Effect of KOH concentration on morphology of ZnO nanostructures

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Abstract

The effect of concentration of base (KOH) in the precursor solution has been studied on the morphology of ZnO . At low base concentration (0.5M), the ZnO nanoflowers composed of thin nanosheets of thickness about 20 nm have been formed and for higher concentration (1M) an octahedral shape with non-uniform size has been observed. For structural and morphological characterizations respectively, X-ray Diffraction (XRD) and SEM analysis have been performed. Ultraviolet–Visible spectroscopy *(UV-Vis) measurements show a band gap variation of the synthesized ZnO structures. For elemental confirmation,* Energy-Dispersive X-*ray spectroscopy (EDS) measurements have been performed.*

1. Introduction:

In past years, ZnO nanostructures have been extensively reported because of their novel properties such as high aspect ratio and surface to-volume ratio, and promising applications for optical, electronic and photocatalytic devices. [1-2] ZnO have attracted much attention in nanoscience based applications, as an ideal component for nanoscale devices such as memory devices, storage devices [3] due to their wide range of nanostructures like rods, belts, wire, flower-like etc. [4-7]. Moreover, ZnO has many excellent unique properties such as direct band gap (3.37eV), strong excitons energy (60 meV) [8]. Because of these properties it is considered as an attractive material for nanolasers [9], light emitting diodes[10], solar cells [11], gas sensors [12],photocatylists [13], photodetectors [14] etc. Innovative and effective techniques have been carried out to synthesize ZnO nanostructures such as facile solution route, hydrothermal process, chemical vapour deposition etc.[15-18] but most of these techniques mentioned above needs complicated equipment, severe conditions or preparation procedures are complex or also have difficulty in controllability and repeatability. Among these, solution route is considered more prominent because of its low equipment cost, low synthesis temperature, high yield. But still it remains significant challenge to synthesize ZnO nanostructures with controllable morphology, size, good uniformity, high reproducibility from the present techniques.

Here, we report a facile route to synthesize ZnO nanostructure and microstructure at low temperature. As the aqueous solution route is very straightforward, environment-friendly, cheap, easily controllable, good uniformity, and the probability of large scale production. We investigated the influence of concentration of reducing agent on the ZnO structure and morphology.

2. Experimental:

Two aqueous solutions were formed with varying concentrations of KOH. A 0.25M of Zinc Nitrate Hexahydrate ($ZnNO_3.6H_2O$) was mixed with 0.5M and or 1M concentrations of base Potassium Hydroxide (KOH) respectively. Both the aqueous solutions were stirred for 3 hours at room temperature. The products were filtered and washed with deionised (DI) water and C_2H_5OH several times to remove any residuals and then dried at 100 ºC for 3 hours. Field Emission Scanning Electron Microscopy (FE-SEM) was used to examine the morphology and microstructure of the samples. Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed to determine the element composition. UV spectroscopy and XRD were used to determine the band gap of structure of ZnO and the crystallinity of synthesized products.

3. Result And Discussion:

Figure 1(a) and (b) shows the FE-SEM images of the product for molar ratio of Zn^{2+}/OH^{-} equal to 0.25/0.5. The low magnification image indicates that flower-like aggregates of ZnO with multipetals of diameters 1–2 µm having approximately uniform morphologies. From the higher magnification FE-SEM image (Fig. 1(b)), each flower is made up of many thin nanosheets with the non uniform thicknesses (range from about 10 to 50 nm), which are assembled to form the architectures. Figure 2a shows the EDX of as synthesized flower like structure. EDX analysis of as synthesized products demonstrates that product is composed of Zn and O elements. Figure 2b shows the XRD pattern of as synthesized product. The XRD analysis reveals that as synthesized product is crystalline in nature and the diffraction peaks corresponding to (100), (002) and (101) planes of ZnO structure. In addition to these commonly observed orientations, the weak orientations such as (102) and (110) are also observed in XRD pattern. The recorded XRD pattern well matched with the JCPDS 89-1397 and confirm that the flower-like are composed of ZnO. The UV-Vis spectrum as shown in figure 2c shows the absorption peak at 365 nm, indicating the approximate band gap of synthesized flower-like nanostructures to be 3.4eV.

