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Single-pot ZnO nanostructure synthesis by chemical bath deposition and their applications

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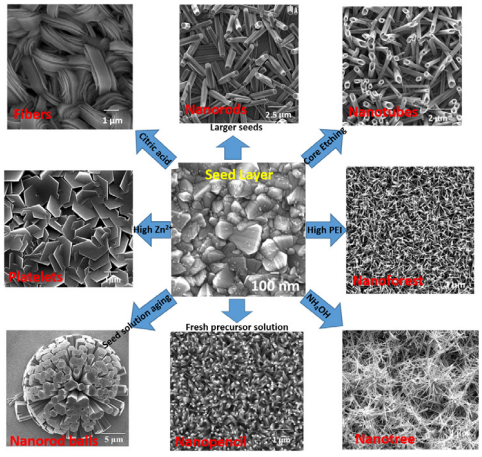
HIGHLIGHTS

- Simple low cost chemical bath deposition was used to design ZnO architectures.
- Variety of ZnO nanostructures were synthesized by chemical bath deposition.
- The effect of additives on the ZnO nanostructure growth was analyzed.

GRAPHICAL ABSTRACT



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ABSTRACT

ZnO is commonly synthesized using many different techniques. Among them, the chemical bath deposition (CBD) technique is appealing as it is low cost and environmentally friendly, owing partly to the low temperature conditions used. An exploration of the variety of ZnO nanostructures that can be synthesized using this technique is presented in this study. ZnO fibers, nanorods, cauliflowers, nanorod balls, nanoforest, nanopencils, ellipsoids and nanotubes are synthesized using CBD by using different additives and conditions that alter the growth of the ZnO nanostructures. The application of these nanostructures in a wide variety of devices is analyzed.

1. Introduction

Rational design and control over morphology and functional properties of inorganic nanostructures is long standing goal in nanoscience and engineering [1]. The physical and chemical

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properties of a material can be changed by designing architectures which can create interfacial effects. Materials with desired properties can be designed using morphology control, leading to potential applications. Therefore there is a need for morphology and property control of materials. Over the last twenty years significant effort to scale the semiconductor and metal oxide nanostructures with the effects at nanoscale has been explored vigorously to improve efficiency of wide variety of devices like solar cells, batteries and fuel cells [2,3].

ZnO is one of the most favorable materials widely used in electronics (transistors) [4,5], sensors [6–8], catalysts [9–11], light emitting devices [12–15], piezoelectric devices [16–20], solar cells [21–23], sunscreens [24,25], lasers diodes [26,27], hydrophobic surfaces [28,29], magnetic data storage [30,31], water disinfection [32], antiviral agent [33,34], anti-cancer agent [35], hazardous waste remediation [36], flexible plastic devices [37], degradation of pollutants [38], energy conversion and storage devices [22,39–41]. ZnO is a wide band gap semiconductor (3.3 eV) with a high exciton binding energy of 60 meV [42] at room temperature.

The properties of the ZnO nanostructures can be altered by tailoring the size, shape, facets, surface area and concentration of the oxygen vacancies. Many useful properties of ZnO nanorods are dependent on the rod diameter, length and number density. The surface band bending of the ZnO nanorods is dependent on the diameter of the ZnO nanorods [43,44]. The performance of the photoelectrochemical cells for water splitting and photovoltaics depends on the rod morphology [45,46]. In hybrid solar cells, a low density of ZnO nanorods on the photoanode is needed to provide void space for P3HT:PCBM infiltration [47]. For applications in surface acoustic wave devices growth along the *a*-axis is required [48]. In the fabrication of composite nanostructures such as nanoparticle-coated ZnO nanorods, tuning the density of the nanorods is required for balancing total surface area against effective coverage of the nanoparticles throughout the length of the nanorod [22,49]. The optoelectronic and gas sensing properties of the ZnO are dependent on the shape of nanostructures [50]. The photocatalytic activity of the ZnO nanorods is enhanced by increasing surface defects and aspect ratio [51,52]. In organic light emitting diodes threefold increase in the efficiency was observed by using triangular shaped ZnO nanoparticles [53]. Blue and white light emission was observed from a ZnO nanoforest under high voltage [54].

