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Preparation of ZnO nanopowder by a novel ultrasound assisted non-hydrolytic sol–gel process and its application in photocatalytic degradation of C.I. Acid Red 249

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ABSTRACT

Rod-like zinc oxide (ZnO) nanopowder was synthesized from zinc acetate via an ultrasound assisted non-hydrolytic sol–gel process. The samples were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV–vis spectroscopy. X-ray diffraction confirmed that the as-prepared nanopowder was excellently crystallized. TEM images displayed the samples consisting of rod-like nanocrystallites of about 30 nm width and 50–70 nm length. A plausible nonhydrolytic alcoholysis route based on the well-known ester-elimination reaction that involved the nucleophilic attack of the hydroxyl group of diethylene glycol on the carbonyl carbon atom of zinc acetate was proposed and confirmed by gas chromatography–mass spectroscopy (GC–MS) analysis. Diethylene glycol not only acted as a solvent, but also acted as a reactant and as a capping agent, limiting particles growth and preventing their agglomeration. Photocatalytic degradation of C.I. Acid Red 249 (AR249) was carried out with synthesized ZnO nanopowder. The blank experiments showed that both UV illumination and the catalyst were necessary for the decomposition of AR249. The influences of various operational parameters such as catalyst dose, dye concentration, pH of the solution on percentage photodegradation of AR249 were investigated. The degradation of AR249 was found to be effective in alkaline media and the kinetic of photodegradation followed pseudo-first-order kinetic model. The rate constant for degradation of AR249 was calculated to be 0.01369 min^{-1}.

1. Introduction

Since the last three decades, semiconductor heterogeneous photocatalysis has been studied extensively for water decontamination [1–3]. Under UV irradiation, heterogeneous photocatalyst is able to decompose and to mineralize bio-recalcitrant organic pollutants in the form of CO_2 and H_2O. TiO_2 is the most widely used for photocatalysis due to its high photosensitivity, chemical stability and non-toxicity [4]. However, zinc oxide (ZnO), as a potential semiconductor with wide bandgap (3.37 eV) and large excition binding energy (60 meV) [5], has received increasing scientific interests as its performance is better than that of TiO_2 in the degradation of several contaminations [6–10].

Various synthetic routes, such as chemical vapor deposition (CVD) [11], template-assisted growth [12], sol–gel process [13], hydro/solvothermal method [14,15], and microwave methods [16] have been developed to prepared ZnO with various morphologies. Recently, non-hydrolytic sol–gel processes have been successfully applied to the preparation of various nanocrystals of transition metal oxides, such as TiO_2 [17], ZrO_2 [18], ZnO [19], and so on. By the high-temperature thermal decomposition of metal precursors at high-boiling-point solvents such as amines or alcohols, high-quality monodisperse nanocrystals are obtained [20–22]. In this method, the alcohol or amine itself not only acts as a solvent, but also acts as a capping agent and as a surfactant agent, limiting particle growth and preventing their agglomeration. The size and morphology of the obtained nanocrystals can be steered by tuning the reaction temperature and the chemical nature of the reaction media. However, in order to yield highly crystalline particles, the reaction must be carried out at high temperature (>150 °C).

Nowadays ultrasound assisted synthesis has been proven to be a useful technique for preparing nanocrystalline materials [23]. During sonication, ultrasonic waves are radiated through the solution. Millions of bubbles form, grow and immediately collapse, which generates high pressures of up to ~1800 atm and high temperatures followed by high rate of cooling [24]. The energy released from this process, known as acoustic cavitations, can improve chemical reactivity and reaction rates [25].

C.I. Acid Red 249 (AR249) is an azo dye and widely used in the dyeing of leather, paper, silk, wool and nylon. In the present investigation, photocatalytic degradation of AR249 under UV light in the presence of ZnO nanopowder synthesized by a novel ultrasound assisted non-hydrolytic sol–gel process was reported. The probable reaction mechanism was proposed and discussed. The effects of various parameters such as catalyst dosage, concentration of dye, pH of

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the dye solution and irradiation time on the photodegradation efficiency of AR249 were investigated.

2. Experimental

2.1. Reagents and materials

Zinc acetate dihydrate ($Zn(CH_3CO_2O)_2 \cdot 2(H_2O)$) and diethylene glycol (DEG, $HOCH_2CH_2OCH_2CH_2OH$) were purchased from Sinapharm Chemical Reagent Co., Ltd. Commercial TiO_2 (P25) was obtained from Degussa.AR249 (disodium 3-[(5-chloro-2-phenoxyphenyl)azo]-4-hydroxy-5-[[(p-tolyl)sulphonyl]amino]naphthalene-2,7-disulphonate, molecular formula $C_{29}H_{20}ClN_3Na_2O_{10}S_3$ and molecular weight 747.5) was obtained from local dye suppliers, and the structure of AR249 was shown in Fig. 1. All the chemicals were used without further purification.

2.2. Preparation of photocatalyst

In a typical synthetic process, 1.756 g (8 mmol) zinc acetate dihydrate was completely dissolved in 40 mL DEG. The solution was treated by ultrasonic horn (manufactured by Nanjing Xian'ou Instrument Co. Ltd., China) for 2 h on 2 s pulse mode (2 s on mode and 2 s off mode). The titanium tip of the horn was located at the center of the solution and immersed 1 cm deep in it. The system was operated with 40% amplitude, giving theoretical dissipation rate ($0.40 \times 1200 = 480$ W). At the end of sonication, a white precipitate was collected by centrifugation at 10,000 rpm for 10 min. The collected white precipitate was washed with absolute alcohol and distilled water for several times and dried under vacuum at 80 °C.

