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Importance of precursor type in fabricating ZnO thin films for photocatalytic applications

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ABSTRACT

Here, the importance of choosing an appropriate precursor with right molarity for the fabrication of zinc oxide (ZnO) films by spray pyrolysis for the photocatalytic application is reported. Films were grown on glass substrates by using three different zinc precursors such as zinc acetate, zinc chloride, and zinc acetylacetonate. The structural, morphological, and optical characterizations were performed on the ZnO films. A preferential orientation along (002) plane, crystallite size distribution in the range 21–59 nm, and the nanostructures such as nanothorns, hexagonal nanorods, hexagonal layers and elongated grains, were acquired from the characterization studies. Further, the photocatalytic activity was tested using indigo carmine dye, obtaining 100% of dye degradation using the ZnO thin films deposited with zinc acetate, whereas films from zinc chloride and zinc acetylacetonate precursors showed 20% and 10% of degradation respectively.

1. Introduction

Environment pollution is a major threat to the living things. The land, water, and air are being contaminated by several mediums like waste water and gas emissions [1–3]. Contaminated water resources affect the aquatic ecosystems, in turn, disrupts the food chain. The various water contaminants include dyes, pharmaceuticals, petrochemicals, plastics, fertilizers and oil spills [4–8]. Indigo carmine (*IC*) is a major dye used by textile, cosmetics and food industries (at low concentration). When it accumulates in higher concentrations, it may become toxic and lead to intestinal and respiratory diseases [9–12]. Therefore, it is necessary to treat the *IC* dye before releasing it to the environment. Scientists are treating water that contains indigo carmine by electrochemical, adsorption using de-oiled soya/charcoal/chitin and chitosan, and photocatalysis [13–17]. Among these practices, photocatalysis is cost effective, environmentally friendly and able to degrade complex compounds [18].

By keeping this as the main issue, we focused on the decomposition of dye containing water by photocatalysis. The various semiconductor materials used as photocatalyst are ZnO, TiO_2, and SnO_2. However, zinc oxide (ZnO) is a favorite semiconductor among researchers for the possibility of utilizing it in different applications like gas sensors, light emitting diodes, lasers, thin film transistors, solar cells and photocatalytic degradation [19–24]. Besides, ZnO is a unique material that can be synthesized in several forms of nanostructures such as rods, wires, belts, flowers, hexagons, towers, spheres, tubes and pyramids with extraordinary physical properties by using appropriate physical or chemical techniques [25–33]. Thus, the special characteristics of ZnO motivated us to work on it. Further, though the thin film form of ZnO can be obtained by several fabrication techniques (sputtering, thermal evaporation, sol-gel, spray pyrolysis, laser ablation, etc.), we picked spray pyrolysis since it offers numerous advantages: simple exploratory setup, reproducibility, cost and time effective [34–38].

Two of the most used Zn precursors to obtain ZnO films by spray pyrolysis are zinc acetate and zinc chloride, where the later is preferred to grow ZnO nano or micro rods [39–42]. However, none of them justify the use of this precursor. A previous work showed that the use of zinc acetate leads to the formation of random non-uniform morphology (or nanoflakes), while zinc chloride produces vertically oriented nanorods [43].

We found that even though the final product of different Zn precursors is ZnO, the properties of the sprayed films were different. Thus, the precursors have a strong impact on the final properties. The surface morphology is particularly important for photocatalysis applications, because chemical reactions take place on the catalyst's surface. So, the greater the exposed surface of the semiconductor, the greater the efficiency of the material.

In this work, we report the importance of the type of zinc precursor

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Table 1
Solution conditions for the ZnO thin film fabrication.

Sample name	Type of precursor	Molarity (M)	Solvent (ml)
ZAA-1	Zinc acetylacetonate	0.1	Methanol (147 ml)
ZAA-2	$C_{10}H_{14}O_4Zn\ H_2O$	0.2	+ acetic acid (3 ml)
ZAA-3		0.3	
ZAC−1	Zinc acetate Zn	0.1	deionized water
ZAC−2	$(CH_3COO)_2 2H_2O$	0.2	(150 ml)
ZAC−3		0.3	
ZCL−1	Zinc chloride $ZnCl_2$	0.1	deionized water
ZCL−2		0.2	(150 ml)
ZCL−3		0.3	

and the molar level of the solution for the deposition of ZnO thin films by spray pyrolysis, on their structural, morphological, optical and photocatalytic characteristics. We discuss how the decomposition mechanisms of each precursor affects the film's growth.

2. Experimental

The deposition of ZnO thin films was performed on glass substrates (Corning glass) using spray pyrolysis. Initially, glass substrates were ultrasonically cleaned using the following solutions one by one: trichloroethylene (Meyer, ACS grade), acetone (Meyer, ACS grade) and methanol (Sigma-Aldrich, ACS reagent) and dried with nitrogen gas (Praxair, high pure).

