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Ultrasonic-assisted synthesis of Ce doped cubic–hexagonal ZnTiO₃ with highly efficient sonocatalytic activity



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ABSTRACT

Ce doped ZnTiO₃ as a novel catalyst with highly efficient and stable sonocatalytic activity was synthesized via an ultrasound-assisted sol–gel method using non-ionic surfactant Pluronic F127 as structure directing agent. Synthesized samples were characterized by using various techniques, such as XRD, TEM, SEM, EDX, XRF, BET, DRS, and PL, and their sonocatalytic activity studied toward degradation of p-Nitrophenol as a model organic compound. The synthesized mesoporous Ce/ZnTiO₃ had mixed cubic–hexagonal phase with large surface area (118.2 m² g⁻¹) and narrow pore size distribution (4.9 nm). The effects of cerium concentration, calcination temperature, and calcination time on the structure and the sonocatalytic activity of Ce/ZnTiO₃ were studied in detail. XRD results were suggested that the relation between the phase structure and the catalytic activity is considerable. Significant decrease in band-gap and PL intensity was observed with increasing the cerium concentration in the ZnTiO₃. It became clear that the Ce/ZnTiO₃ (0.81 mol%) shows high sonocatalytic activity compared with pure ZnTiO₃ and other Ce/ZnTiO₃ samples as well as commercial TiO₂-P25. The possible mechanism for the enhanced sonocatalytic activity of Ce/ZnTiO₃ was discussed in details. The electrical energy consumption was also considered during sonocatalytic experiments.

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1. Introduction

TiO₂ and ZnO as wide band-gap oxide semiconductors with several desirable attributes and a great variety of applications have received a lot of attention in either single or composite (ZnO–TiO₂) form [1]. The concurrent synthesis of a ZnO–TiO₂ composite typically results in the formation of three known compounds, including ZnTiO₃ (cubic, hexagonal), Zn₂Ti₃O₈ (cubic), and Zn₂TiO₄ (cubic, tetragonal) [2]. Recently, a great deal has been received in zinc titanate (ZnTiO₃) due to its favorable catalytic properties. For instance, ZnTiO₃ is identified as one of the most efficient photocatalysts for environmental applications [3–5].

ZnTiO₃ is a perovskite-type oxides (ABO₃) that its perovskite structure gives the adaptability to change the arrangement of the A and B sites and to incorporate a combination of cations at the A and B sites to compose superseded perovskites. In fact, the electronic properties of perovskite-type oxides varies with changes in the stoichiometry or doping with a cation of a different valence

state [6,7]. Doping technique can be a potent strategy to modify the structural and the catalytic properties of the perovskite-type oxides. So that a suitable doping can prevent the recombination of photoinduced electron–hole pairs and enhances the photocatalytic activity of perovskite-type oxides such as ZnTiO₃ [3,4]. Lanthanide ions can be one of the best candidates for doping, as regards the lanthanide ions with 4f electron configurations can act as an efficient electron reservoir to trap electrons in the conduction band of photocatalysts [8,9]. It was also reported that lanthanide ions doping can increase light sensitivity and provide a means to concentrate the target molecules at the substrate surface [9,10]. To the best of our knowledge, although there are few reports on the photocatalytic applications of ZnTiO₃, its catalytic activity under ultrasonic irradiation has not yet been reported. It is known that the sonoluminescence caused by ultrasonic irradiation involves an intense UV-light that is able to excite the oxide semiconductors to act as a photocatalyst during sonication [11,12]. Ultrasonic irradiation by generating microjets from the collapse of cavitation bubbles inside the solution provides a very strong stirring environment. In addition, it can overcome the main disadvantages of UV-light assisted photocatalytic processes, such

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as the low penetration rate of UV-light and shielding effects of catalyst particles [13,14].

The ultrasonic-assisted method has proved to be a useful tool for the synthesis of nanostructured inorganic materials [15–21]. Utilization of ultrasonic irradiation during sol–gel synthesis method can affect morphology, size, and crystallinity of particles [9,22]. The implosive collapse of the cavitation bubbles during ultrasonic irradiation generates many local hot spots with extremely high temperatures (>10,000 K) and high pressures (>500 atm). The extreme conditions caused due to ultrasonic irradiation leading to intense micromixing improve solute transfer and nucleation rate in aqueous suspension, which lead to the formation of nanosized particles [15–21]. Further, ultrasonic irradiation is responsible for the prevention of agglomeration of particles [16–19] and uniform incorporation of dopant species into host lattice [9,23].

