Effect of Microwave Irradiation on Physical Adsorption Accuracy and Photocatalytic Activity of Nano-ZnO Materials

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Abstract. Trace toxic organic compounds, such as dyes and polymer additives, can cause serious environmental pollution and threaten human health. Therefore, photocatalytic degradation of organic dye pollutants as an abiotic means has attracted much attention. In the process of preparing ZnO by precipitation method, a series of nano-ZnO materials were obtained by microwave radiation with different power. The crystal structure, morphology and surface physicochemical properties of the synthesized materials were characterized. The results show that the surface area has different degrees of increase compared with the ZnO prepared by the ordinary precipitation method. After different power microwave irradiation, the photocatalytic activity of ZnO has been improved to different extents, and is significantly higher than the commercially available P25 and ZnO without microwave irradiation.

1. Introduction
Among many metal oxide semiconductors, ZnO, an environmentally friendly material, can be used as a green photocatalyst for treating industrial wastewater due to its wide band gap, high exciton binding energy, low cost and non-toxicity [1]. Since the properties of inorganic materials are largely determined by their crystal size and crystal structure, in recent years, people have been working on new synthetic methods for obtaining semiconductor materials with well-formed morphology and good crystal structure [2]. Among them, the research on the theory and technology of semiconductor photocatalysis has attracted extensive attention due to the degradation and mineralization of semiconductors in the photocatalytic reaction process [3]. Photocatalytic degradation using semiconductors is a modern water treatment technology rising in recent years. Compared with traditional water treatment methods, it has the characteristics of high efficiency, stability, non-selectivity, full utilization of renewable resources solar energy and deep and thorough oxidation of refractory organic toxicants [4]. As a result, it has gradually become a new sewage treatment technology with broad application prospects. Compared with traditional methods, photocatalytic technology has more advantages, and it is also a green environmental protection technology with broad application prospects [5]. Therefore, photocatalytic technology is becoming a green environmental protection technology with practical application prospects [6].

With the rapid development of modern industry and the growth of daily life consumption, solving environmental pollution and developing renewable energy have become one of the most important issues in the international community [7]. At present, many kinds of nanostructured ZnO have been synthesized, such as bivertebral, dumbbell, ellipsoid, sphere, whisker, nanotube, hexagonal cylinder of nanoring, etc. The change of properties of ZnO is closely related to its synthesis method [8]. At present, the commonly used methods for synthesizing ZnO are sol-gel, hydrothermal, thermal evaporation and precipitation methods. The ZnO morphology obtained by these methods is mainly rod like, spherical, flake and bullet shaped [9]. In principle, when a semiconductor is irradiated by a light source, the
generated electrons and holes form a highly active substance through a series of reactions, namely hydroxyl radicals, which are capable of degrading dye molecules [10]. As a semiconductor material ZnO with a broad band gap and a large exciton binding energy, it possesses both semiconductor and piezoelectric properties, and has attracted extensive research interest. In addition to anatase titanium dioxide among many semiconductor catalysts, ZnO has become a rising star of semiconductor catalysts with its excellent properties. Related studies have shown that ZnO has certain photocatalytic properties under ultraviolet light. In addition, the photocatalytic reaction does not have a unified microscopic mechanism of action necessary to verify the lower section, or an incomplete research field, and the efficient and stable photocatalytic system still needs further development.

2. Methodology

It is a very effective method to treat organic pollutants in wastewater by using semiconductor materials as photocatalysts. In recent years, with the in-depth study of ZnO, some researchers have tried to combine precious metals with ZnO. Using the SPR effect of Ag nanoparticles, Ag is captured as a center of visible light and electrons. Related research shows that photocatalytic oxidation technology with good effect on environmental pollutants is becoming a new darling to solve environmental pollution problems. The electrons and holes generated by the excitation of the catalyst are newly recombined, resulting in low quantum yield. As a common metal semiconductor material, ZnO's unique optical and electrical properties make it widely used not only in nanolasers, solar cells and some functional devices, but also in photocatalytic degradation of certain organic pollutants. Significant effect. Because photocatalytic treatment of organic pollutants can directly use light energy to react at room temperature, and the catalyst used is generally non-toxic, harmless and easy to recover, the products obtained are usually inorganic ions, CO2 and hydrogen peroxide, without secondary pollution. Because of the strong anisotropic growth rate of ZnO on the c-axis, one-dimensional nanostructured ZnO, such as nanowires, nanoribbons, nanorods and nanotubes, has been studied extensively. Therefore, proper modification of zinc oxide has become a research topic of great concern.

