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Morphological studies of ZnO nanostructures in the presence of trigol

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ABSTRACT

The present investigation discloses the synthesis of uniform leaf and flower shaped zinc oxide (ZnO) nanostructures using a simple hydrothermal technique. Morphological variations of ZnO nanostructures were thoroughly studied by varying concentrations of triethyelene glycol (trigol) and precursor zinc acetate. Specific morphological nanostructures were achieved by properly maintaining the concentration of trigol and precursor zinc acetate. The optimized methodologies for the synthesis of uniform leaf and flower shaped ZnO nanostructures and their morphological characterizations are reported in this manuscript.

Keywords: *Nanoparticles; electron microscopy; leaf and flower shaped ZnO nanostructures; Trigol*.

1. INTRODUCTION

Due to the smaller size and larger surface area nanomaterials show unique properties when compared to bulk. Nanotechnology is an emerging technology which is used in fabricating the sophisticated electronic devices, optoelectronics etc. Especially for the bottom-up approaches to nanoelectronics, nano building blocks such as quantum dots, nanorods, nanosheets, nanowires, nanocomposites have been investigated thoroughly [1,2].

ZnO is a gifted material in the field of electronics due to its huge exciton binding energy at room temperature and the wide band gap of around 3.37 eV. Not only in the field of electronics, ZnO nanoparticles have many applications such as the performance of glass slides coated with various percentages of ZnO nanoparticles as an antibacterial agent and their excellent bactericidal effect was demonstrated by Applerot et al. [3]. Strunk et al. [4] used ZnO nanomaterials as heterogeneous catalysts in methanol synthesis.

There are many reports to synthesize ZnO nanoparticles. But the formation of ZnO nanostructures depends on many factors such as the nature of reactants and their concentrations, counter ions charge and type, reaction time and temperature, the presence of dispersant etc., [5]. Especially recent reports on flower shaped ZnO structures uses cyclic feeding CVD technique [6], solvo/hydrothermal methods [7-9], reflux synthesis [10], heating the precursor solutions at 60 ^{o}C for 24 hours, flower growth formation using silicon substrates and Zn powder at 1000 ^{o}C [11], and using stabilizers/complexing agents like ethyleneglycol [8] and Triethylamine [9]. Bamboo leaf shaped ZnO nanostructures was reported using magnetron co-sputtering by oxidation Zn/SiO2 composite films [10]. Latest literatures have demonstrated many synthesis techniques for the synthesis of different ZnO nanostructures [11-21]. All the above said methods include high temperatures, long time and complicated methodology. So creating the nanomaterials with particular shapes and size by simple methods is crucial. Although the cooling technique was used to manipulate the structure of ZnO by thermal evaporation of zinc powders in the presence of oxygen using a silicon substrate [22], in the present attempt a simple technique was presented to manipulate the structures of ZnO nanostructures in solution phase. In the present manuscript, we disclose the synthesis of leaf shaped and flower shaped uniform ZnO nanostructures in the presence of trigol as a surfactant.

2. EXPERIMENTAL SECTION

ZnO nanoparticles were prepared by dissolving zinc acetate dihydrate in trigol solution. An appropriate amount of NaOH pellets was dissolved in trigol solution. Both the solutions were cooled in ice bath. Then NaOH was added dropwise using a peristaltic pump to the zinc acetate dihydrate solution with stirring at 550 rpm by a propeller. This mixture resulted to a turbid solution which on heating on a water bath at 75°C synthesized ZnO nanostructures. We investigated the morphological variances and sizes of ZnO nanostructures by (i) keeping trigol concentration as 0.5M, NaOH as 20 mM and various concentrations of zinc acetate as (a) 1mM, (b) 2mM, (c) 4mM, (d) 6mM and (e) 8mM; (ii) keeping zinc acetate concentration as 1mM, NaOH (20mM) and varying the trigol concentration as (a) without trigol, (b) 0.05M, (c) 0.1M, (d) 0.25M, (e) 0.5M and (f) 0.75M trigol; (iii) keeping zinc acetate concentration as 4mM, NaOH (80mM) and varying the trigol concentration as (a) without trigol, (b) 0.05M, (c) 0.1M, (d) 0.25M, (e) 0.5M and (f) 0.75M trigol.

The synthesized ZnO nanostructures were characterized by XRD (Bruker D8 Advance Diffractometer, Bruker AXS, Germany) with Cu Kα radiation (λ= 1.54Å). XRD pattern of ZnO

samples was recorded over a 2θ range of 10-90° at a step size of 0.02° and scanning rate of 4°/min.

