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Preparation of ZnO Nano-Photocatalysts and Their Performance on Photocatalytic Degradation of Coking Wastewater

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ABSTRACT

ZnO photocatalysts were prepared by hydrothermal synthesis method. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). The photocatalytic activities of the prepared catalysts were evaluated by the photocatalytic degradation of coking wastewater under a xenon lamp irradiation. The results showed that the prepared products were hexagonal wurtzite structure of ZnO. Photocatalytic degradation of coking wastewater reached 69.48% in 120 minutes under the irradiation of xenon lamp light (λ=365nm).

INTRODUCTION

Coking wastewater is a kind of toxic and refractory industrial wastewater, which gets accumulated in the environment around the world (Meng et al. 2015, Chu et al. 2012). Since it is difficult to be biodegraded, the traditional biological treatment technology need pretreatment unit to reduce the biological toxicity in coking wastewater treatment, which was costly and inefficient. Due to the advantages of environment friendly and high efficiency, semiconductor photocatalytic oxidation technology received widespread attention in environmental pollution control. Recently, some studies were carried out on the degradation of coking wastewater by semiconductor photocatalysts (Guo et al. 2011, Meng et al. 2015). Among various semiconductors studied, ZnO has been identified as a promising host material and proved to be the most suitable catalyst for widespread environmental applications because of its high photosensitivity, excellent mechanical characteristics, low cost and environmentally safe nature (Singhal et al. 2008, Shen et al. 2008).

The discharge volume of the coking wastewater is about $2.85\times10^8 m^3$ every year in China. The toxic and refractory material's accumulation in the environment increased rapidly, thus posing a bigger threat to the environment for its degradation-resistance. There are several methods to treat coking wastewater, such as biological methods like anaerobic-aerobic (Joshi et al. 2016, Lai et al. 2008), anaerobic-anoxic-aerobic (A2/O) (Sahariah et al. 2015) and sequencing batch reactor (SBR) (Yu et al. 1997) wastewater treatment. With fast, convenient and efficient advantages, photocatalytic method is widely used in the removal of toxicity in the wastewater. At present, studies are mainly concentrated on the research of photocatalytic materials such as TiO_2 (Zhao et al. 2010, Zhao et al. 2013, Pereira et al. 2013), Mg-Al (Jacome-Acatitla et al. 2014) and so on, but research on the treatment with the ZnO is reported less.

To get more knowledge of ZnO nano-photocatalytic materials, in the present work, ZnO nano-photocatalytic materials were prepared by hydrothermal synthesis method. And the properties of the nanoparticles have been characterized by XRD and SEM. Furthermore, the photocatalytic activities of the materials have been evaluated by degradation of synthetic coking wastewater in the photodegradation process, which is an effective way to solve the environmental issue of the extensive use of coking wastewater.

MATERIALS AND METHODS

Catalyst Preparation

The main reagents in the experiments included zinc acetate (CAS number: 557-34-6), sodium hydroxide (CAS number: 1310-73-2), sodium dodecyl benzene sulphonate (CAS number: 69669-44-9), absolute ethyl alcohol (CAS number: 64-17-5) and deionized water (CAS number: 7732-18-5).

The main process was: 4.39 g zinc acetate ($(CH_3COO)_2{\cdot}2H_2O$) was dissolved in the 100 mL distilled water. Then sodium dodecylbenzenesulphonate was added into the solution, and Zn^{2+} content in the last solution contained was 0.2 mol/L. The sodium hydroxide solution (2.0 mol/L)

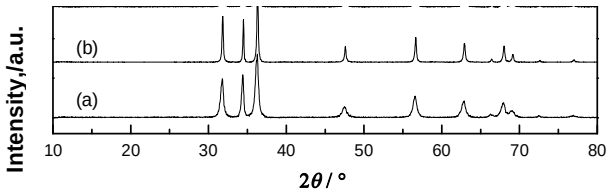

Fig. 1: XRD patterns of the samples ZnO nanoparticles.

was dripped slowly into the solution until the pH = 10 with magnetic stirring and the solution continued to stir for 30 minutes. Then the solution was transferred into a polytetrafluoroethylene lining reaction kettle with 80% fullness. The solution was placed in drying oven and heated for 8h at 120°C, and then cooled naturally to room temperature. The cooled liquid was centrifuged and separated, and the solid was prepared. With 3 times been washed with deionized water and anhydrous ethanol respectively, the prepared solid was dried for 10h at 70°C. Lastly, the solid was smashed and grinded, and then ZnO nano-materials were obtained.

