Hindawi
Journal of Chemistry
Volume 2017, Article ID 1728345, 7 pages
https://doi.org/10.1155/2017/1728345

Research Article

Effect of Surfactant on Growth of ZnO Nanodumbbells and Their Characterization

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Received 15 March 2017; Accepted 22 May 2017; Published 25 July 2017

Academic Editor: Renal Backov

We report the controlled synthesis of dumbbell shaped ZnO micro/nanostructures using anionic surfactant sodium dodecyl sulphate (SDS) by simple one-step hydrothermal method. The morphology changes of ZnO were characterized by using scanning electron microscopy, X-ray diffraction, and energy dispersive spectroscopy. It is found that the size of the dumbbell increased with increase in concentration of SDS. Systematic growth mechanism with increase of concentration of SDS polymer is studied. Our results will help in the growing face selective ZnO for many functional applications.

1. Introduction

Zinc oxide (ZnO) is an important II-VI group semiconductor material. ZnO has a wide direct-band gap of 3.37 eV and high-exciton-binding energy of 60 mV at room temperature. ZnO has been extensively studied because of its fascinating wide range of applications such as chemical sensors and biosensors, piezoelectricity, optoelectronics, photocatalysis, and photoelectrochemical water splitting [1–8]. In many of the applications, ZnO functional properties are highly affected by the morphology of the nanostructure. In recent years, various research groups have reported the formation of different types of morphologies using surfactants. Surfactants (cationic, anionic) act as growth-directing agents in the reaction and show a dramatic effect on the shape and size of the ZnO nanostructures. Zhang et al. used polyvinyl pyrrolidone (PVP) as a growth directing reagent for preparing different type of ZnO morphology [9]. Tang et al. used surfactant cetyltrimethylammonium bromide (CTAB) for growing Zinc-HDS mesocrystal sheets [10]. In recent period, ZnO nanodisks and dumbbells shaped morphology have gained interest due to their potential application in the field of catalysis due to their face selective adsorption of various gases [11–13]. Thus, face selective growth of ZnO nanostructure can enhance the many application properties.

In this paper, we report the growth of ZnO nano/microdumbbell nanostructures using SDS by simple one-step hydrothermal process. The effect of SDS concentration on the morphology of ZnO nanostructures has been studied.

2. Experimental Section

All the chemicals were of analytical reagent grade purchased from Sigma Aldrich and used as received without further purification. In a typical experimental procedure, 1 g of zinc nitrate hexahydrate $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved in 50 ml of deionized water in a beaker under magnetic stirring and 0.1 g of sodium dodecyl sulphate (SDS) anionic polymer was added. In this solution, 2 ml NH_4OH solution was added drop by drop under vigorous stirring. The solutions were transferred to a 50 ml autoclave and placed in a thermal oven for 10 hours at 150°C. After cooling, the collected powder was washed with ethanol for 3 times and placed in oven for drying at 80°C overnight. To study the influence of SDS in the morphology, different amount of SDS was varied from 0.1 g to 0.5 g. Surface morphology of the ZnO nanostructures was investigated by field emission scanning electron microscopy (FESEM, Hitachi S-4800). The structural properties were investigated by X-ray diffraction (XRD, Rigaku D/MAX-RC) using Cu Kα radiation with a Ni filter.

