Influence of Phosphine-Free Solvents On the Structural and Optical Properties of Oleylamine Assisted Synthesis of CdS Nanocrystals

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Research Article

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Abstract

Synthesis of cadmium sulphide (CdS) nanocrystals was carried out using hot-injection method through oleylamine as solvent and capping ligand at 220°C. From the UV-visible absorption spectra, the band gap of the synthesized nanocrystals was estimated as 2.5 eV. X-ray diffraction pattern confirms the presence of wurtzite phase with their characteristic reflections. TEM analysis of the synthesized nanocrystals show that the nanocrystals are having nearly spherical shape with the diameter 5-10 nm. For the comparison, different solvent mixtures were employed to prepare the CdS nanocrystals and the structural and optical results show that the solvents have significant influence on the optical properties of the prepared nanocrystals. The results are discussed in detail.

1. Introduction

Colloidally prepared semiconductor nanocrystals are widely applied for different kind of promising sectors such as solar cell, photodetector, photocatalysis and photodiodes [1]. Preparation of semiconductor nanocrystals using colloidal method has emerged as one of the versatile approaches to deliver nanocrystals with different morphologies. Specifically, hot-injection method has been used to prepare variety of chalcogenide nanocrystalline materials for the solution processed applications [2, 3]. In this method, easily decomposable precursors are actively reacting in hot-coordinating solvents under high temperature and result highly monodispersed, crystalline nanomaterials. The contribution of hot-injection method to the preparation of cadmium chalcogenide nanomaterials is remarkable and several research findings are dealing about their preparation under different solvents [4, 5, 6]. By varying the physical parameters, the size and shape of the nanocrystals are cleverly managed in order to use them for different applications. Out of others, cadmium chalcogenides nanomaterials are commonly explored for several promising applications including solar cells, photocatalysis, light emitting diode (LED), bio-imaging etc. For the core-shell preparation also CdS nanocrystals are playing important role in reducing surface defects of nanocrystalline materials such as cadmium selenide (CdSe), cadmium telluride (CdTe). Although several research findings are dealing about the synthesis of CdS nanocrystals under different conditions [7, 8, 9, 10] higher boiling point solvent assisted colloidal synthesis always has some advantages [11]. Higher boiling point solvents such as oleylamine (OLA)m, oleic acid (OA) and 1-octadecene (1-ODE) have been extensively used in recent years to produce monodispersed, highly crystalline semiconductor nanocrystals for the solution processed fabrication of optoelectronic devices [12, 13]. Importantly, the morphology of the resultant nanocrystals is hardly influenced by these solvents under the controlled conditions and it is also greatly influenced by their binding ability. The composition, phase and optical properties of the semiconductor nanocrystals are often influenced by these solvents. With different kind of amines and acids, single molecular cadmium precursor such as dithiocarbamate, thiosemicarbazide, thiosemicarbazone etc. have shown formation crystalline CdS nanocrystals with different morphologies [14, 15, 16]. Having the boiling point over 300°C, OLAm is enormously used to produce variety of metal chalcogenide and metal oxide nanocrystals by decomposing simple molecular precursors under optimized conditions [17, 18]. The reducing ability of OLAm is additionally favour to
achieve semiconductor nanocrystals with desired phase [19]. Other than functioning as solvent and ligand, OLAm also influencing on the disproportionation of the precursors in the reaction medium in order to control the growth of the nanocrystals [20]. Furthermore, the activity of OLAm together with other coordinating and non-coordinating solvents such as OA and 1-ODE is found to be different and this critically influence on the different facets of the nanocrystals which results in different morphologies [21, 22]. Hence, it is essential to explore the role of OLAm in synthesizing metal sulphide nanocrystals and its activity with other solvents. In this present work, we investigate on the synthesis of CdS nanocrystals using OLAm as solvent and influence of different solvents with OLAm on the structural and optical properties of the synthesized CdS nanocrystals.

2. Experimental Section

(a) Chemicals

Cadmium chloride (CdCl₂), Oleylamine (OLAm), Oleic acid (OA), 1-Octadecene(1-ODE), 1-dodecanethiol (1-DDT), sulphur powder (S) and isopropanol were purchased from Sigma Aldrich and used without further purification.

