

3 Characterization of the semiconductor nanoparticles

One of the crucial steps in the development of nanosensors is the characterization of their optical and/or electronic properties of the nanomaterials. In this work, TGA-CdTe, 2MPA-CdTe and cysteine-ZnS nanocrystals were investigated as sensing probes for different substances (captopril, histamine, kanamycin and thyroxine). Therefore, these nanomaterials were characterized using different techniques in order to evaluate their size distribution, their optical absorption profile and their luminescence characteristics. Techniques such as spectral and time-domain luminescence spectroscopy, spectrophotometry, transmission electron microscopy (TEM) and dynamic light scattering (DLS) were employed.

3.1 Characterization of TGA-CdTe and 2MPA-CdTe nanoparticles

3.1.1 Optical properties of TGA-CdTe nanoparticles

Three batches of synthesized TGA-CdTe nanoparticles (each one submitted to different reflux times) has their optical properties (molecular absorption and fluorescence) studied. The emission spectra (normalized in intensity) of these TGA-CdTe quantum dots exhibited maximum photoluminescence (using excitation at 350 nm) at 515, 545 and 580 nm when reaction systems were refluxed for 10, 30 and 60 min respectively (Figure 11). As the reaction time increased, the crystal size of nanoparticles increased and the longer was the wavelength bathochromic shift. This trend in the decreasing of the emitted energy is due to the decrease of the band gap energy as the nanoparticle size increased. The electronic energy levels of quantum dots are discrete, hence, an increase in size, due to addition of atoms, results in the decreasing of boundaries of the band gap, therefore, excited electrons have a shorter energy decay as they return to the ground (at longer wavelength). These symmetric and sharp photoluminescence profiles (with full width at half maximum, FWHM,

about 35, 43, 53 nm) indicated a fairly homogeneous and symmetric nanoparticle size distribution.

In Figure 12, the broad wavelength excitation spectrum, characteristics of quantum dots is shown. Such feature is ideal for sensing applications as the excitation wavelength can be chosen out of the spectral interference imposed by complex samples in contrast to what is obtained with conventional photoluminescent probes (organic dyes) where the absorption spectrum is narrow. In Figure 13, the absorption spectra of these nanoparticles at 490, 509 and 539 nm is shown. The absorption shoulder, which indicates the 1st excitonic, moves towards longer wavelength as the crystal grows by the increasing of the reaction time.

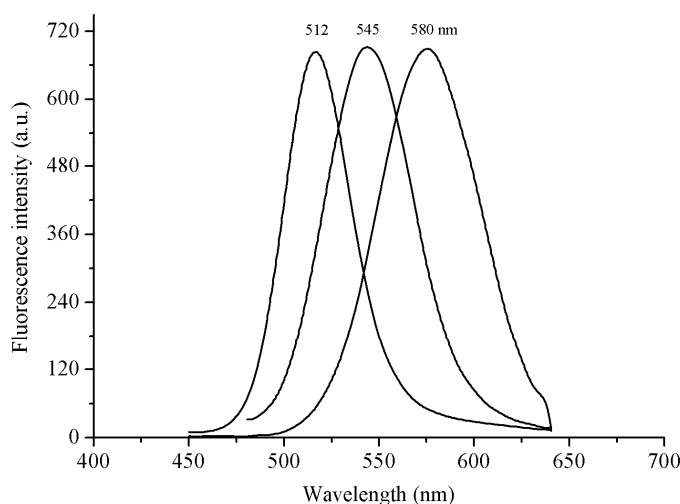


Figure 11- Photoluminescence emission spectra of TGA-CdTe nanoparticles.

