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Influence of structural properties of oleic acid-capped CdSe/ZnS quantum dots in the detection of Hg²⁺ ions

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Abstract

Oleic acid-capped CdSe/ZnS quantum dots (QDs) were used to investigate their photoluminescence (PL) response to Hg^{2+} ions as a function of the surface properties of QDs. Three distinctly-size CdSe/ZnS QDs were obtained by varying the molar ratio of shell precursors, which were characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HR-TEM), Fourier-Transform infrared (FT-IR), X-ray photoelectron spectroscopy (XPS), absorption spectroscopy, and time-resolved fluorescence spectroscopy. Results revealed the obtention of zinc blende nanocrystals with sizes ranging from 2.7 to 3.2 nm (± 0.5) and ZnS thickness between 0.3 and 1.0 monolayer (ML). The variation of the [S]/[Zn] molar ratio introduced chemical species that act as traps, affecting the PL properties differently. Depending on the thickness of the shell and chemical speciation on surface, Hg^{2+} ions could induce quenching or enhancement of PL. Detection of mercury ions was evaluated in terms of Stern-Volmer equation, where the limit of detection (LOD) for the PL quenching system was 11.2 nM, while for the PL enhancing systems were 8.98 nM and 10.7 nM. Results demonstrate the performance of oleic acid-capped CdSe/ZnS QDs to detect Hg^{2+} and their capacity to turn the PL on/off depending on surface properties.

1. Introduction

Quantum dots (QDs) of semiconductors are nanocrystals with particle sizes between 1 and 10 nm, which have found applications in different fields, such as sensors, lasers, photovoltaics, and light-emitting diodes [1]. II-VI semiconductors like CdSe are mainly characterized by a broad absorption spectrum and a narrow and intense emission that could be multicolor since it depends on their size due to the quantum confinement effect [2]. These characteristics are very appreciated for metal ion sensing applications [3, 4].

Indeed, for QD-based metal ion detection, CdSe QDs have been modified with different ligands to avoid aggregation, enhance stability, and improve their selectivity and sensitivity [5]. With this goal, the CdSe QDs surface has been modified with hydrophilic ligands, resulting in a fluorescence signal intensity that could be quenched or enhanced as a response to metal ions [5, 6]. For instance, quenching of fluorescence has been reported with L-cysteine-capped CdSe QDs to detect Pb^{2+} ions [7], mercapto acetic acid-capped CdSe QDs have been applied in the detection of Ag^+ ions [8], and mercaptoethanesulfonate-capped CdSe QDs for Cu^{2+} determination [9]. Equally, enhancement of PL has been reported with L-cysteine-capped CdSe to detect Zn^{2+} ions [9] and L-carnitine-capped CdSe/ZnS QDs to detect Hg^{2+} [10]. Other QDs types have also been reported considering the enhancement of PL intensity induced by cations. For example, mercaptopropionic acid-capped CdTe QDs in the presence of Cd^{2+} [11], mercaptoethanol-capped PbS QDs in the presence of mercapto acetic acid-capped InP QDs in the presence of Hg^{2+} ions [12] and L-cysteine capped CdS QDs in the presence of Ag^+ ions [13].

Mercury ions, the most potent neurotoxin in human physiology, are selected as analyte in this investigation due to the severe environmental and public health problems in counties that use mercury in gold extraction mining. Many fluorescent-based optical sensors [14] have been applied to detect Hg^{2+} ions in real time with high sensitivity, selectivity, and signal-to-noise ratio [15].

For QDs-based mercury ion sensors, the interaction between analyte and nanocrystals leads to many pathways that affect photoluminescence intensity.

According to the affinity of metal ions and QDs, cation exchange could be produced by replacing cations of starting QDs with cations of the analyte, preserving the original anion sublattice [16]. This cation exchange reaction forms small particles on the QDs surface, causing non-radiative recombination of excited electrons and holes that finally quenches fluorescence [17].

