

Effects of dodecyl sulfate anionic surfactants on the crystal growth of ZnO through hydrothermal process

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The effects of dodecyl sulfate anionic surfactants on the synthesis of ZnO nanostructures were investigated at low temperature hydrothermal conditions in an aqueous solution. We used anion surfactants which have the same length of alkyl chain with different counter-ions, such as sodium dodecyl sulfate (NaDS), ammonium dodecyl sulfate (NH₄DS) and lithium dodecyl sulfate (LiDS) as additives. As a result, single-crystalline ZnO nanorods with various morphologies, sizes and aspect ratios were synthesized depending on the different counter ions of the surfactants. From the series of experiments, it was observed that the anionic surfactants affect the surface energy of ZnO crystal faces by adsorption of their hydrated counter-ions on negatively charged zinc hydrate precursor (Zn(OH)₄²⁻), and this phenomenon continuously occurs through the whole crystal growth process. So, it promotes the control of the crystal growth along a specific direction. The various ZnO morphologies depending on the type of dodecyl sulfate surfactants were explained by the differences in electrostatic interaction between the surface charge of ZnO and the counter-ions of the surfactant molecules.

Key words: Zinc oxide (ZnO), Nanowires, Hydrothermal process, Dodecyl sulfate anionic surfactants, Counter ions.

Introduction

Technology to control crystallization is a crucial requirement for the synthesis, purification, and application of materials in various industrial fields. In particular, ZnO (zinc oxide) is one of the most valuable materials in the study of crystal control because of its electronic and optical properties which are strongly influenced by the various morphologies, crystal sizes, dimensions and aspect ratios [1].

So far, much effort has been made in the synthesis of one dimensional (1D) zinc oxide with various morphologies, including nanorods, nanowires, nanobelts, nanotubes, whiskers, nanocrystals, and other superstructures, because of their advantageous chemical and physical properties. It has been recognized as one of the materials with wide applicable possibilities in nanoelectronics, gas and piezoelectric sensors, emitters, transparent electrodes in solar cells, and in catalysis nanotechnology [2-4].

Additionally, ZnO, as one of the most popular n-type semiconductor metal oxides (SMOs), exhibits a wide band gap (3.37 eV) and a high mechanical stability at room temperature with a high exciton binding energy of 60 meV. The strong exciton binding energy of ZnO (~60 meV) is much larger than that of GaN(25 meV), which can ensure an efficient exciton at room temperature under a low exciton energy [5]. Room temperature UV lasing properties have also been demonstrated by many other research groups [6-8].

These days, many synthetic methods have been developed for the synthesis of 1D ZnO nanostructures, such as vapor-phase deposition (thermal evaporation) [9, 10], a microemulsion method [11], template-assisted growth [12] and electrochemical deposition [13]. However, these techniques require complicated synthetic steps, high-temperature conditions and special equipment with a low yield of products. To overcome the drawbacks of these techniques, a simple solution synthetic process needs to be developed for the mass production of one dimensional ZnO nano structures with a high aspect ratio. Among the various types of solution processes, recently the hydrothermal process has been proposed to be an effective method for the synthesis of fine ZnO nanostructures. Unlike conventional vapor-phase methods, the hydrothermal process is a simple environmental method which has many advantages. It has been developed as a large scale manufacture at low temperature, with easy to control crystal shape, simple synthetic steps and has successfully prepared single crystalline ZnO nanorods with various morphologies. Besides, a hydrothermal method also has the advantages of organic additives such as polymers and surfactants which can be used to influence the size and shape of crystals.

In this paper, we report an easy approach to synthesize single crystalline ZnO with various morphologies and aspect ratios using different dodecyl sulfate anionic surfactants through a low temperature hydrothermal process (120 °C). More-over, the influences of different types of hydrated counter-ions of anionic surfactant molecules on the morphology of ZnO are investigated and a mechanism is also proposed.

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Experimental Section

Materials: All chemicals used in this experiment, such as zinc chloride (ZnCl_2 salt, reagent grade, 98%, ZAlrich), sodium carbonate (Na_2CO_3 , 99.99-105%, Aldrich) sodium dodecyl sulfate (NaDS salt, 99.9%, Acros organics), lithium dodecyl sulfate (LiDS salt, Fluka) and ammonium dodecyl sulfate (NH_4DS solution, ~30% in water, Aldrich), were all analytical grade reagents and used without further purification. Water (electrical resistivity of 18.2 M) was purified with a Rios and Milli Qsystem (Millipore).

