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RESEARCH ARTICLE

Growth of ZnO Nanostructures in Organic Solvent

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Abstract

The growth of zinc oxide (ZnO) nanostructures of varied morphology in organic solvents was always a challenge as the release of hydroxyl ions necessary for the growth of ZnO is very slow. However, organic solvents have many advantages that make them attractive for use in nanomaterial synthesis. In this work, ZnO nanostructures were successfully synthesized using an organic solvent n-hexane. In order to affix the nanostructures on substrates, pre-synthesized nanoparticles were deposited on glass substrates using cetrimonium bromide (CTAB) as an ionic carrier for zincate ions and the interface between n-hexane and methanol as an alignment tool for CTAB.The seeding of the substrates was successfully carried out which was confirmed using SEM.Nanorods of ZnO with width in the range of 150-200 nm and lengths in the range of 6–7 µm grew through the solvothermal process. The nanorods were found to be tapered, which can be attributed to the decrease in concentration of the reactants with growth time and subsequent increase in pH from 6.8 to about 10. The ZnO nanorods were found to be of wurtzite crystal structure from XRD analysis. Some nanostructures of ZnO like nanobelts, nanorods, and nanocubeswere also observed to grow at the interface of n-hexane and methanol.

Keywords: *Zinc oxide, Nanostructure, Solvent, Organic, Solvothermal*

1. Introduction

ZnO is one of the most explored nanomaterials for advantages like ease of synthesis under mild conditions(1; 2) and unique properties that open up possibilities of applications in numerous fields like photocatalysis(3; 4; 5; 6), sensing(7; 8; 9), solar cells(9), super hydrophobicity(10), communication(11; 12), wound healing(13), etc. Research over the last two decades has shown maximum morphologies of ZnO in the nano size(1; 14; 15; 16).The most preferred method of solvothermal synthesis of ZnO nanostructures is the hydrothermal synthesis in aqueous solvent with zinc and hydroxyl sources through the control of parameters like temperature, concentration of reactants and pH. Even though controlled synthesis of spherical ZnO nanoparticles have been successfully carried out in various alcohol solvents like ethanol, methanol, isopropanol, etc., the growth of ZnO nanostructures like nanowires, nanorods, nanoflowers, nanocubes, etc. in organic solvents have not been explored systematically. The growth of ZnO nanostructures on seeded substrates in organic solvents can pave the path for new applications considering the advantages of organic solvents over water. Many advantages of organic solvents over water are reported in the literature(17). Organic solvents increase separation selectivity as well as separation efficiency. High separation voltages and background electrolyte (BGE) ionic strengths are possible to be used in organic solvents because of lower electric current as compared to water. Further, it can be safely assumed that due to comparatively high field strengths that can be used in organic solvents, the time taken for

analysis is shorter than in water. This work reports the successful growth of ZnO nanostructures in an organic solventn-hexane and the characterization of the synthesized nanostructures. Seeding on glass substrates was carried out using CTAB as an ionic carrier for zincate ions and the interface between n-hexane and methanol as an alignment tool for CTAB.

2. Experimental

Variable amounts of sodium hydroxide NaOH were added to solution containing CTAB and zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ in methanol CH_3OH. 4mM NaOH was added to a solution containing 30ml CH_3OH, 1mM CTAB, and 1 mM $Zn(NO_3)_2 \cdot 6H_2O$. Approximately 7-8ml of each solution was poured into a petri dish, in which glass substrates had been placed on glass supports. N-hexane was subsequently added on top of this solution in a 2:1 ratio. The petri dish was then heated to 50°C until both solvents completely evaporate. The substrates were then annealed at 150°C for approximately 15 min and then rinsed with acetone and deionized (DI) water. ZnO nanorods were then grown on some of these samples using conventional hydrothermal synthesis using equimolar solutions of $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylene tetramine $C_6H_{12}N_4$ for 10 h. Figure 1 illustrates the experimental setup.

