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Formation and Photoluminescence of Zinc Sulfide Nanorods

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Abstract: Zinc sulfide nanorods of wurtzite structure have been grown using a simple sol-gel method via ultrasonication, in the presence of a capping agent. X-ray diffraction, scanning electron microscopy, low and high resolution transmission electron microscopy and selected area electron diffraction techniques have been used to characterize the crystal structure, morphology and growth direction of the obtained nanorods. The possible mechanism of the shape evolution was investigated, which revealed that the crystal growth along the unique c axis resulted in the rod like ZnS. The photoluminescent spectrum of ZnS nanorods exhibited green emission, which may find applications in optoelectronic devices.

Key words: Sol-gel, ultrasonication, synthesis, nanostructures, nano rods

INTRODUCTION

In recent years, much attention has been focused on the preparation of one-dimensional (1D) nanostructures, such as nanorods (Chen *et al.*, 2003), nanowires (Nian and Teng, 2006), nanobelts (Pan *et al.*, 2001a) and nanotubes (Wang *et al.*, 2002) because they exhibit physical and chemical properties different from their bulk counterparts. The growth of nanostructures in a controllable manner is a critical issue in nanoscience. Zinc sulfide (ZnS) an important II-VI semiconductor has a wide band gap of 3.7 eV at 300 K (Fang *et al.*, 2007). It is one of the most important semiconductor material used in the electronics industry. It crystallizes in two forms, namely, wurtzite and sphalerite. Hexagonal wurtzite is a thermodynamically metastable phase and cubic sphalerite is the most stable under ambient conditions. The hexagonal structure can be transformed to cubic phase in presence of organic molecules (Murkowski *et al.*, 1998). The cubic phase can also be converted to hexagonal phase over 1020°C (Shionoya and Yen, 1999). ZnS has a wide range of applications covering electroluminescence, nonlinear optical devices, LEDs, flat panel displays, IR windows, sensors and lasers (Moore and Wang, 2006; Hu *et al.*, 2004; Shen *et al.*, 2006). It has been reported that the growth of 1D nanostructures with different morphologies, sizes, compositions and microstructure was mainly affected by temperature and duration of the reaction (Pan *et al.*, 2001b; Gudiksen *et al.*, 2001; Wen *et al.*, 2005; Cao *et al.*, 2005). It has been found that ZnS nanocrystallites have been generally synthesized using

colloidal chemistry methods by controlling the reaction conditions such as precursor concentration, nature of the solvents, capping and stabilizing agent (Nanda *et al.*, 2000; Sugimoto *et al.*, 1998; Yang *et al.*, 1997; Kulkarni *et al.*, 2001). Semiconductors such as ZnO, ZnS have been reported to exhibit polar ends with either anion or cation terminated surfaces. During the growth process the cation terminated surfaces serve as self-catalysts and the polar charges influence the growth of nanostructures and are further driven by minimizing the energy (Wang, 2003). Sol-gel is a very simple and effective method for achieving nanomaterials in large scale. The sonochemical method is yet another technique used extensively to generate novel materials with unusual properties since they form particles of much smaller size and higher surface area. The chemical effects of ultrasound appear from acoustic cavitation, that is formation, growth and implosive collapse of bubbles in a liquid. The implosive collapse of bubbles generated a hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble.

In this communication, we report a simple chemical route of sol-gel via ultrasonication towards the growth of well faceted and crystalline ZnS nanorods using mercaptoethanol as the capping agent. The significance of this procedure can be visualized by the successful and well-ordered growth of perfect crystalline ZnS nanorods under easy and mild reaction conditions. Photoluminescent (PL) spectrum exhibit green emission, which may find applications in optoelectronic devices.

