Applied Catalysis A: General 459 (2013) 106–113

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

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

Synthesis, characterization and enhanced photocatalytic degradation efficiency of Se doped ZnO nanoparticles using trypan blue as a model dye

Bhavani P. Nenavathu[a], A.V.R. Krishna Rao[b], Anshu Goyal[c], Ashok Kapoor[c], Raj Kumar Dutta[a,b,*]

[a] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India
[b] Centre of Nanotechnology, Indian Institute of Technology Roorkee, Roorkee 247667, India
[c] Solid State Physics Laboratory, Lucknow Road, Timarpur, New Delhi 110054, India

ARTICLE INFO

Article history:
Received 7 September 2012
Received in revised form 30 March 2013
Accepted 2 April 2013
Available online 13 April 2013

Keywords:
Photocatalytic dye degradation
ZnO nanoparticles
Selenium doping
Thermo-mechanical
Reactive oxygen species
X-ray photoelectron spectroscopy

ABSTRACT

Se doped ZnO nanoparticles (NPs) were successfully synthesized by thermo-mechanical method whose band gap increased with concentration of Se doping. Transmission electron microscopy of 5 wt% Se doped ZnO NPs revealed spherical nanoparticles of average size of 9.5 nm. X-ray photoelectron spectroscopy (XPS) revealed Se 3d binding energy at 59.5 eV, confirmed SeO_2 in the doped ZnO NPs. Fluorescence emission spectroscopy of Se doped ZnO NPs revealed oxygen vacancies which increased with the concentration of Se doping. The photodegradation efficiency of trypan blue (TB) using 30 W UV lamp was higher for Se doped ZnO NPs than pristine ZnO NPs, depended on Se doping concentrations, UV illumination, concentrations of photocatalyst and pH of the dye solution. The batch of 0.6 mg of 5 wt% Se doped in ZnO NPs per mL of TB dye maintained at pH 5 exhibited maximum photodegradation efficiency ($89.2 \pm 3.1\%$). Higher photocatalytic degradation efficiency for Se doped ZnO NPs was correlated with incorporation of oxygen vacancies due to Se doping, which were likely intermediate levels for transiting photoexcited charge carriers for generation of hydroxyl radicals and consequently facilitated photodegradation. Terephthalic acid assay confirmed formation of hydroxyl radicals in dye solution treated with photocatalyst.

1. Introduction

Industrial wastewater containing toxic dye effluents and its byproducts formed through oxidation, hydrolysis or other chemical reactions has raised severe environmental threat [1,2]. Primarily, there are two methods for removal of toxic dye from wastewater, i.e., adsorption of dye on a suitable substrate [3] and degradation of dye to nontoxic metabolites [4]. In the adsorption method, the toxic dye is merely transferred from the wastewater to a solid phase which further requires disposal of the sludge and would therefore render environmental pollution. In this context, degradation of dye by chemical or biological oxidation is suitable and has been widely explored [5,6]. However, new generation dyes are synthesized to resist microbial attack and as a result conventional biological wastewater treatment might be inefficient for degradation [7]. In this regard, advanced oxidation processes (AOPs) based on generation of reactive oxygen species, is a suitable option for treating contaminants of drinking water and industrial effluents [8–10]. Heterogeneous photocatalysts, namely TiO_2 is a well known material for decontaminating organic pollutants from aqueous system [11]. Lately, metal oxide nanoparticles illuminated by UV or visible light are reported to exhibit higher photocatalytic degradation efficiency as compared to their bulk counterpart and are therefore gaining importance for degradation of toxic dye [12]. Irradiation with photon energy greater than the band gap of the photocatalyst leads to formation of electrons (e^-) and holes (h^+), where electrons are promoted to conduction band and holes occupy valence band. The electrons could be utilized for reduction of oxygen bound to the surface of photocatalyst and result in the formation of highly reactive superoxide anions followed by generation of reactive oxygen species (ROS), e.g., hydroxyl radical ($OH^\bullet$). Similarly, the holes can oxidize adsorbed water on the photocatalyst to form highly reactive hydroxyl radical ($OH^\bullet$), and eventually participate in photocatalytic degradation of toxic compounds. It is evident that the limiting factor for photocatalytic degradation depends on the ability to suppress recombination of photogenerated electron–hole pairs. Doping photocatalyst with metals has been a successful method for inhibiting electron–hole recombination [13,14]. An extensive literature survey revealed reports of pristine and metal doped TiO_2