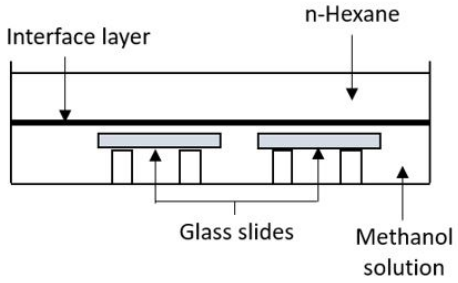

Figure 1: Experimental setup used for seeding. The glass substrates were placed at the bottom of the Petri dish upon glass supports in order to position them closer to the interface layer

During the drying process, the remnants of the thin film developing at the interface were gently dragged using a pipette to the edge and were allowed to agglomerate without being disturbed by the convection currents. Following evaporation, the fragments were deposited upon a glass substrate, which was subsequently annealed at 150°C for 15 min and rinsed with acetone and water. The substrate was then stored after a thermal treatment at 50°C for 30 min in order to evaporate any remaining solvent. The synthesis was carried out twice to check repeatability. Characterization of the synthesized ZnO nanomaterials was carried out in a JEOL JSM-6301F Field Emission Scanning Electron Microscope (FESEM)operating at 15KV.X-ray Diffraction Spectroscopy was carried out in a Bruker D8 Discover XRD. Samples for Scanning Electron Microscopy were sputtered with Au as ZnO is a semiconductor.

3. Results and Discussion

During the evaporation process, a hazy film-like structure was formed at the interface between the two liquids. Furthermore, bubble-like emulsions were observed just underneath this film. When these bubbles reached the "zone of no growth" in the center of the film, they burst at the film's edges, extending the film-like structure further. This film was very fragile, however, as it quickly disintegrated when disturbed in any way (mostly by the convection currents inside the methanol solution). When such an event took place, the film never grew back, and the fragments underwent constant agglomeration and disintegration. Figure 2 shows SEM micrographs of the top and cross-sectional views of the ZnO nanostructures grown on the substrate on the first trial. Measurements carried out on the SEM micrographs using ImageJ software show the width of the nanorod like structures in the range of 150-200 nm with lengths in the range of 6-7µm. The nanorods were observed to have a tapered end, possibly due to the decrease in concentration of the reactants with growth time and subsequent increase in pH from a near neutral (6.8) to about 10.

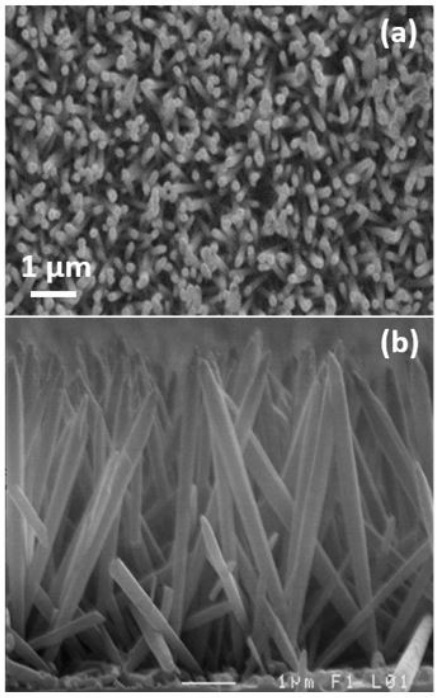

Figure 2: Scanning electron micrographs of the nanomaterial grown on glass substrate during the first trial (a) top view (b) cross-sectional view

The second trial also yielded nanorods with comparable morphology and dimension establishing the consistency and repeatability of the process. A top view of the nanorods from the second trial is shown in Figure 3. The width of the nanorods were measured and found to be in the range of 120-180 nm and lengths in the range of 5-6µm.

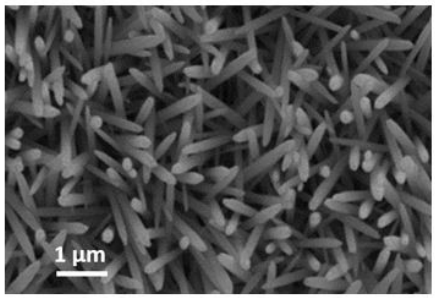

Figure 3: Scanning Electron micrograph showing the top view of the nanorods grown in the second trial

Figure 4 shows the SEM images of the interfacial film-like structures that grew at the interface of n-hexane and methanol. From the images, it can be seen that the film is primarily composed of long nanobelts, nanorods, and nanocubes of ZnO.

