



# Influence of Li-doping on structural characteristics and photocatalytic activity of ZnO nano-powder formed in a novel solution pyro-hydrolysis route

Ibram Ganesh\*, P.S. Chandra Sekhar, G. Padmanabham, G. Sundararajan

Laboratory for Photoelectrochemical (PEC) Cells and Advanced Ceramics, International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), Balapur PO, Hyderabad 500005, A.P., India

## ARTICLE INFO

### Article history:

Received 15 May 2012

Received in revised form 16 July 2012

Accepted 16 July 2012

Available online 23 July 2012

### Keywords:

ZnO

Li-doped ZnO

Photocatalysis

Methylene blue degradation

Band gap energy

## ABSTRACT

Different types of Li-doped ZnO (LDZ) (Li=0–10 wt.%) powders were prepared by following a novel pyro-hydrolysis route at 450 °C, and were thoroughly characterized by means of thermo-gravimetry (TG), differential scanning calorimetry (DSC), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier-transform infrared (FT-IR), Fourier-transform Raman (FT-Raman) spectroscopy, diffuse reflectance spectroscopy (DRS), ultra-violet visible (UV-Vis) spectroscopy, Brunauer–Emmett–Teller (BET) surface area (SA), and zeta potential ( $\zeta$ ) measurements. Photocatalytic activity of these powders was evaluated by means of methylene blue (MB) degradation experiments conducted under the irradiation of simulated and natural solar light. Characterization results suggest that both pure ZnO and LDZ powders are quite thermally stable up to a temperature of 700 °C and possess band gap (BG) energies in the range of 3.16–3.2 eV with a direct band to band transition and  $\zeta$  values of –31.6 mV to –56.4 mV. The properties exhibited by LDZ powders were found to be quite comparable to those exhibited by *p*-type semi-conducting LDZ powders. In order to study the kinetics of MB degradation reaction under the irradiation of simulated solar light, the Li (0.2–10 wt.%) and Al (0.5 wt.%) co-doped ZnO (0.2LADZ to 10LADZ) powders were also synthesized and employed for this purpose. The photocatalytic degradation of MB over LADZ catalysts followed the Langmuir–Hinshelwood (L–H) first order reaction rate relationship. The 10LDZ catalyst exhibited highest photocatalytic activity among various powders investigated in this study.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

Recently, the conversion of CO<sub>2</sub> into value added chemicals such as, methanol using solar energy (artificial photosynthesis (PS)) has received a great deal of attention from the scientific community as it harnesses the solar energy in the form of chemical energy, combats CO<sub>2</sub> associated global warming problems today world is facing, uses process-waste CO<sub>2</sub> streams as a fuel source, and utilizes the most abundant sources of energy and hydrogen, being sunlight and water, respectively [1–7]. Methanol is a potential liquid fuel that can be directly used in the automobile vehicles without major modifications of the internal combustion engines. Photo-electrolysis of water or photoelectrochemical (PEC) reduction of CO<sub>2</sub> requires thermodynamic energy inputs of 1.23 and 1.5 eV, respectively [8]. In fact, the reduction of CO<sub>2</sub> with 6 protons (H<sup>+</sup>) and 6 electrons (e<sup>-</sup>) into methanol (CO<sub>2</sub> + 6 H<sup>+</sup> + 6e<sup>-</sup> → CH<sub>3</sub>OH + H<sub>2</sub>O) is an exothermic

reaction that does not need any energy like the dark reaction of the natural PS. However, the production of H<sup>+</sup> and e<sup>-</sup> from water needs energy like the light reaction of the natural PS [8]. For the first time, the PEC reduction of CO<sub>2</sub> into methane, methanol, ethanol, and formic acid was demonstrated by Halmann in 1978 in a PEC cell using *p*-GaP as a photocathode and certain amount of external bias voltage [6]. In another study, Inoue et al. [9] studied the photo-catalytic reduction of CO<sub>2</sub> into formaldehyde, formic acid, methanol, and trace amounts of methane and carbon monoxide using an array of semiconductors: tungsten trioxide (WO<sub>3</sub>), titanium dioxide (TiO<sub>2</sub>), zinc oxide (ZnO), cadmium sulfide (CdS), GaP, and silicon carbide (SiC) with limited success. For the first time, without employing any external bias voltage, Nozik [10], has successfully photo-oxidized water in a PEC cell using two photo-anode and photo-cathode simultaneously. He has employed *n*-type TiO<sub>2</sub> as photoanode and a *p*-GaP as photo-cathode. Since, *p*-GaP undergoes severe photo-corrosion in aqueous medium; Nojik's process could not takeoff for commercial practice. The so far reported information in the literature on artificial PS suggests that stable oxide based *n*-type and *p*-type semi-conducting materials with suitable BG energies and band edges are required for successful conversion

