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Sonocatalytic performance of Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 in organic dye degradation

Jingqun Gao, Renzheng Jiang, Jun Wang*, Baoxin Wang, Kai Li, Pingli Kang, Ying Li, Xiangdong Zhang

Department of Chemistry, Liaoning University, Huanggu District #66, Shenyang 110036, PR China

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ABSTRACT

In this study, the Er^{3+}:$YAlO_3$ as up-conversion luminescence agent, which can transfer the visible light part in the sonoluminescence to ultraviolet light, was synthesized by nitrate–citrate acid and sol–gel method. And then the Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 composite as a sonocatalyst was prepared by ultrasonic dispersion and liquids boil method. The prepared Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 composite was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The sonocatalytic activity of Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 composite was examined through the degradation of organic dye in aqueous solution under ultrasonic irradiation. The influences of key preparation conditions such as Ti/Fe molar ratio, heat-treated temperature and heat-treated time on the sonocatalytic activity of Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 composites were studied. The results indicated that the Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 composite with 1:1 molar ratio of Ti/Fe heat-treated at 500 °C for 20 min displays the highest sonocatalytic performance in the degradation of Acid Red B. For the degradation of other organic dyes, the Er^{3+}:$YAlO_3/TiO_2$–Fe_2O_3 composite also demonstrates a good sonocatalytic activity.

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1. Introduction

In the wake of continuous investigation, sonochemical technology has become one of the advanced oxidation processes (AOPs). It is also based on the production of various reactive oxygen species (ROS), often the hydroxyl radicals ($^•OH$) that are able to induce the degradation and transformation of a number of organic and inorganic pollutants in the wastewater containing anthropogenic toxins [1]. The $^•OH$ are generated through the acoustic cavitation, which can be defined as the cyclic formation, growth and collapse of microbubbles which leads to the formation of hot spots with extremely high local conditions of temperature and pressure and sonoluminescence [2]. Under these conditions, organic pollutants with an elevated fugacity character are pyrolyzed, while non-volatile compounds are degraded by $^•OH$ coming from water and oxygen dissociation [3]. Particularly, at present in wastewater treatments the ultrasound is the most effective way of all the AOPs to decompose organic dyes in non- or low-transparent effluents. However, in actual applications, the efficacy using ultrasound alone to degrade organic compounds is relatively low. Many recent studies have been focused on the ultrasonic irradiation (US) in combination with photocatalysts [4–8]. Compared with the ultrasound alone, US/photocatalysts exhibit a higher degradation efficiency. It is because that the solid photocatalyst enhances mass transfer of organic pollutants between the liquid phase and the catalyst surface. Moreover, it provides additional nuclei for bubble formation, more active surface area due to ultrasound de-aggregating and more $^•OH$ generated from the activated photocatalyst excited by ultrasound-induced light which has a wide wavelength [8].

To effectively use the sonoluminescence (ultrasound-induced light) and increase the ultrasonic degradation efficiency, as a most promising catalyst, TiO_2 could reasonably be used due to its high efficiency, stability and low cost. However, the fast recombination rate of photogenerated electron–hole pairs and the low efficient absorption of ultrasound-induced light because of its band gap (E_g = 3.2 eV) hinder its efficiency of the photocatalysis. Fortunately, combining TiO_2 with other semiconductor can provide a beneficial way to restrain the recombination of photogenerated electron–hole pairs, such as Fe_2O_3–TiO_2 [9–11]. What is more, Fe_2O_3 as a semiconductor has relatively narrow bandgap (E_g = 2.2 eV) and a wide respondent spectrum. Hence, to some extent, TiO_2 coupling Fe_2O_3 improves the utilization of visible light. But the lifetime of holes in the Fe_2O_3 is so short that are especially vulnerable to photo-induced corrosion. Therefore, it is unsuitable to degrade the organic pollutants continuously. Thus, in recent years many efforts have been made to develop systems combining semiconductor with up-conversion luminescence agents (for example: Er^{3+}:$YAlO_3$) in photocatalytic degradation. It can convert visible light to the ultraviolet light that can activate the TiO_2 photocatalyst [12–14]. And it is considered to be a feasible method to expand the responsive spectrum of TiO_2 besides impurity doping of nonmetal ions [15–17]. In the Er^{3+}:$YAlO_3$, the $YAlO_3$ acting as the host offers a suitable crystal field for the absorption and emission of light [18], while the Er^{3+} ion is a very attractive optical activator and displays the richest

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* Corresponding author. Tel.: +86 024 62207861; fax: +86 024 62202053.
E-mail address: wangjun890@126.com (J. Wang).

