

# Aqueous Synthesis of CdPbS Quantum Dots Capable of NIR Emission

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## Introduction

Water-based synthesis and thiol ligands of PbS nanoparticle (i.e. quantum dot, QD) synthesis for Infrared imaging purposes have been studied in the past years; so far there are some problems in terms of real application. First, the reported luminescence spectral range through the literature is usually 1000–1500nm [1], which is still far from the optimal NIR window of 650–900 nm for efficient tissue penetration [2]. Second, our experiments indicate that the luminescence of MPA-capped PbS QDs is not as bright as other common visible-irradiative QDs such as ZnS, CdS and so on. Third, there is a stability issue relative to the dissolubility of PbS particles in alkaline aqueous solutions due to the amphoteric feature of the Pb element. With regard to the electronic and optical properties of semiconductor materials, we present a hybrid QDs of PbS along with CdS using the co-precipitation method in an aqueous solution; we attempt to achieve a better PL performance that includes proper wavelengths and an acceptable intensity. In the process, a series of processing parameters including composition, pH, and concentration are studied. By exploring different synthesis conditions, we wish to identify the key elements for the best PL performance of the process.

## Experimental

The aqueous CdS–PbS ( $Cd_{1-x}Pb_xS$ ) QDs were synthesized according to the following co-precipitation method at room temperature. A typical process for synthesis, such as a sample of 30/70 Cd/Pb molar ratio in the precursor, involved mixing  $Cd(NO_3)_2$  (0.04M, 0.6ml) and  $Pb(NO_3)_2$  (0.04M, 1.4ml) with 3-mercaptopropionic acid (MPA) (11.38M, 14 $\mu$ l) as capping molecule previously dissolved in DI water while stirring. The pH of the solution was then adjusted through the addition of a 1M tetrapropylammonium hydroxide solution (TPAH) (Alfa Aesar). While stirring at ambient temperature, various volumes of a  $Na_2S$  (0.04M) precursor was instantly injected into the solution to obtain a CdS–PbS colloidal suspension. An excess 2ml of 0.04M  $Cd(NO_3)_2$  was then dropwisely added until the pH of the suspension rose to about 12 by additional TPAH solution. A solution of MPA:( $Cd^{2+}+Pb^{2+}$ ):S having a total molar ratio of about 1:1:x ( $x=0.125\sim 0.3125$ ) was synthesized for a final volume of about 50ml with a nominal concentration based on the concentration of sulfur. The size analysis and XRD pattern of the resulting QDs were examined with a TEM (TECNAI 20, Philips) and an X-ray diffractometer (LabX XRD-6000), respectively. As to elementally quantitative analyses, atomic absorption spectrometer (SpectrAA-30) was employed to measure the metallic ions

concentration. UV–visible absorption spectra and Photoluminescence (PL) of the QDs suspension were obtained with a Model UV–2450 UV–visible spectrometer and a QM–4/2005 spectrofluorometer (Photon Technology International) coupled with a suit of Ocean Optics USB4000 (Ocean Optics), respectively.

## Results and Discussion

Fig.1(a) shows that the QDs are quite uniform in size and their mean size and deviation are 3.38nm and 0.4nm respectively. Fig.1(b) shows the XRD patterns of the powders from the precipitate of the final precipitate, which confirms that the produce is sulfides of the CdPbS composite.

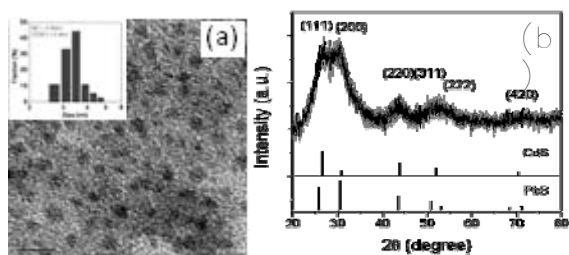


Fig. 1. (a)TEM image of CdPbS nanoparticles; (b)X–ray diffraction patterns of the final precipitate.