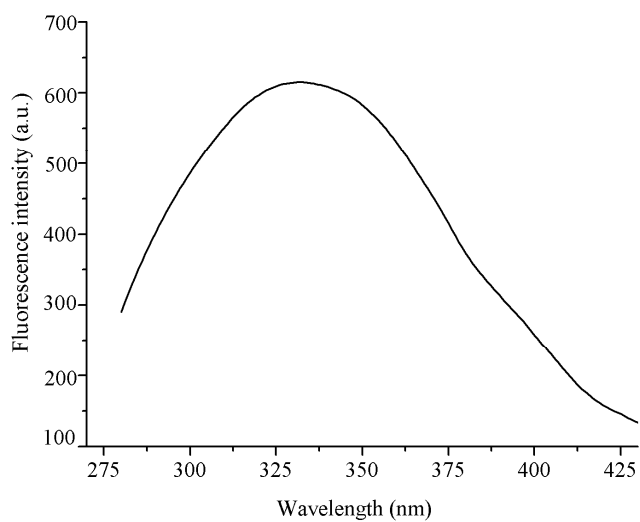


Figure 12- Photoluminescence excitation spectra of TGA-CdTe nanoparticles.

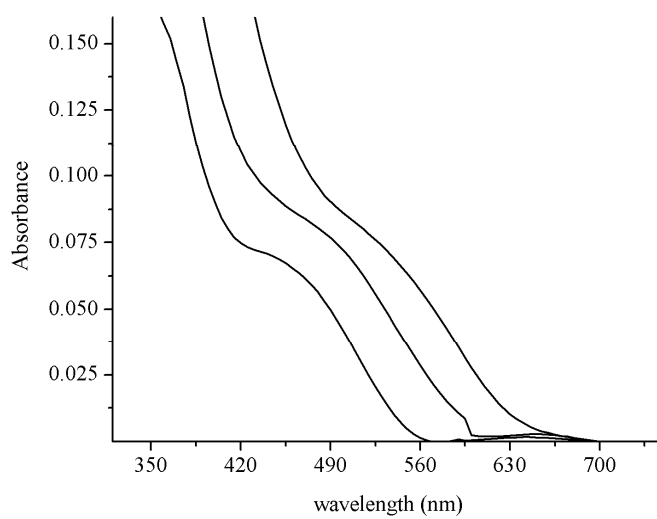


Figure 13-TGA-CdTe quantum dots electronic absorption spectra with 1st excitonic at 490, 509 and 539 nm.

3.1.2 Optical properties of 2MPA-CdTe nanoparticles

The quality of the 2MPA-CdTe nanocrystals was monitored through its optical properties. In Figure 14, the absorption spectrum presented a well resolved absorption band with maximum at 480 nm. In Figure 15, a strong, narrow and symmetric photoluminescence emission band (with maximum at 512 nm and FWHM of 40 nm) is shown for the 2MPA-CdTe upon excitation at 350 nm. The increase of the photoluminescence emission intensity with the increasing concentration of quantum dots, with no shift in emission wavelength, is shown in Figure 16. This behavior suggests that quantum dots are uniformly distributed and presents small amount of surface defects.

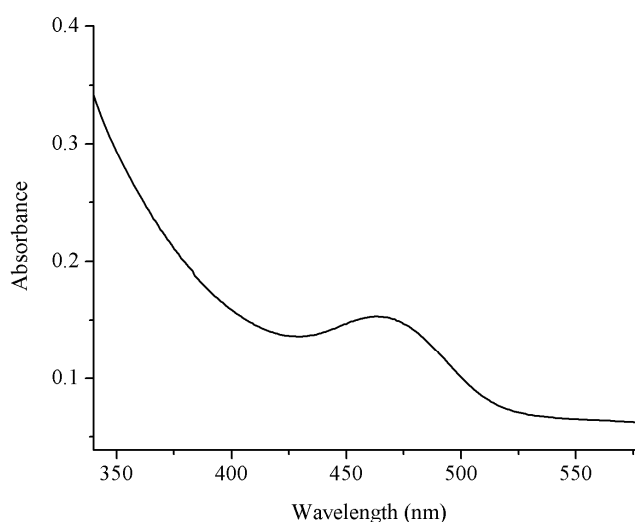


Figure 14- 2MPA-CdTe quantum dots electronic absorption spectra.

