Morphology Controlled Synthesis of ZnO Nanostructures via Facile Hydrothermal Method

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ABSTRACT

Zinc Oxide (ZnO) nanostructures due to their intrinsic characteristics such as chemical stability, non-toxic and biocompatibility gained attention in energy, environmental and biomedical sectors. Controlled engineering on its physiochemical characteristics such as morphology and particle sizes enhance its performance and efficiency during real applications. The present work focuses on synthesizing well-crystalline, floret patterned ZnO nanopowders using a facile, hydrothermal synthesis process. Unlike the existing methodologies, the present process avoided the usage of any surfactants and capping agents and explored the method that is more economical and eco-friendly. The study examines the influences of the reaction periods of the precursors on the final morphology of the ZnO nanostructures. The study reveals that the higher reaction periods favor the formation of ordered, floret structures of ZnO nano-rods. The final powders were systematically characterized for their crystallinity and functional properties using XRD and UV, FTIR analyses. The variation in the morphological characteristics with respect to the reaction period was further examined through FESEM analysis. The study further discusses the plausible mechanism of the formation of floret ZnO nano-rods.

KEYWORDS

ZnO, Hydrothermal method, Nano-rods, and Floret structure.

1. INTRODUCTION

Over the past decades, researchers have been developing innovative and environmental friendly method for synthesis of nanomaterials for various fields, including electronics, medicine and environmental science. In accordance with the application requirements, they engineered the characteristics of nano metal-oxides by modifying various parameters of synthesis including temperature, time, pH, and precursor concentrations [1]. Amongst, Zinc oxide (ZnO) is considered as one of a multifunction material due to its exceptional physio-chemical properties including high chemical stability, high photo-stability, wide range of radiation absorption, biodegradability and biocompatibility. In addition, ZnO nanomaterials are versatile to engineer their morphological structures including one-dimensional structures like nanorods, nanowires, and nanotubes, two-dimensional structures like nano-plates, nano-sheets, and nano-pellets, and three-dimensional hierarchical formations like nanoflowers, dandelions, and snowflakes.

ZnO nanomaterials have been synthesized by various synthesis methods such as mechano-chemical process, co-precipitation, chemical vapor deposition, emulsion method, green synthesis, sol-gel, hydrothermal method [2]. Among, hydrothermal method is mostly desired to synthesize-ZnO nanomaterials as it is more facile and economical and has several significant advantages including high product purity and homogeneity, crystal symmetry, metastable compounds with unique properties and narrow particle size distributions under mild reaction conditions [3].

P. Ramasamy et al., synthesized flower-like ZnO nanostructures using ethanol as solvent and explained the formation mechanism of its floret structure [4]. E.M. Abdel-Fattah et al., synthesized two distinct forms of flower-like ZnO nanostructures via hydrothermal methods and studied the influence of various growth times, temperatures and zinc precursors on its morphology. In another study, zinc nitrate and NaOH were used to synthesize lotus-flower-like ZnO nanostructures, while zinc chloride, NaOH and CTAB were utilized in synthesis of tulip-flower-like ZnO nanostructures [5]. A. Ejsmont et al., studied the morphology control of ZnO flowers-like nanostructures by varying the factors such temperature, pH and capping agent [6].

In the present work, the focus was anchored towards synthesizing well-crystalline, flower-like ZnO nanostructures through an eco-friendly and cost-effective hydrothermal method. More specifically, the present work attempted to produce floret ZnO nanostructures without utilizing any capping agent and surfactants which were employed in the hitherto approaches [4 – 6]. To our surprise, the similar floret ZnO nanostructures were produced in this study without the usage of any capping or surfactant agents but by merely varying the reaction periods. Further, the direct addition of the required precipitator (NH_4OH) to the precursor solution rather than the regular dropwise additions also aided to achieve the eventual floret ZnO nanostructures. The resultant ZnO powders were systematically characterized using various analyzes such as X-Ray Diffractometry (XRD) and Fourier Transform Infrared (FTIR) Spectroscopy to confirm their phase formation and functional properties. Further, their optical properties were analyzed through UV-Vis spectroscopy (UV-Vis) and their surface morphology was characterized through by Field Emission Scanning Electron Microscopy (FESEM). In addition, the plausible mechanism for the formation of the floret ZnO nanostructures is also discussed.

2. MATERIALS AND METHODS

2.1 Materials

The precursors used for the synthesis of ZnO nanostructures were Zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$], aqueous ammonium solution (NH_4OH) and Distilled water (DW). The chemicals used were purchased from HIMEDIA and are of analytical grade with 99% purity.