Fig.2(a) presents the PL spectrum for the optimal excitation wavelength of QD suspension, which showing a well defined NIR emission peak at about 830nm under photoluminescence excitation(PLE) at 470nm. Fig. 2(b) illustrates the overall mechanism involving excitation and emission, the reason for the irradiation can be assigned to that because the different crystalline structure between CdS(wurtzite) and PbS(rocksalt), when the Cd atom in CdS is thermodynamically exchanged by a lead ion, defects and

vacancies will be created at the interface to act as a new PL center at the interface in the CdS/PbS system [3]. The CdS shell formed after the addition of excess Cd precursor serves as a diffusion barrier to restrain the PbS inside from dissolving; hence, the QDs can resist higher pH solutions for a longer period of time. For example, a QDs solution with pH 12 restored at 4°C does not show any significant decay in PL intensity even after 10 months. Further, because CdS has a higher band gap than PbS, using CdS for surface passivation can be expected to improve the optical properties of quantum dots, such as quantum yield and photobleaching.

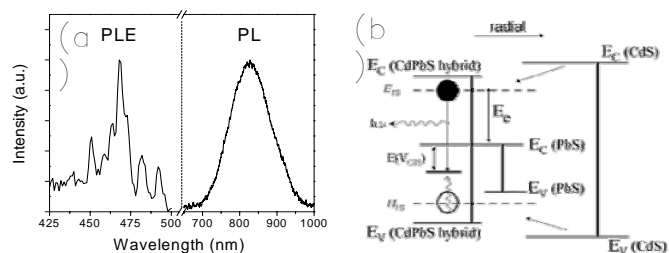


Fig. 2. (a)The PL spectra of the suspension; (b)The schematic representation of the electron–hole recombination process.

Fig. 3(a) is a plot describing the changes of the band edge and the PL photon energy of CdPbS QDs prepared with different Cd/Pb molar ratios in the precursor. Both the energies slightly decreased with the increased molar ratio of Pb in the precursor. When 60% Pb was used during the precipitation of QDs, only one IR emission peak could actually be measured in the PL spectrum, since the visible light emission had been almost quenched. In addition, because the concentration of total cations is fixed, less Cd ions participated in the reaction, and the relative content of CdS in the

particles was reduced, which led to the decreasing energies observed in the spectra. Fig. 3(b) exhibits the concentration–normalized PL map as a function of pH during the precipitation and total sulfur concentration. As can be seen, the maximum intensity was located near a pH of 10.5, along with a concentration of 0.8mM sulfur. Beyond this area, the intensity apparently decreased.

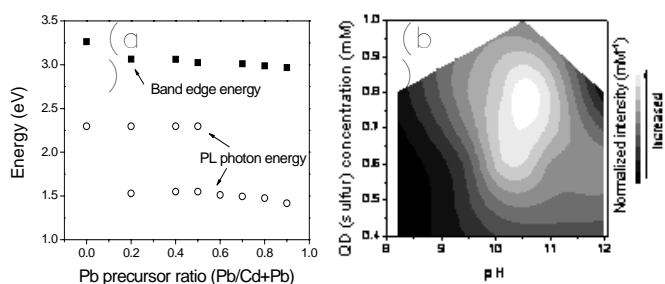


Fig. 3. (a) Absorption edge energy and the PL photon energy of CdPbS QDs prepared with different Cd/Pb molar ratios in the precursor; (b) PL intensity map as functions of pH during the precipitation and total sulfur concentration.

## Conclusion

MPA–capping CdPbS QDs aqueous suspension was synthesized, which exhibit a well defined NIR emission of wavelength ca. 830nm as excited. The mechanisms of particle formation and of radiation assigned to the defects at the interface of the heterogeneous structure are discussed. Also, a PL map recording the intensity distribution of QDs suspension prepared at a series of processing parameters has been established.

## References

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