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Grau de Química

Treball Final de Grau

Nanostructuration of II-VI semiconductor materials for quantum communications technologies
Nanoestructuració de materials semiconductors tipus II VI per tecnologies quàntiques de la comunicació

Núria Ponsa Espinet

June 2026

Universitat de Barcelona

B:KC Barcelona Knowledge Campus
Campus d'Excel·lència Internacional

Quan creus que ho tens tot resolt, canvien les preguntes.

Joan Fuster

Primer de tot, vull agrair a la meva tutora Marta Estrades Bofarull i a l'Albert Figuerola Silvestre pels seus esforços, per ajudar-me sempre que han aparegut dubtes i fer que realment aprengués i gaudis d'aquest treball. També gràcies a tot el meu grup de recerca LM2N, en especial a la Gara, a l'Eloi i a la Coral, per fer-me sentir acompanyada en tot moment, per fer que cada dia anés amb ganes al laboratori i fer-me sentir una més al grup.

També donar les gràcies a la meva família, per haver-me recolzat i acompanyat durant tot el procés. Al David, per haver-me escoltat i ajudat en els mals dies. I a tots els meus amics per treure'm un somriure sempre que he estat amb ells. A tots ells, gràcies per acompanyar-me i fer-me costat durant tot aquest procés.

REPORT

IDENTIFICATION AND REFLECTION ON THE SUSTAINABLE DEVELOPMENT GOALS (SDG)

This work focuses on the synthesis and characterisation of CdSe semiconductor nanocrystals using various synthesis methods, with a primary emphasis on solvothermal synthesis. These nanomaterials exhibit highly tuneable optical and electronic properties, making them particularly attractive for applications in optoelectronics, bioimaging and emerging photonics technologies. However, their synthesis relies on the use of heavy metals, in our case cadmium, which are potentially toxic materials, as well as organic solvents and demanding reaction conditions, all of which can have an impact on the environment and human health.

This work aims to improve synthesis methods to make them safer and more sustainable, as well as optimise control over optical properties in order to expand their technological applications. Within the five main areas of the Sustainable Development Goals (SDGs), known as the 5Ps, and defined by the United Nations, the ones most relevant to this project are: Planet, People and Prosperity. On the one hand, the use of heavy metals and the generation of chemical waste may have negative impacts on the environment (Planet). On the other hand, exposure to toxic substances such as cadmium can pose risks to human health (People). Finally, the development of semiconductor nanomaterials for applications in optoelectronics contributes to the technological and industrial process (Prosperity).

Some of the most relevant SDGs for this work are shown below:

- Goal 12: Responsible consumption and production

  A closely related objective is the SDG 12, which promotes the management of chemicals and waste from the synthesis. In these syntheses toxic precursors based on cadmium, a heavy metal, are used; in addition, organic solvents are also employed. Therefore, it is necessary to develop a more efficient, safer and less polluting synthesis method. In this work, we aim to contribute to the study of solvothermal synthesis as an alternative to colloidal synthesis in order to improve the sustainability of the process, particularly with regard to scalability and reproducibility. However, heavy metals, such as cadmium, are still used, which shows that research into new, safer materials and methodologies that are more respectful of the environment must continue.

- Goal 9: Industry, innovation and infrastructure

  We can also relate our work to goal 9, as it contributes to the scientific research of advanced materials with technological applications. Based on the comparative study of solvothermal and colloidal synthesis, we aim to investigate how synthesis conditions affect optical and structural properties. In this way, we can improve control over their properties and optimise the synthesis processes. This may favour its future application at an industrial scale.

- Goal 7: affordable and clean energy

  Goal 7 promotes access to affordable, reliable and sustainable energy. In this work, cadmium selenide quantum dots exhibit interesting optical and electronic properties for applications in photovoltaic devices (solar cells) and can contribute to the development of more efficient energy technologies. However, it is important to keep in mind that the sustainability of these technologies also depends on the synthesis processes used, which highlights the need to develop more environmentally friendly methods.

CONTENTS

1. SUMMARY

In recent years, the study of semiconductor nanocrystals with quantum properties has gained increasing interest, especially following the award of the 2023 Nobel Prize in Chemistry to the discovery and development of quantum dots. These materials have demonstrated great potential in optoelectronic applications and are nowadays proposed for quantum communication technologies. This work focuses on the synthesis of cadmium selenide (CdSe), which exhibits highly tunable optical properties depending on nanocrystal size because of the quantum confinement effect.

The main objective of this study is to synthesise CdSe semiconductor nanocrystals using different methods: colloidal synthesis via the hot injection technique and solvothermal synthesis. In particular, is evaluated the potential of solvothermal synthesis as an alternative to conventional colloidal synthesis by studying aspects such as size control, morphology, optical properties, reproducibility, and its potential for large-scale application. This method has not been widely used for the synthesis of colloidal quantum dots, especially in CdSe-based systems. It is also intended to evaluate whether solvothermal synthesis can be a safer and simpler alternative from an experimental point of view compared to colloidal synthesis.

To carry out this synthesis, CdSe samples were prepared by both colloidal and solvothermal methods under different reaction conditions. In the case of the solvothermal synthesis, two coordination cadmium precursors, based on stearic acid and myristic acid, were employed. The colloidal synthesis is based on the rapid injection of precursors into a hot medium to induce burst nucleation followed by controlled growth of the nanocrystals, which enables the production of highly monodisperse nanocrystals. On the other hand, solvothermal synthesis is carried out under high temperature and pressure conditions inside an autoclave, where similar nucleation and growth processes take place, yielding nanocrystals with good crystallinity using less stringent experimental conditions and a simpler and easily scalable procedure.

Finally, the samples obtained were purified by precipitation and centrifugation processes and subsequently characterised using optical and structural techniques, including UV-Vis spectroscopy and photoluminescence, as well as high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction. These techniques allow establishing a relationship between the synthesis conditions and the size, morphology, crystallinity, and optical properties of the CdSe nanocrystals, as well as evaluating the potential of the solvothermal synthesis as an alternative to the colloidal synthesis

Keywords: quantum dots, CdSe, quantum confinement, colloidal synthesis, solvothermal synthesis, hot injection, nanocrystals, semiconductors, photoluminescence, and optoelectronics.

2. RESUM

En els últims anys, l'estudi dels nanocristalls semicoductors amb propietats quàntiques ha guanyat interès, especialment rere l'atorgament del Premi Nobel del 2023 per al descobriment i el desenvolupament dels punts quàntics. Aquests materials han demostrat un gran potencial en aplicacions optoelectròniques i tecnologia de comunicació quàntica. Aquest treball es centra en la síntesi de CdSe, el qual presenta unes propietats òptiques altament ajustables en funció de la mida del nanocristall a causa del fenomen de confinament quàntic.

L'objectiu principal d'aquest estudi és poder sintetitzar els nanocristalls semiconductors de CdSe a partir de diferents mètodes: la síntesi col•loidal mitjançant la tècnica de hot injection i la síntesi solvotèrmica. En particular, es pretén avaluar el potencial de la síntesi solvotèrmica, un mètode que fins ara, no havia estat utilitzat per la síntesi de quantum dots col•loidals especialment en sistemes basats en CdSe, com a alternativa a la col•loïdal convencional, estudiant aspectes com el control de la mida, la morfologia, les propietats òptiques així com la seva reproductibilitat i la seva possible aplicació a gran escala. També es vol avaluar si la síntesi solvotermal pot ser una alternativa més segura i senzilla des del punt de vista experimental en comparació amb la síntesi col•loidal.

Per a dur a terme aquesta síntesi s'han preparat mostres de CdSe mitjançant síntesi col•loidal i solvotèrmica sota diferents condicions de reacció. En el cas de la síntesi solvotermal s'han utilitzat dos compostos de coordinació de cadmi com a precursors basats en àcid esteàric i àcid mirístic. La síntesi col•loidal es basa en la injecció ràpida dels precursors en un medi calent per tal d'induir una nucleació ràpida seguida d'un creixement controlat dels nanocristalls, i així obtenir nanocristalls monodispersos. D'altra banda, la síntesi solvotermal es duu a terme sota condicions d'elevada temperatura i pressió dins d'una autoclau, on tenen lloc processos similars de nucleació i creixement, obtenint nanocristalls amb bona cristal•linitat mitjançant condicions experimentals menys estrictes i un procediment més senzill i més fàcilment escalable.

Finalment, s'han purificat les mostres obtingudes mitjançant processos de precipitació i centrifugació per posteriorment caracteritzar-les mitjançant tècniques òptiques i estructurals utilitzant espectroscòpia UV-Vis i fotoluminescència així com per microscòpia electrònica de transmissió d'alta resolució (HRTEM) i difracció de raig (XRD). Aquestes tècniques permeten relacionar les condicions de síntesi amb la mida, la morfologia, la cristal·linitat i les propietats òptiques dels nanocristalls de CdSe i determinar el potencial de la síntesi solvotèrmica com a alternativa de la síntesi col•loidal.

Paraules clau: "quantum dots", CdSe, confinament quàntic, síntesis col•loidal, síntesis solvotermal, "hot injection", nanopartícules, semiconductors, fotoluminescència, optoelectrònica.

3. INTRODUCTION

3.1. SEMICONDUCTOR NANOCRYSTALS: PROPERTIES AND APPLICATIONS

In recent years, semiconductors nanocrystals have gained significant importance due to their unique physical and chemical properties, making them highly attractive materials for applications in optoelectronics, fluorescent bioimaging, photovoltaic devices, chemical and biological sensors, as well as quantum communications technologies.[1, 2, 3]

Currently, CdSe nanocrystals are being investigated by the QComms research group at the Institut de Ciències del Cosmos lof the Universitat de Barcelona (ICCUB) as tunable materials for Single Photon Source (SPS) applications in emerging quantum photonic technologies. For these studies, it is necessary to obtain CdSe nanocrystals with an emission wavelength around 600 nm, as this spectral region is of particular interest to the ongoing research programme of the QComms group.

3.2. SEMICONDUCTORS AND ELECTRONIC STRUCTURE.

Materials can be classified according to their electrical properties as conductors, semiconductors and insulators. Semiconductors are characterized by exhibiting intermediate conductivity, which is determined by their electronic structure. In these materials there is a forbidden energy region between the valence band and the conduction band, known as the band gap. This is, by definition, the energy required to excite an electron from the valence band to the conduction band, creating an electrostatically bound electron-hole pair, known as the exciton.[1, 4, 5]

3.3. QUANTUM DOTS AND QUANTUM CONFINEMENT

Within the field of semiconductor nanocrystals, quantum dots (QDs) are a specific type of nanoparticle that has been extensively studied. These are nanocrystals with dimensions ranging from 1 to 10 nm. At such small scales, the size of the exciton (electron-hole pair) is comparable to the size of the nanocrystal, so that the movement of the hole-electron pair is confined within the nanoparticle.[1, 6]

This phenomenon, known as quantum confinement, leads to a change in energy levels, which shift from being continuous, as would be the case with bulk materials, to being discrete, causing an increase in the system's energy, which translates as an increase in the band gap as the size of the nanocrystal decreases. As a consequence of quantum confinement, the optical and electronic properties of QDs depend directly on their size (Figure 1).[7]

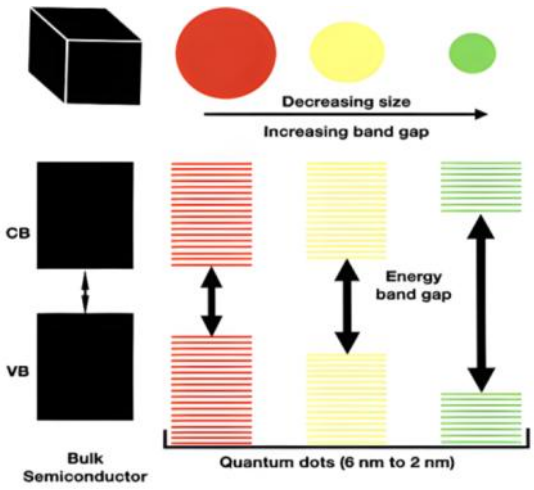

Figure 1. Comparation of energy band structures in bulk and nanoparticulate semiconductors.[6]

3.4. Optical properties and photoluminescence

The optical properties of quantum dots refer to their ability to interact with light, both in absorption and emission processes. Among these properties, photoluminescence stands out, which is the capacity to absorb light and re-emit it at a specific wavelength.

