Materials Science in Semiconductor Processing 27 (2014) 197–206

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Controlled synthesis of zinc oxide nanoflowers by succinate-assisted hydrothermal route and their morphology-dependent photocatalytic performance

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ARTICLE INFO

Available online 11 July 2014

Keywords:
Zinc oxide
Hydrothermal
Succinate
Photocatalytic activity

ABSTRACT

Hierarchical flower-like zinc oxide (ZnO) nanostructures were successfully synthesized by using facile succinate and PEG assisted hydrothermal process. The as-prepared ZnO samples were characterized by X-ray diffraction analysis (XRD), field emission scanning electron microscopy (FE-SEM), photoluminescence (PL) spectroscopy and UV–visible spectroscopy. The effect of dilution of precursor concentration on the formation of distinctive morphology was systematically studied. The flower-like morphology of ZnO can be effectively tuned by simply varying the precursor concentrations. A plausible growth mechanism for the formation of different hierarchical nanostructures is also proposed. Further, photocatalytic activities of the as-prepared samples were studied by photodegradation of Rhodamine B (RhB).

1. Introduction

Zinc oxide (ZnO) is an important functional oxide semiconductor with a wide band gap (3.37 eV) and a large exciton binding energy (60 meV). It is highly preferred multitasking metal oxide having a vast list of attractive properties [1]. Due to its unique optical and electrical properties [2,3], it is regarded as a potential material in optoelectronic applications operating in the visible and near ultraviolet spectral regions. The areas in which it is used include, UV light-emitting diodes [1,4,5], nanolasers [6], gas sensors [7], highly-efficient green phosphors [8], photocatalysts and photovoltaic devices [9,10], field-effect transistors [11], chemical sensor [12], transparent conductors and varistors [13,14]. Moreover, it also possesses excellent thermal and chemical stability, a large piezoelectric coefficient and an easily modifiable electrical conductivity.

The remarkable interest in ZnO is due to its unique ability of structure dependent properties [15]. Properties like electrical and thermal transport, in addition to optical and mechanical properties could be varied with respect to particle size, shape, morphology, orientation and aspect ratio. Hence, morphology and dimensionality-controlled growth of zinc oxide has become a challenging topic to design novel functional devices. Accordingly, ZnO with different morphologies such as nanowires, nanorod arrays, nanocombs, nanobelts, nanorings, nanocables have been synthesized by various processes such as thermal evaporation deposition, template-mediated growth, metal–organic vapor phase epitaxy and carbothermic method [16–21]. However, most of these synthesis techniques require high temperature, vacuum, or complicated controlling processes.

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http://dx.doi.org/10.1016/j.mssp.2014.06.040
1369-8001/

Therefore, it is of great importance and necessity to develop a technique operating at mild reaction conditions. Hydrothermal method has been proven to be versatile approach for preparation of ZnO due the convenience and simplicity in the operation.

Recent studies have shown that the use of organic additives in the aqueous solution can effectively tune the shape of product by selective adsorption and subsequent controlled removal of organic additives at interfaces [22,23]. In this perspective, Yin et al. employed water-soluble biopolymer sodium carboxymethyl cellulose (CMC)-assisted hydrothermal method for synthesis of hierarchical ZnO nanorod-assembled hollow superstructures for catalysis and photoluminescence applications [24]. Wu et al. have developed a facile amino acid histidine assisted hydrothermal route to synthesize ZnO hierarchical architectures, including prism, flower and hollow microspheres, and they exhibit different photocatalytic activities [25]. Moreover, in this context, several different soft templates/capping agents such as ethylene diamine [26], water-soluble diblock copolymers [27] and surfactants [28] have been successfully used to tune the size and shape of ZnO nanostructures. In most of these methods the externally added surfactants or capping agents were adsorbed preferentially on some crystal planes of the growing particles which alter the growth kinetics and relative stability of the crystal faces and hence either promote or inhibit crystal growth in some particular crystal planes, resulting in the formation of anisotropic ZnO nanostructures. These studies showed high control on the morphology of ZnO; however, most organic additives used in these methods were expensive long chain molecules. A non-ionic surfactant, polyethylene glycol (PEG) has been used previously [29,30]. Uniform and ordered chain structure of PEG is easily adsorbed at the surface of metal oxide colloids, and from the view of kinetics of colloid growth, if the colloid adsorbs the polymer on some area of its surface, the growth rate of colloid in certain direction would be confined. Therefore, the addition of PEG in the metal oxide colloids will modify the growth kinetics of colloid, leading to anisotropic growth of crystals [31–33].