2.2 Hydrothermal Synthesis Method

0.15M of Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) was dissolved in 60 ml of distilled water under constant stirring conditions. Appropriate amount of aqueous ammonium solution (NH_4OH) was added directly to the aqueous zinc nitrate solution to reach 12 as a final pH. The stirring was continued for another 30 minutes to obtain homogenous mixture and the resultant solution was treated in an autoclave unit at 180°C for a period of 1hour and 3 hours. The resultant precipitate was rinsed in distilled water to remove impurities and any unreacted components and further dried in a hot air oven at 100 °C for 12 hours.

2.3 Characterization

The structural, optical, and morphological characteristics of hydrothermally synthesized ZnO nanostructures were investigated through comprehensive characterization techniques. The crystallinity and phase purity of the as-prepared ZnO nanostructures were investigated by Bruker X-Ray diffractometer. The functional group of ZnO were observed by Shimazu (IR Tracer-100) Fourier transform infrared spectroscopy and the surface morphology was analyzed by Zeiss Sigma Field Emission Scanning Electron Microscope. Further, the absorption spectra was examined by Shimazu UV-Visible Spectrophotometer.

3 RESULTS AND DISCUSSION

The entire procedure followed in this study for synthesizing ZnO is shown as a flowchart in fig.1

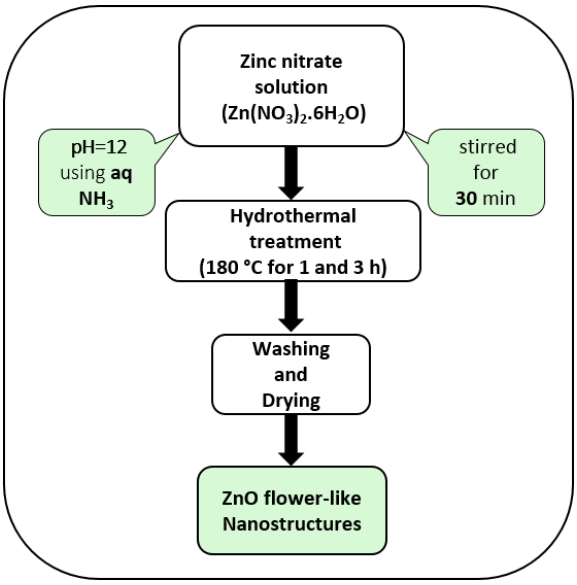

Fig. 1. Flowchart for synthesizing ZnO nano-florets

3.1 XRD Analysis

XRD pattern of hydrothermally synthesized ZnO nanostructures is shown in Fig.1. Diffraction peaks at 31.98, 34.74, 36.36, 47.66, 56.78, 63.01, 68.08 and 69.23º were assigned to (100), (002), (101), (102), (110), (103), (112) and (201) planes respectively. All the corresponding peaks were indexed to hexagonal wurtzite phase of ZnO as reported in Joint Committee on Powder Diffraction Standard (JCPDS) card No. 36-1451. The hexagonal structure of ZnO with very good having well defined crystallinity was confirmed by the sharp, intense diffraction peaks. All the peaks were corresponding to ZnO wurtzite phase and no other peaks related to unreacted compounds were found in the pattern. Debye-Scherrer calculations showed the average crystallite sizes as 23 and 34 nm for the of ZnO nano-florets obtained from the reaction periods of 1 hour and 3 hours respectively. The variation of peak intensities along (101), (002) and (100) planes indicted hat the growth of obtained nanoparticles was predominant along c-axis [7].

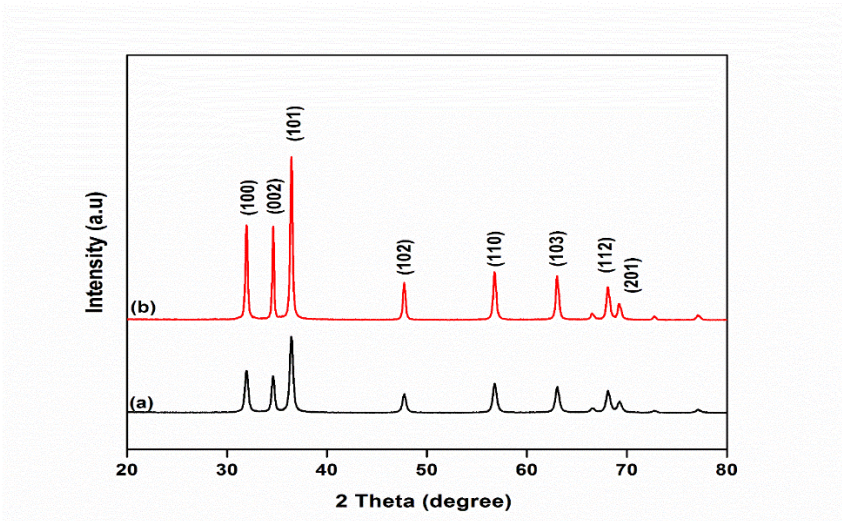

Fig. 2. XRD pattern of ZnO obtained by varying the reaction period of (a) 1h and (b) 3h

