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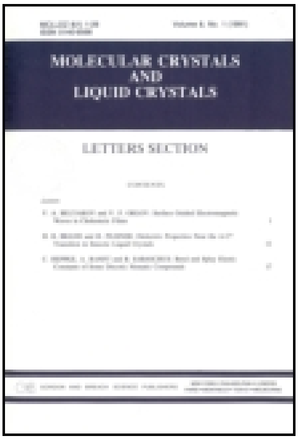

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Facile Synthesis, Characterization, and Optical Properties of Ag^+Doped ZnS Nanocrystals via Co-precipitation Method using Thioglycerol as a Capping Agent

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Facile Synthesis, Characterization, and Optical Properties of Ag^+ Doped ZnS Nanocrystals *via* Co-precipitation Method using Thioglycerol as a Capping Agent

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Zinc sulfide (ZnS) nanocrystals (NCs) doped with transition metal ions (Ag^+) ($ZnS{:}Ag^+$) were synthesized by a low temperature co-precipitation method using thioglycerol as a capping agent. The X-ray photoelectron spectroscopy (XPS) study suggested that Ag dopant was successfully doped into the $ZnS{:}Ag^+$ NCs matrices. The zinc blende structure of the $ZnS{:}Ag^+$ NCs was confirmed by X-ray diffraction (XRD) analysis. The UV/Vis absorbance spectra for all of the synthesized NCs showed a gradual red shift while Ag^+ ions concentrations were increased. Photoluminescence (PL) peak for un-doped ZnS NCs exhibited at 465 nm. On the other hand, doping of Ag^+ ions into ZnS NCs in the presence of thioglycerol resulted in PL peaks shifted towards red shift in accordance with the increasing Ag^+ ions concentration.

Keywords Co-precipitation method; doping; optical properties; semiconductor nanocrystals

1. Introduction

Currently, transition metal ions doped semiconductor nanocrystals (NCs) have attracted much interests of researchers in academic and industries, because quantum size effects result their properties dramatically different from the bulk materials [1,2]. Doping with optically active materials rearrange the band structure of the NCs and attribute intense emissions in a wide range of wavelength depending on the impurity type, concentration and crystal dimensions, thus influencing their practical applications. Besides, significant structural manipulations can also occur due to doping which is important for fundamental understanding of the structure and optical phenomena in semiconductors [3,4]. Especially, ZnS NCs is a direct-transition semiconductor with the widest energy band gap semiconductor having exciton Bohr radius, RB = 2.5 nm among the groups II–VI compound

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semiconductor materials, and is an important material with an extensive range of applications from blue/green light-emitting diodes (LEDs) and electroluminescence devices (ELDs) to optoelectric modulators, data storage, data transfer and coatings which are sensitive to UV light [5–8]. In addition, the most striking feature of ZnS NCs is that their chemical and physical properties differ dramatically from those of the bulk solids. This is particularly due to the high dispersity of nanocrystlalline system, i.e. the number of atoms at the surfaces is comparable to the number of those located in the crystalline lattice [9–11]. Moreover, their luminescence properties strongly depend on the doped ions because these ions can lead to the formation of novel luminescent centers in ZnS NCs.

Many studies have been focused on the transition metal ions doped ZnS NCs using different techniques. Till date, several methods have been developed to prepare the doping semiconductors, such as matrix-mediated growth technique, chemical route, coating method, and sol–gel processing [12–14]. Bhargava et al. reported Mn^{2+} doping into ZnS NCs efficiently generated yellowish-orange emission [15]. Some more reports on the photoluminescence (PL) properties of ZnS nanostructures doped by various types of impurities, such as Cu^{+}, Cr^{2+}, Co^{2+} and Eu^{3+} etc. have been demonstrated [16,17]. Un-doped ZnS NCs emit in the blue region with broad bandwidth. But doping causes the visible light emission, due to the intermediate transitions under UV light excitation. However, controlled synthesis of metal-doped semiconductor NCs is still remained in a great challenge. The main limitation is the difficulties in composition and nanosize-controlling during the preparation of metal-doped semiconductor NCs.

In this paper, we report the synthesis and optical studies of ZnS:Ag^{+} NCs using thioglycerol as a capping agent. Ag^{+} doped (0.5–2.0%) ZnS NCs were synthesized through chemical co-precipitation method. The characterization of the samples was accomplished by respective analytical studies. The optical properties of the samples were studied by UV-vis and PL spectroscopy.