Conversely, the strategies reported by literature that led to increased fluorescence for determining cation ions are less frequent. Surface state passivation of QDs removes the traps that facilitate non-radiative recombination pathways [18]. Understanding the role of trap states is challenging. In its simplest form, a trap can be described as a stable nonbonding orbital of an undercoordinated atom. This orbital usually lies deep in the bandgap, where it can act as an electron or hole trap. Metal ions on QDs surface can produce non-coordinative atoms and dimers [19], indirectly affecting the number of dangling bonds and the presence of traps [20].

In this context, the growth of a shell of semiconducting material with a larger bandgap ($3.7 > 1.7$ eV) [2] than CdSe, such as ZnS, plays a determinant role since the shell passivates the traps and defects of core [21, 22], improving stability [1, 21], and photoluminescence [2, 23, 24]. This type of system is known as a type I core/shell system, characterized by the confinement of the exciton (an electron-hole pair) to the core. Type I structures are the most studied in analytical applications since this configuration provides the best confinement of the exciton (an electron-hole pair) and the highest rates of radiative electron-hole recombination (i.e., the brightness of the photoluminescence). <https://doi.org/10.1016/j.jlumin.2019.116627> However, excess shell (greater than 2.2 monolayers [25]) can cause the opposite effect in the PL because the lattice mismatch between CdSe and ZnS is 12%, which generates a strain at the interface [26] that creates non-radiative recombination sites impairing the properties of PL [22, 27, 28].

Our group has previously studied Hg^{2+} detection by PL measurements using CdSe/ZnS QDs modified with two ligands of differing water affinity, such as L-glutathione and oleic acid [29]. Both QDs produced PL quenching. The affinity of Hg^{2+} ions with QDs surface could generate the displacement of Cd^{2+} ions of CdSe

(or Zn^{2+} of ZnS), forming HgSe (or HgS) particles that lead to fluorescence quenching. The chemical displacement of surface Cd^{2+} (or Zn^{2+}) by Hg^{2+} is expected because of the low K_{sp} values of HgSe and HgS.

The cation exchange reactions could be a strategy for tunable optical properties of QDs. (<https://doi.org/10.1002/chin.200826224>) Wang et al. (<https://doi.org/10.1007/s00604-021-04871-5>) reported the fluorescence enhancement using CdSe/ZnS QDs to detect Hg^{2+} . The $\text{Zn}^{2+}/\text{Hg}^{2+}$ cation exchange in the ZnS shell increases the separation of electrons and holes, reducing the recombination rate.

Since oleic acid-capped CdSe/ZnS could detect metal ions, we used these nanomaterials to induce PL quenching and enhancement. We used the variation of the molar ratio of shell precursors to obtain three nanocrystals with different shell thicknesses, forming traps that affected PL properties in different ways. We discuss the fluorescence response of QDs regarding the shell thickness, $[\text{S}]/[\text{Zn}]$ molar relation, surface properties, and PL decay dynamics. Surface properties are characterized by FT-IR, XPS, TEM, and HR-TEM measurements. Results show that an adequate molar ratio of shell precursor could passivate the trap sites of surface QDs. In addition, a thicker ZnS shell (0.7-1.0 ML ranging) protects the core from exchange cation reactions, avoiding the quenching of PL in the presence of Hg^{2+} ions. Thus, we demonstrate the shell dependence to turn PL on/off induced by mercury ions and other metal cations.

2. Experimental section

2.1 Materials.

Cadmium oxide powder (99.9%), trioctylphosphine (TOP, 99%), selenium powder (99.9%), hexamethyldisilathiane ((TMS)₂S, 99%), diethylzinc (Et₂Zn, 1.0 M/hexane), oleic acid (OA), and 1-octadecene (ODE, tech. 99%) were purchased from Sigma-Aldrich. Metal chloride (HgCl₂, MnCl₂, CoCl₂, NiCl₂, ZnCl₂, CdCl₂, PbCl₂), ethanol (99.5%), acetone (99.8%), methanol (99.5%), and acetonitrile (CH₃CN, 99%) were obtained from Panreac. All reagents were analytical grade and used without further purification. Ultrapure water (18 MΩ) was used to prepare aqueous solutions.

