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Photocatalytic Degradation of Reactive Brilliant Blue X-BR in Aqueous Solution Using Quantum-sized ZnO

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Abstract

Quantum-sized ZnO was prepared using sol–gel method with Zinc acetate dehydrate (Zn (CH₃COO)₂·2H₂O) and lithium hydroxide monohydrate (LiOH·H₂O) as raw material. The ZnO particles annealed at different temperature were characterized by means of X-ray diffraction (XRD), Infrared absorption spectroscopy (IR) and UV-Vis spectroscopy. The degradation rate of reactive brilliant blue X-BR in aqueous solution was used to evaluate the photocatalytic performance of the quantum-sized ZnO. The experimental results indicated that the photocatalytic property of the ZnO was excellent. The photocatalytic efficiency of quantum-sized ZnO was significantly influenced by the calcining heat. When calcined at 300°C, its size is 6.78 nm and the photocatalytic performance is the best. The degradation rate of reactive brilliant blue X-BR could exceed 90% in 15 min at 35°C, when the concentration of the quantum-sized ZnO was 0.35 mg/L.

Keywords

sol-gel; zinc oxide; reactive brilliant blue X-BR; photocatalytic degradation

1.Introduction

Semiconductor photocatalytic oxidation is a new modern water treatment technology. It has many advantages such as high efficiency, low energy-consumption, moderate condition, extensive applicability and decrease in secondary pollution. Zinc oxide is one of the most promising materials for optoelectronic application because of its wide band gap (3.37 eV) and large exciton binding energy (60 meV). It can be used as catalyst and photocatalyst under the ultraviolet radiation ($\lambda \leq 368$ nm) to resist bacteria, eliminate odor, disinfect, refine and protect the environment. Therefore, ZnO will play an important role in the treatment of contamination.

Nano-ZnO has been widely studied as catalyst. Especially in recent years, ZnO was used as effective, inexpensive, nontoxic semiconductor for the degradation of a wide range of organic chemicals [1–6]. Gouvea et al. [7] have reported that the activity of nano-ZnO was higher than nano-TiO₂. They also compared three methods used to prepare nano-ZnO, and the results

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indicated that the smaller the particle was, the higher the photocatalytic activity was. Yeber et al. [8] did similar researches with different kind of dye. Studies were carried out to investigate the effect of the degradation conditions: initial concentration of the contaminants [9–11], pH [12,13], reaction temperature [11], catalyst loading [14–16], intensity of the light [14], et al.. ZnO nanoparticles and its nano-crystalline particles were prepared and used to degrade methylene blue, and the results showed that the photocatalytic degradation capacity of the ZnO nanoparticles was higher than that of the ZnO nano-crystalline particles [17]. The suitability of ZnO nanoparticles (both as suspension and thin films) to sense and photodegrade several common organic contaminants were tested by C. Hariharan [18], who reported that a wide variety of aromatic and aliphatic chlorocompounds listed as contaminants present in water could quench the fluorescence from ZnO-nano; hence this system had been used to sense the presence of contaminants and to photodegrade them effectively. The photocatalytic degradation of C.I. Acid Red 27 (AR27), an anionic monoazo dye of acid class, in aqueous solutions was investigated with immobilized ZnO catalyst on glass plates in a continuous-mode [19], and the removal percent increases with increasing the photoreactor volume and light intensity but it decreased when the flow rate was increased.

In order to research the photocatalytic property of quantum-sized ZnO, the samples synthesized by sol-gel technique was prepared and its characterizations were described in detail in this article. Its photocatalytic property was investigated with reactive brilliant blue X-BR solution as the model contaminant.

2.Experimental

2.1.Photocatalyst Determination

Infrared spectra were obtained as KBr pellets using Nicolet FT-IR Nexus 870 infrared spectrometer. The crystalline structure was investigated by X-ray diffraction (XRD) on x'Pert. Pro. MPD X-ray diffractometer with Ni filtered Cu K_{α} radiation of 1.542 Å (40 kV, 40mA) at the scan rate of $0.05^{\circ}\text{s}^{-1}$. The UV-Vis absorption spectra of ZnO were carried out on HITACHI U-3310 UV-Vis spectrophotometer. All the chemicals and solvent used in present study were of AR grade. Anhydrous ethanol were refluxed over magnesium strips and then distilled.

2.2.Photocatalyst Preparation

Quantum-sized ZnO was synthesized via an improved sol-gel method referring to the literatures [20,21]. A 1.10 g (5 mmol) sample of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 50 ml anhydrous ethanol at 80°C under vigorous stirring. A 0.29 g (7 mmol) sample of $\text{LiOH} \cdot \text{H}_2\text{O}$ was dissolved in 50 ml anhydrous ethanol at room temperature in an ultrasonic bath. The hydroxide-containing solution was added to the $\text{Zn}(\text{Ac})_2$ solution under vigorous stirring at 50°C for 40 minutes. The reaction mixture became transparent ZnO sol and was distracted into a conical bottle. More than twice as much hexane in volume was added to the conical bottle and then the bottle was stored at the temperature under 4°C overnight to prevent particles growing rapidly. The white precipitate would appear and became white powder after separated with the liquid above by centrifugal machine. The powder was calcined for 2h in muffle at different temperature: 200°C , 300°C , 400°C , 500°C and 600°C .