---

[*] Corresponding author at: Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India. Tel.: +91 1332285280; fax: +91 1332286206.
E-mail address: duttafcy@iitr.ernet.in (R.K. Dutta).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.04.001

nanoparticles (NPs) as a photocatalyst for dye degradation applications [9,11–16]. Though ZnO NPs have similar band gap (3.37 eV) as that of TiO_2 at room temperature, and they are easy to fabricate than that of TiO_2 nanoparticles, but its application as a photocatalyst has been limited [17,18]. Higher photosensitivity and thermal stability of ZnO NPs are the other advantages of ZnO NPs over TiO_2 NPs are [19]. Guovea et al. has confirmed that ZnO exhibited better photodegradation efficiency of some reactive dyes in aqueous solution than TiO_2 [20]. Photodegradation applications of ZnO NPs and metal doped ZnO NPs were reported to corroborate with the results of metal doped TiO_2 NPs [21].

The purpose of doping a semiconductor nanoparticles for photocatalytic activity could be of diverse nature, e.g., to alter the band structure, create defect sites and incorporate impurities for facilitating mobility of charge carriers. A recent study on doping of ZnO with non-metals revealed increase in the band gap and changes in the opto-electronic properties as compared to the un-doped ZnO NPs [22]. It would be interesting to explore other applications, especially its photocatalytic activity of non-metal doped ZnO NPs. In the present study, we have explored the option of Se doping in ZnO NPs to study its photodegradation of toxic dye. Selenium was chosen due to its suitable chemical property, ease of synthesis of Se doped ZnO. Moreover, high reduction potential of Se is thought to be a favorable condition for extracting photoexcited electrons from conduction band and hence can facilitate generation of ROS. Here we report a cost effective, thermo-mechanical method of synthesis and characterization of Se doped ZnO nanoparticles and studied its ROS induced UV light sensitized photocatalytic effect toward degradation of trypan blue (TB), used as a model toxic dye. Terephthalic acid assay has been used to confirm ROS generation. The role of ROS was further confirmed by reduced the photocatalytic activity in the presence of a ROS scavenger *viz*., histidine.

2. Materials and methods

2.1. Materials

Trypan blue dye, histidine and terephthalic acid were obtained from HIMEDIA Chemicals, India. Zinc acetate dihydrate, given as $Zn(O_2CCH_3)_2{\cdot}2(H_2O)_2$, was procured from SRL Pvt. Ltd., India and selenium metal powder was obtained from SD Fine-Chemicals Ltd., India. Oxalic acid dihydrate ($H_2C_2O_4{\cdot}2H_2O$) was procured from Ranbaxy Laboratories Ltd., India. All the chemicals and solvents were used without further purification.

2.2. Synthesis of Se doped and pristine ZnO NPs

In a typical synthesis of Se doped ZnO NPs, 5.48 g of zinc acetate dihydrate, 3.78 g of oxalic acid and required amount of selenium metal powder (2 wt%, 5 wt% and 10 wt%) of precursor Zinc acetate dihydrate were mixed and grinded in an agate mortar at room temperature for 20 min to form $ZnC_2O_4{\cdot}2H_2O$. The product was transferred to a quartz crucible and heated at 450 °C for 30 min in a muffle furnace comprising a proportional–integral–derivative (PID) controller for ensuring stability in the temperature. The temperature was set at 450 °C as thermogravimetric analysis of $ZnC_2O_4{\cdot}2H_2O$ revealed thermal degradation at 400 °C due to decomposition to ZnO (Fig. S1, supporting information), and agreed well with the reported literature [23]. Similarly a batch of pristine ZnO NPs without Se doping was prepared by following the same process as described above, except addition of selenium metal. The as-synthesized NPs were washed with ethanol and kept for overnight drying at 60 °C.

