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Effect of preparation parameters on the morphologically induced photocatalytic activities of hierarchical zinc oxide nanostructures

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Abstract

Hierarchical zinc oxide nanostructures were successfully synthesized by facile hydrothermal and sonochemical routes using citrate and PEG as structure directing agents. The effect of precursor concentration and preparation methods on the formation of typical morphology was systematically studied under hydrothermal and sonochemical conditions. Different concentrations of zinc acetate, sodium citrate and NaOH under hydrothermal and sonochemical methods generate different hierarchical structures such as flower-like, cabbage-like, and ellipsoidal ball-like morphologies, depending on the preparation conditions. The as-prepared ZnO samples were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission election microscopy (TEM), photoluminescence (PL) spectroscopy, Fourier transform infrared spectroscopy (FTIR) and particle size distribution (PSD) analysis. Catalytic activities of the as-prepared samples were studied by photodegradation of Methylene blue.

Keywords: Zinc oxide; Hydrothermal; Sonochemical; Methylene blue; Photocatalytic activity

1. Introduction

Zinc oxide (ZnO) is an important functional oxide semiconductor with a direct wide band gap (3.37 eV), deep violet/borderline ultraviolet (UV)) and a large exciton binding energy (60 meV). It is a highly preferred multi-tasking 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], photo-catalysts and photovoltaic devices [9,10], field-effect transistors [11], chemical sensors [12], transparent conductors and varistors [13,14]. Also, it possesses excellent thermal and chemical stability, a large piezoelectric coefficient, and an easily modifiable electrical conductivity.

The tremendous interest in ZnO is due to its unique ability of possessing 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 lately to design novel functional devices. Accordingly, many types of ZnO nanostructures, such as nanowires, nanorod arrays, nanocombs, nanobelts, nanorings, nanocables, and other nanostructures have been synthesized by various processes, such as thermal evaporation deposition, template-mediated growth, metal-organic vapor phase epitaxy and the carbothermic method [16–21]. However, most of the synthesis techniques require high temperature, vacuum, or complicated controlling processes. Therefore, it is of great importance and necessity to develop a technique operating at mild reaction conditions. Hydrothermal and sonochemical methods have been proven to be

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a versatile approach for preparation of ZnO due the convenience and simplicity in their operation.

More recently, ZnO architectures with different morphologies synthesized via template-assisted hydrothermal or sonochemical methods have been greatly highlighted [22,23]. 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-like and flower-like structures and hollow microspheres, and they exhibit different photocatalytic activities [25]. Mishra et al. have reported synthesis and growth of flower-like ZnO nanostructures using starch assisted sonochemical method [26]. Moreover, in this context, several different soft templates/capping agents such as ethylene diamine [27], water-soluble diblock copolymers [28] and surfactants [29] have been successfully used to tune the size and shape of ZnO nanostructures. Vaishampayan et al. have reported a low temperature (4 °C) synthesis of crystalline flower-like ZnO by using an aminolytic reaction at the air-liquid interface in an aqueous media at an alkaline pH. They have further reported that nanobelts overlap systematically to form petals of the flower-like structure. The photodegradation of methylene blue over the flower-like ZnO catalyst was observed which was attributed to sub-bands formed due to surface defects facilitating separation of charge carriers which increases their lifetime [30]. In most of these methods of preparing hierarchical ZnO nanostructures, the externally added surfactants or capping agents were adsorbed preferentially on some crystal planes of the growing particles that ultimately 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 morphology controllability of ZnO; however, most organic additives used in these methods were expensive long chain molecules. Polyethylene glycol (PEG), an inexpensive non-ionic surfactant has been used to assist the formation of metal oxides in previous researches [31,32]. PEG with uniform and ordered chain structure is easily adsorbed at the surface of metal oxide colloid. When this occurs, the surface activity of colloid would greatly decrease. 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 some certain direction would be confined. Therefore, the addition of PEG in the metal oxide colloids will modify the growth kinetics of colloid, which finally leads to anisotropic growth of crystals [33–35].

In this article, we report a facile synthesis of ZnO with different morphologies via hydrothermal and sonochemical processes with PEG, trisodium citrate and zinc acetate as the Zn^{2+} source. Citric acid is a weak organic acid and often used as chelating agent. Herein, PEG was introduced as an assembling and structure directing agent along with sodium citrate for controlled synthesis of ZnO architectures assisted by hydrothermal and sonochemical processes. We have studied the effect of precursor concentration and the effect of preparation methods on the morphology of the resulting ZnO nanostructures. Different experimental conditions plays a vital role during the formation of hierarchical morphologies of ZnO such as flower-like, cabbage-like, ellipsoidal ball-like and flake-like structures. The as-synthesized ZnO samples were investigated in terms of their morphology, crystallinity, growth mechanism and photocatalytic efficiency towards degradation of methylene blue dye.

2. Experimental

2.1. Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2\,H_2O$) and sodium hydroxide (NaOH) were purchased from Merck (India). Trisodium citrate dihydrate and PEG-400 was purchased from SRL (India). Double distilled water was used to prepare solutions throughout all experiments.

2.2. Preparation of hierarchical ZnO nanostructures

In a typical preparation method, 50 mL of 0.1 M aqueous $Zn(CH_3COO)_2 \cdot 2\,H_2O$ and 50 mL of 0.34 M aqueous Sodium citrate solutions were added to 30 mL PEG-400 under magnetic stirring. Then, 20 mL of 1.8 mM aqueous NaOH solution was added drop-wise to the above emulsion. The resulting mixture was magnetically stirred for 30 min at room temperature and then treated under hydrothermal and sonochemical conditions. For hydrothermal treatment, the reaction mixture was transferred into a Teflon-lined stainless-steel autoclave with a capacity of 200 mL, sealed and maintained at 120 °C for 12 h. The autoclave 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 8 h.

Similarly, for sonochemical treatment, the magnetically stirred reaction mixture was irradiated with ultrasound probe (Sonics Vibra cell, USA) for 2 h (with 5 s pulse ON and 1 s pulse OFF at amplitude of 30%). The obtained precipitate was then centrifuged, washed and dried as earlier.

In order to investigate the influence of precursor concentration and the preparation method on the morphology of ZnO nanostructures, a series of experiments were carried out by varying the concentration of the reactants by keeping the quantity of PEG constant. More specifically, the molarity of zinc salt, trisodium citrate 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.