As the size of the nanocrystal decreases, the energy of the electronic transitions increases. As a result, smaller nanoparticles emit light at shorter wavelengths (in the blue region of the spectrum), whereas larger ones emit at longer wavelengths (red region). By controlling the size of the quantum dots, it is possible to tune the wavelength at which they absorb and emit light (Figure 2).

The scientific importance of quantum dots was internationally recognised with the awarding of the 2023 Nobel Prize in Chemistry to Moungi G. Bawendi, Louis E. Brus and Alexei I. Ekimov for the discovery and development of quantum dots. Their work established the fundamental understanding of size-dependent optical and electronic properties of semiconductor nanocrystals as well as the controlled synthesis of highly monodisperse quantum dots suitable for technological applications.[4, 5, 8-10]

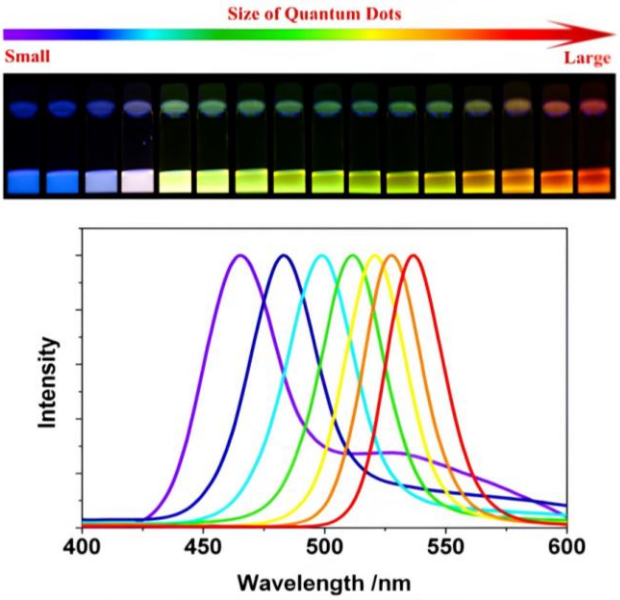

Figure 2. Size-dependent optical properties of quantum dots.

(Image extracted from Debasis Bera et al., Materials 2010, 3, 2260–2297)

3.5. Classification of quantum dots

Quantum dots are classified according to their chemical composition, with particular emphasis on group II–VI semiconductors (such as CdSe, CdS, ZnS) and group III–V semiconductors (such as InP, GaAs), among others. Among these, those of the II-VI group have been extensively studied because they exhibit excellent optical properties and a high photoluminescence efficiency.[6]

This work focuses on CdSe quantum dots, an II–VI semiconductor. Although other materials such as CdS or ZnS are also of interest in optoelectronic applications, CdSe stands out for its excellent optical properties and its easily tunable emission within the visible region of the spectrum. In the case of CdS, with its wider band gap exhibits more limited emission in the visible region, while ZnS with an even larger band gap, further restricts visible emission despite its lower toxicity. Furthermore, CdSe is one of the most widely studied model systems in the field of quantum dots, with extensive literature available on its synthesis and characterisation.[1, 4]

When this material is in the bulk state it exhibits a fixed band gap energy of approximately 1.76 eV; however, when it is reduced to the nanometer scale, this band gap energy ceases to be constant and varies depending on the nanoparticle size, due to quantum confinement. As a result, CdSe nanocrystals can emit light across a broad range of wavelengths within the visible spectrum, making them useful for both biological imaging and various types of optoelectronic devices, including solar cells and light-emitting diodes (LEDs).[1, 7]

3.6. METHODS OF SYNTHESIS OF QUANTUM DOTS

Quantum dots synthesis methods are important for determining and controlling their size, shape, crystallinity and other factors that can influence their optical and electronic properties. These methods must allow precise control of nanocrystal size in order to optimize its functionality and obtain a monodisperse solution. [6]

3.6.1. Size control: nucleation and growth

Nanocrystal formations take place in multiple phases, mainly nucleation and growth based on the La Mer model (Figure 3).[11]

3.6.1.1. Nucleation

Initially, nucleation takes place, which is the process by which small aggregates (nuclei) form from the precursors in our solution. At this stage the energy barrier is very high and a high degree of supersaturation is required to overcome it and initiate the nucleation process. Once the nuclei have formed and exceeded the critical radius, the size at which they become stable and they can grow the degree of supersaturation decreases as the precursors are consumed, and the nucleation process terminates on its own. This stage occurs over a short period of time and is known as burst nucleation, in which many nuclei form simultaneously.

Although burst nucleation does not guarantee a uniform size distribution, it is essential for its size control, ensuring that almost all nuclei exhibit the same growth history.[12]

3.6.1.2. Nanocrystal growth

The second stage of the process is nanocrystals growth, which occurs through the incorporation of reactive species from the solution. During this stage, the smaller particles grow faster than the larger ones, a phenomenon known as size focusing, resulting in a more uniform size distribution. However, at later stages the phenomenon of Ostwald ripening may occur, in which the smaller particles dissolve and the material redeposit onto the larger ones, causing an increase in the average size and a broader size distribution.

Precise control of these stages is essential to obtain quantum dots with tunable optical properties and suitable for applications such as LEDs, bioimaging and photovoltaic devices.[5, 14]

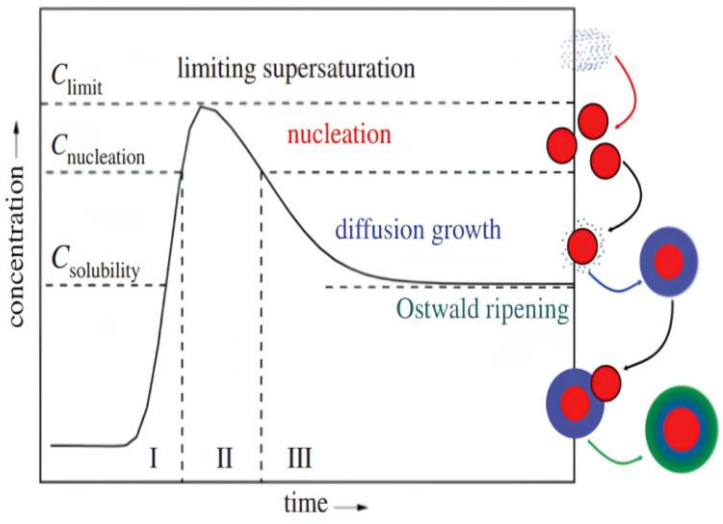

Figure 3. Schematic representation of nanocrystal formation based on the LaMer model, showing the evolution of supersaturation during nucleation and growth stages.

(Image extracted from Dunne P. W. et al. *Philos. Trans. R. Soc.* 2015, 373, 20150015)

3.6.2. Colloidal synthesis - Method description - Advantages

In this work, CdSe quantum dots have been synthesised using different methods. First, they were prepared by a colloidal method, with the aim of obtaining high-quality, monodisperse nanoparticle with tunable optical properties.

This method is based on the reaction of liquid-phase inorganic or organometallic precursors in the presence of organic solvents and stabilising agents (ligands), allowing control over the growth of the nanocrystals and preventing aggregation. The ligands adsorb onto the surface of the nanocrystals, regulating their size and colloidal stability (Figure 4 left side). One of the most widely used techniques in this synthesis is the hot injection method, in which the precursors are rapidly injected into a hot medium, generating a high supersaturation that leads to rapid nucleation (burst nucleation), followed by a controlled growth stage (as described in the La Mer crystal growth theory).[11]

Through this synthesis it is possible to obtain precise control over the size of the quantum dots by adjusting parameters such as temperature, precursor concentration and reaction time. This allows the production of nanocrystals with a narrow size distribution (high monodispersity) and can be obtained well-defined optical properties. Note that the discovery of colloidal synthesis allowed the confirmation of the La Mer thus enabling for the first time the semiconductor nanocrystals and their optical size dependence properties, which, as mentioned above, was awarded years later with the Chemistry Nobel Prize 2023.[4, 5, 8-10]

Importantly, this synthesis methodology was later on applied to obtain other nanomaterials, such as magnetic (Fe_3O_4, γ-Fe_2O_3, etc.) and plasmonic (Au, Ag and Pd) nanosctructures (Figure 4 right side), also achieving also precise control over their size and shape.

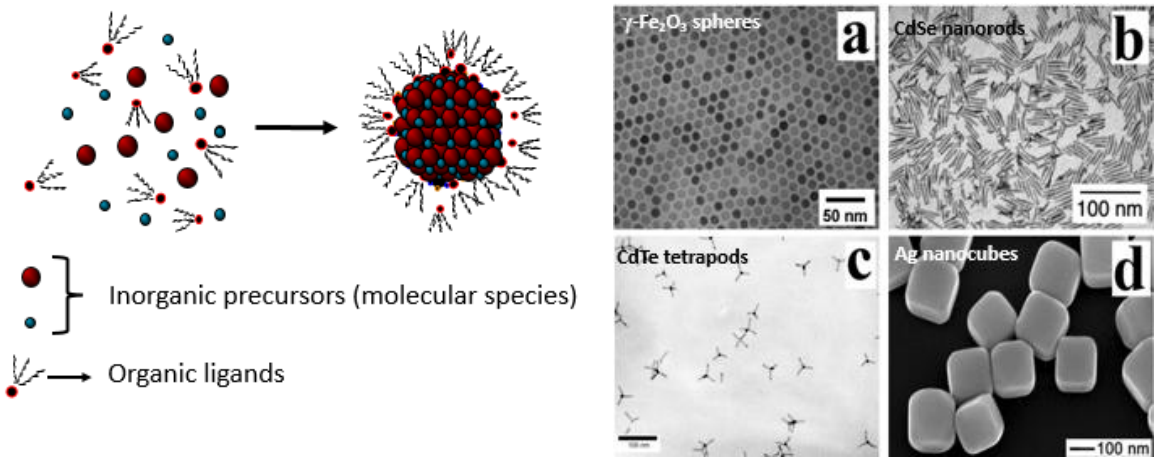

Figure 4. Schematic representation of nanocrystal formation and growth during colloidal synthesis (left) and examples of nanocrystals of different nanomaterials with dissimilar morphologies synthesised through colloidal methods (right).

(Image adapted from lecture material provided by Dr Marta Estrader Bofarull, University of Barcelona)

3.6.3. Limitations of the colloidal method

Despite its advantages, colloidal synthesis presents some limitations. Firstly, the use of potentially toxic precursors, especially in the case of cadmium-based quantum dots, can lead to significant environmental and health concerns.

Secondly, the method requires rigorous control of reaction parameters, such as precise temperature control, the atmosphere (often inert) and the injection rate. Small variations in these conditions can significantly affect reproducibility.

Finally, this method has a significant limitation which is scalability, as mentioned previously, the need for precise control over the synthesis and the difficult of maintaining a homogeneous distribution over large volumes, makes large-scale production challenging.

3.6.4. Solvothermal synthesis - Method description - Advantages - Comparison with colloidal

In recent years, as an alternative to the colloidal method, solvothermal synthesis has begun to be used to prepare semiconductor nanocrystals in systems based on CdS, CdSe and CdTe, where the ability to control their size and shape and their optical properties has been demonstrated. [2, 13, 14] However, this type of method it is still in its infancy of exploration.

