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REVIEW ARTICLE

Nano ZnO structures synthesized in presence of anionic and cationic surfactant under hydrothermal process

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Abstract Uniform ZnO nano structures are synthesized in the presence of anionic surfactant, sodium dodecyl benzene sulfonate (SDBS) and cationic surfactant, cetyl tri methyl ammonium bromide (CTAB) at 100 °C using NaOH as the reactant. The particle size, morphology and structure of the nano ZnO particles are collected by X-ray diffraction, scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectra. Rod and cone shaped ZnO nano structure is observed. It may vary in morphology from pure ZnO structure due to the presence of surfactants. The results show that there is an extrinsic relation between the morphology of the samples. Based on the relation, we proposed that there might be two kinds of interactions between SDBS and CTAB with ZnO particles, i.e., inter- and intra-interactions.

Keywords Sol–gel growth · Infrared spectroscopy · X-ray diffraction · Microporous materials · Nanostructures

Introduction

Zinc oxide (ZnO) is a versatile material. Nanosized ZnO crystals have attracted a great deal of attention because of their size-dependent opto-electronic properties. A chemical synthesis of nano-sized ZnO crystals in aqueous solution, which was suitable for a large-scale production, has been developed (Usui 2009).

During the past decades, reports on the synthesis of various structures of ZnO have increased rapidly, viz., rods, wires, tubes, towers, stars, dendrite, flower like, etc. These structures are expected to have more potential applications in building functional electronic devices with special architectures and distinctive opto-electronic properties. Therefore, it is attempted to synthesize ZnO nano or microstructures in a controllable shape and size to meet the demand and to explore the potentials of ZnO. It is still a challenging task for material scientists, to directly fabricate large-scale ZnO crystals with controlled morphology (Xie et al. 2009; Aslani et al. 2011; Ahmed and Al-Owais 2012). In recent years, many researchers are inclined to prepare ZnO crystals at a low temperature to reduce energy consumption, improve large-scale production, and obtain special properties (Gu et al. 2012).

In recent years, many researchers are inclined to prepare ZnO crystals at a low temperature to reduce energy consumption, improve large-scale production, and obtain special properties. However, synthesis of ZnO crystals generally need a catalyst (such as PVP, CTAB, and SDBS) and long reaction time because of the poor ZnO crystallization at a low temperature. The effect of SDBS and CTAB on the ZnO nucleation has been investigated in detail by many researchers. They found that the ZnO nucleation was promoted (or) depressed with a different amount of surfactant at certain temperature.

In the present study, ZnO nano rods and nanocones were synthesized hydrothermally using SDBS and CTAB as a surfactant. The results suggested that, using SDBS and CTAB as a precursor, morphology of ZnO could be changed in hydrothermal process.

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Preparation

Preparation of ZnO with surfactant (SDBS and CTAB)

A typical hydrothermal synthesis procedure is depicted as follows: molar ratio of $Zn^{2+}/OH^{-} = 1{:}6$ and 1:7. 4 mol L^{-1} NaOH (30 ml/35 ml) was added drop wise into 20 ml of 1 mol L^{-1} $ZnCl_2$ aqueous solution with intense magnetic string at room temperature. Then 5 ml SDBS/CTAB (0.2 mol) and 45 ml/40 ml distilled water were introduced into the above mixture to get a 100 ml clear solution. After that, the 1:6 solutions were kept at room temperature for 1.5 h under strong stirring to obtain solution with precipitate.

The 1:7 solutions was aged for 1.5 h under rest position and then the solution was kept at room temperature for 1.5 h under strong stirring to obtain white precipitate. The precipitate-containing solution was transferred to ground-glass stopped conical flask and aged at 100 °C for 4 h. For comparison, two parallel experiments were carried out by getting rid. The white products deposited on the bottom of the conical flask were collected, washed with distilled water for several times, and dried in at 100 °C in air.

Instrumental analyses

The phase structure of synthesized ZnO was performed using X-ray diffraction (Philips PW1370) with Cukα ($\lambda = 1.54056$), operating at 35 kV and a scanning rate of 0.02 %. The chemical structure of the prepared particles was performed using a Fourier transform infrared (FTIR) Raman spectrometer (Nicolet Avatar impact 330 series) was used for measuring the ultraviolet absorption spectra in the region of 400–4,000 cm^{-1} frequency range. The samples were characterized with a scanning electron microscope (SEM, JSM–5610 LV).

