Research on Preparation of Diatomite and Graphene Oxide Materials

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Abstract. The sol-gel method and negative pressure and load method, diatomite as carrier, are used to prepare diatomite, nano-zinc oxide and graphene oxide composite materials, the sample was characterized and analyzed, the structure and morphology of diatomite was and graphene oxide materials were studied, and the influence graphene oxide on photocatalytic performance was analyzed. The results show that the loading of diatomite on nano-zinc oxide is better than the ordinary load method.

1. Introduction
Zinc oxide is an n-type semiconductor with 3.37 eV band gaps, which has high photosensitivity, photocatalysis and can promote redox reactions, the temperature range required for zinc oxide photocatalysis is wide and the cost is low, it has certain application prospects for environmental governance. However, zinc oxide nanometer particles have uneven dispersion, difficulty in fixation and other disadvantages, and their electron are easy to recombine, and the photon efficiency is low, the multi-order ordered pores of diatomite are used, and the surface area is strong and strongly adsorbed. Characteristics such as properties and surface electrical properties are used as carrier materials; diatomite is used as carrier material by its multi-order ordered pores, large specific surface, strong adsorption and surface electrical properties. Graphene oxide connects a large number of oxygen-containing groups on two-dimensional space formed a layer of carbon atoms, such as -OH, COO, C=O and COOH, Graphene oxide has higher electron mobility and higher specific surface area at room temperature, and can inhibit recombination of photon-generated carrier, and improves the photocatalytic efficiency of the photocatalyst. At present, one of the most promising photocatalyst modification methods is the modification research of graphene oxide on photocatalysts, Zinc oxide hollow spheres is prepared by ultrasonic chemistry are attached to composite photocatalytic material in graphene oxide, the photocatalytic reaction showed that the photocatalytic performance was improved by 150% compared with the pure zinc oxide nanoparticles, The composite material of zinc oxide and graphene with loading structure was prepared, which showed that the photocatalytic activity increased by 200%. Graphene oxide, diatomite and zinc oxide are combined to complement each other in performance and produce synergistic effect, the new composite photocatalytic material is superior to the original material in comprehensive performance. In this paper, a new sol-gel and negative pressure loading method was used to produce zinc oxide and load it on diatomite, the graphene oxide on photocatalytic performance of diatomite and zinc oxide was studied.
2. Experiment

2.1. Raw Materials
Diatomite, concentrated sulfuric acid (98%), zinc nitrate hexahydrate, citric acid; polyethylene glycol 6000; absolute ethyl alcohol (99%); ammonia water (25%); natural flake graphite (200 mesh); potassium permanganate; hydrogen peroxide (30%); hydrochloric acid (37%); sodium nitrate; barium chloride; Rhodamine B solution, experimental water is distilled water.

2.2. Experimental Methods

2.2.1. Preparation of diatomite and nano-zinc oxide. After grinding and acid leaching, diatomite is filtered and dried. Zinc nitrate and citric acid were mixed at 20:1 and put in distilled water stirred evenly, absolute ethyl alcohol was added slowly, ammonia water was added slowly, micro-polyethylene glycol was added, then ultrasonic treatment was carried out for 60 minutes, magnetic current stirred for 2 hours at 80°C water temperature, a certain amount of diatomite after acid leaching was put into flask, the flask was pumped into vacuum, the supersonic suspension was slowly injected into the flask with a syringe, then placed for 1 hour, dried, grinded, and calcined at 600°C for 2 hours in a high temperature furnace to prepare diatomite and nano-zinc oxide composite photocatalytic material powder for use.

2.2.2. Preparation of graphene oxide. Graphene oxide is prepared by Hummers method: taking a certain amount of natural flake graphite, the graphite was stirred in a beaker containing concentrated sulfuric acid, Stir well and weigh proper amount of potassium permanganate and sodium nitrate and put into the beaker, stir in mixture at 0°C and control temperature not to exceed 20 °C, and continue to stir up to 35°C after 30 min reaction, After the medium-temperature reaction is complete, up to 80°C, react with distilled water for 30min, after the high temperature reaction was completed, 5% hydrogen peroxide was added to make the solution bright yellow, Finally, 10% HCl was repeatedly rinsed to no sulfate and barium chloride was used to test to no precipitation. The graphene oxide centrifuged repeatedly, washed to neutral, 55°C drying in the oven, then grind into powder.

2.2.3. Preparation of diatomite and graphene oxide. The different amounts of graphene oxide was weighed (1%, 3%, 5%, 7%, 10% of diatomite, nano-zinc oxide powder) and disperse it in water by ultrasonic wave and achieve hydrosol of graphene oxide. The diatomite powder was weighed and added to the graphene oxide after ultrasonic wave treatment for a period of time, and then it was dried and grinded to prepare composite photocatalytic materials diatomite, nano-diatomite, graphene oxide.