This method is based on the reaction of precursors in a liquid medium under high temperature and pressure conditions, typically using organic solvents. It enables the formation of nanocrystals with high crystallinity and good control of morphology. Furthermore, unlike colloidal synthesis by hot injection, it requires less strict experimental reaction conditions, making it more reproducible and easier to scale up. However, it still uses potentially toxic precursors based on heavy metals such as cadmium.

In this work, II-VI group semiconductor nanocrystals, specifically CdSe, have been synthesised using the solvothermal method with the aim of evaluating their effectiveness in controlling size, morphology and optical properties, as well as their potential application in large-scale processes.

4. OBJECTIVES

The main objective of this work is to synthesise CdSe quantum dots using two methods, placing greater emphasis on the solvothermal approach than on the colloidal one in order to assess its effectiveness in controlling size, morphology and optical properties. It also aims to determine whether the solvothermal method for quantum dot synthesis can be a viable alternative to the colloidal approach. To achieve this main goal, the research work was conducted through specific subobjectives:

- Acquire the basic skills associated with working in a nanomaterials chemistry laboratory.
- Synthesise CdSe quantum dots using both the colloidal synthesis and the solvothermal method with emission wavelengths within the spectral region of interest for the research activities of the QComms group.
- Study the influence on solvothermal method of reaction parameters in nanocrystal growth and optical properties.
- Compare solvothermal synthesis with colloidal synthesis in terms of reproducibility, scalability and safety.
- Investigate the dependence of the nanocrystal size on optical properties as a result of quantum confinement.
- Characterise the CdSe nanocrystals in terms of their optical, structural and morphological properties using UV–Vis absorption spectroscopy, photoluminescence spectroscopy, X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM).

5. EXPERIMENTAL SECTION

5.1. MATERIALS AND METHODS

Materials:

Myristic acid ($C_{14}H_{28}O_2$, MA, 99%), stearic acid ($C_{18}H_{36}O_2$, SA, 97%) and oleic acid (OA, 90%) were purchased from Sigma-Aldrich. Trioctylphosphine oxide (TOPO, 90%), Tri–n-octylphospine (TOP, 97%), Selenium powder (Se, 99,99%) and cadmium oxide (CdO, 99%) were purchased from Strem Chemicals. Octadecyldiphosphonic acid (ODPA, 99%) was purchased from Polycarbon Industries. Selenium powder (Se). Toluene (99.5%) was acquired from PanReac AppliChem. Methanol (99%) was acquired from Thermo Scientific.

Methods:

Synthesis

Two synthesis methods were employed in this work. The first consisted of a colloidal synthesis using the hot-injection method (detailed in Section 5.2.1), while the second involves a solvothermal synthesis using two different cadmium coordination compounds as precursors: one derived from stearic acid and the other from myristic acid (detailed in Section 5.2.2).

Laboratory equipment:

The equipment used in these syntheses included a Schlenk line for working under an inert atmosphere and a 50 mL Teflon-lined of a stainless steel autoclave for the solvothermal synthesis. A glovebox was used in both cases for handling oxygen and moisture sensitive reagents. Heating was carried out using a heating mantle equipped with temperature control and magnetic stirring. Additionally, a high-temperature oven was employed to perform the solvothermal treatment. For sample purification, a centrifuge was employed.

Optical measurements:

- ABSORPTION MEASUREMENTS: For absorption characterization, the samples were analyzed with a UV/Vis/NIR spectrophotometer (PerkinElmer brand, model Lambda 950). The measurements were carried out in transmission mode. To prepare the samples, the nanoparticles of CdSe were dispersed in toluene and measured in liquid suspension using a quartz cuvette. Toluene was first introduced into the cuvette, which had been previously cleaned by rising with toluene and the nanoparticle dispersion was subsequently added drop wise until an adequate concentration was achieved. The solution was mixed to ensure homogeneity, and absorbance spectra were recorded at room temperature.
- PHOTOLUMINISCENCE MEASUREMENTS: For fluorescence characterization, the samples were analyzed with a spectrofluorometer (Edinburgh Instruments, model FS5). It is equipped with a photon-counting PMT detector for visible-range fluorescence spectra and an absorption detector. The photoluminescence spectra were recorded at room temperature. To prepare the samples, the CdSe nanoparticles were dispersed in toluene and measured in liquid suspension using quartz cuvette. The cuvette was cleaned by rinsing it with toluene prior to the measurements. The samples were measured directly in liquid suspension after dilution with toluene to obtain an appropriate concentration and the solution was mixed before measurements and spectra were recorded directly from the liquid suspension.

Physical measurements:

- HIGH-RESOLUTION TRANSMISSION ELECTRON MICROSCOPY (HRTEM): Morphological and structural characterization of the CdSe nanocrystals was carried out using a JEOL J2100 high-resolution transmission electron

microscope (HRTEM) equipped with a LaB_6 thermionic electron gun and operated at an accelerating voltage of 200 kV. Images were recorded using a Gatan Orius CCD camera. For sample preparation, the nanocrystals were dispersed in toluene and sonicated to ensure good dispersion. A drop of the resulting suspension was deposited onto a copper TEM grid coated with an amorphous carbon film and allowed to dry prior to analysis.

- X-RAY POWDER DIFFRACTION (XRD): XRD was performed to characterize the crystalline phase and purity of the synthesized nanocrystals (NCs). Measurements were conducted using a benchtop PANalytical Aeris powder diffractometer (CuKα radiation and Ni filter), operated at 40 kV/7.5 mA in Bragg-Brentano geometry. The data were collected over a 2θ range from 4° to 90°, with a step size of 0.0217°. The obtained XRD patterns were analyzed using XPert HighScore Plus Software and peak positions and intensities were compared with reference patterns from standard database. To prepare the samples for analysis, the NCs were dispersed in toluene and drop casted onto a glass substrate and allowing the solvent to evaporate.

5.2. SYNTHESIS OF CDSE QUANTUM DOTS

5.2.1. Colloidal synthesis: hot-injection method

The colloidal synthesis of CdSe was carried out using the hot injection method described by Carbone et al.[16] applying the original protocol with slight modifications introduced by the research group. This method is based on the rapid injection of selenium into a hot solution containing the cadmium precursor and the ligands (see Figure 5).

In this synthesis, TOPO, ODPA and CdO were mixed in a 25 mL three-neck round-bottom flask, heated to 150°C under vacuum in the Schlenk line for 2 hours. Then, the solution was heated to 350 °C to dissolve the CdO until it turns optically clear with slight coloration. At this point, the TOP was injected in the flask. The solution should become even more transparent after this. Then the temperature was increased to 390 °C and when was stabilized the Se-TOP was rapidly injected. The reaction was allowed to proceed for approximately 40 seconds, during which the formation of a dark brown solution was observed. To stop the reaction, the heating mantle was removed while maintaining continuous magnetic stirring during cooling.

After the synthesis, the nanocrystals were precipitated with methanol. They were washed by repeated cycles of redispersion in toluene followed by precipitation with methanol. A detailed step-by-step description of the synthesis procedure is provided in Appendix 2.

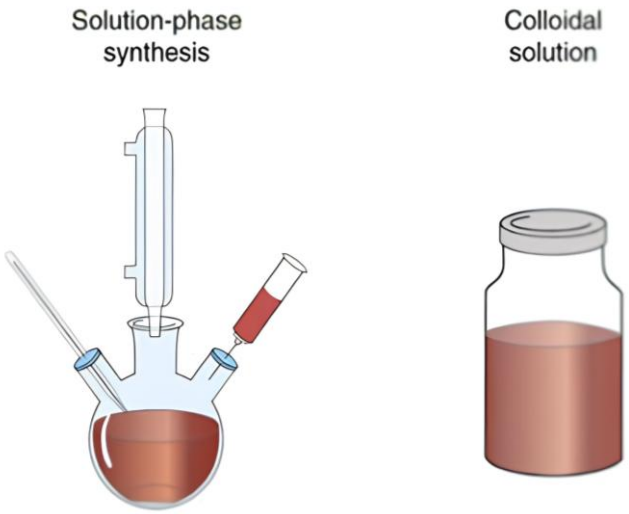

Figure 5. Schematic representation of the hot injection method for CdSe nanocrystals, showing precursor injection into a hot reaction mixture and the formation of a colloidal nanocrystal solution.[7]

5.2.2. Solvothermal synthesis

The two CdSe quantum dot syntheses were carried out using two similar procedures reported in the literature and based on different cadmium coordination precursors employed: cadmium stearate[15] and cadmium myristate.[2, 14]

5.2.2.1. Stearic acid-based synthesis

Preparation of the cadmium precursor

In a 25 mL three-neck round-bottom flask, 0.2568 g of CdO (2 mmol), previously handled in the glovebox, 2.275 g of stearic acid (8 mmol) and a magnetic stirring bar were added, and the side necks were sealed with septa.

The flask was placed in a heating mantle and with nitrogen flow and the temperature was gradually increased to 200 °C at which point a slight yellowish tint was observed. The nitrogen flow was then stopped, and the reaction mixture was allowed to cool to around 100–110°C. Once this temperature was reached, 5 mL of toluene was added while maintaining stirring.

Before transferring the solution to the beaker or crystallizer and after the septa had been removed, the neck of the flask used for the transfer was heated with a heat gun to facilitate maximum recovery of the cadmium precursor, as it tends to solidify rapidly upon cooling due to its low solubility at lower temperatures. The solution was then transferred to the recipient, which contained one-third to one-quarter of the volume of toluene previously added (about 20 mL). The mixture was stirred for several minutes using a magnetic stirrer for ensure complete homogenization. Stirring was then stopped and the magnetic stir bar was removed. The solution was allowed to cool to room temperature, after which a white solid precipitate was formed at the bottom of the recipient after approximately 5 minutes.

Finally, the product was filtered using a Büchner funnel to isolate the solid corresponding to cadmium stearate.

Preparation of the selenium precursor

All materials used were handled inside the glovebox and prepared in 4 mL borosilicate vials with standard screw caps.

First, 0.06 g of Se (0.76 mmol) and 0.1 g of TOP were added to the vial. The vial was then removed from the glovebox and shaken until a homogeneous mixture was obtained. Since the Se did not dissolve completely, mild heating was applied using a heat gun, alternating with agitation using a vortex mixer. In the case that wasn't sufficient, the mixture was sonicated for a few minutes, to promote its dissolution. However, the Se did not fully dissolve, therefore, it was considered sufficient to obtain a homogeneous black solution with the minimum amount of undissolved selenium (Se-TOP).

Solvothermal synthesis of CdSe quantum dots:

First, 0.2717 g of cadmium stearate (0.4 mmol), previously obtained, was transferred to a 40 mL beaker, and 0.131 mL of oleic acid (0.4 mmol) together with 2 mL of toluene were added. The mixture was heated on a heating mantle up to 100 °C under constant magnetic stirring until a clear solution was obtained.

While the solution of cadmium precursor was being heated, the Se-TOP precursor solution was prepared in parallel. Toluene was then gradually added in portions to the Se–TOP solution in the 4 mL vial until a final volume of 10 mL was reached. After each addition, the solution was agitated using a vortex mixer to ensure homogenization and it was transferred to the 50 mL Teflon-lined stainless autoclave, to ensure complete transfer of the solution of selenium precursor. When the cadmium solution became clear, it was transferred into the Teflon-lined autoclave containing the previously added Se-TOP solution, using a heat gun to ensure complete transfer, because the mixture tends to solidify when it cools down.

Finally, once all the solutions had been transferred to the Teflon-lined, the autoclave was sealed, and maintained at 180 ºC in the pre-heated oven at 180 ºC for different reaction times: 5, 6 and 15 hours. After the solvothermal synthesis, colour changes in the solutions were observed as a function of reaction time: at 5 hours, dark red solutions were obtained, at 6 hours a mixture of dark red and brownish tones were observed. As the reaction time increased to 15 hours, progressively darker suspensions were form, resulting in a dark brown colour.