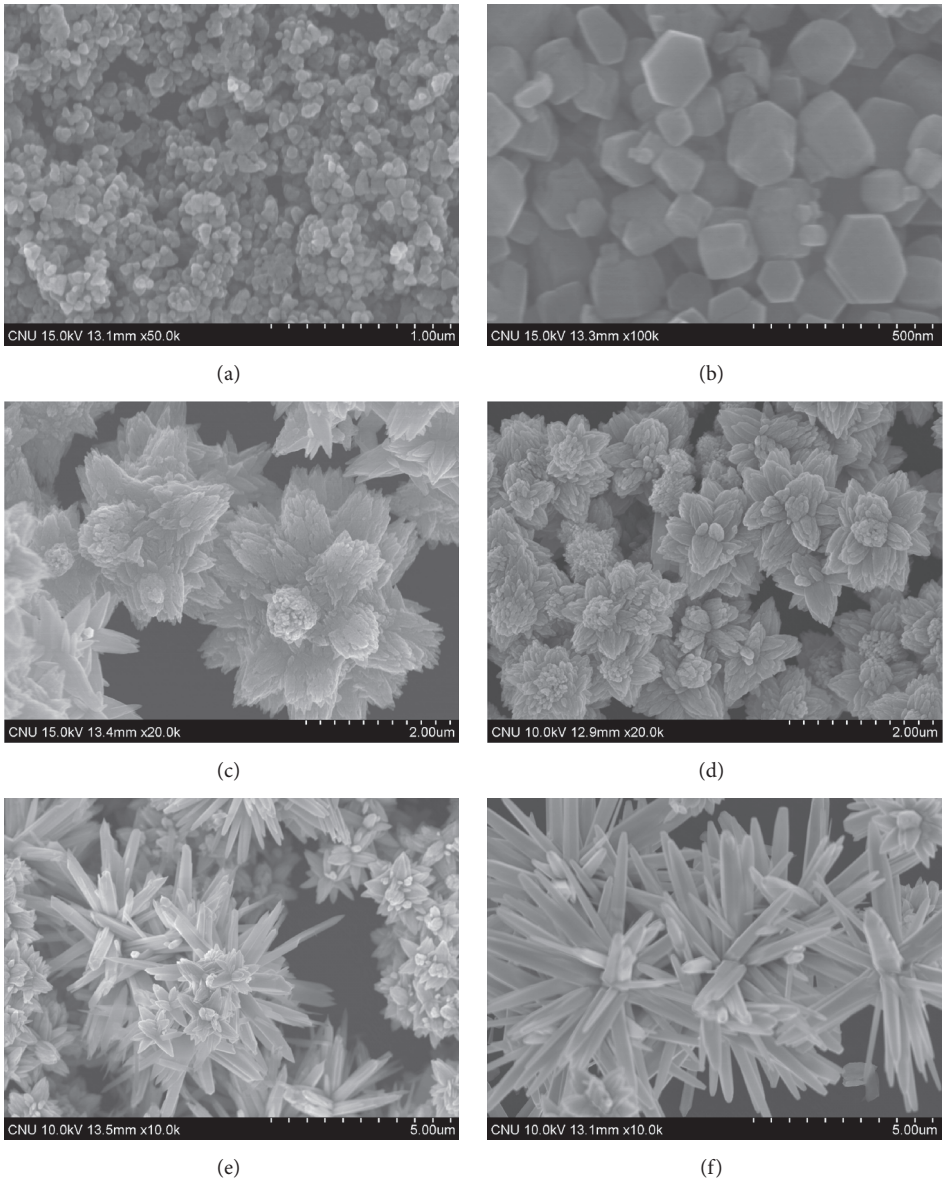


Figure 1: Typical FESEM images of ZnO nanostructures grown with different NH_4OH concentrations of (a) 0.1 ml, (b) 0.5 ml, (c) 1.0 ml, (d) 2.0 ml, (e) 2.5 ml, and (f) 3.0 ml and growth temperature and growth time of 150°C and 10 hours, respectively.

3. Results and Discussion

The shape and size controlled growth of ZnO in a hydrothermal process is affected by many factors such as temperature, concentration of precursors, surfactants, organic solvents, and growth time. To have proper understanding of SDS polymer effect on ZnO growth, first we studied the growth of ZnO nanostructures with effect to NH_4OH concentration only and with no SDS. Figure 1 shows the FESEM of different ZnO nanostructures obtained with various concentrations of NH_4OH, for 10-hour growth time. It can be clearly seen that with increase in NH_4OH concentration morphology changes from nanoparticles to nanorods. The size of the nanoparticles ranges within Avg. 50 nm~70 nm. Figure 1(a) shows the images of nanoparticles obtained at 0.5 ml of NH_4OH, and Avg. particles sizes are ranges within 200 nm~300 nm. Further increase in NH_4OH concertation in the solution morphology changes from nanoflowers. Figures 1(c)–1(f) show steady grow of nanoflowers with increase in the length of the rods, with Avg. nanorods size from 1 μm, 1.5 μm, 2 μm, and 3 μm, respectively.