Synthesis: The experimental procedure was followed: for the hydrothermal method, 50 ml of deionized water containing 0.05 M ZnCl_2 (0.35 g), 5 M Na_2CO_3 (26 g) and 1.5 g of NaDS (for the later comparison experiments, NaDS was replaced with LiDS or NH_4DS) were firstly prepared and stirred for 30 minutes at room temperature. Then the mixture was transferred into a Teflon-lined stainless steel autoclave of 100 ml capacity. The sealed autoclave was put into an oven and heated at 120 °C for 12 h. When the reaction was completed, the autoclave was cooled down to room temperature naturally. Finally, the white precipitates were collected and washed with hot deionized water (about 60 °C), and ethanol several times prior to drying in an oven at 80 °C for 12 h.

Characterization: The morphology and crystal structure of the resulting products were characterized by field-emission scanning electron microscopy (FE-SEM, JSM-6700F), transmission electron microscopy (TEM, JEM-2000EXII), selected area electron diffraction (SAED) and high resolution transmission electron microscopy (HRTEM, JEOL-2010 model, voltage of 200 KV). The powder X-ray diffraction (XRD) patterns of the as-prepared samples were taken by a Rigaku-D/MAX RINT 2000 X-ray diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at a scanning rate of $10^\circ/\text{minute}^{-1}$, and photoluminescence (PL) spectroscopy (Sci-Tech Instruments - LabRam HR) was used to evaluate the effect of as-prepared ZnO nanostructures on luminescence.

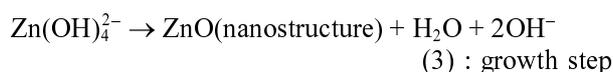
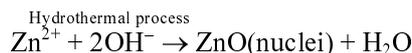
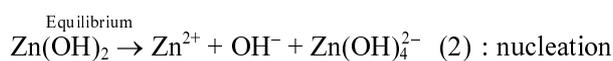
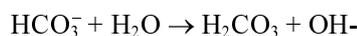
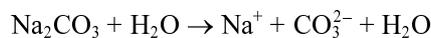
Results and Discussion

Influence of sodium carbonate on the formation of ZnO nanostructures

The experiments without using anionic surfactants through the hydrothermal process were carried out to understand the influence of anionic surfactants on the synthesis of ZnO nanostructures. The reaction mechanism of ZnO nanostructures synthesized without using surfactants is as follows;

It can be divided into two stages of nucleation and crystal growth. In the first step, $\text{Zn}(\text{OH})_2$ precursor is prepared in an equilibrium with the existence of Zn^{2+} , OH^- and $\text{Zn}(\text{OH})_4^{2-}$ precursor on the reaction mechanism (1) and (2). Next, the Zn^{2+} , OH^- and $\text{Zn}(\text{OH})_4^{2-}$ concentration

reaches a supersaturated degree, and it leads to the rapid nucleation and growth of ZnO nanostructures through the hydrothermal process. (reaction mechanism (2) and (3)).



When the mixture contains above a certain concentration of Na_2CO_3 , the excessively produced ($\text{Zn}(\text{OH})_4^{2-}$) precursor reaches a supersaturated degree faster than usual and forms much smaller nuclei through a short homogeneous nucleation process [14].

The XRD patterns of ZnO nanorods prepared by the hydrothermal process without using anionic surfactants are shown in Fig. 1. All diffraction peaks are well indexed as the ZnO nanostructure with lattice parameters $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$, which are consistent with the values in the 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 ([001] direction) and the strong (100) and (001) peaks indicate a high aspect ratio of the ZnO nanowires. The sharp and narrow diffraction peaks indicate that the ZnO nanostructure has good crystallinity, and characteristic peaks of the intermediates such as $\text{Zn}(\text{OH})_2$ and ZnCO_3 cannot be detected.

Fig. 2 shows SEM images of ZnO nanorods. The as-synthesized ZnO products were composed of rod-like and wire-like ZnO nanostructures 30 to 100 nm in width and several tens micrometres in length. Further inves-

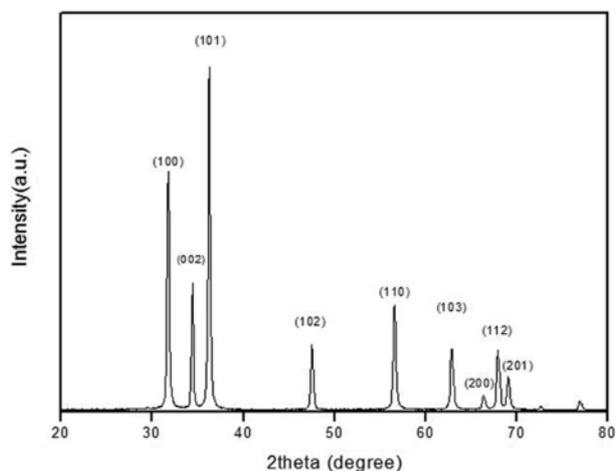


Fig. 1. XRD pattern of the ZnO nanostructures synthesized by the hydrothermal process in the absence of anionic surfactants.

