

Synthesis and optical properties of functionalized CdS nanoparticles with different sizes

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Water soluble CdS nanoparticles were synthesized using a simple aqueous method that enables us to obtain functionalized nanoparticles with different sizes, optical absorption and emission features. These differences were reached using several Cd^{2+} to S^{2-} molar ratios and various capping agents. The size of the nanoparticles ranges were from 2.6 to 3.88 nm depending on the synthesis conditions. CdS nanoparticles prepared could be used as biolabels because their nanometric dimensions, luminescence signal and most important to their functionalization with organic molecules, which have functional groups that can attach them to biomolecules or cells.

Keywords: Luminescence; Nanomaterials; Semiconductors; Optical materials and properties

1. Introduction

In the last two decades, semiconductor nanoparticles have been intensively investigated due to their unique size-dependent properties [1-3]. CdS is one of the most studied materials because it has a well established relationship between the optical absorption and the size of the particle; the first investigations in this area were focused in the improvement of the synthesis method [4-6], in the last five years the investigation has focused in the preparation of nanoparticles for applications in the biological field as molecular probes or biolabels [7]. In order to be applied in the biological field, it is desirable for the prepared semiconductor nanoparticles to be water soluble and have an appropriate functionalization [3, 8], that dictates the final application of the nanoparticles [9]. In this work, water-soluble CdS nanoparticles were synthesized using a simple aqueous method that enables us to obtain functionalized nanoparticles with different sizes and optical properties.

Table 1. Band gap and average particle size for every sample prepared in this work.

Sample	Band Gap (eV)	Particle Diameter (nm) ^a
1:0.5	3.88	2.39
1:1	3.5	2.74
1:2	3.3	3.00
1:15	2.6	6.26
TG	3.5	2.74
TGA	2.75	4.57
CYS	3.17	3.23

^a We used the Brus equation assuming that CdS nanoparticles are spherical because in a previous report we observed this morphology for the same sort of nanoparticles. See Ref. [12].

2. Experimental

2.1 Synthesis using different $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratios

Under ambient conditions and using magnetic stirring, 100 mL of a 2 mM solution of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ (ACS reagent, 99%) were placed in a reaction vessel and mixed with 1.8 mmol of 1-thioglycerol (Sigma, 98%). After 5 minutes of stirring, pH was adjusted to 10 with NH_4OH (30% w/w aqueous solution, ACS Reagent) and then a specific amount of $(\text{NH}_4)_2\text{S}$ (20% w/w aqueous solution, Sigma) was added to form de CdS nanoparticles. The $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratios used were 1:0.5, 1:1, 1:2 and 1:15.

2.2 Synthesis using different stabilizing agents

100 mL of a 2 mM solution of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$ were placed in a reaction vessel and mixed with 1.8 mmol of 1-thioglycerol, TG, thioglycolic acid (Sigma-Aldrich, 98%), TGA; or L-cysteine (Aldrich, 97%), CYS. After 5 minutes of magnetic stirring, pH was adjusted to 10 with NH_4OH and then a specific amount of $(\text{NH}_4)_2\text{S}$ was added to form de CdS nanoparticles. The $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratio used was 1:1.

2.3 Characterization

The optical analyses were made using the obtained stable dispersions. Fluorescence analysis was carried out by an Ocean Optics SF2000 fiber optic spectrophotometer, the excitation source was a uv air cooled nitrogen laser with an excitation wavelength at 337 nm. Absorption measurements were obtained with an Ocean Optics S2000 UV-VIS fiber optic spectrometer.