The plot of pH of the solution with volume of NH_4OH is shown in Figure 2. It can be noted that the pH of the solution increased with NH_4OH concentration. Figure 3 shows the XRD patterns of the grown ZnO nanostructures with different NH_4OH concentration in the solution. All the diffraction peaks can be indexed to know ZnO hexagonal wurtzite structure with major peaks of (100), (002), and (101), respectively. Furthermore, we studied the effect of SDS polymer with change in NH_4OH concentration on ZnO

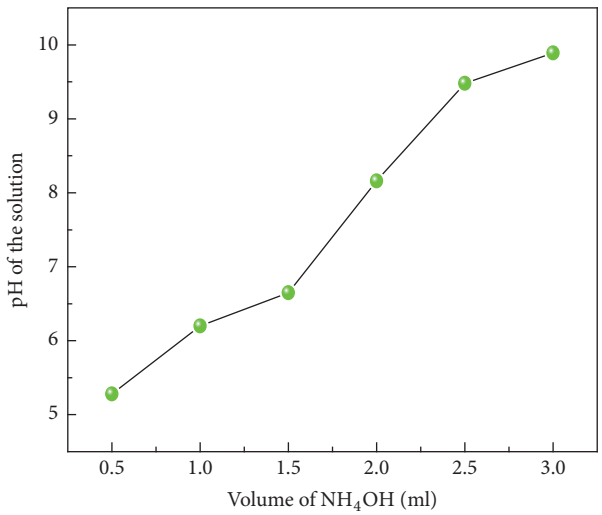


Figure 2: The plot of pH versus NH_4OH concentration.

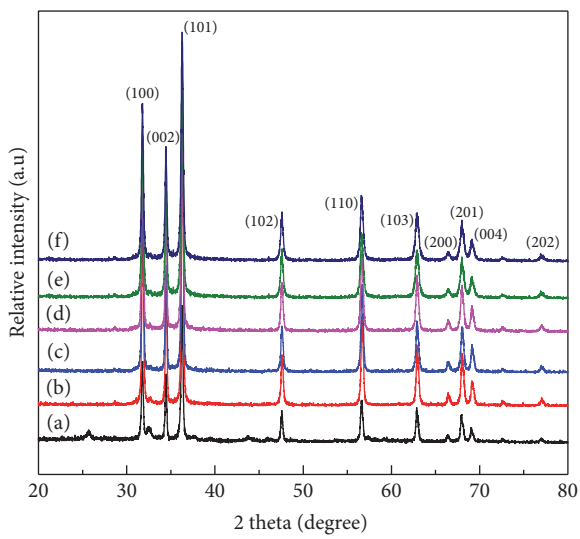
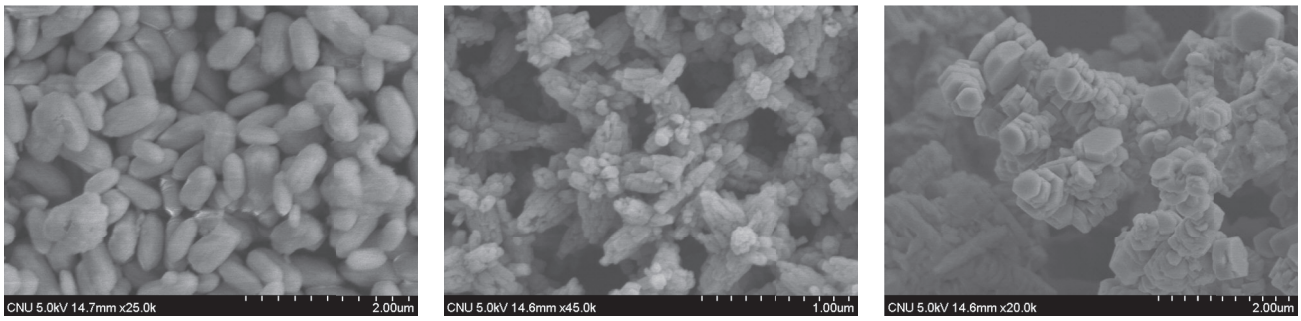