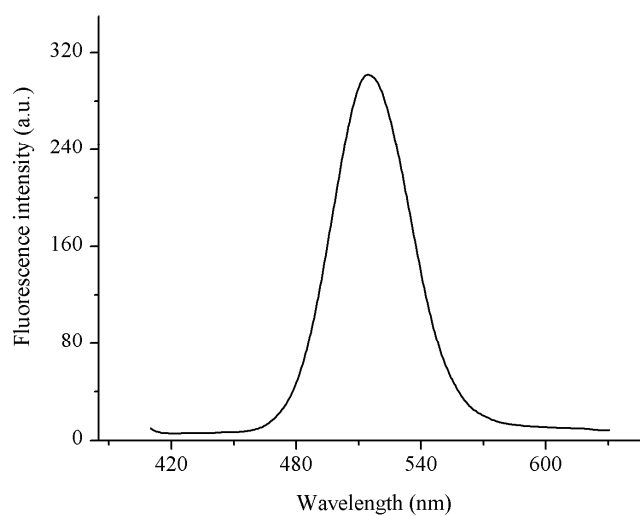


Figure 15 - 2MPA-CdTe quantum dots photoluminescence spectra upon excitation at 350 nm.

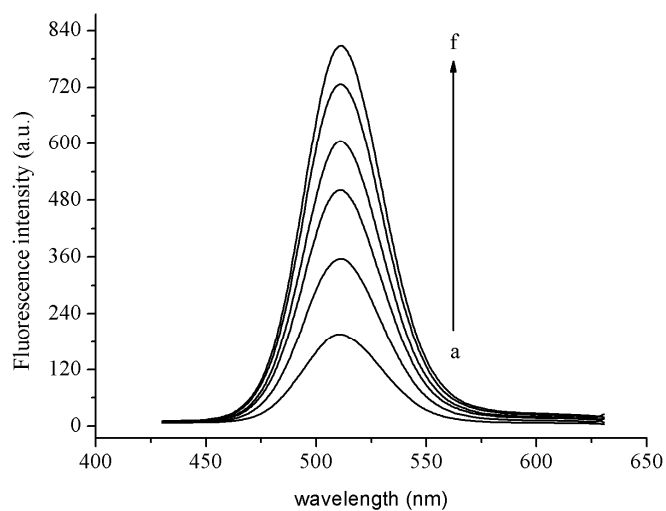


Figure 16 - 2MPA-CdTe quantum dots concentrations dependent photoluminescence:
 (a) 7×10^{-8} , (b) 1.4×10^{-7} , (c) 2.1×10^{-7} , (d) 2.8×10^{-7} , (e) 3.5×10^{-7} , (f) 4.2×10^{-7} mol L⁻¹.

3.1.3 Nanoparticle size determination

3.1.3.1 Size determination by UV-vis spectrophotometry

From the UV-vis absorption spectra, it is possible to determine the size of the quantum dots, which is an important factor that influences their characteristics. Peng *et al.* developed a formula to determine the approximate size of quantum dots, using the 1st exciton peak of the absorption spectra. By replacing the wavelength value of the 1st exciton peak into Equation 3.1 (when the optical density is kept between 0.15 and 0.25), the size of the quantum dots core may be determined [150]. From the electronic absorption data, the concentration and extinction coefficient is easily calculated. From the molar absorptivity (ϵ) of nanoparticles, the apparent concentration of quantum dots (considering it as a real solution) in the stock dispersion can be determined from Beer-Lambert law. This is a very practical and simple approach to find out the concentration of nanoparticles in solution.

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + (1.0064)\lambda - 194.84 \quad (3.1)$$

Where D is the nanocrystal size and λ is the wavelength of 1st excitonic. From the nanocrystal size, determined from equation 3.1, the ϵ value can be calculated from Equation 3.2.

$$\epsilon = 10,043 (D)^{2.12} \quad (3.2)$$

Once the extinction coefficient is known for a given batch of quantum dots, the concentration of the solution can be easily found using the Beer-Lambert Law (Equation 3.3).

$$A = \epsilon C b \quad (3.3)$$

Where C is the apparent concentration of the quantum dots and b is the optical pathlength.

