



Preparation of rare earth-doped ZnO hierarchical micro/nanospheres and their enhanced photocatalytic activity under visible light irradiation

Jin-Chung Sin, Sze-Mun Lam, Keat-Teong Lee, Abdul Rahman Mohamed*

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia

Received 13 September 2013; received in revised form 26 October 2013; accepted 27 October 2013

Available online 1 November 2013

Abstract

Rare earth-doped ZnO hierarchical micro/nanospheres were prepared by a facile chemical precipitation method and characterized by X-ray diffraction, field-emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, UV-visible diffuse reflectance spectroscopy and photoluminescence spectroscopy. The results showed that the as-synthesized products were well-crystalline and accumulated by large amount of interleaving nanosheets. It was also observed that the rare earth doping increased the visible light absorption ability of the catalysts and red shift for rare earth-doped ZnO products appeared when compared to pure ZnO. The photocatalytic studies revealed that all the rare earth-doped ZnO products exhibited excellent photocatalytic degradation of phenol compared with the pure ZnO and commercial TiO₂ under visible light irradiation. Nd-doped ZnO had the highest photocatalytic activity among all of the rare earth-doped ZnO products studied. The optimal Nd content was 2.0 at% under visible light irradiation. The enhanced photocatalytic performance of rare earth-doped ZnO products can be attributed to the increase in the rate of separation of photogenerated electron–hole pairs and hydroxyl radicals generation ability as evidenced by photoluminescence spectra.

© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Powders: chemical preparation; C. Optical properties; D. ZnO; E. Functional applications

1. Introduction

Nowadays, “green life” has been inspiring people to pay more and more attention to the removal of hazardous substances in the wastewater, especially organic pollutants. The photocatalytic reaction has become a desirable method to convert the organic pollutants into simpler and harmless compounds to eliminate the environmental pollution. As an important functional oxide, ZnO has received broad interest as a photocatalyst due to its unique chemical and physical properties, environmental stability, abundant availability and low cost, as compared to other metal oxides [1,2]. However, ZnO is a wide band gap (~ 3.3 eV) semiconductor, which means only radiation with shorter wavelength ($\lambda < 385$ nm) can be utilized to generate electron–hole pairs. Therefore, the activity of ZnO is limited to the ultraviolet region which only covered no more than 5% of the whole solar spectrum [3]. Hence, various strategies have been adopted to extend the photoresponse of ZnO toward the visible spectral

region such as doping with metal or non-metal ions, sensitizing by dyes and coupling with semiconductors [1,3–6]. On the contrary, the fast recombination of photogenerated electron–hole pairs on ZnO unavoidably hindered the outward diffusion of the charge carriers. Thus, the photocatalytic process occurring at the semiconductor/fluid interface is prohibited, which is another important limiting factor to the photocatalytic efficiency [6]. Recently, some studies have reported doping with rare earth ions was a useful way to overcome the aforementioned two drawbacks of ZnO [5,7–9]. The doping of rare earth ions on the ZnO can produce impurity energy levels in band gap and expanded its visible light response. Furthermore, rare earth ions doping can produce traps for photogenerated charge carriers and decreased the electron–hole pairs recombination rate. The La-doped ZnO nanoparticles [7], Ce-doped ZnO nanorods [8], Sm-doped ZnO nanorods [5] and Nd-doped ZnO nanoneedles [9] were the different rare earth-doped catalysts that have been successfully fabricated and appeared to be very efficient for the photodegradation of organic pollutants. In particular, hierarchical micro/nanostructures have become a class of attractive materials owing to their peculiar structure and unique properties [10–12].

*Corresponding author. Tel.: +60 45996410; fax: +60 45941013.

E-mail address: chrahman@eng.usm.my (A.R. Mohamed).

For example, Lu et al. [10] reported that flower-like ZnO hierarchical microarchitectures synthesized via a citrate-mediated hydrothermal route showed higher photocatalytic activity compared with the mono-morphological nanostructures. Wang et al. [11] prepared peanut-like ZnO hierarchical superstructures possessing enhanced photocatalytic performance for the degradation of methyl orange because of their peculiar structure. Our previous work revealed that the unique hierarchical porous structure and large surface area of ZnO hierarchical micro/nanospheres offered greater opportunity for the diffusion and mass transportation of phenol molecules and hydroxyl radicals in the photochemical reaction of phenol degradation [12]. Meanwhile, there is insufficient information available on the application of rare earth-doped ZnO hierarchical structure as photocatalyst.

In this study, three different rare earth-doped ZnO hierarchical micro/nanospheres (RE/ZnO) photocatalysts including Nd/ZnO, Eu/ZnO and Ce/ZnO were synthesized by a simple chemical precipitation route without any organic solvent or surfactant. The morphology evolution and mechanism on the formation of the 3D ZnO hierarchical structure were investigated. The as-synthesized ZnO products were characterized by different techniques and used for the photocatalytic degradation of phenol under visible light irradiation. The mechanism by which rare earth ions enhanced photocatalytic activities was also discussed.