2.2 Synthesis of oleic acid-capped CdSe/ZnS QDs

The CdSe/ZnS QDs were prepared using the method previously reported [17]. Three CdSe/ZnS samples with different sizes were obtained by varying the amount of Et₂Zn as follows: 31 μL (0.031 mmol), 140 μL (0.14 mmol), and 280 μL (0.28 mmol),

while the amount of (TMS)₂S kept constant (0.28 mmol). The details of the synthesis process are in supporting information.

2.3 Characterization

2.3.1 HR-TEM analysis

The High-Resolution Transmission Electron Microscopy (HR-TEM) images of the QDs were taken using a Tecnai F20 Super Twin TMP Microscope, Field emission source, resolution of 0.1 nm at 200 kV, maximum magnification at TEM 1.0 MX, GATAN US 1000XP-P camera. EDX Oxford Instruments XMAX detector. STEM Analysis - FISCHIONE Instruments Model M3000 FP5360/22 HAADF Detector 120/200 kV. The samples were dispersed in chloroform using an ultrasonic bath. After, a drop was deposited on a carbon film grid; then, the sample was dried and analyzed in the transmission microscope using 450.000 x magnification. Image-J software was used to calculate the average diameter and d-spacing [111] of QDs with HR-TEM micrographs.

The shell thickness parameter is the value of the difference between the size of QDs core-shell (CdSe/ZnS) and size core (CdSe) from HRTEM analysis (equation 1).

$$\textit{Shell thickness} = \textit{Size CdSe/ZnS QDs} - \textit{Size CdSe core QDs} \quad (\text{equation 1})$$

The monolayer number (ML) was calculated as the ratio value between the experimental shell thickness parameter and ZnS zinc blende theoretic monolayer size (0.70 nm) (equation 2) [30].

$$\textit{Monolayer number (ML)} = \frac{\textit{shell thickness experimental}}{0.70 \textit{ nm}} \quad (\text{equation 2})$$

2.3.2 XRD patterns

Panalytical X'Pert3 Pro Multipurpose Diffractometer with CuK_α radiation source (45 kV and 40 mA) was employed to measure the powder XRD patterns. The diffraction dataset cards from the Joint Committee of Powders Diffraction Standards (JCPDS) were used to compare the obtained patterns.

2.3.3 FT-IR analysis

Infrared spectra of quantum dots were recorded with a Thermo Nicolet Nexus 670 FTIR spectrometer at a resolution of 4 cm⁻¹ using a KBr pellet, summing 50 scans.

2.3.4 X-ray Photoelectron Spectroscopy (XPS)

The XPS experiments were recorded using the XPS/ISS/UPS- ACenteno surface characterization platform built by SPECS (Germany). The platform is equipped with a PHOIBOS 150 2D-DLD energy analyzer. A monochromatized Al K α X-ray source (FOCUS 500) operated at 100 W was used for the measurements. The pass energy of the hemispherical analyzer was set at 100 eV for general spectra and 20 eV for high-resolution spectra. The samples were mounted on copper conductive tape in stainless steel metal sample holders for analysis and provided by the manufacturer SPECS. These sample holders are electrically connected to the spectrometer. CasaXPS program (Casa Software Ltd) for data analysis and the SPECS Prodigy library for RSF values were used.

2.3.5 UV-Vis spectroscopy

Electronic absorption spectra were measured on a UV-Vis spectrophotometer EMC-11-UV. Samples were measured in dilute solution in 1 cm pathlength quartz cells.