2. Experimental

Materials

Zinc acetate dihydrate [$Zn(Ac)_2.2H_2O$], thioglycerol, sodium thiosulfate pentahydrate ($Na_2S_2O_3.5H_2O$), $AgNO_3$ and solvents were used as received. All of the above chemicals were purchased from Aldrich, Yongin, Korea.

Preparation of ZnS:Ag^{+} NCs

First, a desired molar proportion of $Zn(Ac)_2.2H_2O$ in 50 ml de-ionized water and $AgNO_3$ (wt% in Zn = 0.5%, 1%, and 2%) in 50 ml de-ionized water were dissolved and 2 ml thioglycerol as capping agent was added to control the growth of the NCs during the reaction. Subsequently, the $Na_2S_2O_3$ (50 ml) was added drop wise to the above mixture using an additional funnel. For each experiment, the equimolar amounts of $Zn(Ac)_2$ and Na_2S were used. Un-doped ZnS NCs were synthesized by following the similar procedure without doping and capping agent. During the whole reaction process, the reactants were vigorously stirred at 80°C. The as-prepared NCs were separated from the solution by centrifugation. After that, NCs were washed repeatedly using deionized water and then dried at 60°C. Finally, the powder samples of ZnS:Ag^{+} NCs were obtained.

Measurements

The chemical composition of the synthesized ZnS:Ag$^+$ NCs was investigated using a X-ray Photoelectron Spectroscopy (XPS) (Thermo VG Multilab 2000) in ultra high vacuum with Al Kα radiation. The crystallographic states of the samples were determined by a Philips X'pert-MPD system diffractometer (the Netherlands) with Cu Kα radiation. The morphology was studied by Transmission Electron Microscopy (TEM) using a Joel JEM 2010 instrument (Japan) with an accelerating voltage of 200 kV. The absorption spectra were obtained using Perkin-Elmer Lambda 40 Ultraviolet-visible Spectrophotometer. PL spectra were recorded on an F-4500 spectrofluorometer (Hitachi, Japan).

3. Results and Discussion

The II–VI semiconductor nanoparticles are well known to exhibit a dramatic change of their optical properties when their size is tuned into a few nanometers scale in controlled manner. It is known that surface capping agents are very useful to control NCs size and shape. In this work, thioglycerol was used as capping agent to prepare Ag$^+$ doped ZnS NCs because of its dual activity namely catalytic and stabilizing properties [18]. The formation mechanism of ZnS:Ag$^+$ NCs can be explained in such a way that thioglycerol catalyzes the conversion of $Na_2S_2O_3$ into free S^{2-} ions, which reacts with Zn^{2+} to afford ZnS NCs. In the co-precipitation system, the aqueous solution of $AgNO_3$ produce Ag$^+$ ions which spontaneously diffuse into the crystal lattice of ZnS NCs to afford zinc blende ZnS:Ag$^+$ NCs. The structure, morphology and optical properties of ZnS:Ag$^+$ NCs were systematically investigated.

XPS was employed to investigate the chemical composition of ZnS:Ag$^+$ NCs as shown in Fig. 1. The detailed scan for Zn2p spectra comprises of two peaks with binding energies

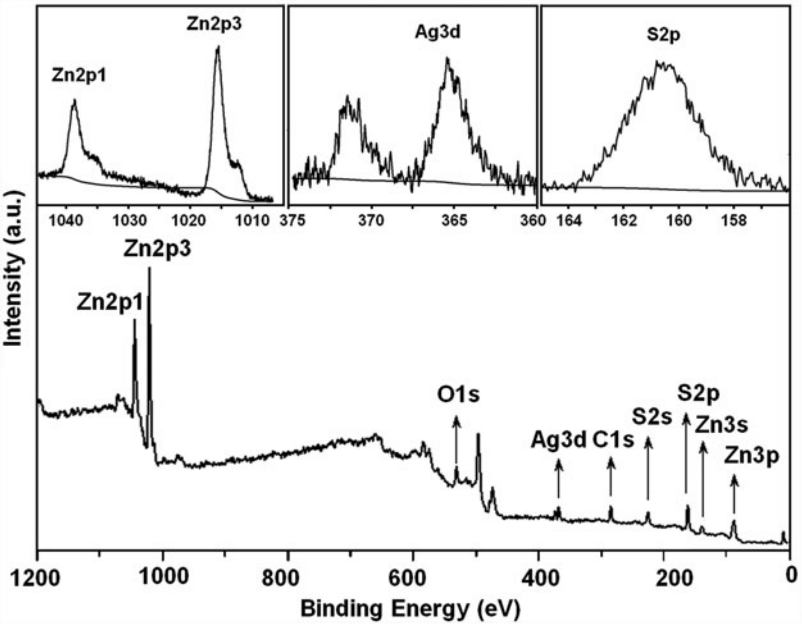

Figure 1. XPS survey scan of ZnS:Ag$^+$ NCs (insets, core-level spectra).

