Photocatalytic properties of ZnO powder sensitized by ZnTPP

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Abstract: In this study, ZnTPP-ZnO composite photocatalyst was prepared by impregnation method, and the samples prepared were characterized and analyzed by UV-Vis technology and TEM technology. The effects of light duration and ZnTPP loading on the photocatalytic degradation of methyl orange by ZnO were investigated. The experimental results show that ZnTPP is mainly loaded on the surface of ZnO particles in the form of surface adsorption, and plays the role of generating excited electrons and transferring electrons in photocatalysis. The degradation of methyl orange by the composite photocatalyst is mainly due to the photodegradation and the absorption peak is blue shift. The longer the light duration, the more degradation of methyl orange; The photocatalytic activity of ZnO is the highest when the sensitizer loading is 6 µmol.

1. Introduction
Although China is rich in land and resources, fresh water resources are very scarce, accounting for only 2200 cubic meters of water per capita. However, the water environment on which we live is still being destroyed, because of the improper treatment of domestic waste, and the use of pesticides, dyes and halogenated organic compounds produced by industry. Some of these organic pollutants can not be effectively removed by traditional treatment techniques. Therefore, a more efficient and environmentally friendly sewage treatment technology has become a key scientific research project in recent years[1,2].

ZnO is a new type of II-VI direct band gap, wide band gap (3.37 eV) semiconductor piezoelectric material, similar to the TiO2, which has good photocatalytic performance[3,4]. However, the application of ZnO in natural photocatalysis has great limitations due to its low quantum efficiency and narrow spectral absorption range. Therefore, in order to further broaden the spectral absorption range of ZnO, researchers focus on photosensitizers with strong light capture ability, such as porphyrin[5], phthalocyanine[6], etc. Porphyrin is often used as sensitizer of semiconductor materials because of its strong light absorption in 400 ~ 450nm (B band) and 500 ~ 700nm (Q band)[7].

In many previous studies, TiO2 was mainly used as a semiconductor object sensitized by porphyrin, and good results were obtained[8,9]. Although ZnO and TiO2 have similar photocatalytic mechanism, there are few reports on their sensitization. W. J. Sun and J. Li[10] prepared the CuTPP-ZnO composite photocatalyst and found that the photocatalytic activity of the composite photocatalyst was significantly higher than pure ZnO. Z. J. Xu et al.[11] successfully prepared porphyrin ZnO composite photocatalyst by using ZnO nanorods sensitized by novel naphthalimide functionalized free radical porphyrin (H2TPP) and Zn (Cu/Fe/Mn/CO)TPP. The results show that not all porphyrin sensitizers can improve the photocatalytic activity of ZnO.
2. Experiment

2.1. Preparation of ZnTPP-ZnO photocatalyst

The ZnTPP-ZnO composite photocatalyst was prepared by impregnation method[12]. The specific operation was as follows: a certain amount of ZnTPP-ZnO catalyst was added into an appropriate amount of anhydrous ethanol, and then a certain amount of ZnO catalyst was added into the catalyst after it was completely dissolved by magnetic stirring and continued stirring for 2 h. Finally, ZnTPP-ZnO composite photocatalyst with corresponding load was obtained after drying, grinding and drying.

2.2. Photocatalytic degradation of methyl orange with ZnTPP-ZnO sensitizer

A proper amount of catalyst was added into methyl orange solution with a concentration of 50 mg/L, and the reaction was carried out under the dark condition after constant temperature stirring for 1 h. After T min, an appropriate amount of suspension was extracted for centrifugal separation. Finally, supernatant was absorbed for UV-Vis spectroscopic analysis and detection.

3. Results and analysis

3.1. Influence of illumination time and ZnO catalyst on the absorbance of methyl orange solution

![Fig.1 UV-Vis spectra of methyl orange solutions under different conditions](image)

The following conclusions can be drawn from the figures: 1. Methane orange solution has strong light absorption in the visible region, and its absorbance is the highest at 464nm. The position of absorption peak does not change with the illumination time, indicating that methyl orange does not decompose to generate new substances under the illumination condition. 2. The degradation of methyl orange solution by ZnO catalyst is mainly due to the photocatalytic degradation, and the absorption peak is blue shift, and the spectral response range is broadened. When the ZnO photocatalyst was illuminated for 30 to 60 min, the increase of net light degradation rate of methyl orange was the largest (23.0%), indicating that the degradation rate of methyl orange solution also had a limit value[13,14]. With the extension of illumination time, the photoinduced charge (including photogeneration and photogeneration) increases, and the activity of ZnO photocatalyst increases[15]. However, the total amount of photoinduced charge generated by a certain amount of catalyst is certain, so the degradation rate will reach a peak.
3.2. Effect of ZnTPP loading on absorbance of methyl orange solution

![Graph showing absorbance vs wavelength for different ZnTPP concentrations.]

