SYNTHESIS OF ZINC OXIDE NANOFLOWER USING EGG SHELL MEMBRANE AS TEMPLATE

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ABSTRACT

In this study, the nanocomposite of eggshell membrane is synthesized with ZnO by the chemical bath deposition (CBD) method, and eggshell membrane, which is used as a template, and decomposed. The end product obtained is nanoflowers of zinc oxide (ZnFs). The petals of nanoflowers obtained are of hexagonal cross-section similar to the unit cell structure of zinc oxide. The CBD parameters of temperature, reaction time, and solution pH were varied extensively during this study to obtain optimized parameters for the growth of ZnFs. The obtained nanoflower structure was analyzed using various characterization techniques of Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), X-Ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR).

Keywords: Nanostructure, Nanoflower, Zinc Oxide, Chemical Bath Deposition, Egg Shell Membrane (ESM), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDX), X-Ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR).

INTRODUCTION

Synthesizing ZnO nanoflowers (ZnFs) by using a low-cost approach of environment-friendly eggshell membranes without using chemical etching techniques is the novelty of this study. Expected to give exceptional properties, this study focuses on the synthesis of the 3D nanostructure of ZnO, which can have several applications, such as sensors. ZnO is also biocompatible material and has numerous applications in photonics and electronics. It also has applications in triboelectric and piezoelectric devices, and its behavior is micro or nanostructure-dependent, which can be easily molded by various techniques (Aminullah et al., 2020; Gan et al., 2009; Kilinc et al., 2014; Liu et al., 2011; Ramesh et al., 2021; Schlur et al., 2018; She et al., 2007; She et al., 2008; Tang et al., 2014; Wang et al., 2010; Wang et al., 2020; Xu et al., 2024; Yang et al., 2009; Zhang et al., 2006). Green electricity can be generated from the fabricated ZnFs in this study by utilizing ambient mechanical energy of human motion as input energy using the concept of triboelectricity. Triboelectricity or triboelectric behavior of the material is structure-dependent along with material composition and can be easily altered by changing the micro or nanostructure of the material. Another material, eggshell membrane, used in this study is also a biomaterial, which is a waste product and thrown with eggshells as kitchen or hotel waste material. It is composed of collagen-based multi-layered fibers in the form of a porous matrix, which can be easily extracted manually or by dissolving the eggshell (Dong et al., 2007; Meng & Deng, 2016; Ray & Roy, 2016; Sah & Rath, 2016; Su et al., 2011; Zhang & Buitenhuis, 2007; Zhou et al., 2007).

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1. Materials and Methodology

In this study, biocompatible and biodegradable material zinc oxide (ZnO) is used to synthesize its' unique nanostructure in the form of nanoflower using novel technique of fibrous natural waste biomaterial eggshell membrane as template. ZnO nanostructures are synthesized by using the chemical bath deposition method. The eggshell membrane acts as a biofibrous template in this process. The ESM was extracted manually from the raw hen egg shell from the poultry farm. Then the ESM was washed out in deionized water to remove dirt and unwanted organic material. After that, it was kept drying at room temperature for 2 hours. The homogeneous solution of distilled water, 0.05 M zinc nitrate hexahydrate (Zn(NO3)2.6H2O) and 0.05 M hexamethylenetetramine or HMTA ((CH2)6N4) precursors, was heated on the heater, and ESM was dipped into the solution. The different temperatures and reaction times for the synthesis of the ESM-ZnO composite were used to study their effect on the growth of the ZnO nanoparticles on the surface of ESM. The successful formation of the ESM-ZnO composite required for this study was observed when the temperature of the solution was kept at 85 °C and the reaction time was 3.5 hours. The pH of the homogenous solution was maintained at 6.0. The temperature, reaction time, and pH play a very important role in forming zinc oxide nanoflowers. After drying the water from the composite, it was placed in the temperature-controlled tube furnace for annealing. The temperature of the furnace was raised linearly in the interval of half hours. During this time, from the ESM-ZnO composite, the ESM template started to decompose, and only zinc oxide nanostructures in the form of white powder were obtained. The solution was filtered out with filter paper and dried at room temperature to extract ZnO nanoparticles.

The equations of the reaction are,

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + NO_3$$

$$(CH_2)6N_4 + 6\,H_2O \rightarrow 4\,NH_3 + 6\,HCHO$$

$$Zn^2+ + 2OH- \rightarrow Zn(OH)_2 \downarrow$$

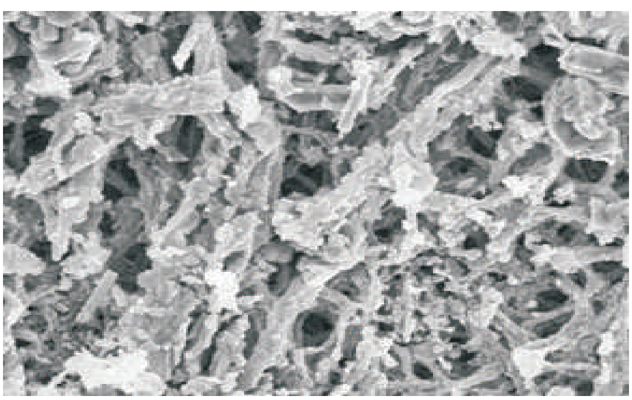
$$Zn(OH)_2 + 2\,OH- \rightarrow Zn(OH)_2^{\ 4-}$$