5.2.2.2. Myristic acid-based synthesis

Preparation of the cadmium precursor:

The procedure for synthesizing the cadmium precursor from myristic acid was analogous to that described for stearic acid, using following the same experimental protocol. However, in this case 0.2568 g of CdO (2 mmol) and 1.928 g of myristic acid (8 mmol) were added to the 25 mL three-necked flask. The reaction was heated to 210 °C under constant stirring and under nitrogen inert atmosphere for 10 minutes.

Subsequently, the same purification procedure described above was followed, consisting of dissolving in toluene, cooling and filtration of the resulting solid (see Figure 6).

Figure 6. Purified cadmium myristate (Cd-MA) precursor used in the solvothermal synthesis of CdSe quantum dots. The cadmium stearate (Cd-SA) precursor showed an analogous appearance.

Preparation of the selenium precursor:

The procedure for preparing the selenium precursor remained the same, with only proportions of the reagents being modified. In this case, 0.004 g of Se (0.051 mmol) and 0.08 g of TOP were added to the vial.

It was observed that the Se dissolved more easily, resulting in a transparent solution, without the need for heating with a heat gun. Complete dissolution was achieved by manual shaking and vortex mixing.

Solvothermal synthesis of CdSe quantum dots:

The synthesis of CdSe was carried out following a procedure analogous to that previously described for the stearic acid-based synthesis, with the main difference being in the proportions of the reactants. In this case, 0.0567 g of cadmium myristate (0.1 mmol), 0.131 mL of oleic acid (0.4 mmol) and 2 mL of toluene were added to a 40 mL beaker, and heated until a clear solution was obtained.

In parallel, the Se-TOP solution was prepared while the cadmium precursor solution was being heated. The Se-TOP solution was diluted with 10 mL of toluene following the procedure described above and then transferred stepwise to the 50 mL Teflon-lined stainless steel autoclave. When the solution of cadmium precursor became clear, it was added to the autoclave containing de Se-TOP solution. As in the stearic acid-based synthesis, the transfer was assisted with a heat gun to ensure complete recovery of the cadmium precursor, as the solution tends to solidify upon cooling due to its low solubility.

Finally, the autoclave was sealed and maintained at 180 °C in the oven (previously pre-heated at 180 ºC) for 15 hours, yielding a dark red suspension as the final product.

5.2.3. Purification of CdSe

The purification of the CdSe quantum dots, both for the synthesis based on stearic acid and for the myristic acid based one, was carried out following the same procedure.

First, the suspension obtained from the autoclave after the solvothermal treatment, once cooled to room temperature, was transferred to a borosilicate vial (40 mL). Subsequently, in order to precipitate the nanocrystals from the reaction mixture, 15 mL of methanol and 15 mL of acetone were added, and the sample was centrifuged at 4000 rpm for 5 minutes.

Finally, the supernatant was discarded as it appeared colourless, and the washing process was repeated two additional times to improve the purification of the sample. In cases where the supernatant did not appear completely colourless after centrifugation, it was transferred to a new vial and centrifuged again. Small additional amounts of methanol and acetone were added to promote complete precipitation of the nanocrystals.

The final product was redispersed in a small amount of toluene (see Figure 7).

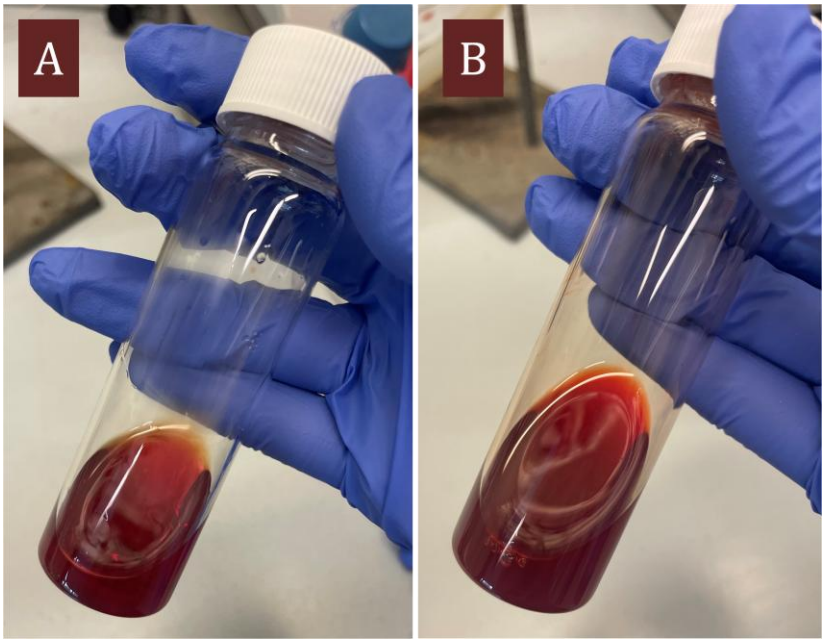

Figure 7. Purified CdSe quantum dot dispersion obtained by the solvothermal synthesis after redispersion in toluene. Image A corresponds to the sample prepared from Cd-MA, while image B corresponds to the sample prepared from Cd-SA.

6. RESULTS AND DISCUSSION

6.1. SOLVOTHERMAL SYNTHESIS: PRECURSOR AND OPTICAL CHARACTERIZATION

6.1.1 FTIR characterization of cadmium precursors

Fourier-transform infrared spectroscopy (FTIR) was used to verify the successful synthesis of the cadmium precursors, both cadmium stearate and cadmium myristate. In each case, they were compared with their respective acid in order to confirm the

coordination of the ligand to the cadmium and, thus, the formation of the precursor. The IR spectra corresponding to cadmium stearate and cadmium myristate are shown in Figures 8 and 9, respectively.

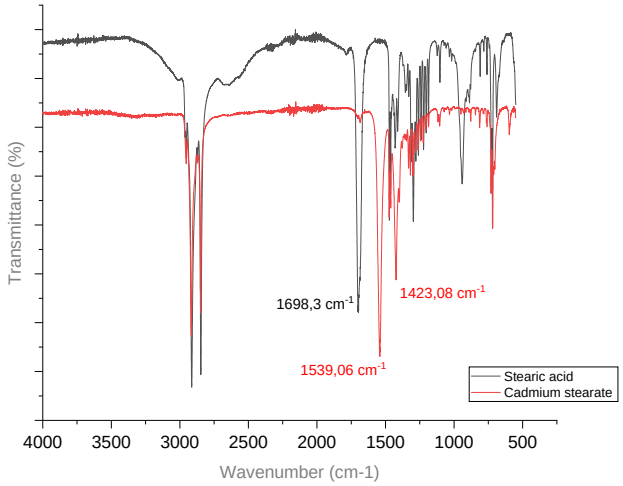

Figure 8. FTIR spectrum of stearic acid vs cadmium stearate.

From this FTIR spectrum, the synthesis of cadmium stearate could be confirmed, since stearic acid features a carboxylic group (C=O), as shown by a band at 1698.3 cm^{-1}. In contrast, in the spectrum of cadmium stearate this signal disappears and two new bands corresponding to the carboxylate group (COO^-) appear, at 1539.06 cm^{-1} (asymmetric stretching) and 1423.06 cm^{-1} (symmetric stretching), appear. This change from carboxylic to carboxylate group confirms the ligand coordination to cadmium, and therefore the successful formation of the precursor.

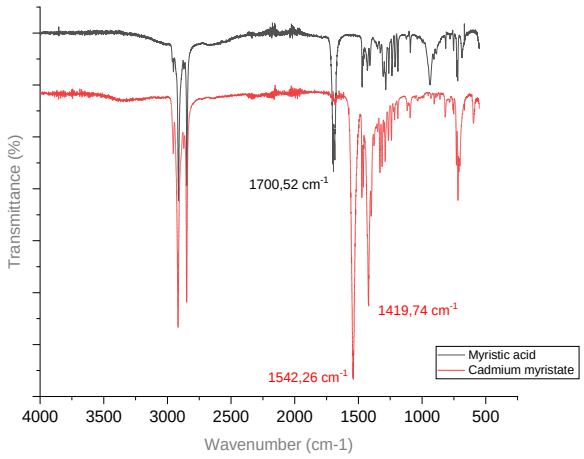

Figure 9. FTIR spectrum of myristic acid vs cadmium myristate.

In this spectrum the same change is observed as in the case of cadmium stearate, showing how the band of carboxylic group (1700.52 cm^{-1}) disappears and a two bands of carboxylate group (1542.26 cm^{-1} and 1419.74 cm^{-1}) forms. This confirms the formation of the cadmium myristate precursor.

The slight differences in peak positions between cadmium stearate and cadmium myristate can be attributed to the different lengths of the hydrocarbon chains. In the case of the sterate, which has a longer chain, the van der Waals interactions are stronger, slightly affecting the vibrations of the carboxylate group. Consequently, the shifted peaks appear at lower wavenumbers. In contrast, in cadmium myristate this behaviour is less pronounced because it has a shorter chain lenght. [17]

6.1.2 Optical characterization: UV–Vis absorption and photoluminescence

The optical properties of the synthesised CdSe nanocrystals were studied by UV–Vis absorption and photoluminescence (PL) spectroscopy. Figure 10 shows a representative spectrum (sample 5SA) of the results obtained for the different samples. CdSe nanocrystals were synthesized using both myristic acid (MA) and stearic acid (SA) and the values discussed below correspond to this representative sample.

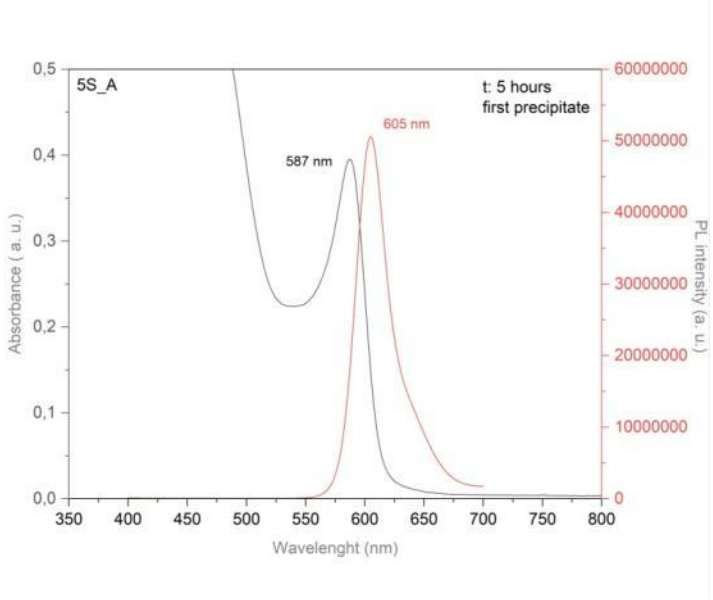

Figure 10. Representative UV–Vis absorption and photoluminescence spectra of CdSe nanocrystals synthesized using myristic acid (MA) (sample 5SA), selected from multiple samples.

The UV-Vis absorption spectrum shows a band with a maximum at 587 nm (2.11 eV), corresponding to the first excitonic transition of the CdSe nanocrystals. As shown in Figure 10, the position of this maximum is blue-shifted compared to bulk CdSe (1.71 eV; 713 nm), which confirms the presence of quantum confinement in the synthesized nanocrystals. From this result, it has been confirmed that the decrease in nanoparticle size causes a reduction in the value of λmax, which implies an increase in the effective band gap. Therefore, the position of the first excitonic peak represents a direct indicator of nanocrystal size.

Furthermore, from the value of λmax the average size of the synthesised CdSe nanocrystals was estimated. This estimate was based on relationships described in the literature by W. William Yu et al.[18] In this case, the absorption maximum at 587 nm corresponds to a diameter of 4.0607 nm, consistent with the quantum confinement regime. This result is consistent with the expected size-dependent optical properties of CdSe nanocrystals.