2.3. Characterization of Se doped and pristine ZnO NPs

The X-ray diffraction measurements of the pristine and Se doped ZnO NPs were performed with powder diffractometer (Bruker ARS D8 Advance) operated at 40 kV using graphite monochromatized Cu K_α radiation source with a wavelength of 1.54 Å in a wide-angle region from 20° to 80° on a 2θ scale. The morphology and particle size distribution of pristine ZnO NPs and Se doped ZnO NPs were characterized using transmission electron microscopy coupled with energy dispersive X-ray analyzer (TEM EDX), using FEI Technai-G^2 microscope operated at 200 kV. The corresponding elemental constituents of the nanoparticles were determined by the EDAX. The samples for TEM analysis were prepared by placing a drop of dispersed and diluted Se (5 wt%) doped ZnO NPs on a carbon coated 150 mesh copper grid and dried at room temperature. The thermogravimetric analysis of $ZnC_2O_4{\cdot}2H_2O$ and the batch of 5 wt% Se doped ZnO NPs was carried out at a heating rate of 5 °C min^{-1} from ambient temperature up to 1000 °C under a nitrogen flow (200 mL min^{-1}) using Perkin Elmer Pyris Diamond, to ensure mass loss in the sample due to thermal degradation of $ZnC_2O_4{\cdot}2H_2O$. The absorption spectroscopy of the as-synthesized nanoparticle dispersion was measured by UV–vis spectrophotometer (Shimadzu, UV-1800) in the range of 200–800 nm. The band gaps of the different batches of NPs were determined from Diffuse Reflectance Spectra (Shimadzu, UV-2450) with $BaSO_4$ as the reference scattering material. The emission spectra are recorded using fluorescence spectrophotometer (Shimadzu, RF-5301 PC) at excitation wavelength (λ_{ex}) of 380 nm. The chemical constituents in the pristine and Se doped ZnO nanoparticles were determined from X-ray photoelectron spectroscopy (XPS) using multi-technique surface analysis system of Omicron Nanotechnology, Germany. The XPS analyses were carried out using monochromatic Al K_α X-ray source of 1486.7 eV, with an operating voltage of 15 kV and emission current of 15 mA. The samples for XPS analysis of pristine and Se doped (5 wt%) ZnO NPs were made pellets using hydraulic press.

2.4. Photocatalytic degradation study

The degradation of trypan blue in the presence of Se doped ZnO nanoparticles under UV light illumination was similar to those discussed recently to mimic photocatalytic degradation of organic pollutants [24–26]. In our study, a purple colored trypan blue (TB) dye test solution of 2×10^{-5} M concentration was prepared and the batches of the test solution were treated with 0.6 mg/mL of 2 wt% and 5 wt% Se doped ZnO nanoparticles and compared with pristine ZnO NPs and control sample (without nanoparticles). The effect of concentration of photocatalyst was studied by treating batches of dye solution with different concentrations of 5 wt% Se doped ZnO NPs, e.g., 0.1 mg/mL, 0.4 mg/mL, 0.6 mg/mL and 0.9 mg/mL. The dye solution treated with different batches of NPs were first ultrasonicated for 20 min in dark to ensure minimal ROS formation during dispersion of the catalyst for attaining proper adsorption and desorption equilibrium. All the batches were then subjected to continuous stirring in the presence of 30 W UV light (λ = 340–360 nm), kept at a distance of 30 cm for a period of 6 h. These experiments were carried out in a laminar airflow workstation with a UV illumination facility. The kinetic study of the dye degradation was performed by measuring decolorization of dye in the 1 mL of an aliquot withdrawn from the sample solution at an interval of 1 h. The absorbance of the aliquot was measured at λ = 590 nm after separating the dispersed nanoparticles by centrifuging at 15,000 rpm at 25 °C for 5 min in Beckman Coulter^{TM} Allegra^{TM} X-22R Centrifuge. The decolorization of the dye was compared with a positive control comprising same concentration of dye solution without treating with Se doped ZnO NPs. The effect of decolorization of the dye by Se doped ZnO NPs was also compared