Synthesis and Characterization of Chalcogenides Nanocrystals

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ABSTRACT

Considerable studies have been conducted in the imaging of living cells, using visualization tools based on fluorescent markers. The present work is focused on the synthesis of CdS and ZnS nanocrystals, by a two-phase technique. Nanocrystals were synthesized in water, coated with a suitable surfactant and mobilized into an organic phase before getting aggregated. UV-Vis and PL measurements indicate the formation of CdS and ZnS nanocrystals with an estimated size around 2.4 nm.

Keywords: calcogenides, nanocrystals, two-phases, CdS, ZnS.

1. INTRODUCTION

During the past 15 years there has been a remarkable growth in the use of fluorescence in the biological sciences [1]. Fluorescence is used for cellular identification and sorting in flow cytometric and cellular imaging to reveal the localization and movement of intracellular substances by means of fluorescence polarization immunoassays. However, conventional labels, such as organic fluorescent dyes or green fluorescent proteins (GFP), lack the photo-stability to allow the tracking of cellular events that happen over a period from minutes to days. Semiconductor nanocrystals exhibit interesting size-tunable optical properties due to the confinement of the electronic wave functions. Over the past decade, much progress has been made in the synthesis and characterization of monodisperse nanocrystals of a wide variety of so-called II-VI semiconductors [1, 2]. These type of nanocrystals would find versatile applications for light emission applications.

Various methods of nanoparticle synthesis have been developed. Two main soft-chemical routes have been developed over the last two decades: *in situ* synthesis in the water pools of reverse micelles developed in the 1980s by Pileni et al. [3] and the phase-transfer method developed by Brust et al. in the 1990s. A mixed approach combining the aqueous synthesis and phase-transfer method was developed by Kasuya et al for cadmium selenide (CdSe) [4]. In continuation of our previous work [5], we studied the applicability of the two phase synthesis route for CdS and ZnS nanoparticles.

2 EXPERIMENTAL

2.1 Materials

All reactants were used as received. $ZnSO_4.7H_2O$, $Na_2S.9H_2O$; $CdSO_4$ were used as precursor materials. Trisodium nitrilo- triacetic acid (SNTA), $[N(CH_2COONa)_3]$, was used as complexing agent. Decylamine was added to restrict crystal growth.whereas methanol was selected as co-surfactants. The pH of the solution was adjusted between 10 and 11 in al tsts.

2.2 Synthesis of CdS and ZnS Nanocrystals:

CdS nanocrystals were synthesized at 60 ^oC and atmospheric pressure. Cd solutions at various concentrations (0.1M or 0.19M) were prepared in the presence of $1.75X10^{-3}$ moles SNTA, water and methanol. This solution was acidified with HCl 10% (w/w). The formation of CdS was obtained after contacting the Cd solution with a Na_2S solution at different concentrations to achieve Cd/S mole ratios, 'R', between 0.8 and 3.5. Toluene was added under gentle mixing right after addition of the sulfide solution, to promote the rapid mobilization of nanocrystals into the organic phase. ZnS QDs

were synthesized by same route as for CdS. In this case disodium sulfide, Na_2S, was used as the source of sulfide ions.

2.3 Products Characterization

Structural analysis of produced nanocrystals were carried out in a Siemens D5000 x-ray diffractometer (XRD) using the Cu-Kα radiation (1.5405Å). The infrared spectra were obtained using a FT-IR Digilab FTS-1000 spectrophotometer. UV-vis spectra of the CdS nanocrystals in toluene were recorded in a UV-vis Beckman Coulter DU 800 spectrophotometer. For PL measurements, CdS nanocrystals suspended in toluene were excited at 400 nm using an HORIBA Jobin-Ybon Fluoro Max-2 spectrofluorimeter.