(b) Synthesis of CdS nanocrystals

Synthesis of CdS nanocrystals was carried out using colloidal hot-injection method. Firstly, 0.5 mmol of CdCl₂ was taken in a three-neck flask together with 10 mL of OLAm and 10 ml of 1-ODE. This mixture was degassed for 30 minutes in order to avoid oxidation. Then, the mixture was heated to 220°C for an hour to achieve Cd-Oleate complex. At the same time, about 0.5 mmol of elemental sulphur powder was taken in an another three-neck flask together with 10 mL of OLAm and 10 ml of 1-ODE. This mixture was heated at 150°C until the solution colour turn out to reddish brown. Then, this solution was taken in a glass syringe and injected into Cd-OLAm complex mixture. Appearance of yellow colour indicate the formation of CdS nanocrystals in solution. This mixture was further allowed to 5 minutes and cooled to room temperature. This was again centrifuged with 5000 rpm for 15 minutes. With the crude mixture, 10 mL of iso-propanol was added and purified by repeating the centrifugation process. The resultant nanocrystals were dried under ambient conditions and subjected to further analysis using different characterization techniques.

3. Results And Discussion

X-ray diffraction pattern of the synthesized CdS nanocrystals using pure OAm is given in figure 1. For the comparison, CdS nanocrystals under different solvent mixtures OAm/OA and OAm/1-DDT were prepared in order to find the effect of solvents on the physical properties. The XRD pattern shows that the prepared nanocrystals have exhibited wurtzite phase (JCPDS No: 41-1049). Interestingly, in all cases we have observed formation of wurtzite phase through the similar characteristic peak positions and there is no phase change observed with the solvent mixtures. This clearly show that almost all kind of solvents
investigated in the present study are suitable to synthesis CdS nanocrystals under the optimized conditions. However, compared with other samples, the nanocrystals prepared using OLA/1-DDT mixture showed a slightly broader diffraction pattern compared with the samples prepared using pure OLA and OLA/OA. This is probably due to the slow release of sulphide (S^2−) from the 1-DDT in solution at higher temperature. This slow release of S^2− ions resulted a broad distribution of the nanocrystals in the reaction mixture due to the different size and cause broadening of peaks in XRD pattern.

The UV-visible spectra of the synthesized CdS nanocrystals under different solvent conditions is given in figure 2. Although there is no phase change observed in the XRD measurements, the prepared samples possess different band gap values because of the influence of solvents. The nanocrystals prepared using pure OLA exhibits with band gap 2.5 eV. Since the bulk bandgap value of CdS is 2.4 eV, the observed value show that the prepared particles exhibit in nanodimension. When CdS nanocrystals are prepared using the mixture of solvents i.e. OLA/1-DDT and OLA/OA, we see there is a change in the band gap values. The sample prepared using OLA/1-DDT exhibit band gap 2.38 eV whereas the sample prepared using OLA/OA exhibit 2.25 eV.

This lower bandgap value of the nanocrystals synthesised using OLA/OA is probably due to the larger size during the synthesis because of the dual ligands capping. Increase in the bandgap compared with the sample prepared by pure OLA show that these samples are significantly influenced by other solvents 1-DDT and OLA. This also reveals that there is significant variation in the size of the synthesized nanocrystals due to the influence of different solvents. Furthermore, the obtained bandgap values clearly showing that there is a significant influence when OLA is mixed with OLA and 1-DDT during the synthesis of nanocrystals. The active role of these solvents on the surface of the nanocrystals together with OLA however, should further be examined in detail.

Lattice strain and crystallite size of the nanocrystals were calculated from the diffraction data using Williamson-Hall plot (W-H). W-H plot is drawn between sinθ and βcosθ in x and y-axis respectively (figure 3) using the equation (1).

\[ β\cosθ = \frac{kλ}{D} + 4ε\sinθ \]  

