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ScienceDirect
Optical Materials 29 (2007) 1579–1583
OPTICAL Materials
www.elsevier.com/locate/optmat

Annealing of ZnS nanocrystals grown by colloidal synthesis

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Received 20 October 2005; accepted 13 July 2006
Available online 28 September 2006

Abstract

ZnS nanocrystals (NCs) capped with tetramethylammonium (TMAH) were synthesized from $ZnCl_2 \cdot 2H_2O$ and thiourea using a wet chemical process. Further treatments of the nanocrystals such as aging, and annealing have been conducted to examine the stability of the grown samples. The X-ray diffraction spectra show that the crystal has a zinc blende structure with particle size of about 2 nm. The evidence of nanocrystalline character is also clear in the UV–Vis absorption that shows an excitonic peak at about 236 nm (5.2 eV) arising from band edge transitions. A photoluminescence emission peak centered at about 450 nm (2.7 eV) is attributed to transitions between shallow donors and Zn^+ vacancies. Both absorption and photoluminescence spectra show that sample aging does not affect the characteristics of the sample, possibly due to protection by TMAH capping. Annealing at 700 °C and 900 °C results in the red shift of the photoluminescence.

PACS: 78.55.Et; 78.55.m

Keywords: ZnS; Nanocrystals; Annealing; Photoluminescence emission

1. Introduction

Research concerned with nanocrystals (NCs) has greatly accelerated recently and many applications are emerging. One of the unique properties of the semiconductor NCs is their band gap increase with decreasing particle size due to carrier confinement effects. Luminescence from within the band gap is also affected by the grain size and nanoparticle composition. Among different materials explored in the nanoparticle form ZnS has a relatively high direct band gap (3.68 eV) [1], strong fluorescence, and resistance to high electric field [2] and therefore it has potential application in areas such as solar cell and infrared windows, laser, sensors and displays [3]. ZnS has a low exciton Bohr radius (2.5 nm) that makes its nanoparticles interesting as small biomolecular probes for fluorescence and laser scanning microscopy. ZnS is also currently used as a shell or capping layer in core/shell nanoprobes such as CdSe/ZnS core/shell structures [4].

There have been a numbers of experiments concerned with synthesis and characterization of ZnS both through colloidal preparation [1,5,6] and other methods such as ultrasonic-assisted successive ionic layer adsorption and reaction method [7], microwave irradiation [8], solid-state reaction [2], and wire technique [9]. Photophysical properties of ZnS nanoclusters have been studied by Kumbhojkar et al. [1] where the quantum size effect has been clearly observed. These authors reported a significant effect of capping agents on optical properties demonstrated through variations of the emission peak energies of ZnS nanoclusters

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0925-3467/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.optmat.2006.07.019

with different capping agents. It was also found that uncapped ZnS nanoclusters have their excitonic peak located at higher wavelengths. Moreover, the capping agents further stabilize the nanocrystals. This is because at higher temperatures, the surfactant molecules are dynamically adsorbed to the surface of the growing crystal where they provide access sites for the addition of monomer units to the growing nanocrystal and at the same time preventing their aggregation. At low temperatures the surfactants are strongly bound to the surface of the nanocrystals where they provide solubility in organic solvents [10].

Despite progress in the synthesis of the ZnS NCs many unresolved problems still remain. Marked discrepancies of the evolution of the band edge emission in the ZnS NCs with nanocrystal size are reported in various studies. In addition, the origin of visible luminescence, other than the band gap emission, observed in many NCs is still uncertain. It is well known that due to their very small diameter the NCs have a very high ratio of surface to volume that makes them susceptible to various surface defects. Therefore further refinement of the synthesis conditions and post-growth treatments are needed to understand and control the properties of ZnS NCs. Up until now only isolated works reported the sample treatments used to determine the NC stability. Among those, Goswami and Sen [9] have studied water-induced stabilization of ZnS nanoparticles. In the present work we employed colloidal synthesis and subsequent sample treatments such as aging and annealing. The characterization was aimed at determining the sample stability.

