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Facile synthesis of gradient alloyed $Zn_xCd_{1-x}S$ nanocrystals using a microwave-assisted method

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ABSTRACT

We have synthesized $Zn_xCd_{1-x}S$ nanocrystals (NCs) using a microwave assisted method. $Zn(Ac)_2$, $CdSO_4$ and $Na_2S_2O_3$ were used as the precursors and thioglycerol (TG) was used as the capping agent. $Na_2S_2O_3$ is a photo and heat sensitive material, which supplies S species needed for the reaction upon dissociation. In this facile method, microwave irradiation provides the activation energy for the dissociation of $Na_2S_2O_3$ in and leads to the formation of $Zn_xCd_{1-x}S$ NCs in 2 min. The question that to what extent Zn is incorporated into CdS structure was addressed using UV–Vis spectroscopy, X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Our results showed that the real value of x in $Zn_xCd_{1-x}S$ NCs is less than the initial values of Zn. Also we have given evidence indicating the formation of a gradient alloyed structure for $Zn_xCd_{1-x}S$ NCs. The NCs sizes were calculated by effective mass approximation, using real calculated x values. Photoluminescence spectra indicated a blue-shift by increasing x value, which is consistent with band gap shift.

1. Introduction

Semiconductor nanocrystals (NCs) demonstrate unique physical and chemicals properties, which depend strongly on size due to the well-known quantum confinement effects [1]. II–VI semiconductors such as CdS and ZnS are among direct band gap semiconductors which are suitable for using in light emitting diodes [1–3], solar cells [4], biolabeling [5], and sensors [6]. CdS and ZnS have so far attracted a great deal of attention, because of easy synthesis and having proper band gap for some applications [7–9].

In the last two decades, a wide range of work on the synthesis of binary, ternary, quaternary and core–shell NCs has been reported [10–12]. Among them, ternary NCs have the specific advantage that their properties can be tuned either by the change in size or the change in composition, while they can be synthesized more easily compared to quaternary NCs. Although the band gap of binary NCs can be tuned by reducing the size, in sizes below about 2 nm they become chemically unstable. Alloying NCs with a wider band gap semiconductor is an alternative method to change the band gap without decreasing chemical stability. On the other hand, in some cases alloying results in band gaps which is smaller than the band gap of either parent materials. An example is alloying CdSe with CdTe [13]. Also it has been reported that ternary alloyed NCs may show better luminescent properties than parent binary NCs, as demonstrated in case of $Zn_xCd_{1-x}Se$ [14].

There are various reported methods for the synthesis of alloyed NCs; such as hot injection in non-polar solutions [15,16] microwave-assisted [17,18], simple chemical synthesis in aqueous solutions [19] and reverse micelles techniques [20]. In many of these methods, reaction temperature or reaction time is too high. A very fast microwave irradiation method was already reported for synthesis of CdS NCs in our group [21].

Here $Zn_xCd_{1-x}S$ alloyed NCs have been synthesized using a facile and rapid microwave assisted method in an aqueous media. Thioglycerol (TG) was used as the capping agent molecule. Optical, structural and compositional properties of NCs at various Zn values were investigated and the incorporation of Zn atoms in CdS lattice has been studied in detail.

2. Experimental

All chemicals used were of analytical reagent grade without further purification. $3CdSO_4{\cdot}5H_2O$, $Na_2S_2O_3{\cdot}2H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and thioglycerol (TG) were purchased from Merck chemical Co.

$Zn_xCd_{1-x}S$ NCs were synthesized using $CdSO_4{\cdot}5H_2O$, $Zn(CH_3COO)_2{\cdot}2H_2O$ and $Na_2S_2O_3$ as the precursors. TG was used as capping agent. $Zn_xCd_{1-x}S$ NCs were synthesized through a microwave assisted reaction between $CdSO_4$., $Zn(CH_3COO)_2$. and $Na_2S_2O_3$. $Na_2S_2O_3$ is a photo and heat sensitive material, which provides S