2.3. Characterization of and diatomite oxide composite photocatalytic materials
The micro-morphology of the samples was observed by FESEM. X-ray diffractometer was used to analyze the XRD spectra of the samples. The specific surface area were measured by specific surface and pore size analyzer.

2.4. Photocatalytic performance test
BL-GHX-I photocatalytic reactor was used to test the photocatalytic performance. Rhodamine B was used as degradant. 0.1g graphene oxide photocatalytic materials with different mass fractions (0, 1%, 3%, 5%, 7%, 10%) were weighed by electronic balance. The composite photocatalytic materials were irradiated under 250W high pressure mercury lamp at room temperature and the amount of 10mg pre-configured at 100mL was taken. The rhodamine B solution was put into 250 mL glass reactor dish for photocatalytic degradation experiment. After sampling at different time, the supernatant was measured by UV-1200 ultraviolet-visible spectrophotometer, and the degradation rate was calculated.

\[ \eta = \left[1 - \left( A_t / A_0 \right) \right] \times 100\% \]

Among them, \( A_0 \): preliminary concentration of Rhodamine B, \( A_t \): the concentration of Rhodamine B after \( t \) minutes.
3. Results and Discussion

3.1. Effect of negative pressure loading on preparation of diatomite

Fig.1 is a SEM photograph of nano-zinc oxide and diatomite, nano-zinc oxide. From Fig.1a, it can be seen that nano-zinc oxide particle is easy to agglomerate. In Fig. 1b, almost all nano-zinc oxide particles are loaded on the surface of diatomite disc, and the zinc oxide particles agglomerate to form large particles with poor dispersion. As shown in Fig.c, zinc oxide particles are grown and loaded into diatomite pore by negative pressure method, which not only solves the problem of poor dispersion of particles, but also regulates the pore of diatomite and produces more multi-stage pore. Fig. 2 shows the adsorption isotherms (a) and pore size distribution curves (b) of diatomite and diatomite, nano-zinc oxide. According to Fig. 2 (a), the adsorption isotherms of diatomite and diatomite, nano-zinc oxide are type IV isotherms with H3 hysteresis loops, it shows the existence of mesoporous structure in the composites. The pore size distribution can be obtained from Fig.2 (b). When the pore size is between 0 and 10 nm, the diatomite loaded with nano-zinc oxide has more mesoporous, while the composite photocatalytic material and single diatomite loaded with ordinary method have fewer mesoporous. When the pore size of single diatomite is around 100 nm, the distribution of diatomite loaded with nano-zinc oxide is more. The results show that nano-zinc oxide plays an important role in regulating the pore size of diatomite.

![Fig. 1](image)

![Fig. 2](image)

3.2. Structure and morphology analysis of diatomite and graphene oxide composite photocatalyst material

3.2.1. Analysis of XRD results. Fig.3 is the XRD spectrum of the sample, it can be seen from the image that the characteristic peaks of diatomite SiO2 are at 28 degrees, and the characteristic peaks of zinc oxide are at 31 degrees, 35 degrees and 56 degrees. Compared with the standard comparison card, the diffraction peaks are the same and belong to hexagonal wurtzite, which are consistent with the SEM images of Fig. 1a. The diffraction peaks at 26.3 and 43.9 degrees are characteristic peaks of graphene oxide. The diffraction peaks of graphene oxide appear at 43.9 degrees of diatomite, nano-zinc oxide,
graphene oxide and are weak. However, it shows that graphene oxide exists in the composite sample, and there are no other impurity peaks in XRD, and it shows that purity of samples is very high.

3.2.2. Analysis of BET results. Table 1 shows the specific surface area of the samples; we can see the specific surface area of nano-zinc oxide is 10.2 m$^2$/g, mainly due to the agglomeration and uneven dispersion of nano-particles. When nano-zinc oxide is loaded on diatomite, nano-particles are dispersed on the carrier, the adsorption points on the surface increase, and the specific surface area of diatomite, nano-zinc oxide reaches 25.7 m$^2$/g. Compared with nano-zinc oxide, the specific surface area of nano-zinc oxide is increased by 60.2% and the average particle size decreases. After compounding with graphene oxide, the specific surface area of nano-zinc oxide is greatly increased to 32.4 m$^2$/g, which is 68.5% higher than that of nano-zinc oxide. The reason is that graphene oxide itself has a larger specific surface area. On the one hand, it provides more adsorption points for zinc oxide, and on the other hand, it provides more adsorption, the diatomite shell is wrapped or dispersed on the surface of the diatomite disc. In the process of photocatalysis, high specific surface area can effectively adsorb and transfer organic molecules, thus improving the photocatalytic performance of the composite materials.