The synthesis methods of nano ZnO crystals include sol-gel method, microemulsion method, gas phase precipitation method, hydrothermal method, chemical precipitation method and homogeneous precipitation method. Therefore, in order to study the effect of different synthetic processes on the photocatalytic activity of ZnO composites, the pure ZnO nanopowders and 3% (mole fraction) ZnO composite nanopowders were prepared by sol-gel method through one-step and two step methods respectively. The photocatalytic properties of the samples prepared by different photocatalytic processes were compared with those of photocatalytic degradation of methyl orange. A comparative study. At the same time, the microwave radiation power is different, and the morphology of ZnO is obviously different. With the change of microwave power, there are various forms such as nanoparticles, elliptical nanoclusters, nanosheets and spherical nanoclusters. Among them, ZnO is a relatively important semiconductor photocatalytic material, and researchers have done a lot of research on it, and reported many preparation methods for nano-scale ZnO. For example, sol-gel method, solution evaporation decomposition method, template-assisted growth method, chemical synthesis method and gas phase reaction method, and synthesized ZnO of various morphological structures, such as double vertebral body, dumbbell type, ellipsoid, Spheres, nanotubes, etc.

As can be seen from Fig. 1, compared with the results of microwave direct photolysis, the above three photocatalytic materials have certain photocatalytic activity under microwave irradiation.
According to the existing research reports, the typical preparation methods of ZnO nanocomposites can be divided into one-step method and two-step method. The application of microwave heating in chemical synthesis began in the late 1980s. Compared with the traditional heating method, this method has more uniform heating, higher reaction rate and selectivity. Microwave-enhanced photocatalysis experiment uses microwave electrodeless lamp as light source. MDEL consists of quartz tube filled with metal mercury and inert gas Ar. Its ultraviolet emission region is mainly located near 280 nm. Its power is 15W, its shape is U-shaped, and the output power of microwave reactor is 600W. When a small amount of precious metals contact with the surface, the carriers in the system will redistribute, and the photoelectrons will transfer from the higher Fermi level to the lower Fermi level precious metals until the Fermi level is the same. While increasing the utilization of light by ZnO, the recombination of photogenerated electron-hole pairs is also reduced, the photocatalytic efficiency of ZnO is greatly improved, or ZnO is modified by a composite method. In the synthesis process, the precursor can be reacted more rapidly by the microwave, thereby obtaining a nano semiconductor material having excellent performance. Therefore, microwave-assisted synthesis has certain advantages in the synthesis of photocatalytic semiconductor materials, and this paper aims to investigate the morphology and photocatalytic properties of ZnO nanomaterials by microwave-assisted synthesis.

Microwave-assisted synthesis is a new assistant technology for synthesis of nanomaterials in recent years. Moreover, the average particle size and loading of the nanocrystals are also achieved by adjusting the concentration of metal salts in the precursors. Compared with the traditional heating method, the microwave radiation method has more uniform heating, higher reaction rate and selectivity. However, zinc oxide is prone to light decay under ultraviolet irradiation and dissolves easily in extreme values, which greatly reduces the catalytic activity of zinc oxide in aqueous solution and hinders its application of photocatalytic properties. It is expected that the synergistic effect between them can be used to improve the photocatalytic oxidation ability of zinc oxide. Of course, some studies to improve the activity of ZnO by improving the morphology of ZnO are also good research ideas. In the research of photocatalytic degradation of organic pollutants, many photocatalysts are mainly used in semiconductor materials such as TiO2 and ZnO. Among them, ZnO is one of the most important semiconductor photocatalytic materials, and researchers have done a lot of research on it. A number of methods for the preparation of nanoscale ZnO have been reported. Under the condition that the microwave radiation time and period are fixed, the changes of ZnO structure and morphology are studied by changing the microwave radiation power. The degradation of Rhodamine B (RhB) in ZnO samples under UV and microwave assisted photocatalysis was investigated.

