Journal of Photochemistry and Photobiology B: Biology 130 (2014) 11–19

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology B: Biology

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

# Highly active lanthanum doped ZnO nanorods for photodegradation of metasystox

P.V. Korake [a], R.S. Dhabbe [a], A.N. Kadam [a], Y.B. Gaikwad [b], K.M. Garadkar [a,*]

[a] Nanomaterials Research Laboratory, Department of Chemistry, Shivaji University, Kolhapur 416 004, Maharashtra, India
[b] Department of Zoology, Shivaji University, Kolhapur 416 004, Maharashtra, India

ARTICLE INFO

*Article history:*
Received 27 June 2013
Received in revised form 15 October 2013
Accepted 16 October 2013
Available online 30 October 2013

*Keywords:*
Zinc oxide nanorods
Lanthanum doping
Optical properties
Pesticide
Photocatalytic activity
Cytotoxicological study

ABSTRACT

La-doped ZnO nanorods with different La contents were synthesized by microwave assisted method and characterized by various sophisticated techniques such as XRD, UV–Vis., EDS, XPS, SEM and TEM. The XRD patterns of the La-doped ZnO indicate hexagonal crystal structure with an average crystallite size of 30 nm. It was found that the crystallite size of La-doped ZnO is much smaller as compared to pure ZnO and decreases with increasing La content. The photocatalytic activity of 0.5 mol% La-doped ZnO in the degradation of metasystox was studied. It was observed that degradation efficiency of metasystox over La-doped ZnO increases up to 0.5 mol% doping then decreases for higher doping levels. Among the catalyst studied, the 0.5 mol% La-doped ZnO was the most active, showing high photocatalytic activity for the degradation of metasystox. The maximum reduction of concentration of metasystox was observed under static condition at pH 8. Reduction in the Chemical Oxygen Demand (COD) of metasystox was observed after 150 min. The cytotoxicological studies of meristematic root tip cells of *Allium cepa* were studied. The results obtained indicate that photocatalytically degraded products of metasystox were less toxic as compared to metasystox.



## 1. Introduction

Semiconductor materials, such as $TiO_2$, ZnO are the promising candidates in air purification, water disinfection, hazardous waste remediation and water purification. In recent years considerable attention is owing to their photocatalytic ability in the degradation of various environmental pollutants. ZnO is one of the most promising material which is applied to many fields such as transparent conductive contacts, solar cells, laser diodes, ultraviolet lasers, thin film transistors, optoelectronic and piezoelectric applications, surface acoustic wave devices, gas sensors. It is an interesting semiconductor material, which has a wide direct band-gap (3.3 eV) and remarkable optical properties [1–5]. Although $TiO_2$ is universally recognized as the most photo active catalyst, ZnO is a suitable alternative to $TiO_2$ due to similar band gap energy (3.2 eV) [6] and lower cost which shows better performance in the degradation of dye molecules in both acidic and basic medium than $TiO_2$ [7–10].

Recently, transition metal (TM) and rare earth doped II–IV semiconductor nanoparticles have received much attention due to modification of optical properties. Usually, semiconducting nanoparticles are known to exhibit exotic physico-chemical properties due to quantum confinement effect. Especially, doped nanoparticles are predicted to show improved optical properties, viz., luminescence efficiency, and delay time and band edge emission with respect to particle size variation. These properties have opened up a number of new areas of applications such as DNA markers, biosensors, light emitting diodes, lasers as well as in spintronics and photocatalysis [11–15].

Rare earth metals are known for their ability to trap the electrons, which can be effectively reduce the recombination of photogenerated electron–hole pairs. La-doped ZnO nanorods has attracted much attention in the photocatalytic process owing to its high photocatalytic activity for the degradation of organic contaminants. The luminescence properties of rare earth doped ZnO have aroused great interest to many researchers [16–23]. There are only few studies were carried out on photo-oxidative degradation of toxic compounds [24] using ZnO semiconductor doped with rare earth metal ions, the photocatalytic activity in particular of La doped ZnO in the degradation of monocrotophos [25]. La-doped $TiO_2$ nanoparticles have attracted much attention in the photocatalytic processes owing to its high photocatalytic activity for the degradation of organic contaminants [26–28]. To date there are no reports available on the preparation of La doped ZnO nanorods and their photocatalytic activities towards the degradation of metasystox present in water. In present study La doped ZnO nanorods were prepared by simple microwave assisted method which is environmental eco friendly and energy saving technique. In case of

* Corresponding author. Tel.: +91 0231 2609161; fax: +91 0231 2692333.
*E-mail address:* kmg_chem@unishivaji.ac.in (K.M. Garadkar).

1011-1344/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jphotobiol.2013.10.012

microwave heating, energy is transferred throughout the material via molecular interaction thus producing uniform heating without thermal gradients and stress. This often results in materials with finer microstructures and particles with narrow size distribution.

Metasystox R is a organophosphorous pesticide (Scheme 1), also known as Oxydemeton-Methyl (ODM) which is a systemic acting cholinesterase – inhibiting organophosphate. Based on the specificity of its action against aphids, mites, leafhoppers and other plant destroying insects, highly water soluble ODM is widely used in agriculture. The degradation of metasystox is not possible by conventional biological treatment, due to its toxicity to the microorganism. However, due to chemical stability and high toxicity, metasystox resists to biodegradation. Therefore it is an important to explore a new methodology to reduce the contamination of water with metasystox. Photocatalysis is considered to be one of the most potential water pollution remedy in recent decades. Here we report for the first time on the synthesis and characterization of La-doped ZnO catalyst and its photocatalytic activity for the degradation of metasystox by influencing different parameters such as light sources, pH, and amount of catalyst loading.