$$Zn(OH)_2^{\ 4-} \rightarrow ZnO\,(Nanoflower) + H_2O + 2\,OH$$

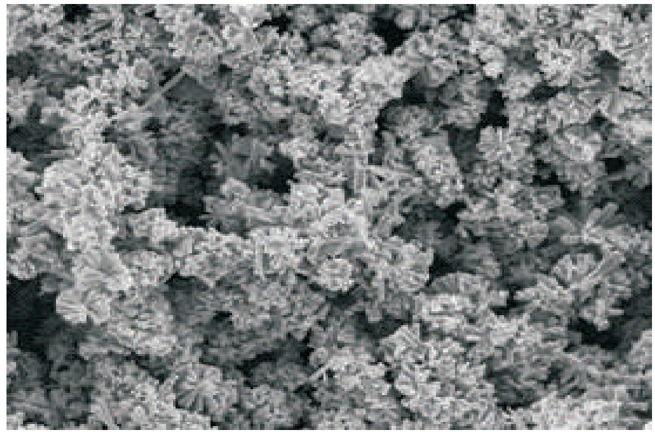
2. Results and Discussion

Studies have developed different types of nanostructures of the ZnO for various applications and reported the variation in the properties due to their different structures. In this study, ZnO nanoflower (ZnF) is synthesized with hexagonal cross-sectioned ZnO nanostructures using a novel method of waste biomaterial eggshell membrane (ESM). In this method, the organic nanofibers of eggshell membrane are used as a template to synthesize ZNFs, as shown in Figure 1 (a). First, the composite of ESM with zinc oxide is synthesized by the chemical bath deposition process, by immersion of dry ESM in the precursor solution. After immersion in the solution, the swelling of ESM is observed as the precursors adsorbed in porous biofibers of biotemplate ESM. The biofibers were then removed by the heat treatment method, and only the inorganic material ZnO remains with a hexagonal cross-section.

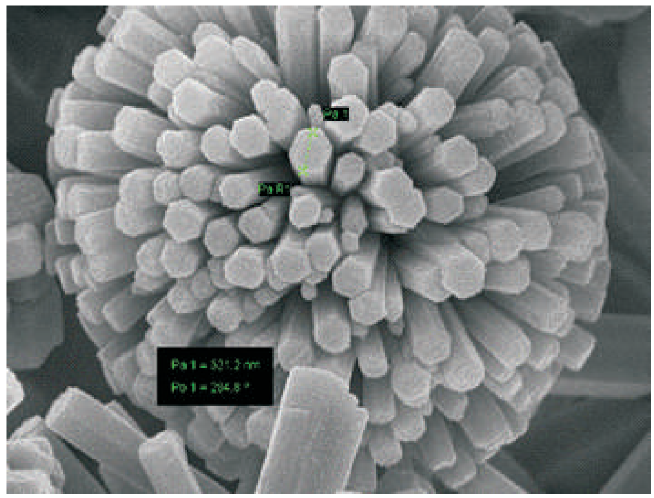
As the temperature and reaction time are the important parameters along with the template in the CBD method, a number of experiments were performed to achieve the proper adsorption of ZnO in the fibers of ESM to form the ESM-ZnO composite, which is achieved at 85 °C, 3.5 hours of the reaction time, and 6.0 pH of solution. Temperature and time duration are also important parameters to decompose the ESM present in the composite and to synthesize ZnFs, which are present as inorganic material in the biocomposite. The thermal analysis of the ESM-based composite is required to understand mainly the decomposition behavior of the biomaterial. The temperature of the thermogravimetric analysis device was increased at a rate of 10 degrees per minute, and the loss of mass of ESMZF was observed after 200 °C. Complete ESM decomposition was observed at 500 °C, and the material left was zinc oxide in the form of white powder. So the required physical shape of the ZnO material present in its' composite with ESM is decided by the action of increasing temperature for a particular time duration. This treatment removes the organic biofibers of the eggshell membrane template and results in the formation of crystalline ZnO nanorods arranged in the form of ZnO nanoflowers, as shown in the SEM micrograph in Figure 1 (b). The diameter of hexagonal cross-sectional-shaped each petal of nanoflower is of the order of 321 nm and length 1.307 μm, as observed in SEM images in Figure 1 (c). For characterization analysis, the FTIR spectrum of the ZNFs obtained shows strong absorption peaks beyond 500 cm-1, which was due to the presence of ZnO crystals in the sample. The flat FTIR transmission spectrum is due to the uniform composition of the material, ZnO, which is the basic composition of the ZNFs, as shown in Figure 2 (a). The XRD plot of the ZNT is shown in Figure 2 (b). The crystalline peaks were observed around 31.870, 34.680, 36.520, 47.790, 56.410, 63.120, 66.400, 67.690, 69.190, 72.70, and 770 values of 2 (θ) theta with their corresponding miller indices 100, 002, 101, 102, 110, 103, 200, 112, 201, 404, 202. These indices are calculated from the reference JCPDS cards, as shown in Figure 2 (c). These values are analyzed and compared using X'Pert High Score Plus software, and these peaks were identical to the peaks in JCPDS card number 36-1451, a reference card of zinc oxide. EDX analysis attached with the SEM apparatus also confirms the presence of ZnO in the tested sample. These characterizations give a detailed picture of the material's structure, surface morphology, and thermal stability. The ZnFs fabrication method proposed in this study using a novel technique of waste biomaterial eggshell membrane as a template is very low cost and an effective way for the development of complicated desired shapes of inorganic nanomaterials in a controlled manner.