To determine the morphologies of the ZnO nanostructures, the images of various ZnO nanostructures were taken using Scanning electron microscope (SEM, Carl Zeiss oxford instrument) and further taken High Resolution Transmission electron microscope (HR- TEM) using JEOL JEM 2100 HR-TEM.

3. RESULTS AND DISCUSSION

The X-ray powder diffraction pattern of the synthesized flower shaped nanostructure was presented in Figure S1 (Supporting information). From the X-ray diffractogram, it was clear that formation of pure hexagonal ZnO phase was in good agreement with the JCPDS Card No.00-036-1451. No other peaks of impurities were observed. Highly crystalline nature was confirmed from the sharp and strong intense diffraction peaks. The lattice constants of these ZnO nanostructures matched exactly with the values of hexagonal ZnO phase having space group P63mc.

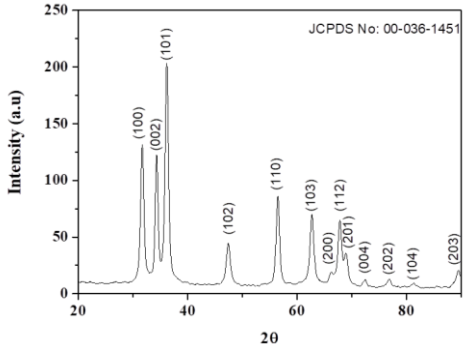

Figure S1. XRD Pattern of ZnO leaf shaped nanostructures (SEM image shown in Fig. 1B).

Electron microscopic studies were performed to characterize the morphology of the synthesized ZnO nanostructures. SEM images of ZnO nanostructures show morphological variations of ZnO nanostructures in 20mM NaOH and 0.5M tirgol solution after changing the concentrations of precursor zinc acetate (Figure 1a-1f). It is very clear from the microscopic images at low concentrations of zinc acetate (1mM), the formation structures were in the intermediate stage and no clear leaf shapes was observed. With increasing concentration of precursor, we noticed the formation of very clear and uniform leaf shaped nanostructures with 2mM, two dimension flower growth with 4mM, three-dimensional flower structures with 6mM and stacked flower growth with 8mM precursor concentrations, respectively. Interestingly we noticed no structural growth when the concentration of precursor was 10mM.

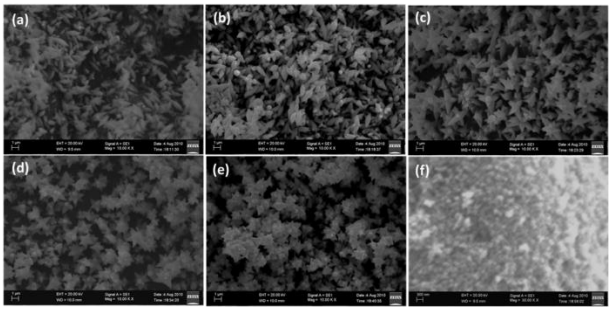

Fig. 1. Scanning electron microscopic view of ZnO nanostructures in the presence of 0.5M Trigol and 20mM NaOH at various concentrations of Zinc acetate as (a) 1mM, (b) 2mM, (c) 4mM, (d) 6mM and (e) 8mM.

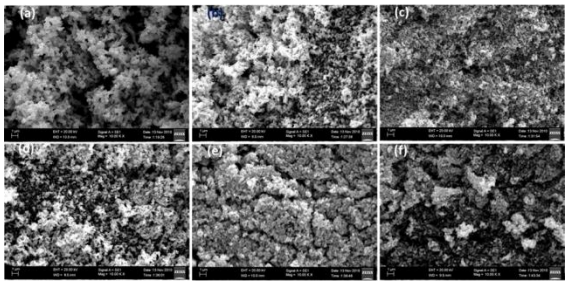

Fig. 2. Scanning electron microscopic view of ZnO nanostructures (leaf shaped) in the presence of 1mM Zinc acetate and 20 mM NaOH by varying trigol concentration as (a) without trigol (b) 0.05M, (c) 0.1M, (d) 0.25M, (e) 0.5M and (f) 0.75M.

