Study on properties of zinc ferrite, titanium dioxide and their composites

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Abstract: In this paper, the methods of sulfuric acid leaching and chemical coprecipitation were used to prepare products such as purified zinc ferrite, synthetic zinc ferrite, synthetic titanium dioxide and its complex with purified zinc ferrite. The morphology and microstructure of the above samples were characterized and analyzed by XRD and SEM. The results showed that the purified zinc ferrite contained a small amount of ZnO, SiO_2, Al_2O_3 and $PbSO_4$. Its particle size was the largest and the crystallinity was the best, but the surface was not smooth, the particle size distribution was not uniform and there was agglomeration phenomenon. The purchased zinc ferrite had high purity, the smallest particle size and the worst crystallinity. Its surface was smooth, particle size distribution was uniform, and it was loose and porous. The synthetic zinc ferrite had high purity, smooth surface, uniform particle size distribution and obvious agglomeration. The prepared titanium dioxide had no other impurities, good crystallinity, smooth surface and certain agglomeration phenomenon. For the zinc ferrite/titanium dioxide composite, adding a small amount of purified zinc ferrite would change the crystallinity of titanium dioxide, but it had little effect on the grain size of titanium dioxide. The surface was rough, the particle size distribution was not uniform, and there was agglomeration phenomenon.

1. Introduction

In recent years, with the continuous development of industrial production, the discharge of industrial wastewater is large, so how to effectively carry out comprehensive treatment of industrial wastewater is crucial. As the main industrial wastewater, dye wastewater is difficult to treat. Photocatalytic technology is an effective wastewater pollutant decomposition technology, which can effectively degrade pollutants by oxidation-reduction decomposition of many organic substances into inorganic small molecules such as CO_2, H_2O, HX and mineralized substances, and has the characteristics of environmental friendliness. For example, nano-zinc ferrite and nano-titanium dioxide are used as photocatalytic oxidation catalysts because of their good physical properties. Zinc ferrite is an important material and has been widely used as a magnetic material, a gas sensor, a catalyst, a photocatalyst, an absorption material, etc[1-3]. Spinel zinc ferrite nanoparticles can be prepared by many physical and chemical methods, such as sol-gel method, chemical coprecipitation method, hydrothermal synthesis method, high-temperature calcination method, solid phase synthesis method, microemulsion method and mechanochemical synthesis method. Titanium dioxide is a kind of semiconductor material with three crystal forms of anatase, rutile and brookite. Titanium dioxide has the characteristics of stable chemical properties, non-toxic, strong light stability, high oxidation efficiency and environmental friendliness[4-7]. However, in the practical application of photocatalysis technology, different materials and different preparation methods have certain effects on their photocatalytic properties, such as their composition, morphology, structure and other physical properties, thus affecting their chemical properties. Therefore, in this paper, sulfuric acid leaching zinc calcine was used to prepare purified zinc ferrite, chemical coprecipitation was used to prepare synthetic zinc ferrite and chemical coprecipitation was used to prepare titanium dioxide and its composite with purified zinc ferrite. On the basis of XRD and SEM, focus on the purification characterization of purified zinc ferrite, purchased zinc ferrite, synthetic zinc ferrite, synthetic titanium dioxide and its composite with purified zinc ferrite, laying a foundation for the subsequent exploration of the application of products in photocatalytic wastewater treatment.

2. Sample preparation

Put 100g zinc calcine into a beaker and added 100ml of 4mol/L sulfuric acid solution. After sealing, it was heated in 80℃ water bath and leached for 2 hours with stirring speed of 300r/min. After cooling, the supernatant was poured out, filtered and fully washed. After the filter cake was dried, it was pulverized, screened and reduced for sample preparation. The obtained sample is purified zinc ferrite, denoted as PZ.