Figure 3: XRD profile of ZnO nanostructures grown with different NH_4OH concentrations of (a) 0.1 ml, (b) 0.5 ml, (c) 1.0 ml, (d) 2.0 ml, (e) 2.5 ml, and (f) 3 ml.

nanostructures. Figure 4 shows the FESEM images of ZnO nanostructures grown with fixed SDS (0.1 g) and different NH_4OH concentrations of (a) 0.1 ml, (b) 1.0 ml, and (f) 2.0 ml for 10-hour growth time and 150°C growth temperature. We can see that the SDS polymer affects the morphology different from the only NH_4OH grown ZnO nanostructures. Figure 4(a) shows the rice type morphology, with Avg. length and diameter of 600 nm and 200 nm, respectively. Figure 4(b) shows the agglomeration of rice beads into flower petals morphology. It is interesting to note that the morphology of rice beads changes to dumbbell shaped morphology as shown in Figure 4(c). To explore more on dumbbell shaped morphology of ZnO in our experiment, we fixed the temperature and concentration of zinc nitrate and NH_4OH, changed the SDS amount in the solution, and studied the effect on the final morphology of ZnO. Figure 5 shows the FESEM images of ZnO nanostructures prepared in the experiment. Figure 5(a) shows the ZnO nanoflowers obtained without using any surfactant in the reaction. The nanoflowers basically consist of nanorods. The nanorods were grown to be 2 μm in length and 300 nm in diameter. The morphology of the ZnO nanoflowers changed to nanodumbbells on addition of SDS surfactant. Figures 5(b)–5(f) show the FESEM images of nanodumbbells obtained at different concentration of SDS. The size of the dumbbells increased with the increase in the concentration of the SDS from 0.1 g to 0.5 g. It was noticed that in Figure 5(b) when the concentration of SDS is 0.1 g, the Avg. size of dumbbell is 900 nm and 2.5 μm in diameter and height, respectively. In Figure 5(c), with increase in SDS to 0.2 g, it was noticed that the diameter of nanodumbbell increased to 2 μm and the change in height of the dumbbell was 2.8 μm in length. At concentration 0.3 g of SDS, as shown in Figure 5(d), the diameter of nanodumbbell increased to 2.8 μm in size and there was no considerable change in length of nanodumbbell, which specifies decrease in the aspect ratio. In further addition of 0.4 g SDS in the solution we obtained dumbbells with 4.4 μm and 6.5 μm in length and diameter, indicating growth along the side (100) faces increasing as shown in Figure 5(e). And finally at higher concentration 0.5 g of SDS, perfect hexagonal cylinder type morphology was observed. The hexagonal cylinders were highly symmetrical with 10 μm × 10 μm heights and diameters, respectively. Figure 6 shows the XRD patterns of the grown ZnO nanostructures with and without the addition of SDS polymer in the solution. All the diffraction peaks can be indexed to know hexagonal wurtzite structure. The results indicated that the nanodumbbells consist of pure crystalline phase and the peak intensities of the prepared ZnO nanodumbbells increased with the concentration of the SDS indicating the formation of greater enhancement of crystallization. It is observed that the peak intensities of the nanoflowers are higher than the dumbbells structures.