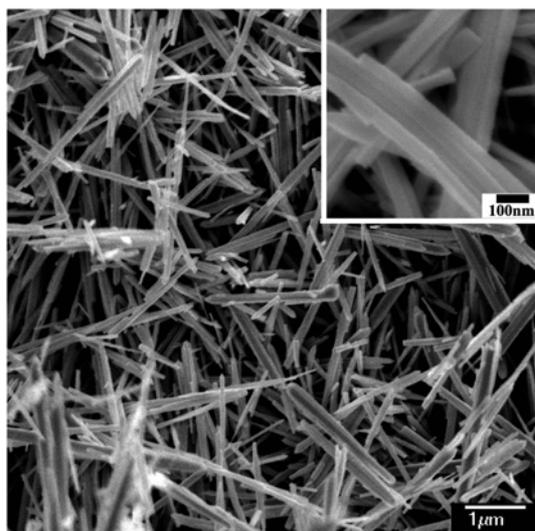


Fig. 2. SEM images of the ZnO nanostructures prepared in the absence of surfactants (inset is a magnified image).

tigation of the ZnO nanorods and nanowires has been carried out by TEM and image is shown in Fig. 3 and a SAED pattern (see inset of Fig. 3). Fig. 3 exhibits a typical TEM image of ZnO nanorods and nanowires grown along the [001] direction. The inset of Fig. 3 shows the SAED pattern which reveals that the ZnO exhibits the single-crystal structure with a [001] growth direction (along the *c*-axis). It can be indexed as the hexagonal ZnO phase, which is in accordance with the XRD results in Fig. 1.

So, a certain molar ratio of ZnCl_2 to Na_2CO_3 is considered to play an important role in the crystal shape control. Generally, the concentration of the $\text{Zn}(\text{OH})_4^{2-}$ precursor increased as amount of Na_2CO_3 added was increased and it is considered that the Na^+ ions also affects the crystal growth of ZnO nanorods and nanowires.

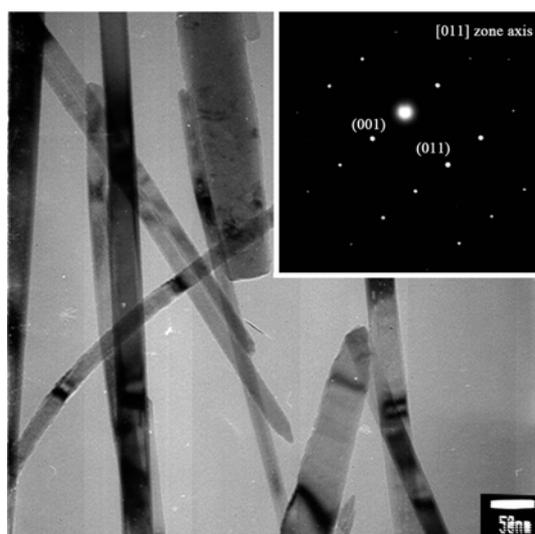


Fig. 3. TEM image of the ZnO nanostructure prepared in aqueous solution without surfactants. The corresponding selected area electron diffraction pattern of ZnO nanostructures is shown in the inset.

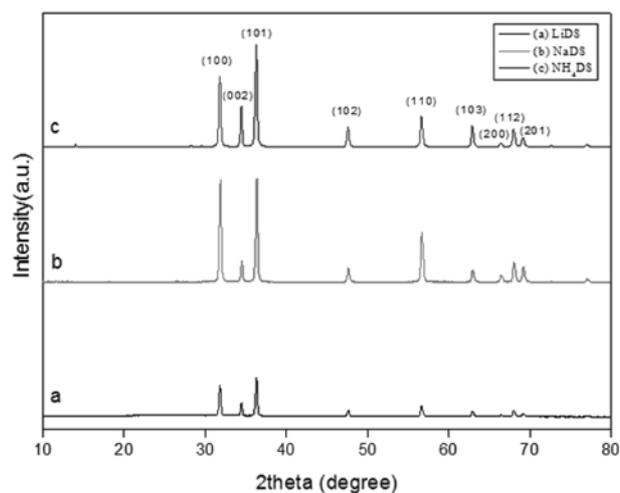


Fig. 4. XRD patterns of the ZnO nanostructures synthesized by the hydrothermal process in the presence of anionic surfactants (a) LiDS, (b) NaDS, and (c) NH_4DS at the low temperature.

