



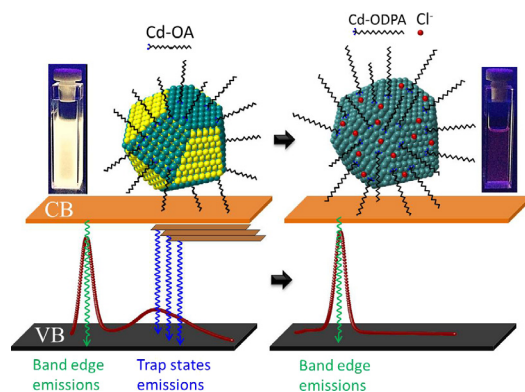
Synthesis of trap emission free cadmium sulfide quantum dots: Role of phosphonic acids and halide ions



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GRAPHICAL ABSTRACT



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ABSTRACT

Changing the capping ligands of CdS nanocrystals during their synthesis controls the optical properties of these nanocrystals. Addition of a little amount of CdCl₂:Phosphonic Acid (PA) completely eliminates the surface state emission with an increase in quantum yield of band edge emission from these nanocrystals. The role of halide ions in surface passivation along with the structural dependence of these nanocrystals on surface states has also been studied. These as prepared nanocrystals are uniform as well as monodispersed and their size can be tuned by varying the reaction time. These nanocrystals have been well characterized using a combination of optical and structural techniques.

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1. Introduction

The capping of cadmium chalcogenide nanocrystals (NCs) surrounded by organic ligands has attracted significant attention for applications in materials science and nanotechnology [1–3]. It has long been accepted that proper passivation of surface sites is essential for obtaining high luminescence quantum yield from col-

loidal quantum dots such as CdSe and CdS [4–7]. In order to enhance the photoluminescence (PL) intensity, a proper combination of radiative and non-radiative decay pathways is essential, with more of the radiative decay part. The non-radiative decay pathways which are more likely associated with unpassivated surface atoms or dangling bonds of semiconductor NCs could be eliminated by effective surface passivation using suitable surface capping agents [8,9]. Some progress has been achieved in improving the PL intensity through modifying the semiconductor NCs surface [10]. The effects of ions and ligands on the surface states of

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cadmium sulfide NCs have also been investigated by various groups [11–14]. There are a few articles that report the synthesis of semiconductor NCs with white-light emission from CdSe and CdS quantum dots by controlling the surface traps [15–17]. These trap states emission in CdS quantum dots are mainly said to originate from the surface deep trapped electrons at the surface Cd with sulfur vacancy sites [18] and thus by appropriate ligand passivation, the thermodynamics of excitonic population which is in equilibrium between the band edge exciton and the surface of nanocrystals can be controlled effectively [17,19].

On the basis of number of electrons involved and identity of electron donor and acceptor groups, metal ligand interaction has been classified into three types [20,21]. Firstly, L type ligands (RNH_2 , R_3P and R_3PO) which are neutral two electron donors with a lone electron pair that coordinates with surface metal atoms. Secondly, X type ligands (RCOO^- , RS^- , Cl^-) which are neutral ligands or monovalent ions that bind with opposite charge at the nanocrystals surface. And thirdly, Z type ligands such as ($\text{Pb}(\text{OOCR})_2$, CdCl_2) which bind through the metal atom as two electron acceptors [22]. Specifically these small X type ligands (OH^- or Cl^-) can be incorporated on the NCs surface intentionally or unintentionally through side reactions during synthesis. A hybrid passivation scheme that involves introducing halide anions (X type ligand) during the end stages of the synthesis process, which can passivate trap sites that are inaccessible to much larger organic ligands has also been studied by Ip et al. [23] for lead sulfide NCs.

Here, we report the role of phosphonic acid, halide ions and cadmium ions on controlling the band-edge PL and surface-trap-state PL emission from CdS NCs. Almost all the surface traps can be eliminated by using suitable amount of CdCl_2 :PA during the course of the reaction. Our results show strong excitonic emission and no trap emission with increase in luminescence efficiency of these NCs. We have also studied the effect of alkyl chain length of phosphonic acid and role of individual ions on nucleation, growth and surface reconstruction of CdS NCs. The same procedure was applied for ZnS NCs and it was found that surface traps can be completely eliminated from this system as well.