2.3.6 Photoluminescence (PL) measurements

Steady-state PL measurements were performed in an Agilent Varian Cary Eclipse Fluorescence spectrophotometer, using optically dilute solutions in 1cm x 1cm quartz cells. The PL quantum yield (PLQY, Φ) of CdSe/ZnS QDs (dissolved in chloroform) was calculated using rhodamine 6G in methanol solution as standard ($\Phi_s = 94\%$), with excitation wavelength (λ_{exc}) at 500 nm. Equation 3 was employed to calculate PLQY [31]

$$\Phi_x = \Phi_s \left(\frac{A_s}{A_x} \right) \left(\frac{I_x}{I_s} \right) \left(\frac{n_x^2}{n_s^2} \right) \quad (\text{equation 3})$$

A is the absorbance at the excitation wavelength, I is the area under the emission band, n is the refractive index of the solvent, s is the standard solution, and x are values of the unknown solution.

2.3.7 Time-resolved photoluminescence (TRPL)

TRPL measurements were carried out using a Horiba Fluorolog Time-Correlated Single Photon Counter (TCSPC) system, using a 560 nm nano LED as the pulsed excitation source (1 MHz; FWHM = ca. 1 ns). Measurements were performed at room temperature.

2.4 Changes optical induced by Hg²⁺

Hg²⁺ detection was carried out as follows: 100 μ L of Hg²⁺ ions in an aqueous solution (0.3 mM - 5.0 mM) were added to 3000 μ L of a solution containing CdSe/ZnS QDs (240 ppm) dissolved in chloroform and ethanol (1:1). The mixtures containing Hg²⁺ and QDs systems were stirred at room temperature, and then PL spectra were measured using $\lambda_{exc} = 380$ nm, slit: 3 (excitation) and 2 (emission), integration time: 0.3 s.

2.4.1 Effect of other metal ions

The changes in the fluorescence intensity originated from several metal ions (Mn²⁺, Co²⁺, Pb²⁺, Ni²⁺, Ba²⁺, Cd²⁺, and Zn²⁺) were determined with experimental conditions similar to the detection of Hg²⁺. In a typical experiment, 100 μ L of metal salt in an aqueous solution (5.0 μ M) were added to 3000 μ L of CdSe/ZnS QDs dissolved in a CHCl₃/EtOH 1:1 (240 ppm). The mixtures containing cations and QDs systems were stirred at room temperature, and then PL spectra were measured using $\lambda_{exc} = 380$ nm, slit: 3 (excitation) and 2 (emission), integration time: 0.3 s.

3. Results and Discussion

3.1 Structural characterization

3.1.1 TEM and HR-TEM analysis

CdSe QDs were synthesized by injecting Cd and Se precursors into a hot 1-octadecene and oleic acid solution. The growth of the ZnS shell around CdSe core was performed by a reaction of Et_2Zn and $(\text{TMS})_2\text{S}$ at 80 °C. The molar ratio of $[\text{S}]/[\text{Zn}]$ precursors was 9.0, 2.0, and 1.0 to obtain particles with variations in the size and thickness of the shells (**Figure 1** and **Table 1**). From TEM and HR-TEM images, the average diameters of QDs are 2.7 nm, 3.0 nm, and 3.2 nm (± 0.5 nm), corresponding to an amount of ZnS monolayer (ML) of 0.3 (QD-0.3 ML), 0.7 (QD-0.7 ML), and 1.0 nm (QD-1 ML), respectively. ZnS monolayer around CdSe was calculated from the difference between the core diameter (2.5 nm) from HR-TEM images shown in **Figure S1** and the theoretical value of one monolayer (equations 1 and 2) [30]. TEM images also revealed the obtention of spherical structures with good crystallinity and reasonable, narrow size distributions. There is no evidence of an interface between the core and shell, meaning that the shell growth process occurs in a coherent epitaxial region, as described in previous reports [22].