Figure 2 is a comparison of pure ZnO and ZnO/C core-shell nanocables prepared with different amounts of glucose: samples, H-0.1, H-0.2 and H-0.3 photocatalytic degradation of MB.
3. Result Analysis and Discussion

Microwave assisted as an auxiliary technology for the synthesis of nanomaterials, it has the characteristics of fast heating, high thermal energy utilization, good selectivity, sensitive reaction and high product quality. However, due to the low utilization of sunlight and the easy recombination of photogenerated electron-hole pairs during photocatalysis of ZnO, researchers have begun to try to combine precious metals or other semiconductor oxides with ZnO. Because of the formation of the Schottky potential gold, the precipitated precious gold has become an effective trap for capturing the scorpion, promoting the effective separation of photogenerated electrons and holes, prolonging the lifetime of the holes, thereby improving the catalytic activity of the photocatalyst. The microwave enhanced photocatalytic reactor is reported in our previous studies. Previous studies have found that after doping noble metals into zinc oxide to form complex, photogenerated electrons can be quickly transferred to the metal surface, which is conducive to the separation of photogenerated carriers, thus greatly improving the photocatalytic activity of zinc oxide. Among all noble metals, Ag is a commonly used dopant due to its low relative cost and low toxicity. When microwave irradiation is applied to synthesis, the morphology of synthesized products is often affected. The morphology of synthesized products is better, the size of particles is different, the pore size distribution is more uniform, and the crystallization process of synthesized products is shortened.

In addition, microwave-assisted synthesis (MAS) is a new assistant technology for the synthesis of nanomaterials in recent years. It has the characteristics of fast heating speed, high thermal energy utilization, good selectivity, sensitive reaction and high product quality that traditional synthesis methods do not possess. Considering the short cycle, simple process, easy operation and low cost, it is necessary to optimize the preparation of ZnO composite photocatalyst by sol-gel method. In the synthesis process, because microwave can make the precursor react more quickly, nano-semiconductor materials with excellent properties can be obtained. Some scholars have prepared nitrogen-doped titanium dioxide nanotubes from titanium dioxide synthesized by microwave-assisted method, whose photocatalytic activity is three times higher than that of samples prepared by P25. On the one hand, microwave radiation is expected to have an effect on the physical properties and photocatalytic properties of the synthesized sample. On the other hand, considering that Ag has an SPR effect and has good absorption of visible light, it can change the electron conduction mode in photocatalysis to some extent, reduce the recombination probability of photogenerated electron-holes, and improve the efficiency of photocatalytic reaction. To this end, some auxiliary methods such as template method and microwave radiation synthesis have emerged. Obviously, microwave-assisted synthesis has certain advantages in the synthesis of photocatalytic semiconductor materials.

From the data in Table 1, it can be seen that the atomic percentages of Ag, O and Zn are close to the theoretical feeding ratios. Among them, the content of Ag in mcd-Ag/ZnO samples is significantly
higher than that of the other two samples in the detection range. Although SEM-EDS analysis is only a semi-quantitative analysis method, it is only a detection of sub-surface of samples.

Table 1 Contents of O, Zn and Ag in c-Ag/ZnO, mc-Ag/ZnO and mcd-Ag/ZnO

| Sample         | Element | Weight (%) | Atomic fraction (%) |
|----------------|---------|------------|---------------------|
| c-Ag / ZnO     | O       | 16.58      | 45.64               |
|                | Zn      | 75.56      | 56.38               |
|                | Ag      | 1.25       | 1.69                |
| mc-Ag / ZnO    | O       | 17.39      | 51.69               |
|                | Zn      | 82.67      | 46.13               |
|                | Ag      | 2.46       | 1.25                |
| mc-Ag / Zn O   | O       | 15.32      | 35.34               |
|                | Zn      | 91.58      | 49.67               |
|                | Ag      | 3.42       | 1.95                |

In order to study the main active species in Ag/ZnO-ZrO2 photocatalytic reaction system, the capture experiments were carried out as shown in Fig. 3.