Result and discussion

It has been well known that the use of additives leads to dramatic changes in crystal growth and these effects have been investigated by many research groups. However, the effects of anionic and cationic surfactants in an aqueous solution on the crystal growth of ZnO nanostructure are not clearly explained. In this study, we used anionic and cationic surfactants as additives which have the same length of alkyl chain, but different counter-ion (head groups) such as SDBS and CTAB, and investigate the effects of counter-ions in an anionic and cationic surfactant solution when ZnO nanostructures.

The XRD patterns of ZnO nanorods prepared by the hydrothermal process using SDBS are shown in Fig. 1. All diffraction peaks are well indexed as the ZnO nanostructure with lattice parameters $a = 3.25$A and $c = 5.21$A, which are consistent with the values in JCPDS card No. 36-1451. Compared to the standard card patterns, the (002) diffraction peak exhibited the growth orientation of ZnO nanorods along the c-axis ([100] direction) and the strong (100) and (0010) peaks indicate a high aspect ratio of the ZnO nanorod. The sharp and narrow diffraction peaks indicate that the ZnO nanostructure has good crystallinity. Larger crystalline size of 32.82–59.10 nm is obtained for the ZnO crystals in the SDBS solution. The difference in the crystalline size indicates that there are some differences in size in morphology of the ZnO crystals (Sridevi and Rajendran 2009; Maiti et al. 2008).