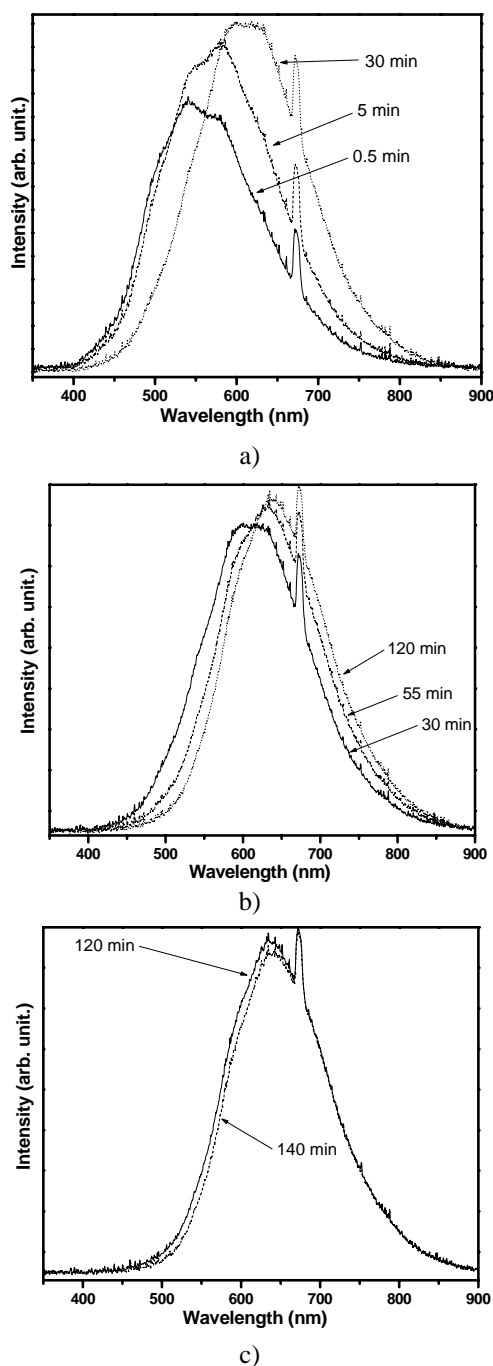


Figure 1. Emission spectra taken at different reaction times.

3. Results and discussion

3.1 Synthesis kinetics

Figures 1a, 1b and 1c show an emission spectra taken at different reaction times during the synthesis of the CdS nanoparticles prepared with TG as capping agent and with a $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratio of 1:15. Figure 1a shows spectra taken at 0.5, 5 and 30 minutes of reaction time. As we can see, after the addition of ammonium sulfide, CdS

nanoparticles were immediately formed due to the low solubility of CdS in water, CdS nanoparticles have a bimodal size distribution which can be deduced from spectrum at 0.5 min; it had two maximums, at 541 nm and 574 nm respectively. After five minutes of reaction the spectrum grows in intensity due to the formation of new particles nucleated with the remaining ions and, after thirty minutes of reaction time, the spectrum still grows and the two maximums shift to the red giving only one broader band. From 30 minutes to 2 hours of reaction, the spectrum slightly varies, it just grows in intensity and the band becomes narrower (Figure 1b). After two hours of reaction, the formation of nanoparticles stops and nanoparticles start growing via the Ostwald ripening mechanism, i.e. larger particles grew on account of the dissolution of the smaller ones, this result in an increment on particle size and a decrement in the total number of particles formed. The increment in particle size produce a red shift in the maximum of the emission band, and the decrement in the total number of particles produce a decrement in intensity (Figure 1c). These results confirm those reported by Hirai *et. al.* [10], where the kinetics of the reaction was followed using the absorption spectra.

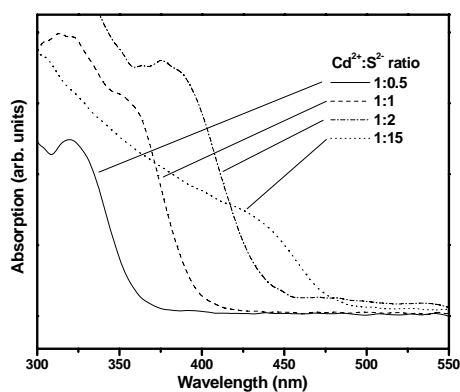
3.2 Effect of the use of different $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratios

Figure 2 shows the absorption spectra of the samples prepared using different $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratios (these $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratios were not measured in CdS nanoparticles, they correspond to the concentrations of Cd^{2+} and S^{2-} used in the synthesis). It can be seen that all samples present a blue shift in its absorption edge comparing with that of the bulk CdS (2.4 eV, 490 nm). Table 1 shows the band gap and the average particle size for every sample calculated from its absorption spectra and using the Brus equation [11].

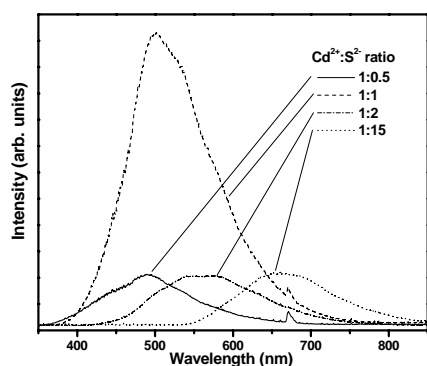
$$E_g = E_g(\text{bulk}) + \frac{h^2}{2d_p^2} \left(\frac{1}{m_e} + \frac{1}{m_h} \right) - \left(\frac{3.6e^2}{4\pi\epsilon_0 d_p} \right)$$

Where E_g is the band gap of the nanoparticle, $E_g(\text{bulk}) = 2.4$ eV, h is Planck's constant, d_p is the particle diameter, $m_e/m_0 = 0.19$, $m_h/m_0 = 0.8$, e is the electron charge and $\epsilon/\epsilon_0 = 5.7$.