FIG.3 Photocatalytic Capture of Ag/ZnO-ZnO under Ultraviolet Light

At present, the modification methods of monomer ZnO mainly include semiconductor composite, noble metal doping and the change of synthesis methods. The photocatalytic properties of the materials will be significantly affected by the different preparation processes. Because of the different Fermi levels of Ag and ZnO and Schottky barrier formed between precious metal Ag and ZnO in the photocatalytic process, there is electron transfer between semiconductor ZnO and metal Ag. To a certain extent, the recombination rate of photogenerated electrons and holes is reduced, so the research of ZnO-supported Ag composite photocatalysts has been increasing recently. However, zinc oxide materials with small specific surface area, poor surface adsorption performance, excitation band in the ultraviolet range, and the existence of severe light decay candles under ultraviolet irradiation hinder their wide application in the field of photocatalysis. Therefore, the study considers the incorporation of Ag into the material under the action of microwave radiation. At the same time, it is considered that both ZrO2 and ZnO are light retort materials with better performance. The conduction band of ZnO is lower than the conduction band of ZrO2, and the electrons on the conduction band can be utilized in the photocatalytic reaction process, thereby effectively reducing the recombination of photogenerated electrons and hole pairs, and improving photocatalytic efficiency and quantum yield. While increasing the utilization of light by ZnO, the recombination of photogenerated electron-hole pairs is also reduced, and the photocatalytic efficiency of ZnO is greatly improved.

At present, in the research of photocatalytic degradation of organic pollutants, the most widely used photocatalysts are mainly semiconductor materials such as titanium dioxide and zinc oxide. In addition, the photocatalytic activity of ZnO was investigated under various photocatalytic modes in order to obtain nano-photocatalytic materials with high photocatalytic activity. In addition, it is well known that high mobility is very important to improve photocatalytic performance by improving photogenerated hole separation. Generally speaking, the synthesis methods of nanocomposite ZnO mainly include sol-gel method, microemulsion method, gas phase precipitation method, hydrothermal method, chemical
precipitation method and homogeneous precipitation method. These methods require more rigorous experimental instruments and synthetic conditions, or the morphology of synthesized products is difficult to control and the size is different. In addition, since the surface of the spherical ZnO nanoclusters is composed of ZnO nanorods and has a layered skeleton structure inside, the layered skeleton structure increases the pore volume, which is also an increase in the pore volume and specific surface area of the spherical ZnO nanoclusters. Another reason, the photocatalytic properties of ZnO strongly depend on changes in its structure and surface morphology. The influence of ZnO crystal morphology, growth direction, crystal size, orientation and crystallinity on its catalytic performance has been reported.

According to the data in Table 2, the specific surface area and pore volume of the synthesized samples c-Ag / ZnO, mc-Ag / ZnO and mcd-Ag / Zn O are small, which should be related to the selected synthesis method.

Table 2 Specific surface area, average pore diameter and pore volume of c-Ag/ZnO, mc-Ag/ZnO and mcd-Ag/ZnO

| Sample   | SBET/(m²·g⁻¹) | D/nm | Vtotal/(cm³·g⁻¹) |
|----------|---------------|------|------------------|
| c-Ag / ZnO | 2.59          | 3.2  | 0.006            |
| mc-Ag / ZnO | 3.16          | 4.3  | 0.009            |
| mcd-Ag / Zn O | 1.48          | 4.6  | 0.006            |

4. Conclusions
A series of nanocomposites ZnO were prepared by microwave assisted, temperature programmed solvothermal and calcination. Due to the influence of microwave radiation, the physical properties of absorbance, surface morphology, specific surface area and pore size of the obtained ZnO samples were significantly changed compared with those without microwave treatment. At the same time, the multi-mode photocatalytic activity of Ag/ZnO-ZrO2 synthesized under microwave irradiation is higher than that of P25, ZnO and Ag/ZnO-ZrO2 synthesized under the same conditions. The higher photoactivity is not only derived from Ag, SPA effect, synergy between ZnO and ZrO2. Moreover, it is related to the influence of microwave radiation treatment on the morphology of Ag/ZnO-ZrO2. ZnO in the three-step process of microwave irradiation, temperature programmed solvothermal and calcination exhibited regular hexagonal prismatic crystals, while spherical particles of Ag aggregated on the surface. The high photocatalytic activity of ZnO nanoclusters under microwave irradiation is attributed to the excellent morphology of ZnO after microwave-assisted synthesis. With the increase of microwave power, the surface morphology of nanoparticles, elliptical nanoclusters, nanosheets and nanospheres shows a variety of morphologies, and the ZnO particles are dispersed to aggregate again. In microwave-enhanced photocatalytic degradation, ZnO synthesized by microwave-assisted synthesis showed excellent photocatalytic activity.

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