Co$_3$O$_4$ nanoparticles decorated Ag$_3$PO$_4$ as heterostructure for improving solar-light-driven photocatalysis

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Abstract: As a common photocatalytic material, Ag$_3$PO$_4$ still faces the challenge including the fast recombination of photo-generated electron-hole (e$^-$-h$^+$) pairs. In this work, we prepared Co$_3$O$_4$/Ag$_3$PO$_4$ heterojunction with good optical properties by an in-situ precipitation method. Compared to pure Ag$_3$PO$_4$, the Co$_3$O$_4$/Ag$_3$PO$_4$ exhibited greatly improved photocatalytic activities for degradation methylene blue (MB) and bisphenol A (BPA) under the visible light irradiation. Here, the degradation rate of MB could reach up to 12% which is about 35% higher than that of pure Ag$_3$PO$_4$, after 18 min irradiation. The degradation rate of BPA could reach up to 33% which is about 45% higher than the pure Ag$_3$PO$_4$. This work may provide insight for finding a new Ag$_3$PO$_4$ photocatalyst for promoting the photocatalytic performance.

1. Introduction
Preparing semiconductor photocatalyst is an effective strategy for solving increasingly severe environment trouble [1-3]. Co$_3$O$_4$ is one of p-type semiconductors, which has the following advantages: thermal arrest, chemical stabilization, low dissolubility, magnetism, catalytic performance and narrow band gap (1.2~2.1 eV) [4]. Based on the advantage above, Co$_3$O$_4$ can be applied as a photocatalyst or co-catalyst in visible-light-driven degradation reaction. According to previous report, it is found that the photocatalytic activity of Co$_3$O$_4$/BiOCl in photocatalytic degradation of methyl orange (MO) and rhodamine B (Rh B) was significantly better than the pure BiOCl. However, it always faces the challenges of photo-corrosion phenomenon and slight soluble in water. Those shortcomings such as poor stability in photocatalysis and photo-generated e$^-$-h$^+$ pairs, limited the catalyst’s practical application [5]. When solving above difficulties, Co$_3$O$_4$ will put up excellent photocatalysis performance. We all know that the microstructure of composite photo-catalyst playing an important role in photo-catalyst process. Therefore, researches are looking for appropriate semiconductor to load on Ag$_3$PO$_4$ composite as electron acceptor material. It can reduce the recombination rate of e$^-$-h$^+$ pair and improve its activity and stability.

In this work, the Co$_3$O$_4$/Ag$_3$PO$_4$ with good optical properties was prepared by an in-situ precipitation method. Compared to pure Ag$_3$PO$_4$, the Co$_3$O$_4$/Ag$_3$PO$_4$ exhibited greatly improved photocatalytic activities for degradation methylene blue (MB) and bisphenol A (BPA) under the visible light irradiation. Co$_3$O$_4$ hexagonal nanoplates were decorated on the surface of Ag$_3$PO$_4$ nanoparticle forming heterojunction which can make composites take shape compact interface and separate...
photo-generated e⁻h⁺ pairs effective. Meanwhile, Co₃O₄ nanoparticle loaded on the surface of Ag₃PO₄ can protect the Ag₃PO₄ from dissolution in aqueous solubility which enhances composite material’s stability during the degradation process.

2. Experiment section

2.1 Synthesis of the samples

The pure Ag₃PO₄ was prepared using an in-situ precipitation method. Firstly, AgNO₃ (0.340 g) was dissolved in 20 mL distilled water. Subsequently, Na₃PO₄·12H₂O (0.25 g) was dissolved in 30 mL deionized water [6]. Then, the Na₃PO₄·12H₂O solution was added into the AgNO₃ solution. The reaction process was carried out under the condition of the water bath. The temperature was kept at 60ºC while keep stirring. It generated yellow substance during the procedure. After adding, the progress was stirring for 30 min while avoiding light. Afterwards, the solution containing the Ag₃PO₄ was washed by ethanol and deionized water for 3 times. Later, drying at 60 ºC in the drying oven.