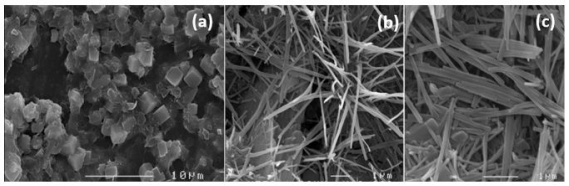

Figure 4: Scanning electron micrographsof the nanostructures that grew at the interface. They were a mix of three prominent morphologies (a) nanocubes (b) nanofibers and (c) nanobelts

The formation of ZnO both on the substrates and the interface was confirmed through EDS of the nano structures, which are shown in Figure 5. The Si, Na and Ca peaks in the EDS spectra are from the glass slides. Au peaks are from the sputteringduring sample preparation. The nanostructures that were formed are likely either ZnO or some composite containing ZnO and sodium. The same holds true for the nanocubes, which also gave prominent zinc, oxygen, and sodium peaks. So far, no literature is available that document the formation of stable ZnOnanocubes under the given conditions in organic solvents. There are many possible explanations for the formation of these varied morphologies. It is possible that a temperature and heat capacity differential between n-hexane and methanol may be the reason for certain crystal planes of the wurtzite ZnO structure to undergo preferential growth. The wurtzite structure was confirmed through powder XRD analysis (Standard JCPDS pattern for ZnO (file no: 043-0002)as shown in Figure 6. In addition, the change in the polarity of the solvent at the interface may also have aneffect on the growth rates of the individual crystal planes. Further, the interfacial activity of CTAB may also be playing a role in the selective growth of the crystal planes.

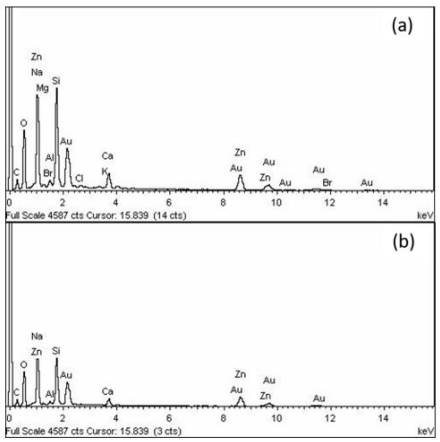

Figure 5: Energy Dispersive X-ray Spectrographs of the ZnO nanostructures grown on (a) glass substrate and (b) n-hexane and methanol interface

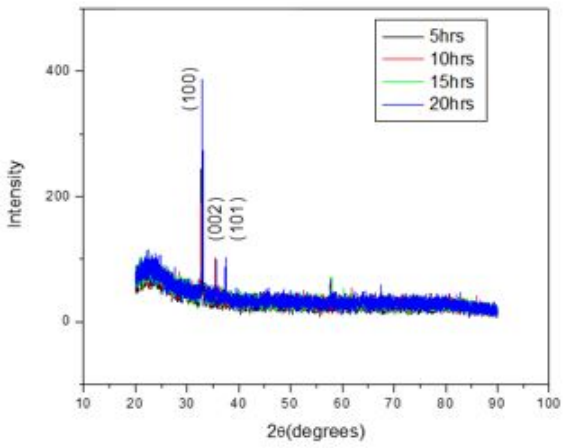

Figure 6: Powder XRD spectra of the ZnO nanostructuresfor different growth durations: 5 h, 10 h, 15 h and 20 h. Major peaks of wurtzite structure (100), (002) and (101)) are indexed and the growth of these planes was found to be prominent in all the samples

4. Conclusion

ZnO nanostructures were successfully synthesized using an organic solvent n-hexane on seeded sub-

strates.Scanning electron microscopy confirmed proper seed and nanostructures growth from the seed nucleation sites. Measurements carried out on the SEM micrographs show that the widths of the nanorod like structures grown through the solvothermal process are in the range of 150-200 nm and lengths in the range of 6–7 µm. The nanorods were found to be tapered, which can be attributed to the decrease in concentration of the reactants with growth time and subsequent increase in pH from 6.8 to about 10. Growth of ZnO nanostructures was also observed at the interface of n-hexane and methanol. These film-like structures are found to be primarily composed of long nanobelts, nanorods, and nanocubes of ZnO. EDS and XRD analysis confirmed the nanostructures of ZnO are of wurtzite crystal structure.

Conflict of Interest The authors declare no conflict of Interest in this reported communication.

References

[1] S. Baruah and J. Dutta, "Hydrothermal growth of ZnO nanostructures," *Science and technology of advanced materials*, 2009, publisher: Taylor & Francis.

[2] R. Kitsomboonloha, S. Baruah, M. T. Z. Myint, V. Subramanian, and J. Dutta, "Selective growth of zinc oxide nanorods on inkjet printed seed patterns," *Journal of Crystal Growth*, vol. 311, no. 8, pp. 2352–2358, 2009, publisher: Elsevier.