2. Experimental section

2.1. Chemicals

Hexyl phosphonic acid (HPA) and tetradecyl phosphonic acid (TDPA) were prepared according to Arbuzov procedure reported by Katritzky, et al. [24]. Cadmium oxide, (CdO, 99.5%), 1-octadecene (ODE, 90%), oleic acid (OA, 90%), oleylamine (OLA, 70%), octadecyl phosphonic acid (ODPA, 97%) and sulfur powder (99.9%) were purchased from Sigma-Aldrich.

2.2. Characterization

UV–VIS absorption spectra were acquired on Perkin Elmer Lambda 1050 UV/VIS/NIR spectrophotometer. Dilute solutions of semiconductor NCs dispersed in hexane were placed in four window 1 cm quartz cuvettes, and their absorption and corresponding fluorescence were measured. The fluorescence spectra were recorded on Perkin-Elmer LS-55 spectrometer and excitation wavelength employed was 350 nm. Powder X-ray diffraction (XRD) studies were carried out on a Bruker D8 Advance diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation. Transmission electron microscopic (TEM) images were recorded on a Technai G2 20 electron microscope operated at an accelerating voltage of 200 kV. Samples were prepared on 200-mesh carbon coated Cu grids by dropping NCs solution dissolved in hexane.

2.3. Synthesis of CdS nanocrystals (NCs)

CdS NCs were synthesized by previously reported methods with slight modifications [25]. Briefly, Sulfur solution is prepared by dissolving 0.5 mmol sulfur in 3 mL ODE in an inert atmosphere at 100 °C. 0.47 mmol CdO and 5 mmol OA were added to 13 mL ODE and heated to 280 °C with continuous stirring under an Ar atmosphere until a colorless solution was obtained. After attaining a constant temperature, sulfur solution was injected swiftly into the Cd solution. The temperature dropped down to 250 °C. The reaction was allowed to proceed until the desired size of the NCs was achieved. The solution was cooled down and washed twice in a 1:1 mixture of hexane-methanol to remove unreacted precursors. The NCs were precipitated by ethanol and re-dissolved in hexane.

2.3.1. Preparation of CdCl_2 :L solution where L = ODPA, HPA, TDPA

0.24 mmol L and 2.64 mmol CdCl_2 were dissolved in 10 ml OLA and heated to 100 °C for 16 h in an inert atmosphere.

2.3.2. Preparation of CdCl_2 :OA solution

0.24 mmol OA and 2.64 mmol CdCl_2 were dissolved in 10 ml OLA and heated to 100 °C for 16 h in an inert atmosphere.

2.3.3. Preparation of CdO:OA solution

10.56 mmol OA and 2.64 mmol CdO were dissolved in 10 ml ODE and heated to 250 °C in an inert atmosphere.

2.4. Synthesis of CdS NCs with CdCl_2 :PA

After 20 s of S injection in the procedure described above for CdS NCs synthesis, an aliquot was collected and then CdCl_2 :PA solution was added and reaction was quenched after 20 s. Different amounts of CdCl_2 :PA solution was added to achieve only band edge emission and no surface trap emissions. Finally the optimised amount of CdCl_2 :PA was achieved and the results have been explained further. The purification procedure is the same as for plain CdS NCs.

3. Results and discussion

The UV–Vis absorbance and Photoluminescence (PL) spectra of CdS NCs are shown in Fig. 1, before and after the addition of CdCl_2 :ODPA solution. The PL spectrum of CdS NCs shows two spectral

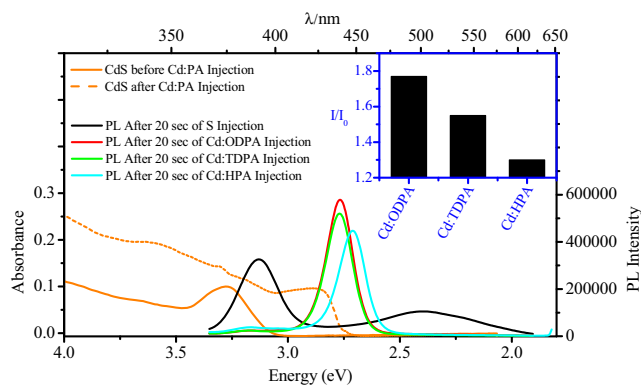


Fig. 1. UV–Vis absorbance, and PL spectra of CdS NCs (orange and black respectively). PL spectra for CdS/ CdCl_2 :ODPA, CdS/ CdCl_2 :TDPA and CdS/ CdCl_2 :HPA in red, green and cyan respectively. In inset ratio of PL intensities of CdS NCs after and before addition of CdCl_2 :ODPA, CdCl_2 :TDPA and CdCl_2 :HPA. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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