With regard to photoluminescence, an emission peak is observed at 605 nm. This peak appears at higher wavelengths compared with the absorption maximum (587 nm), indicating a redshift characteristic of semiconductor quantum dots associated with exciton relaxation processes.

This shift between absorption and emission, known as the Stokes shift, is associated with the energy relaxation processes that occur after light absorption and before exciton radiative recombination, resulting in emission at slightly longer wavelengths. In this case, the observed Stokes shift is 18 nm, corresponding to the difference between the absorption maximum (587 nm) and the emission maximum (605 nm). The relatively small Stokes shift suggests a narrow size distribution and good crystallinity of the nanocrystals.[7] Additionally, surface defects may influence the photoluminescence by creating trap states that promote non-radiative relaxation processes, thereby affecting both the intensity and spectral position of the emission.

The samples synthesized using myristic acid (MA) and stearic acid (SA) exhibit noticeable variations between them in both UV-Vis absorption and PL spectra within each set of samples (see Appendix 1). The absorption and emission maxima differ from sample

to sample, reflecting variations in nanocrystal size and size distribution. Some samples exhibit well-defined and intense optical features, whereas others show broader and less resolved peaks, indicating differences in the quality of the synthesized nanocrystals.

The UV-Vis absorption and PL spectra of the different samples obtained using the same Cd precursor (ie., either Cd-MA or Cd-SA), including their replicates and at various reaction times during the synthesis process (Appendix 1), exhibit similar optical characteristics and at the expected positions (approximately 600 nm). Furthermore, no significant differences are observed in the position of the absorbance and emission between the different samples and their replicates, synthesised under the same conditions and different reaction times. This behaviour indicates that the nanocrystal size remains practically invariant under the conditions studied and confirms the good reproducibility of the synthesis.

However, the samples synthesised for 15 h exhibited a dark appearance and a strong tendency to aggregate after the solvothermal treatment. Due to this aggregation, stable dispersions could not be obtained and reliable UV-Vis and PL measurements could not be performed. Therefore, these samples were excluded from further characterisation (see Figure 11).

Figure 11. CdSe nanocrystals synthesised by the solvothermal method for 15 hours, showing significant aggregation.

To evaluate the effectiveness of the purification procedure, a detailed study was carried out for the sample 2S obtained through the solvothermal method using the Cd-SA precursor and 5 hours of reaction time (see Figure 12). The different replicates obtained after each purification step were analysed by UV-Vis absorption and PL spectroscopy.

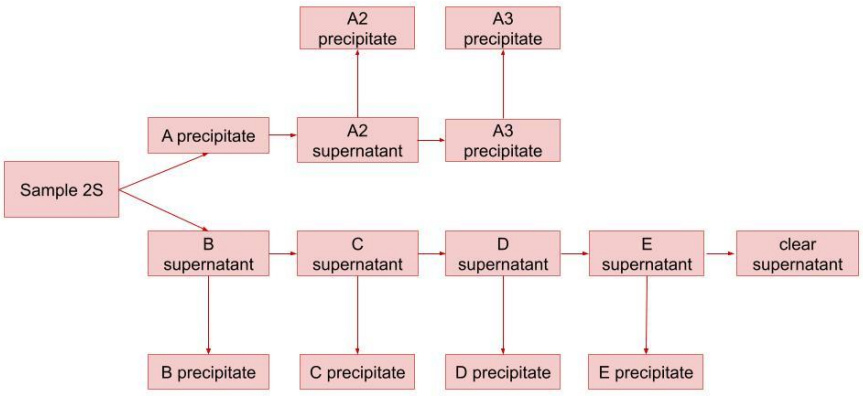

Figure 12. Schematic representation of the purification procedure applied to solvothermal sample 2S. Successive precipitation–redispersion and centrifugation cycles were performed, generating precipitate and supernatant fractions (B–E) until a clear colourless supernatant was obtained.

Moreover, the fact that the spectra are similar after the purification process (Appendix 1, Figure 20 to 25), based on successive centrifugation steps and the use of an antisolvent to precipitate (see subsection 5.2.3), indicates that the different precipitates analysed are, in fact, composed by the same nanocrystals (both in terms of size and composition). As these nanocrystals are very small, it is likely that by using faster centrifugation speed and other antisolvents, the whole mass of nanocrystals could be obtained in a single centrifugation (i.e., purification) step.

The only observed exception is the sample 4S_D, in which a second band appears at the PL spectra (see Appendix 1, Figure 29) which may be associated with a measurement error or the presence of a secondary population of nanocrystals, although additional analyses, such as TEM, would be required to confirm its origin.

Finally, given that the optical properties are not affected between reaction times of 5 and 6 hours, it is considered preferable a synthesis time of 5 hours as it appears to be sufficient to obtain CdSe nanocrystals with comparable characteristics. This would reduce both processing time and energy consumption. Nevertheless, it would be necessary to optimise the abovementioned purification procedure up to a single step in order to improve the precipitation and recovery of the CdSe nanocrystals and thus, being feasible to assess the reaction yield.

6.2 STRUCTURAL CHARACTERIZATION: XRD AND HRTEM ANALYSIS

6.2.1. HRTEM Characterization of CdSe Nanocrystals

The morphologies of the CdSe synthesized nanoparticles were characterized by high resolution transmission electron microscopy (HRTEM). Representative images of samples synthesized using both Cd-SA and Cd-MA precursors are shown in Figures 13 and 14, respectively.

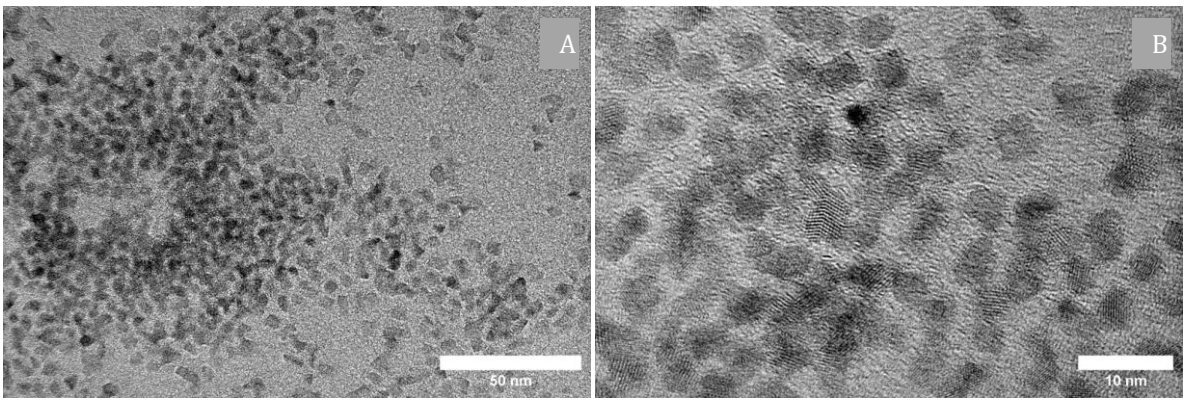

Figure 13. HRTEM images of CdSe nanocrystals synthesized Cd-SA precursor.

The Figure 13 contains two different TEM images of the CdSe nanocrystals synthesized via the solvothermal method using Cd-SA precursor and reaction time of 5 hours. In image A, a relatively uniform distribution of particle size and quasi-spherical morphology is observed. In image B crystal plans are clearly observed. The average size was determinate through statistical analysis by measuring approximately 200 nanoparticles from de HRTEM images, resulting in an average size of 3.291 nm. This value is consistent with the expected size based on the results reported in the literature.[15] The HRTEM studies confirm that the CdSe QDs have nearly monodisperse size distributions and well-defined crystalline structure.

The structural information obtained by HRTEM is consistent with the UV-Vis and PL spectra, figure 10 where the average size of the nanocrystals (3.291 nm) is within the quantum confinement regime for CdSe quantum dots and agrees with the optical properties observed. We can also confirm that the relatively narrow emission band indicates a reasonably homogeneous size distribution, in accordance with the uniform morphology observed in the HRTEM images in Figure 13.

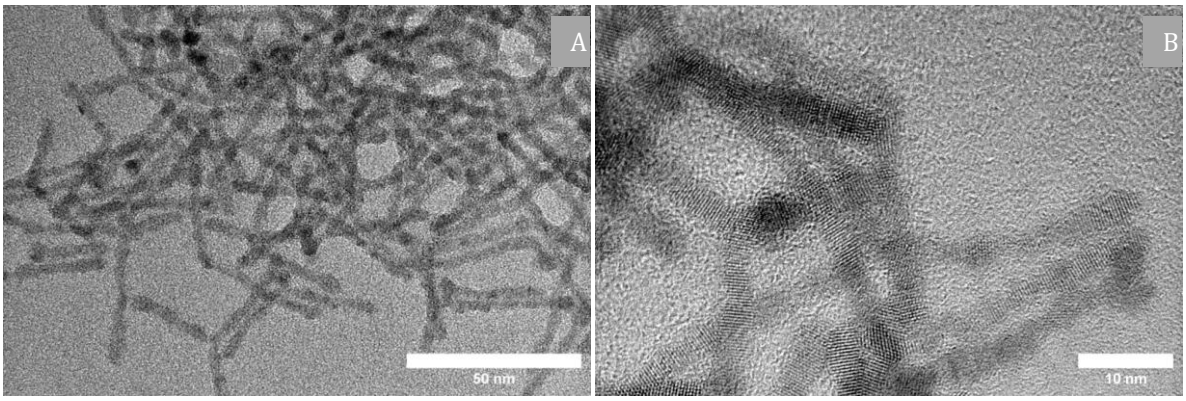

Figure 14. HRTEM image of CdSe nanocrystals synthesized using Cd-MA precursor.

Figure 14 shows HRTEM images of the CdSe nanocrystals synthesised using Cd-MA precursor and reaction time of 5 hours. In image A, nanoparticles with a predominantly elongated morphology s are observed. In Image B the crystal planes can be clearly distinguished, confirming the crystalline nature of the nanocrystals.

These results differ from those initially expected, as previous works reported in the literature describe CdSe nanocrystals with a spherical morphology.[2,14] In contrast, this sample exhibits a morphology tending nanorods.

Also, it should be noted that the experimental procedure was followed as described in the literature[2, 14], except for the use of a larger capacity autoclave. In our procedure we used an autoclave of 50 mL while in the literature they use 30 mL autoclaves. It is possible that this change of scale may have affected certain reaction conditions, such as the pressure inside the autoclave, and this may have influenced the growth process of the nanocrystals. However, this hypothesis would require more detailed investigation to be confirmed.

Furthermore, this observation corresponds to only one of the replicated samples synthesised. Therefore, additional HRTEM analysis would be necessary on the other available replica to determine whether this morphology is characteristic of the solvothermal synthesis with Cd-MA precursor or is simply a variation specific to one sample.

6.2.2. XRD characterization of of CdSe Nanocrystals

The crystal structure and phase composition of the synthesized CdSe nanocrystals were investigated by X-ray diffraction (XRD).

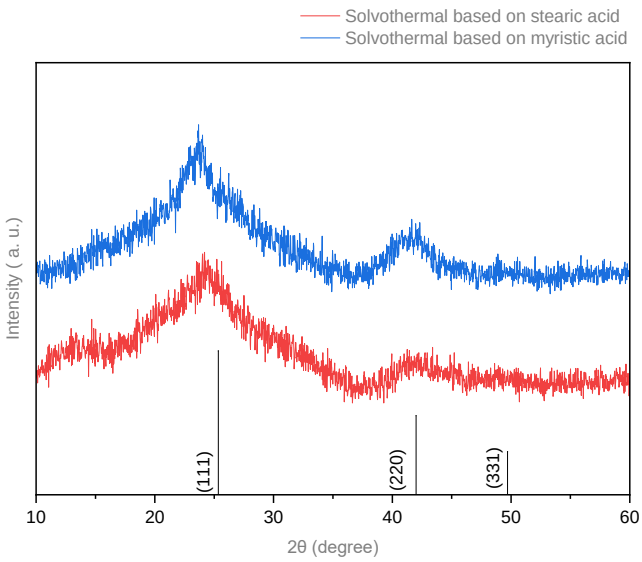

Figure 15. XRD patterns of CdSe nanocrystals synthesized using MA and SA acids and compared with the reference patterns of cubic CdSe (JCPDS No. 77-2307).