3 RESULTS AND DISCUSSION

3.1 UV-Vis Measurements

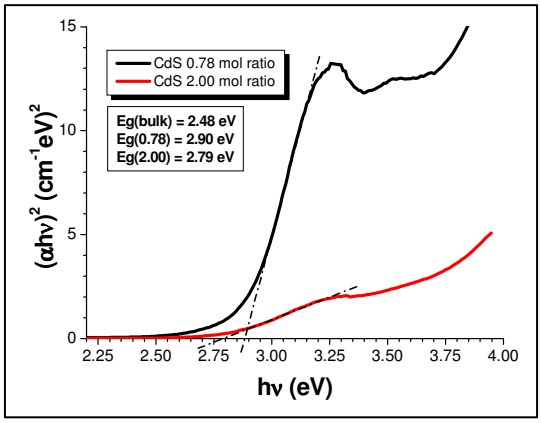

Figure 1. Figure 1.UV-vis spectra for CdS nancrystals synthesized at different Cd/ S mole ratios, 'R'.

Figure 1 shows the UV-Vis spectra of CdS nanocrystals synthesized at 60 ^{0}C without aging. The blue shift in the absorption peak in comparison with bulk CdS is attributed to the quantum confinement effect. From plot of $(\alpha h\nu)^2$ vs hν, the extrapolated intercept on the hν axis gives an E_g of 2.90 eV for 'R'=0.78 2.79 eV for a 'R' of 2.0. The UV-Vis absorption spectra for CdS nanocrystals synthesized at different concentrations of SNTA are shown in Figure 2. The Cd/S mole ratio was 0.78. The spectra confirm the strong dependence of the clusters formation with the SNTA concentration. For SNTA concentrations around 0.25M, the absorption spectrum shows a highly pronounced absorption edge and a very sharp exciton peak, evidencing the narrow size distribution in the cluster sizes. The corresponding cluster size can be estimated at 1.5 nm For SNTA concentrations below 0.25M the suspensions gave a poor optical respons. We also observed that suspensions were not stable and CdS powder sedimented after a few hours, suggesting a poor coating by decylamine; i. e., clusters growth and/or aggregation was not inhibited.

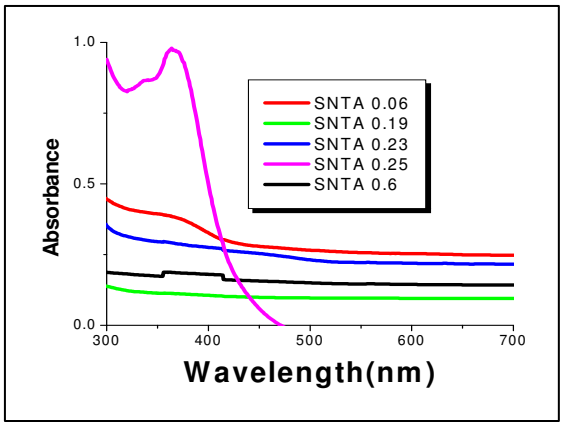

Figure 2.Uv-vis Spectra of CdS at differents concentrations of SNTA. 'R' was 0.78.

3.2 Photoluminescence- Analyses

PL spectra shown in Figure 3 evidence a blue shift in emission wavelength for CdS. The photoluminescence is weak for CdS, (for 'R'=6.7) indicating polydispersity in the nanocrystals. The monodispersity has been enhanced for 'R'= 0.78; the CdS nanocrystals exhibited a tendency to red shift at lower Cd/S mole ratios.

3.3 XRD Analyses

ZnS nanoparticles were not capable to get mobilized into the toluene phase. Instead, they were transferred to the interface toluene/water. A possible solution to this problem could be the use of thiolates as phase transfer agents [7].Figure 4 shows the x-ray diffraction patterns of ZnS powders synthesized by the two-phases approach at different Zn/S mole ratios. XRD analyses revealed the coexistence of both cubic and hexagonal ZnS phases [5]. It can be observed

