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Study of quantum size effects and optical characteristics in colloidal $\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ quantum dots

ABSTRACT

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In this work, we report, optical properties of $\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ quantum dots ($x = 0.05, 0.10$ and 0.15) synthesized in water using thioglycolic acid (TGA) as a modifier agent. The optical characterization of the samples was performed through absorption (UV) and photoluminescence spectra (PL). A red shift absorption and fluorescent emission peaks was observed which can be related to the increase of nanocrystals diameter with pass the reaction time. This size dependent phenomenon is concerned to the known “quantum confinement” effect and the highest quantum yield has been achieved under our experimental conditions (using thioglycolic acid (TGA) as a modifier agent) when the processing time reached to 150 min.

Keywords: *Semiconductor nanocrystals; Colloidal quantum dots; Quantum yield; Crystalline growth; Quantum confinement.*

INTRODUCTION

In the past few decades, luminescent semiconductor nanocrystals have been intensely studied due to their unique optical properties [1]. In particular, quantum dots semiconductor are very attractive as biological labels because of their small size, emission tunability, superior photostability and longer photoluminescence decay times in comparison with conventional organic dyes [2–6]. These highly luminescent nanoparticles have photophysical properties superior to organic dyes but the high temperature required to synthesize them can be problematic for some applications [4, 5, 7]. One of the major challenges is to obtain water-soluble nanocrystals with a high PL quantum efficiency. Arrested precipitation in water in the presence of stabilizers (e.g., thiols) is a faster and simpler method to synthesize water-soluble nanocrystals and has been applied to several semiconductors potentially relevant to biolabeling (e.g., CdS, CdSe, CdTe) applications.

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In this work, following to this method for synthesis of CdS and CdSe, which yielded nanocrystals with defect-related emission and low quantum efficiency [8, 9], we attempted to study synthesis and optical properties of wet chemically grown semiconductor quantum dots (QD). These kind materials, because of the quantum confinement effect, show size dependent optical properties and a proper passivation of the surface can yield sufficiently strong emission [10–13]. Our initial purpose in this work was to obtain infrared or near infrared emitting colloidal QDs through the chemical modification of CdTe nanocrystal precursors by Sn^{2+} ions doping.

EXPERIMENTAL

Materials

All chemicals, Cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, Merck), tin chloride (SnCl_2), tellurium (Te reagent powder), and sodium borohydride (NaBH_4), Thioglycolic acid (TGA) supplied by Merck were of analytical grade and used without any further purification. Deionized water was used throughout the experiments.

Characterization

A Varian Cary 100 spectrophotometer in the range of 200–800 nm was used to record the UV-Vis absorption spectra. The PL emission measurements were performed at room temperature on a photoluminescence spectrophotometer Ls-50B Perkin Elmer equipped with Xe lamp ($\lambda=320$ nm) as an excitation light source. A JEON 360 Transmission Electron Microscope (TEM) operated at 100 W was used to observe morphology and size of the synthesized nanocrystals.

Synthesis CdSnTe nanocrystals

In a typical synthesis procedure, in a three-necked flask, 2.5 mmol of CdCl_2 , 2.5 H_2O and 5, 10, 15 weight percent of Sn^{2+} precursor were dissolved in 110 mL of water in stirring and added by 12 mmol of TGA as stabilizer agent. In this stage, the reaction mixture, after adjusting pH to an appropriate values by dropwise addition of NaOH (1M) was added a solution of NaHTe (a purple clear liquid prepared by the reaction of 2.4 mmol of Te powder with 5 mmol NaBH_4 in 8 mL water and

stirred and cooled then in an ice bath for 10 min) under stirring in the three-necked flask under nitrogen atmosphere for 20 min. The precursors obtained were then converted to CdSnTe nanocrystals by refluxing the reaction mixture at 95°C under inert-gas condition.

RESULTS AND DISCUSSION

Optical properties of $\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ nanoparticles

Figures 1, 2, 3 represents photoluminescence (PL) and absorptions (UV) spectra of series of CdTe quantum dots doped with different percent of tin. These spectra were recorded for the as-prepared colloidal solutions taken from the refluxing reaction mixtures at different intervals of times. A clearly resolved shift of absorption maximum from the first electronic transition of $\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ quantum dots ($x=0.05, 0.10$ and 0.15) to the longer wavelength were observed when the particles grow in the reaction process. The size growing of CdSnTe nanocrystals can be therefore controlled by the duration of reflux time and can easily be monitored by absorption and PL spectra. In other word, the PL excitation spectra display electronic transitions at lower energies when the heating time is extended from 30 min to 300 min in the presence of thioglycolic acid used as the stabilizer agent (Table 1). So, PL technique allows the detection of luminescence emitted by particles with a selected size.