[3] S. Baruah, R. F. Rafique, and J. Dutta, "Visible light photocatalysis by tailoring crystal defects in zinc oxide nanostructures," *Nano*, vol. 3, no. 05, pp. 399–407, 2008, publisher: World Scientific.

[4] S. Baruah, S. S. Sinha, B. Ghosh, S. K. Pal, A. Raychaudhuri, and J. Dutta, "Photoreactivity of ZnO nanoparticles in visible light: Effect of surface states on electron transfer reaction," *Journal of Applied Physics*, vol. 105, no. 7, p. 074308, 2009, publisher: American Institute of Physics.

[5] S. Baruah, M. A. Mahmood, M. T. Z. Myint, T. Bora, and J. Dutta, "Enhanced visible light photocatalysis through fast crystallization of zinc oxide nanorods," *Beilstein journal of nanotechnology*, vol. 1, no. 1, pp. 14–20, 2010, publisher: Beilstein-Institut.

[6] B. Sarkar, A. V. Daware, P. Gupta, K. K. Krishnani, S. Baruah, and S. Bhattacharjee, "Nanoscale wide-band semiconductors for photocatalytic remediation of aquatic pollution," *Environmental Science and Pollution Research*, vol. 24, no. 33, pp. 25 775–25 797, 2017, publisher: Springer.

[7] R. Borgohain, P. K. Boruah, and S. Baruah, "Heavy-metal ion sensor using chitosan capped ZnS quantum dots," *Sensors and Actuators B: Chemical*, vol. 226, pp. 534–539, 2016, publisher: Elsevier.

[8] R. Borgohain, R. Das, B. Mondal, V. Yordsri, C. Thanachayanont, and S. Baruah, "ZnO/ZnS core-shell nanostructures for low-concentration NO 2 sensing at room temperature," *IEEE Sensors Journal*, vol. 18, no. 17, pp. 7203–7208, 2018, publisher: IEEE.

[9] R. Borgohain and S. Baruah, "Development and testing of ZnO nanorods based biosensor on model Gram-positive and gram-negative bacteria," *IEEE Sensors Journal*, vol. 17, no. 9, pp. 2649–2653, 2017, publisher: IEEE.

[10] K. Das and S. Baruah, "Quantum dots for solar energy harvesting." *Current Science (00113891)*, vol. 115, no. 4, 2018.

[11] H. Zheng, Y. Jiang, S. Yang, Y. Zhang, X. Yan, J. Hu, Y. Shi, and B. Zou, "ZnO nanorods array as light absorption antenna for high-gain UV photodetectors," *Journal of Alloys and Compounds*, vol. 812, p. 152158, 2020, publisher: Elsevier.

[12] M. Bashirpour, M. Forouzmehr, S. E. Hosseininejad, M. Kolahdouz, and M. Neshat, "Improvement of terahertz photoconductive antenna using optical antenna array of ZnO nanorods," *Scientific reports*, vol. 9, no. 1, pp. 1–8, 2019, publisher: Nature Publishing Group.

[13] M. Kaushik, R. Niranjan, R. Thangam, B. Madhan, V. Pandiyarasan, C. Ramachandran, D.-H. Oh, and G. D. Venkatasubbu, "Investigations on the antimicrobial activity and wound healing potential of ZnO nanoparticles," *Applied Surface Science*, vol. 479, pp. 1169–1177, 2019, publisher: Elsevier.

[14] S. Baruah and J. Dutta, "pH dependent growth of ZnO nanorods," *Journal of Crystal Growth*, vol. 311, no. 8, pp. 2549–2554, 2009.

[15] D. Li and H. Haneda, "Morphologies of zinc oxide particles and their effects on photocatalysis," *Chemosphere*, vol. 51, no. 2, pp. 129–137, 2003, publisher: Elsevier.

[16] I. J. Peter, E. Praveen, G. Vignesh, and P. Nithiananthi, "ZnO nanostructures with different morphology for enhanced photocatalytic activity," *Materials Research Express*, vol. 4, no. 12, p. 124003, 2017, publisher: IOP Publishing.

[17] S. P. Porras and E. Kenndler, "Are the asserted advantages of organic solvents in capillary electrophoresis real? A critical discussion," *Electrophoresis*, vol. 26, no. 17, pp. 3203–3220, 2005, publisher: Wiley Online Library.