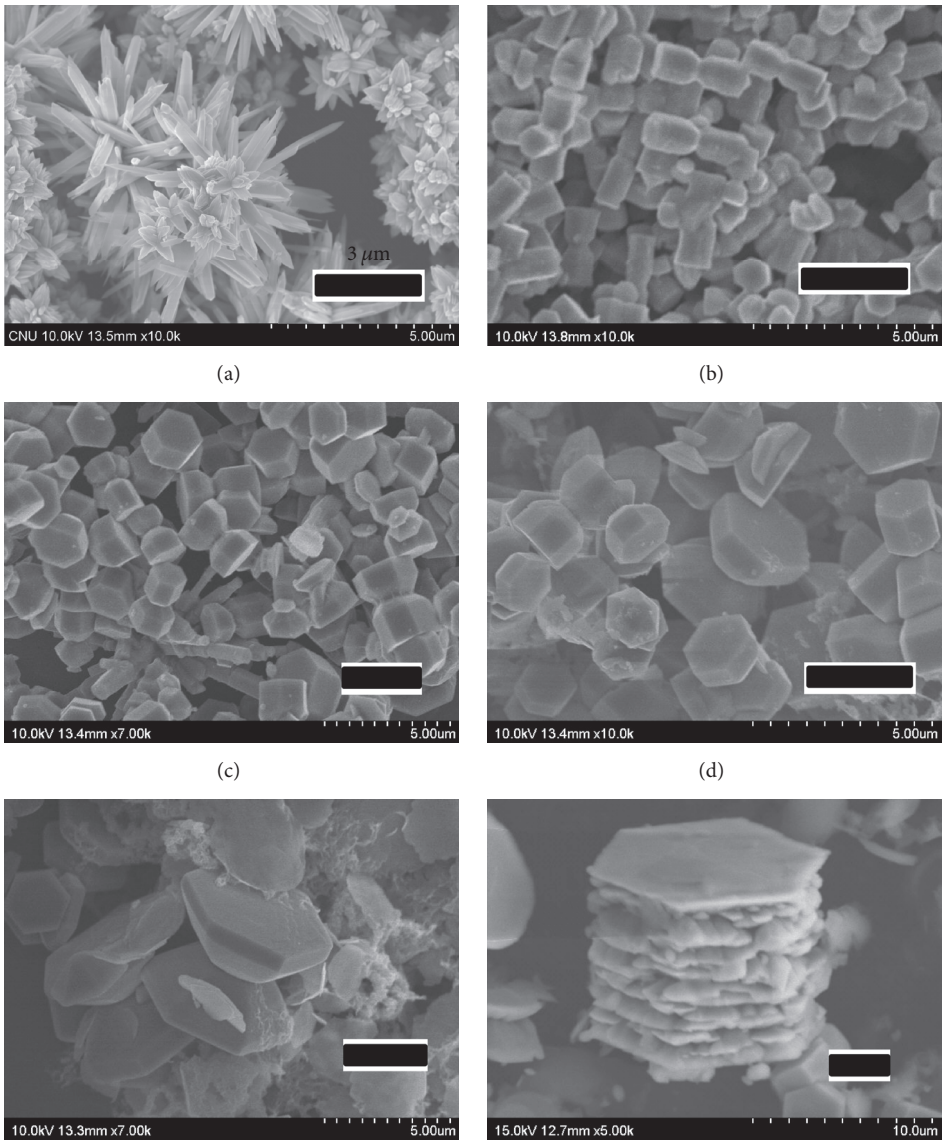
It is evident that the SDS played important role in the formation of nanodumbbells and act as growth template. $CH_3(CH_2)_{11}OSO_3Na$ (SDS) in aqueous solution ionize into Na^+ (S) and $CH_3(CH_2)_{11}OSO_3^-$ (DS^-) and attack on the polar faces of the ZnO and inhibit the growth along [0001] directions forming nanodumbbells. Without SDS, the formation of nanoflowers can be explained by Wolf's principle, a crystal growing under equilibrium conditions, crystal faces with maximum specific surface energy *(σhkl)* values grow at maximum rate values compared to their faces with minimum *σhkl*. In case of ZnO, the polar (0001) face of ZnO has high surface energy compared to other faces [14]. ZnO grows faster in [0001] direction forming nanoflowers type morphology when the reaction was performed without the surfactant.

The formation of nanodumbbells morphology in addition of SDS can be clearly observed. Figure 7 shows the typical shape of a crystallization curve for a ZnO where the evolution of the crystal-length is plotted as a function of the concentration of SDS. The growth rate and nucleation of crystal are greatly affected by the SDS. Formation of dumbbell shape morphology was demonstrated by various researchers [15–17]. Wang et al. reported the dumbbell-like twinning crystal,



(a) (b) (c)

Figure 4: Typical FESEM images of ZnO nanostructures grown with SDS polymer (0.1 g) and different NH_4OH concentrations of (a) 0.1 ml, (b) 1.0 ml, and (c) 2.0 ml and growth temperature and growth time of 150°C and 10 hours, respectively.



