light irradiation, the MB removal was ascribed to the adsorption rather than the photo-degradation. MB absorbed by pure Ag₃PO₄ and HGMs-KH550 is only about 15%, while about 54% of MB were adsorbed by HGMs3, 46% of MB adsorbed by HGMs2 or HGMs4, and 32% of MB adsorbed by HGMs1. For the floating HGMs-Ag₃PO₄ composites, the amount of adsorption was as follows: HGMs3 > HGMs2 > HGMs1 > HGMs-KH550. The more Ag₃PO₄ was loaded on the floating microspheres, the more MB was adsorbed. The adsorption capability of HGMs-Ag₃PO₄ composites was better than that of HGMs-KH550 support and pure Ag₃PO₄ catalyst. Ag₃PO₄ was dispersed on microspheres, increased the specific surface area of Ag₃PO₄ and enlarged the contact area with MB solution, resulting in the enhanced adsorption capacity. The superfluous Ag₃PO₄ particles for HGMs4 aggregated on the HGMs (figure 2(e)) and decreased the adsorption capacity.

When they were exposed under the irradiation of simulated visible light for an hour, the only a small amount of MB was degraded by HGMs-KH550. For the HGMs-Ag₃PO₄ composites or pure Ag₃PO₄, as expected, and the MB concentration decreased much with the increasing of the exposed time. After an hour, the MB removal was as follows: HGMs3 (96%) > HGMs2 (91%) > HGMs4 (87%) > Ag₃PO₄ (80%) > HGMs1 (79%). The BET surface area of HGMs was 0.760 m² g⁻¹ and that of pure Ag₃PO₄ was 1.299 m² g⁻¹, while the BET surface area of HGMs3 was 0.779 m² g⁻¹, little higher than that of raw HGMs, which may have promoted the adsorption of MB on HGMs-Ag₃PO₄ and enlarged the contact area with MB solution, resulting in the enhanced adsorption capacity. The superfluous Ag₃PO₄ particles for HGMs4 aggregated on the HGMs (figure 2(e)) and decreased the adsorption capacity.

Since the MB removal was very different during the adsorption process for HGMs-KH550, the HGMs-Ag₃PO₄ composites or pure Ag₃PO₄, the photo-catalytic degradation rate of MB over HGMs-Ag₃PO₄ composites and pure Ag₃PO₄ was concerned. In addition, the Ag₃PO₄ content of floating HGMs2 and HGMs3 was less than that of pure Ag₃PO₄, but the catalytic properties were better than pure Ag₃PO₄, which could be attributed to the better adsorption performance of HGMs-Ag₃PO₄ composites and the larger light contact area.

Since the MB removal was very different during the adsorption process for HGMs-KH550, the HGMs-Ag₃PO₄ composites or pure Ag₃PO₄, the photo-catalytic degradation rate of MB over HGMs-Ag₃PO₄ composites and pure Ag₃PO₄ was concerned rather than the MB removal in the photo-catalytic process. When the concentration of dyes is very low, the Langmuir-Hinshelwood model is suitable for the kinetics photocatalytic degradation, which expression is \[ \frac{dC}{dt} = -k \frac{KC}{1+KC} \]. In this formula, \( \frac{dC}{dt} \), \( k \), \( K \) and \( C \) are the reaction rate, reaction rate constant, adsorption coefficient and the reactant concentration, respectively. When C is very small, \( \ln \frac{C}{C_0} = kt \) is obtained, \( k \) is the apparent constant (first order rate). The photo-catalytic degradation of MB over
Ag₃PO₄ and HGMs-Ag₃PO₄ composites followed the pseudo-first-order kinetics, as shown in figure 7(b). ln(C₀/C) versus t is a straight line and the slope of this fitted line is the photo-catalytic rate, recorded as k. In order to simulate the quiescent state of rivers and lakes in practical application, no stirring was used in the photo-degradation. The apparent rate constants (k) for floating HGMs3 and HGMs2 were 0.0444 and 0.0297 min⁻¹, which are larger than those for sinking HGMs4 (k = 0.0229 min⁻¹) and pure Ag₃PO₄ (k = 0.0242 min⁻¹). HGMs3, which had the best photocatalytic performance herein, was actually loaded with 0.0768 g Ag₃PO₄ per gram of sample (see table 2). Compared with the same mass of pure Ag₃PO₄, the mass of Ag₃PO₄ contained in HGMs3 is only 7.68% (∼8 wt% of the composite shown in table 1), but its photocatalytic efficiency (k = 0.0444 min⁻¹) is nearly twice that of pure Ag₃PO₄ (k = 0.0242 min⁻¹, see figure 7(b)). However, as shown in table 1, to enhance the photocatalytic activity of Ag₃PO₄-composite, the proportion of Ag₃PO₄ often exceeds 50% [18, 20, 24, 25, 30]. Therefore, the superiority of the HGMs-Ag₃PO₄ composite is obvious.

In views of the loading of Ag₃PO₄ catalyst, the floating HGMs-Ag₃PO₄ composites as the photo-catalyst could not only greatly decrease the input of Ag₃PO₄ and the cost, but also obviously enhance the photo-degradation efficiency. Moreover, it is easy to salvage and recover in practical applications, indicating that the floating HGMs-Ag₃PO₄ composites can work as an efficient and promising visible-light photo-catalyst.