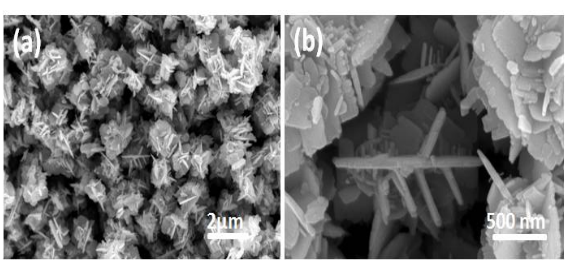
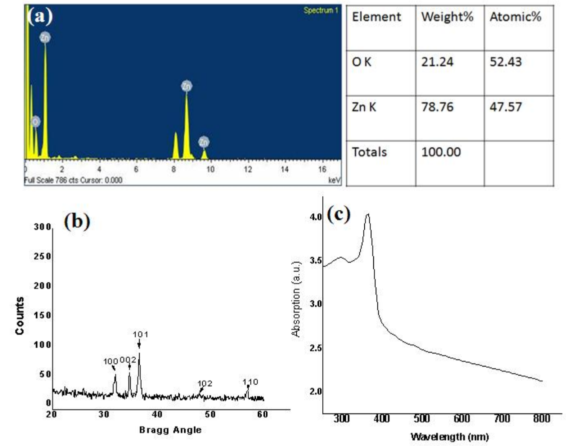


Figure 1 SEM images of flower like structure obtained when molar ratio of Zn^{2+}/OH^{-} is 0.25/0.5. (a) shows flower like structure with uniformity and (b) higher magnified image shows flower consist of sheets.



Element	Weight%	Atomic%
O K	21.24	52.43
Zn K	78.76	47.57
Totals	100.00	

Figure 2 (a) EDX spectrum and table shows product comprising of Zn and O elements only, (b) XRD pattern for ZnO flower like structure (c) UV-Vis spectrum for the flower like structure.

Effect of concentration on morphology of ZnO

The experiment showed the existence of hydroxide ion played an important role in the formation of ZnO structures. It is found that the morphologies of the ZnO structures are sensitive to the amount of KOH. Figure 3 shows the morphological change of the product with different concentrations of KOH. Figure 3 shows the FE-SEM image if the obtained ZnO structure formed for the molar ratio of Zn^{2+}/OH^{-} equal to 0.25/1. The octahedral-like structure of micrometer range is observed. This may due to the more basic nature of the solution due to which recrystallization occurs which give rise to microstructure. The size of the particles goes on increasing with increase in PH of the solution [19]. Therefore, it could be speculated that amount of KOH in solution can adjust the ZnO crystal growth and facilitate the structure nucleation and growth, which may reduce the interfacial activation energy.

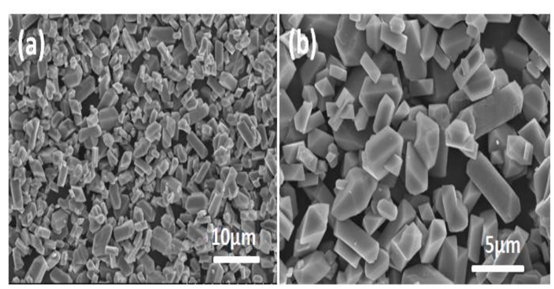


Figure 3 SEM images of ZnO octahedral-like microstructure ((a) at lower magnification and (b) at higher

magnification) synthesized when molar ratio of Zn^{2+}/OH^{-} is 0.25/1.

4. Conclusion:

ZnO microstructure and nanostructure were obtained by changing concentration of base (KOH) in a solution. At high concentration (Zn^{2+}/OH^{-}:: 0.25/1) of KOH, we observed octahedral shape microstructure while at low concentration (Zn^{2+}/OH^{-} ::0.25/0.5) the flower like structure composed of nanosheet of thickness of 20 nm have been observed. The synthesized flower-like structure has band gap of 3.4eV and UV-Vis spectrum shows absorption peak at 365 nm. XRD pattern demonstrates synthesized product has crystalline nature and EDX give the ZnO composition of synthesized flower-like structure.

Reference:

[1] U. Ozgur, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho and H. Morkoc, "A comprehensive review of ZnO materials and devices" , *J. Appl. Phys.* 98, 2005, 041301.

[2] A. B. Djurišić, X. Chen, Y. H. Leung and A. M. Ching Ng, "ZnO nanostructures: growth, properties and applications" , *J. Mater. Chem.* 22, 2012, 6526-6535.

