Synthesis and characterizations of Mn doped alloyed $Zn_xCd_{1-x}S$ nanocrystals

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Abstract

Composition regulation of semiconductors can engineer the band gap and thus tune the optical properties. For effective utilization of orange emitting phosphors in color conversion applications blue excitation is necessary. Here in this work, absorption and photoluminescence spectroscopic measurements have been done to study the variation in band gap energy by changing the composition of $Zn_xCd_{1-x}S$ nanocrystals. Further, ternary Mn doped $Zn_xCd_{1-x}S$ semiconductor nanocrystals have been synthesized via an aqueous route over a wide composition range by adjusting the molar ratio of precursors which leads to tunable bandgap, thus propagate the progressive growth of light absorption and photoluminescence spectra. The variation in tunability of bandgap is due to the change in Cd/Zn ratio. By changing Cd/Zn ratio excitation wavelength shifts from UV to blue colour. Copyright © 2017 VBRI Press.

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Introduction

Semiconductor nanoparticles (NPs) have spawned great fundamental and technical interest as they possess unique size-tunable properties and, accordingly, exhibit potential applications as optoelectronic devices and biomedical tags [1]. There are various parameters which should be effectively controlled so as to tune the properties. Controlling size, composition, and structural complexity, during synthesis is always an enthralling topic since the properties can be effectively tuned by regulating these parameters. Engineering the bandgap is the crucial aim in such regulations. As known, the bandgap of semiconductor can be tuned by modifying the size near Bohr radius or by adjusting the composition via alloying. In the past two decades, the main efforts have been focused on the preparation of different color-emitting binary or core-shell nanocrystals with different particle sizes [1] using simple and inexpensive chemical routes. Among a variety of semiconductor materials, the wide-band gap binary II–VI compounds and their alloys have been investigated most extensively for their potential application in different fields such as opto-electronic devices, nonlinear optical and luminescence devices because of the quantum-size effect, especially their tunable optical property. Apart from binary compositions, exploration of tunable optical properties of ternary compositions has become an alternative way to produce desired wavelength by changing their stoichiometries and/or the doping [2]. Yang and co-workers reported ternary $Zn_xCd_{1-x}Se$ alloyed nanocrystals with luminescent properties comparable or even better than the best-reported binary CdSe based nanocrystals [3]. Recent advances have led to the exploration of tunable optical properties by changing their constituent stoichiometries in ternary nanocrystals. As an important semiconductor with great potential in light emission [4], photocatalysis [5] and solar cells [6], the ternary sulfide $Zn_xCd_{1-x}S$ could cover the bandgap ranging from 2.42 eV for CdS [7] to 3.8 eV for ZnS [8] by adjusting the composition ($0 \leq x \leq 1$), which enables the light emission from green to ultraviolet. Mediated growth of composition-tunable ternary $Zn_xCd_{1-x}S$ nanocrystals over a wide composition range by changing the ratio of Zn and Cd precursors results in tuning of the bandgaps. This study provides a convenient approach for engineering the composition and bandgap of ternary $Zn_xCd_{1-x}S$ nanocrystals, which could be applicable to some other alloyed chalcogenide nanocrystals. The composition effect has been attributed to arising from a strong dependence of the electronic energy of nanocrystals on the effective exciton mass [9, 10]. Currently, the ternary II–VI semiconductor materials have attracted more interest than the binary II–VI compounds due to their better physical properties compared to other materials, especially their tunable optical properties which could be controlled by their constituent mole-fraction, particle size, and morphology. The optical properties of doped nanomaterials differ from the corresponding host nanomaterials as the dopants form deep trap levels and act as luminescence centers. Discrete energy states can be

introduced in the band gap of semiconducting host by doping with transition metals such as Cu, Ag and Mn [11]. Thus, alloy nanocrystals are increasingly important in many areas of nanoscale engineering because of the continuous tunableness of their physical and optical properties through the gradual Variation of their composition. Alloyed semiconductor nanomaterials provide a wealth of opportunities for the controlled development of new materials and devices, such as electronic devices [12], light-emitting diodes [13], electromagnetic-radiation detectors, catalysts [14], and biological labels [10].

In this paper, Mn doped $Zn_xCd_{1-x}S$ nanoparticles have been synthesized via a co-precipitation route by varying the composition of Zn and Cd precursors. Here it has been studied that by changing the composition of Zn and Cd, the band gaps are tuned accordingly. Thus Mn doped $Zn_xCd_{1-x}S$ nanoparticles with tunable band gap have been synthesized by using an inexpensive and simple procedure.

Experimental

Materials/ Chemicals details

Materials: zinc acetate ($Zn(CH_3COO)_2 \cdot 2H_2O$), 99.99%) purchased from Aldrich, cadmium acetate dihydrate ($Cd(CH_3COO)_2 \cdot 2H_2O$) from Himedia, sodium sulfide ($Na_2S.\ 9H_2O$) from Merck, 3-Mercaptopropane-1,2-diol ($C_3H_8O_2S$) or thioglycerol (TG), manganese acetate tetrahydrate (($CH3COO)_2Mn.4H_2O$) from Merck were used without further purifications.