Crystal phases of QDs were determined with the interplanar distance spacing of selected areas in the HRTEM images, applying the Fast Fourier Transform (FFT) of ImageJ software (in **Figure 1**, micrographs at right). The interplanar spacing is 0.31 nm for QD-0.3 ML, 0.31 nm for QD-0.7 ML, and 0.30 nm for QD-1 ML, which match the lattice spacing of (111) plane of cubic ZnS ($d_{111} = 0.31$ nm for zinc blende ZnS)[32]. By comparing it with CdSe (**Figure S1**), the spacing value of the (111) plane is 0.34 nm, which matches the bulk cubic zinc blende of CdSe. These results are evidence of the growth of the ZnS shell on the CdSe core [32].

3.1.2 XRD patterns

Figure 2 compares the X-ray powder diffraction (XRD) patterns of CdSe/ZnS samples with the CdSe pattern. For CdSe/ZnS samples, the diffraction peaks are centered around 25.5, 42.7, and 50.2 degrees, corresponding respectively to the

(111), (220), and (311) lattice planes of cubic zinc blende CdSe (see reference CdSe pattern) [33]. Compared to CdSe, diffraction peaks of core/shell samples show more intense peaks and the characteristic shift to higher reflection angle positions due to the formation of ZnS shell [34, 35].

3.1.3 FT-IR spectra

Figure 3 shows FTIR spectra in the region 2000-1000 cm^{-1} of CdSe core and CdSe/ZnS QDs, which are compared with the oleic acid spectrum. The bands at 1460 cm^{-1} , 1412 cm^{-1} , and 1282 cm^{-1} , respectively, due to O-H, CH_3 , and C-O groups of the pure oleic acid [36] are observed in all samples of QDs. However, for CdSe and CdSe/ZnS samples, the C-O band is shifted to higher wavenumbers, and the intense band at 1707 cm^{-1} , characteristic of C=O group of oleic acid, decreased significantly. FT-IR spectra of QDs samples show two bands around 1534 cm^{-1} and 1407 cm^{-1} , which are respectively attributed to the asymmetric and symmetric stretching of the carboxylate anion (COO^-), indicating a complexation between $-\text{COO}^-$ group of oleic acid and a cation (Cd^{2+} , Zn^{2+}) of QDs surface. Separating asymmetric and symmetric carboxylate bands ($\Delta\nu = \nu_{\text{asymCOO}^-} - \nu_{\text{symCOO}^-}$) reveals the coordination mode between QDs surface and ligand. In the present case, the separation range is 127 cm^{-1} and 136 cm^{-1} , suggesting a bidentate coordination mode [36, 37].

FT-IR spectra show a shift of the asymmetric band to higher wavenumbers as the shell thickness increases. This shift allows us to determine the cation affinity on QDs surface and $-\text{COO}^-$ group. Since the amount of ZnS shell is different, the sites on QDs surface associated with the cation (Cd^{2+} , Zn^{2+}) must vary. CdSe is a reference sample with Cd^{2+} ions bound to oleic acid. QD-0.3 ML sample (with 0.3 monolayers) has Cd^{2+} and Zn^{2+} exposed on the QD surface, while QD-1 ML sample should have more Zn^{2+} ions exposed on surface to bind with oleic acid. According to the hard-soft acid-base (HSAB) theory [38], strong bonds are formed by electrostatic interaction between hard Lewis acid-base pairs and covalent interaction between soft pairs.

In contrast, a weak association is observed between members of opposite groups. In the present case, oleic acid, with oxygen-containing headgroups, is a hard base

with more affinity to Zn^{2+} because it has a greater hardness than Cd^{2+} . [16, 38] Therefore, the stronger affinity of -COO^- group and Zn^{2+} of QDs surface produced a shift to higher wavenumbers of the asymmetric band. The observed shift indicates that QD-0.7 ML and QD-1 ML samples have more species of Zn^{2+} exposed on surface compared with QD-0.3 ML sample, which has more Cd^{2+} species (with a lower affinity to -COO^- group of ligand).