Characterization of Catalysts

The crystal phase and crystallinity of the sample were measured by X ray diffraction (D8ADVANCE, Brooke AXS Company, Germany, Cu target K α radiation at wavelength of 0.15406 nm, working voltage of 40 kV, accelerating current of 200 mA, scan step of 0.02°/0.5 s, scan area of 10°-80°). The morphology of the catalyst surface was observed with scanning electron microscopy (SEM) (S-4800, Hitachi, Japan).

Catalyst Evaluation

Light catalyst activity was evaluated using BL-GHX-V photochemical reaction apparatus with light source from xenon-lamp (300 W) at wavelength range of 320-800 nm. In light of the catalytic reaction, initial COD concentration of the synthetic coking wastewater solution was 2000 mg/L and volume 50 mL. The catalyst dosage was 0.6 g/L. Before the photocatalytic reaction, the suspension containing the light catalyst was stirred for 30 min in the dark in order to achieve the adsorption equilibrium. At this time, the remaining COD concentration of the wastewater was 1360 mg/L, and the concentration does not change with time, which can be considered that the photocatalytic materials have reached the adsorption equilibrium. After opening the light source (365 nm xenon-lamp source), 3-4 mL sample at interval time was taken to be centrifuged at high speed and separated. The supernatant fluid was measured for the absorbance using ultraviolet-visible spectrophotometer (UV-765, Shimadzu, Japan) in maximum absorption wavelength (λ=365 nm). The concentration C and degradation rate X was calculated according to the fitting equation (1):

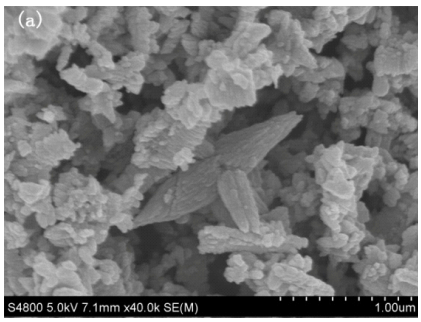

Fig. 2: SEM pictures of ZnO nanoparticles.

$$X = (C_0 - C_t) / C_0 \times 100\% \quad ...(1)$$

Where, C_0 is the original COD concentration; C_t is the retained COD concentration in solution.

The process of using nanoparticles and recycling residual nanoparticles is as follows: Firstly, the nanoparticles are fully mixed with synthetic coking wastewater for above the reaction. After the reaction, the polyvinylidene fluoride (PVDF) membrane (mean pore size 0.001 μm, Zhejiang Qiushi Membrane Company, Hangzhou, China) is used to filter the solution to recycle the residual nanoparticles, the filtrate is the effluent. The residual nanoparticles can be used again.

RESULTS AND DISCUSSION

XRD Analysis

Fig. 1 is the XRD spectrum of the prepared samples. The diffraction peak of the sample was sharp and half peak width was narrow. This were in accordance with the hexagonal system wurtzite ZnO (JCPDS No. 36-1451). The corresponding crystal planes were (100), (002), (101), (102), (110), (103), (200), (112) and (201). The standard peak of crystal plane about ZnO samples (002) was stronger than standard peaks, which showed that crystal grew perpendicularly in the directions preferential to the C axis.

The average grain size D of the sample was calculated according to the Scherrer formula: $D = 0.89\lambda / (\beta \cos\theta)$, (101) crystal plane as the characteristic diffraction peak.