Figure 15 displays the XRD patterns of the CdSe nanocrystals synthesized via the solvothermal method using SA and MA acids. It can be observed the both samples have the same diffraction peak centred at 25°, corresponding to the (111) plane of cubic CdSe. Also, two different peaks can be observed at 43° grades and 49° corresponding to the (220) and (311) reflections, respectively. These diffraction peaks can be assigned to the zinc blende (ZB) phase of CdSe (JCPDS No. 77-2307). The low intensity of these peaks, particularly the (311) reflection, which appears less well-defined, may be attributed to peak broadening. This broadening is characteristic of nanocrystalline materials and indicates that the nanocrystals are within the quantum confinement regime.

7. COMPARISON BETWEEN SOLVOTHERMAL AND COLLOIDAL SYNTHESIS

A characterisation of a representative sample obtained through the colloidal synthesis was carried out in order to compare it with the samples attained by the solvothermal synthesis.

For this sample, a UV–Vis and photoluminescence were measured. As shown in Figure 16, this spectrum is used to compare it with that obtained from the samples synthesized by the solvothermal method (Figure 8).

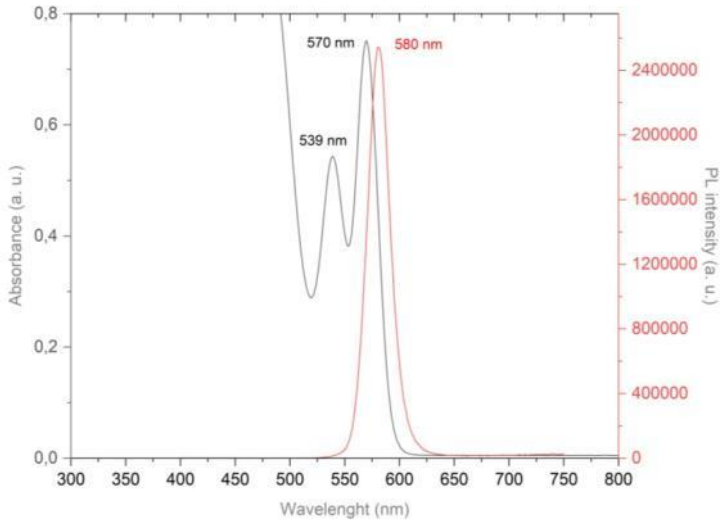

Figure 16. Representative UV–Vis absorption and photoluminescence spectra of CdSe nanocrystals synthesized using colloidal method, selected among the samples synthesized.

As shown in Figure 16, in the UV-Vis absorbance spectrum we observe band around 570 nm which corresponds to the first excitonic transition of the CdSe nanocrystals. We can also see a second band at 539 nm that can be attributed to higher-energy excitonic electronic transitions, commonly observed in CdSe nanocrystals with a narrower size distribution and therefore a high degree of monodispersity. [19]

In contrast, for the solvothermal-synthesised nanoparticles, only a single, broader absorption band is observed (Figure 8), which suggests a wider size distribution, and consequently, a lower degree of monodispersity. As a result, the second excitonic transition observed in the colloidal samples is likely obscured in the UV-Vis spectra of the solvothermal samples.

Apart from that, in the photoluminescence spectrum of the CdSe QDs is a narrow and well-defined emission band centred at 580 nm. This narrow band indicates a narrow size distribution and, therefore, a higher degree of monodispersity in the sample. In contrast, in the sample synthesised via solvothermal (see Figure 8), we observe a broader emission band, which suggests a lower degree of monodispersity, in agreement to the aforementioned UV-Vis data. Although these differences, the optical properties

obtained are quite enough similar to the ones attained by the colloidal synthesis, thus rendering these results as very promising for future optical optimization.

The average size of the CdSe quantum dots has been estimated from the value of λmax using the relationship described in the literature (see section 6.1.2). In this case, the absorption band located at 548 nm corresponds to a diameter of approximately 3.00 nm, consistent with the quantum confinement phenomenon and very similar to the size estimated for the CdSe quantum dots obtained via solvothermal synthesis. Additional UV-Vis absorption spectra corresponding to other colloidal synthesis CdSe samples are provided in Appendix 1.

Finally, structural and morphological characterization was carried out using two techniques: high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD), as shown in Figures 14 and 15, respectively.

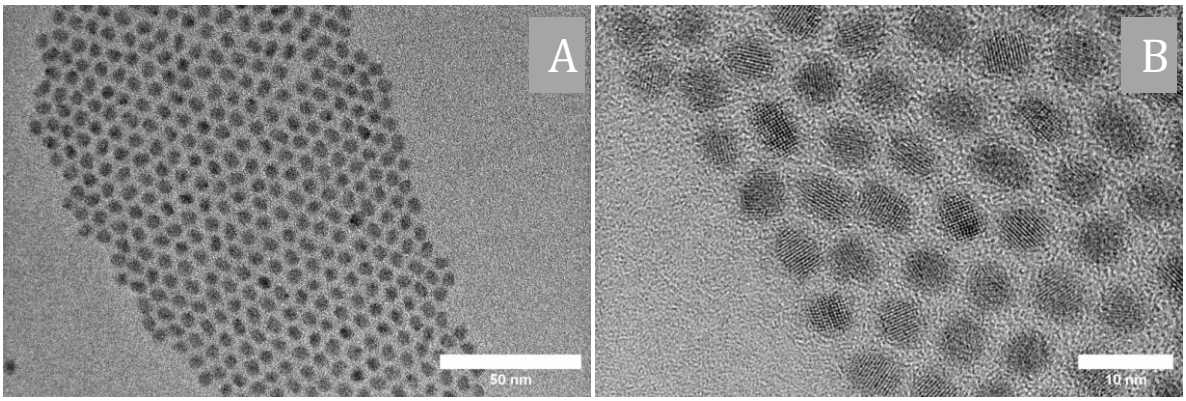

Figure 17. HRTEM image of CdSe nanocrystals synthesized using colloidal method.

In Figure 17, we can observe two different HRTEM images of CdSe nanocrystals obtained via colloidal synthesis: in image A a uniform distribution of particle sizes and a dot-shaped morphology is observed, and in image B crystal planes are seen.

The comparison between the CdSe nanocrystals obtained by colloidal and solvothermal synthesis shows relatively small differences. The colloidal sample exhibits slightly highly ordered arrays of NPs, a more homogeneous size distribution and NPs with a more spherical morphology, whereas the solvothermal sample shows some aggregation in the HRTEM image A and a slightly less well-defined morphology. However, the observed differences are small and both routes allow for the production of CdSe nanocrystals with comparable morphology and crystallinity.

To complete the monodispersity analysis of the nanoparticles, it would be interesting to supplement these results with Dynamic Light Scattering (DLS) measurements, which would provide additional information on the hydrodynamic size and size distribution of the dispersed nanoparticles in solution.

Additionally, X-ray diffraction (XRD) analysis was performed to investigate the crystal structure of the CdSe quantum dots obtained via the colloidal synthesis.

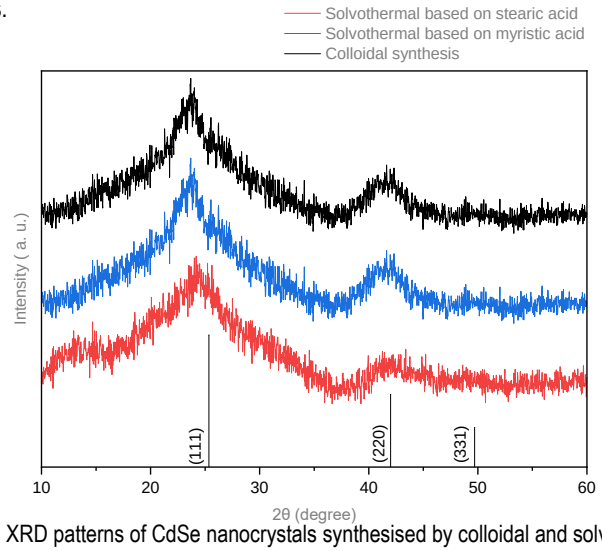

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Figure 18. Comparison of the XRD patterns of CdSe nanocrystals synthesised by colloidal and solvothermal methods, together with the reference patterns of cubic CdSe (JCPDS No. 77-2307)

In Figure 18, shows a comparison between the XRD patterns of quantum dots synthesised via colloidal and solvothermal methods using stearic and myristic acids.

As observed, both syntheses yield the same zinc blende (ZB) crystal structure, with peaks corresponding to the reflections: (111), (220) and (311). As can be seen, the diffraction peaks are broad and relatively low intense, especially for the (311) reflection, as well as poorly defined, characteristics of nanocrystalline materials indicating that the nanocrystals are within the quantum confinement regime.

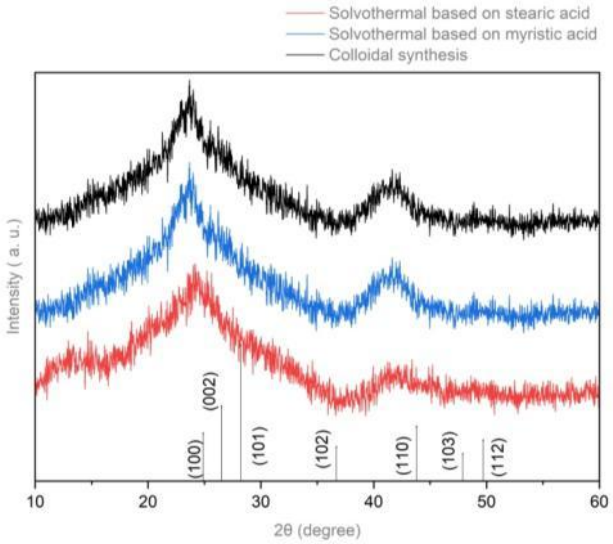

Figure 19. Comparison of the XRD patterns of CdSe nanocrystals synthesised by colloidal and solvothermal methods, together with the reference patterns of hexagonal CdSe wurtzite (JCPDS No. 08-0459).

To confirm the crystalline phase of the samples, the experimental diffractograms were compared with the reference patterns for hexagonal wurtzite-type CdSe (WT) as you can see in Figure 19 (JCPDS 08-0459) . The main observed diffraction peaks are more consistent with the characteristic reflections of the cubic phase, assigned to the (111), (220) and (311). In contrast, the additional reflections characteristic of the wurtzite phase, such as those associated with the (100), (002) and (101) planes, are not clearly observed. For this reason, the predominant presence of wurtzite CdSe can be ruled out. .

8. CONCLUSIONS

In conclusion, CdSe quantum dots have been synthesised using two routes studied: colloidal hot-injection synthesis and solvothermal synthesis, for the last one using both cadmium stearate and cadmium myristate coordination compounds as cadmium precursors. The main objective has been to evaluate the potential of solvothermal synthesis as an alternative to colloidal synthesis for the production of CdSe semiconductor nanocrystals.

FTIR characterisation has confirmed the correct formation of the cadmium precursors, both cadmium stearate and cadmium myristate, by the presence of the carboxylate group (COO-).