In this study, pure and Ce doped ZnTiO₃ nanoparticles were synthesized via a sol–gel method using non-ionic surfactant Pluronic F127. Ultrasonic irradiation was employed during synthesis for a uniform incorporation of cerium ions into ZnTiO₃ lattice. The synthesized samples were structurally characterized by various techniques and their sonocatalytic activity studied toward degradation of p-Nitrophenol (PNP) as a model organic compound. Finally, the effects of synthesis key factors such as cerium concentration, calcination temperature, and calcination time on the structures and sonocatalytic activity were studied. The interactions between effective variables on degradation efficiency of the PNP and electrical energy consumption were established by the 3D response surface and the 2D contour plots using response surface methodology (RSM). The RSM is a widely used mathematical and statistical technique in process optimizing and modeling. This procedure utilizes mathematical and statistical techniques for analyzing the effects of different variables and their interactions on response and optimizing the process. In addition to these benefits, RSM technique significantly decreases the total number of experimental runs, resulting in saving experimental costs and time [24,25]. Box-Behnken and central composite design are the most commonly selected methods in RSM technique [26]. A significant division of the operating expenses on using an ultrasound-assisted catalytic process for cleaning polluted waters is electrical energy consumption. In the following, the reusability of samples was evaluated and the effects of various radical and charge carrier scavengers on the sonocatalytic activity studied.

2. Materials and methods

2.1. Chemicals

Titanium tetra-n-butoxide, zinc acetate dihydrate, cerium(III) nitrate hexahydrate, ethanol, coumarin, sodium carbonate, potassium periodate, tert-butyl alcohol, ammonium oxalate, and PNP as a model organic compound, were purchased from Merck Co. (Germany). Triblock copolymers pluronic F127 (EO₁₀₆–PO₇₀–EO₁₀₆) was purchased from Aldrich Co. (England). All chemical reagents were in analytical grade.

2.2. Synthesis of cerium doped ZnTiO₃

For synthesis of Ce/ZnTiO₃, an ultrasound-assisted sol–gel method was used according to the following steps; First, 0.8 g pluronic F127 as a template was dissolved in ethanol under ultrasonic irradiation provided by a probe sonicator (700 W–20 kHz, Qsonica Q700, Newtown, CT, US). Then, 3.86 mL titanium tetra-n-butoxide was slowly added to the above solution. This was denoted solution A. In another process, 2.19 g of Zn(CH₃COO)₂·2H₂O was

dissolved in 11.6 mL deionized water with stirring at room temperature. This was denoted solution B. The hydrolysis process was performed under ultrasonic irradiation by adding solution B drop by drop into a flask containing solution A by a syringe pump (Fanavaran Nano-Meghyas, model SP. 1000, Iran). After 2 h, an appropriate concentration of cerium (0.4, 0.6, 0.9, 1.2, and 1.4 mol%), was added to the mixed solution and the obtained solution sonicated for 1 h. A small amount of ethylene glycol was added to the solution as a chelating agent. The resulting transparent colloidal suspension was aged in an autoclave at 100 °C for 3 days. The white solids formed were washed thoroughly with deionized water and ethanol, and finally calcined at various temperatures (630, 700, 800, 900, and 970 °C) for various times (80, 120, 180, 240, and 280 min). In addition, for the purpose of comparison, pure ZnTiO₃ was also prepared by the similar procedure.

2.3. Characterization of the synthesized samples

The average crystallite size and phase content of prepared samples were characterized by a Philips X'pert MPD diffractometer using Cu K α radiation ($\lambda = 0.15478$ nm). The hexagonal phase content was calculated approximately from the ratio of areas of hexagonal phase reflections to the areas of all reflections by the following equation [27];

$$H(\%) = \frac{A_h}{A_{all}} \times 100 \quad (1)$$

where A_h and A_{all} are the areas of hexagonal phase reflections and the areas of all reflections, respectively.

The average crystallite size of the particles based on the main X-ray diffraction (XRD) reflection was calculated using the Scherrer's equation [28];

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where, D is the average crystallite size (nm), λ is the wavelength of the X-ray radiation, k is a constant taken as 0.89, β is the full width at half maximum intensity, and θ is the half diffraction angle.

The size of the particle was obtained by transmission electron microscopy (TEM) instrument (EM 208 Philips, 80 keV) and surface morphology recorded with KYKY-EM3200 Digital SEM. The scanning electron microscopy (SEM) was equipped with an energy dispersive X-ray spectroscopy (EDX) for analyzing the chemical composition of the sample. The actual contents of cerium in the prepared samples were determined by means of X-ray fluorescence (XRF) on a Fischerscope XRAY XAN FD instrument. Photoluminescence (PL) emission spectra of the samples were recorded using a Varian Cary-Eclipse luminescence spectrometer (Agilent Technologies) with excitation wavelength at 320 nm. UV–Vis diffuse reflectance spectroscopy (DRS) was obtained using AvaSpec-2048 TEC spectrometer for determination of the optical band-gap of samples and calculated by the following equation [29];

$$E_g = \frac{hc}{\lambda} \quad (3)$$

where, E_g is the optical band-gap energy (eV), h is the Planck's constant, c is the light speed ($m\ s^{-1}$), and λ is the wavelength (nm).

2.4. Sonocatalytic activity experiments

The sonocatalytic activity of samples was studied toward degradation of PNP under ultrasonic irradiation provided by a probe sonicator in a batch reactor. In each run, 100 mL of PNP solution with initial concentration of 10 mg L⁻¹ and 100 mg of catalyst were transferred into the reactor and sonicated with an output power

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