(a) (b) (c) (d) (e) (f)

Figure 5: Typical FESEM images of ZnO nanostructures grown with different SDS surfactant concentrations of (a) 0 g, (b) 0.1 g, (c) 0.2 g, (d) 0.3 g, (e) 0.4 g, and (f) 0.5 g.

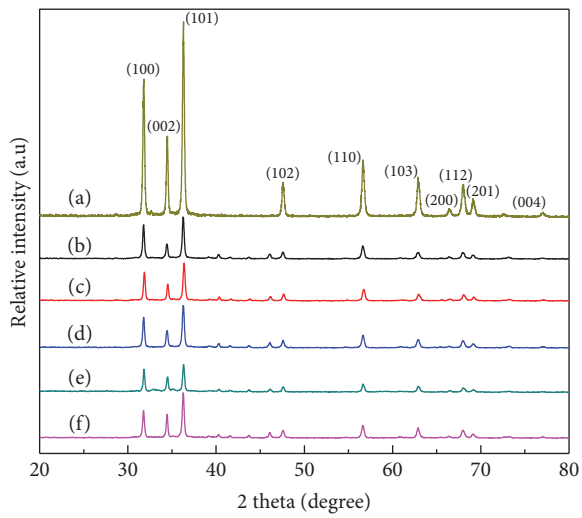


Figure 6: X-ray diffraction plot of ZnO nanostructures grown with different SDS surfactant concentrations of (a) 0 g, (b) 0.1 g, (c) 0.2 g, (d) 0.3 g, (e) 0.4 g, and (f) 0.5 g.

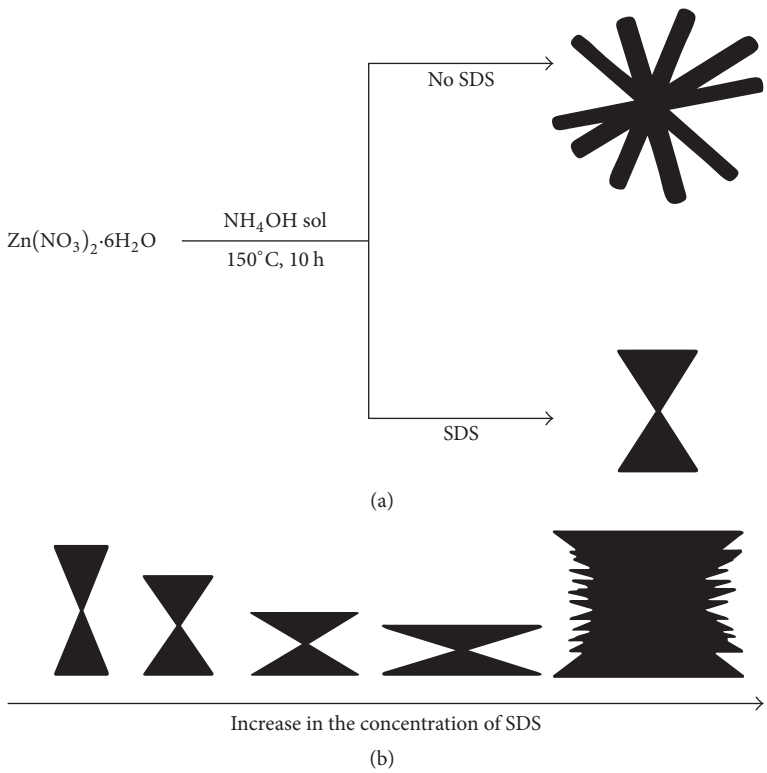
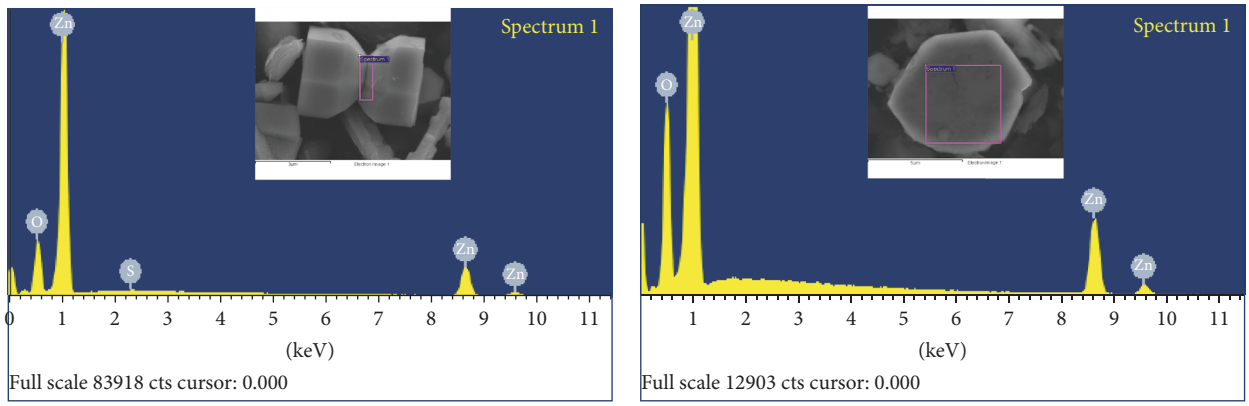