For the samples obtained through the solvothermal synthesis, the optical characterisation by UV-Vis and photoluminescence spectroscopy confirmed the formation of CdSe quantum dots within the quantum confinement regime. The absorption and emission peaks are within the expected values for this type of nanocrystal and have allowed the estimation of the average size of these quantum dots to be between 3 and 4 nm. This highlights the dependence of the optical properties on nanocrystal size, a typical characteristic of semiconductor nanocrystal. Furthermore, it has been observed that the optical properties of the CdSe nanocrystals are very similar from one synthesis to another (between replicas and between samples obtained at different reaction times), indicating that the resulting nanomaterials are comparable from an optical standpoint.

Structural characterisation by HRTEM confirmed that colloidal and solvothermal syntheses using stearic acid have produced monodisperse quantum dots with a narrow size distribution. Furthermore, X-ray diffraction patterns have confirmed the formation of CdSe with a zinc-blende cubic structure in all samples analysed.

The comparison between the two synthesis routes shows that colloidal synthesis produces slightly more homogeneous nanocrystals, with narrower absorption and emission bands and a somewhat more uniform morphology. However, the observed differences with respect to the solvothermal samples are very small, and both methods allow the production of CdSe nanocrystals with comparable structural and optical characteristics.

In practical terms, solvothermal synthesis offers greater reproducibility, since different replicates synthesised under the same conditions at various reaction times exhibit very similar optical properties. It has also been observed that increasing the reaction time in solvothermal synthesis does not lead to significant changes in optical properties; therefore, a reaction time of five hours is considered sufficient to obtain nanocrystals with properties comparable to those of samples synthesised over longer periods. Furthermore, this synthesis method requires less stringent experimental conditions, with no need to reach such high temperatures or perform hot injections, making it a potentially simpler and safer alternative. Furthermore, this synthesis allows multiple syntheses to be carried out simultaneously using multiple autoclaves, thus making it a more easily scalable method than colloidal synthesis.

Moreover, the emission wavelengths obtained fall within the spectral region of interest for the research activities currently being developed by the QComms group.

Overall, the results of this work demonstrate that solvothermal synthesis is a promising alternative to conventional colloidal synthesis for the preparation of CdSe quantum dots, as it allows the production of nanocrystals with comparable structural and optical properties, maintaining good reproducibility and offering potential advantages in terms of experimental simplicity, safety and scalability.

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10. ACRONYMS

CdSe: Cadmium Selenide

CdS: Cadmium Sulphide

CdTe: Cadmium Telluride

QDs: quantum dots

UV-Vis: Ultraviolet-Visible

PL: Photoluminescence

FTIR: Fourier Transform Infrared Spectroscopy

XRD: X-ray Diffraction

HRTEM: High-Resolution Transmission Electron Microscopy

SPS: Single-Photon Source

ICCUB: Institut de Ciències del Cosmos de la Univeritat de Barcelona

Qcomms: Quantum communications research group

JCPDS: Joint Committee on Powder Diffraction Standards

LED: Light-Emitting Diode

TOP: Tri-n-octylphosphine

TOPO: Trioctylphosphine Oxide

ODPA: Octadecylphosphonic Acid

OA: Oleic Acid

SA: Stearic acid

MA: Myrisctic Acid

CdO: Cadmium Oxide

Se: Selenium

COO^- : Carboxylate group

C=O: Carboxylic group

GB: Glovebox

DLS: Dynamic Light Scattering

ZB: Zinc Blende

WZ: Wurtzite

eV: Electronvolts

nm: Nanometers

a.u.: Arbitrary units

ºC: Degrees Celsius

º: Defrees

cm^{-1}: Inverse centimeter

mg: Miligrams

g: Grams

µL: Microliters

mL: Mililiters

mmols: Milimols

rpm: Revolutions per Minute

APPENDICES

APPENDIX 1: UV–VIS ABSORPTION AND PHOTOLUMINESCENCE SPECTRA OF CDSE NANOCRYSTALS

Solvothermal method:

Samples using stearic acid (SA)

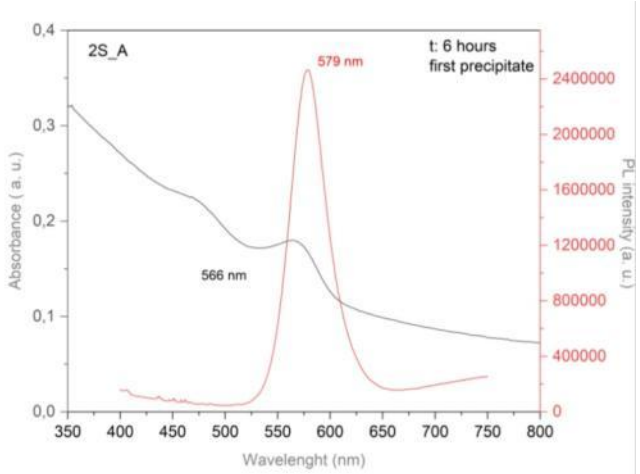

Figure 20. UV–Vis and PL spectra of sample 2S_A obtained from the Cd-SA precursor.

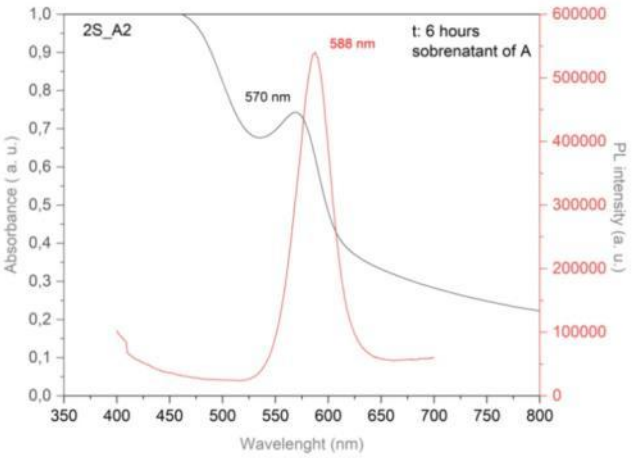

Figure 21. UV–Vis and PL spectra of sample 2S_A2 obtained from the Cd-SA precursor.

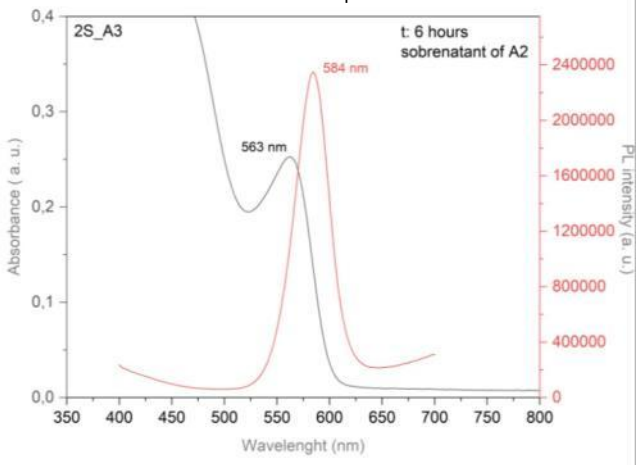

Figure 22. UV–Vis and PL spectra of sample 2S_A3 obtained from the Cd-SA precursor.

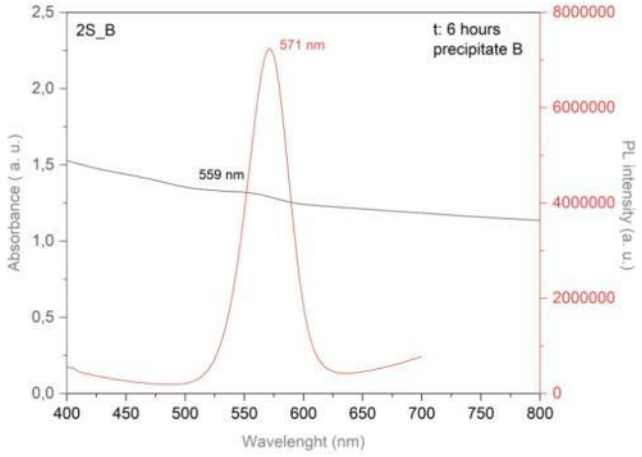

Figure 23. UV–Vis and PL spectra of sample 2S_B obtained from the Cd-SA precursor.

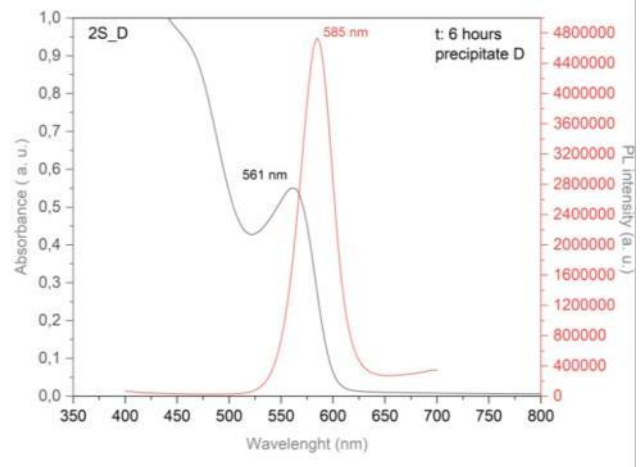

Figure 24. UV–Vis and PL spectra of sample 2S_D obtained from the Cd-SA precursor.

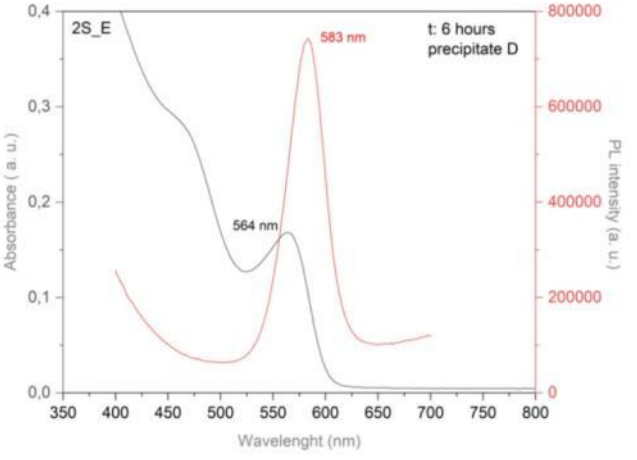

Figure 25. UV–Vis and PL spectra of sample 2S_E obtained from the Cd-SA precursor.

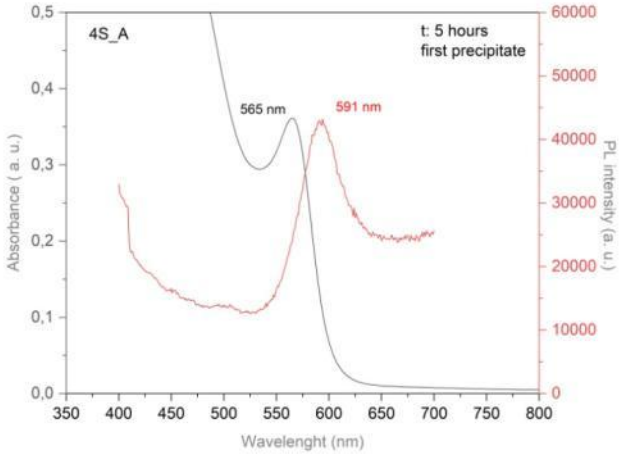

Figure 26. UV–Vis and PL spectra of sample 4S_A obtained from the Cd-SA precursor.

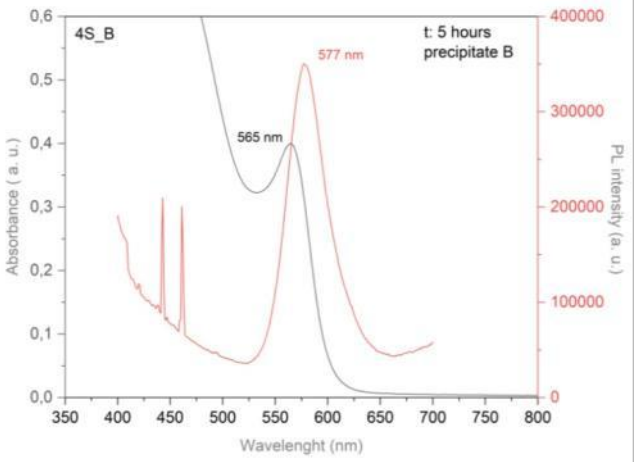

Figure 27. UV–Vis and PL spectra of sample 4S_B obtained from the Cd-SA precursor.