Influence of counter-ions of dodecyl sulfate anionic surfactants on the formation of ZnO nanostructures

It has been well known that the use of additives leads to dramatic changes in crystal growth [15], and these effects have been investigated by many research groups [11, 16, 17]. However, it has not been clearly explained the effects of anionic surfactants in an aqueous solution on the crystal growth of ZnO nanostructure. In this study, we used anion surfactants as additives which have the same length of alkyl chain but different counter-ion (head groups) such as sodium dodecyl sulfate (NaDS), ammonium dodecyl sulfate (NH_4DS) and lithium dodecyl sulfate (LiDS), and investigate the effects of counter-ions in an anionic surfactant solution when ZnO nanostructures were formed as single crystals.

Fig. 4 shows XRD patterns of ZnO nanostructures prepared with different anionic surfactants (a) LiDS, (b) NaDS and (c) NH_4DS in aqueous solution. As shown in Fig. 4, all XRD patterns of diffraction peaks are well indexed as the hexagonal phase of ZnO with lattice parameters $a = 3.25 \text{ \AA}$ and $c = 5.21 \text{ \AA}$ (JCPDS card No. 36-1451). In particular, the (002) peak of Fig. 4-(b) indicates that the ZnO nanorods prepared in the NaDS aqueous solutions have [001] oriented growth and the strongest (100) and (001) diffraction peaks, compared to the standard ZnO XRD pattern, show an increase of length of the ZnO nanorods. The as-synthesized ZnO nanorods were well crystallized, according to the intensity and the patterns.

SEM images of ZnO nanostructures prepared in the presence of NH_4DS , NaDS and LiDS are shown in Fig. 5. Based on these images, the morphologies and size of each sample varied depending on the counter-ions of the anionic surfactants. In particular, the edge morphologies of individual ZnO nanorods and nanowires were synthesized into totally different shapes (see inset images). As shown in Fig. 5-(a), the average diameter and length of the nanorods are about 60 nm and 3 μm , respectively. When ZnO was synthesized