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Took a certain amount of ferric nitrate nine-hydrate and zinc nitrate hexahydrate according to the substance ratio of 2:1, dissolved them in a beaker, and adjusted the pH value of the solution to 10 with sodium hydroxide. The supernatant was removed after magnetic stirring for 12h, standing for layering, and fully washed with ultra-pure water. The precipitation was dried in an oven at 80℃, and the precursor zinc ferrite was obtained. The precursor was moved to a crucible and calcined in a resistance box furnace at 400℃, 500℃, 600℃ and 700℃, respectively, and then taken out after holding for 2 hours. The calcined product was ground, screened and reduced to prepare sample. The obtained samples are synthetic zinc ferrite, denoted as SZ400, SZ500, SZ600 and SZ700.

30g titanium oxide sulfate and 200ml ultra-pure water were placed in a beaker and stirred magnetically at 60℃ until the solution was clarified. Then 45ml concentrated ammonia water was added and moved to a water bath at 60℃ for 40min at a rotating speed of 500r/min. The precursor of titanium dioxide was obtained by vacuum filtration, full washing and drying. The precursor was moved to a crucible and calcined in a box resistance furnace at 300℃, 400℃, 500℃ and 600℃ respectively, and then taken out after holding for 2 hours. The calcined product was ground, screened and reduced to prepare sample. The obtained samples are synthetic titanium dioxide, denoted as T300, T400, T500, T600 and T700.

Took 30g of titanium sulfate and added 200ml of ultra-pure water, stirred it magnetically at 60 ℃ until the solution was clear, then added purified zinc ferrite, and then added 45ml of concentrated ammonia water, moved the mixture into a water bath at 60℃, stirred it for 40min at a speed of 500r/min to obtain a white viscous mixed solution, and then decompressed and filtered it, fully washed it and dried it to obtain zinc ferrite/titanium dioxide precursor. Moved it to a crucible and placed it in a box-type resistance furnace for calcining at 400℃ and 500℃ respectively, and then took it out after holding for 2h. The calcined product was ground, screened and reduced to prepare sample. The samples obtained are synthetic titanium dioxide/purified zinc ferrite composite, recorded as T400/PZ (5%), T500/PZ (5%) and T500/PZ (10%).

3.1 XRD analysis

The X-ray diffraction analysis results of purified zinc ferrite, synthetic zinc ferrite and purchased zinc ferrite are shown in Figure 1 and Table 1. It showed that the diffraction peaks of synthetic zinc ferrite at the calcination temperature of 500~700℃ were roughly the same as the main diffraction peaks of purified zinc ferrite and purchased zinc ferrite. The 2θ diffraction angles of purified zinc ferrite, purchased zinc ferrite and synthetic zinc ferrite at different calcination temperatures were 30.080°, 35.084°, 37.066°, 42.953°, 53.153°, 56.809° and 62.339°, respectively. It corresponded to the standard pattern of zinc ferrite (PDF #87-7412). In addition, no other impurity peaks were observed between synthetic zinc ferrite and purchased zinc ferrite, indicating that its purity is high. However, in addition to the above diffraction peaks, the 2θ diffraction angle of purified zinc ferrite showed obvious diffraction peaks at 31.393°, 34.548°, 36.547°, 47.667°, 62.972°, 68.052° and 68.170°. And it corresponded to (100), (002), (101), (102), (103), (112) and (201) crystal planes in standard zinc oxide atlas (PDF#34-1651). There were also some weak diffraction peaks in the purified zinc ferrite, which were SiO_2, Al_2O_3, $PbSO_4$ and so on by phase retrieval analysis. The content of $ZnFe_2O_4$ in the purified zinc ferrite by XRD semi-quantitative analysis was 82.4%. From the point of view of the diffraction peak intensity, the diffraction peak of synthetic zinc ferrite gradually became higher and sharper with the increase of calcination temperature, indicating that the degree of crystallization gradually becomes better. The degree of crystallization of purchased zinc ferrite was not as good as that of synthetic zinc ferrite and purified zinc ferrite. The crystallinity of purified zinc ferrite was the best. The reason may be that the zinc concentrate is oxidized and calcined sufficiently, and the by-product zinc ferrite crystal is fully developed. In addition, the peak value of synthetic zinc ferrite shifts to the left when the calcination temperature was 400℃, which may be due to the fact that high calcination temperature is usually required for the preparation of zinc ferrite by precipitation method, but the calcination temperature is relatively low at 400℃, which causes incomplete lattice growth and distortion.