MATERIALS AND METHODS

The method employed here is very similar to the method adopted (Vogel *et al.*, 2000), with some modifications to obtain ZnS nano rods. Zinc chloride and sodium sulfide were purchased from E-Merck, India and used as such without further purification. Mercaptoethanol supplied by Sd's Fine chemicals was doubly distilled. Doubly distilled water was used for the analysis. In a three necked round bottom glass vessel (250 mL), 10 mL of 50 mM concentration of zinc chloride was continuously stirred and 20 mL of mercaptoethanol was added in drop wise to get a homogeneous stabilized mixture. The pH of the above solution was adjusted to around 10 by adding 1 M NaOH solution and 10 mL of sodium sulfide solution (50 mM) was injected into the reaction mixture and magnetically stirred. The reaction mixture was continuously stirred for 6 h to get a homogeneously stabilized dispersion. The round bottom flask containing the above mixture was subjected to ultrasonic irradiation which was accomplished with a high intensity ultrasonic pro bath (Toshniwal, KLN W. Germany). The reaction mixture was dialyzed for 12 h; dialysis membrane supplied by Sigma. The dialyzed samples were further mixed with ethanol and isopropanol with 1:2 volume ratios and stirred. The solution was centrifuged and dried in a vacuum oven to obtain a white powder. The powder was then calcined at 800°C for 6 h to obtain ZnS nanorods. Crystallinity of the as synthesized ZnS nano rod was confirmed using X-ray diffractometer (Shimadzu model XRD 6000) fitted with a filtered Cu K α radiation. The morphology of as-synthesized product was observed using through the JEOL model JSM 6360 Scanning Electron Microscopy (SEM). Further, Transmission Electron Microscopy (TEM), High Transmission Electron Microscopy (HRTEM) images and Selected Area Electron diffraction (SAED) patterns were captured with a JEOL 2010 to reveal the morphology of the ZnS nano structures. Photoluminescence (PL) spectrum was recorded on a Jobin Yuon Fluorolog 3-11 Spectrofluorometer.

RESULTS AND DISCUSSION

The morphology of the as-synthesized ZnS nanorods at temperature about 800°C for 6 h by a simple sol-gel route via ultrasonication was first analyzed by SEM. Figure 1a represents a typical SEM image of randomly distributed one dimensional nanostructures with diameters in the range of 30-50 nm. It is notable from the appearance of the individual crystals in Fig. 1b that the nanorods are straight and have highly faceted hexagonal

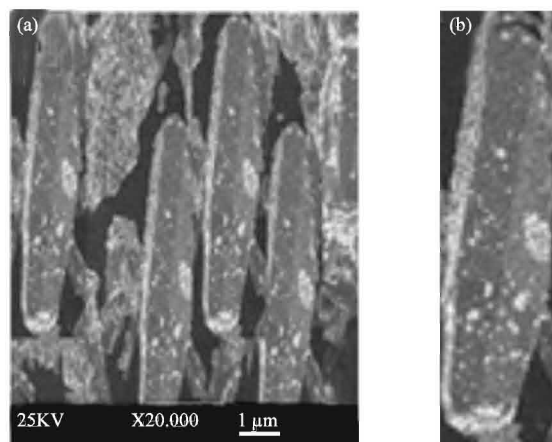


Fig. 1: (a) Scanning electron micrographs of ZnS nano rods (b) magnified scanning electron micrograph of a single ZnS nano rod

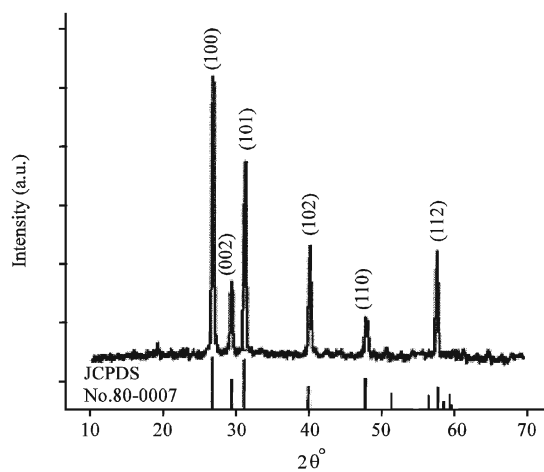


Fig. 2: X-ray diffraction patterns of ZnS nano rods

cross-sectional shape with truncated pyramids at their ends. The well-defined highly faceted hexagonal cross-sectional shape is indicative of the single-crystal nature of the ZnS nanorods. Similar observations were also made for ZnS nano tubes (Yin *et al.*, 2005), ZnS nano wires (Zhu *et al.*, 2004) and ZnO nano rods (Ge *et al.*, 2007).

An X-ray diffraction (XRD) pattern of the ZnS nanorods is shown in Fig. 2. All the sharp reflection peaks could be indexed to the wurtzite-type ZnS structure with accordance to the standard JCPDS card No. 80-0007. The intensity and sharpness of the peaks lead to perfect crystallization and larger particles. From the XRD pattern we find a predominant (100) plane, which may be attributed to the crystallographic structure and morphology of ZnS. In case of 1D nanostructures like nano rods the growth would be longitudinal (along the (002) plane), with the

