Ultrasonics - Sonochemistry 40 (2018) 361–372

Contents lists available at ScienceDirect

Ultrasonics - Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

Heterogeneous sonocatalytic degradation of anazolene sodium by synthesized dysprosium doped CdSe nanostructures

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ARTICLE INFO

Keywords:
Nanocatalyst
Sonocatalyst
Doped CdSe nanoparticles
Sonocatalysis

ABSTRACT

Undoped and Dy–doped CdSe nanoparticles are synthesized and then characterized by the SEM, XRD, FT–IR, XPS and BET methods, which verify successful preparation of the doped catalyst. The sonocatalytic degradation of anazolene sodium as a model azo dye is higher than sonolysis process and the 2% Dy–doped CdSe with band gap of 1.42 eV exhibits the greatest sonocatalytic performance. The decolorization efficiency (DE%) of sonocatalysis with 2% Dy–doped CdSe, undoped CdSe and sonolysis after 90 min of the process is 91.32%, 56.13% and 39.14%, respectively. In addition, the sonocatalytic degradation of anazolene sodium increases with enhancement of the dopant, catalyst dosage, ultrasonic power, dissolved gasses and decreasing of initial anazolene sodium concentration. Furthermore, with addition of chloroform, sulfate, chloride and ethanol as the radical scavengers, the DE% decreases indicating the controlling mechanism of free radicals for the dye degradation. Besides, the results reveal the appropriate reusability of the catalyst and various degradation by–products are identified using the GC–MS technique. Eventually, the empirical kinetic model is expanded by nonlinear regression analysis for prediction of pseudo first–order constants in various operational conditions.

1. Introduction

Environmental pollution can be occurred by releasing of untreated hazardous industrial effluents into the limited natural water sources resulting in unfavorable consequences in the ecosystem and shortage in available domestic and commercial water. Hence, wastewater treatment comprising organic contaminants is essential to protect the environment from serious threats [1,2]. Textile industries consumes significant amounts of water and dyes during involved processes, which eventually generates colorful wastewaters containing organic pollutants with high chemical oxygen demand. Extensively used azo dyes and their reductive cleavage intermediates like aromatic amines are toxic and carcinogenic substances, which need to be removed from water efficiently to permissible levels [3].

Advanced oxidation processes (AOPs), which are based on direct, quick and non–selective oxidation of the contaminants by in situ generated reactive species particularly hydroxyl radicals ($^{\cdot}OH$), are promising green technologies for degradation and mineralization of the organic pollutants into CO_2, H_2O and mineral acids [4]. Active radicals are generated utilizing diverse routes including ozone, hydrogen peroxide, homogeneous or heterogeneous catalyst without or in the exposure of energy sources like ultraviolet (UV) or ultrasonic (US) irradiations [2].

Environmental sonochemistry is an environmentally friendly process, which is applied for organic compounds degradation. Acoustic cavitation is generated using the US irradiation through which tiny microbubbles form, grow and finally collapse resulting in high localized temperature and pressure. It causes to split water molecules to $H^{\cdot}$ and $^{\cdot}OH$ radicals within or out of the hot spots at the bubble–liquid interface [3,4]. However, practical application of sonolysis is restricted by high operational cost, which is owing to the remarkable loss of input energy in thermal form. Consequently, development of processes such as heterogeneous sonocatalysis or sonophotocatalysis using various catalysts is desired to improve the degradation efficiency [3].

Different semiconductors including, TiO_2, ZnO and etc. as sonocatalyst have been applied for treatment of refractory pollutants [5,6]. Nanostructured catalysts have advantages of high surface area, low cost, proper catalytic activity and low toxicity. Cadmium selenide (CdSe) is considered as a proper catalyst for application in water treatment due to its narrow band gap (1.7 eV) and rapid generation of electron–hole pair (charge carriers). However, low adsorption capacity and fast

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http://dx.doi.org/10.1016/j.ultsonch.2017.07.021
Received 10 June 2017; Received in revised form 12 July 2017; Accepted 12 July 2017

recombination of the generated pairs are the main limitations of its application, which can be improved by preparing doped catalyst with rare earth ions [7]. Doped semiconductors with trivalent lanthanide (Ln^{3+}) ions modify their physico–chemical properties. Moreover, the Ln^{3+} direct excitation is not effective, which restrain their catalytic applications; so, transferring energy from the host excited semiconductor to Ln^{3+} ions is the acceptable way to overcome this restriction.

