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Nano ZnO synthesis by modified sol gel method and its application in heterogeneous photocatalytic removal of phenol from water

Khizar Hayat[a], M.A. Gondal[b,*], Mazen M. Khaled[a], Shakeel Ahmed[c], Ahsan M. Shemsi[d]

[a] Chemistry Department, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
[b] Physics Department and Center of Excellence in Nano Technology (CENT), King Fahd University of Petroleum & Minerals, Box 372, Dhahran 31261, Saudi Arabia
[c] Center for Refining & Petrochemical, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia
[d] Center for Environment & Water, Research Institute, King Fahd University of Petroleum & Minerals, Dhahran 31261, Saudi Arabia

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ABSTRACT

Zinc oxide nanoparticles were synthesized by precipitation and modified sol gel methods. The influence of calcination temperature on morphology and crystallite size of ZnO was studied by varying temperature from 400 to 700 °C. The nano-structured ZnO particles were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDXS) and tranmission electron microscopy (TEM). The photo catalytic activity of as-prepared ZnO was evaluated by degradation of phenol under UV laser irradiation. The Photocatalytic degradation (PCD) efficiency of ZnO was found to decrease with the increase in calcination temperature due to agglomeration of particles and the increase in particle size. In addition to the effect of calcination temperature, the influence of various other parameters such as photocatalyst concentration, initial pH and the initial phenol concentration was also investigated to achieve the maximum PCD of phenol. The operational parameters show the expected influence regarding the efficiency of the photocatalytic degradation process. The results follow the pseudo-first order rate kinetics.

1. Introduction

Sol–gel preparation of solid catalysts has been reported by many research groups since the 1980s [1–5]. Within the broad family of functional materials, metal oxides are particularly attractive with respect to applications in catalysis, sensing, energy storage and conversion, optics, and electronic devices [6]. Although they have been extensively studied by materials scientists for many years but still research is going on to synthesize metal oxides with well-defined shape, size and composition. The soft-chemistry routes especially sol–gel procedures offer unique advantages such as the possibility of obtaining metastable materials, achieving superior purity and compositional homogeneity of the products at moderate temperatures with simple laboratory equipment [7].

Semiconductor photo-catalysts offer huge potential for elimination of toxic chemicals [8]. The photocatalytic degradation of organic pollutants in water and air, using semiconductors such as TiO_2 and ZnO have been focus of research recently due to their unique ability in the environmental detoxification [9–12]. ZnO, with bang gap = 3.37 eV, has become promising in the past few years because of its distinctive optoelectronic, catalytic, and photochemical properties [13,14]. The quantum efficiency of ZnO is also significantly larger than that of TiO_2 [15]. In some cases, ZnO has revealed better activity than TiO_2 [16]. The ZnO-mediated photocatalytic process has been successfully used to degrade organic pollutants [17,11]. ZnO is available at low cost and it absorbs over larger fraction of the solar spectrum than TiO_2 [18]. For this reason, ZnO is considered to be more suitable material for photocatalytic degradation of organic pollutants.

Phenol and phenolic compounds are widely used in industry and daily life. The presence phenol and phenolic compounds in the resulting wastewaters is an issue of environmental concern. Their high toxicity, even at low concentrations, have motivated the search and improvement of many waste treatment techniques. They have caused considerable damage and threat to the ecosystem in water bodies and human health due to their high stability, high toxicity and carcinogenicity. Removal of phenol and phenolics in wastewater effectively is a burning issue worldwide. Traditional wastewater treatment techniques include activated carbon adsorption, chemical oxidation and biological digestion, in which photocatalytic degradation assisted by titanium dioxide under ultraviolet light is extensively studied. More research has been focused recently on the search for new catalysts beyond TiO_2, modification of the catalyst and the factors influencing photocatalytic rate and the reaction kinetics [19–21]. A few studies regarding photo-oxidation of phenol are reported in the literature [22–25].

* Corresponding author. Tel.: +966 38602351; fax: +966 38602293.
E-mail address: magondal@kfupm.edu.sa (M.A. Gondal).

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Highly efficient catalysts are still being sought to eliminate these toxic materials. Thus, development of new photocatalysts for pollution treatment is of current interest [26,27].

In the present work, nano ZnO catalyst was synthesized using two different methods and characterized by XRD, FESEM and TEM, the photocatalytic activity of synthesized ZnO by two methods is evaluated for the degradation of phenol under ultraviolet laser irradiation. The influence of various parameters such as calcination temperature, the amount of the catalyst, laser exposure time, initial pH and initial phenol concentration on the rate of photocatalytic degradation of phenol is also investigated.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate [Zn $(NO_3)_2]\cdot 6H_2O$, polyvinyl alcohol, ammonium carbonate $(NH_4)_2CO_3$, ethanol [C_2H_5OH] were purchased from Sigma–Aldrich. The commercial ZnO nanoparticles were obtained from Aldrich (particle size <100 nm, and BET surface area of 25 $m^2\,g^{-1}$). The ZnO nanoparticles (particle size, ranging from 15 to 51 nm) were synthesized by precipitation method and sol gel method. Phenol ((Aldrich, >99%) was obtained from Sigma–Aldrich and used without any further purification. Reagent-grade sodium hydroxide, nitric acid, and HPLC-grade methanol were purchased from Merck. De-ionized water was used throughout this study.