3.2 FTIR Analysis

The broad vibration band perceived in the range 2700 - 3750 cm^{-1} with peaks at 3371 and 2880 cm^{-1} were assigned to O-H stretching vibrations of absorbed water molecule and surface hydroxyl group [8,9]. The absorption peaks at 1606 and 1405 cm^{-1} indicated C=O vibrational mode of carboxylate group and O-H bending H_2O respectively [10,11]. The peak observed at 1066 cm^{-1} was assigned to C-H vibration [12] originated from ethanol during characterization. The intense peak at 478 cm^{-1} attributed to the characteristic peak of ZnO that further confirmed the purity of the samples [13].

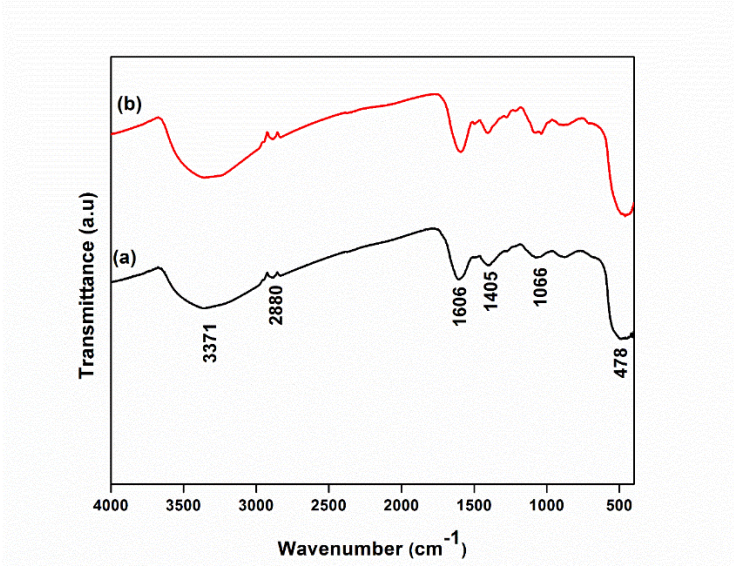

Fig. 3. FTIR spectra of ZnO (a) 1h (b) 3h

3.3 UV-Vis Analysis

Fig. 4 shows the UV-Vis absorption spectra of ZnO nanostructures synthesized at various time period (1 and 3h). The spectrum reveals a characteristic absorption peak at 370 and 372 nm for all ZnO [14].

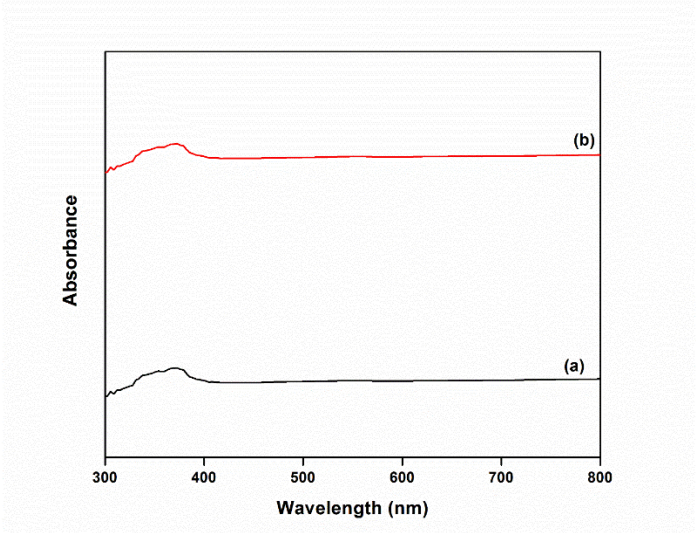

Fig. 4. UV-Vis Absorption Spectra of ZnO (a) 1h (b) 3h

3.4 FESEM Analysis

FESEM images of ZnO nano-stuctures prepared with different hydrothermal reaction time are shown in Fig. 5. As proposed in the earlier sections, it is evident from the fig.5 that synthesizing the floret-structured ZnO nano powders is possible by merely varying the reaction periods between 1 hour and 3 hours coupling with direct addition of ammonia solution for precipitation. Further, it can be observed that the formation of flowers with self-assembly of hexagonal shaped nanorods was obtained for 1h reaction (Fig. 5(a,b) while well structured, uniform floret morphology through self-assembly of short nanorods was observed for the reaction periods of 3 hours (Fig. 5(c,d)).

