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PREPARATION AND PHOTOCATALYTIC ACTIVITY OF SILVER PHOSPHATE MODIFIED BY NANO-SILVER METAL

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Since the 21st century, a variety of photocatalytic materials have been developed, in which the properties are not the same, but the photocatalytic degradation activity of Ag_3PO_4 is much higher than other known visible light catalysts, and Ag_3PO_4 exhibits excellent performance under visible light. Photocatalytic performance has received attention. In order to prepare a more stable and efficient Ag_3PO_4 photocatalytic material, the photocatalytic performance of Ag_3PO_4 was improved by nano-metal Ag modification of Ag_3PO_4. Nano-modified silver phosphate was prepared by coprecipitation method and hydrothermal method using silver nitrate and potassium dihydrogen phosphate as raw materials, and analyzed by x-ray diffraction (XRD), scanning electron microscope (SEM), Photoluminescence (PL), ultraviolet diffuse reflection and photodegradation etc. The performance improvement effect of the prepared nano-metal modified silver phosphate was examined. In this experiment, Rhodamine was used as the degraded solution. Through the photodegradation experiment, that is, under the illumination of LED lamps, it can be observed that the performance of nano-metal Ag-modified silver phosphate is improved compared with pure Ag_3PO_4, and the prepared nano-metal Ag is modified. The degradation rate of rhodamine at Ag_3PO_4 can reach 99% at 10 minutes.

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1. Introduction

Many chemical industry departments now directly release their organic and inorganic pollutants into water sources, which are the main water pollutants. [1-4] The water pollution caused by this industrial pollution affects aquatic organisms and other living things, which in turn affects human life. Among these pollutants, waste organic dyes from many industrial processes are highly dangerous and carcinogenic and need to be carefully treated before being released into the water. [5–7] However, due to the expensive and time consuming waste disposal process, they are often directly discharged into local water bodies, affecting the environment. This problem can be overcome with the help of semiconductor photocatalytic technology, which is an economical, rapid and environmentally friendly method for degrading organic and inorganic contaminants.

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Whether it is in environmental management, agricultural development, clean energy and other aspects of semiconductor photocatalytic materials have shown its excellent performance. [8] It is precisely because of this that many researchers have discovered the broad application prospects of semiconductor photocatalytic materials, and began to study the photocatalytic properties of semiconductor photocatalytic materials, and tried to improve and improve its photocatalytic performance. [9] In the early 1970s, some scientists who were at the forefront discovered that TiO_2 can decompose water under photocatalytic conditions. [10-15] Subsequently, a corresponding article was published on Nature, and thus the multiphase photocatalyst began to receive the attention of the scientific community. In the following years, some people began to carry out a series of pollutant degradation experiments using semiconductor photocatalysts, and made breakthroughs. At this point, the way of photocatalyst has been greatly expanded. After the 1990s, with the rapid development of nanotechnology, nanomaterials have been widely used in many fields such as environmental protection, building materials, and health care. [16] Therefore, research on nanoscale photocatalytic materials has become a major trend. As a world problem, environmental pollution and treatment are getting more and more attention. Therefore, semiconductor photocatalysts with excellent degradation properties have been recognized by most scientists. [17] Under such a background, semiconductor photocatalytic materials have gradually developed.

Although a variety of photocatalytic materials have been developed, many of which have relatively mature photocatalytic materials such as titanium dioxide, etc., in general, the utilization of visible light in these photocatalytic materials on the market is still relatively low. On the horizontal line, it is precisely because of the urgent need for a photocatalytic material that uses visible light more efficiently, and the application of silver phosphate photocatalytic materials. The first to discover the high photocatalytic activity of silver phosphate was Professor Ye Jinhua from Japan. After extensive experiments, he confirmed the high photocatalytic activity of silver phosphate. Professor Ye Jinhua then published the results in the material version of the journal Nature. This is the first report of a new photocatalyst. [18-20] Professor Ye Jinhua's team found that the maximum visible light absorption wavelength of silver phosphate is 520 nm, and its quantum yield under visible light is 90%. It is the strong oxidizing ability of silver phosphate under visible light, which has attracted the attention of researchers. In the oxygen production experiment, the ratio of Ag_3PO_4 under visible light is much higher than other visible light response catalysts. At the same time, in the methylene blue photocatalytic degradation experiment, silver phosphate showed excellent degradation ability. [20-22] The rate of degradation of equivalent methylene blue under visible light far exceeds that of other photocatalysts, such as titanium dioxide. However, due to the low cost performance, low stability and high probability of electron-hole recombination of Ag_3PO_4 [16], silver phosphate photocatalytic materials are still in the stage of research and modification, and have not been widely promoted. Because of this, improving the stability of silver phosphate is our main task at present.