2. Experimental details

2.1. Preparation of catalysts

All the reagents used in this work were of analytical grade without further purification. The ZnO hierarchical micro/nanospheres were prepared by a facile chemical precipitation method as described earlier [12]. The RE/ZnO catalysts were prepared according to the same procedure in the presence of added metal salt ($\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{Cl})_3 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$) into the solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. For each RE-doped catalyst, 5.0 mmol $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and a stoichiometric amount of rare earth salt were dissolved in 80 mL of deionized water. Then 30 mmol NaOH was added into the above solution and stirred continuously for 3 h at room temperature. After stirring, the as-formed precipitates were filtrated, washed with deionized water for several times, dried at 60 °C for 12 h and finally calcined at 450 °C for 2 h.

2.2. Characterization

The products were characterized by X-ray diffraction (XRD) analysis on a Philips PW1820 diffractometer equipped with $\text{Cu K}\alpha$ radiation over a range from 20° to 80°. Field-emission scanning electron microscopy (FESEM) was performed with a Quanta FEG 450 instrument together with energy-dispersive X-ray spectral (EDX) analysis. Diffuse reflectance spectroscopy (DRS) of catalysts was carried out with a Perkin-Elmer Lambda 35 UV–visible spectrometer. Spectra were recorded in the range of 350–650 nm, with BaSO_4 as reference standard.

Photoluminescence (PL) spectroscopy of synthesized products was taken at room temperature on a Perkin-Elmer Lambda S55 spectrofluorometer using a Xe lamp with an excitation wavelength of 325 nm.

2.3. Measurement of photocatalytic activity

The photocatalytic activity of the as-synthesized ZnO products was evaluated by the degradation of phenol. Experiment was as follows: 100 mg catalyst was placed into 100 mL of 20 mg/L phenol aqueous solution in a beaker. Before photocatalytic reaction, the solution was magnetically stirred in dark for 1 h to ensure the establishment of an adsorption–desorption equilibrium between the catalyst and phenol. The phenol concentration after equilibration was monitored using a high-performance liquid chromatography (HPLC) and taken as the initial concentration (C_o). Then, the solution was irradiated under a 55 W compact fluorescent lamp. The average light intensity striking the surface of the reaction solution was about 14,500 lx, as measured by a digital luxmeter. This lamp was fixed about 12 cm above the reaction solution. The details of the photocatalytic process and HPLC system have already been discussed in our earlier papers [5,13]. HPLC separations were performed at 254 nm with a mobile phase mixture of water and acetonitrile in the ratio of 70:30 (v/v) at a flow rate of 1 mL/min. The photocatalytic reaction temperature was kept at room temperature by using cooling fans to prevent any thermal catalytic effect. After the elapse of a period of time, 2 mL of the solution was drawn and the concentration of phenol (C) was determined. Meanwhile, the comparison studies with commercial TiO_2 (100% anatase) were also conducted.

According to the Langmuir–Hinshelwood kinetics model [5,9,14,15], the photocatalytic process of phenol can be expressed as the following pseudo-first-order kinetics equation [15]:

$$\ln(C_o/C) = kt \quad (1)$$

where k is the observed rate constant (min^{-1}), C_o is the equilibrium concentration of phenol (mg/L) and C is the concentration of phenol at time t (mg/L). In order to determine the reproducibility of all the results, at least duplicated runs were carried out for each condition for averaging the results, and the experimental error was found to be within $\pm 4\%$.

2.4. Analysis of hydroxyl radicals ($\bullet\text{OH}$)

Terephthalic acid photoluminescence probing technique (TA-PL) was used in the detection of $\bullet\text{OH}$. Terephthalic acid readily reacted with $\bullet\text{OH}$ to produce highly fluorescent product, 2-hydroxyterephthalic acid. The method relied on the PL signal at 425 nm of 2-hydroxyterephthalic acid. The PL intensity of 2-hydroxyterephthalic acid was proportional to the amount of $\bullet\text{OH}$ formed. In the detection experiment, a basic terephthalic acid solution was added to the reactor instead of phenol and the concentration of terephthalic acid was set at 5×10^{-4} M in 2×10^{-3} M NaOH solution. The PL spectra of generated 2-hydroxyterephthalic acid were measured by a Perkin-Elmer Lambda S55 spectrofluorometer. At the given irradiation time,

Download English Version:

<https://daneshyari.com/en/article/10625744>

Download Persian Version:

<https://daneshyari.com/article/10625744>

[Daneshyari.com](https://daneshyari.com)