The Co₃O₄ nanosheets were prepared by hydrothermal method and calcination method. First, the Co(NO₃)₂·6H₂O (0.38 g) and PVP (0.5 g) were mixed was evenly dispersed into 20 mL deionized water and ethanol (V/V = 1:1) mixed solution [4]. After stirring for 30 min, NaOH (20 ml, 0.4 M) was added slowly into the above solution. The mixture was stirring until the solution changed from red to blue. Then, the solution was fall into a reaction still and heated at 200ºC for 12 h. This process can obtain the precursor Co(OH)₂. The precursor Co(OH)₂ was collected and separated by centrifuge. Later, product washed by ethanol and deionized water for several times. It was followed by that the product was heated at a rate of 1 ºC /min to reach a temperature of 300 ºC, and the tempered at this temperature for another 2h in an air atmosphere. In the end, this process can obtain the black Co₃O₄ nanosheets.

To obtain Co₃O₄/Ag₃PO₄ photocatalysis composite, the generated Co₃O₄ was put into 20ml deionized water and disperse by ultrasound. 0.340 g Ag₃PO₄ was dissolved in it. Then 30ml Na₃PO₄·12H₂O solution was added to the above solution. The reaction was carried out under water bath at 60ºC and stirring continuously. During this process, yellow particles were gradually generated. Later, the mixture was stirred for 1 h by avoid light. Finally, the photocatalyst collected and washed with deionized water and ethanol for three times, then dried at 60 ºC in drying oven. According to the weight ratio of Co₃O₄ compared with Ag₃PO₄, the composites were noted as 1% Co₃O₄/Ag₃PO₄, 2% Co₃O₄/Ag₃PO₄, 3% Co₃O₄/Ag₃PO₄, 5% Co₃O₄/Ag₃PO₄.

3. Results and discussion

The X-ray diffraction (XRD) patterns can analyze the as-prepared Co₃O₄/Ag₃PO₄ samples crystal texture. From Figure 1, the peaks located at 18.85°, 31.16°, 36.84°, 44.74°, 59.38° and 65.38° correspond to the (100), (220), (311), (400), (511), (440) crystal planes of Co₃O₄ (JCPDS card No.43-1003) [7]. Compared with the pure Ag₃PO₄, the peaks located at 0.88°, 29.69°, 33.29°, 36.59°, 42.48°, 47.79°, 52.69°, 55.02°, 57.28°, 61.64°, 65.84°, 69.91°, 71.90° and 73.87° correspond to the (110), (200), (210), (211), (220), (310), (222), (320), (321), (400), (330), (420), (421) and (332) crystal plane of Ag₃PO₄ (JCPDS card No.06-0505) [8]. The disappearance of the (311) crystal plane of Co₃O₄ in the composites is because this peak is close to Ag₃PO₄ characteristic diffraction peaks and the content is relative low.
Figure 1. XRD patterns of the as-prepared samples.

The microstructure of samples was characterized by scanning electron microscope (SEM). As shown in Figure 2(a), the pure Co₃O₄ shows hexagonal nanoplate structure with the size of 150-300 nm. This kind of structure can shorten the charge transfer distance and provide flat surface for the loading of other components. It can be observed that the Ag₃PO₄ nanoparticles were successfully loaded on the surface of Co₃O₄. (Figure 2(a), (b)) The Figure 2(d-g) show that elements such as Ag, P, O and Co were dispersed evenly on the as-prepare sample, further demonstrating the uniform dispersion of the Ag₃PO₄ by the in-situ loading method.

Figure 2. SEM images of the samples: (a) Co₃O₄, (b-c) 2% Co₃O₄/Ag₃PO₄, Element mapping of the 2% Co₃O₄/Ag₃PO₄, (d) Ag, (e) P, (f) O, (g) Co.

The light absorption capacity of sample is shown in Figure 3a. Pure Ag₃PO₄ has strong light absorbance in the visible light with wavelengths less than 500 nm and ultraviolet region. With the increase of the content of Co₃O₄ in the Co₃O₄/Ag₃PO₄ composites, the light absorption capacity of the composites increases gradually. Compared with the pure Ag₃PO₄, the absorbance of the composites is significantly enhanced in the visible light with the wavelength greater than 500 nm. Therefore, the composite can utilize more solar energy in typical photocatalytic reaction.