Although there are many photocatalysts that start very early, some of them have excellent performance, but without exception, they all have big defects, such as titanium dioxide. [23] However, with the increase of the use time, the disadvantage of TiO_2 as a common photocatalytic material is gradually exposed, and most of the visible light is not within its absorption range. This results in a relatively low photocatalytic ability of TiO_2, which is not satisfactory. As a novel photocatalyst, silver phosphate is slightly soluble in water, resulting in greatly reduced structural stability. In addition, when silver phosphate is exposed to air, it is easily oxidized, that is, during long-term contact with air, silver phosphate produces photochemical corrosion and produces silver, and the resulting black silver element remains in phosphoric acid. [24-25] The surface of the silver particles reduces the utilization of light by silver phosphate and greatly reduces the activity of silver phosphate. In addition, the process of preparing silver phosphate requires a large amount of Ag consumption, which is expensive and limits its large-scale application.

It is precisely because of the slight corrosiveness of silver phosphate and the easy reduction of Ag¬+ to Ag elementality, which leads to a decrease in the Ag+ concentration in the photocatalytic material, which causes the catalytic efficiency of silver phosphate to decrease. In this paper, nano-metal Ag was used to modify silver phosphate to reduce the optical corrosion of silver phosphate, and to study the morphology, structure and photocatalytic performance of nano-metal Ag modified silver phosphate. This experiment aims to prepare a better and more stable silver phosphate photocatalyst by modification of nano-metal Ag.

2. Materials and methods

2.1. Preparation of silver phosphate by coprecipitation

Weigh 0.02 mol of AgNO3 and mix it with 50 ml of distilled water, and stir until dissolved. Dilute 5 times diluted dilute ammonia water, continue to drop after the brown precipitate appears, stop the addition when the precipitate just disappears. Dilute 5 times diluted dilute nitric acid into the configured silver ammonia solution until the pH of the silver ammonia solution Stop at =8. Weigh 0.03mol KH2PO4 and mix with 50ml of distilled water, stir to dissolve, form KH2PO4 solution, and add KH2PO4 solution to the silver ammonia solution dropwise, stir for 30 minutes. After stirring, let stand at room temperature for 15 minutes. Then, it was washed three times with deionized water and absolute ethanol, and dried in a vacuum oven at 70 ° C for 40 minutes.

2.2. Preparation of nanometer metal Ag modified silver phosphate

Weigh 0.003 mol of AgNO3 and mix it with 50 ml of distilled water and stir until dissolved. Dilute the diluted ammonia water by 5 times, add the brown precipitate and continue to drop. When the precipitate just disappears, stop the dropwise addition. Dilute the diluted nitric acid by 5 times in the configured silver ammonia solution and adjust to the silver ammonia solution. Stop at pH=8. Weigh a certain amount of nano-metal Ag into the configured silver ammonia solution and stir for 20 minutes. The stirred solution was sonicated for 30 minutes. Weigh 0.001mol of KH2PO4 and mix it with 50ml of distilled water, stir until dissolved, form KH2PO4 solution, and add the configured KH2PO4 solution to the silver ammonia solution dropwise, stir for 20 minutes. After stirring, let stand at room temperature for 15 minutes, then use Ionized water and absolute ethanol were washed three times and placed in a vacuum oven at 70 ° C to dry.

2.3. Characterization

The powder X-ray diffraction (XRD) of Ag_3PO_4, X%Ag/Ag3VO4 was recorded by Panalytical Empyrean diffractometer. The morphology and structure of all samples were characterized byscanning electron microscopy (SEM S4800). The morphology and structure of all samples were characterized by

Photoluminescence spectra (PLFLS920) and UV–Vis diffuse reflectance spectroscopy (DRS,PerkinElmer Lambda 950) were used to characterize the optical properties of as-prepared samples.