Table 1. λ_{Max} of photoluminescence for colloidal $\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ (with $x=0.05, 0.10$ and 0.15) as a function of time

Time(min)	$\lambda_{\text{Max}}(\text{nm})$		
	$\text{Sn}^{2+}, \text{mol}\%$		
	5%	10%	15%
30	651	683	707
90	670	701	726
150	682	713	738
210	702	733	758
270	731	762	786

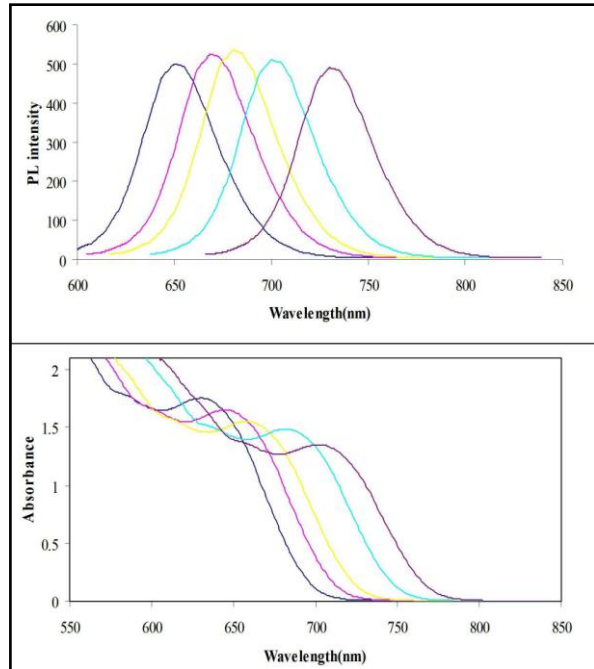


Fig. 1. Fluorescence and absorptions spectra of CdSnTe (5%) quantum dots prepared at different reaction times.

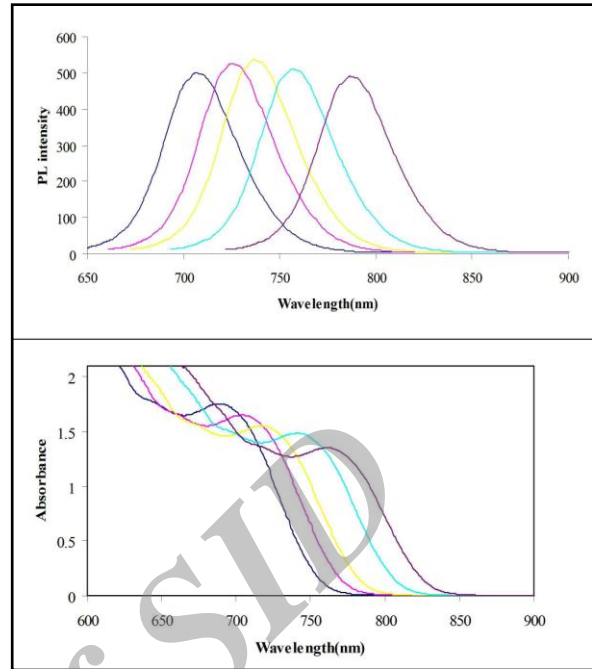


Fig. 3. Fluorescence spectra and absorptions of CdSnTe (15%) nanoparticles prepared at different reaction times.

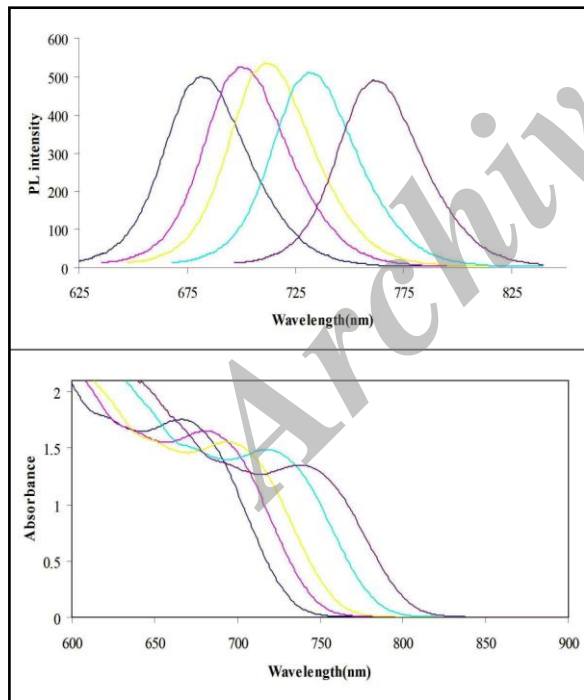


Fig. 2. Fluorescence spectra and absorptions of CdSnTe (10%) nanoparticles prepared at different reaction times.