Among various routes for synthesis of nanostructured materials, hydrothermal method has some advantages compared to sol–gel [8], microwave [9], chemical precipitation [10], solvothermal [11], ultrasonic irradiation [12], electrochemical [13] methods including no need for toxic organic reagents, high temperature and sophisticated equipment. In addition, one pot high yield synthesis of controllable size nanoparticles with no post–heat treatment make it suitable for industrial applications [7,14].

In the present work, CdSe nanoparticles was synthesized by efficient and uncomplicated hydrothermal method. Dysprosium (Dy) was specifically selected as dopant in order to improve CdSe sonocatalytic properties. The physical characteristics of the prepared catalysts were analyzed by SEM, XRD, FT–IR, XPS and BET. Then, the performance of synthesized CdSe and Dy–doped CdSe nanostructures were studied as sonocatalyst for the anazolene sodium degradation; then, the kinetic of the treatment process was perused. Eventually, the generated degradation intermediates of the anazolene sodium were detected using GC–MS technique. To the best of our knowledge, there isn't any report about the use of Dy–doped CdSe nanoparticles as the sonocatalyst for the anazolene sodium degradation.

2. Experimental details

2.1. Materials and methods

All reagents and chemicals used in this study were analytical grade and were applied as supplied without any purification. Hydrazine monohydrate ($N_2H_4{\cdot}H_2O$ 80%), cadmium acetate dihydrate ($Cd(CH_3COO)_2{\cdot}2H_2O$ 98%) and sodium selenite (Na_2SeO_3 99%) were provided from Loba Chemie company (India). NaOH, H_2SO_4 (98%), NaCl, Na_2SO_4 and chloroform ($CHCl_3$ 99.6%) were obtained from Merck company (Germany). Dysprosium (III) nitrate hexahydrate ($DyN_3O_9{\cdot}6H_2O$ 99.99%), and ethanol (96%) were supplied from Sigma Aldrich, USA. anazolene sodium was purchased from Shimi Boyakhsaz company (Iran).

2.2. CdSe and Dy–doped CdSe synthesis

CdSe and Dy–doped CdSe nanoparticles with diverse Dy mole fractions (2, 4 and 6%) were synthesized by hydrothermal method. In a classic synthesis, 4 mmol of Na_2SeO_3 powder, proper molar ratios of $DyN_3O_9{\cdot}6H_2O$, 2 mmol of $Cd(CH_3COO)_2{\cdot}2H_2O$ and 2 pellets of NaOH were dissolved in distilled water. $N_2H_4{\cdot}H_2O$ was dropwisely added to the mentioned solution, under moderate stirring. The ultimate solution was transferred into a stainless–steel Teflon-lined autoclave (110 mL), put in an oven for 24 h at 180 °C, then the autoclave was permitted to cool down till room temperature. The resulted precipitate was collected and washed several times with distilled water and ethanol to eliminate residual impurities. Then, the resulted black powder was dried for 6 h at 60 °C.