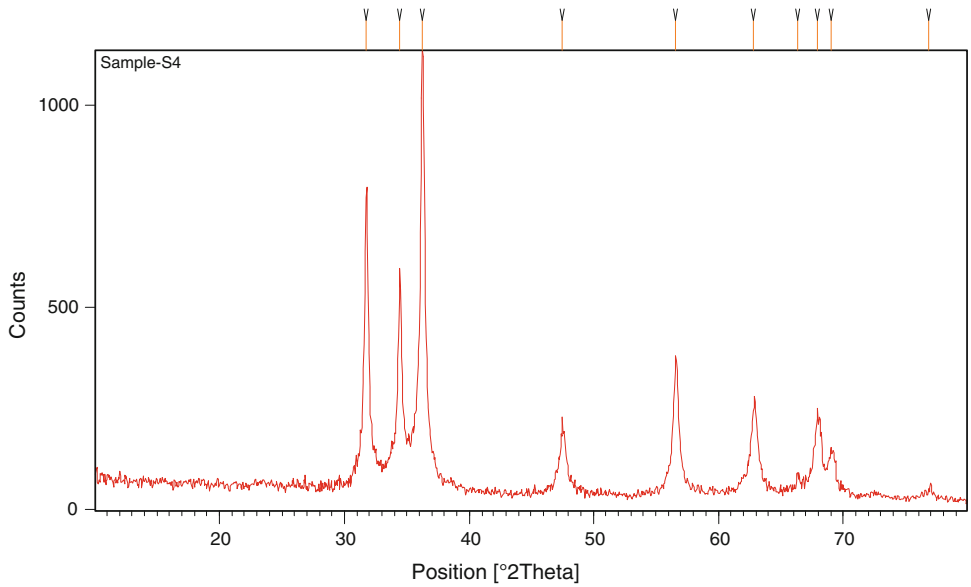

Fig. 1 X-ray powder diffraction pattern of ZnO-SDBS

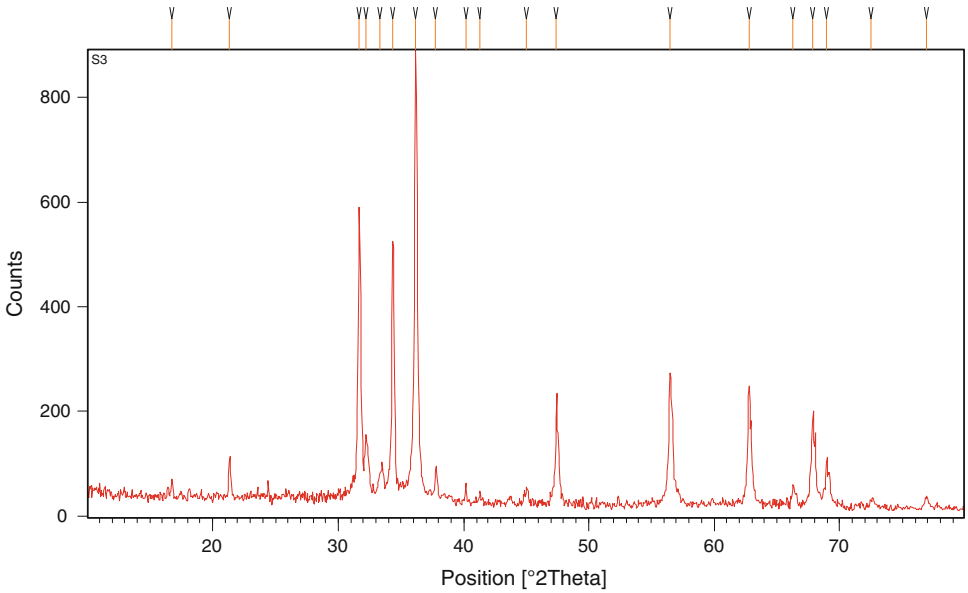

Fig. 2 X-ray powder diffraction pattern of ZnO-CTAB

Table 1 Particle size estimated from the diffraction spectrum of ZnO + SDBS and ZnO + CTAB by using FWHM

	Pos. [°2Th.]	FWHM [°2Th.]	d-spacing [Å]	Particle size
ZnO + SDBS	20.6137	0.1367	4.30528	59.10
	21.1082	0.1610	4.20551	50.22
	23.5458	0.1539	3.77536	52.76
	25.2755	0.1918	3.52078	42.47
	26.7888	0.2331	3.32523	35.05
	30.2081	0.1446	2.95618	56.94
	32.8975	0.2330	2.72039	35.57
	34.8127	0.2072	2.57499	40.20
	39.4172	0.1608	2.28415	52.51
	40.2453	0.1596	2.23904	53.04
	41.9742	0.2464	2.15073	34.55
	46.2596	0.2819	1.96097	30.66
	48.1387	0.2293	1.88872	37.97
	55.1868	0.2262	1.66302	39.65
	59.9677	0.2206	1.54135	41.60
	61.5801	0.2931	1.50480	31.57
	65.5546	0.2380	1.42286	39.72
	68.2215	0.2925	1.37359	32.82
ZnO + CTAB	20.5302	0.1741	4.32259	46.40
	31.6162	0.2803	2.82765	29.47
	32.2026	0.3926	2.77749	21.07
	37.7358	0.2771	2.38197	30.31
	41.1955	0.2191	2.18956	38.76
	61.6002	0.3538	1.50436	26.16

Figure 2 shows the typical XRD patterns of ZnO synthesized using CTAB with the higher and narrower diffraction peaks implied a good crystallization of ZnO (Geetha and Thilagavathi 2010). The sharp diffraction peaks indicated the good crystallinity of the prepared crystals (Sheng-Yuan and Tser-Min 2000; Li et al. 2008; Zhai et al. 2008; Yiamsawas et al. 2009). Larger crystalline size of 21.16–39.05 nm is obtained for the ZnO crystals. The crystal size of the ZnO nanoparticles calculated from FWHM was tabulated in Table 1.

$Zn(OH)_2$ is indeed a good adsorbent and possibly adsorbs the SDBS molecules. This adsorption can be detected by FTIR spectroscopy. The comparison of the IR transmittance spectra of SDBS and CTAB is displayed in Fig. 3a. The band at around 1,200 cm^{-1} is assigned to an S=O stretching vibration of $–SO_4$ from SDBS molecules. The peaks at around 2,926, 2,850, 1,469, and 1,083 cm^{-1} are due to C–H stretching and bending. A broadening peak at around 3,440 cm^{-1} is proposed to be due to H–O–H stretching. The bands at asymmetric C=O stretching of zinc chloride, O–H bending of hydroxyl groups at 567 cm^{-1} of ZnO. The peak at 470 cm^{-1} is a characteristic peak of Zn–O stretching.