that all XRD peaks correspond to ZnS

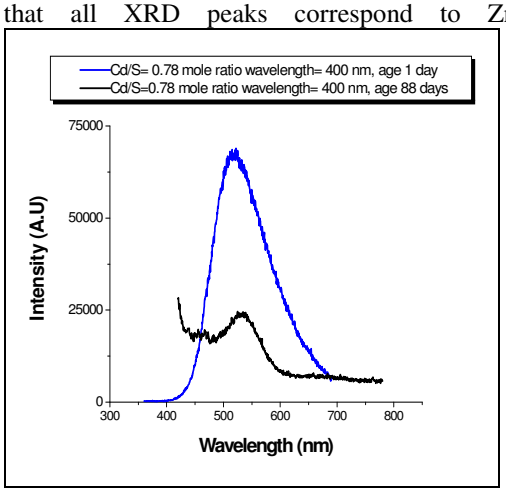

Figure 3. Comparison between curves of emission for CdS were used for characterization of CdS excited at different wavelengths (275, 350,400 nm) at room temperature.

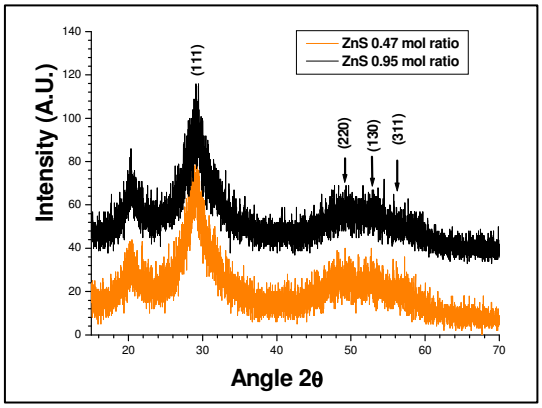

Figure 4. XRD spectra of ZnS at different mol ratio.

except two peaks at approximately 2Θ =13 and 20.5 degrees. These impurity peaks may be attributed in principle to possible formation of $Zn(OH)_2$ and Na_2S salts, but their presence was discarded after verifying their corresponding peak positions and intensities from the literature[5,6]. In general terms, most of the peaks can be assigned to the cubic ZnS structure, although the one corresponding to the (103) suggests the co-existence of the both phases in nanocrystalline ZnS. The average crystallite size, estimated by using the Deybe Scherrer's equation for (111) peak, was 2.19nm .

3.4 FT-IR Analyses

The FTIR spectra for ZnS (figure 5) synthesized at two 'R' values showed similar absorption peaks at 1611.25 and 1061.39 corresponding to N-H bending and C-N stretching vibrational modes from the decylamine used as surfactant. In addition, C-H bands from decylamine were observed in the interval 2800-2900 cm^{-1}. The absorption bands for the metal to sulfur bond should appear in the far-IR region.

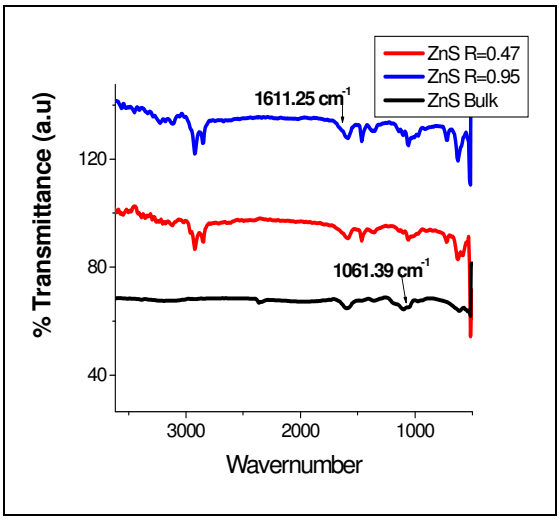

Figure 5: FT-IR spectra for ZnS synthesized at 'R' 0.47 and 0.95.

4 CONCLUDING REMARKS

The syntheses of CdS and ZnS were accomplished successfully by using the two-phase approach. Obtained results suggest a high crystallinity, monodispersity and stability against aggregation of produced CdS clusters. On the other hand, strongly aggregated ZnS nanoparticles were formed that could not be transferred into the organic phase. In general, the optical properties of these nanocrystals can vary according to their size as evidenced from the UV-vis and PL spectra.

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