Quantum yield

The most reliable method for recording quantum yield, Φ_F is the comparative method of Williams et al. [8] which involves the use of well characterized standard samples with known Φ_F values. In this method, only two quantities need to be known; the number of photons absorbed and the number of photons emitted per unit of time:

$$\Phi_f = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

Reliable measurements of these quantities are unfortunately hard to obtain. We only considered the easiest case of dilute solution. In this method, the measurement has been performed using standard absorption and emission spectra [9] and Q_Y can be calculated by using following equation:

$$\Phi_x = \Phi_s \times f_s / f_x \times F_x / F_s \times \eta_x^2 / \eta_s^2$$

Where, Φ_x and Φ_s are the photoluminescence quantum yield of the sample and that of the standard (oxazine), respectively. F_x and F_s are the integrated intensities (surface areas)

of the sample and standard spectra, respectively (in units of photons); fx is the absorption factor (also known under the absolute term “absorbance”) [9], the fraction of the light impinging on the sample that is absorbed; the refractive indices of the sample and reference solution are η_x and η_s , respectively. The photoluminescence Q_Y measured results for colloidal $\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ (with $x = 0.05$) nanoparticles on function of time are given in Table 2. This results show that the highest quantum yield has been achieved after 150 min under our experimental condition and using thioglycolic acid (TGA) as modifier agent.

Table 2. Quantum yield calculated for colloidal $\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ (with $x = 0.05$) nanoparticles on function of time

Time	F_x	F_s	Emission range / nm	Quantum yield
30	25000	32800	600-800	0.83
90	27500	32800	600-800	0.92
150	32200	32800	600-800	1.0
210	30800	32800	600-800	1.0
270	31200	32800	600-800	1.0

Morphological characteristics of CdSnTe nanocrystals

• TEM studies

Figure 4 Shows TEM image of cubic and spherical crystalline form deposited from colloidal quantum dots reaction solution doped with 5% thin. This image confirms formation of the crystalline structure of thin doped CdTe in the form of quantum dots surrounded by TGA as stabilizer agent. The grain size estimated to be about 3-8 nm.

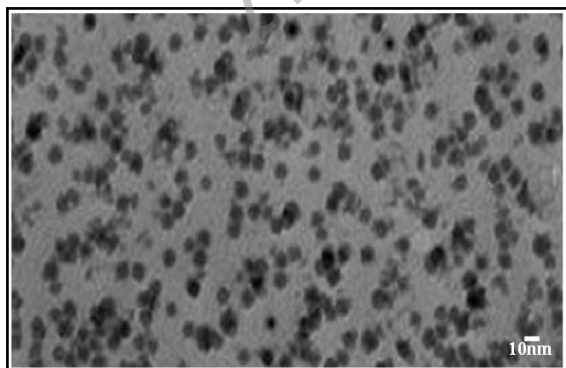


Fig. 4. TEM image of CdSnTe (5%) nanocrystals deposited from the colloidal CdTe quantum dots CdSnTe with 5% thin.

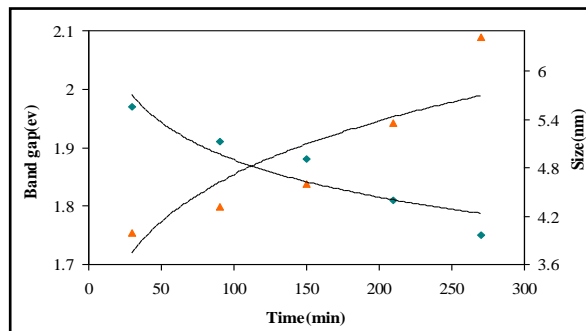


Fig. 5. Band Gap and Size of CdSnTe nanoparticles compared at different reaction times.

CONCLUSIONS

In this work, colloidal CdTe and thin doped CdTe nanocrystals ($\text{Cd}_{1-x}\text{Sn}_x\text{Te}$ with $x=0.05$, 0.1 and 0.15) in water have been prepared using thioglycolic acid (TGA) as a modifier agent and studied using absorption and photoluminescence spectroscopy. The results obtained showed a red shift in absorption and photoluminescence emission spectra due to the crystalline size increase of the prepared CdSnTe nanoparticles when recording time was prolonged. This size dependent phenomenon is concerned to the known “quantum confinement,” effect that in which, the allowed electronic states of exciton energy are varied when its position is related to the dimensions of its parent crystal in a manner analogous to the particle in a box. The highest quantum yield has been achieved in our experiment condition when the processing time reached to 150 min.

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