(a)

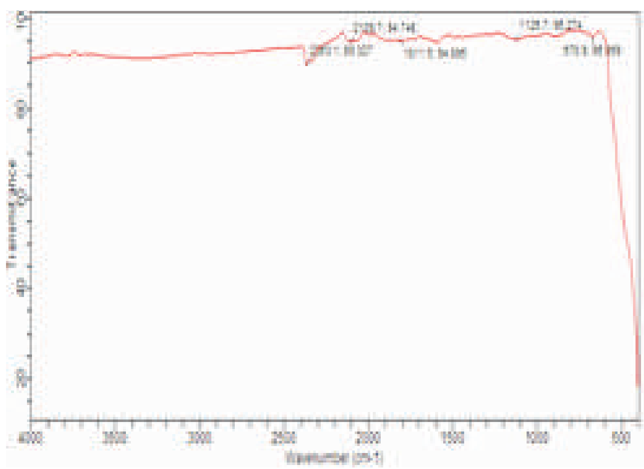


(b)

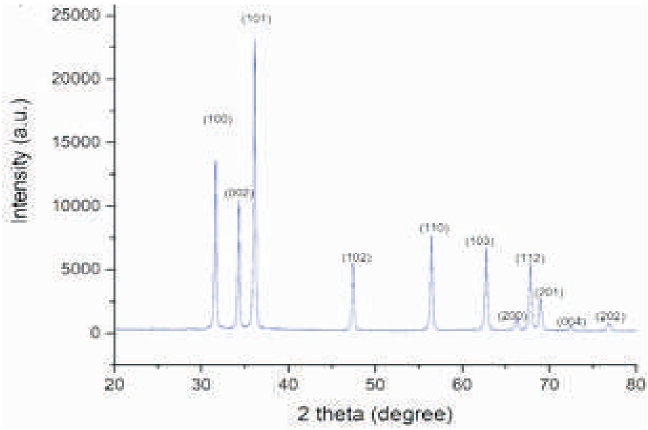


(c)

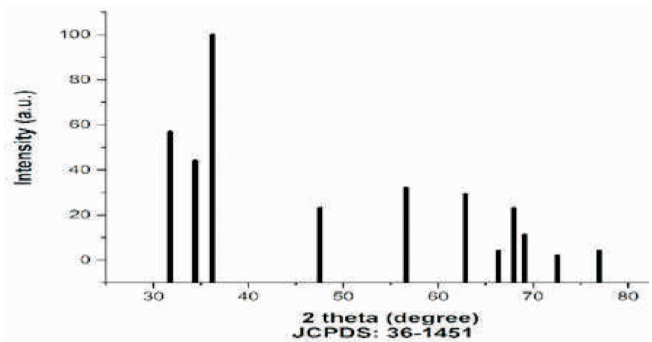
Figure 1. (a) Eggshell Membrane Fibers (b) ZnO Nanoflower on ESM Mebrane (c) ZnO Nanoflower



(a)



(b)



(c)

Figure 2. (a) FTIR Analysis (b) XRD Analysis (c) ZnO JCPDS Card

Conclusion

ZnO nanoflowers (ZnFs) are synthesized using an eggshell membrane as a template. The temperature, reaction time, and solution pH play a crucial role in the formation of the desired nanostructure, along with the type of template used for the synthesis. The optimized parameters were obtained after a number of experiments in this study to obtain ZnFs with hexagonal crosssection of each petal of nanoflower. The ZnFs fabrication method proposed in this study using a novel technique of waste biomaterial eggshell membrane as a template is very low cost and an effective way for the development of complicated desired shapes of inorganic nanomaterials in a controlled manner.

Declarations

Conflict of Interest

The authors declare no competing interests.

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