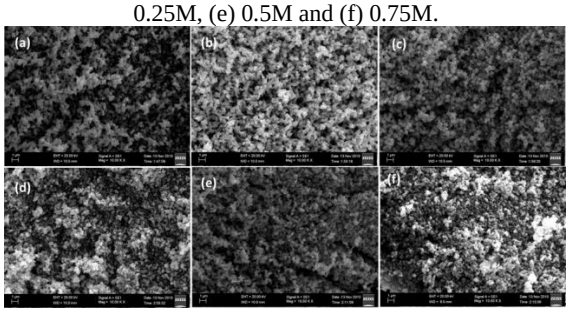

Fig. 3. Scanning electron microscopic view of ZnO nanostructures (small flowers) in the presence of 4mM Zinc acetate and 80 mM NaOH by varying trigol concentration as (a) without trigol (b) 0.05M, (c) 0.1M, (d) 0.25M, (e) 0.5M and (f) 0.75M.

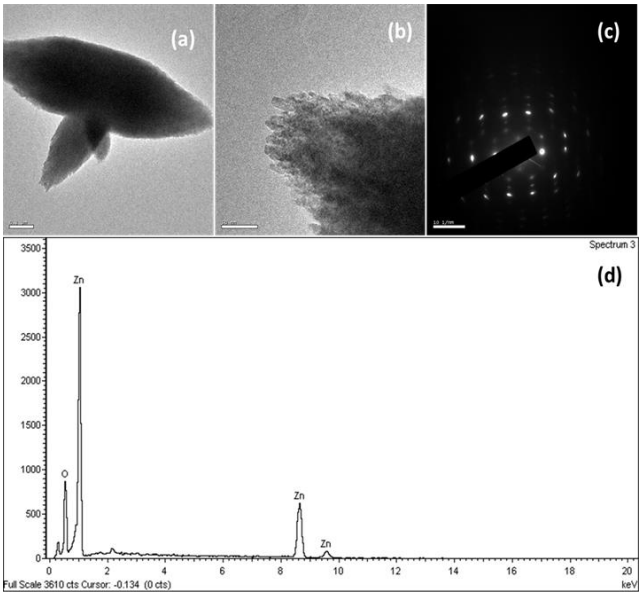

Fig.4. (a,b) HR-TEM images, (c) SAED pattern and (d) EDS spectrum of leaf shaped ZnO nanostructures.

SEM images of ZnO nanostructures show the morphological variation of ZnO nanostructures with 1mM zinc acetate precursor and 20 mM NaOH in water by varying the concentrations of trigol (Figure 2a-2f). Interestingly synthesized nanostructures using 1mM precursor in water show good leafy structure and the introduction of trigol leads to a gradual decrease

in the size of the leaf structures with 0.05M and 0.1M trigol respectively. The least size of 250 nm sized leafs was achieved in the presence of 0.1M trigol. Beyond 0.1M trigol concentration i.e. with 0.25M, 0.5M and 0.75M trigol, the nanostructures showed similar leaf structures with little increase in the size of leafs in all cases.

In order to test the concentration effect of trigol on flower structures, we chose the precursor concentration as 4mM zinc acetate, 80mM NaOH and varying concentrations of trigol from 0.05 to 0.75M. Similarly, 4mM precursor containing sample showed a small flower-shaped structures. The least sized flower structures were achieved with 0.5M trigol concentration and afterward the size of flowers remained more or less same with increasing trigol concentrations (Figure 3a-3f).

Further HR-TEM images of leaf-shaped ZnO nanostructures (Fig. 4a-c) clearly support the formation mechanism of ZnO nanostructures. Initially, zinc precursors react with NaOH in order to form $Zn(OH)_4^{2-}$ growth units which then self-assemble into nanorods and further these nanorods align together forming leaf and flower shaped nanostructures [23]. This self-assembly occurs by simply heating the solution containing zincate ions. EDS spectrum of the ZnO leaf shaped nanostructures shows the presence of Zn and O atoms without any other impurities which confirm its purity (Fig. 4d). Selected area diffraction pattern (SAED) further confirms the formation of hexagonal ZnO (Fig. 4c).

4. CONCLUSION

An optimization protocol was given to produce the ZnO leaf and flower shaped nanostructures of desired sizes. Uniform nanostructures and sizes can be achieved with this method. Leaf-shaped ZnO can be achieved even in the absence of trigol at a particular concentration of zinc acetate dihydrate i.e., at a concentration less than 2mM. NaOH concentration also plays an important role. Flower shaped ZnO can be achieved even in the absence of Trigol at a particular concentration of zinc acetate dihydrate i.e., at a concentration greater than 2mM. Concentrations of zinc acetate dihydrate beyond 9mM results in irregular shape (no shape). Introduction of trigol in this method plays an important role in controlling the size at a particular precursor concentration. The smallest sized leaf/flower shaped ZnO nanostructure was achieved at 0.1M trigol concentration. Concentration less than or greater than 0.1M trigol results in increased size of leaf/flower shaped ZnO nanostructures.

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