In our previous research, we have obtained flowerlike, ellipsoidal and cabbage-like hierarchical ZnO architectures by adjusting the reaction conditions using sodium citrate and PEG [34]. In the present study, we report a facile synthesis of ZnO with different morphologies via sodium succinate and PEG assisted hydrothermal process. Herein, succinate was used as an assembling and structure directing agent for controlled synthesis of ZnO architectures along with PEG in a one-step hydrothermal process. Succinate plays an important role in the formation and self assembly of different flower-like ZnO architectures. The morphology has significant influence on the photocatalytic performance.

2. Experimental

2.1. Materials

Zinc acetate dihydrate (Zn $(CH_3COO)_2 \cdot 2H_2O$) and sodium hydroxide (NaOH) were purchased from Merck (India). Sodium succinate hexahydrate ($C_4H_4O_4Na_2 \cdot 6H_2O$) and PEG-400 were purchased from SRL (India). Double distilled water was used for all the experiments.

2.2. Preparation of hierarchical ZnO nanostructures

In a typical preparation method, 40 mL of 0.25 M aqueous $Zn(CH_3COO)_2 \cdot 2H_2O$ and 40 mL of 0.72 M aqueous sodium succinate solutions were added to 30 mL PEG-400 under magnetic stirring. Then, 20 mL of 2.5 M aqueous NaOH solution was added drop-wise to the above solution. The resultant mixture was magnetically stirred for 30 min at room temperature and then transferred into a Teflon-lined stainless-steel autoclave (250 mL capacity). The autoclave was sealed and heated upto 120 °C for 12 h and subsequently cooled to room temperature naturally. The obtained precipitate was centrifuged at 5000 rpm for 15 min, washed with distilled water several times and finally dried at 60 °C in air for 12 h.

In order to investigate the influence of precursor concentration on the morphology of ZnO nanostructures, a series of experiments were carried out by varying the concentration of the reactants. More specifically, for studying the effect of dilution of precursor concentration on ZnO morphology, the molarity of zinc acetate, sodium succinate and NaOH was decreased systematically by keeping the quantity of PEG and water same. The various preparation conditions and the resultant morphologies are summarized in Table 1.

2.3. Characterization

The surface morphology of prepared samples was investigated by Field Emission Scanning Electron Microscope (FE-SEM) using JEOL-JSM Model 6700F field-emission scanning electron microscope. The phase identification of the ZnO powders was obtained by X-ray diffraction (XRD) recorded using a Rigaku Miniflex X-ray diffractometer with CuKα radiation at $\lambda = 1.5406$ Å. The room-temperature

Table 1
Reaction parameters for the preparation of different ZnO nanostructures and their morphology.

Sr. no.	Sample	$[Zn(OAc)_2]$ 40 mL (M)	[Sodium succinate] (mol)	[NaOH] 40 mL (M)	[PEG] (mL)	Morphology obtained
01	ZSP-1	0.17	0.018	0.93	30	Flower
02	ZS	0.17	0.018	0.93	–	Sheet-like
03	ZP	0.17	–	0.93	30	Undefined
04	ZSP-2	0.17	0.018	1.4	30	Vesicular
05	ZSP-3	0.17	0.018	0.46	30	Undefined
06	ZSP-4	0.08	0.009	0.46	30	Flower
07	ZSP-5	0.04	0.004	0.23	30	Flower