The FTIR spectrum of synthetic ZnO powder (Fig. 3b) shows main absorption bands due to O–H stretching of hydroxyl group at 3,401 cm^{-1}, asymmetric and symmetric C=O stretching of Zinc acetate at 1,634 and 1,506 cm^{-1}, O–H bending of hydroxyl group at 569 cm^{-1}, and Zn–O stretching of ZnO at 428 cm^{-1}. These data are similar to the results of Suwanboon (2008) and Hong-xia et al. (2011).

Based on these images, the morphologies and size of each sample varied depending on the counter-ions of the anionic and cationic surfactants. In particular, the edge morphologies of individual ZnO nanorods and nanocones were synthesized into totally different shapes (see inset images of Fig. 4). SEM images of the prepared ZnO with

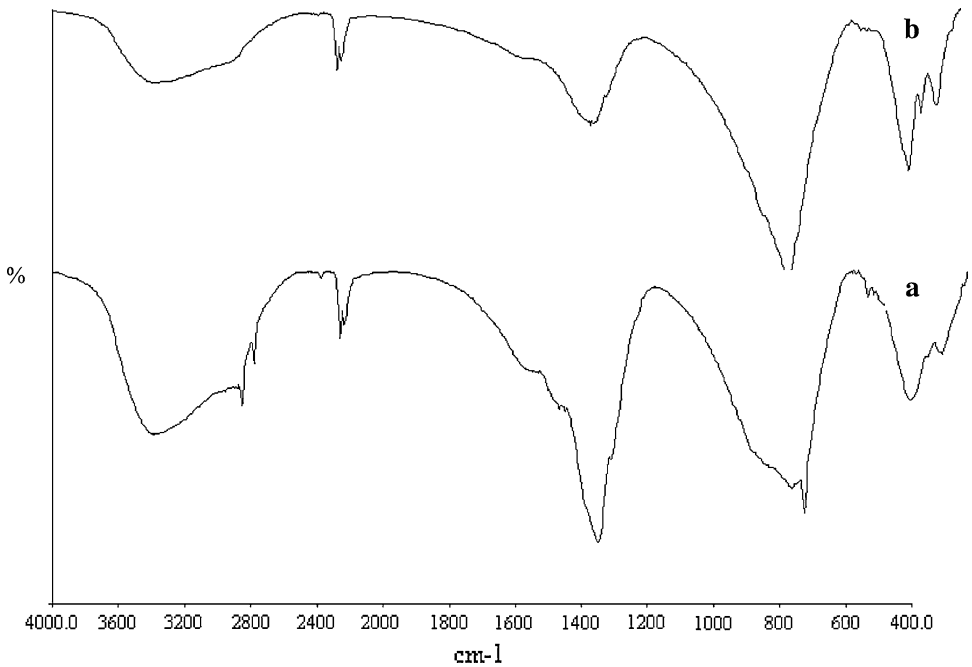

Fig. 3 FTIR spectra of ZnO nanostructures synthezied with SDBS (**a**) and CTAB (**b**)

SDBS samples are shown in Fig. 4. Figure 4a shows the SEM image of the ZnO nanorods rich area. It is found that the products are composed of well-defined rod like structures on large scale. All the rods are highly oriented and the morphology of the branch rods like structure is hexagonal which can be seen clearly from the amplified image for 10, 5, 4, 3, 2, 1 μm and 500 nm in Fig. 4a–d. The average top, middle, and bottom width of the obelisk-like rods have the equal diameter and average length around 3 and 2 μm is shown in Fig. 4c.

The shape of pure ZnO materials are also affected by surfactant in the synthesis with the presence of SDBS, the morphologies of ZnO did change dramatically from spherical to rod-like structure. However, conspicuous difference occurred when the SDBS is added to the reaction system. As shown in Fig. 4c, rod-like ZnO having a rectangular base produced on the surface was observed at 2 μm and irregular sponge-like ZnO was observed at 500 nm in Fig. 4d.