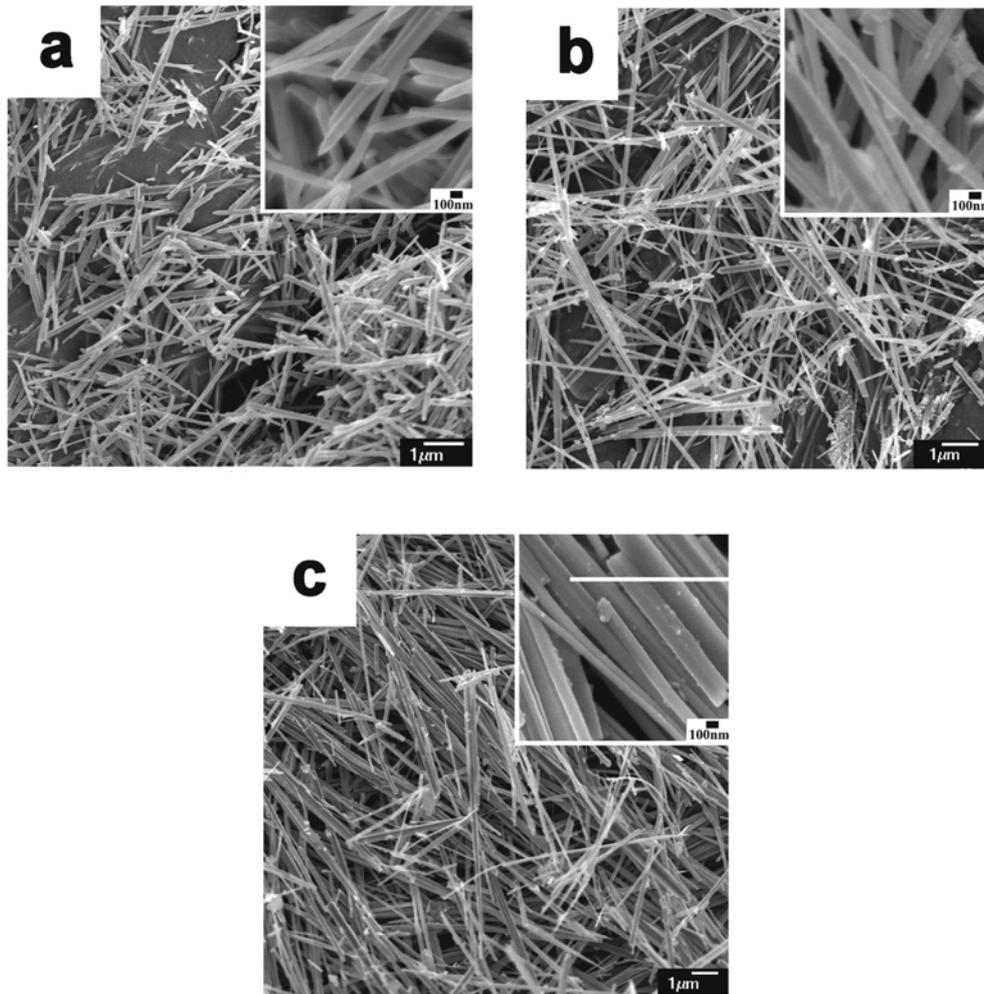


Fig. 5. SEM images of the ZnO nanostructures prepared by the hydrothermal process in the presence of anionic surfactants (a) LiDS, (b) NaDS and (c) NH_4DS .

in the LiDS aqueous solution, the morphology of ZnO nanorods indicates a shorter length and narrower diameter than the other ones, and the edge shape is sharp and rough due to the influence of the strong hydrated lithium ion as shown in an inset image of Fig. 5-(a). Fig. 5-(b) shows that the ZnO nanostructures prepared in the NaDS aqueous solution consist of a large number of ZnO nanorods and nanowires with lengths in the range of several tens micrometres and width ranging from 20 to 100 nm. Fig. 5-(c) shows a width of approximately 100-150 nm and length of about tens micrometres. It is observed that the as-prepared ZnO sample in the NH_4DS aqueous solution has a rod-like morphology, a larger size and longer length.

As shown in the TEM images in Fig. 6, the shape and aspect ratio of the as-synthesized ZnO nanostructures vary due to the effects of different hydrated counter-ions. Fig. 6-(a) a TEM image of ZnO nanostructures synthesized in the LiDS aqueous solution exhibits rod and wire-like ZnO nanostructures with narrower and shorter morphologies than ZnO nanostructures prepared in the NaDS and NH_4DS solutions. This image shows the morphological features of nanorods and nanowires with a diameter of about 20

to 100 nm, and averaged around 60 nm which correspond with Fig. 5-(a). The morphology of ZnO nanorods and nanowires is comparatively well observed in Fig. 6-(b). It can be seen that most of the ZnO nanostructures have diameters of about 40-120 nm and lengths of $\sim 10 \mu\text{m}$. Fig. 6-(c) of ZnO nanorods prepared in the NH_4DS containing aqueous solution shows a thinner thickness and higher aspect than the other ones. These nanostructures are straight and consist of many wire-like nanostructures ZnO.

Further structural characterization of the ZnO nanostructures was investigated by high-resolution TEM with the results shown in Fig. 7. The HRTEM images and the corresponding selected area electron diffraction (SAED) patterns reveal the detailed lattice fringes of the ZnO nanorod and nanowire structures. The regularly repeated lattice indicates the single crystal nature of the as-synthesized ZnO. The lattice separation is about 0.51 nm, which corresponds to the spacing the (002) plane of ZnO, indicating the crystal growth along c-axis direction.

The HRTEM images of Fig. 7-(b) and Fig. 7-(c) show that the lattice fringes become curved in the surface area, depending on the surfactants with different hydrated