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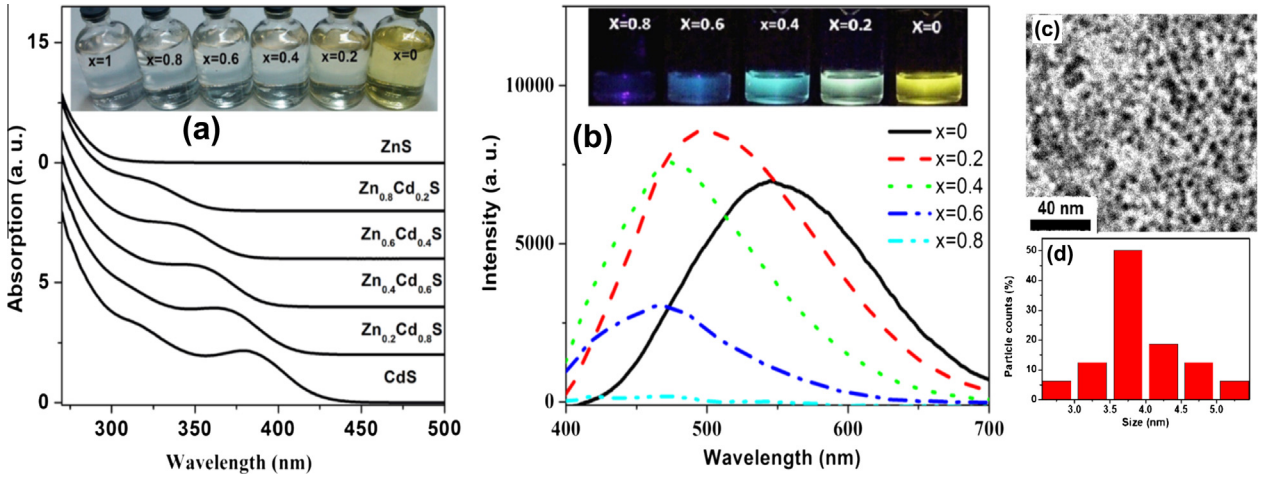

Fig. 1. Absorption (a) and photoluminescence spectra (b) of $Zn_xCd_{1-x}S$ NCs. Inset of 1a shows these NCs in ambient light condition. Inset of 1b shows image of luminescent NCs that are exposed to UV light. TEM image of sample with $x = 0$ (c) and the size distribution extracted from tem image (d).

species through dissociation [22]. In this work, the reaction temperature was rapidly increased to boiling point of water by microwave irradiation which leads to dissociation of $Na_2S_2O_3$ and the $Zn_xCd_{1-x}S$ NCs formation.

For the synthesis of $Zn_xCd_{1-x}S$ NCs, 30 ml mixed aqueous solution of $CdSO_4$, $Zn(CH_3COO)_2$ and $Na_2S_2O_3$ was prepared, in a way that the initial concentrations were x mM, $(1-x)$ and 50 mM, respectively. The x values were selected 0, 0.2, 0.4, 0.6, 0.8, and 1. Here, x in $Zn_xCd_{1-x}S$ is referred to the initial Zn mole fraction.[1] Then 20 ml of a 0.4 M solution of TG was added to the mixed aqueous solution of precursors. NH_4OH was used to adjust pH value of the solution to 8. The prepared solution was put at the center of a microwave system (2.45 GHz) and irradiated just for 2 min in constant power of 450 W. After the temperature of solution reached to room temperature, acetone was added as a non-solvent to precipitate. Then it was centrifuged, extracted and redispersed in 1 ml DI water. The final dispersed NCs in water were dried in vacuum for the XRD and XPS analysis.

Optical transmission was measured using a Perkin Elmer, Lambada 25, UV–Visible (UV–Vis) spectrometer. Photoluminescence (PL) measurements were performed by exciting with a high pressure Hg lamp with a 360 nm filter, and the emission of the solutions was collected through an optical fiber and measured using an Avantes spectrometer (AvaSpec-2048 TEC). TEM image was taken by a JEOL JEM-1400F transmission electron microscope. X-ray diffraction (XRD) was performed on the centrifuged and extracted particles using a Philips MRD X'pert Pro system equipped with a cobalt target. XPS analysis was measured using Al anode of a V.G.Microtech XR3E2 X-ray source and a concentric hemispherical analyzer (Specs model EA10 plus).

