Preparation of ZnO photocatalysts and study on photocatalytic degradation of antibiotic wastewater

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Abstract. Nano ZnO/graphene composites were prepared by the oxidation of graphite and nano ZnO as the precursors under the condition of water temperature at 120℃. The photocatalytic activity of the composite was detected to treat simulated antibiotic wastewater by using the solution of tetracycline hydrochloride with 300W xenon lamp light source. The optimal conditions for the degradation of the composite material were obtained by single factor test. The optimized conditions were obtained as follows: the amount of catalyst, the time and the pH value was at 20mg, 4 hours and 5 respectively. The degradation rate of the solution of tetracycline hydrochloride could reach 86.7%.

Introduction

Zinc oxide, with band gap energy of 3.37eV, has high photocatalytic activity and low cost.Zinc oxide has great potential in terms of antibiotic wastewater treatment .Zinc oxide is a well-known semiconductor and has been applied in many significant field. Zinc oxide nanoparticles have been used in gas sensors, the fabrication of solar cells, transparent conductors, coatings and catalysis.

In recent years, grapheme with the thickness of 0.335nm is regarded as a very popular a kind of new exciting material. There are several reports on the syntheses of graphene-metal oxide nano-composites using techniques such as microwave-assisted reduction , solvothermal and ultrasonic spray pyrolysis, hydrothermal . However, there has been no report on Zinc oxide - graphene composites in the treatment of antibiotic wastewater applications.

In the present work, the preparation of ZnO/rGO nanocomposites via a simple hydrothermal method is reported. Moreover, Zinc oxide and graphene composites for antibiotic wastewater treatment effect are also being investigated.

Experimental

Materials.

Graphite flakes, 98% sulfuric acid, 37% hydrochloric acid (HCl), 30% hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), zinc chloride ($ZnCl_2$), sodium hydroxide (NaOH), and absolute ethanol. All chemicals were analytical grade without further purification.

Preparation of graphene oxide (GO) sheets.

Graphite oxide (GO) was synthesized from natural flake graphite powder by a modified Hummers method. In the typical modified synthesis, H_2SO_4(100 ml) was concentrated,and 2.0 g of graphite powder was put into it. Then the temperature of the H_2SO_4 was kept to be below 10℃and $KMnO_4$ (8.0 g) was added gradually under stirring. The reaction temperature was controlled below 10℃,and the reaction mixture was continued for 2 h . Successively, added 100 ml deionized (DI)water into the mixture, stirred, and kept the mixture temperature below 35℃. The addition of water was performed in an ice bath to keep the temperature below 100℃,because the process, addition of water in concentrated sulfuric acid medium, released a great amount of heat. Continue

stirred the mixture for 1 h. After that adding all of the 100 mL of DI water, and was further diluted to approximately 300 mL with DI water. There was 20 mL of 30% H_2O_2 what was added to the mixture in order to remove the residual $KMnO_4$. The color of the mixture changed into brilliant yellow and released a large amount of bubbles. Finally, the mixture was filtered, and then washed with 5% HCl aqueous solution (800 mL) to remove metal ions followed by 1.0 L of DI water to remove the residual acid. The resulting solid was dried at 60℃for 24 h. For further remove residues, the as-obtained graphite oxide was re-dispersed in DI water and then was dialyzed for one week to remove residual acids and salts.

Preparation of ZnO/GO nanocomposite.

20 mg of graphite oxide and 200 mg of zinc acetylacetonate ($Zn(acac)_2$) were dispersed in 45 mL of ethylene glycol (EG) with ultrasonication for 30 min. 20 mL of hydrazine hydrate was slowly added into the mixture with stirring. Subsequently, the mixture was put into an autoclave and heated at 180 8C for 16 h. The synthesized product was isolated by centrifugation, washed three times with water and ethanol, respectively, and finally dried in a vacuum oven at 60 8C for 24 h. For comparison, the synthesis was also carried out using water instead of EG as reaction medium under the same other conditions. In addition, graphene and ZnO were synthesized in EG in the same way as the composites in the absence of $Zn(acac)_2$ and GO, respectively.

Characterizations of the samples.

The surface morphology, structure and composition of the nanocomposites were characterized by X-ray diffraction. The result of experimental is shown in Figure 1.

Photocatalytic experiments.

The result of experimental is shown in Figure 2. In order to determine the solution pH value of wastewater of tetracycline hydrochloride degradation effect, 20 mg tetracycline hydrochloride was dissolved in the water and added deionized water. After that, the solution is diluted to 1 L . The solution pH value was set to 1、3、5、7、9、11、13 .100 ml tetracycline hydrochloride of solution was concentrated and 20 mg of ZnO/graphite powder was put into it. The solution was fully mixed for 30 min. Then 300W of xenon lamp power supply was opened for photocatalytic experiment. After 3h a certain amount of solution was removed, the solution was handled through centrifuge centrifuge, the supernatant was removed and the solution concentration was calculated.