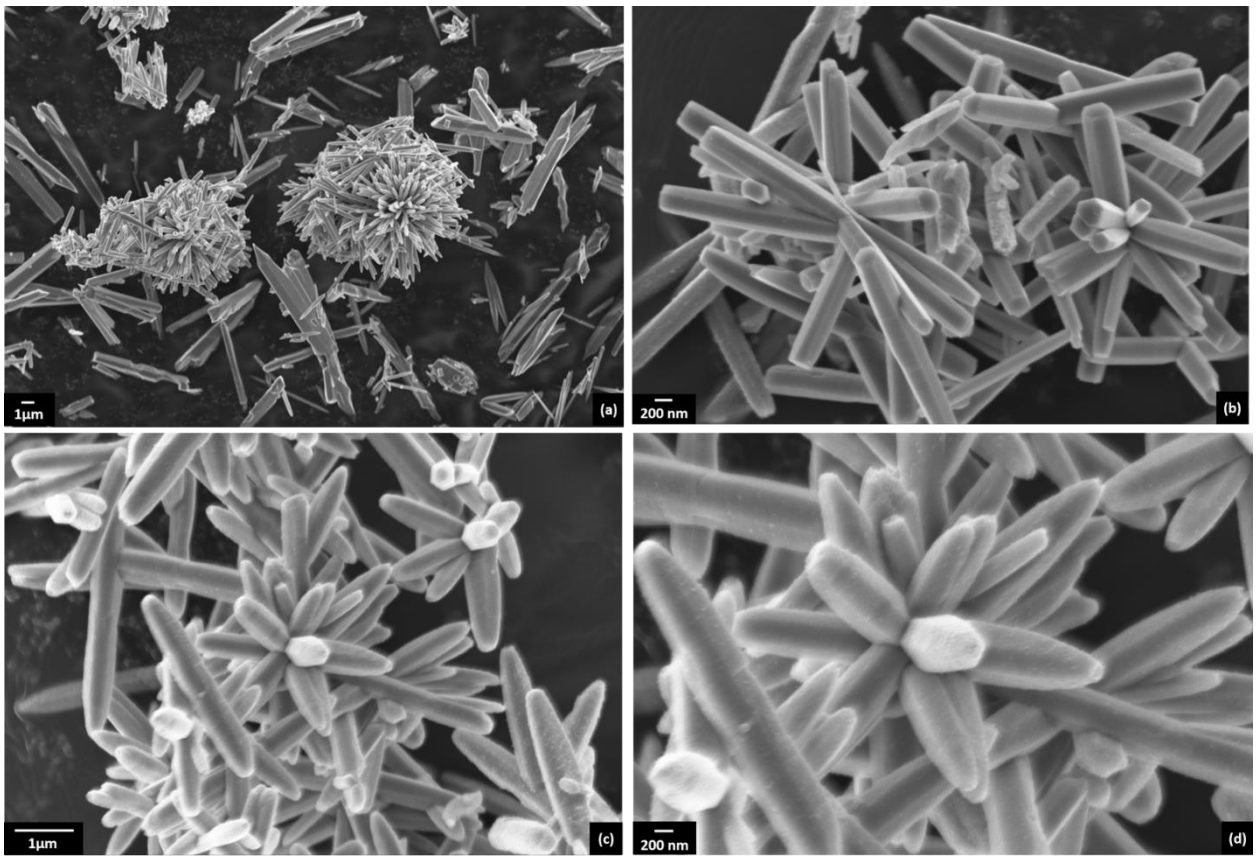

Fig. 5. FESEM images of ZnO (a,b) 1h and (c,d) 3h

3.4 Growth Mechanism

The formation of flower-like morphology of ZnO nanostrucrues was explained on the basis of nucleation, growth and self-assembly of the $Zn(OH)_2$ nuclei. The whole addition of ammonia solution leads to formation of $Zn(OH)_2$ and zincate $[Zn(OH)_4]^{2-}$[15]. These complexes decompose to form ZnO nanostructures during hydrothermal treatment. For both reaction times, rod like structure was obtained due to the increased growth rate of the formed ZnO nuclei along (101) as evident from Fig. 2. Hexagonal nanorods with high aspect ratio were obtained at 1 h to maintain the hexagonal symmetry of ZnO crystal structure [16]. Uniform flower morphology with self-assembly of ZnO nanorods at 3 h might result from dissolution and re-precipitation. The high surface energy and electrostatic interactions between charges of (0001) polar face of ZnO nanorods lead to self-assemble to form flowers in both cases [17,18].

