

Photocatalytic activity of La-doped ZnO for the degradation of monocrotophos in aqueous suspension

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Abstract

La-doped ZnO nanoparticles with different La contents were synthesized and characterized by various sophisticated techniques such as XRD, UV–vis, AFM, XPS, and HR-SEM. The XRD results revealed that La³⁺ is uniformly dispersed on ZnO nanoparticles in the form of small La₂O₃ cluster. It was found that the particle size of La-doped ZnO is much smaller as compared to that of pure ZnO and decreases with increasing La loading. Rough and high porous surface of La-doped ZnO was observed by AFM, which is critical for enhancing the photocatalytic activity. The photocatalytic activity of La-doped ZnO in the degradation of monocrotophos (MCP) was studied. The effects of the adsorption of MCP, lights of wavelength, and the solution pH on the photocatalytic activity of La-doped ZnO with different La loading were studied and the results were compared with pure ZnO and pure TiO₂. It was observed that the rate of degradation of MCP over La-doped ZnO increases with increasing La loading up to 0.8 wt% and then decreases. It was found that the doping of La in ZnO helps to achieve complete mineralization of MCP within a short irradiation time. Among the catalyst studied, the 0.8 wt% La-doped ZnO was the most active, showing high relative photonic efficiencies and high photocatalytic activity for the degradation of MCP.

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1. Introduction

Metal oxide semiconductor materials, such as TiO₂, ZnO have attracted considerable attention in the recent year owing to their photocatalytic ability in the degradation of various environmental pollutants, such as pesticides, detergents, dyes, and volatile organic compounds into carbon dioxide, water, and mineral acids under UV light irradiation [1–4]. Although TiO₂ is universally recognized as the most photo active catalyst, ZnO is a suitable alternative to TiO₂ as it has similar band gap energy (3.2 eV) [5] and its lower cost and better performance in the degradation of organic dye molecule in both acidic and basic medium than TiO₂ has stimulated many researchers to further explore the properties of this oxide in many photocatalytic

reactions [6–9]. It has been recently shown that ZnO colloids are more effective in production of H₂O₂ and photocatalytic degradation of organic acids than TiO₂ colloids. In addition, the emitting properties of ZnO, which are developed in the system due to various kinds of intrinsic defects such as oxygen vacancies, zinc vacancies, zinc interstitials, oxygen interstitials, and antisite defect, can help to set up a catalytic system which is able to sense and shoot environmental contaminants [10–12].

ZnO has also several drawbacks including the fast recombination rate of photogenerated electron–hole pair and a low quantum yield in the photocatalytic reactions in aqueous solutions, which obstruct commercialization of the photocatalytic degradation process [13,14]. Consequently, there has been a lot of interest in improving the photocatalytic activity by suitable modification of semiconductors for the degradation of organic compounds in water. It has been found that the interfacial electron transfer efficiency and rate of the recombination of electron–hole pairs of semiconductor materials can be easily tuned by various surface

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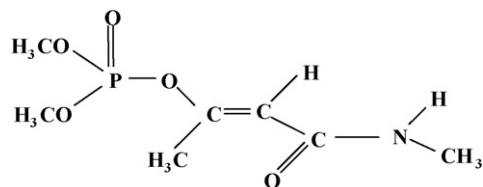


Fig. 1. Structure of monocrotophos (MCP).

modification methods such as surface chelation, surface derivatization, platinization, and selective metal ion and nitrogen doping [15–20]. It has been also demonstrated that the presence of heavy metals such as Pt, Pd, Au, and Ag on semiconducting metal oxides or zeolite supported TiO₂ can enhance the degradation efficiency of photocatalytic reactions [21–28]. Very recently, La-doped TiO₂ nanoparticle has attracted much attention in the photocatalytic processes owing to its high photocatalytic activity in the degradation of organic contaminants because of the suppression of electron–hole recombination, large content of oxygen vacancies, and strong absorption of OH[−] ions on the surface of the catalyst [23–25]. Unfortunately, there has been no report available on the preparation of rare earth-doped ZnO nanoparticles and their photocatalytic activities towards the degradation of pollutants present in water though it has almost similar band gap energy as that of TiO₂.