\* Corresponding author. Fax: +91 40 24442699.

E-mail address: [ibranganesh@arci.res.in](mailto:ibranganesh@arci.res.in) (I. Ganesh).

of solar energy into chemical energy via artificial PS process. The most widely studied semi-conducting material in aqueous based PEC cells is  $\text{TiO}_2$ , which is an *n*-type. Since, conversion of  $\text{TiO}_2$  from *n*-type to *p*-type has been found to be not so state forward, the focus has been diverted to ZnO, which is also an *n*-type material, but can be converted into *p*-type by doping of certain elements. In certain instances, larger quantum efficiency and higher photo catalytic activity than  $\text{TiO}_2$  have been noted for ZnO [11,12]. However, this material was found to be not much stable in aqueous medium under low pH conditions (<3) at which it dissolves into water due to its high basic nature.

ZnO possesses wide BG energy (3.37 eV), large exciton binding energy (60 meV), hexagonal wurtzite crystal structure apart from photo-conducting, piezoelectric and optical waveguide properties. Owing to these properties, ZnO was employed for short-wavelength optoelectronic devices, ultraviolet light emitting diodes, laser diodes, optical and magnetic memory devices, solar cells (transparent conducting electrodes), transducer, surface-acoustic-wave device, and chemical sensors [13–21]. In recent years, a considerable number of efforts have been made to create *p*-type ZnO by doping with group-V elements such as N, P, As and Sb [22–25], but their acceptor levels were theoretically identified to be deep with low solubility limits. Formation of *p*-type ZnO is limited by its self-compensating effects and by deep acceptor level and low solubility of acceptor dopants [19]. In view of these difficulties, there has been a continuous quest for identifying optimal choice of acceptor species [13–25]. Theoretical calculations predicted that group I elements substituting for ZnO possesses shallower acceptor levels than group V elements substituting for O suggesting that group I elements are considered to be better dopants than group V elements in terms of acceptor levels for ZnO. Especially, the acceptor level of Li substituting for Zn ( $\text{Li}_{\text{Zn}}$ ), is 0.09 eV [22], which is a shallowest value among the energy levels of acceptor dopants reported. However, optically detected magnetic resonance experiments showed that Li also introduces a deeper acceptor state [23,24]. Nevertheless, it was found that about 30% of the Zn sites have been occupied by Li in single crystal ZnO [25]. In an article, Water et al. [13] reported that doped Li atoms in ZnO films substitute for Zn atoms and act as acceptors that compensate the donors (excess Zn atoms). Recently, the so-called combustion synthesis route has been employed for successful preparation of LDZ powders, which were utilized as primary materials for the fabrication of *p*-type ZnO films by following radio frequency magnetron sputtering technique [12,26–28]. However, the crystallite size (CZ) of the powder formed in this combustion route was found to be on the higher side (>364 nm), and the higher temperatures generated during combustion were found to be responsible for forming such large size crystals with an average particle size of about 0.2–0.4  $\mu\text{m}$ . Since, the activity of any photocatalytic material is highly influenced by the size of the particles and crystals; it is highly desirable to develop a simple and in-expensive powder synthesis route to prepare the LDZ powders with much finer average crystallite and particle sizes [29].

In this investigation, different amounts of LDZ (Li=0–10%) powders were prepared by following a novel yet simple solution pyro-hydrolysis (combustion) route. The synthesized powders were thoroughly characterized by means of various spectroscopic and non-spectroscopic techniques and were finally evaluated by photo-catalytic degradation of MB reaction conducted under the irradiation of simulated as well as natural solar lights. For comparison purposes, Li and Al co-doped ZnO (LADZ) powders were also synthesized in order to study the kinetics of MB degradation reaction. The obtained results are analyzed, presented and discussed in this paper to understand the real effects of Li-doping on structure–property relationship of ZnO.

