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pH-dependent growth of zinc oxide nanorods

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ABSTRACT

Here we study the effect of pH variation on the dimension and morphology of zinc oxide (ZnO) nanorods grown through hydrothermal process at temperatures less than 100 °C. ZnO nanorods were grown on pre-seeded glass substrates using zinc nitrate hexahydrate as the source of Zn ions and hexamethylenetetramine as the source of hydroxyl ions. The pH of the reaction bath was found to change gradually from 6.4 to 7.3 in 5 h during the growth process. The growth of the ZnO nanorods was observed to be faster, both laterally and longitudinally, when the growth solution was in basic conditions. However, flower petal like ZnO nanostructures were obtained when the growth process was initiated in basic condition (pH 8–12), indicating that initial acidic conditions were required to obtain nanorods with well-defined hexagonal facets. ZnO is known to erode in acidic condition and the final dimension of the nanorods is determined by a competition between crystal growth and etching. ZnO nanorods of different dimensions, both laterally (diameters ranging from 220 nm to 1 μm) and longitudinally (lengths ranging from 1 to 5.6 μm) were successfully synthesized using the same concentration of zinc nitrate and hexamine in the reaction bath and the same growth duration of 5 h simply through appropriate control of the pH of the reactant solution between 6 and 7.3.

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1. Introduction

Numerous reports on the growth and characterization of one-dimensional nanowires of elemental and compound semiconductors such as silicon (Si) [1], germanium (Ge) [2], indium phosphide (InP) [3], gallium arsenide (GaAs) [4] and zinc oxide (ZnO) [5–7] are available in the literature. Nanostructures of ZnO such as nanowires and nanorods [8], nanocombs [9], nanorings [10], nanoloops and nanohelices [11], nanobows [12], nanobelts [13] and nanocages [14] have been reported. These structures have been synthesized under controlled growth conditions [15,16]. Zinc Oxide nanostructures can be synthesized either through gas-phase synthesis or through solution-phase synthesis. Gas-phase synthesis is carried out in a gaseous environment in closed chambers at high temperatures (500–1500 °C). Some commonly used gas-phase methods are vapor-phase transport, which includes vapor solid (VS) [17] and vapor liquid solid (VLS) [18] growth, physical vapor deposition (PVD) [19], chemical vapor deposition (CVD) [20], metalorganic chemical vapor deposition (MOCVD) [21] and thermal oxidation of pure Zn [22] followed by condensation. In the solution-phase synthesis, the growth process is carried out in a liquid. Normally aqueous solutions are used and the process is then referred to as hydrothermal growth process. Some of the solution-phase synthesis processes reported are the zinc acetate hydrate (ZAH) derived nano-colloidal sol–gel route [23], ZAH in alcoholic solutions with sodium hydroxide (NaOH) [24], tetra methyl ammonium hydroxide (TMAH) [25] or lithium hydroxide (LiOH) [26], template-assisted growth [27] or spray pyrolysis [28,29] and electrophoresis [30].

One of the most energy-efficient strategies for synthesizing ZnO nanorods is the hydrothermal process that does not require high temperature and complex vacuum environment. The hydrothermal process induces an epitaxial, anisotropic crystal growth in a solution [26,31] (normally aqueous solution). The hydrothermal process is usually substrate independent [32] and the morphology of the nanorods can be easily controlled through slight changes in the reaction conditions [33]. There are reports on the successful growth of ZnO nanowires on flat substrates like Si [15], glass [33,34], TCO [35], polyethylene fibers [8], carbon cloth [36] and Al foil [37].

In one of the reported processes [31], an equimolar solution of zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] and hexamethylene tetramine [$C_6H_{12}N_4$], popularly known as hexamine is utilized to epitaxially grow ZnO rods on substrates by fixing pre-synthesized ZnO nanoparticles on the substrate as seeds. The ZnO crystal is hexagonal wurtzite and exhibits partial polar characteristics [16]

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with lattice parameters a=0.3296 and c=0.52065 nm. The anisotropy in the crystal structure of ZnO assists the growth of the nanorods. The most common polar surface is the basal plane (0 0 1). One end of the basal polar plane terminates in partially positive Zn lattice points and the other end terminates in partially negative oxygen lattice points. The anisotropic growth of the nanorods takes place along the c-axis in the [0 0 0 2] direction.

It was reported by Sugunan et al. [33] that hexamine, a non-ionic tertiary amine derivative and a non-polar chelating agent, would preferentially attach to the non-polar facets of the ZnO crystal as it builds up, thereby exposing only the (0 0 1) plane for epitaxial growth [33]. Thus a preferential growth along the [0 0 0 2] direction is made possible. Seeding of the substrate with ZnO nanoparticles was found to lower the thermodynamic barrier by providing nucleation sites, further improving the aspect ratio of the synthesized nanorods. Seeding of the substrate is thus an important parameter for the uniform growth of ZnO nanorods through hydrothermal process. Seeding can be done by dip coating [8] and spin coating [32] using a colloidal solution of ZnO nanoparticles or sputtering a thin layer of ZnO on the substrate [38].