3. Characterization analysis

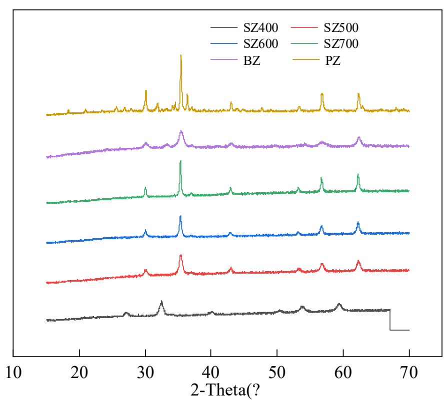

Fig. 1 XRD patterns of different kinds of zinc ferrite

Table 1 Crystal size of different kinds of zinc ferrite

Sample	SZ400	SZ500	SZ600	SZ700	BZ	PZ
Peak FWHM	0.558	0.497	0.368	0.269	0.675	0.227
Grain size/nm	31.33	35.19	47.51	65.00	25.91	77.04

Table 1 showed that the particle size of synthetic zinc ferrite increased with the increase of calcination temperature, ranging from 31.33nm to 65nm. The particle size of purchased zinc ferrite was 25.91nm, and the particle size of purified zinc ferrite after screening was 77.04nm.

The X-ray diffraction analysis results of titanium dioxide at different calcination temperatures are shown in Figure 2 and Table 2.

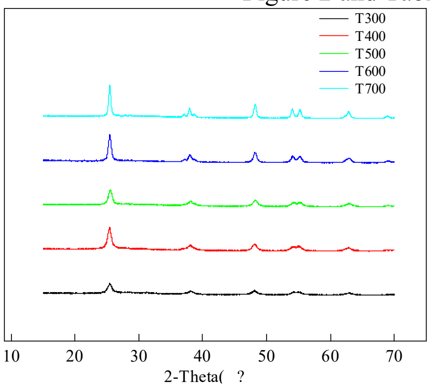

Fig. 2 XRD patterns of titanium dioxide at different calcination temperatures

It showed from Figure 2 that the positions of diffraction peaks of titanium dioxide prepared at calcination temperature of 300~700℃ were basically the same. However, the width and intensity of diffraction peaks changed with the increase of calcination temperature. The main diffraction peaks with 2θ center positions at 25.447°, 37.977°, 48.055°, 54.033°, 55.199°, 62.744° and 68.888° corresponded to the (101), (004), (200), (105), (211), (204) and (116) crystal planes of the standard atlas of anatase titanium dioxide PDF #21-7212, respectively. No diffraction peaks of other impurities and rutile and brookite titanium dioxide were found, which indicates that anatase titanium dioxide with high purity can be obtained by chemical coprecipitation method at calcination temperature of 300~700℃. In addition, with the increase of calcination temperature, the diffraction peak of titanium dioxide gradually became narrow and high, which indicates that the increase of calcination temperature is beneficial to the improvement of its crystallinity.

Table 2 Crystal size of titanium dioxide at different calcination temperatures

Sample	T300	T400	T500	T600	T700
Peak FWHM	0.610	0.573	0.612	0.490	0.382
Gain size/nm	15.12	16.10	15.08	18.83	24.15

It showed from Table 2 that the particle size of titanium dioxide prepared by chemical coprecipitation method varied slightly due to different calcination temperatures, and generally showed an upward trend, ranging from 15.12 to 24.15nm.

The X-ray diffraction analysis results of purified zinc ferrite/titanium dioxide composite with different mass ratios are shown in Figure 3 and Table 3.