The image depicts uniform coverage of such features over the surfaces. SDBS is a peculiar surfactant, which acts like a template and catalyzes the self assembled growth of rod-like nano structures. It has been recently explored to modify the morphology of ZnO (Kiomarsipour and ShojaRazavi 2012; Kim and Yong 2012).

The radial-shaped ZnO rods are obtained from the SDBS solution and also from aqueous solution at Zn^{2+} poor condition without any additive. We suggest that the origin of the radial shape is an insufficient supplement of Zn^{2+} for ZnO seeds. The negatively charged SDBS ions are assembled and form spherical micelle which encapsulated ZnO seeds. The micelles limit a supplement of Zn^{2+} ions for the encapsulated ZnO seeds, which leads a formation of chemically activated lattice defeats on the surface. These lattice defects will be nucleation sites of new ZnO rods growing in random directions. Once randomly oriented rods are formed, the crystal growth preferentially occurs at the outer edge of the randomly oriented rods. We consider the morphology of the radial shaped rods is formed with the spherical out line (Polsongkrama et al. 2008).

Figure 4e–h shows the general morphologies of the CTAB-assisted hydrothermally synthesized ZnO urchin-like structures (Ni et al. 2005). As shown in Fig. 4e, most of the structures are uniform for 10 μm. Fig. 4f Shows an individual ZnO urchin-like structure. CTAB-assisted hydrothermal synthesize of various morphologies such as rod-like, spherical, hexahedron structures, and other irregular structures. They reported that the formation of urchin-like nanocones is much more difficult in CTAB-assisted hydrothermal synthesis of ZnO. In Fig. 4g, the picture of ZnO products are hollow-cone-shaped architecture with the size of 2 μm. The hollow center core of the ZnO multigonal star is clearly indicated in the Fig. 4h. The ZnO multigonal urchine-like cone shape is formed through the aggregation of many hollow hexagonal cones. The straight arms of the ZnO cones have occured during the process of growth mechanism. Some of them transform into sharp close-ended tips, while others still have well-defined hexagonal facets on the tips (Zhang et al. 2005; Ni et al. 2008).

The growth process of ZnO in the presence of CTAB is different. Because of the existence of surfactant, the surface tension of solution is reduced, which lowers the energy to form a new phase and ZnO crystal, therefore, needed could form in a lower super saturation. On the other hand, CTAB could also be considered to influence the