Figure 3b shows the photocurrent-time curve of pure Ag₃PO₄ and 2% Co₃O₄/Ag₃PO₄ composite. It can explain that the photocurrent intensity of 2% Co₃O₄/Ag₃PO₄ is higher than the photocurrent intensity of pure Ag₃PO₄. 2% Co₃O₄/Ag₃PO₄ has a relatively stable photoelectric response intensity. The formation of a heterostructure between the complexes can accelerate the transmission efficiency of photogenerated electrons and holes and enhance the stability of the catalyst.
Figure 3. (a) UV-vis absorption spectra of the samples: Co$_3$O$_4$ and (b) Photocurrent-time dependence under visible light irradiation of the samples: Ag$_3$PO$_4$ and 2% Co$_3$O$_4$/Ag$_3$PO$_4$.

The photocatalytic activity of materials was measured by methylene blue (MB) and bisphenol A (BPA) degradation experiments. From the Figure 4(a), 2% Co$_3$O$_4$/Ag$_3$PO$_4$ displays the best performance and the degradation rate of MB reaching up to 12% which is about 35% higher than that of pure Ag$_3$PO$_4$ after 18 min irradiation. The photocatalytic performance showed a trend of increasing first, then decreasing with the increase of the proportion of the composite. More Co$_3$O$_4$ loaded on Ag$_3$PO$_4$ lead to decreased photocatalytic performance, probably because too much Co$_3$O$_4$ will block the light absorption of Ag$_3$PO$_4$ and induce aggregation. As shown in Figure 4(b), it indicates that 2% Co$_3$O$_4$/Ag$_3$PO$_4$ can effectively degrade MB dye under visible light irradiation. To further verify the activity of the composite photocatalyst, BPA was degraded by samples (Figure 5). The degradation rate of BPA could reach up to 33% which is about 45% higher than that of pure Ag$_3$PO$_4$ after 21 min irradiation.

The conduction band (CB) and valence band (VB) of Ag$_3$PO$_4$ are 0.45 eV and 2.9 eV respectively. And the conduction band (CB) and valence band (VB) of Co$_3$O$_4$ are 0.41 eV and 2.48 eV, respectively. The band position of Co$_3$O$_4$ is slightly higher than Ag$_3$PO$_4$. According to previous reports, it can make the following assumption that Co$_3$O$_4$ and Ag$_3$PO$_4$ form a heterostructure in the composite.
Photo-generated electron-hole pairs are generated under visible light irradiation by Co$_3$O$_4$ and Ag$_3$PO$_4$ respectively. Then, the electrons in the Ag$_3$PO$_4$ conduction band recombine rapidly with the holes in the Co$_3$O$_4$ valence band. At the same time, the reduction reaction in the conduction band of Co$_3$O$_4$ generates H$_2$O$_2$, which can enhance the photocatalytic pollutant degradation effectively. As shown in **Figure 6**, the photo-generated electrons of the Ag$_3$PO$_4$ conduction band are transferred effectively which avoids photo-corrosion of the catalyst and improves the stability of the catalyst.

![Figure 6. Schematic diagram of 2% Co$_3$O$_4$/Ag$_3$PO$_4$ composite photocatalyst.](image)

### 4. Conclusion

In summary, Co$_3$O$_4$/Ag$_3$PO$_4$ photocatalyst was prepared successfully by in-situ synthesis method. Ag$_3$PO$_4$ nanoparticles and Co$_3$O$_4$ nanosheets were tightly combined to form a heterostructure. By degradation experiments, 2% Co$_3$O$_4$/Ag$_3$PO$_4$ is the best ratio of the composite. It has the highest degradation efficiency. The degradation rate of MB could reach up to 12% which is about 35% higher than that of pure Ag$_3$PO$_4$. The degradation rate of BPA could reach up to 33% which is about 45% higher than that of pure Ag$_3$PO$_4$. The dissolved oxygen forms H$_2$O$_2$ which promotes the organic degradation during the photocatalytic reaction. The transference of photo-generated electrons from the Ag$_3$PO$_4$ conduction band to the Co$_3$O$_4$ valence band increases the separation of charge effectively. And Co$_3$O$_4$ loaded on the surface of Ag$_3$PO$_4$ enhances the stability of samples. Those characteristics can improve the photocatalytic performance of the composite which have potential application value for environmental protection.

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