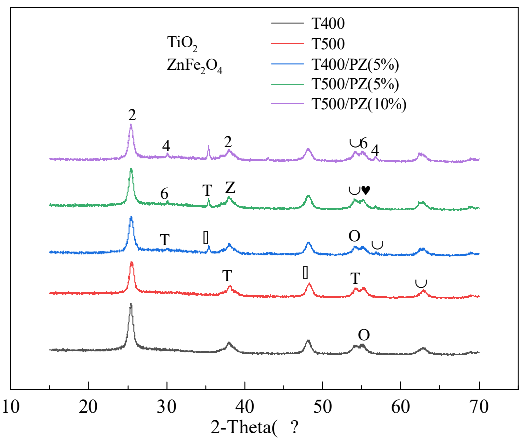

Fig. 3 XRD spectrum of titanium dioxide and purified zinc ferrite/titanium dioxide composite

Table 3 Grain size of titanium dioxide and purified zinc ferrite/titanium dioxide composite

Sample	T400	T500	T400/PZ(5%)	T500/PZ(5%)	T500/PZ(10%)
Peak FWHM	0.573	0.612	0.611	0.566	0.588
Gain size/nm	16.10	15.08	13.97	15.09	14.52

It showed from Figure 3 that only the characteristic peak at zinc ferrite (311) was detected because the doping amount of zinc ferrite was small. The diffraction peak intensity of titanium dioxide weakens with the increase of the amount of zinc ferrite added, indicating that the crystallinity of titanium dioxide will be changed by doping a certain amount of purified zinc ferrite and preparing titanium dioxide under parallel conditions. It showed from Table 3 that the grain size changed only slightly, and the particle size decreased by about 1nm.

3.2 SEM analysis

Figure 4(a) shows the SEM images before and after the purification of purified zinc ferrite powder, Figure 4(b) shows the SEM images of the purchased zinc ferrite, and Figure 5 shows the SEM images of the synthetic zinc ferrite at different calcination temperatures. It showed from Figure 4 and Figure 5 that the surface of purified zinc ferrite was smooth, the particle size distribution was uneven, the crystal was well developed, the crystal was seriously bonded, and only a few pores exist. The purchased zinc ferrite had smooth surface, uniform particle size distribution, better crystal development, and loose porosity. The surface of synthetic zinc ferrite was smooth, the particle size distribution was uniform, the crystal development was complete, and the adhesion between grains was serious at different calcination temperatures. The grain size increased with the increase of calcination temperature, which was basically consistent with the above XRD analysis results.

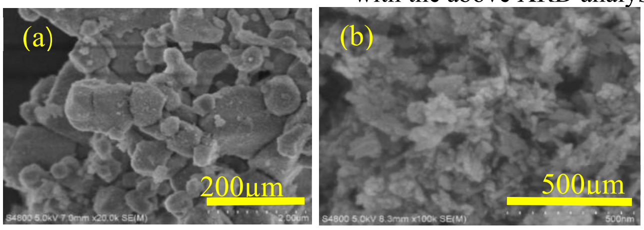

Fig. 4 SEM photographs of various samples: (a) SEM of powdered purified zinc ferrite; (b) SEM of purchased zinc ferrite

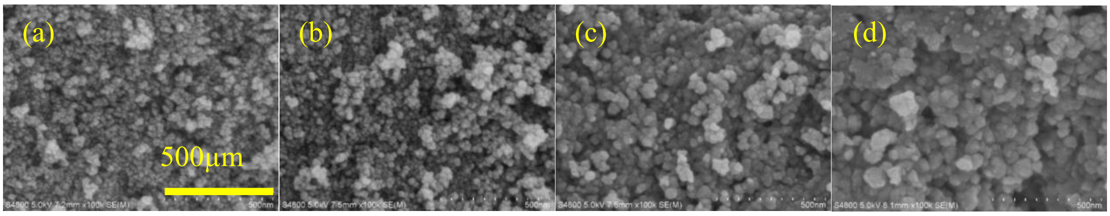

Fig. 5 SEM of synthesized zinc ferrite at different calcination temperatures: (a) SZ400; (b) SZ400; (c) SZ400; (d) SZ400