3.1.4 XPS analysis

Figure 4 shows the high-resolution XPS spectrum of QDs samples. We compare the C1s and O1s spectra from oleic acid bound to CdSe and CdSe/ZnS surfaces. The C1s region is shown in **Figure 4A**. The single peak of C1s of the CdSe core is deconvoluted into two components at 284.5 eV, associated with C-C and C-H bonds, and at 288.3 eV attributed to the bidentate carboxylate (-COO^-) [39]. For core/shell samples, C1s peak is broader than the core's spectrum, and the carboxylate peak around 288 eV is significantly reduced. QDs sample spectra are deconvoluted into two components: at 284.3 eV, attributed to C-C (or C-H) of oleic acid, and near 285.0 eV associated with the carbon adjacent to the carboxylic group, $\underline{\text{C}}\text{-COO}$ [40]. The O1s peak is shown in **Figure 4B**, and a few changes between core and core/shell samples could be appreciated. Core/shell samples show a broader noisy peak, which is deconvoluted into two components at 530.7 eV, attributed to C-O and C=O of monodentate carboxylate, and at 532 eV assigned to bidentate carboxylate. Results demonstrate the chemical bonding between oleic acid and QDs surface [17]. **Figure 5** shows Cd3d, Se3d, Zn2p, and S2p spectra of core and core/shell samples. **Figure 5A** shows the Cd3d region. For CdSe core, the characteristic doublet of Cd^{2+} is seen at 405.1 eV and 411.9 eV, which is attributed to $\text{Cd}3d_{5/2}$ and $\text{Cd}3d_{3/2}$, respectively. For the QD-0.3 ML sample, the Cd3d spectrum remained almost unchanged (compared with core). For samples with a thicker shell (QD-0.7 ML and QD-1 ML), Cd3d doublet is moved to slightly higher binding energies. Additionally, the doublet is deconvoluted into two components, indicating different environments of Cd^{2+} on surface, e.g., Cd^{2+} binding to Se^{2-} (or COO^-) and underpassivated Cd^{2+} [41].

The Se3d peak for the core sample is observed at 54.1 eV (**Figure 5B**), a characteristic of metal selenides [42]. The Se3d spectra for core/shell samples are very similar to those obtained for CdSe core; however, the signal is less intense and noisier due to the shell on core.

The Zn2p region of core/shell samples is shown in **Figure 5C**. QD-0.3 ML sample shows the Zn2p peak resolved into two splitting peaks at 1045.7 eV and 1022.6 eV, corresponding to Zn2p_{1/2} and Zn2p_{3/2}, respectively. The separation between them is 23.1 eV, characteristic of Zn²⁺ species [43]. QDs with a thicker shell (QD-0.7 ML and QD-1 ML) have similar profiles. The Zn2p doublet is shifted to higher binding energies. The peaks are asymmetrical and broader compared with QD-0.3 ML sample. These changes reveal the presence of various Zn²⁺ species, such as Zn²⁺ bound to S²⁻ and oleic acid and the under-passivated Zn²⁺. These Zn²⁺ species could be more evident in the samples with a thicker shell since the molar ratios of Zn and S precursors were more equivalent than QD-0.3 ML.

The S2p region is shown in **Figure 5D**. For QD-0.3 ML, the broad peak centered at 161.0 eV could be due to different sulfur species (S²⁻ bonded to Zn²⁺ or underpassivated S²⁻) generated from S²⁻-rich solutions. In samples with the thicker shell, S2p peak is sharper and shifted to higher binding energies, indicating that when ZnS shell grows up from Zn and S concentrations with a molar equivalence, the under-passivated S²⁻ species are diminished.