2.3.Photocatalytic activity

The experiments were carried out with 100 ml reactive brilliant blue X-BR solution prepared with distilled water in 200 ml beakers. The beakers were put under the ultraviolet light maintaining the distance between the light source and the surface of the solution about 10 cm. The known amount of ZnO was added to the solution. After a known period of time, the solution was centrifuged at 2000 rpm for 10 min and then filtered to remove the catalyst particles

completely. The absorbency was measured with 722 UV-Vis spectrophotometer ($\lambda_{\text{max}} = 594$ nm), and the degradation rate (η) was calculated according to the equation below:

$$\eta = (A_0 - A) / A_0 \times 100\%$$

A_0 is the initial absorbency of the reactive brilliant blue X-BR solution;

A is the absorbency of reactive brilliant blue X-BR solution after degradation.

3. Results and Discussions

3.1. Photocatalyst Determination

X-ray diffraction patterns of ZnO calcined at different temperature are shown in Fig. 1. We can conclude that the ZnO particles prepared are wurtzite structure attached to hexagonal system according to the standardized JCPDS card. According to Scherrer equation, the size of the ZnO particle non-calcined is 8.81 nm, and the sizes of ZnO calcined at 200°C, 300°C, 400°C, 500°C and 600°C are 6.88 nm, 6.78 nm, 12.60 nm, 25.21 nm and 35.29 nm respectively. When the temperature was lower than 300°C, the sizes didn't change a lot, but the peak width became wider and wider with an increase in temperature, and the particles grew obviously. It reveals that the calcined temperature is an important factor which can influence the size of the particle.

Infrared absorption spectroscopy patterns of ZnO calcined at different temperature are shown in Fig. 2. From the figure we can see that the absorption-vibration peak zone is between 472 cm^{-1} and 476 cm^{-1} . When the temperature was higher than 300°C, the spectra remained similar and the crystallites began to sinter [22] with the particle sizes slightly increasing up to 35.29 nm. The vibration peak brought by the Zn-O band became wide, which was probably due to the growth and mass of the particles with an increase in temperature.

Fig. 3 shows the UV-Vis spectra of ZnO at different temperature. The spectrum of the sample calcined at 300°C shifts to the blue compared with the samples non-calcined and calcined at 500°C, which demonstrates obvious quantum size effect.

3.2. Photocatalytic property and reaction condition

A series of experiments were carried out to assess the effect of relevant conditions such as the calcining heat, the reaction temperature, the catalyst loading on the degradation rate.

As shown in Fig. 4, when the temperature was lower than 300°C, the photocatalytic ability boosted up gradually with an increase in temperature. But when the temperature was higher than 300°C, the photocatalytic property weakened sharply. When the particle size ranges from 1 nm to 10 nm, the quantum size effect will appear. The size of the sample calcined at 300°C is 6.78 nm, and it demonstrates obvious quantum size effect, which enhances the oxidation-reduction ability of electron-cavity. Due to the size-quantization, the rate of the charge movement increases in the semiconductor, and the recombination probability of the hole-electron pairs become lower, which lead to the increase of the photocatalytic efficiency.

Fig. 5 and Fig. 6 are the graphs respectively showing the degradation rate (Fig. 5) and adsorption rate (Fig. 6) of 30mg/L reactive brilliant blue X-BR solution with (Fig. 5) and without (Fig. 6) UV light illumination when the concentration of ZnO was 0.2 g/L and the reaction time was 1 h. From the graphs, we see that, with UV light illumination, the degradation rate somehow increases with an increase in temperature, but when the temperature is higher than 35°C, it begins to go down. However, the adsorption amount on the catalyst decreases

with an increase in temperature. Although the increase of the temperature is helpful to the photocatalytic reaction, it prevents the contaminants and the oxygen from being adsorbed. In addition, an increase in temperature helps to compete more efficiently with $e^- - h^+$ recombination and caused an increase in removal reaction rate [11]. When the temperature is overhigh, the function of restraining adsorption plays a leading role, which results in the decrease of the photocatalytic degradation rate.

To investigate the relationship between the catalyst loading and the degradation rate of the dye, the amount of ZnO varied from 0.1 g/L to 0.9 g/L in a series of experiments at constant condition: dye concentration= 30mg/L, reaction temperature=35°C, time=1h. Fig. 7 shows that when the amount of the catalyst increases, the degradation rate goes up first and then keeps unchangeable in certain scale, but when the amount exceeds 0.7 g/L, the degradation rate goes down. It is probably due to the aggregation of the free catalyst particles and the “screening” effect [23,24]. The result is consistent with many other researches that there are an optimal amount of catalyst loading [25]. When the concentration of the catalyst is below the optimal value, the effective surface of the catalyst and the absorption of the light are the main factors which determine the photocatalytic degradation rate [26]. The adsorbability was weak and the photon energy from the light source can't be made full use of, which results in lower reaction rate. With the increase of the ZnO loading, the adsorbability to the contaminants is enhanced and the degradation rate goes up. When the amount of ZnO exceeds 0.7 g/L, the ZnO particles will lead the light to scatter and prevent the light from permeating the solution, therefore the degradation rate goes down. Given that the degradation rate does not change a lot when the concentration ranges from 0.35 g/L to 0.7 g/L, we chose 0.35 g/L as the optimal concentration of the catalyst.