ZnO nanorods can be grown in situ from a variety of substrates through procedures such as chemical bath deposition [55,56], electrodeposition [57–59], chemical vapor deposition [60,61], thermal deposition [62], laser ablation in liquid [63,64], vapor–liquid–solid growth [65], thermal annealing using catalyst [66], flame transport synthesis [33], plasma synthesis [67], combustion synthesis [68], microwave synthesis [69] and pulse laser deposition [70]. Among these, chemical bath deposition (CBD) has the advantage of being low temperature, low cost, suitable for large area processing for industrial applications, and environmentally benign. CBD is a two-step process, beginning with the deposition of a "seed layer" of ZnO nanocrystals on the substrate, from which nanorods are subsequently grown in the "chemical bath", an aqueous solution of a zinc precursor with additives to modify the growth.

In this study we have grown a variety of ZnO nanostructures, and their suitability to different applications based on the size, shape, surface area is discussed. This article provides an overview of the synthesis of the different ZnO structures and their suitable application.

2. Experimental

2.1. Reagents and materials

Zinc nitrate hexahydrate, hexamethylenetetramine (HMTA), polyethyleneimine, citric acid, cobalt nitrate hexahydrate, ammonium hydroxide and ethanol were purchased from Sigma-Aldrich (USA) and were ACS grade. SnO_2: F glass (FTO, transmission $>$ 80% in the visible spectrum; sheet resistance 8 Ω/square) was purchased from Hartford Tec Glass (USA).

2.2. ZnO seed crystal synthesis

The formation of ZnO seeds began with the dissolution of 5 mM zinc acetate dihydrate in ethanol by stirring for 3 h at room temperature [71]. Deionized water is added to the seed solution for increasing the size of the ZnO seeds [72].

2.3. Pre-cleaning of FTO substrates

The FTO substrates were cleaned in RBS 35 detergent with 2% (v/v) solution using sonication for 5 min. RBS sonicated FTO substrates were rinsed in deionized water and sonicated in ethanol and acetone for 5 min each. After sonication the samples are dried in the flow of nitrogen.

2.4. Seed layer deposition

The seed crystals synthesized as described in Section 2.2 were deposited on the precleaned FTO substrate using drop coating technique. Drops of seed crystal solution (10 μL) were deposited onto the pre cleaned FTO substrates using a calibrated micropipette. The drops were allowed to dry for 1 min under room temperature in laboratory conditions. After drying of the seed layer the FTO substrate was rinsed in ethanol and dried in the flow of nitrogen gas. Two seed layers were deposited on all the substrates. After the deposition FTO glass is sintered at 350 °C for 30 min on Ti hot plate and allowed to cool down to room temperature.

2.5. ZnO nanofiber synthesis

Nanofibers were grown by using chemical bath deposition. The precleaned FTO substrates were placed in an aqueous solution of 50 mM zinc nitrate hexahydrate, and 12 mM citric acid in a 100-ml glass bottle at 90 °C for 24 h.

2.6. ZnO nanotubes synthesis

Nanotubes were grown by using chemical bath deposition. The seeded substrate was covered with scotch tape to decrease the area of deposition by 50%. The seeded FTO substrates were placed in an aqueous solution of 50 mM zinc nitrate hexahydrate, and 6 mM polyethyleneimine in a 100-ml glass bottle at 90 °C for 24 h. The glass bottle was left for one hour for cooling before the sample was removed and cleaned in ethanol and dried in the stream of nitrogen.

2.7. ZnO nanoflowers synthesis

Nanoflowers were grown by using chemical bath deposition. Precleaned FTO substrates are coated with 1 day aged seed layer solution. The FTO substrates were placed in an aqueous solution of 50 mM zinc nitrate hexahydrate, and 0.35M ammonium hydroxide in a 100-ml glass bottle at 90 °C for 24 h.

2.8. ZnO nanorods synthesis

Nanorods were grown from the ZnO seeds by chemical bath deposition. The seeded FTO substrates were placed in an aqueous solution of 45 mM zinc nitrate hexahydrate, 50 mM hexamethylenetetramine and 6 mM polyethyleneimine in a 100-ml glass bottle at 90 °C for 24 h.