Figure 7: (a) Schematic presentation of formation of ZnO nanodumbbells and (b) changes of nanodumbbells size as function of amount of SDS surfactant.

in which ZnO_4^{6-} growth units bond bridge between them in the presence of K^+ or Na^+ ions and grow along the [0001] direction [18]. Li et al. explained the possibility of formation of dumbbell by the electrostatic attraction between ZnO nuclei along (0001) face and the negatively charged sulphate groups of the SDS and slows the growth rate, since crystal will grow along the (000-1) face [19], which according to ZnO velocities of growth rate of faces is the slowest face [20]. On the basis of the experimental results we obtained, we think that the growth of the nanodumbbell is uneven, and both dumbbells are not equal in size. In our case, twining starts from formation of growth template by SDS and dumbbell size increased with SDS concentration [21]. According to Shi et al., NMR experiments show that, with increasing in the temperature, SDS aggregates to form large uniform circular disks and the size of the disk increases with the concentration of the



(a) (b)

Figure 8: EDX spectra of ZnO nanodumbbells measured at different surfaces: (a) the twin junction and (b) basal plan of ZnO dumbbell.

SDS in the solution. In this process, disk shapes SD-(SO_4^{2-}) get attracted to the (0001) face of ZnO from a twin structure and the SD- is sandwiched between two (0001) faces and ZnO crystal growth takes place along (000-1) faces. To confirm it and to see if there is any sulfur incorporation in the twin junction, we observed the EDX spectra. Figure 8 shows the EDX spectra of twin junction and (000-1) faces of ZnO dumbbell. It was noticed that sulfur (atomic% 0.3) was present in the twin junction and EDX spectra taken on the (000-1) faces, we only see Zn and O composition, and atomic% of O (56%) is more that Zn (43%), which indicates (000-1) face. The growth takes place along (000-1) faces and surface adsorbed Na^+ ions reduce the growth rate of the faces by hindering the steps on the crystal surface, thereby increasing the surface area of the hindered face, finally forming dumbbells.

4. Conclusions

ZnO nanodumbbells nano/macrostructures were grown with the help of anionic surfactant sodium dodecyl sulphate (SDS). It is observed that SDS affects the ZnO morphology by selective adsorption on the crystal faces and size selective growth of nanodumbbells can be grown by controlling the SDS concentration. Our approach can be a novel way for growing ZnO dumbbells with different size for a wide range of applications.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This study was fully funded by Kumoh National Institute of Technology, Republic of Korea. The authors would like to acknowledge the support of Ministry of Trade, Industry and Energy (MOTIE) Project 10063553 in 2016. The authors would also like to acknowledge and are thankful to WC 300 Project by Business for Global Cooperative R&D by Korea Small and Medium Business Administration in 2015.

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