Material synthesis

The bottom up wet chemical synthesis route was used to synthesize orange emitting nanoparticles with various composition. The ZnCdS nanoparticles with different composition were doped with Manganese (Mn).

Synthesis of $Zn_xCd_{1-x}S$:Mn nanoparticles

ZnCdS nanoparticles have been synthesized via an aqueous route directly in water at room temperature. 0.1 M solution of zinc acetate in 10 ml distilled water and 0.1 M cadmium acetate in 10 ml distilled water with varying Zn_x/Cd_{1-x} ratio, 0.1 M in 10 ml solution of manganese acetate has been prepared and stirred for half an hour. After that Cd and Mn precursors were dropwise added into Zn precursor while stirring. Add TG solution (100μl in 10 ml) dropwise into the reaction solution and then freshly prepared sodium sulfide (0.1M in 10 ml) was injected into the solution. Then the mixture was stirred for 3 hrs at 80ºC. The precipitate was separated by centrifugation and washed several times with ethanol. Then the washed precipitate was dried at 80ºC to collect the finally prepared QDs.

Characterizations

The absorbance spectra were measured with Shimadzu UV 2600 UV-visible spectrophotometer. The

photoluminescence studies were done by using Edinburg FLS-980 florescence spectrophotometer with a Xe lamp as the excitation source. XRD measurements were done.
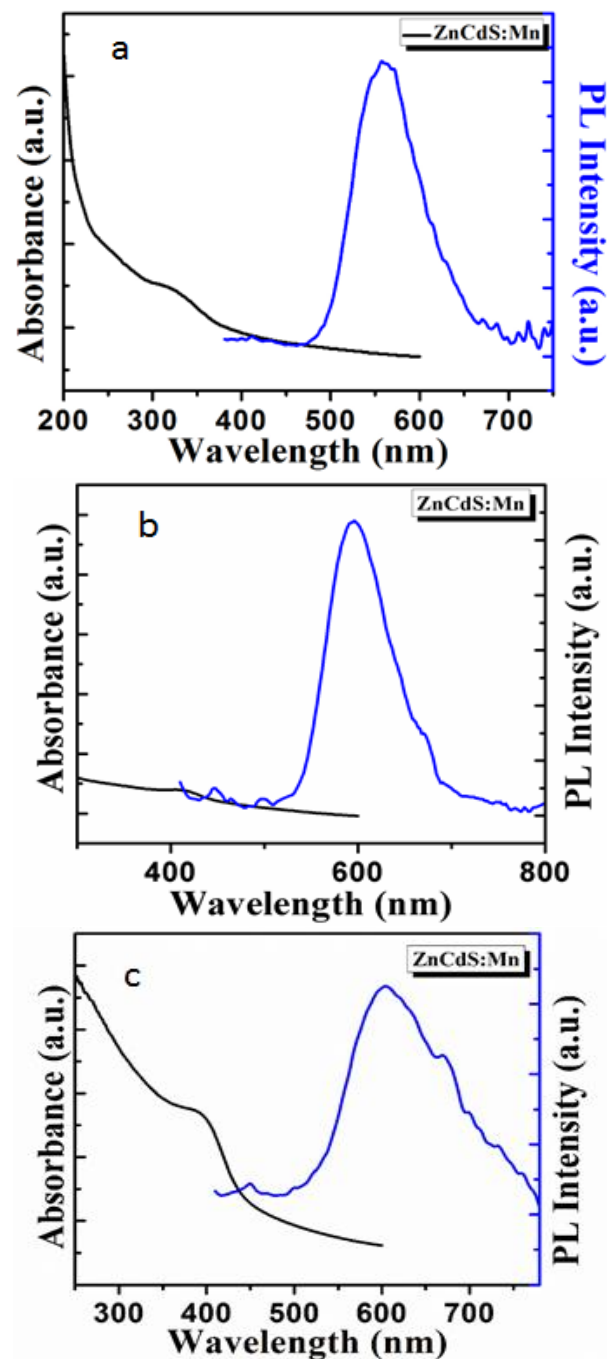

Fig. 1. Pl emission of (a) $Zn_{75}Cd_{25}S$:Mn (b) $Zn_{50}Cd_{50}S$:Mn (c) $Zn_{25}Cd_{75}S$:Mn.

Results and discussion

Fig. 1 (a) shows the normalized UV-vis absorbance and PL spectra for Mn doped $Zn_{75}Cd_{25}S$ nanoparticles. It shows absorbance value at 300 nm as there is more concentration of Zn precursor. The absorbance value and the PL emission peak red shifted as the concentration of cadmium increases. The emission value at 600 nm is due

to the presence of dopant. Manganese (Mn) is used as dopant. PL emission spectrum indicates the formation of deeper trap levels due to Mn, hence dopant related emission ($^4T_1$-$^6A_1$) is observed. They give bright emission in orange region. The concentration of precursors has been varied. **Fig. 1(b)** and **Fig. 1(c)** demonstrate the normalized UV-vis absorbance and PL spectra for Mn doped $Zn_{50}Cd_{50}S$ nanoparticles and Mn doped $Zn_{25}Cd_{75}S$ nanoparticles respectively.