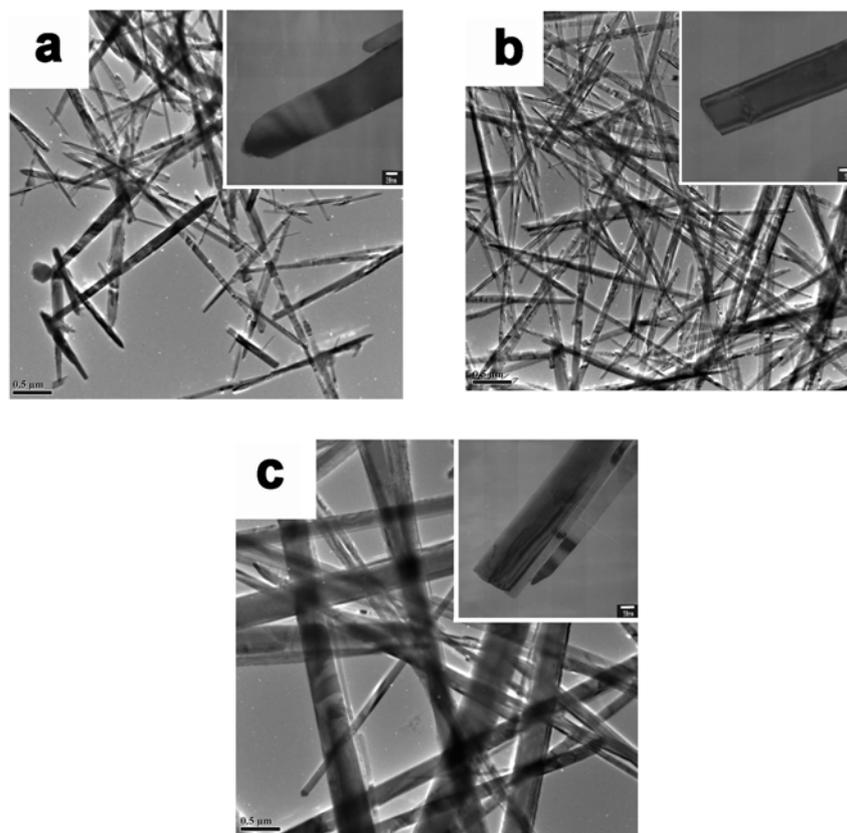


Fig. 6. TEM images of the ZnO nanostructures in aqueous solution surfactants (a) LiDS, (b) NaDS and (c) NH₄DS. (inset are magnified images).

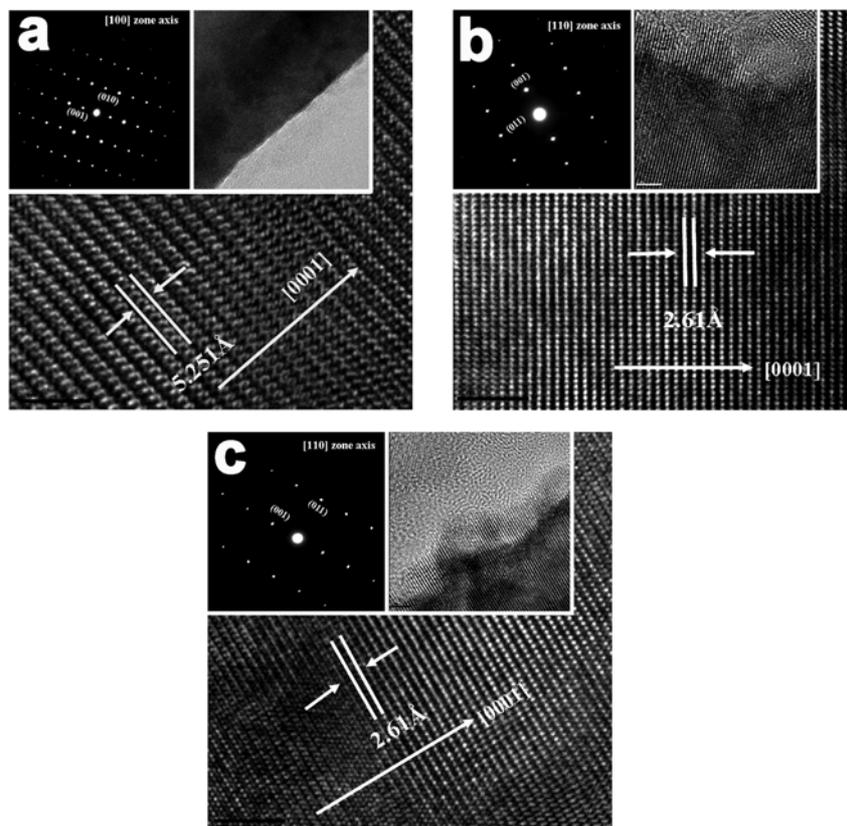


Fig. 7. HRTEM images of the ZnO nanostructures (a) LiDS, (b) NaDS and (c)NH₄DS and selected area electron diffraction patterns (SAED). (inset).

counter-ions (see inset images). However, the inset image of Fig. 7-(a) has a very smooth surface. Therefore, we can state that the different degree of electrostatic effects of each hydrated ion acts on the surface of the crystal, and it also caused some different defective growth on their surfaces. All selected area electron diffraction (SAED) patterns taken from one of these ZnO nanostructures show the complete diffraction patterns of single crystalline ZnO nanostructure grown along the [001] direction (see inset images of Fig. 7-(a), (b) and (c)).

The size of non-hydrated counter-ions increase in the order $\text{Li}^+ < \text{Na}^+ < \text{NH}_4^+$ but the hydrated ion size shows the reverse order $\text{Li}^+ > \text{Na}^+ > \text{NH}_4^+$ due to the greater hydration of a lithium ion compared to sodium and ammonium ions. The highly charged bare cationic ion becomes a much larger hydrated ion due to the strong binding interaction with water molecules, and it can also be understood that the repulsive forces between similar hydrated ions appear to increase in the order of $\text{Li}^+ > \text{Na}^+ > \text{NH}_4^+$ (see Fig. 8).