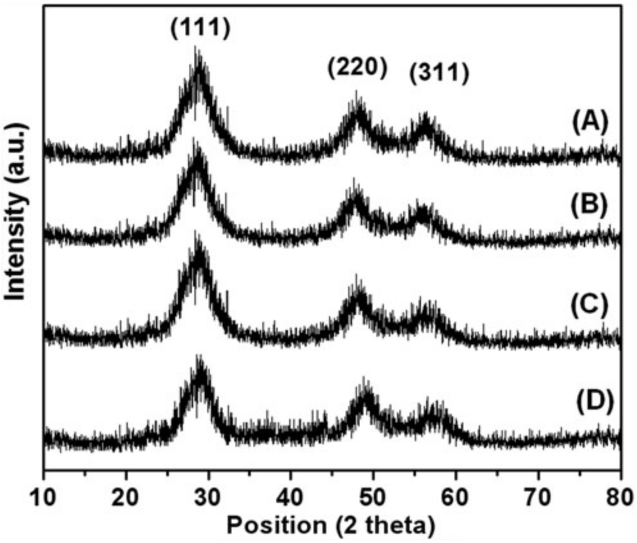

Figure 2. XRD spectra of (A) un-doped ZnS NCs, and (B–D) ZnS:Ag^+ NCs at 0.5, 1.0, 2.0% Ag^+.

(BE) at 1038.8 eV and 1016.7 eV due to $Zn2p_{3/2}$ and $Zn2p_{1/2}$, respectively. The BE of S2p is correspond to 161.2 eV. It should be noted that the characteristic peak of Ag element is not much strong as those of the other elements, which can be attributed to Ag being doped into the interior of particles. In addition, the XPS spectra in the Ag3d region consisted of two peaks at 366.1 ev and 371.7 ev, which correspond to $Ag3d_{5/2}$ and $Ag3d_{3/2}$, respectively, indicated that the Ag was successfully doped into the NCs matrices.

The XRD patterns of the ZnS NCs and ZnS:Ag^+ NCs show broad diffraction peaks, which are the characteristics of nanosized materials (Fig. 2). All the peaks of ZnS NCs in the diffraction pattern are indexed according to the JCPDS data (No. 05-0566) those are very well matched with the zinc blended cubic structure (Fig. 2A) [7]. The peaks in the XRD pattern of ZnS:Ag^+ NCs at 28.53°, 47.89°, and 57.23° for ZnS NCs correspond to crystal planes (1 1 1), (2 2 0) and (3 1 1), respectively (Fig. 2B–D). These results suggest that the ZnS:Ag^+ NCs retained the zinc blende structure of ZnS NCs. The pattern also indicates that there is no distinct diffraction peaks from silver impurity. Thus it is suggested that the Ag^+ ions were well organized in the ZnS NCs lattice.

The morphology of the as-synthesized NCs was investigated by TEM measurement. Figure 3 demonstrates the TEM images and the size distribution diagram of Ag^+ doped ZnS NCs. The result shows that the ZnS:Ag^+ NCs are in narrow size distribution, and the shape of the well-separated nanoparticles is nearly spherical. The mean diameter of ZnS:Ag^+ NCs was found to be *ca.* 6.3 nm, which is in good agreement with that of the XRD results. Moreover, the TEM image of the ZnS:Ag^+ NCs shows continuous lattice fringes with an observed d-spacing of 0.31 nm, which is in line with the lattice spacing in the (111) planes of cubic ZnS NCs (Fig. 3B). The discrete bright spots in Selected Area Electron Diffraction (SAED) pattern of ZnS:Ag^+ NCs consisting of three concentric sharp rings corresponding to (111), (220) and (311) diffraction of the cubic structures (Fig. 3C).