2.3. Characterization instruments

Scanning electron microscopy (SEM) (SEM, S–4200, Hitachi, Japan) was utilized to investigate the morphology and surface structure of the prepared catalysts. The size distribution of the synthesized sample was studied using Manual Microstructure Distance Measurement software (Nahamin Pardazan Asia company, Iran). X–ray diffraction (XRD) analyses of the catalysts were done by a Siemens X–ray diffractometer (D8 Advance, Bruker, Germany) via Cu Ka radiation (l = 1.54065 Å) at an emission current of 30 mA and an accelerating voltage of 40 kV. Fourier transform infrared spectroscopy (FT–IR) spectrometer (Tensor 27, Bruker, Germany) was conducted to record the FT–IR spectra of the catalysts utilizing KBr pellet technique. X–ray photoelectron spectroscopy (XPS) measurements were performed by using a Thermo Scientific spectrometer (K–ALPHA, UK). The porosity and pore size of the samples were measured using adsorption of N_2 at 77 K with a Gmini series, Nitrometrics (Japan). Band gap of nanocatalysts was calculated via measuring the absorbance (200–800 nm) by a UV–vis spectrophotometer (WPA Lightwave S2000, England) after sonicating the mixed sample with distilled water for 15 min. The produced by–-products during the anazolene sodium degradation process were discovered by Agilent 6890 gas chromatography–mass spectrometry (GC–MS) coupled with an Agilent 5973 mass spectrometer (Canada).

2.4. Sonocatalytic degradation procedure

The decolorization of anazolene sodium was investigated in the presence of CdSe and Dy-doped CdSe nanoparticles utilizing an ultrasonic bath (Ultra 8060, England) with process time of 90 min. A particular amount of nanocatalyst was added to anazolene sodium solution (100 mL) with a definite concentration. At specific time intervals, samples were withdrawn and the absorbance of the solution was evaluated by a UV–vis spectrophotometer at the maximum absorbance wavelength of the dye (λ_{max} = 571 nm); the (DE%) is obtained by Eq. (1):

$$\text{DE}\ \% = \frac{A_0 - A}{A_0} \times 100 \tag{1}$$

where A_0 and A are the absorbance of the anazolene sodium solution at the initial and a specific time of the process, respectively.

3. Result and discussion

3.1. Characterization of nanocatalysts

Fig. 1(a, b) and (c, d) show the SEM images of CdSe and Dy–doped CdSe nanoparticles, respectively. The SEM figures of CdSe indicate the spherical and uniform structure with the diameter of about 50–100 nm. By doping CdSe with Dy, the lower nanoparticle size is observed. Reducing the size of the nanoparticles can be attributed to the formation of Cd–Se–Dy phase on doped catalyst surface, which prevents the growth of crystalline grains. Majority of the diameter size distribution for the 2% Dy–doped CdSe is in the range of 20–30 nm.

The XRD patterns of the CdSe and Dy–doped CdSe are indicated in Fig. 2. The XRD diffraction peaks at 2θ of 24.32°, 25.4°, 30°, 35.15°, 42.28°, 45.76° and 49.6° can be attributed to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) plane reflections, and is related to the hexagonal crystal structure of CdSe according to standard powder diffraction data (JCPDS 8-459) [15,16]. No extra peaks are observed which can confirm the unchanged crystal structure of CdSe in the presence of the dopant. So, it can be deduced that, applied hydrothermal method is the promising method in synthesizing the catalyst samples. The intensity of XRD peaks demonstrates the high crystallinity of the synthesized nanoparticles [7].

Fig. 3 shows the FT–IR spectra of the CdSe and Dy–doped CdSe with different ratios to determine the surface functional groups. The peaks at 3400, 1600 and 720 1/cm are ascribed to the stretching vibration of hydroxyl, adsorbed hydroxyl in CdSe structure and stretching vibration of Cd–Se, respectively. By increasing the dopant (Dy) percentage, Cd–Se vibration decreases that can be related to the substitution of Dy^{3+} in the crystal structure of CdSe.

In order to study the composition information of the synthesized samples, the XPS analysis is carried out. Fig. 4 indicates the XPS spectra of CdSe and 2% Dy–doped CdSe samples nanoparticles. The Cd 3d, Se 3d and Dy 3d peaks confirm the presence of Cd, Se and Dy elements and the binding energies of 404.52, 411.3 eV are related to Cd $3d_{5/2}$ and Cd $3d_{3/2}$ peaks, respectively. Moreover, the broad peak at approximately