From these calculations, the average particles size of the three different synthesized TGA-CdTe quantum dots and of the 2MPA-CdTe quantum dot were calculated as indicated in Table 3.

Table 3 -Average sizes of the TGA-CdTe and 2MPA-CdTe nanoparticles caculated from the 1st exciton peak of the absorption spectra

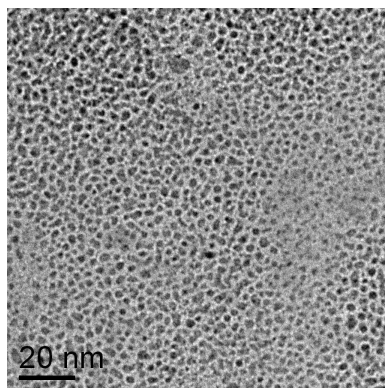
Nanoparticles	$\lambda_{\text{emission}}$	λ_{abs} (nm)	Average diameter (nm)
Small TGA-CdTe	515	490	2.1
Medium TGA-CdTe	545	509	2.6
Large TGA-CdTe	580	539	3.2
2MPA –CdTe	512	480	2.0

3.1.3.2 Size determination by transmission electron microscopy

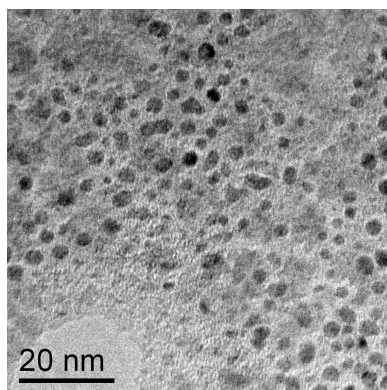
One important tool to determine the size of nanoparticles is through transmission electron microscopy (TEM). TEM makes use of beam of electrons passing through thin specimen of sample. The electrons, after interacting with sample, form an image when they are captured by a charge-coupled device (CCD) camera or photoluminescent screen or by a photographic film. The images of the different sizes TGA-CdTe show that these nanoparticles are spherical and monodispersed in the nanometer scale (Figure 17). Due to the lack of proper software, the exact size of the particle was difficult to obtain, however, it can be observed that the average particles size of the nanoparticles from the three batches refluxed increases as the reaction reflux time increases from 10 to 60 min (Figure 14 a-c).

The 2MPA-CdTe nanoparticles were also characterized by TEM with magnification of both 20 nm and 50 nm. The results also showed nanoparticles monodispersed in nanometer scale (Figure 18). Comparing the results obtained from TEM with the ones of Table 3, larger size values were achieved for all the

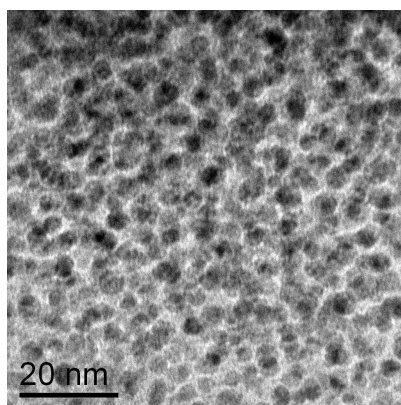
nanoparticles (Table 4). This can be explained by the fact that the Peng's method uses the 1st excitonic that only consider the core size and the stabilizing ligands (2-MPA and TGA) are not take into account



a.

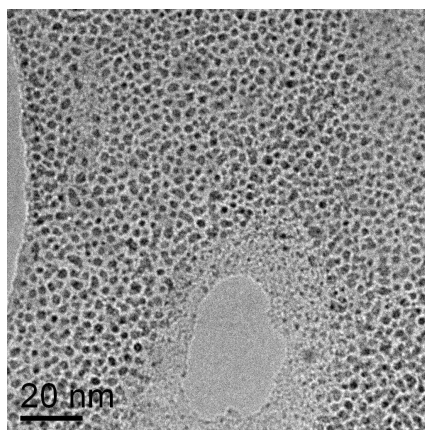


b.