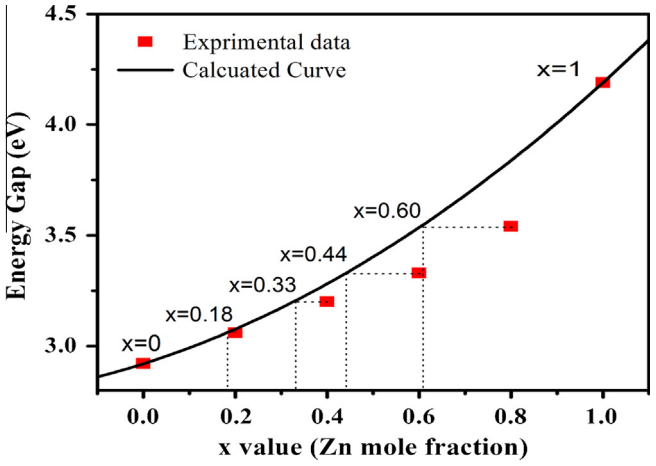

Fig. 2. Energy gap versus x value. Solid curve is Vegard's law that follows Eq. (1) and the red squares are the corresponding experimental data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3. Results and discussions

Microwave irradiation in the synthesis of ZnCdS nanocrystals provides homogeneous heating of the entire solution, enhances reaction rates, and facilitates formation of uniform nucleation centers which leads to an energy efficient synthesis as compared to other methods [23]. As we have already reported, $Na_2S_2O_3$ is the heat and photo sensitive agent which releases S^{2-} ions, therefore if the activation energy of some sort is not provided, releasing rate of S^{2-} ions is very slow [25]. If microwave irradiation is not used and the samples are put in a dark place at room temperature, ZnCdS nanocrystals grow extremely slowly and it takes about 24 h to have NCs with the same size.

Fig. 1(a) shows the absorption spectra of the synthesized $Zn_xCd_{1-x}S$ NCs. As x increases, the absorption edge is shifted to higher energy (400–290 nm), towards the band edge energy of ZnS. There is an excitonic peak in absorption spectrum of $Zn_xCd_{1-x}S$ with $x = 0$ which can be attributed to narrow size distribution of this sample and quantum confinement (because Bohr radii for CdS is smaller than ZnS). Inset of Fig. 1(a) is an image of the $Zn_xCd_{1-x}S$ NCs in ambient media. Change of the NCs color from CdS to ZnS is clear. Fig. 2(b) indicates PL spectra of $Zn_xCd_{1-x}S$ synthesized NCs under UV illumination with excitation wavelength of 360 nm. The PL spectra indicate a broad band emission related to surface defects of NCs that can be used in white LED [26]. The PL peak is shifted from 550 nm for initial x of 0 to 445 nm for initial x of 0.8, which confirms band gap widening when Zn is incorporated to CdS lattice. For x values greater than 0.4 intensity of luminescence of NCs is decreased so that $Zn_xCd_{1-x}S$ NCs with $x = 1$ (i.e. ZnS) is not luminescent anymore even under illumination of excitation wavelength of 254 nm. It may be due to defect energy states that cause non-radiative recombination in x values of greater than 0.4. The inset of Fig. 2b shows the luminescence of $Zn_xCd_{1-x}S$ NCs under UV illumination. TEM image of the sample with $x = 0$ is shown in Fig. 1c. The obtained size distribution for this sample (Fig. 1d) demonstrates an average size of 3.8 nm.

In this synthesis method, initial values of x were 0.2, 0.4, 0.6 and 0.8, however Zn incorporation in CdS structure may be different from these initial values. Here we have determined the real x using these UV–Vis, XRD and XPS. The real x value can be calculated by measuring the band gap and lattice constant of NCs and comparing with the existing models that predict band gap and lattice constant

[1] [Zn]/([Cd]+[Zn]).