In order to investigate the effect of the initial MB concentration on the photo-catalytic properties of floating HGMs3 and sinking HGMs4, the degradation rates of MB solution with three different initial concentrations were measured under visible-light irradiation demonstrated in figure 8. When the initial MB solutions increased from 5 to 20 mg l⁻¹, the MB removal efficiency of floating HGMs3 and sinking HGMs4 decreased much, but the high removal efficiency could be reached after a longer contact time. It was consistent with the results reported in previous works [44]. With the increasing of initial MB solutions, the apparent rate constants (k) of the floating HGMs3 for three initial MB solutions of 5, 10 and 20 mg l⁻¹ (in figure 8(a)) were respectively 0.0444, 0.0119 and 0.0037 min⁻¹, while the values of the sinking HGMs4 were only 0.0229, 0.0069 and 0.0016 min⁻¹. These results illustrated that the floating HGMs3 has larger light contact area and better photo-catalytic performance than the sinking HGMs4.

The cycling photo-degradation tests were carried out to investigate the stability of floating HGMs-Ag₃PO₄ composites under visible-light irradiation, as exhibited in figure 9(a). After each cycle, the amount of MB adsorbed on HGMs3 decreased gradually, the apparent rate of photo-degradation reaction gradually slowed down. This result is due to the fact that Ag₃PO₄ was reduced to Ag (Ag⁺ + e⁻ → Ag⁰) under light exposure [32]. As described in figures 3(e) and 4, silver component was proven in the HGMs-Ag₃PO₄ composites. The photocatalytic efficiency of the sample HGMs3 after five cycles was poor, but we can use it as a catalyst for chemical reduction to degrade 4-NP (p-Nitrophenol) and MO (Methyl Orange), as shown in figure 9(b). With the addition of excess reducing agent sodium borohydride (NaBH₄), the degree of degradation of 0.1 mmol l⁻¹ 4-NP and MO is very low, but after adding the 0.25 g l⁻¹ 5-cycled HGMs3, both 4-NP and MO can be almost fully degraded within 10 min. In this process, the reducing agent NaBH₄ plays two roles: in-situ reduction of the remaining Ag₃PO₄ on the 5-cycled HGMs3 to Ag⁰ and reduction of 4-NP and MO. In other words, 5-cycled HGMs3 can also be used as a catalyst to degrade organic pollutants and further exert its effectiveness.

### 3.3. Possible photo-catalytic mechanism

The following reasons may account for the improved photo-catalytic properties of floating HGMs-Ag₃PO₄ composites. In the first place, with hollow glass microspheres as the carrier of Ag₃PO₄, Ag₃PO₄ dispersed on the
surface of HGMs not only can improve the light contact chance to enlarge the active surface area of the composites, but also enhance the lattice defects to generate new active centers and improve the performance of Ag₃PO₄. Secondly, the as-prepared HGMs-Ag₃PO₄ composites can be floating on the treatment solution, enlarging the light contact area and improving the photo-catalytic efficiency. Thirdly, Ag₃PO₄ particles loaded on the surface of HGMs showed rhombic dodecahedrons using facile ion exchange method, which had higher surface energy values for {110} facet and provide more catalytic active sites than other crystal forms, leading to improved adsorption capacity of dye molecules and better photo-catalytic properties. In addition, Ag₃PO₄ itself has excellent photo-catalytic properties, mainly due to the high dispersion of the conduction band (CB, +0.45 V versus NHE) and the large negative charge induced effect of PO₄³⁻ in Ag₃PO₄, resulting in the separation of photo-generated electrons and holes. As depicted in figure 10, the electrons on the valence band (VB) of Ag₃PO₄ absorb the photon energy larger than the bandgap of Ag₃PO₄ (2.45V versus NHE) to jump to the conduction band, leaving holes with oxidative properties at the original valence band position. These photo-generated holes could oxidize H₂O into strongly oxidative ·OH radicals and the electrons on the CB of Ag₃PO₄ combine with the absorbed O₂ to produce ·O₂⁻. These reactive species ·OH, h⁺, and ·O₂⁻ play a conducive role in the oxidative degradation of organic pollutants MB. Four methyl groups of MB can facilitate attack on MB by electrophilic species (·OH or h⁺ or ·O₂⁻) in the demethylation process and be advantageous for accelerating the photocatalytic oxidative degradation of MB. However, photogenerated electrons have a negative effect at the same time in photocatalytic degradation of MB. With the extension of visible-light illumination time, Ag replaces more active sites of Ag₃PO₄ for Ag₃PO₄ is easily reduced to Ag by photogenerated electrons under light, thus the amount of photo-generated holes is declined and the
photocatalytic performance of Ag₃PO₄ is decreased without any sacrificial agent [53]. Therefore, the further investigation was necessary to improve the stability of Ag₃PO₄.

4. Conclusions

In summary, Ag₃PO₄ was attached to the surface of the inorganic material HGMs via a facile ion exchange process to prepare the floating HGMs-Ag₃PO₄ composites using silane coupling agent as a bridge. The photocatalytic properties were assessed by the MB photo-degradation under the visible-light irradiation. The photocatalytic rate of the floating HGMs-Ag₃PO₄ composites was much larger than that of pure Ag₃PO₄ and the sinking HGMs-Ag₃PO₄ composites. The floating samples could float on the treatment solution and enlarge the contact area significantly between the photo-catalyst and the light, which is beneficial to enhance the efficiency of photo-degradation. The floating HGMs-Ag₃PO₄ composites, a promising photocatalyst that provides a potential approach for large-scale practical application on the removal of organic dye contaminants, which greatly cut down the cost and enhance the photo-catalytic properties under the visible-light irradiation.

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Conflicts of interest

There are no conflicts to declare.

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