2.3. Characterization of photocatalyst

X-ray pattern of ZnO was recorded using power X-ray diffraction (XRD) at room temperature on a Panalytical X-pert diffractometer with Cu Kα radiation ($\lambda = 0.154$ nm), running at 40 kV and 30 mA, scanning from 10° to 80° at 3°/min. The size and the morphology of the particles were determined using a JEOL JEM-2100 transmission electron microscope (TEM) with an acceleration voltage of 300 kV. All TEM samples were prepared by depositing a drop of diluted suspension in ethanol on a carbon film coated copper grid. The UV–vis absorption spectra of the prepared samples were recorded in the wavelength range from 250 to 750 nm using a Cary5000 UV–vis recording spectrophotometer.

GC/MS analysis was performed on SHIMADZU GCMS-2010 QP Ultra equipped with AOC-20i AUTO injector and a RXi-5 ms column (30 m × 0.25 mm × 0.25 μm). Helium was used as carrier gas at a constant flow rate of 1 mL/min. 1 μL of sample was injected using a cold on column injection part. The GC temperature program was set as follows: 4.0 min at 50 °C, 5 °C/min to 70 °C, 25 °C/min to 150 °C, 5 °C/min to 170 °C, 15 °C/min to 280 °C and hold for 20 min. Using scan mode a mass range from 50 to 1000 m/z at 1400 scan/s was defined.

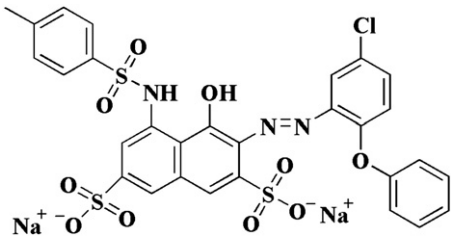

Fig. 1. The structure of AR249.

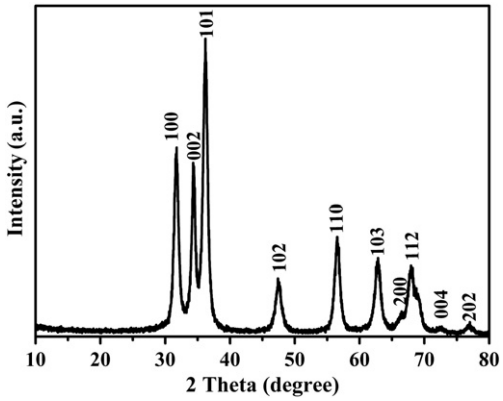

Fig. 2. XRD patterns of the prepared ZnO.

2.4. Photocatalytic activity test

The photocatalytic activity of synthesized ZnO was evaluated by the degradation of AR249 under UV irradiation at room temperature. Prior to irradiation, the suspension containing AR249 and photocatalyst was magnetically stirred in a dark condition for 1 h until the adsorption equilibrium was established. In all the experiments, 50 mL of dye solution of known concentration containing a known weight of ZnO powder was irradiated under the ultraviolet light lamp (15 W, $\lambda = 365$ nm) maintaining the distance between the light source and the surface of the suspension of about 10 cm. At the given time intervals, 3 mL of the suspension was taken out and centrifuged at 10,000 rpm for 10 min to remove the catalyst particles completely. The concentration of solution was analyzed by measuring the absorbance at λ_{max} with a UV–vis spectrophotometer.

The decolorization efficiency (%) was calculated as:

$$\text{Degradation}(\%) = \frac{(C_0 - C)}{C_0} \times 100.$$

Where C_0 is the initial concentration of dye and C is the concentration of dye after photo irradiation at different intervals of time.

The mineralization of AR249 was measured by the reduction of total organic carbon (TOC), as measured using a multi N/C 2100 TOC analyzer (AnalytikJena, Germany).

3. Results and discussion

3.1. Characterization of ZnO nanopowder

Fig. 2 shows the XRD pattern of the prepared ZnO. The characteristic peaks at 31.7°, 34.4°, 36.2°, 47.5°, 56.5°, 62.8°, 67.9°, and 69.0°are identified to be (100), (002), (101), (102), (110), (103), and (112) diffraction peaks of wurtzite ZnO, which indicate that the prepared ZnO possess a hexagonal crystal structure (JCPDS No. 36-1451). The sharp and intense peaks show that the synthesized ZnO has good crystallinity. The relatively high intensity of the (101) peak suggests the anisotropic growth and a preferred orientation of the crystallites [26]. No impurity peaks are detected indicating that the product is of high purity.

The morphology of the synthesized ZnO nanopowder was studied by transmission electron microscope (TEM). The typical TEM micrographs of the prepared samples are shown in Fig. 3. It is clearly shown that the as-obtained ZnO product is uniform, rod-like in shape and in nano-region with little aggregation. The nanorods have a width of about 30 nm and lengths of 50–70 nm.

UV–vis spectrum of the ZnO nanopowder re-dispersed in absolute alcohol is shown in Fig. 4. The curve of ZnO nanopowder has no clear absorption in the visible range. An absorption peak at 366 nm is observed,