Changes on the Stokes Shift in Large CdSe Colloidal Quantum Dots by a Ligand Exchange

Sandra Alvarenga, Hamilton Ponce, Ignacio González Oliva, Carlos Rudamas
Laboratorio de Espectroscopía Óptica, Escuela de Física
Facultad de Ciencias Naturales y Matemáticas, Universidad de El Salvador
Final 25 Av. Norte, San Salvador, El Salvador, Central America
ar12015@ues.edu.sv; hamilton.ponce@ues.edu.sv; ignacio.gonzalez@ues.edu.sv; carlos.rudamas@ues.edu.sv

Abstract *-* In this work, we have studied the optical properties of CdSe colloidal quantum dots (CQDs) that undergo a ligand exchange. The QDs were synthesized by the thermal decomposition method and characterized by using optical spectroscopy techniques and Density Functional Theory (DFT) calculations. Trioctylphosphine (TOP) and Oleic acid (OA) ligands were replaced by Formic acid. This ligand exchange seems to cause an increment of the Stokes shift on the nanostructures. As a result a surface underpassivation of the nanostructures appears. This could be related to the generation of non-radiative states that decreases the quantum yield in our samples and a redistribution of the band edge electronic states that explain to some extent our observed results.

Keywords: Colloidal Quantum Dots, Ligand Exchange, Optical Properties, Stokes Shift, CdSe, Formic Acid.

1. Introduction

Colloidal quantum dots (CQDs) have been studied on the last decades in solid state physics and materials science due to the wide range of applications they have such as bioimaging systems, lasers, LEDs and photovoltaics [1-8]. Some of the CQD properties are the relatively easy synthesis process and the simple tunnability of their emission. The latter, is directly related to QD size, explained by the quantum confinement effect. In these nanostructures, surface interactions play one of the most important roles when it comes to the performance of their optoelectronic properties. During the synthesis process long chain ligands like Trioctylphosphine (TOP) are used. These long chains are capable of giving colloidal stability and assure the formation of the quantum dots. However, these long chains could work against efficient carrier transport [5]. Thus to improve their performance a ligand exchange is required. By performing a ligand exchange, it is possible to obtain results such as enhancement of the efficiency, a broadening of the emission bands, aggregation of the nanostructures and Stokes shift changes [5, 9]. Despite the wide variety of studies related to the characterization of nanostructures, there is still a long way to obtain a better understanding of these effects. In this work, we discuss the effects of ligand exchange on the Stokes shift when Formic acid replaces long chains on the surface of the nanostructures.

2. Experiment

Colloidal QDs were synthesized following the thermal decomposition method proposed by Boatman *et al*. and previously reported in other publications [10-12]. In summary: a Se precursor solution (solution A) is prepared by combining 30 mg of Se, 5 mL of octadecene and 0.4 mL of TOP at 200 °C and cooled at room temperature. A Cd precursor solution (solution B) is later prepared by adding 13 mg of CdO, 0.6 mL of oleic acid (OA) and 10 mL of octadecene and heated at 225 °C. Then 1 mL of solution A is added. Due to the dependence of the resulting size of the QDs with the reaction time, aliquots were taken at different times from the nucleation. They were quenched and stored at room temperature.

The aliquot samples were washed three times in methanol and redispersed in toluene. Formic acid was then added to each sample. Here, the ligand excess was fixed to be around 10 times the concentration of the CdSe atoms in solution. The resulting solution was stored at room temperature. Absorption spectra were measured using an USB4000 UV-VIS spectrograph with a spectral resolution around 1.50 nm, with an entrance slit of 25 µm and a Tungsten lamp as light source. PL spectra were measured with an USB4000-FL spectrograph with a spectral resolution around 10 nm, and an entrance slit of 200 µm using a LED with $\lambda_{exc} = 395$ nm as excitation source. All of them were manufactured by Ocean Optics.

To estimate the size of the CQDs we used the semi-empirical model reported by Yu and co-workers [13]. To support this estimation, we have also performed density functional theory (DFT) calculations, as described elsewhere [15].