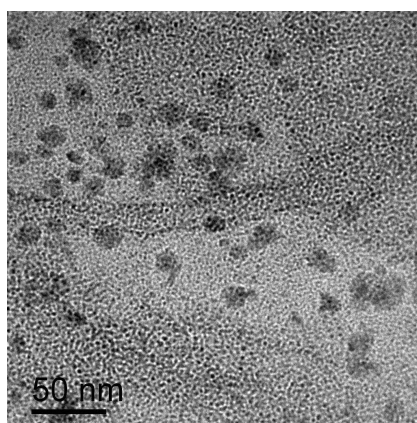


c.

Figure 17 - TEM images of TGA-CdTe nanoparticles synthesized with reaction times of 10 (a), 30 (b) and 60 (c) min. The magnification of 20 nm was used for all the measurements.



a.



b.

Figure 18 - TEM images of 2MPA-CdTe nanoparticles with magnification of 20 nm (a) and 50 nm (b).

Table 4 - Estimated average particle sizes of TGA and 2MPA modified CdTe nanoparticles from TEM images.

Nanoparticles	Reaction time (min)	Average diameter (nm)
TGA-CdTe	10	3.0
TGA-CdTe	30	5.0
TGA-CdTe	60	8.0
2MPA –CdTe	30	2.8

3.1.3.3 Size determination by transmission dynamic light scattering

Dynamic light scattering (DLS) also known as photon correlation spectroscopy is another tool used to determine the hydrodynamic diameter (size) of quantum dots. The technique relies on the fact that particles are in constant movement in solution due to Brownian motion. When a coherent light source, like a laser of known frequency, is directed at these particles, the light is scattered at a different frequencies and due to Doppler effect. This frequency change is known as Doppler shift or Doppler broadening. For measurement purposes, this shift in light frequency is associated with the size of the particle that interacts with the light.

The average hydrodynamic diameter of the TGA-CdTe (obtained with reaction time of 30 min) and 2MPA-CdTe quantum dots obtained by DLS were 20.7 nm and 15.0 nm respectively (as shown by the distributions indicated in Figure 19 and Figure 20). These DSL measured sizes are considerably larger when compared to the results obtained by UV-vis spectrophotometry and TEM. This can be attributed to the fact that DLS technique measures the mean hydrodynamic diameter of the quantum dots cores surrounded by solvation layers and organic molecule used as stabilizer [151]. However it is probable that these larger sizes measured are due to the aggregation of nanoparticles in the experimental conditions required for DSL measurements.

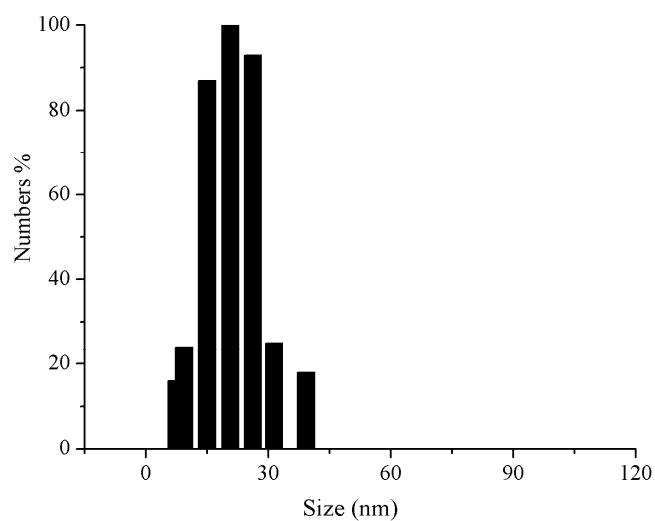


Figure 19 - DLS histogram for the TGA-CdTe nanoparticles synthesized with 30 min reflux time.