2.4. Photocatalytic activity evaluation

The degradation performance of the prepared photocatalysts wastested by using Rhodamine B (5 mg/L, 30 mL) as an organic pollutant in 50 mL quartz glass vessel under the illumination of 50 W 410 nm Light Emitting Diode (LED). The distance between the LED light source and the reactor was adjusted to 50 mm. Typically, the required amount of photocatalyst is 50.0 mg, and the degradation percentage of Rhodamine B was tested by spectrophotometer (721G, Shanghai Precision Instrument Co.,Ltd) every two minutes.

3. Results and discussion

In this experiment, we selected nano-metal Ag to modify silver phosphate to improve its photocatalytic performance. The loading of Ag was 0.01g, 0.02g, 0.03g, 0.04g, 0.05g, 0.06g, 0.07g, 0.08g, 0.09g, A representative sample of photocatalytic performance superior to pure silver phosphate and a representative sample with poor photocatalytic performance compared to pure silver phosphate in the photodegradation test were selected for further analysis by XRD, SEM, PL, UV diffuse reflection, etc. .

In order to observe the photocatalytic effect of silver phosphate when the silver loading is 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, we have done a photocatalytic degradation test. The result is shown in Figure 1.

The ten sets of experiments in Fig. 1 are pure silver phosphate prepared by co-precipitation method and silver phosphate with different Ag loadings (1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9). %) Degradation of Rhodamine B. From Fig. 1, we can clearly observe that the photocatalytic performance of the sample with only 1% and 2% of supported Ag is better than that of pure silver phosphate. When the amount of Ag is 3%, the catalytic performance is the same as that of pure silver phosphate. After that, as the amount of supported Ag increases (4%-9%), the catalytic performance of the sample gradually decreases, so we can conclude that when the amount of Ag supported exceeds 2%, the catalytic performance of the sample will not increase. Therefore, if you want to improve the catalytic performance of pure silver phosphate, you should control the amount of supported Ag within 2%.

In order to analyze the composition of silver phosphate with a nano-metal silver loading of 1% and 5%, we performed an XRD test. The results are shown in Fig. 2.

Because in the photodegradation test, we found that when the loading of silver exceeds 3%, the photocatalytic performance of nano-metal Ag-modified silver phosphate deteriorates, so we have selected a group that has improved photocatalytic performance of silver phosphate (1) %),selected a group of silver phosphate photocatalytic performance decreased (5%), and the factors affecting the photocatalytic performance of silver phosphate were analyzed by these two groups.

Fig. 2 shows the XRD pattern of nano-metal Ag-modified silver phosphate. We can clearly observe that the diffraction peak of Ag in nano-metal-modified silver phosphate corresponds to the diffraction peak of nano-metal Ag (JCPDS.NO.65-2871); The diffraction peaks of silver phosphate in the sample correspond to the diffraction peaks of silver phosphate (JCPDS.NO.06-0505). So we can conclude that in these two sets of experiments, nano-metal Ag has been successfully loaded onto silver phosphate. At the same time, by comparing the XRD patterns of the two sets of nano-metal Ag-modified silver phosphate with the XRD pattern of silver phosphate, we can observe that as the nano-metal Ag incorporation increases, the diffraction peak-to-peak value of silver phosphate is decreased, indicating that the increase in the amount of nano-metal Ag incorporated affects the crystallinity of silver phosphate.

In order to observe the morphology of silver phosphate with a silver loading of 1% and 5%, we performed a scanning electron microscope test and an EDS test. The results are shown in Fig. 3.

The general particle size and morphology of the silver phosphate sample prepared by the coprecipitation method were characterized by SEM as shown in Fig. 3(a). Fig. 3 (a)shows that the silver phosphate prepared this time is a mixture of small spherical particles and polyhedrons, but the morphology of the cubic phase is dominant.Because the cubic phase morphology of silver phosphate has greater photocatalytic activity than the spherical morphology of silver phosphate, this also indicates that the silver phosphate produced this time has higher activity. The electron micrograph of 5% nano-metal Ag-modified silver phosphate showed more adhesion of Ag than that of 1% Ag-modified silver phosphate.But at the same time, we can also observe that the particle size of silver phosphate produced in this experiment is different, the larger grains have about 500nm, and the smaller ones are only tens of nanometers.This also illustrates the randomness of the growth of silver phosphate grains during the preparation of silver phosphate by the coprecipitation method. At the same time, we can observe the Ag particles attached to the above, the shape is irregular, the diameter is about tens of nanometers, and it is randomly attached to the silver phosphate particles. It can be seen from Fig. 3(b) that the particles on the edge of Ag_3PO_4 are indeed elemental to Ag, which fully indicates that Ag does adsorb to the surface of Ag_3PO_4.