2.2. Catalyst preparation

2.2.1. Synthesis of nano ZnO by precipitation method

The aqueous solutions of [Zn $(NO_3)_2]\cdot 6H_2O$ and $(NH_4)_2CO_3$ were prepared in deionized water in a required molar ratio. The zinc nitrate solution was added dropwise into the ammonium carbonate solution. The mixed solutions were stirred continuously for two hours. The resulting precipitates from the reaction between the Zn $(NO_3)_2$ and $(NH_4)_2CO_3$ solutions were collected by filtration using a 0.2 μm. Membrane filter and washed many times with deionized water and ethanol, respectively. The precipitates collected after washing were dried at 100 °C to form the precursors of ZnO. The precursors obtained after drying were calcined at a temperature of 500 °C for 7 h in programmable furnace to get the nano-sized ZnO particles.

2.2.2. Synthesis of nano ZnO by sol gel method

Zinc oxide nanoparticles were prepared by modified sol–gel method from aqueous precursor solutions. The method adopted to prepare nano-ZnO in this study is described in Ref. [28]. The conditions used for synthesis such as aging, drying temperature, calcination time and temperatures are different. The zinc nitrate and polyvinyl alcohol (PVA) solutions of desired molar ratio were prepared. A stoichiometric amount of zinc nitrate hexahydrate [Zn $(NO_3)_2\cdot 6H_2O$] and PVA were accurately weighed and dissolved in deionized water. The two prepared solutions mixed in a beaker and stirred with a magnetic stirrer at room temperature for three hours. Subsequently, the mixed solution was heated at a temperature of 80 °C for 60 h to obtain the gel. The obtained gel was dried at 100 °C for 24 h then ground into a fine powder. The temperature of the dried precursor powder was increased at the rate of 1 °C/min to attain the required temperature and then allowed the sample to stay at that temperature for seven hours to obtain the final product (i.e., ZnO nanoparticles). Thermal treatment was performed at five different calcination temperatures 400 °C, 500 °C, 550 °C, 600 °C and 700 °C, in order to study the effect of calcination temperature on the particle size and photocatalytic activity of nano ZnO and the obtained catalysts were labeled as ZnO-400, ZnO-500, ZnO-550 and ZnO-600, ZnO-700. The ZnO powder obtained from calcination was grounded for more than one hour to obtain homogenous nano powder. The calcined ZnO nano powders were then characterized by micrographic techniques.

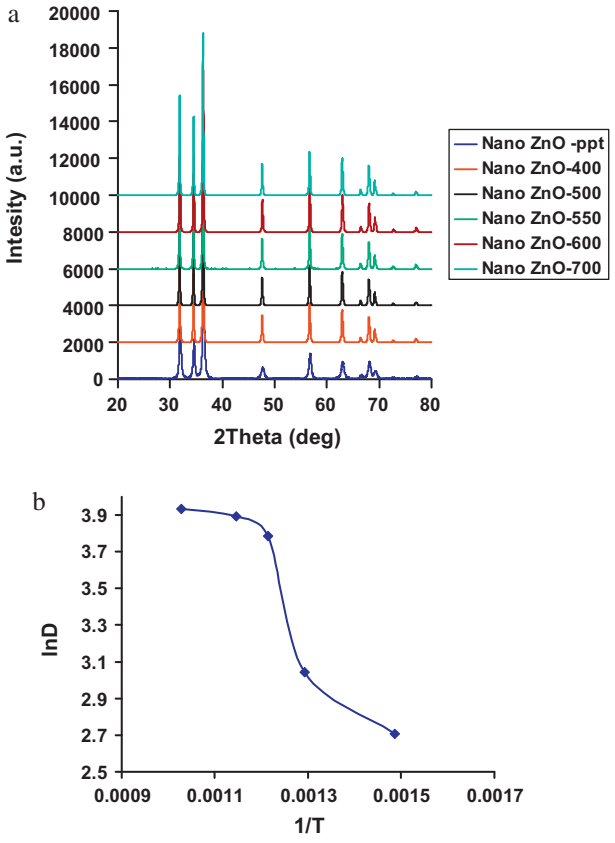

Fig. 1. (a) X-ray diffractrograms for Nano ZnO-ppt, Nano ZnO synthesized by sol gel and calcined at 400 °C, 500 °C, 550 °C, 600 °C and 700 °C. (b) A plot of ln*D* vs time for nano ZnO-ppt, nano ZnO synthesized by sol gel and calcined at 400 °C, 500 °C, 550 °C, 600 °C and 700 °C.

2.3. Characterization of photocatalysts

2.3.1. X-ray diffraction analysis

Powder X-ray diffraction (XRD) patterns of the synthesized nano ZnO powders were recorded in the range $2\theta = 20–80°$ with a step size = 0.02 on a Philips X'Pert MPD rotatory target diffractometer, using Cu Ka radiation (=0.15406 nm) as X-ray source, operated at 40 kV and 100 mA. The particle size was further verified with the help of FESEM and TEM results. The crystallite dimensions of ZnO were calculated using Scherrer's equation [29,30].

$$D = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

where λ is the wavelength of the X-ray (0.15418 nm), *B* is the full width at half maximum (FWHM, radian), and θ is the Bragg angle (degree). The value of FWHM was obtained by performing profile fitting using an XRD pattern processing software. The X-ray diffraction patterns of the nano ZnO prepared by precipitation and sol gel method calcined at different temperatures such as 400 °C and 500 °C, 550 °C, 6 00 °C and 700 °C are presented in Fig. 1a. The average crystalline size of the nano-ZnO product was estimated according to the Scherrer equation and it was observed that nano ZnO synthesized by precipitation method has estimated size (47 nm) while the size of ZnO nanoparticles prepared by modified sol gel method at different temperatures (400–550 °C) range from