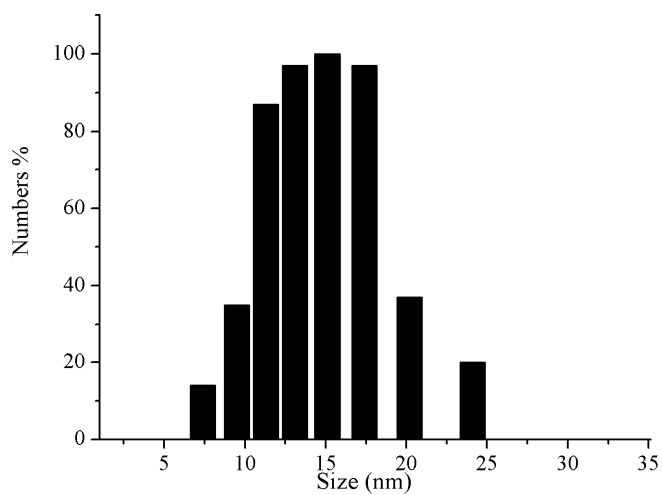


Figure 20 - DLS histogram for the 2MPA-CdTe quantum dots.

3.1.4 Photoluminescence quantum yield

The integrated photoluminescence intensities versus either the absorbance of the dispersion of TGA-CdTe quantum dots or the absorbance of rhodamine B at different concentrations are shown in Figure 21. The quantum yield of the TGA-CdTe (with 515 nm photoluminescence emission) was estimated in 28.8%. While the quantum yield of the 2MPA-CdTe (with photoluminescence emission at 512 nm) was found to be 38.2% (Figure 22). Those values were achieved by the comparative approach using rhodamine B dissolved in ethanol as the fluorophor standard [148]. The higher quantum yield of 2 MPA-CdTe (38.2%) in comparison to the TGA-CdTe (28.8%) may be better surface protection of nanopartciles due to 2MPA. Therefore, the quantum dots capped with 2MPA had better absorption when excited at 355 nm.

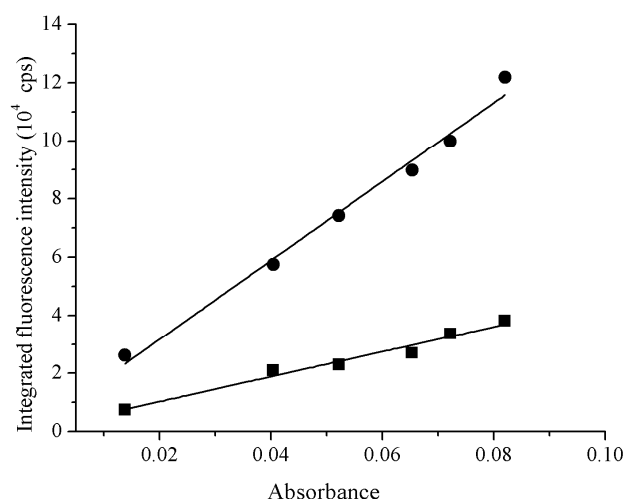


Figure 21-Integrated photoluminescence intensity in function of the absorbance of the aqueous TGA-CdTe quantum dots (■) and for the standard rhodamine B (●).

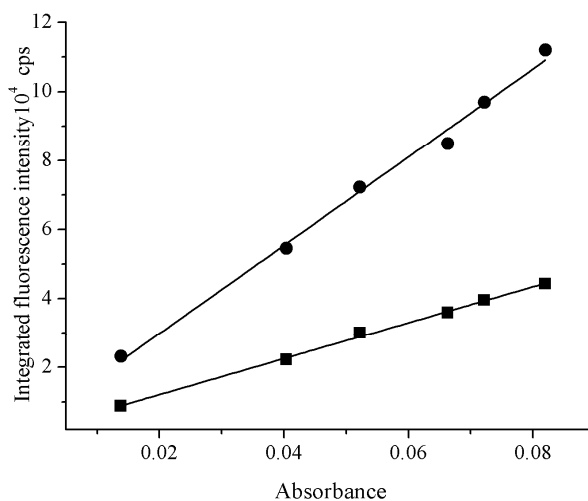


Figure 22- Integrated photoluminescence intensity in function of the absorbance of the aqueous 2MPA-CdTe quantum dots (■). Data for the standard rhodamine B (●).

