Spectroscopy characterization and quantum yield determination of quantum dots

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Abstract. In this paper we show the characterization of two kinds of quantum dots: hydrophilic and hydrophobic, with core and core/shell respectively, using spectroscopy techniques such as UV-Vis, fluorescence and Raman. We determined the quantum yield in the quantum dots using the quinine sulphate as standard. This salt is commonly used because of its quantum yield (56%) and stability. For the CdTe excitation, we used a wavelength of 549nm and for the CdSe/ZnS excitation a wavelength of 527nm. The results show that CdSe/ZnS (49%) has better fluorescence, better quantum dots, and confirm the fluorescence result. The quantum dots have shown a good fluorescence performance, so this property will be used to replace dyes, with the advantage that quantum dots are less toxic than some dyes like the rhodamine. In addition, in this work we show different techniques to find the quantum dots emission: fluorescence spectrum, synchronous spectrum and Raman spectrum.

1. Introduction
In the last 20 years, quantum dots (QDs) have been widely used as luminescent materials. Among their advantages are that they are versatile, and have the tight fluorescence bands, high quantum yield, heat stability and light stability [1]. QDs are formed by hundred to thousands atoms, and their size can be between 1nm and 20nm [2,3]. In this work we used QDs with size between 2nm and 7nm. By changing its size, the fluorescence wavelength can be in the visible spectrum or NIR [4].

The optical properties of QDs can be modelled as a particle in a box model. Energy in the excited state decreases when the particle’s size increases [4,5]. The energy in the excited state depends on the QDs material [6]. We characterized CdTe and CdSe/ZnS with spectroscopy techniques like UV-Vis, fluorescence and Raman [7,8]. The efficiency in the fluorescence mechanism is measured by the quantum yield. It is defined as the relation between the number of emitted photons and the number of absorbed photons [9–11].

2. Experimental procedure
2.1. Preparation of samples
We prepared the samples using 2.5mg of CdTe in water and 2.5mg of CdSe/ZnS in n-hexane. The first samples had a concentration of 100ppm, so we did two dilutions: 40ppm and 20ppm.

2.2. UV-Vis and fluorescence characterization
We used the UV-Vis spectrophotometer Shimadzu Corporation 2401PC with photomultiplier detector R-928. To determine the maximum absorption for each sample, we realised a full scanning from 800nm
to 300nm, with monochromator from 190 to 900nm±0.2nm, and a step beam of 0.1nm. We used quartz cell with 10mm optical path.

For the fluorescence spectrum, we used spectrofluorimeter Photon Technology International (PTI) QM-40, xenon lamps and photomultiplier detector 814. We added the samples in the Starna quartz cell with 10mm optical path and 3.5mL nominal volume.

For the spectrum determination, we used the same parameters: slit width in excitation and emission spectrum of 0.25nm, step size of 1nm and integration time of one second.

2.3. **Raman characterization**

We used the spectrometer LabRam HR Evolution, Horiba Scientific. We used two kinds of laser: blue (473 nm) and red (785 nm). The detector was a charge coupled device with wavelength in UV-Vis and NIR.

3. **Results and discussion**

3.1. **Preparation of quinine sulphate standard**

We prepared a 1.25x10⁻⁴M solution of quinine sulphate standard (QS) with sulphuric acid 0.1N as solvent. UV-Vis absorption spectra was obtained in a range from 800nm to 300nm in the UV-Vis spectrophotometer. The highest absorbance was in 347nm.

3.1.1. **Fluorescence determination to QS.** In order to obtain the fluorescence spectra, we used the wavelength of highest absorbance in UV-Vis (347nm). From this information, we used the sweep range of fluorescence from 353nm to 630nm to determine the highest emission wavelength. It was in 445nm. In order to obtain better results, we used different wavelengths for emission and excitation, and obtained the synchronic spectrum. With the synchronic spectrum, we could see the highest fluorescence with different excitation wavelength and it was in 446nm.

3.2. **CdTe characterization**

A similar approach was used for the CdTe characterization. We determined the highest absorbance in UV-Vis. In this case, the highest intensity was in 505nm when we did a sweep range in 800-300nm. With this result we determined the fluorescence changing the emission wavelength between 510-620nm. The highest value was in 544nm. Then, we changed the emission and the excitation wavelength and obtained the synchronous spectrum (Figure 1(a)). The highest value was in 547nm. We used Raman spectroscopy because it is a fast and sensitive method to determine changes in atoms vibration [12]. We used red laser light (785nm). The highest peaks were in 83.4cm⁻¹ and 155cm⁻¹. They represent tellurium vibrations. In 893cm⁻¹ there was a peak with lower amplitude due to Cd-Te vibrations (Figure 1(b)).

3.3. **CdSe/ZnS**

Using a similar approach, we used the UV-Vis spectroscopy to determine the highest absorption. In this case it was in 511nm. With this sample, we had to thin more, because with the sweep range in UV-Vis, the sample grew up more than the allowable range. Therefore, this sample was diluted in the concentrations: 40ppm and 20ppm.

Then, by changing the excitation and the emission wavelength, we got the synchronous spectrum with the highest data in 531nm (Figure 2(a)). For the Raman characterization, we found two special peaks: one in 143cm⁻¹ owing to Cd-Se interactions, and the other in 202.4cm⁻¹ corresponding to the shell interactions (Zn-S) (Figure 2(b)).

3.4. **Quantum yield determination**

For the quantum yield (QY) we used the equation below. Where \( F \) and \( F_{std} \) are the fluorescence areas in the sample and the standard; \( A \) and \( A_{std} \) are the absorbance in the sample and the standard and; \( n \) and \( n_{std} \) are the refraction index [13].
We used the QS because it is very common to determine the QY for good stability. QY was 0.546 corresponding to 54.6% [14]. In the table below, we can see the data for QY determination.

\[ \Phi_f = \Phi_{f(sol)} \frac{F \cdot A_{sol} \cdot n^2}{F_{sol} \cdot A \cdot n_{sol}^2} \]  

(1)

Figure 1. (a) Synchronous spectrum, the green line the CdTe in 100ppm and the violet line is in 40ppm. (b) Raman spectrum with different vibrational modes.

Figure 2. (a) Synchronous spectrum, the purple line the CdSe/ZnS in 20ppm and the green line is in 40ppm. (b) Raman spectrum with different vibrational modes.
4. Conclusion
The CdSe/ZnS has a better quantum yield (49.7%) than the CdTe (46.5%). It is because the CdSe has a shell that gives it more stability and fluorescence. We could see that the QDs are very fluorescent and have a good quantum yield. This is important because in the future, we can use the QDs as substitution to dyes.

From the conducted experiment, we can conclude that the CdSe/ZnS is a better marker than the CdTe. However, in biological applications it is better to use CdTe, as it is hydrophilic and has less toxicity.

Acknowledgments
The authors gratefully acknowledge the support of this research by LEAM and the Universidad Industrial de Santander.

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