Figure 6 shows the SEM images of synthetic titanium dioxide at different calcination temperatures. Figure 7 shows the SEM image of purified zinc ferrite/titanium dioxide complex. It showed from Figure 6 that the surface of titanium dioxide synthesized at different calcination temperatures was smooth, the particle size distribution was relatively uniform, the grains were in a cohesive state, and the grain size generally increased with the increase of calcination temperature. It showed from Figure 7 that the crystal surface of the purified zinc ferrite/titanium dioxide composite was rough, the particle size distribution was uneven, and the adhesion between grains was serious.

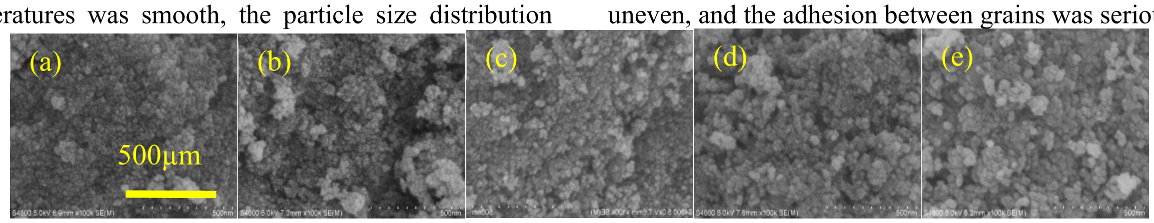

Fig. 6 SEM of titanium dioxide at different calcination temperatures: (a) T300; (b) T400; (c) T500; (d) T600; (e) T700

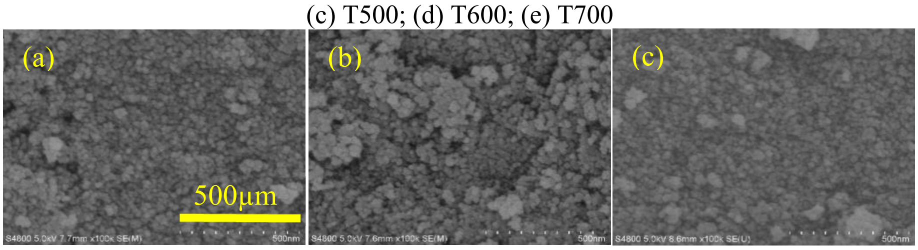

Fig. 7 SEM of purified zinc ferrite/titanium dioxide composite: (a) T500/ (10%); (b) T500/ (5%);

(c) T400/ (5%)

4 Conclusions

(1) The content of zinc ferrite in purified zinc ferrite was 82.4%, and it also contained a small amount of impurities such as ZnO, SiO_2, Al_2O_3 and $PbSO_4$. Its particle size was the largest, with an average particle size of 77.04nm, and the crystallinity was the best, but the surface was not smooth, the particle size distribution was not uniform, and there was agglomeration phenomenon. The purity of purchased zinc ferrite was high, the particle size was the smallest, the average particle size was 25.91nm, and the crystallinity was the worst. Its surface was smooth, particle size distribution was uniform, loose and porous, and agglomeration phenomenon was not obvious. The purity of synthetic zinc ferrite was high, the average particle size was 31.33~65nm, and its particle size and crystallinity were between purified zinc ferrite and purchased zinc ferrite. Its surface was smooth, particle size distribution was uniform, and agglomeration phenomenon was obvious.

(2) The titanium dioxide prepared by chemical coprecipitation method had no other impurities, good crystallinity, particle size of about 15nm, relatively complete crystal growth, smooth surface and certain agglomeration. For the zinc ferrite/titanium dioxide composite prepared by chemical coprecipitation method, adding a small amount of purified zinc ferrite would change the crystallinity of titanium dioxide, but it had little effect on the grain size of titanium dioxide, about 16nm. The composite had rough surface, uneven particle size distribution and agglomeration.

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