3.2 Optical properties of cysteine-ZnS nanoparticles

As L-cysteine is an amino acid has been used for synthesis of water compatible photoluminescent probes. This ligand can bind to the surface of the ZnS nanoparticles through the sulfur atom of the mercapto group while the carboxylic acid group provides water compatibility.

The cysteine-ZnS nanoparticle was characterized through its optical properties. The electronic optical absorption of the nanoparticle presents a maximum at 290 nm (Figure 23) and the photoluminescence maximum was observed at 424 nm using (excitation at 312 nm) and the FWHM value of the emission band was 36 nm (Figure 24). It can be observed that different from the regular quantum dots, that posses strong size dependent optical properties, the cysteine-ZnS nanoparticles always have a fixed absorption profile with a clear maxium at 290 nm. These nanoparticles contain few unit cells in their nanocrystals and have stable structures and unique surface related physical properties. It can be observed that the excitation profile of the cysteine-ZnS is narrower than the profiles of the other characterized nanoparticles [49].

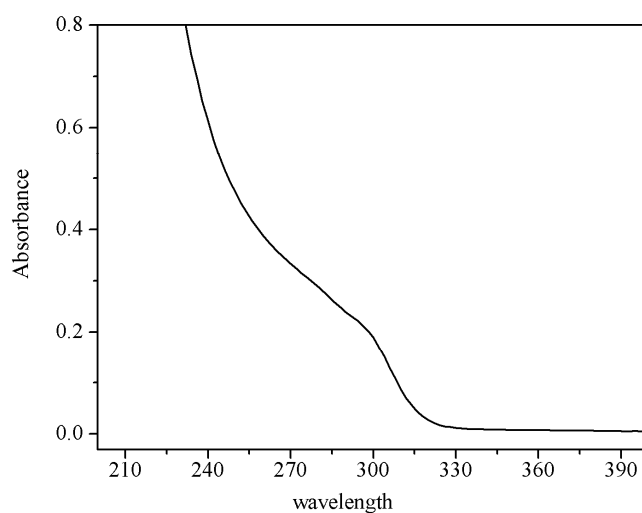


Figure 23 - Cysteine-ZnS quantum dots electronic absorption spectra.

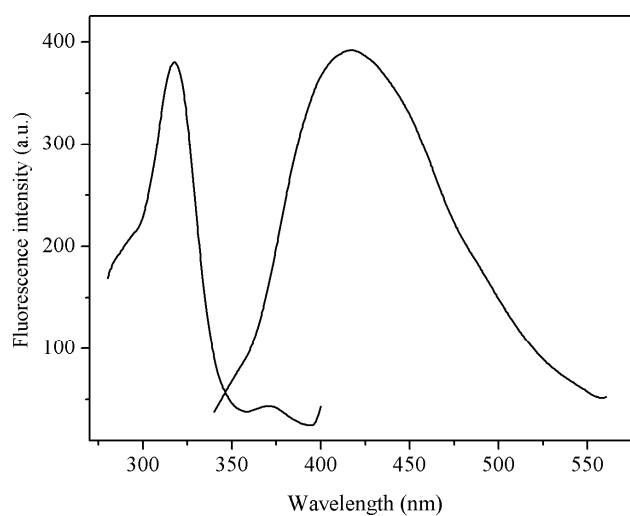


Figure 24 - Photoluminescence excitation and emission spectra of cysteine-ZnS quantum dots.

The photoluminescence intensity of nanoparticles centered at 424 nm sharply increased with the increasing reflux time, reaching a maximum value at 120 min. The photoluminescence intensity then decreases as the reflux time surpass 120 min as indicated in Figure 25. At longer times of reflux, the cloudy appearance of the dispersion indicated the aggregation of the crystals leading to

the formation of bigger particles and consequently less intense photoluminescence.