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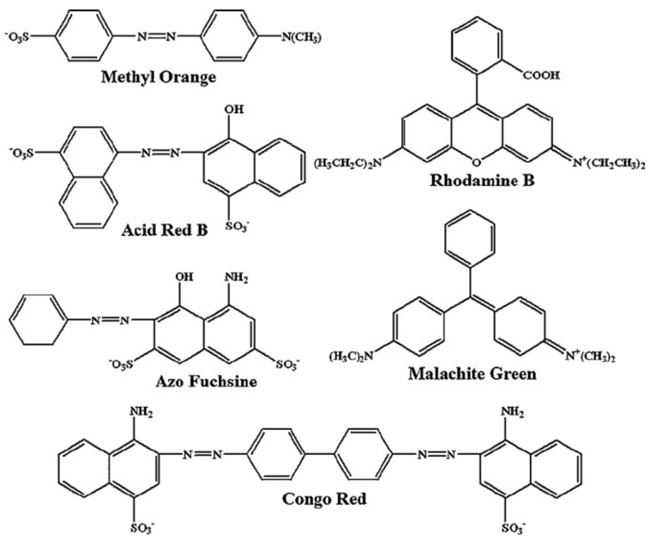

Fig. 1. Molecular structures of used organic dyes.

spectra in the UV–vis–IR range due to its rich energy level structure [19]. In the $YAlO_3$ crystal field, as a special exciton the Er^{3+} ion can absorb two or several low-energy photons (visible light) to emit one high-energy photon (ultraviolet light). Therefore, the Er^{3+}:$YAlO_3$ can provide an effective upconversion process of visible light to ultraviolet light.

In this paper, we design a novel sonocatalyst, Er^{3+}:$YAlO_3/TiO_2–Fe_2O_3$ composite, for enhancing dye degradation in virtue of making effective utilization of sonoluminescence. The purpose was to investigate the sonocatalytic performance of Er^{3+}:$YAlO_3/TiO_2–Fe_2O_3$ composite. And that, Acid Red B dye as a modal target pollutant was selected to examine its sonocatalytic activity. The factors influencing the performance of Er^{3+}:$YAlO_3/TiO_2–Fe_2O_3$ composite, such as Ti/Fe molar ratio, heat-treated temperature and heat-treated time were studied. Besides, the sonocatalytic activity to degrade other organic dyes was also examined. Finally, the mechanisms of upconversion luminescence process of Er^{3+}:$YAlO_3$ and the excitation principle of Er^{3+}:$YAlO_3/TiO_2–ZnO$ composite under ultrasonic irradiation were proposed.

2. Materials and methods

2.1. Materials

Acid Red B ($C_{20}H_{12}N_2O_7S_2Na_2$, molecular weight (MW): 502.44, λ_{max} = 515 nm), Methyl Orange ($C_{14}H_{14}N_3O_3SNa$, MW: 327.34, λ_{max} = 460 nm), Rhodamine B ($C_{28}H_{31}N_2O_3Cl$, MW: 479.02, λ_{max} = 550 nm), Azo Fuchsine ($C_{16}H_{11}N_3O_2S_7Na_2$, MW: 467.38, λ_{max} = 525 nm), Malachite Green ($C_{23}H_{25}N_2Cl$, MW: 364.92, λ_{max} = 617 nm) and Congo Red ($C_{32}H_{22}N_6O_6S_2Na_2$, MW: 696.68, λ_{max} = 498 nm) (analytical pure, Tianjin Kaiyuan Reagent Corporation, China) are used as model organic pollutants and their molecular structures are given in Fig. 1. Er_2O_3 (99.99% purity), Y_2O_3 (99.99% purity) and $Al(NO_3)_3{\cdot}9H_2O$ (analytical pure), citric acid (analytical pure) and HNO_3 (analytical pure) (Veking Company, China) were used for preparing Er^{3+}:$YAlO_3$. TiO_2 (anatase phase, grain size: 25–30 nm, BET: 100 m^2/g, pZC: 6.82) and Fe_2O_3 (α-Fe_2O_3, spherical powder, grain size: 30–35 nm, BET: 36 m^2/g, pZC: 8.10) (Sinopharm Chemical Reagent Co., Ltd., China) were purchased to prepare the $TiO_2–Fe_2O_3$ composite. The solutions were prepared with water from a Millipore Waters Milli-Q water purification system (Millipore Corporation, USA).