Table 1 depicts that when an increase in the concentration of the ion S^{2-} was added to the reaction, the particle size increases, this finding agree with those reported by Vossmeier, *et. al.* [5], they control the size of their CdS nanoparticles with the amount of H_2S used, increasing the size of the nanoparticles with the concentration of the ion S^{2-} available in the reaction. In Figure 2b we can see that CdS nanoparticles prepared with different $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratios present different emission peaks due to its different particle diameter. Particles prepared with ratios 1:0.5 and 1:1 present peaks at 490 and 500 nm respectively, sample prepared with ratio 1:2 presents two peaks the first at 545



a)



b)

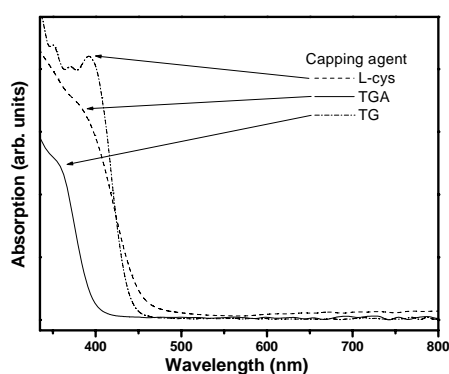
Figure 2. a) Absorption spectra and b) Luminescence spectra of the CdS nanoparticles prepared with different $\text{Cd}^{2+}:\text{S}^{2-}$ molar ratios.

nm and the second at 578 nm, the sample prepared with a ratio 1:15 presents a maximum at 660 nm.

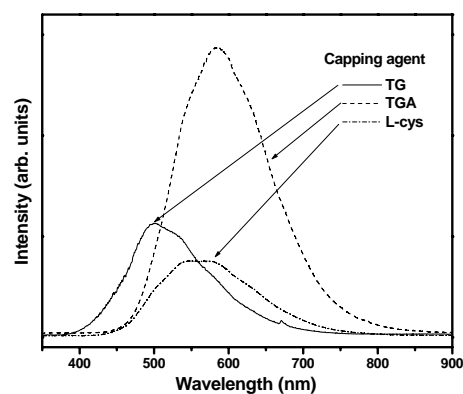
3.3 Effect of the use of different capping agents

Using different capping agents enables us to obtain nanoparticles with different sizes, Table 1 shows the average particle size for the samples prepared with different capping agents calculated using the absorption spectra (Figure 3a) and the Brus equation. The lowest particle size was achieved using TGA; all used capping agents contain at least two functional groups, (i) a thiol group (-SH) which bonds the organic molecule to the nanoparticles through the formation of a covalent bond among the free electrons in S atom of thiol group and the empty orbital of surface Cd atoms in CdS nanoparticles; and (ii) a group which is the responsible of the stabilization [13, 14]. The second group for TG is the hydroxyl group (-OH), for TGA is the carboxylic group (-COOH) and for CYS there are two groups, the amine (-NH₂) and the carboxylic group (-COOH). The differences among the functional groups could be the responsible of the different particle size obtained.

As a consequence of the different particle size, the nanoparticles present different emission peaks (Figure 3b), samples prepared with TG and TGA present a maximum at



a)



b)

Figure 3. a) Absorption spectra and b) Luminescence spectra of the CdS nanoparticles prepared with different capping agents.

500 nm and 584 nm respectively, the sample prepared with CYS present two peaks, at 542 and 578 nm. The intensity of the signal presented by the particles prepared with TGA is almost twice of that presented by the particles prepared with TG and CYS. CdS nanoparticles with sizes comparables to that of the particles prepared in this work were reported by Lakowicz *et al.* [6], that used two different capping agents and obtain particles with different particles size and emission peaks, although the sizes are comparable the emission peaks are not and these findings could be due to the chemistry of the capping agents (a dendrimer and a polyphosphate) this support the idea that the capping agents not only control the particle size and aggregation but also participate in the optical properties of the materials.

The CdS nanoparticles prepared in this work could be used as biomarkers because they have nanometric dimensions, show an important luminescence signal and most important are functionalized with organic molecules which have functional groups that can attach them to biomolecules or cells. Although, according to Alivisatos [8], no obvious toxicity of CdS nanoparticles has been detected, toxicity analysis of these nanoparticles are being investigated by our group in order to have a complete map of the performance of these particles.

4. Conclusions

Functionalized water-soluble CdS nanoparticles were synthesized using a simple aqueous method under ambient conditions; this method enables us to obtain nanoparticles with different particle size just varying the Cd²⁺ to S²⁻ molar ratio and the capping agent. The CdS nanoparticles prepared in this work could be used as biolabels because they have nanometric dimensions, present an important luminescence signal and most important they are functionalized with organic molecules which have functional groups that can attach them to biomolecules or cells.

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