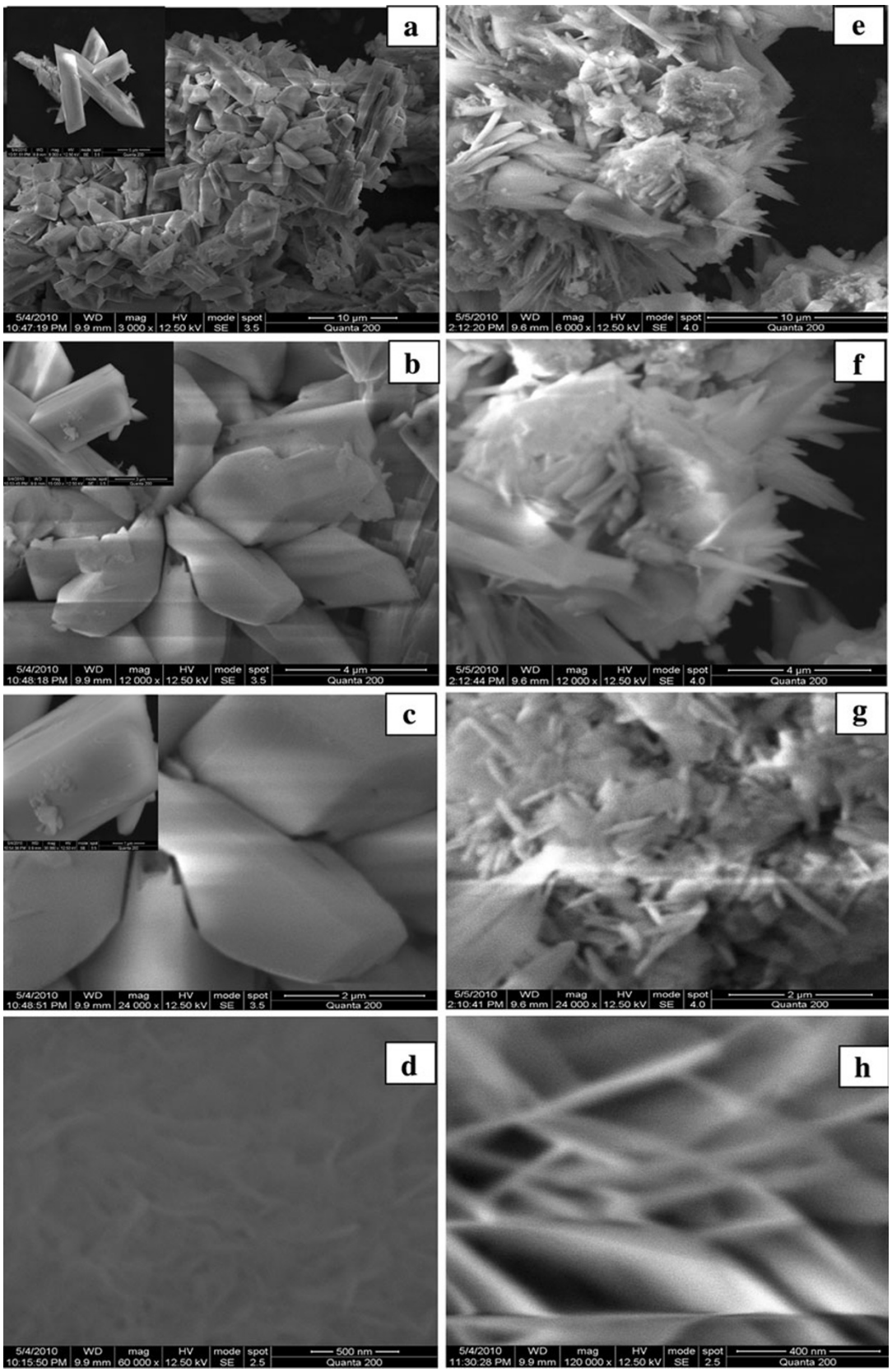

Fig. 4 SEM images of the ZnO at different magnifications (low magnification, medium magnification, high magnification) with SDBS (**a–d**) and CTAB (**d–g**)

erosion process of Zinc and the growth process of ZnO by the electrostatic and stereochemical effects. CTAB is an ionic compound, which ionizes completely in water. The resulted cation is a positively charged tetrahedron with a long hydrophobic tail, while the growth unit for ZnO crystal is considered to be $Zn(OH)_4^{2-}$, which also has a tetrahedron geometry, but it is negatively charged.

The origin of the different morphology can be explained by a chemical interaction between the ZnO seeds with surface and ions produced by the ionization of the additives. For instances, positively charged CTAB ions passivate the ionized oxygen O^- on the surface of ZnO seeds by electrostatic interaction which suppresses the growth of ZnO crystal. Thus, the ZnO nano particles with smaller size are obtained in the CTAB solutions. In the report, the formation of the ZnO nanorods and nanocones structure is due to the presence of a suitable surfactant.

Conclusion

Various types of ZnO nanostructures (including nanorods and nanocones) have been synthesized under low temperature hydrothermal conditions in the presence of SDBS and CTAB. From the experimental results, we proposed that the rate of $Zn(OH)_2$ dissolution to form ZnO particle was inhibited by the adsorption of SDBS molecules onto the $Zn(OH)_2$ surface. Both $Zn(OH)_2$ and ZnO phases were detected in the XRD from the as-powder prepared from the SDBS modified $Zn(C_2H_3O_2)_2{\cdot}2H_2O$ solution. From this work, the size and growth direction of the ZnO particles can be controlled by the addition of SDBS that is adsorbed onto the intermediate colloidal species surface. The surfactant CTAB plays a crucial role in determining the microstructures. The CTAB capped ZnO, the (101) diffraction peak is found stronger and narrower. The morphology of the aggregates is identified by SEM analysis. The SEM image indicates the presence of predominantly rod and urchin-like structure. The hydrothermal route employed in our case is cost effective and free of pollution and therefore, the technique can be extended to prepare many other important semiconducting metal oxide nanoparticles.

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