![Fig. 3 XRD pattern of diatomite, nano-zinc oxide, graphene oxide (a), diatomite, nano-meter zinc oxide (b), nano-zinc oxide (c), graphene oxide (d)](image)

3.2.3. Analysis of IR results. Fig.4 is the infrared spectrum diagram of the samples, the curve A is the infrared spectra of graphene oxide, there are lots of oxygen-containing groups on the base surface of graphene oxide, the obvious absorption peaks are O-H stretching vibration in the range of 3411-3698 cm$^{-1}$, C-O absorption peaks are in the range of 2340-2500 cm$^{-1}$ and C-O absorption peaks are in the range of 1560-1586 cm$^{-1}$. The curve C is the infrared spectra of diatomite, nano-zinc oxide. The absorption peak at 3418-3624 cm$^{-1}$ is caused by the Si-O-H on the surface of diatomite. The bonding action forms Si-O-Zn bond. Curve B is the infrared spectra of diatomite, nano-zinc oxide, graphene oxide composite. Compared with curve c, the stretching vibration peak of C=C and C-O-O after diatomite, nano-zinc oxide, graphene oxide composite increases [9], which indicates that graphene oxide is introduced.
Fig. 4 IR spectra of Graphene oxide (a), diatomite, nano Zinc Oxide, graphene oxide (b) and diatomite, nano zinc oxide (c)

3.2.4. Analysis of SEM results. Fig. 5 (a) and (b) are SEM photos of diatomite, nano-zinc oxide and graphene oxide composite photocatalytic materials, respectively. The nano-zinc oxide in diatomite in Fig. 5A was observed. The distribution of nano-zinc oxide particles was more uniform in most areas. The distribution of zinc oxide in the pores of diatomite was more than that in other areas. At the same time, multistage pore size distribution was prepared for diatomite. In Fig. 5b, some flakes of graphene oxide were dispersed on and near the disks of diatomite loaded with nano-zinc oxide, and the introduction of graphene oxide avoided the introduction of diatomite particles. The agglomeration also makes some nano-zinc oxide adhere to graphene oxide, which increases the dispersion of nano-zinc oxide.

Fig. 5 SEM images of diatomite, nano zinc oxide (a) and diatomite, nano zinc oxide, graphene oxide (b)
3.3. Photocatalytic performance of diatomite, nano-zinc oxide, graphene oxide composite photocatalyst material

It can be seen from Fig. 6 that the degradation ability of graphene oxide composites with different mass fractions is higher than that of pure nano-zinc oxide, graphene oxide and diatomite. The degradation rate of rhodamine by diatomite increases rapidly at first and then decreases. It is due to the porous structure of diatomite, which adsorbs rhodamine B rapidly but does not degrade and releases it after saturation. The content of graphene oxide increased from 0% to 10%. The degradation rate of rhodamine B by diatomite, nano-zinc oxide, graphene oxide composite photocatalyst increased at first and then decreased, and reached the maximum at 5% mass fraction, reaching 88.7%. It was 63% higher than pure nano-zinc oxide at the same time, 81.9% higher than graphene oxide and 81.9% higher than diatomite.83.3%. This is due to the interaction of graphene oxide, diatomite and nano-zinc oxide. The high specific surface area of graphene oxide and diatomite provides more reaction sites for photocatalytic active substances. The porous structure of diatomite can adsorb pollutant molecules first, and then degrade them by using zinc oxide in the pore and on the surface. In addition, graphene oxide can adsorb zinc oxide. The rapid movement of electrons between graphene oxide and graphene oxide decreases the probability of electron-hole recombination, so the photocatalytic performance of the composites is improved. The main reason is that graphene oxide produces electrons and holes under high pressure mercury lamp radiation, as zinc oxide does, so there will be light competition between excessive graphene oxide and nano-zinc oxide. graphene oxide has a large specific surface area. When graphene oxide is excessive, electrons and holes collide and recombine on the surface, so the photocatalytic performance of the composite material decreases.

4. Conclusion

The negative pressure loading method is superior to the conventional loading method in diatomite when loading nano-zinc oxide, hierarchical pore of diatomite is prepared, which improves the shortcoming of single pore structure of diatomite. The specific surface area of diatomite, nano-zinc oxide prepared by negative pressure loading method is 43.4% larger than that of single diatomite. The introduction of graphene oxide can greatly improve the photocatalytic performance of diatomite and graphene oxide. When the mass fraction of graphene oxide is 5%, the photocatalytic degradation rate of diatomite, nano-zinc oxide, graphene oxide composite photocatalyst materials reaches the maximum 88.7%, which is 63% higher than that of pure nano-zinc oxide, and 83.3% higher than that of diatomite.

Fig. 6 degradation rate of rhodamine B in samples at different time
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