In order to observe the recombination rate of silver phosphate photogenerated electron-hole when the silver loading is 1%, 5%,We did a photoluminescence test and the results are shown in Figure 4.

It can be seen from Fig. 4 that when the amount of nano metal metal Ag added is 1%, the fluorescence luminosity of the composite silver phosphate is weaker than that of the pure silver phosphate prepared by the coprecipitation method, and the opposite is true at 5%. It is indicated that in the three groups, the silver metal phosphate has a lowest probability of electron-hole pair recombination when it is added at 1%.Among them, the electron-hole pair recombination is the highest when the addition amount of the nano metal metal Ag is 5%.

Fig. 5 is a graph showing the light absorptivity of three samples when the nano metal Ag loading was 0%, 1%, 5% measured by an ultraviolet visible diffuse reflectance spectrometer. Figure 6 is a Tauc plot corresponding to three samples, with the abscissa (hv) and the ordinate (ahv)2. It can be seen from Fig. 5 that the maximum light absorption boundary value of the pure Ag_3PO_4 sample is about 520 nm, which is consistent with the narrow band gap of Ag_3PO_4. When the nano metal Ag loading is 1%, the maximum light absorption boundary value of the sample is around 540 nm, and the absorption edge appears red shift. When the nano metal Ag loading is 5%, the maximum light absorption boundary value of the sample is on the left side of 500 nm, and the absorption edge appears blue shift. It can be seen from Fig. 6 that when the nano-metal Ag loading is 1%, the forbidden band width is narrower than that of pure Ag_3PO_4. Combined with fluorescence spectrum analysis, the photogenerated electron-hole pairing ratio inside the material is relatively low, thus making it High catalytic activity. When the doping amount of nano-metal Ag is 5%, the forbidden band width is slightly higher than that of pure Ag_3PO_4. Combined with fluorescence spectrum analysis, the photo-generated electron-hole pairing ratio inside the material is relatively high, which makes the catalytic activity worse.

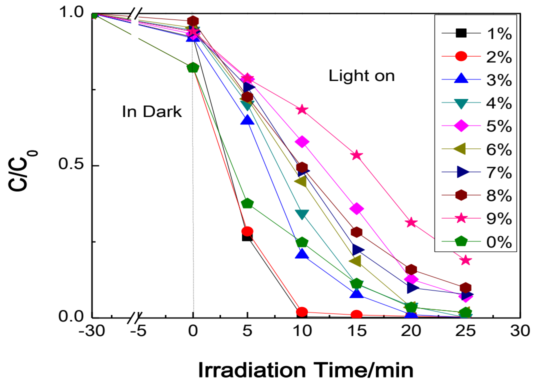


Fig. 1. Photodegradation curve of nanometer metal Ag modified silver phosphate by precipitation method.

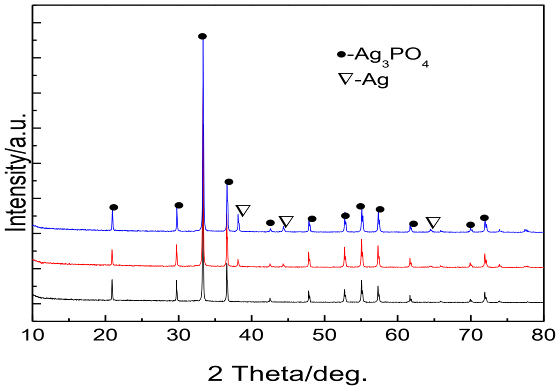
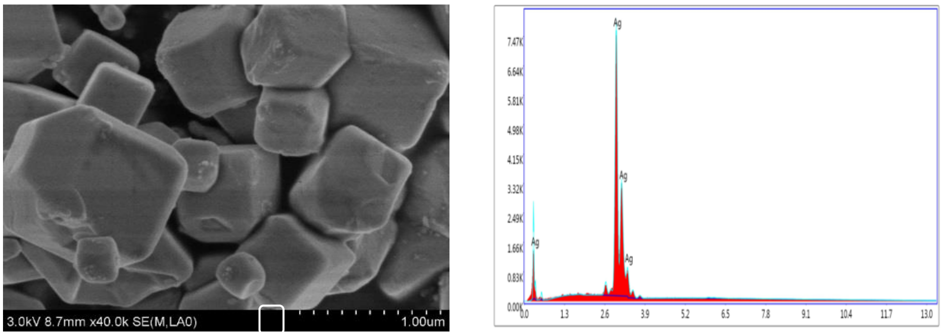