2. Experimental

The ZnS NCs were synthesized in a wet chemical reaction [11]. The reagents used were $ZnCl_2 \cdot 2H_2O$ (14.68 mmol) and thiourea (14.68 mmol) respectively for Zn and S. The solvent was ethylene glycol (EG), 99+% from Sigma Aldrich. The $ZnCl_2 \cdot 2H_2O$ and 10 ml, 20% tetramethylammonium hydroxide (TMAH) were dissolved into 100 ml EG and heated to 100 °C. The thiourea was separately dissolved into another 100 ml EG and heated up to 100 °C. The two solutions were then mixed in a vessel and heated to 160 °C under magnetic stirring. The pH of the solution was adjusted to the value of 9 by adding HCl and NaOH. The reaction aliquots were collected at various times from the beginning of the synthesis and re-dispersed in methanol for optical characterization. The annealing of ZnS nanocrystals was performed by first carefully evaporating the as synthesized nanoparticle solution on an electric hotplate then followed by annealing in an oven in oxygen atmosphere at selected temperatures. The annealed particles were re-dispersed by sonification in different solvents before spectra were measured. Very weak background spectra were observed (not shown here). UV–Vis absorption spectra were measured using a double beam Varian spectrophotometer CARY5E with ZnS NCs solutions placed in a 10 mm path length quartz cuvettes. The fluorescence emission was measured with Fluorolog-Tau-3 spectrometer (Horiba Jobin-Yvon, NJ). The X-ray diffraction (XRD) spectra were taken on Philips PW1830 XRD system with following slit settings: 0.5° for source and 0.2° for detector. The SEM image was recorded on a JEOL system with maximum resolution of 5 nm.

3. Results and discussion

In order to ensure that during our synthesis the ZnS NCs are indeed formed we first conducted X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. Fig. 1 shows a typical wide-angle X-ray diffraction pattern of the ZnS nanocrystals. It shows wider features in comparison to bulk ZnS (see Ref. [6]) indicating the nanoscale size of crystals. A typical diameter of the NCs based on the analysis of the XRD linewidth and calculated using Debye-Scherrer [6] formula, is about 2 nm. Such relatively small size of the synthesized ZnS crystals is typical of high pH used in this experiment, and in agreement with earlier reports that with increasing pH the nanoparticle size decreases [12]. With respect to crystalline structure the characteristic XRD features of the nanocrystallites match the bulk zinc blende pattern. These diffraction features appearing at about 28.5°, 47.5°, and 56.3° correspond to the (1 1 1), (2 2 0), and (3 1 1) planes of the zinc blende phase of ZnS [6]. Further evidence of NCs is shown in the SEM image (Fig. 2). Due to the system resolution limit of 5 nm the smallest, single NCs cannot be clearly resolved, but the presence of small nanoclusters is apparent.

Further we carried out optical characterization of the synthesized nanocrystals. They produced reasonably narrow and well-defined room temperature absorption spectra as shown in Fig. 3. Excitonic spectral features such as those can be observed in nanocrystals even at room temperature due to the increase in excitonic binding [6]. In this growth synthesis the reaction times used to control the size of the NCs influence the absorption properties of the materials.

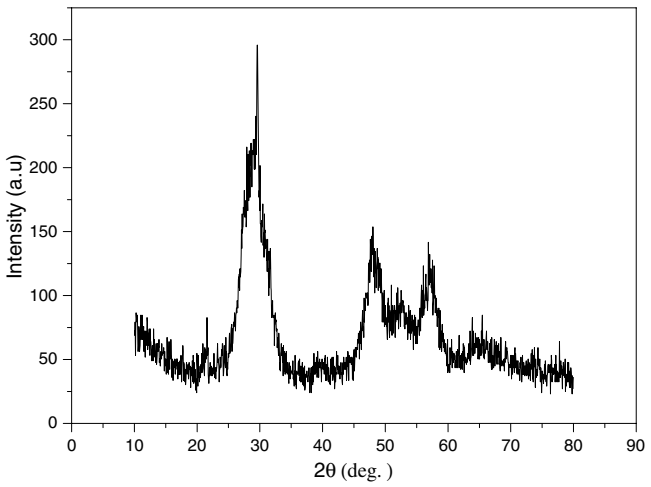

Fig. 1. Typical XRD pattern for nanostructured ZnS revealing the nanoscale size of the crystals.