## 2. Experimental

### 2.1. Synthesis of Li-doped ZnO powders

In this study, different amounts of LDZ (0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0 and 10 wt.%) powders were prepared following a novel pyro-hydrolysis route using zinc nitrate, lithium chloride, oxalic acid, nitric acid and deionized water as starting materials. The required amounts of metal salts and oxalic acid (all are GR grade, Loba Chemie, India) to yield the desired composition of the LDZ materials were dissolved in de-ionized water to which 1 M  $\text{HNO}_3$  solution was added slowly to obtain pH of the solution of about 2 [29]. The molar ratio between lithium and oxalic acid (a chelating agent) was 1:2. The resultant clear solution was evaporated on a water bath till obtaining a white colored transitional-phase metal complex compound. This compound was calcined in air atmosphere at 450 °C for 6 h in a vitrified silica crucible. In the synthesis of Li (0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 6.0, 8.0 and 10 wt.%) and Al (0.5 wt.%) co-doped ZnO (i.e., 0.2LADZ to 10LADZ) powders, aluminum nitrate was employed as the source of Al. In the case of these latter materials synthesis, the remaining procedure was same as employed for LDZ powders.

### 2.2. Photocatalytic activity evaluation

The photocatalytic activity of LDZ and LADZ powders was evaluated by performing MB (Loba-Chemie, Mumbai, India) degradation reactions under the irradiation of simulated as well as natural solar lights. In a typical experiment, 200 mL of 0.01, 0.02 or 0.03 mM aqueous MB solution and 0.24 g fine powder catalyst were taken in a glass dish (150 mm diameter  $\times$  75 mm height, Borosil, India) and was exposed to simulated solar light (Osram 1000 W Xenon short arc display/optic lamp, XBO, Germany, installed in a light-condensing lamp housing, Model No.: SS-1K, Sciencetech Inc., Canada) for 0.5–4 h. The incident light was passed through an AM1.5D air-mass filter and the intensity of the incident light was measured to be about 44.42  $\text{mW}/\text{cm}^2$ . The reaction mixture solution was initially stirred for about 2 h in the dark to reach the adsorption equilibrium. During light irradiation, the reaction mixture was continuously stirred on a magnetic stirrer (Model: 5MLH, Remi, Mumbai, India) and aliquots of the reaction mixture were collected at regular time intervals. The leftover MB concentrations were estimated with the help of UV–Vis spectrophotometer (Lambda 650, Perkin Elmer, Massachusetts, USA). The maximum absorption peak ( $\lambda_{\text{max}}$ ) of MB at about 666 nm was considered to estimate the remaining concentration of MB in aqueous solutions.

## 3. Characterization

A Gemini Micromeritics analyzer (Micromeritics, Norcross, USA) was used for BET SA measurements. The BET SA was measured by nitrogen physisorption at liquid nitrogen temperature (–196 °C) by considering 0.162  $\text{nm}^2$  as the area of cross section of  $\text{N}_2$  molecule. Prior to measurements, the samples were evacuated (up to  $1 \times 10^{-3}$  Torr) at 180 °C for 2 h. Phase analysis, CZ and lattice parameter values of the powders were determined by X-ray diffraction (Bruker's D8 advance system, Bruker's AXS, GmbH, Germany) using  $\text{Cu K}\alpha$  radiation source. To obtain quantitative information of phases, the most intense peak of the individual phase was taken into consideration. The peak heights of all the phases were summed up and the percentage concentration of a particular phase was estimated from the ratio of the strongest peak of that phase to the sum of various phases present in a given system [30,31]. The CZ of the powders were estimated with the help of Debye–Scherrer equation ( $(L)_{hkl} = K\lambda/\beta_{hkl} \cos \theta$ ; where  $K$  is a constant taken as 1, and

Download English Version:

<https://daneshyari.com/en/article/5361495>

Download Persian Version:

<https://daneshyari.com/article/5361495>

[Daneshyari.com](https://daneshyari.com)