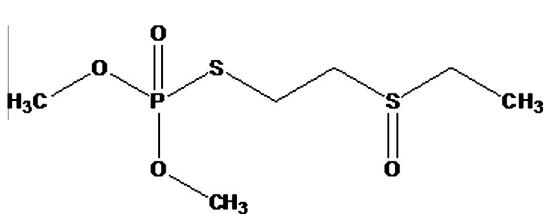
The mutagenic and carcinogenic action of insecticides on experimental animals is well known and several studies have shown that chronic exposure to low levels of pesticides can cause mutations and/or carcinogenicity [29,30]. Pesticide residues can be present in fruit and vegetables risky for human health. Several studies have shown that chronic exposure to low levels of pesticides during prenatal development can cause birth defects associated with carcinogenicity [31]. Pesticides residues persist in soil, water and food posed problems all over the world [32]. To study the toxicity of pesticides and its post-degradation products, plant genotoxicity assays are relatively inexpensive, fast and gives reliable results for the chemicals which cause chromosomal aberration in plant cells [33,34]. The plants are direct recipients of agrochemical toxins, in particular *Allium cepa* assay is one of the plant assay system used widely to study the genotoxic effects of pesticides. Many of such studies have demonstrated the induction of chromosomal aberrations by pesticides [35,36]. In present study the effect of exposure of metasystox and degraded products of metasystox were studied in meristematic root tip cells of *A. cepa.*

## 2. Experimental

### 2.1. Preparation of lanthanum doped ZnO nanorods

Zinc acetate, lanthanum nitrate, sodium hydroxide and high molecular weight Polyvinyl Alcohol (PVA 2000) were purchased from S. D. Fine Chemicals. All solutions were prepared in Millipore water. (Millipore Corp., Bangalore, India). All the chemicals used for the preparation were of analytical grade.

La-doped ZnO nanorods were prepared by microwave assisted method using the precursors of zinc and lanthanum. Then 0.2, 0.5, 1.0 mol% La $(NO_3)_2$ were added in each zinc acetate solutions for various doping. The La-doped ZnO powder was prepared by controlled addition of NaOH (0.1 M) to a mixture of zinc acetate (0.1 M), lanthanum nitrate (0.1 M) solution and PVA until the solution reached to pH = 10. The ratio of PVA to zinc acetate solution was kept 1:1 by taking equimolar solutions of each. A special arrangement was made to add dropwise aqueous solution of sodium hydroxide (0.5 mL $min^{-1}$) into the solution with constant stirring. After complete precipitation, the hydroxide was washed 2–3 times with distilled water and then pure hydroxide was placed in a microwave oven (input power 600 W) about 5 min with on–off cycle. Annealing of the product was carried out at 200 °C for 3 h. in a temperature controlled furnace.




**Scheme 1.** Structure of metasystox (pesticide).

### 2.2. Characterization of catalyst

The La-doped ZnO nanorods were characterized for structural, optical and photocatalytic properties. The structural and phase formations of La-doped ZnO were identified by an X-ray diffractometer (Rigaku Corporation, Japan) (Cu Kα radiation, $\lambda$ = 1.5406 Å) over the $2\theta$ range from 10 to 80°. The EDS was recorded in the binding energy region of 0–10 keV (JEOL, JSM-6360, Japan). The absorption spectra were recorded in the wavelength range 200–700 nm using UV–Vis. spectrophotometer (Shimadzu, Model-UV-3600). X-ray photoelectron spectra were recorded using an ESCA-3000 (VG Scientific Ltd. England) using Al Kα radiation (1486.6 eV) and constant pass energy of 50 eV. The morphological investigation was carried out by a scanning electron microscopy (SEM JEOL, JSM-6360, Japan). The shape and size of catalyst were obtained with TEM (Model: Tecnai G 2 20 Ultra-Twin, FEI, Netherland) working at 200 kV.

### 2.3. Photocatalytic activities of catalysts

The photocatalytic activities of pure and La-doped ZnO photocatalysts under UV and natural sunlight were evaluated by the degradation of metasystox ($1.4 \times 10^{-3}$ M) in an aqueous solution (100 mL). The pH of the solution was adjusted from 4 to 10 by addition of appropriate amount of HCl and NaOH. The aqueous solution of pesticide containing appropriate quantity of catalyst was taken in the quartz reactor and subjected to thorough stirring. The photoreactor was placed inside the reactor setup and the distance between the reactor and the UV lamp (High Pressure Mercury Lamp, 365 nm) was kept 5 cm. The photocatalytic degradation was carried out by taking 100 mL of aqueous metasystox solution and 100 mg photocatalyst. Prior to irradiation, the reaction suspension was stirred for 30 min to reach adsorption–desorption equilibrium. The light is irradiated and after specific time interval, aliquots were withdrawn from the suspension and centrifuged immediately at 3000 rpm, in order to separate the nanoparticles, then filtrate was analyzed by recording the absorbance of metasystox ($\lambda_{max}$ = 266 nm) using UV–Vis spectrophotometer to find out the extent of degradation of metasystox.

### 2.4. Changes in Chemical Oxygen Demand (COD) during photocatalysis

COD of the samples were determined at different time intervals. For the COD determination diluted supernatant solution refluxed with potassium dichromate in the presence of silver and mercury sulfate at a temperature of 100 °C. The refluxed solution was then titrated with ferrous ammonium sulfate (FAS) using ferroin as an indicator. Similar conditions were used for the blank sample (distilled water). COD was calculated by using the formula: COD (mg $dm^{-3}$) = $(A - B) \times N \times 8 \times 1000$ $mL^{-1}$ of sample, where $A$ is mL of FAS required for the blank, $B$ is mL of FAS required for the effluent sample, $N$ is the normality of FAS, and 8 is the milliequivalent weight of oxygen.