[3] Z. R. Tian, J. A. Voigt, J. Liu, B. Mckenzie, M. J. Mcdermott, M. A. Rodriguez, H. Konishi and H. Xu, " Complex and oriented ZnO nanostructures" , *Nature Materials* 2, 2003, 821 - 826.

[4] B. Ling, Y. Wang, X. W. Sun, Z. L. Dong, and N. X. Yang, " Low-Temperature Facile Synthesis of Zno Rod Arrays And Their Device Applications", IEEE *J. Sel. Top. Quant. Electron.* 17, 2011.

[5] M. Li, Y. J. Su, W. Y. Chu, L. J. Qiao, A. A. Volinsky and G. Kravchenko, "Local piezoelectric effect on single crystal ZnO microbelt transverse I-V characteristics", *Appl. Phys. Lett.* 98, 2011, 082105.

[6] X. Wang, J. Song and Z. L.Wang, "Nanowire and nanobelt arrays of zinc oxide from synthesis to properties and to novel devices", *J. Mater. Chem.* 17, 2007, 711-720.

[7] H. Zhang , R. Wu , Z. Chen , G. Liu , Z. Zhang and Z. Jiao, "Self-assembly fabrication of 3D flower-like ZnO hierarchical nanostructures and their gas sensing properties", *CrystEngComm* 14, 2012, 1775-1782.

[8] Z. L. Wang , "Zinc oxide nanostructures: growth, properties and applications", *J. Phys.: Condens. Matter* 16, 2004.

[9] S. Chu, G. Wang, W. Zhou, Y. Lin, L. Chernyak, J. Zhao, J. Kong, L. Li, J. Ren and J. Liu, "Electrically pumped waveguide lasing from ZnO nanowires", *Nature Nanotechnology* 6, 2011, 506–510.

[10] J. H. Na, M. Kitamura, M. Arita, and Y. Arakawa, "Hybrid p-n junction light-emitting diodes based on sputtered ZnO and organic semiconductors", Appl. Phys. Lett. 95, 2009, Article ID 253303.

[11] L. Li, T. Zhai, Y. Bando, and D. Golberg, "Recent progress of one-dimensional ZnO nanostructured solar cells", *Nano Energ.* 1, 2012, 91–106.

[12] W. Guo, T. Liu, H. Zhang, R. Sun, Y. Chen, W. Zeng, and Z. Wang, "Gas-sensing performance enhancement in ZnO nanostructures by hierarchical morphology", *Sensor Actuat. B-Chem.* 166–167, 2012, 492–499.

[13] M. A. Kanjwal, F. A. Sheikh, N. A. M. Barakat, X. Li, H. Y. Kim, and I. S. Chronakis, "Zinc oxide's hierarchical nanostructure and its photocatalytic properties", *Appl. Surf. Sci. 258*, 2012, 3695-3702.

[14] C. Y. Chen, M. W. Chen, C. Y. Hsu, D. H. Lien, M. J. Chen, H. He, "Enhanced Recovery Speed of Nanostructured Zno Photodetectors Using Nanobelt Networks", IEEE *J. Sel. Top. Quant. Electron.* 18, 2012.

[15] J. Wang, H. Luo, T. Chen and Z. Yuan,"A facile shape-selective growth of ZnO nanotips and graded nanowires from its oriented nanorods in a saturated ZnS solution", *Nanotechnology* 21, 2010, 505603.

[16] S. L. Romero, P. Santiago, D. Mendoza, "Assisted-hydrothermal Synthesis and Characterization of Flower-like ZnO Nanostructures", *Adv. Sci. Lett.* 5, 2012, pp. 283.

[17] M. Zhou, C. Feng, C. Wu, W. Ma, and L. Cai, "Superhydrophobic multi-scale ZnO nanostructures fabricated by chemical vapor deposition method", *J. Nanosci. Nanotechnol.* 9, 2009, 4211-4.

[18] D. Raoufi, "Synthesis and microstructural properties of ZnO nanoparticles prepared by precipitation method", *Renew. Energ.* 50, 2013, Pages 932–937.

[19] N. Singh, Dhruvashi, D. Kaur, R. M. Mehra and A. Kapoor, "Effect of Ageing in Structural Properties of ZnO Nanoparticles with pH Variation for Application in Solar Cells", *The Open Renew. Energ. Journal* 5, 2012, 15-18.