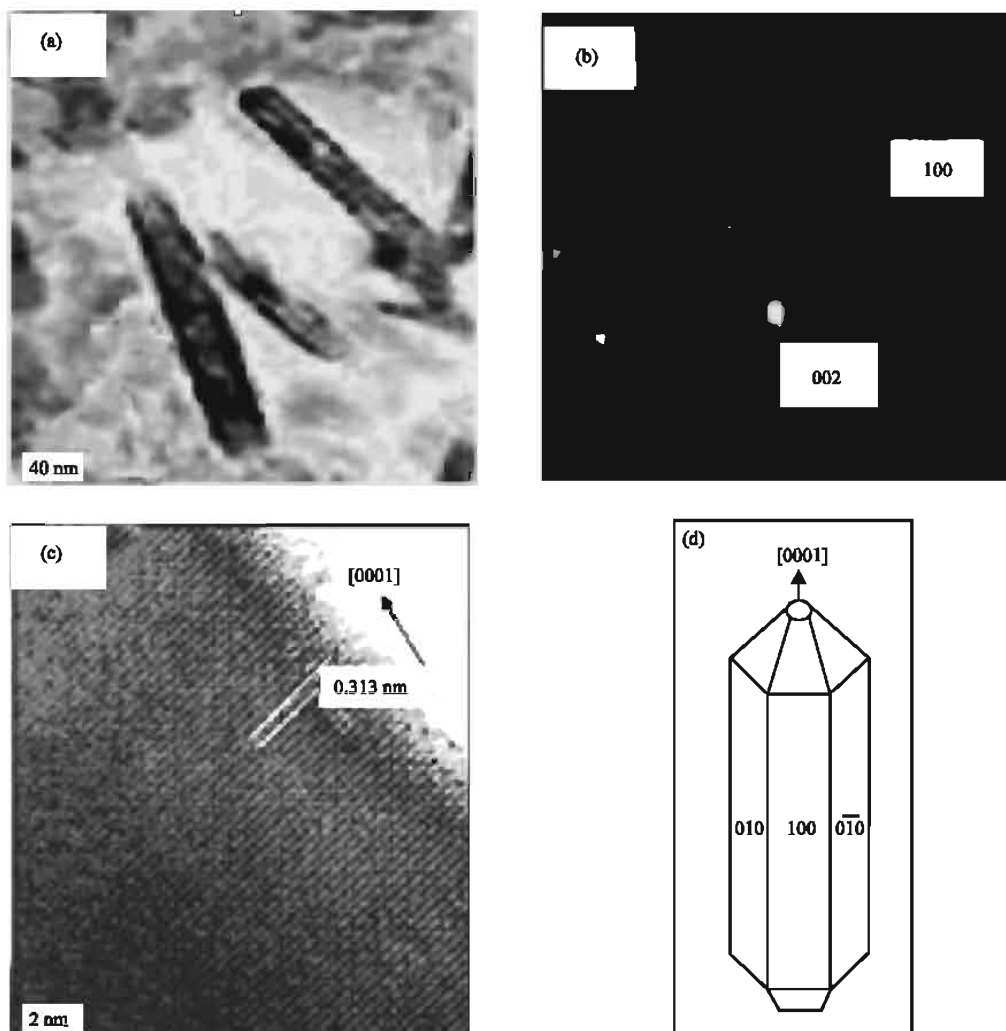


Fig. 3: (a) Low resolutions transmission electron micrographs of ZnS nano rods, (b) selected area electron diffraction pattern (SAED) of ZnS nano rods, (c) high resolution transmission electron micrographs of ZnS nano rods and (d) crystal growth model of ZnS nanorods with truncated pyramidal heads

side facets of the rods made of (100) plane. Whereas, in our case the side facets of the rod may be more exposed to the XRD beam resulting in a stronger (100) peak. Many other researchers were also reported similar observations for the synthesis of ZnO (Ghoshal *et al.*, 2007), formation of ZnS nano tubes (Yin *et al.*, 2005) and ZnS nano wires (Zhu *et al.*, 2004). No peaks related to other impurity phases could be assigned, suggesting that the synthesized ZnS nanorods are chemically pure. The presence of the cubic phase cannot be excluded from the XRD data alone, due to the structural similarities between the two polymorphs of ZnS.

Hence, it is important to analyze, more structural and morphological information of the sample through the low and high resolution Transmission Electron Microscopy

(TEM, HRTEM) and selected area electron diffraction (SAED) pattern. The low resolution TEM (Fig. 3a) images showed the nano rod formation with average particle size to be in the range of 30-50 nm which agrees well with the results obtained from X-ray diffraction patterns. It clearly shows image of ZnS nanorods with hexagonal facets and truncated pyramidal heads growing along the [0001] direction. The SAED pattern shown in Fig. 3b indicates that the nanorods are single crystals. Figure 3c shows the high resolution TEM (HRTEM) image taken from the nanorods. The marked inter-planar d-spacing of 0.313 nm correspond well with that of the [0001] lattice plane of wurtzite ZnS. Further, the HRTEM image suggests that the nanorods are structurally uniform and single crystalline, no defects and dislocations in the area

analyzed. The SAED indicate the growth of the nanorods to be along the [0001] direction. The crystal growth model for hexagonal faceted ZnS nanorods with the truncated pyramidal ends is shown in Fig. 3d. The nanorods grew along the [0001] direction and are closed by the low -index {1000} planes.