Quantum confinement effects generally provide blue-shift in optical absorption edge as caused by band gap widening in the UV region in nanometer scale particle size [19] and the corresponding blue-shift in PL. Doped NCs are of special importance because of both high

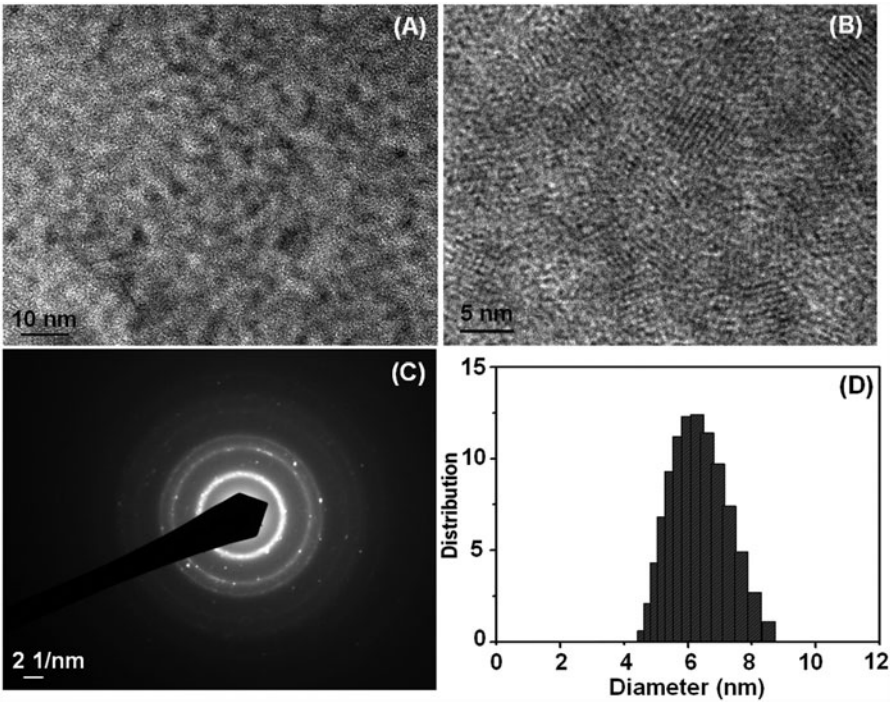

Figure 3. (A, B) TEM images at different magnifications, (C) SAED pattern, and (D) the size distribution diagram of ZnS:Ag^+ NCs.

luminescence-efficiencies and lifetime shortening [15]. In the present study, the effect in optical properties upon the doping of Ag^+ into ZnS NCs at the ranging from 0.5 to 2.0 wt% was investigated. The UV-vis absorption spectra of the un-doped ZnS NCs and ZnS:Ag^+ NCs are depicted in Fig. 4. Blue shift was observed in the absorption band edge of ZnS NCs from the corresponding bulk value of 335 nm (3.7 eV). The excitonic transition appeared at 306 nm (4.02 eV) in undoped ZnS NCs implying quantum confinement effects resulted in the nanoparticles. The passivation layers of the thioglycerol around the ZnS NCs core could both prevent the growth of ZnS NCs and act as a quantum well, which widens the band gap and is responsible for the blue shift in respect of bulk counterparts. The UV–visible absorption band edge of ZnS:Ag^+ red-shifted non-monotonically and the absorption onset was observed at 311, 315, and 321 nm for ZnS:Ag^+ NCs depend on doping of 0.5%, 1.0% and 2.0% Ag^+ dopant, respectively, (Fig. 4B–D). The red shifts were happened due to the change of energy band gap in the NCs. Because Ag^+ ions occupy the Zn^{2+} sites in the lattice, and might form the Zn-Ag-S ternary system, so the band gap would be reorganized by the ratio of Zn and Ag ions in the matrix.

The PL spectroscopy was employed to study the changes in luminance property upon doping of different concentrations Ag^+ ions in ZnS NCs. The PL spectra of un-doped ZnS NCs and Ag^+ doped ZnS NCs are demonstrated in Fig. 5. The emission band for un-doped ZnS NCs was observed at 465 nm with moderate intensity (Fig. 5A). On the other hand, upon doping of Ag^+ ions into ZnS NCs, the band emission peaks shifted towards higher wavelength. As the Ag^+ ions doped concentration increased by 0.5%, 1.0% and 2.0% a gradual red shift were appeared at 472 nm, 478 nm and 481 nm, respectively (Fig. 5B–D).