Fig.2 ZnTPP-ZnO of methyl orange solution absorption spectrum of UV-Vis under different ZnTPP sensitizer concentration

It can be seen from the figure that ZnO sensitized by ZnTPP has stronger photocatalytic performance. With the increase of ZnTPP loading, the degradation of methyl orange solution by the composite photocatalyst first increased and then decreased. From this, the concentration of ZnTPP sensitizer in the composite catalyst is not as large as possible.

3.3. The characterization and analysis of TEM

It can be seen from the low resolution images that the loading of sensitizer can improve the dispersion of ZnO particles in solution and reduce the agglomeration of particles, but excessive loading will also lead to the re-agglomeration of ZnO particles. Compared with the three pictures at high resolution, the boundary of pure ZnO particles is clearer, and the boundary of ZnO particles becomes rougher after loading[16], thus the surface area, which is one of the reasons why loading ZnTPP can improve the catalytic activity of ZnO. TEM images also showed that ZnTPP was successfully loaded on the surface of ZnO particles by physical adsorption[6].

![TEM images showing ZnO and ZnTPP-ZnO materials.]

Fig.3 TEM image of ZnTPP-ZnO and ZnO catalytic materials
3.4. Photocatalytic Degradation Mechanism of ZnTPP ZnO Materials

The results show that ZnTPP molecules are loaded on the surface of ZnO particles in the form of surface adsorption. ZnO is a wide band gap semiconductor material. Only under ultraviolet light, the conduction band of ZnO can excite free electrons ($e^-$) and holes ($h^+$)[17,18]. The excited $e^-$ transitions to the conduction band of ZnO and reacts with O$_2$ in solution, while the left $h^+$ reacts with H$_2$O, OH$^-$ and other molecules adsorbed on the surface of ZnO particles to form $\cdot$O$_2$ and $\cdot$OH with strong oxidizability respectively, which further oxidizes and reduces organic pollutants.

Under visible light irradiation, ZnTPP produces a lot of excited $e^-$ and ZnTPP$^+$, and ZnTPP$^+$ attaches to the surface of ZnO particles, which can effectively adsorb the surrounding organic pollutants. On the one hand, the generated $e^-$ can be directly transferred to the surface of ZnTPP molecule and directly participate in the redox reaction; on the other hand, because the conduction band energy of ZnO is lower than the excited state energy of ZnTPP[19], it can be transferred to the conduction band of ZnO and indirectly participate in the related reduction process.

4. Conclusions

On the basis of ZnO material prepared by sol-gel method, ZnTPP-ZnO composite photosensitizer was prepared by impregnation method. The results show that the photocatalytic degradation efficiency of ZnTPP-ZnO composite photocatalyst is significantly higher than pure ZnO, and the absorption peak of UV-Vis is blue shifted and broadened obviously. TEM results show that ZnTPP molecules mainly attached to the surface of ZnO particles by physical adsorption, which can improve the dispersion of ZnO particles in solution to a certain extent. However, excessive loading intensifies the overlap of ZnO particles, resulting in a decrease of photocatalytic activity. In the experiment of methyl orange degradation, ZnTPP plays three roles. First, free electrons are generated under visible light irradiation, which makes up for the defect that ZnO can only be excited to produce $e^-$ under ultraviolet light irradiation. Second, the generated ZnTPP$^+$ is attached to the surface of ZnO particles and can effectively adsorb organic pollutant molecules. Thirdly, the $h^+$ left by ZnO in the valence band under ultraviolet irradiation can be transferred to promote the separation of photogenerated $h^+-e^-$ pairs, and then more photogenerated $h^+-e^-$ pairs can be produced by ZnO to improve the efficiency of photocatalytic degradation.

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