To calculate the band gap of the synthesized QDs, the fundamental absorption which correspond to the transition from valence band to conduction band was used. The relation between absorption coefficient and incident photon energy can be written as

$$\alpha = A\,(h\upsilon - E_g)^n/h\upsilon$$

where, A is constant, E_g is band gap of material and exponent n depends on the type of transition. The exact value of band gap can be determined by extrapolating the straight-line portion of the $(\alpha h\upsilon)^{1/n}$ versus $h\upsilon$ axis.
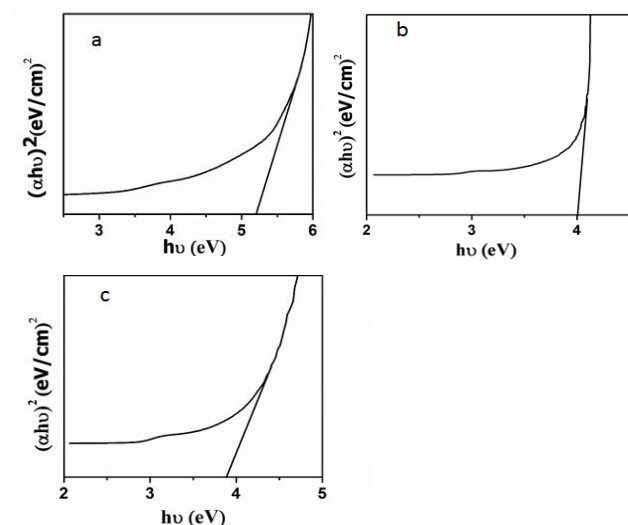

Fig. 2. Optical band gap of (a) $Zn_{75}Cd_{25}S$: Mn (b) $Zn_{50}Cd_{50}S$:Mn (c)$Zn_{25}Cd_{75}S$:Mn.

Fig. 2(a) shows the optical band gap 5.2 eV of Mn doped $Zn_{75}Cd_{25}S$ nanoparticles which has been calculated using the above equation. **Fig. 2(b)** and **Fig. 2(c)** demonstrate the normalized optical band gap 4 eV and 3.88 eV of Mn doped $Zn_{50}Cd_{50}S$ nanoparticles and Mn doped $Zn_{25}Cd_{75}S$ nanoparticles respectively. From here, it has been concluded that the band gap of the material varies as the composition changes. **Fig. 3** shows the XRD pattern of ZnCdS doped with Mn. From XRD results, it concluded the cubic structure with broad diffraction peaks of (111), (220), (311). The average crystallite size has been calculated from XRD peak broadening by using Scherrer formula i. e.

$$(d = 0.9\lambda/\beta Cos\theta)$$

where, d is the calculated particle size in angstrom, β is the full width at half maximum (FWHM), λ is the wavelength of the X- rays used i.e. 1.54 A°. From this, particle size of 2.9 nm has been obtained.
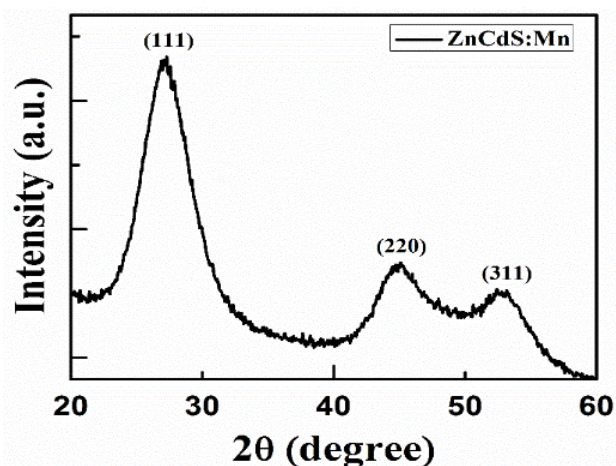
Fig. 3. XRD pattern of Mn doped ZnCdS.

Conclusion

The composition regulation of the $Zn_xCd_{1-x}S$ nanocrystals leads to a tunable bandgap by the progressive evolution of their optical properties. The absorbance in UV-vis spectra changes by changing the *x* values from 0.75, 0.50, and 0.25 respectively. There is variation in band gap which is found due to change in Cd/Zn ratio. For the data it is concluded that for Cd-rich samples, the excitation wavelength shifts from UV to visible light (i.e. blue light). The $Zn_xCd_{1-x}S$ nanoparticles with tunable bandgaps could find their applications in different optoelectronic devices where blue excitable materials are required.

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