The overall shape and aspect ratio of ZnO crystals are determined by the relative growth rates of their various faces. In general, the growth rate of each face is controlled by a combination of internal and external factors, such as the reaction temperature, the use of additives etc. Among the external factors, the use of an additives results in different growth rates along the c-axis and

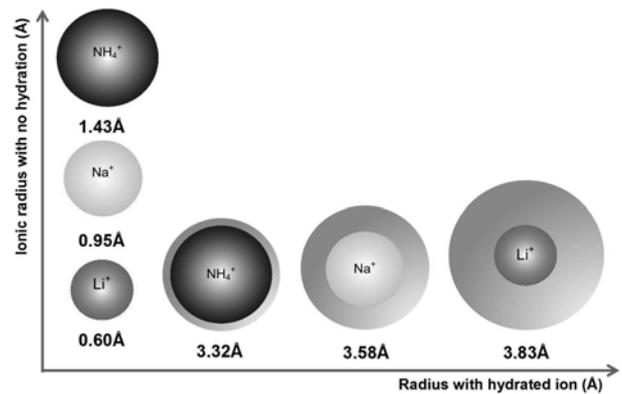


Fig. 8. Values for the nonhydrated and hydrated ionic radius of each counter-ion

had a further affect on the aspect ratio of ZnO nanorods in this study. It is observed that the use of anionic surfactants can reduce the surface energy of specific crystal faces by adsorption of their counter-ions on the negatively charged surfaces (zinc hydrate precursor ($\text{Zn}(\text{OH})_4^{2-}$)) from the experiments, and it can lead to control the crystal growth with high aspect ratio.

Fig. 9 gives the reaction mechanism for the synthesis of ZnO nanostructures with various morphologies. All these results seem to mean that the cationic counter-ions (associated with surfactant molecules) influence the

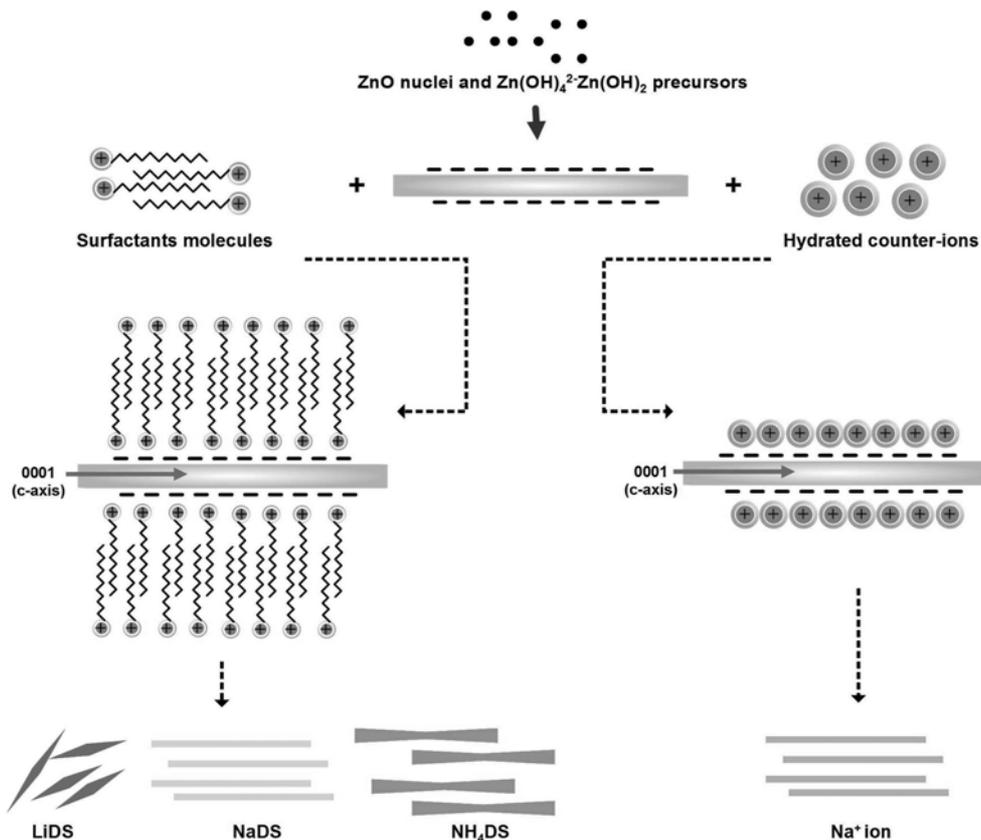


Fig. 9. The reaction mechanism for the ZnO nanorod structures (a) in the absence of additives (b) in the presence of anionic surfactants. (by the adsorption of counter-ions on the surface of ZnO nanostructures).

morphology rather than the molecular structure of ZnO although the crystal structures of ZnO prepared in an aqueous solution indicated no differences whether an anionic surfactant was added or not (see Fig. 2. and Fig. 5). However, in aqueous systems containing anion surfactants, the increased binding of the counter-ions to the surfactant in the order LiDS > NaDS > NH₄DS causes a decrease in the CMC (critical micelle concentration) and an increase in the aggregation number in solution [18, 19].