Fig. 2. XRD pattern of nanometer metal Ag modified silver phosphate by precipitation method.



a)

b)

Fig. 3. Scanning electron microscopy and EDS map of Ag/ Ag_3PO_4 samples.
(a) Scanning electron micrograph of nano-metal Ag-modified silver phosphate.
(b) EDS map of Ag/ Ag_3PO_4 samples

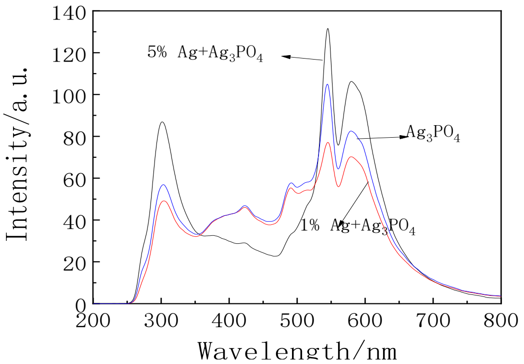


Fig. 4. PL map of nano-metal modified silver phosphate.

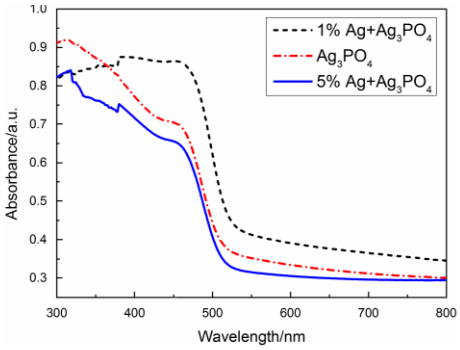


Fig. 5. UV-vis DRS spectra of Ag_3PO_4 samples with different Ag loadings.

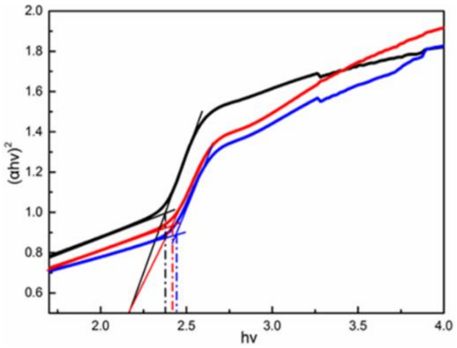


Fig. 6. Forbidden band width map of Ag_3PO_4 samples with different Ag loadings.

4. Conclusions

In the experiment, the nano-metal silver-modified silver phosphate prepared by the co-precipitation method has a higher photocatalytic performance than the pure silver phosphate when the loading of silver is less than 2%.When the loading of silver is more than 2%, the photocatalytic performance of the sample is lower than that of pure silver phosphate.

Through the XRD pattern, we know that the nano-metal silver was successfully loaded onto the silver phosphate. Combined with the SEM and EDS spectra, we can know that the nano-metal silver is indeed loaded on the silver phosphate, which confirms the XRD conclusion. In the PL spectrum, we can see that when the loading of silver is below 2%, the fluorescence of the sample is weaker than that of pure silver phosphate, which indicates that the recombination rate of the electron-hole pairs of the sample decreases.

In the UV diffuse reflectance spectrum, we can see that when the loading of silver is below 2%, the forbidden band width of the sample is narrower than that of pure silver phosphate, which means that the maximum absorption light wavelength of the sample increases at this time.

In summary, we can see that when the loading of silver is 1%, the photocatalytic performance of the sample increases the most.The mechanism is achieved by suppressing the recombination rate of electron holes and increasing the absorption range of visible light.

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