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Phthalocyanine-sensitized hollow ZnO spheres as an efficient visiblie-light photocatalyst for water treatment

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Abstract. A novel phthalocyanine-sensitized hollow ZnO spheres as an efficient visiblie-light photocatalyst had been prepared successfully. Firstly, a unique hollow ZnO microsphere had been prepared by a facile solvothermal method followed by calcination. Secondly, zinc-tetracarboxyl-phthalocyanine (Pc) impregnated onto the surface of hollow ZnO microsphere. The obtained photocatalyst Pc/ZnO was characterized by XRD, SEM and EDS. The hollow Pc/ZnO hierarchical nanostructure improved the electron-hole separation more effectively and Pc loaded on the surface of ZnO microsphere to enhance photocatalytic activity under visible light. In our photocatalytic experiments, the hollow Pc/ZnO microsphere showed excellent photocatalytic performance under visible light for the removal of Rhodamine B (RhB). As a result, our work provided an effective and green photocatalyst for water treatment.

1 Introduction

In the modern society, various pollutants (e.g., dyes, pharmaceuticals and heavy ions), which are produced by many industries, are seriously considered as major pollutants in water pollution [1]. Meanwhile, they threaten human health and living environment. Therefore, it is urgent to find effective methods for the removal of pollutants in waste water. Based on the above inspiration, photocatalysis technology has gained great potential for the elimination of hazardous waste from water environment [2].

As an important semiconductor photocatalyst, ZnO is intensively favored for its non-toxicity and cheapness, especially hollow structure nanoparticle. Hollow ZnO microsphere with adjustable morphology and size has attracted more attentions due to its more active sites and larger surface areas [3]. Nevertheless, the band gap of bare ZnO is 3.20 eV, which limits the application of materials to visible light region [4]. Moreover, the rapid hole-electron recombination of ZnO will reduce the photocatalytic performance [5]. Therefore, among various methods to overcome above shortcomings, phthalocyanine-sensitized ZnO seems to be a facile way to expand absorption light range and improve the photocatalytic activity [6].

In this work, we prepared a novel organic/inorganic green photocatalyst Pc/ZnO. Hollow ZnO microsphere was synthesized via solvothermal and pyrolysis processes. Pc impregnated on the outer surface of ZnO. The synergistic photocatalytic performance of Pc/ZnO was evaluated by RhB. Benefiting from the unique design, the obtained photocatalyst exhibited better photocatalytic activity under visible light irradiation. Above all, this study provided a new strategy for water treatment.

2 Experiment

2.1 Synthesis of Hollow ZnO Spheres

Typically, 0.35 g $Zn(CH_3COO)_2$ and 3 mL ethylene glycol were added in 40 mL ethanol. The solution was stirred for 4 h. Then the solution was transferred into stainless steel autoclaves and maintained at 100 ºC for 12 h. Products were washed for three times with ethanol by filtration processes and dried in vacuum. Finally, hollow ZnO spheres obtained by thermal annealing at 400°C for 1 h.

2.2 Synthesis of Pc/ZnO

Pc was synthesized according to literature [7]. 90 mg ZnO was dispersed into 15 mL deionized water. 10 mg Pc dissolved in 2 mL dimethyl sulfoxide. Then the solution of Pc was added to ZnO with stirring for 24 h at 25 ºC. Following that, the product Pc/ZnO was washed with distilled water and dried in vacuum.

2.3 Photocatalytic experiments

A 300 W xenon lamp with filter acted as visible light source. 10 mg Pc/ZnO was suspended in RhB solution (1.0×10^{-5}mol/L, 30 mL). Before photocatalytic experiments, suspension was stirred for 30 min without light irradiation. Then suspension was irradiated under visible light. The concentration of RhB was detected by UV-Vis spectrophotometer and the absorption

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wavelength was at 554 nm. Photocatalytic degradation efficiency (D) was calculated as follows:

$$D = (C_0 - C)/C_0 \times 100\% \quad (1)$$

C was the concentration during photocatalytic experiments and C_0 was the initial concentration of RhB solution.