MCP is a model pollutant (Fig. 1), which is identified as endocrine disrupting chemicals (EDCs). Endocrine disrupting chemicals (EDCs), an exogenous agent present in the environment, disrupt the endocrine functions such as growth, development and reproduction of humans and animals. Recent research reports [29] have highlighted the existence of these chemicals in surface and ground water via point and non-point sources. A few adverse effects of EDCs are early maturity, defect in child birth and impotence [30]. Hence, the treatment of wastewater containing endocrine disrupting chemicals is imperative.

Here we report for the first time on the synthesis and characterization of La-doped ZnO catalysts and their photocatalytic activity on the degradation of MCP. All the materials have been unambiguously characterized by XRD, FT-IR, UV–vis, XPS, AFM, and HR-SEM analysis. It has been found that the photocatalytic activity of La-doped ZnO is much higher as compared to that of pure ZnO and TiO₂. Moreover, La-doped ZnO photocatalysts require shorter irradiation time for complete mineralization than pure ZnO and TiO₂. The relative photonic efficiency of ZnO, TiO₂, and La-doped ZnO has also been compared and the results have been discussed. Interestingly, the relative photonic efficiency of La-doped ZnO is much higher as compared to that of pure ZnO and TiO₂.

2. Experimental

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) (Analytical grade, Merck Ltd., India) and lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O) (Analytical grade, CDH, India) were used as zinc

and lanthanum sources, respectively. Sodium carbonate anhydrous (Na₂CO₃) was purchased from Merck (Analytical grade), India. The technical grade sample of monocrotophos (MCP) was received from Sree Ramcides Chemicals, India. HPLC grade acetonitrile was purchased from Merck, India. All the chemicals were used without further purification.

2.2. Preparation of photocatalysts

La-doped ZnO nanoparticles were prepared by coprecipitation method using the precursors of zinc and lanthanum. Zn(NO₃)₂·6H₂O and Na₂CO₃ were dissolved separately in double distilled water to obtain 0.5 mol/l solutions. Zinc nitrate solution (250 ml of 0.5 mol/l) was slowly added into vigorously stirred 250 ml of 0.5 mol/l Na₂CO₃ solution. Lanthanum nitrate in the required stoichiometry was slowly added into the above solution and a white precipitate was obtained. The precipitate was filtered, repeatedly rinsed with distilled water, and then washed twice with ethanol. The resultant solid product was dried at 100 °C for 12 h and calcined at 300 °C for 2 h. ZnO particles were also prepared by the same procedure without the addition of lanthanum nitrate solution. The doping concentrations of lanthanum are expressed in wt%.

2.3. Characterization of photocatalysts

The crystallinity of pure ZnO and La-doped ZnO catalysts were analyzed by X-ray powder diffraction using PANalytical X-ray diffractometer with Cu Kα radiation in the scan range 2θ between 10° and 70°. An accelerating voltage of 40 kV and an emission current of 25 mA were used. The UV–vis spectra of pure ZnO and La-doped ZnO catalysts were recorded in the range 200–700 nm using Shimadzu, Model: UV-1601. For recording of the spectra, the catalyst (~5 mg) in paraffin oil (2 ml) was finely crushed and applied over Whatman 40 filter paper. The absorbance spectra were then recorded in the range 200–700 nm for all the catalysts using a filter paper soaked in paraffin oil as the reference.

Pure ZnO and La-doped ZnO surfaces were investigated by an atomic force microscope (Model: Digital Instruments, 3100). The samples were analyzed by contact mode with Si₃N₄ tip having a force constant of 0.12 N/m. The presence of elements and chemical states of the catalysts were examined by ESCALAB 200 X-ray photoelectron spectrophotometer (VG Scientific) with monochromatic Mg Kα excitation source. The pressure was maintained at 6.3 × 10^{−5} Pa. Prior to XPS measurements all as-sprayed samples were calcined at 673 K for 2 h to ensure that any possible residual precursors would decompose completely. The texture and morphology of pure ZnO and La-doped ZnO were measured by a high resolution-scanning electron microscope (Hitachi, Model: S-4800).

2.4. Adsorption studies

Prior to photocatalytic experiments, the adsorption of MCP on ZnO and La-doped ZnO catalysts was carried out by mixing 100 ml of aqueous solution of MCP with fixed weight of

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