The result of experimental is shown in Figure 3. In order to determine the solution the time value of wastewater of tetracycline hydrochloride degradation effect. The solution was fully mixed for 30 min. The time was set 0.5h, 1h, 2h, 3h, 4h, 5h. Then 300W of xenon lamp power supply was opened for photocatalytic experiment.

The result of experimental is shown in Figure 4. In order to determine the solution quality of nanocomposite value of wastewater of tetracycline hydrochloride degradation effect.The quality of nanocomposite was set 5mg, 10mg, 15mg, 20mg, 25mg. After that, 300W of xenon lamp power supply was opened for photocatalytic experiment.

Results and discussion

XRD analysis.

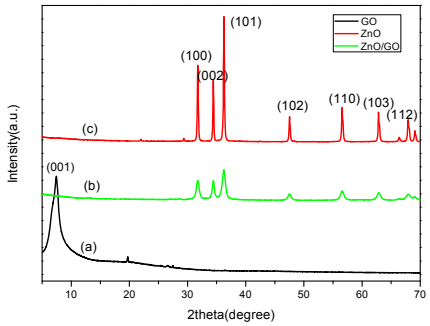
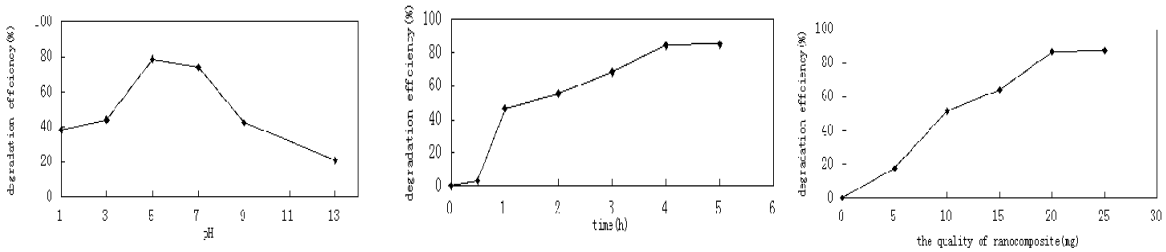


Fig. 1 XRD patterns of ZnO nanoparticles, ZnO/GO nanocomposite and GO

Fig. 1 shows the XRD patterns of ZnO nanoparticles, ZnO/GO nanocomposite, and GO sheets, respectively. All the diffraction peaks in the XRD pattern of ZnO nanoparticles are consistent with the hexagonal phase wurtzite ZnO. The diffraction peak at around 2θ= 8°in the XRD pattern of GO sheets belongs to the (001) reflection of GO, and the interlayer spacing(0.95 nm) is much larger than that of graphite (about 0.37 nm) owing to the introduction of oxygen-containing functional groups on the graphite sheet surfaces. The diffraction peaks of ZnO/GO nanocomposite are similar to those of hexagonal ZnO. Nevertheless, the (001) diffraction peak at 8°of GO dropped profoundly to an almost undetectable level, which may indicate that the regular layered structure of GO has been destroyed and exfoliated GO sheets are formed due to the growth of ZnO nanocrystals. The XRD patterns demonstrate that the ZnO/GO nanocomposite can be obtained in the present system.

The effects of solution factors on the degradation efficiency.



(a) (b) (c)

Fig. 2 effects of solution pH value ,time value and the quality of nanocomposite on the degradation efficiency

Fig. 2(a) shows the effect of pH value on the photocatalytic activity and effect of pH value is obvious.Then,with the increase of pH value, curve shows a trend of reducing the rise.When the solution pH value is 5, the degradation efficiency is 78.8%.Therefore, the solution of pH value is selected as 5.

Fig. 2(b) shows the effect of time value on the photocatalytic activity and effect of time value is obvious. Then the longer photocatalytic, the better the treatment effect could be obtained. When the time value is 4h, the degradation efficiency is 84.4%.Therefore, the time value is selected as 4h.

Fig. 2(c) shows the effect of the quality of nanocomposite on the photocatalytic activity and effect of time value is obvious. Then with the increase of quality of nanocompositehe, photocatalytic effect is better .When the t the quality of nanocomposite is 20mg, the degradation efficiency is 86.7%.Therefore, the quality of nanocomposite is selected as 20mg.

Conclusions

The optimized conditions were obtained as follows: the amount of catalyst was 20mg, the time was 4 hours and the pH value was 5. The degradation rate of the solution of Tetracycline hydrochloride could reach 86.7%.

Acknowledgment

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