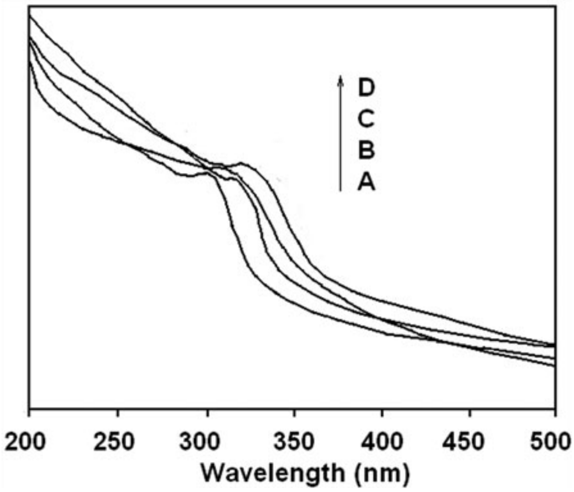

Figure 4. Absorption spectra of (A) un-doped ZnS NCs, and (B–D) ZnS:Ag$^+$ NCs with different doping concentrations (0.5, 1.0, and 2.0%).

It is known that the peak is correlated with native defects, in this case sulfur vacancy. When Ag$^+$ ions were doped into ZnS NCs, more defect states would be incorporated. It is speculated that during the incorporation of (impurity) Ag$^+$ ions into ZnS NCs, the dopant Ag$^+$, entered the lattice by substitution of Zn^{2+} ions or occupation interstices of the lattice, and causes increased Ag$^+$ ions on regular Zn^{2+} sites. In the case of 2.0% Ag$^+$ doping, the enhancement intensity of blue emission (about 481 nm) was observed (Fig. 5D). It may be because of the formation of blue luminescence centre by inclusion of Ag$^+$ ions, resulting in a transition from defect level to the Ag induced t_2 level, [20] while without doping, transition occurs from defect level to the valence level.

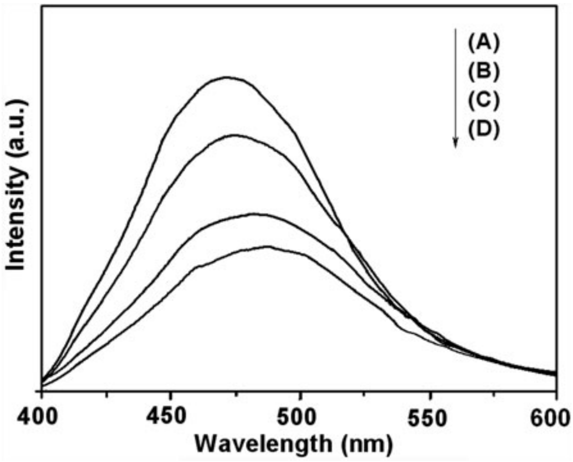

Figure 5. PL spectra of (A) ZnS, (B–D) ZnS:Ag$^+$ NCs to Ag$^+$ wt% of 0, 0.5, 1.0 and 2.0%, respectively.

4. Conclusions

ZnS NCs doped with 0.5–2.0 wt% of Ag^+ were synthesized by aqueous solution co-precipitation method using thioglycerol as capping agent. The synthesized $ZnS{:}Ag^+$ NCs were characterized by XPS elemental mapping analysis. The zinc blende structure of $ZnS{:}Ag^+$ NCs was confirmed by XRD studies. The TEM and SAED studies of the $ZnS{:}Ag^+$ NCs showed well-crystallized cubic crystalline phase which was good agreement with XRD results. The band gap of thioglycerol guided ZnS NCs was observed to be increased from bulk value of 3.7 to 4.11 eV due to quantum confinement effects. Based on dopant ions concentration, the UV/vis absorption spectra of the $ZnS{:}Ag^+$ NCs found to be red shifted in the emission wavelength ranging from 310–320 nm might be due to the formation of Zn-Ag-S ternary system. PL emission spectra clearly showed that the Ag^+ doped (0.5–2.0%) ZnS NCs emitted at the range 472–481 nm which were much higher than that of un-doped ZnS NCs (465 nm). These results clearly demonstrate that by controlled doping of Ag^+ ions using appropriate capping agent the optical properties of ZnS NCs could be tuned in order to attained materials with suitable applications.

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