3 Results and discussion

The morphology of ZnO and Pc/ZnO were investigated by SEM. From **Fig. 1a**, the prepared hollow ZnO were uniform spheres with diameters around 600-800 nm. The surface of hollow ZnO microsphere was rough, which consisted of large numbers of nanoparticles building blocks. Compared with ZnO, there were obvious changes in Pc/ZnO (**Fig. 1b**), which might be due to the effect of Pc attachment on structure of ZnO. The composite photocatalyst Pc/ZnO could still maintain a complete spherical structure.

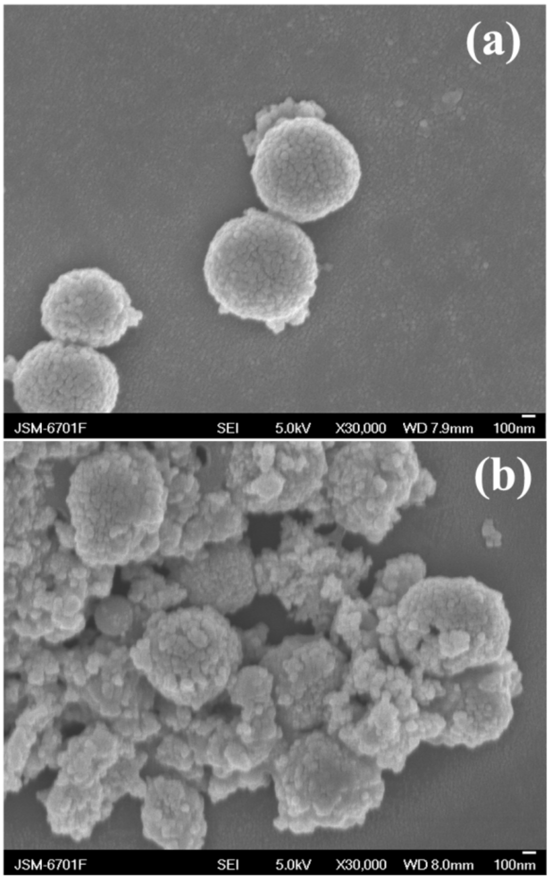

Fig. 1. SEM images of ZnO (a) and Pc/ZnO (b).

The crystalline phases of ZnO and Pc/ZnO were characterized by XRD in **Fig. 2**. The XRD pattern of ZnO showed diffraction peaks with high intensity and all peaks of ZnO matched with the JCPDS card No. 36-1451. Above results showed that the product had high crystallinity. While for Pc/ZnO, the introduction of Pc did not change peak positions of ZnO, indicating synthesis process of Pc/ZnO had little effect on the crystalline structure of ZnO.

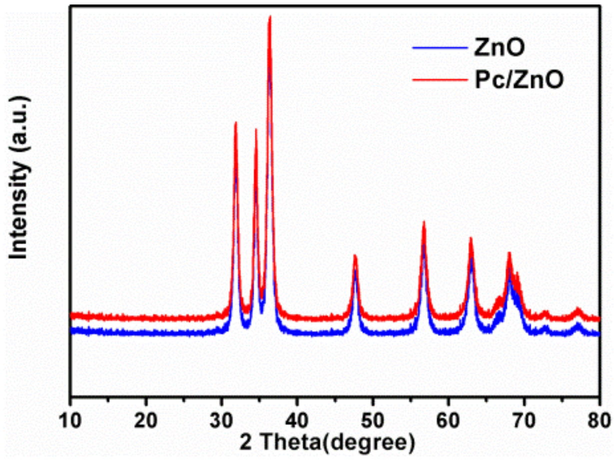

Fig. 2. XRD patterns of ZnO and Pc/ZnO.

EDS patterns of ZnO and Pc/ZnO were also investigated and corresponded to above analysis. As presented in **Fig. 3a**, Zn and O were found from EDS spectrum and had a high content. After Pc-sensitized hollow ZnO spheres in **Fig. 3b,** the low carbon content was found, which demonstrated Pc on the surface of ZnO. And N was not found which might be due to the low content.