The growth of ZnO films was carried by with three different precursors: Zinc acetylacetonate (Alfa aesar), zinc acetate dihydrate (Sigma-Aldrich, ≥ 98%), zinc chloride (Alfa aesar, 98 + %). The type of the precursor and its molarity were used as variables. The sample name and the precursor solution conditions are given in Table 1. The solutions were continuously stirred at room temperature until transparency was achieved and then spray depositions were executed for 12 min by maintaining a substrate temperature of 475 °C using a tin bath. The flow of the solution and carrier gas were kept at 20 and 80 psig, respectively.

The films were characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with a thin film modulus (Cu Kα radiation λ = 0.15418 nm). Scanning Electron Microscopy (SEM) images were taken to observe the morphology with at JEOL 7600 F instrument. The optical properties of the films were studied using a Shimadzu 1800 UV–vis spectrophotometer. Thermogravimetric analysis (TGA) of the precursors were performed using a SDT Q600 V8.3 with a ramp temperature of 10 °C/min. The photocatalytic activity of the films was evaluated by the degradation of an *IC* ($C_{16}H_8N_2Na_2O_8S_2$) dye aqueous solution with a concentration of 5 mgL^{-1}. Each film was immersed in 10 ml of the dye solution and kept in the dark for 30 min under constant stirring to achieve the equilibrium. Then, an UV lamp (26 Wm^{-2}, with emission centered at 380 nm) was turned on to initiate the photocatalytic reactions. The absorbance of an aliquot of the solution was measured each 15 min during the first hour and then each 60 min. The generation of $^{\bullet}OH$ radicals by the ZnO films was measured by the transformation of terephthalic acid (TA) into 2-hydroxyterephtalic acid (HTA) which is a highly luminescent species. For this, a TA solution 0.5 mM was prepared dissolving in a 2 mM water/NaOH solution. The films were immersed in this TA solution for 30 min in the dark and then exposed to UV light at the same photocatalytic conditions. Photoluminescence spectra of the films were performed with a He-Cd laser of 5 mW with emission at 325 nm. Fluorescence measurements of the solution were performed using a Varian Cary Eclipse fluorescence spectrophotometer with excitation at λ = 350 nm.

3. Results

3.1. TGA characterization of precursors

Thermogravimetric analysis (TGA) was performed to know the thermal decomposition behavior of zinc precursors toward formation of ZnO. The TG analysis curves are shown in Fig. 1. All the zinc precursors show a weight loss twice.

The decomposition of zinc acetylacetonate appears to be quite faster than zinc acetate and zinc chloride. From Fig. 1(a) we can observe that the primary loss occurs between 58 and 98 °C (7.92%) in turn specifies

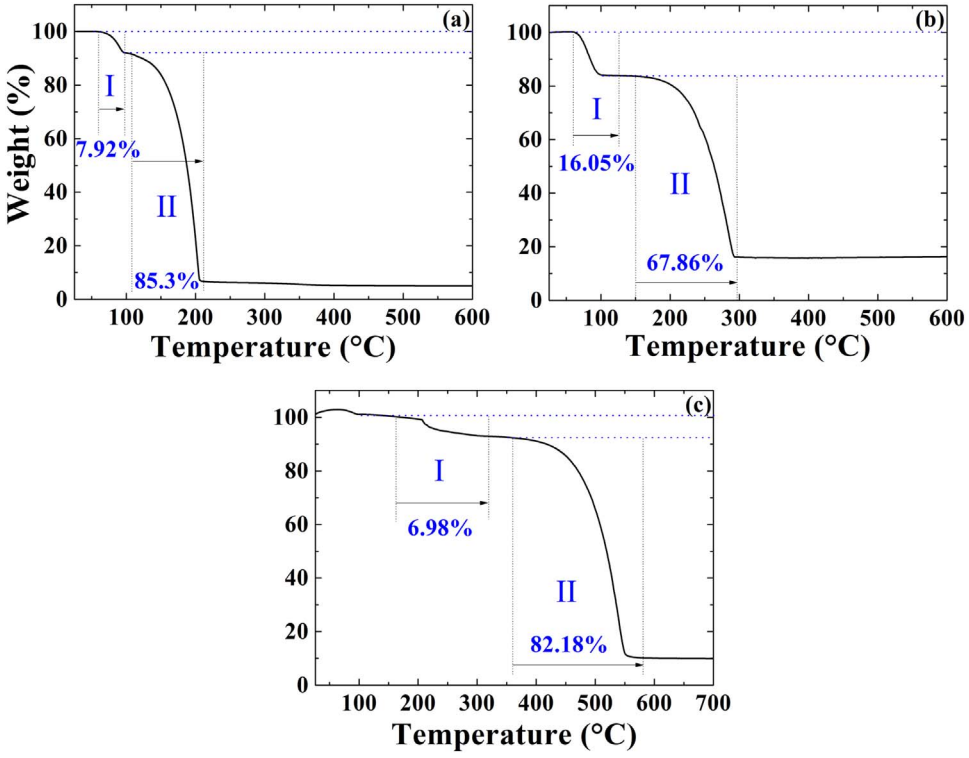

Fig. 1. Thermogravimetric analysis of Zn precursors (a) zinc acetylacetonate, (b) zinc acetate, and (c) zinc chloride.