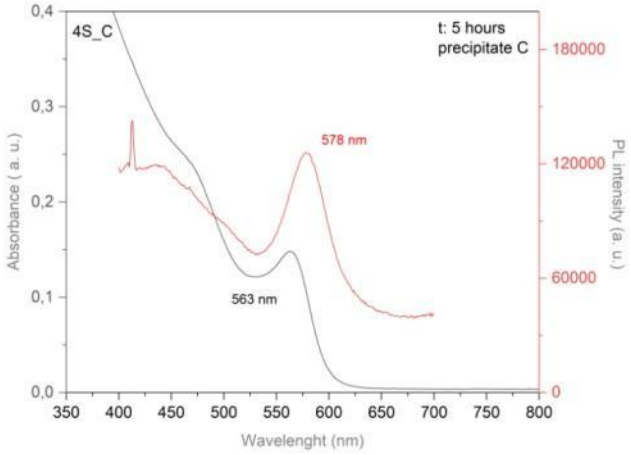

Figure 28. UV–Vis and PL spectra of sample 4S_C obtained from the Cd-SA precursor.

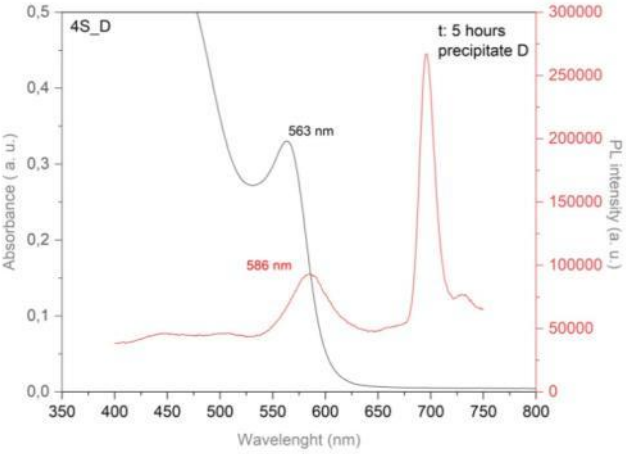

Figure 29. UV–Vis and PL spectra of sample 4S_D obtained from the Cd-SA precursor.

Samples using myristic acid (MA):

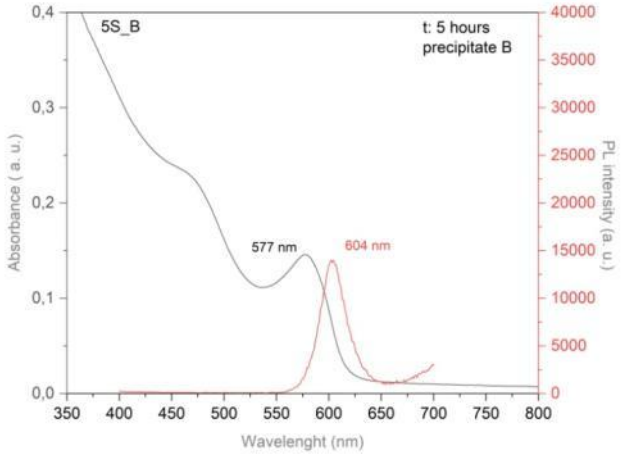

Figure 30. UV–Vis and PL spectra of sample 5S_B obtained from the Cd-MA precursor.

Colloidal method:

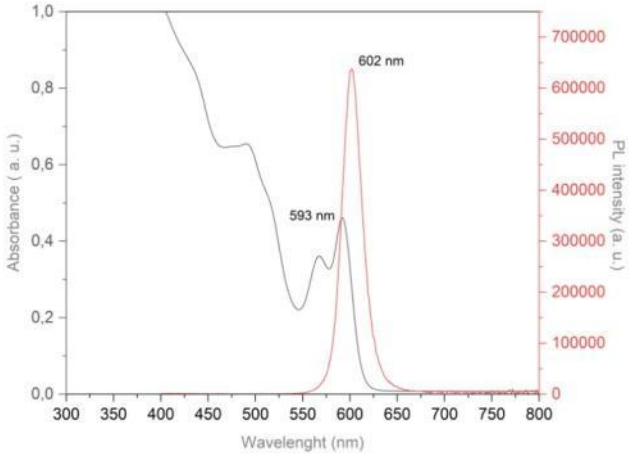

Figure 31. UV–Vis and PL spectra of sample SC_11A obtained from colloidal synthesi.

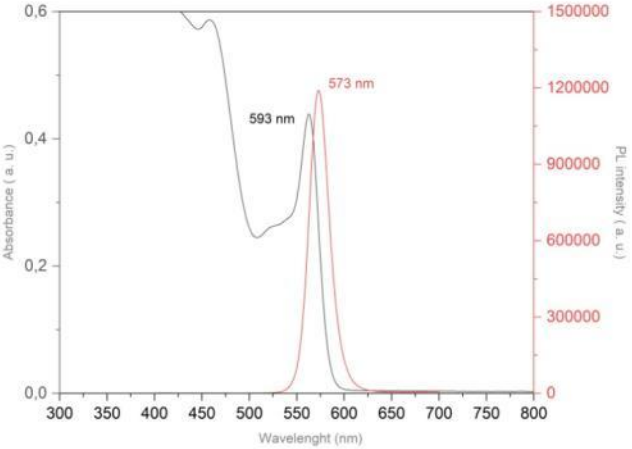

Figure 33. UV–Vis and PL spectra of sample SC_4C obtained from colloidal synthesi.

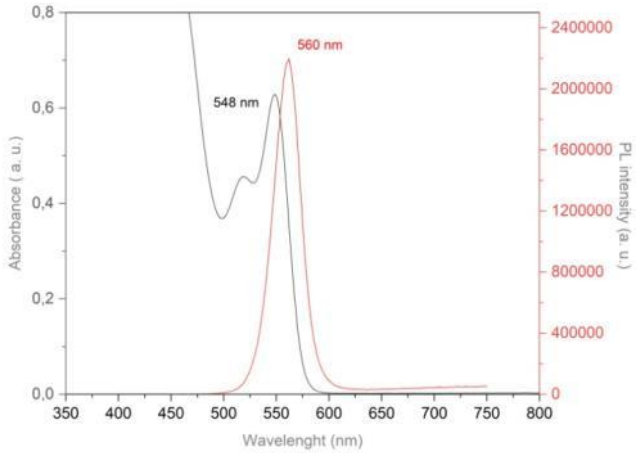

Figure 33. UV–Vis and PL spectra of sample SC_10B obtained from colloidal synthesi.

APPENDIX 2: EXPERIMENTAL PROTOCOL FOR THE COLLOIDAL SYNTHESIS OF CDSE QUANTUM DOTS BY THE HOT-INJECTION METHOD

1. Preparation of precursors in the GloveBox

Three 5 mL borosilicate vials, two septum screw caps and one standard screw cap were introduced into the glovebox antechamber. Prior to entering the glovebox, three vacuum–nitrogen cycles were performed in the antechamber.

Inside the glovebox, prepare the three vials as follows:

1. Vial with 60 mg of CdO sealed with a standard screw cap.
2. Vial with 1.5 g of TOP sealed with a septum screw cap.
3. Vial with 58 mg of Se and 360mg of TOP, sealed with a septum screw cap.
   Note: This vial must be prepared last, as prolonged storage of selenium and TOP before mixing may hinder the formation of a homogeneous precursor solution.

The Se-TOP mixture was manually agitated until homogeneous suspension was obtained. When necessary, mild heating with a heat gun was applied to facilitate selenium dissolution.

After preparation, the precursor vials were removed from the glovebox through the antechamber using three additional vacuum–nitrogen cycles and transferred directly to the laboratory for the synthesis step.

2. Vacuum part in the laboratory

A 25 mL three-neck round-bottom flask equipped with a high-temperature magnetic stir bar was charged, in the following order, with:

- 290 mg of ODPA
- 3 g of TOPO
- 60 mg of CdO (from the glovebox)

The two side necks of the flask were sealed with silicone septa, after which the flask was connected to a Schlenk line (see Figure 34) and subjected to a degassing procedure under vacuum. A thin layer of vacuum grease was applied to the ground-glass joint of the Liebig condenser before connecting it to the central neck of the flask.

The reaction mixture was heated to 150 ºC using a heating mantle and magnetic stirring was initiated once the TOPO/ODPA mixture began to melt. At this stage, the reaction mixture exhibited a characteristic brown colour due to the presence of CdO. A cryogenic trap was placed between the reaction setup and the vacuum pump to prevent contamination of the pump by volatile species.

Once the reaction mixture was completely melted and the temperature had stabilised at 150 °C, the flask was gradually connected to the vacuum line and maintained under vacuum at 150 °C for 2 h. During this process, bubbling was observed as dissolved oxygen and moisture were removed from the system.

3. Nitrogen part in the laboratory

After the 2-hour degassing period, the system must be gradually transitioned to an inert atmosphere of nitrogen.

Once a stable nitrogen flow had been established, the reaction temperature was increased to 350 °C. During heating, the initially brown solution gradually became more transparent as the CdO dissolved, although a slight colouration remained visible.

When the temperature had stabilised at 350 °C and the solution was transparent, the first injection of 1.5g TOP was performed into the reaction flask. Following this addition, the solution became completely transparent.

The digital thermometer probe was then removed and cleaned with toluene. After cooling to approximately 70 °C, the probe was reinserted into the reaction flask through one of the silicone septa using a thick needle. Care was taken to ensure that the magnetic stir bar rotated freely without contacting the probe.

The reaction temperature was subsequently increased to 390°C, and once it had stabilised, the Se-TOP precursor was rapidly injected into the reaction mixture. Immediately after injection, the reaction was allowed for approximately 40 seconds and was saw a solution turned dark brown.

To stop the reaction the heating mantle was removed and the reaction flask was lifted away from the heat source while maintaining continuous magnetic stirring during cooling.

Figure 34. Schlenk line setup used for the colloidal synthesis of CdSe quantum dots under controlled vacuum and nitrogen atmosphere.

4. Purification of CdSe quantum dots

After completion of the reaction, the crude CdSe nanocrystal dispersion was allowed to cool to room temperature. A small amount of toluene was first added, followed by the addition of methanol to precipitate the nanocrystals.

The resulting precipitate was collected and purified through repeated washing cycles consisting of redispersion in toluene followed by precipitation with methanol. After each precipitation step, the samples were centrifuged at 4000 rpm for 5 minutes and the supernatant was inspected. If the supernatant appeared with colour additional precipitation and centrifugation cycles were performed. But when the supernatant was colourless, it was discarded.

This purification procedure was repeated several times until clean nanocrystal dispersion was obtained. Finally, the purified CdSe quantum dots were redispersed in toluene for subsequent optical and structural characterisatio (see Figue 35).

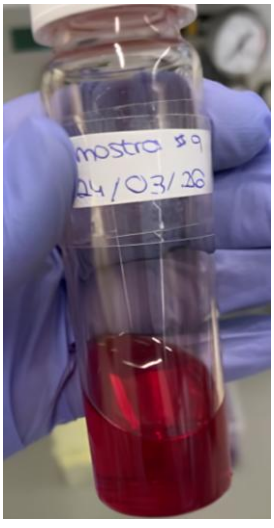

Figure 35. Purified CdSe quantum dot dispersion obtained by the colloidal hot-injection synthesis after redispersion in toluene.