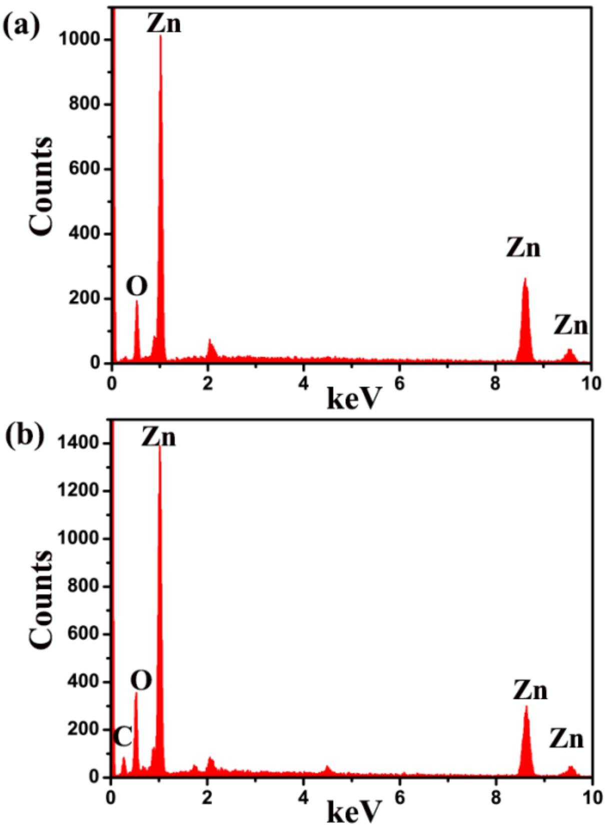

Fig. 3. EDS patterns of ZnO and Pc/ZnO.

To evaluate the photocatalytic activity of Pc/ZnO, RhB was used as model pollutants. ZnO, due to the large band gap, was hardly to removal RhB under visible light. However, Pc sensitized ZnO to sufficiently make use of visible light spectrum. The photocatalytic degradation of RhB by Pc/ZnO was 22 % within 240 min under visible light irradiation showed in **Fig. 4**. Photocatalyst Pc/ZnO showed excellent photocatalytic activity.

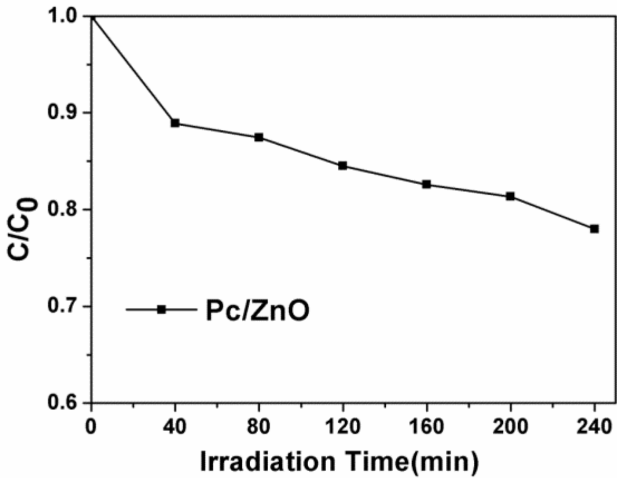

Fig. 4. The degradation curve of RhB by Pc/ZnO under visible light irradiation.

4 Conclusion

In summary, a novel organic/inorganic green photocatalyst Pc/ZnO was prepared. Hollow ZnO microsphere was synthesized via solvothermal and pyrolysis processes. Then Pc impregnated on the surface of ZnO. Pc sensitized hollow ZnO to improve its light response to visible region, which improved photocatalytic activity. Thanks for the reasonable structural design, the efficiency of photocatalyst was improved under visible light. Therefore, this study provided a deeper investigation on hollow Pc/ZnO microsphere, which would be an ideal photocatalyst in water treatment.

Acknowledgments

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