4. Conclusions

The photocatalytic activity of quantum-size ZnO is excellent. This kind of ZnO particle whose size is 6.78 nm demonstrates obvious quantum size effect. The degradation rate of reactive brilliant blue X-BR could exceed 90% in 15 min at 35°C, when the concentration of ZnO was 0.35 g/L. The difference in their activities may arise from a number of factors including the temperature, surface area, concentration, absorption and adsorption efficiency et al. Further studies are in progress for the lifetime of the active species.

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References

1. Gouvea CAK, Wypych F, Moraes SG, Duran N, Nagata N, Zamora PP. Chemosphere 2000;40:433. [PubMed: 10665410]
2. Lizama C, Freer J, Baeza J, Mansilla HD. Catal Today 2002;76:235.
3. Pal B, Sharon M. Chem Phys 2002;76:82.
4. Sakthivel S, Neppolian B, Shankar MV, Arabindoo B, Palanichamy M, Murugesan V. Sol Energy Mater Sol Cells 2003;77:65.
5. Akyol A, Yatmaz HC, Bayramoglu M. Appl Catal B: Environ 2004;54:19.
6. Yatmaz HC, Akyol A, Bayramoglu M. Ind Eng Chem Res 2004;43:6035.
7. Gouvea CAK, Wypych F, Moraes SG. J Chemosphere 2000;40:433.
8. Yeber MC, Rodriguez J, Baeza J. J Water Sci Technol 1999;40(11–12):337.
9. Wu CH. Chemosphere 2004;57:601. [PubMed: 15488922]
10. Qamar M, Saquib M, Muneer M. Dyes Pigments 2005;65:1.

11. Daneshvar N, Rabbani M, Modirshahla N, Behnajady MA. J Photochem Photobiol A 2004;168:39.
12. Zhao H, Xu S, Zhong J, Bao X. Catal Today 2004;93–95:857.
13. Bekbolet M, Balcioglu I. Water Sci Technol 1996;34:73.
14. Konstantinou IK, Albanis TA. Appl Catal B 2004;49:1.
15. Chakrabarti S, Dutta BK. J Hazard Mater 2004;112:269. [PubMed: 15302448]
16. Pera-Titus M, Molina VG, Banos MA, Gimenez J, Esplugas S. Appl Catal B 2004;47:219.
17. Jang, Young Joon; Simer, Cynthia; Ohm, Taein. Materials Research Bulletin 2006;41:67.
18. Hariharan C. Applied Catalysis A: General 2006;304:55.
19. Behnajady MA, Modirshahla N, Daneshvar N. Journal of Hazardous Materials 2006;xxx:xxx.
20. Wong ME, Bonevich JE, Searson PC. J Phys Chem B 1998;102:7770.
21. Meulenkamp Eric A. Synthesis and Growth of ZnO Nanoparticles. J Phys Chem B 1998;102:5566.
22. Daniele, Ste'phane; Ghazzal Mohamed, N.; Hubert-Pfalzgraf Liliane, G.; Duchamp, Christian; Guillard, Chantal; Ledoux, Gilles. Materials Research Bulletin 2006;41:2210.
23. Mehrotra K, Yablonsky GS, Ray AK. Ind Eng Chem Res 2003;42:2273.
24. Sauer T, Neto GC, Jose HJ, Moreira RFPM. J Photochem Photobiol A: Chem 2002;149:147.
25. Akyol A, Yatmaz HC, Bayramoglu M. Appl Catal B Environ 2004;54:19–24.
26. Wang, Huihu; Xie, Changsheng; Zhang, Wei; Cai, Shuizhou; Yang, Zhihong. Yanghai Gui Journal of Hazardous Material 2006:1–8.

Fig. 1. X-ray diffraction patterns of ZnO non-calcined (a), calcined at 200 (b), 300 (c), 400 (d), 500 (e) and 600°C (f)

Fig. 2.
Infrared absorption spectroscopy patterns of ZnO at different heat treatment temperature

Fig. 3.
UV-Vis spectra of ZnO at different calcining temperature

Fig. 4.
Degradation rate of reactive brilliant blue X-BR by ZnO calcined at different temperature

Fig. 5.
Reactive brilliant blue X-BR degradation rate under different temperature

Fig. 6.
Reactive brilliant blue X-BR adsorption rate under different temperature

Fig. 7.
Reactive brilliant blue X-BR degradation rate under different catalyst loading