Where, \( β \) is full width at half-maximum, \( λ \) is the wavelength of the X-ray, \( D \) is the average crystallite size and \( ε \) is the lattice strain of the compound. The obtained values are tabulated and given in Table 1. From the table, it is found that nanocrystals synthesized using OLA are smaller than the nanocrystals obtained using OLA/OA or OLA/1-DDT. It should be noted that the size of the nanocrystals synthesized using OLA calculated by this method is approximately equal with the TEM result of the same. In addition, the W-H plots show that nanocrystals synthesized using pure OLA and OLA/OA (figure 3a and b) have negative slopes from the linear fit, it construes that the nanocrystals have experienced a compressive strain in its lattice. Meanwhile, plot of the nanocrystals prepared using OLA/1-DDT shows positive slope, hence, its lattice is experienced tensile stress (figure 3c). The tensile
strain in OLAm/1-DDT might be due to the elongation in the morphology. Furthermore, it is observed that this strain has ensued peaks shift in the XRD patterns. Chen et al. have found that because of the metal-thiol interaction effect in 1-DDT, larger nanocrystals with lesser thickness are formed [23, 24]. Hence, compressive strain is averted and the lattice experiences tensile strain. Similar kind of effect can also be correlated in the present case. Moreover, from the XRD analysis, it is observed that the metal-thiol interaction leads change in the predominant plane growth.

Transmitte electron microscopy (TEM) analysis of the CdS nanocrystals prepared by pure OLAm is given in figure 4 (a, b). The images clearly show that the prepared nanocrystals exhibit nearly spherical in shape. The diameter of the nanocrystals is estimated as 5-10 nm. Since the intention of the present study is to explore the primary role and effect of OLAm in the synthesis of CdS nanocrystals, the analysis is especially focused on the exploring the structural, optical and morphological properties of CdS nanocrystals prepared by pure OLAm. The TEM images of the prepared nanocrystals in show that the nanocrystals are assembled together quite closely, which may be due to the ligand (i.e. OLAm) induced self-assembly. The lattice spacing of the prepared CdS nanocrystals is calculated as 0.34 nm which further ensure the formed nanocrystals with wurtzite phase (figure 4c). The selected area diffraction pattern (SAED) of the prepared nanocrystals in figure 4 (d) show that highly crystalline nanocrystals are formed with OLAm capping and this is also resembled with the obtained results from XRD analysis.

The formation mechanism of the nearly spherical shaped CdS nanocrystals could be described by the following theory. Because of the long chain (i.e bulky nature), OLAm is significantly influencing on the CdS nanocrystals surface. When OLAm is refluxed with sulphur powder, it forms oleylammonium sulphide which functionally act as the sulphide precursor [25, 26, 27]. Upon injecting into the Cd-oleate complex mixture, formation of CdS nanocrystals rapidly happen through the nuclei formation. According to the Ostwald ripening process, in this situation, growth of nanocrystals takes place under prolonged reaction conditions. The non-spherical nature of the formed nanocrystals in the present study could be due to the steric hindrance provided by the OLAm capping which strongly influence on the growth of facets of CdS nanocrystals. The schematic diagram of the synthesis scheme of CdS nanocrystals through hot-injection method in the presence of OLAm is represented in figure 5.

### Table 1

| Sample          | Crystallite size (nm) | Type of strain | Strain |
|-----------------|-----------------------|----------------|--------|
| OLAm            | 4                     | Compressive    | -0.011 |
| OLAm-OA         | 11                    | Compressive    | -0.002 |
| OLAm-1-DDT      | 10                    | Tensile        | 0.005  |

Conclusion
Oleylamine capped CdS nanocrystals were synthesized using hot-injection method and their structural and optical properties were analysed. The nanocrystals are possessed nearly-spherical shape with the bandgap 2.5 eV. Although there is no phase transformation observed under the influence of different solvents, the obtained results show that solvents have significantly influence on the optical and morphological properties. Hence, it is possible to tailor the functional properties of CdS nanocrystals using suitable ligand chemistry. The results also show that the prepared nanocrystals are suitable for the solution-processed solar cell fabrication applications.

**Declarations**

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**Conflict of interest**

The authors declare that they have no known competing interests.

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Figures
Figure 1

XRD patterns of the CdS nanocrystals synthesized in the presence of different solvents
Figure 2

UV-visible spectra of the synthesized CdS nanocrystal powders
Figure 3

W-H plots of the CdS nanocrystals synthesized using a) pure OLAm b) OLAm/OA and c) OLAm/1-DDT
Figure 4

(a-c) TEM images of the synthesized CdS nanocrystals using pure OLAm and (d) SAED pattern of the CdS nanocrystals
Figure 5

Schematic diagram of the synthesis protocol of CdS nanocrystals by hot-injection method