Considering the FT-IR and XPS results, the growth of a ZnS shell by varying [S]/[Zn] molar ratio in the precursor solutions generated underpassivated ionic species (Cd²⁺, Zn²⁺, and S²⁻), which could be evidenced by the broader and shifted peaks in the XPS spectra, particularly in the Cd3d, Zn2p, S2p regions. QD-0.3ML has more underpassivated S²⁻ species derived from S²⁻-rich solutions. Samples with a thicker shell ([S]/[Zn] molar ratio was 2/1 and 1/1) are characterized by having more underpassivated Zn²⁺ species. As was observed in the FT-IR spectra, for instance, QD-1 ML with more Zn²⁺ species in the QDs surface produced a shift that was more significant in the band related to bond -COO-Zn²⁺.

3.2 Optical characterization

Figure 6 and **Table 2** compare the main characteristics of the absorption and emission spectra of CdSe core and CdSe/ZnS samples. CdSe/ZnS samples show the typical red-shift in the first exciton absorption peak and the emission maximum regarding CdSe. The PLQY enhanced from 0.17 for CdSe to 0.54 for core/shell samples. This enhancement of PLQY is a typical result of the growth of ZnS shell on CdSe core [44]. Literature has demonstrated that ZnS shell passivates defects of core surface, increasing PLQY [22, 45]. However, PLQY is affected when many ZnS monolayers grow on the core [45]. In this work, a relationship between QY and the thickness of the ZnS shell is not observed since QD-0.7 ML has a higher PLQY (0.54), and the sample with one formed monolayer of ZnS shows a reduction of PLQY (0.47). We believe that the variation of the molar ratio of precursors could introduce trap states that affected the PLQY.

Photoluminescence lifetime measurements were performed to understand the role of traps associated with [S]/[Zn] molar ratio and the exciton dynamics (**Figure 7**). Nonexponential kinetics showed the PL decay curves of core and core/shell QDs. Still, they could be mathematically fit by multiple exponentials (equation 4), with relative amplitudes A_i and time constants τ_i . The average fluorescence lifetime (τ_{FL}) is calculated with equation 5.

$$I(t) = I_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}} + A_3 e^{-\frac{t}{\tau_3}} + A_4 e^{-\frac{t}{\tau_4}} \quad (\text{equation 4})$$

$$\langle \tau_{FL} \rangle = \frac{\sum_{i=1}^4 A_i \tau_i}{\sum_{i=1}^4 A_i} \quad (\text{equation 5})$$

Table 3 shows the average fluorescence lifetimes (τ_{FL}). A dependence of τ_{FL} values with shell thickness is observed. The ZnS shell passivates the non-radiative trap states on the CdSe core, making the core more photostable and less affected by non-radiative recombination pathways [23, 45–47]. No direct correlation was found between the average fluorescence lifetime and QY values, due probably to the trapping sites introduced in the nanocrystal structure during the synthesis process. We recall that QD-0.3 ML sample with the thinner shell was prepared from a solution rich in S^{2-} , which generated underpassivated S^{2-} species on QDs surface. The anions (underpassivated S^{2-} species) are known for their role as hole traps [48, 49], affecting PLQY for QD-0.3 ML sample. By contrast, the sample with one monolayer of ZnS

(QD-1 ML), obtained from an equal ratio of [S]/[Zn] precursors, is characterized by having underpassivated S^{2-} and Zn^{2+} species. According to previous investigations, PLQY increases up to a specific shell thickness (1.25 ML of ZnS for Li et al. [50], 1.3 ML of ZnS for Dabbousi et al. [22]). After any further increase in the shell thickness, PL decreases due to the introduction of non-radiative recombination sites [45, 51, 52]. In the present investigation, the reduction of PLQY in QD-1 ML could be due to underpassivated Zn^{2+} and S^{2-} species acting as electron and hole traps [53, 54], respectively decreasing PL.