The tiny different crystal structures of ZnO prepared in anionic surfactant solutions by hydrothermal process were further analyzed by PL spectra. The PL spectra of the as-prepared ZnO samples were measured using a Xe lamp with an excitation wavelength of 325 nm at room temperature. From the measurements, a UV emission at ~390 nm and four different emitting bands, a blue emission band at 430-460 nm, a blue-green at 470-490 nm, a green band at 510-530 nm and a yellow band at 590-620 nm, were observed on the whole. The green band emission corresponds to the singly ionized oxygen vacancy in ZnO nanostructures and results from the recombination of a photogenerated hole with the single ionized charge state of this defect and also implies that there are few surface defects in the ZnO nanostructures [20-22]. The yellow emission is also attributed to interstitial oxygen. For the above-mentioned reasons, it is observed that the ZnO nanostructures synthesized in the NaDS solution (Fig. 10-(a)) have good optical properties compared to those prepared in the NH₄DS and LiDS solution. (Fig. 10-(b), (c)). It is commonly understood that high quality ZnO crystals have a strong room-temperature UV emission property. As shown in Fig. 10-(b), ZnO nanostructures prepared in the NH₄DS aqueous solution show a lower UV emission and the intensity of the defect-related green and yellow emission increases. Fig. 10-(c) shows the PL of ZnO nanostructures synthesized in the LiDS aqueous solution. Not only strong UV emission but also a wide band emission covering the blue, green and yellow regions were observed,

indicating that many oxygen vacancies or the presence of interstitial Zn are in the ZnO nanostructures. Therefore, the PL spectra of the ZnO nanostructures prepared using different counter-ions of anionic surfactants indicated tiny different crystal structures via few surface defects of samples and also verified that the optical properties of ZnO nanostructures are strongly affected by the morphology and aspect ratio.

Conclusions

Various types of ZnO nanostructures (including nanorods and nanowires) have been synthesized under low temperature hydrothermal conditions in the presence of different types of dodecyl sulfate anionic surfactant. It was found from a series of experiments that different counter-ions of anionic surfactants have significant effects on the morphology and aspect ratio of ZnO nanostructures. When we used LiDS (lithium dodecyl sulfate) as an additive, the synthesized ZnO nanorods exhibited the narrowest morphology and a low aspect ratio in comparison with those prepared using NaDS and NH₄DS as additives. It is considered that the adsorption (caused by electrostatic interactions) of hydrated counter-ions on the positively charged zinc hydrate surface leads to the structural changes in the growth of ZnO nanocrystals. Therefore, basically the size (ionic radius) and charge of the bare counter-ions are important key factors in this approach. The highly charged bare cationic ion becomes a much larger hydrated ion due to the binding interaction with water molecules and is strongly affected the surface energy of each crystal face by adsorption. This approach to prepare low dimensional ZnO nanostructures with controlled morphologies and aspect ratios can be effective for the synthesis of other low dimensional metal oxide nanocrystals.

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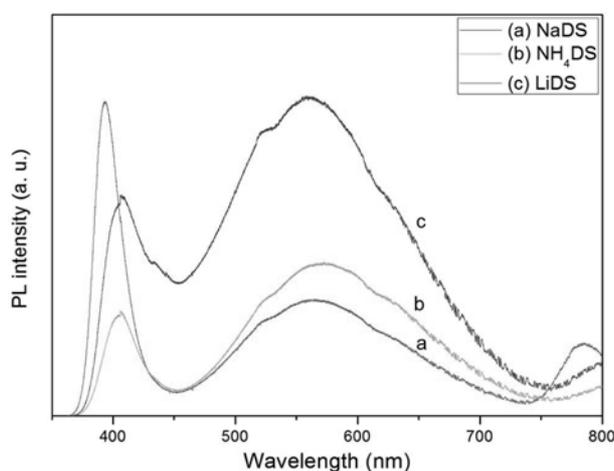


Fig. 10. Shows PL spectra of the ZnO nanocrystals prepared by hydrothermal process in the presence of anion surfactants (a) NaDS, (b) NH₄DS and (c) LiDS.

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