2.2. Synthesis of Er^{3+}(1.0%):$YAlO_3$ and Er^{3+}:$YAlO_3/TiO_2–Fe_2O_3$

The Er^{3+} (1.0%):$YAlO_3$ as up-conversion luminescence agent was synthesized by nitrate–citrate acid and sol–gel method. Y_2O_3, Er_2O_3, $Al(NO_3)_3{\cdot}9H_2O$ and solid citric acid as raw materials were used to prepare the Er^{3+} (1.0%):$YAlO_3$. $Y(NO_3)_3$ and $Er(NO_3)_3$ solutions were prepared by dissolving stoichiometric Y_2O_3 and Er_2O_3 into hot HNO_3. Then the prepared $Y(NO_3)_3$ and $Er(NO_3)_3$ solutions were mixed with $Al(NO_3)_3{\cdot}9H_2O$ under stirring magnetically until a homogenous solution was obtained. At that moment, the solid citric acid was gradually added into the mixture (mol ratio of citric acid:metal ion is 3:1). The final solution was evaporated in the water bath at 85 °C to form a pale-yellow gel. And the amorphous powders were obtained at 120 °C for 24 h and grounded into fine particles. Subsequently, the particles were calcined at 1200 °C for 2.0 h to remove residual organic components and nitrate ions and finally form the Er^{3+}:$YAlO_3$ nanocrystal.

The Er^{3+}:$YAlO_3/TiO_2–Fe_2O_3$ composites as sonocatalyst were prepared by ultrasonic dispersion and liquids boil method. The stoichiometric amounts of TiO_2 and Fe_2O_3 powders (the molar ratio of Ti: Fe = 9:1, 7:3, 1:1, 3:7 and 1:9) were added into 20 mL of deionized water. During stirring, 5.0 wt% Er^{3+}:$YAlO_3$ powder was gradually added to the TiO_2 and Fe_2O_3 suspension, and then dispersed by an ultrasonic bath (KQ-100, 25 kHz, 50 W, Kunshan Ultrasonic Apparatus Company, China) for 5.0 min. After fully dispersed, the suspension was filtered and dried at 100 °C for 24.0 h. The final mixture was calcined at various temperatures (300, 500 and 700 °C) for different times (20, 60 and 100 min) at 10 °C/min, respectively. After calcining, the wanted sonocatalysts were grounded into fine particles for later use.

2.3. Analytical method

The prepared samples were characterized by powder X-ray diffractometer (RINT 2500, XRD-Rigaku Corporation, Japan) using Ni filtered Cu Kα radiation in the range of 2θ from 10° to 70° and scanning electron microscopy (SEM, JEOL JSM-5610LV, Hitachi Corporation, Japan). The surface areas of prepared samples were determined using a BET surface area analyzer (BET, F-Sorb 2400, Beijing Jinaipu United Win Technology Limited, China). The degradation of organic dye was detected by UV–vis Spectrometer (LAMBDA-17, PerkinElmer Company, USA) and ion chromatogram (ICS-90, Dionex Company, USA). The ratios of dye adsorption and reduction were determined from the change in intensity of λ_{max} of organic dye solution using the following equation:

$$\text{Adsorption ratio}(\%) = \frac{C_0 - C_a}{C_0} \times 100$$

$$\text{Absolute degradation ratio}(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

$$\text{Relative degradation ratio}(\%) = \frac{C_a - C_t}{C_a} \times 100$$

where C_0 is the initial concentration of Acid Red B solution, C_a is the dye concentration after adsorption by catalysts and C_t is the instant concentration after ultrasonic irradiation.

2.4. Experimental

Degradation experiments were carried out in a 150 mL conical flask placed in ultrasonic irradiation apparatus (KQ-100, 40 kHz, 50 W, Kunshan ultrasonic apparatus Company, China) for 150 min avoiding light. The distance between the bottom of the reactor and the ultrasonic irradiation source was fixed at 2.0 cm. The reaction temperature was maintained as 25.0 ± 0.2 °C by circulating

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