A lot of factors come into play during the growth of the ZnO nanorods like concentration of the chemical bath, temperature, duration of growth, pH, etc., which directly affect the final morphology of the rods grown. There are reports available in the literature about the synthesis of ZnO nanorods and other morphologies through a variation in pH of the reaction bath [39–41]. However, this study is aimed at optimizing the pH conditions to obtain ZnO nanorods of different dimensions starting with the same concentration of the reactant mixture. It was possible to grow ZnO nanorods of different dimensions (both lateral and longitudinal), with the same concentration of $Zn(NO_3)_2$ and hexamine in the chemical bath and the same growth duration, simply by varying the pH of the growth solution between 6 and 7.3.

2. Experimental

The ZnO nanorods were synthesized modifying a method initially suggested by Vayssieres et al. [31] and proposed by Sugunan et al. [33]. The method consisted of seeding substrates with ZnO nanocrystallites followed by a chemical bath growth of the nanorods as described in Section 2.3.

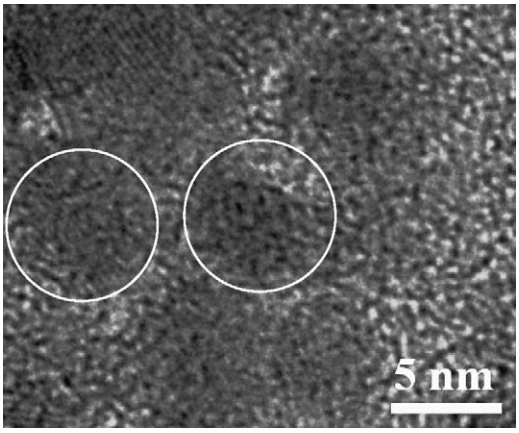

Fig. 1. HRTEM image showing the ZnO nanoparticles synthesized in isopropanol. Measurements of lattice spacings done on images of different particles indicated the presence of the (100), (002), (101) and (102) planes of the wurtzite structure.

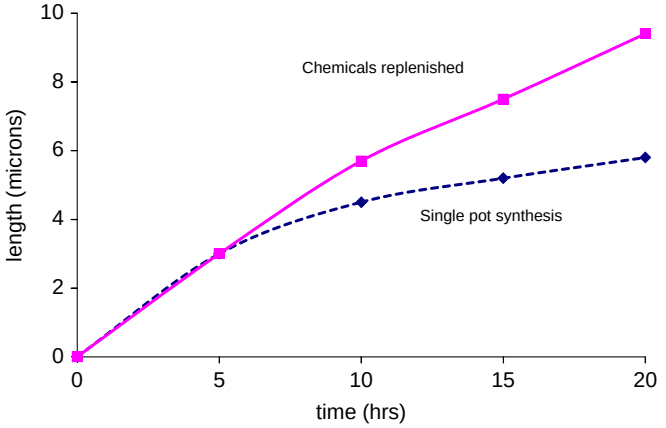

Fig. 2. ZnO nanorod growth rate increased when the chemicals were replenished after every 5 h.

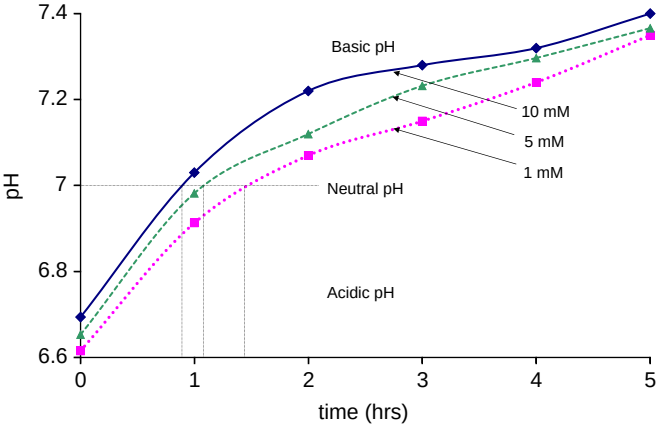

Fig. 3. Change in pH of the reaction bath over a period of 5 h during the growth of ZnO nanorods.

2.1. Materials used

All chemicals used in this study were analytical grade and was used without further purification. Zinc acetate dihydrate [$(CH_3COO)_2Zn \cdot 2H_2O$] procured from Merck was used as the zinc ion source, sodium hydroxide [NaOH] from Merck as the reducing agent and ethanol [C_2H_5OH] from J.T.Baker as the solvent for the synthesis of ZnO nanoparticles. Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, Aldrich, 99% purity] and hexamethylene tetramine [$C_6H_{12}N_4$, Carlo Erba, 99.5%] were used as the reactants in the chemical bath for the ZnO nanorod growth.

2.2. Synthesis of ZnO nanoparticles

The synthesis of ZnO nanoparticles that were used as seeds was carried out following a procedure reported by Bahnemann et al. [42] 1 mM zinc acetate solution was prepared in 2-propanol under rigorous stirring at 50 °C. The solution was then further diluted and cooled, after which aliquots of 20 mM sodium hydroxide in 2-propanol was added under continuous stirring. The mixture was then kept in a water bath at 60 °C for 2 h [43].

2.3. Hydrothermal growth of ZnO nanorods

ZnO nanorods were grown on glass slides, which were first thiolated by dipping in a 1% solution of dodecane thiol in ethanol

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