A chemical reaction between the $ZnCl_2$ and Na_2S in aqueous solution, resulted in ZnS which is highly insoluble in water. Immediately after the solutions are mixed, the nucleation of the ZnS nanocrystallites starts due to the supersaturation of ZnS. The ZnS is consumed in the nucleation resulting in smaller nuclei and as a result of Brownian motion in the liquid, these nuclei collide with each other to aggregate. But, the capping agent and the ultrasonication process prevented the aggregation to form the nanostructures. The temperature, time and capping agent, influence the growth pattern of the nanorods. In this research, we have not used any catalyst or templates to form the nanorods. The formation of the nanorods is related to the structural nature of ZnS crystal. Wurtzite ZnS has a ionic and polar structure with hexagonal close packing of zinc and sulphur atoms in the AB AB sequence. It has no centre of inversion and therefore an inherent symmetry exist along the c-axis, which allows the anisotropic growth of the crystal along the most stable [0001] direction.

It has been observed that the photoluminescent spectra of ZnS nanostructures is complicate due to its sensitiveness to the reaction conditions, crystal size and shape (Weller, 1993; Steiger-Wald and Brus, 1990; Cizeron and Pileni, 1997; Li *et al.*, 2004). The PL spectra were recorded with an excitation wavelength of 280 nm at room temperature, for ZnS nano rods. The PL spectrum of ZnS nanorods presents a single green emission band around 530 nm as shown in Fig. 4. Denzier *et al.* (1998) reported that a strong blue emission around 450 nm was reported for ZnS multicore microcables and they assigned the peak to the defect-related emission of ZnS For ZnS nano belts Sulieman *et al.* (2006) reported three broad emission peaks at 340, 410 and 510 nm. They assigned the peak at 340 nm due to the spontaneous emission due to band to band transition, while the 410 nm peak originated from the surface states and the peak at 510 nm was attributed to the S vacancies in the single crystal. Further it has been explained by other researchers that the observed green emission at 538 nm may be obtained from some self-centered centers, vacancy states or interstitial states associated with the peculiar nano structures (Yin *et al.*, 2005). Mitsui *et al.* (1996) explained that such an emission may be associated with point defects, arose due to isolated Zn vacancy in the single negative charge state

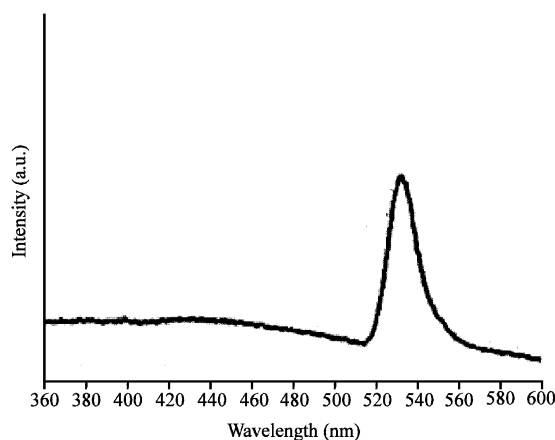


Fig. 4: Photoluminescent spectra of ZnS nano rods

(Mitsui *et al.*, 1996). We have also observed a strong green emission peak centered around 530 nm and this may be attributed to the stoichiometric defects, which might be a vacancy or an interstitial states. It is believed that these ZnS nanorods may have find potential applications in displays, sensors and lasers.

CONCLUSIONS

To summarize, we have synthesized hexagonal-faceted ZnS nano rods by a simple sol-gel route via ultrasonication using mercaptoethanol as a capping agent. The as-synthesized ZnS nanorods have a hexagonal wurtzite structure and grow along the [0001] direction. The important shape guiding parameters and mechanism for the growth of the nanorods were discussed. The shape control was achieved through the preferential growth of the crystallographic axis (c-axis) of the ZnS nano structures during the kinetically controlled growth process. The PL spectrum of the ZnS nanorods shows a strong green emission around 530 nm. The synthesis route can be easily controlled, repeated, mild and feasible and can be applied to fabricate nanorods or wires of other II-VI semiconductors. This high quality, single-crystalline ZnS nanorods with green emission represent good candidates for use in optoelectronic devices.

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