3. Results and Discussion

Figure 1 shows the absorption spectra of several synthesized samples. An absorption band, associated to the band edge absorption, is clearly observed. As stated above, the QD sizes were estimated by using the semi-empirical model reported by Yu *et al.*, as shown in Figure 2, using the band edge absorption peak energy for each sample. The quantum confined effect is observed here as a red shift of the band edge absorption when the size of the QDs increased. DFT calculations, also shown in Fig. 2, support the interpretation of these results. Despite of the underestimation of the energy of the absorption transition, the behaviour of the absorption transition energy when the QD size increases is similar to the obtained experimental results. The underestimation of the absorption transition energies obtained in DFT calculations is understood and has been explained elsewhere [15]
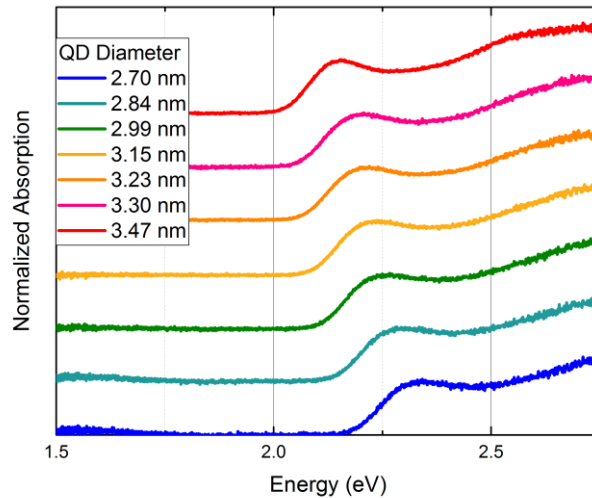

Fig. 1: Normalized absorption spectra. The quantum confinement effect is seen as a red shift in the band edge peak with increasing QD size.
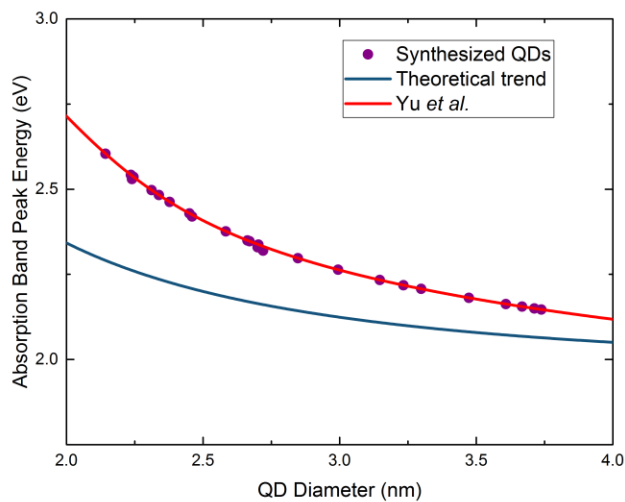

Fig. 2: Theoretical trend and synthesized QD sizes. A similar trend is observed in experimental and theoretical plots.

Figure 3 shows the PL spectra of the synthesized samples. Two emission bands are clearly observed, especially for small QDs. The band at higher energies is associated to the band edge emission whereas the wide band at lower energies has its origin in the recombination of charge carriers trapped in surface defects [11]. A red shift of the band edge emission is also here observed when the QD size increases. We also observe a decreasing of the surface defect band emission for higher QD sizes. This could be understood considering the decreasing on the surface-to-volume ratio with an increasing of the size of the QDs. The surface-to-volume ratio is inversely proportional to the QDs size, meaning in smaller QDs there is a higher ratio of superficial atoms, relative to the total number of atoms on the structure [16].

Figure 4 shows the absorption and PL spectra for the 3.61 nm QDs before and after the ligand exchange process was done. A blue shift is clearly observed in the absorption spectrum. The absorption band edge energy peak is shifted from 2.16 eV for TOP/OA capped QDs to 2.19 eV in the case of Formic acid capped QDs. On the other hand, we observe a band edge emission energy peak shift from 2.12 eV to 2.09 eV in the PL spectra. The ligand exchange treatment produced a similar shift in all our absorption and PL spectra for different CdSe nanostructure sizes.