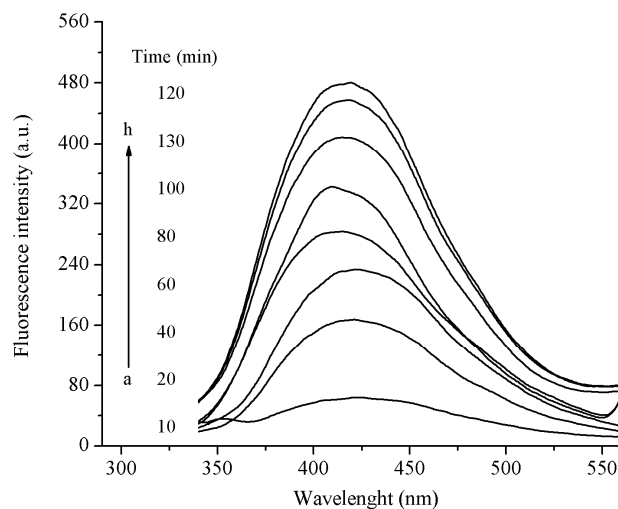


Figure 25- Photoluminescence emission spectra of the cysteine-ZnS nanoparticles synthesized using different reflux times: (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, (f) 100, (g) 130, (h) 120 min

3.2.1 Size determination by scanning transmission electron microscopy

The morphology and structure of functionalized nanoparticles were studied by scanning transmission electron microscopy (STEM). In the Figure 26, the STEM image indicated a large number of assemblies of cysteine-ZnS nanoparticles with almost uniform size and shape. As can be observed, nanoparticles are well dispersed in the size range from 5.1 to 6.6 nm of diameter.

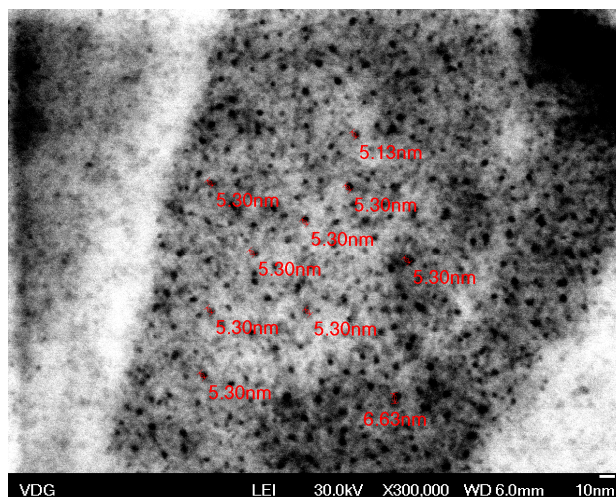


Figure 26- STEM image of cysteine-ZnS nanoparticles.

3.2.2 Size determination by dynamic light scattering

The particle size distribution of cysteine-ZnS was measured by DLS. The hydrodynamic diameter was in the range from 12.7 to 17.2 nm with an average diameter of 14.0 nm. The DLS measurements indicated a certain degree of polydispersity, which shows that cysteine-ZnS nanoparticles are prone to certain degree of aggregation, occurrence that is probably due to sample preparation required for DLS measurements that may have removed surface cysteine stabilizer (Figure 27).

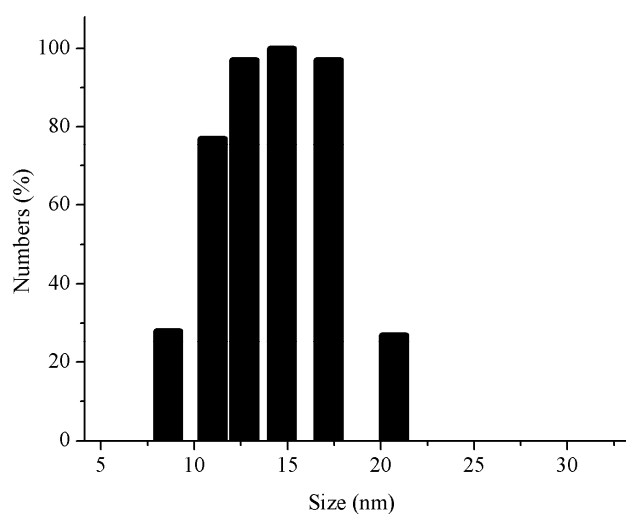


Figure 27- DLS histogram for the cysteine-ZnS nanoparticles.