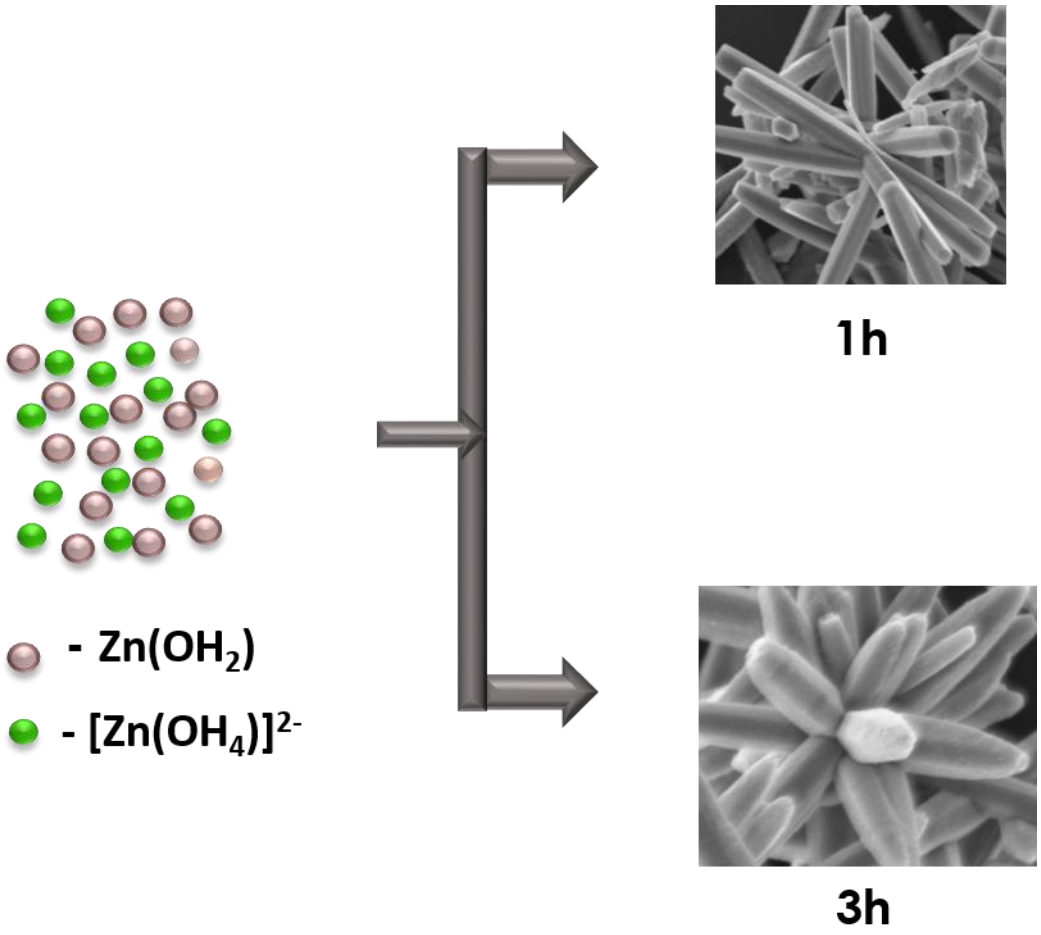

Fig. 6. Growth Mechanism of ZnO

4. CONCLUSION

The synthesis of two different flower-like ZnO nanostructures was successfully synthesized by the novel and eco-friendly hydrothermal method without using any additives such as surfactant and capping agents. The structural analyses confirmed the formation of highly crystallined hexagonal wurtzite phase and the UV and FTIR analyses further ratified its phase purity and optical chacteristics. Examining the resultant ZnO powders through FESEM analyses eventually confirmed the feasibility of synthesizing floret ZnO nanostructures through a facile and economical hydrothermal synthesis followed in the present study. The formation of ZnO nanoflorets is plausibly achieved due to combinations of various mechanisms such as nucleation, dissolution, reprecipitation and growth. As detailed in the present study, direct addition of requisite ammonia for the reactions along with optimized reaction periods are attributed for the formation of floret ZnO nanostructures.

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