Where, λ is incident light wavelength (0.15406 nm), β is half peak width of characteristic diffraction peak for (101) crystal plane, and θ is the diffraction angle.

Morphology Analysis

Fig. 2 shows SEM pictures of ZnO samples. The prepared ZnO nano sheets with inhomogeneous sizes showed that crystals grew perpendicularly in the directions preferential to the C axis, and the result was consistent with XRD spectrum (Fig. 1).

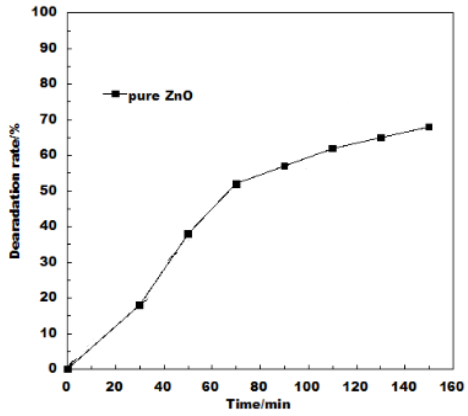

Fig. 3: The influence on photocatalytic activity of ZnO sample (R = 0.9489).

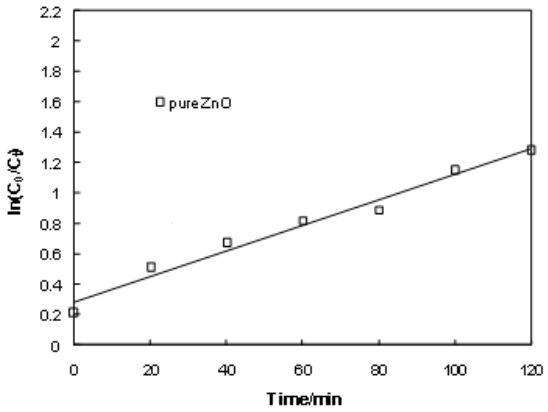

Fig. 4: $\ln(C_0/C_t)$ versus reaction time of ZnO samples (R = 0.9891).

The Activity of Catalysts

The sample was used to degrade coking wastewater in xenon lamp light, whose source of power was 300 W and wavelength range was 320-800 nm. The initial COD concentration in synthetic coking wastewater was 2000 mg/L, solution volume 50 mL, and catalyst dosage 0.6 g/L. Before the photocatalytic reaction, suspension, including light catalyst in the dark was mixed for 30 min in order to achieve the adsorption equilibrium, then the light source was opened to degrade wastewater, and samples were taken after every 20 minutes.

Fig. 3 showed that degradation rate of COD concentration in synthetic coking wastewater catalytic by pure ZnO was 69.48%, which was about 40% greater than that of the biodegradation efficiency. Nanoparticles of zinc oxide had more surface area than regular zinc oxide, which helped the separation of photo-generated electrons and holes, and then the light catalytic activity of ZnO was improved.

hotocatalytic Reaction Dynamics Analysis

The dynamics analysis of the degradation reaction of coking wastewater by pure ZnO was done. The time after adsorption for 30 min in the dark was as zero time, the relationship of the ln (C_0/C_t) and the light reaction time is shown in Fig. 4. The linear relationships of ln (C_0/C_t) and time of the four samples showed that the light catalytic reaction was in line with first order kinetic model "ln (C_0/C_t) = kt". The reaction rate constant corresponding to the light catalyst was 0.008 min^{-1}, which proved that nanometer material significantly improved the photocatalytic reaction rate of ZnO.

CONCLUSIONS

1. ZnO nano-photocatalytic materials were prepared by hydrothermal synthesis method.
2. The photocatalytic activity of ZnO materials is good, whose coking degradation efficiency was 69.48% with xenon lamp light (365 nm) for 2 hours, about 40% greater than that of the pure ZnO degradation efficiency.
3. Coking wastewater photocatalytic degradation reactions of ZnO samples were first order reaction kinetics equation.

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