We believe that the increment of the Stokes shift in our samples suggest an underpassivation in our QDs. Accordance to this, we observed (not shown here) an 8-fold decreasing of the quantum yield after the ligand exchange, which could be associated to the generation of non-radiative traps within this underpassivation. In fact, surface modification trough ligand exchange has been reported to cause different effects on the absorption and PL spectra of QDs, where electronic reconfiguration is one of the main causes of these shifts [13, 17-22]. Underpassivation could also cause changes on the band edge states and a decreasing of the oscillator strength in CQDs, as reported by other authors [23]. This is good agreement with our obtained results.
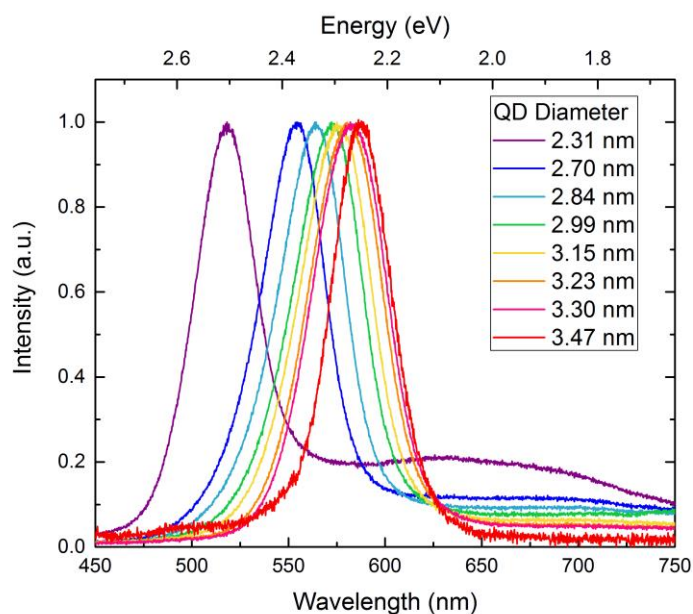

Fig. 3: PL spectra normalized to the band edge maximum for different QD sizes.
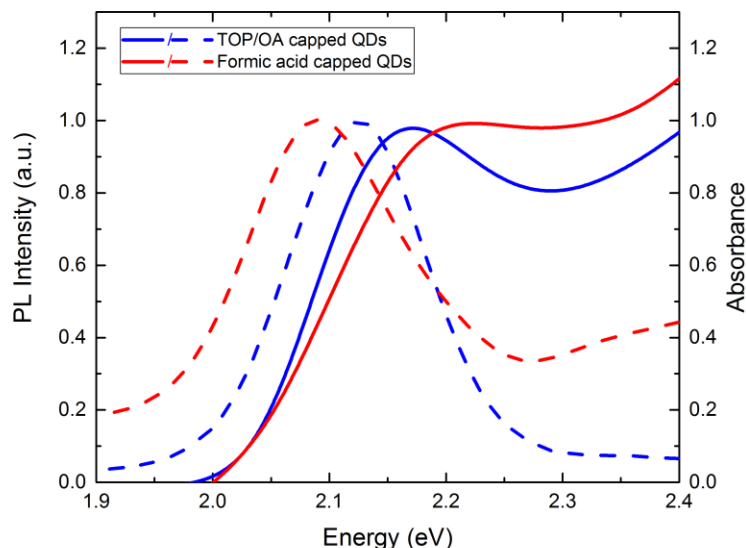
Fig. 4: Normalized absorption (solid lines) and PL spectra normalized to the band edge maximum (dashed lines) for 3.61 nm sized QDs before and after the ligand exchange process.

Formic acid as capping ligand has been used before in ultrasmall CdSe QDs (smaller than 2 nm in diameter) to study white light emitting QDs [5]. The PL red shift observed in our samples differs from the results presented by Rosenthal *et al.*, but this could be related, to some extent, to the size of the studied nanostructures and/or the difference in primary ligands used on each synthesis process.

4. Conclusion

In this work, PL spectra for different QD sizes (QD diameter > 2.31 nm) are presented. An increment of the Stokes shift was observed on CdSe CQDs after a ligand exchange process where Formic acid was added as new capping ligand. This could be related to an effect of underpassivation in our QDs after the ligand exchange. The latter generates non-radiative states that compete against an efficient recombination, what we observed as a decreasing of the quantum yield in our samples, and a redistribution of the electronic states that could explain, to some extent, our obtained results.

Acknowledgements

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