3.2.1 Effect of Hg^{2+} ions on luminescence properties

The changes in the PL spectra of CdSe/ZnS QDs samples induced by Hg^{2+} ions were studied in a homogeneous mixture containing QDs dissolved in chloroform and Hg^{2+} ions dissolved in water. Results show that the PL intensity could be quenched or enhanced by Hg^{2+} ions. The two opposite effects are shown in **Figure 8** and depend on CdSe/ZnS surface properties (thickness shell and surface traps). First, we presented the progressive fluorescence quenching by increasing the Hg^{2+} concentration for QD-0.3 ML sample (**Figure 8A**), accompanied by a shift of 3 nm of maximum emission wavelength. FL quenching by Hg^{2+} could be explained by the metal cation exchange reaction that produces the displacement of Cd^{2+} or Zn^{2+} in the lattice by Hg^{2+} ions generating HgSe (or HgS) particles on surface. This cation exchange is due to the lower solubility constant (K_{SP}) of HgSe or HgS compared with K_{SP} CdSe or ZnS being favored thermodynamically, as discussed previously in several reports [55, 56].

The PL quenching by increasing the Hg^{2+} concentration in the range of 0.3-3.0 μM is evaluated in terms of Stern-Volmer equation (equation 6):

$$I_0/I = 1 + K_{sv}[Hg^{2+}] \quad (\text{equation 6})$$

I_0 and I are the fluorescence intensities at a constant wavelength in a mercury ion-free solution and a given mercury ion concentration, respectively. $[Hg^{2+}]$ is the concentration of Hg^{2+} , and K_{sv} is the Stern-Volmer FL quenching constant. A good linearity is obtained with a correlation coefficient (R^2) equal to 0.9976 (bottom of

Figure 8A). The limit of detection (LOD), calculated with equation $LOD = 3\sigma/k$, where σ is the standard deviation of the y-intercept of the regression line, and k is the slope of the calibration graph, is found to be $0.0112 \mu\text{M}$ (11.2 nM). This value is lower than previously reported using oleic acid-capped CdSe/ZnS in a heterogeneous mixture that produces PL quenching induced by Hg^{2+} [17].

Figures 8B and 8C show the enhancement of PL intensity of the QD-0.7 ML and QD-1 ML samples in the presence of Hg^{2+} in the concentration range from $0.3 \mu\text{M}$ to $5.0 \mu\text{M}$. The enhancement of PL (I/I_0) of these two QDs is evaluated by the equation: $I/I_0 = 1 + K_{sv}[\text{Hg}^{2+}]$, where K_{sv} is the Stern-Volmer constant for the enhanced PL. A good linearity is obtained for both samples (see bottom of Figures 7B and 7C): R^2 is 0.9982, and LOD is $0.00898 \mu\text{M}$ (8.98 nM) for QD-0.7 ML sample. R^2 is 0.9975, and LOD is $0.0107 \mu\text{M}$ (10.7 nM) for QD-1 ML sample. The enhancement of PL by CdSe/ZnS with oleic acid as a capping agent is observed for the first time. The enhanced PL of QDs induced by Hg^{2+} [56] and other metal ions [57] has been reported in other investigations. Results reveal the shell's role in detecting Hg^{2+} . A thicker shell (than 0.3 ML) protects the core from the exchange reaction with Hg^{2+} , providing more stability and brightness. Furthermore, thicker shell samples (QD-0.7 ML and QD-1ML) have more underpassivated Zn^{2+} species on the surface, which are more exposed for the exchange with Hg^{2+} than Cd^{2+} species from core. These results show a significant improvement in the emission properties of oleic acid-capped CdSe/ZnS and an improved capacity to detect Hg^{2+} with lower LOD values.

The influence of Hg^{2+} on the PL lifetimes was investigated. **Figure 9** shows the PL decay curves for CdSe/ZnS samples mixed with an Hg^{2+} aqueous solution. **Table 4** gives the average fluorescence lifetimes, showing that the decays are very sensitive to the surface states of QDs. When Hg^{2+} is present, longer lifetimes occur for samples with a thicker shell (0.7 and 1.0 ML). The increased PL of CdSe/ZnS QDs by mercury ions could be attributed to the Zn^{2+} -to- Hg^{2+} cation exchange in the ZnS shell, which favors the separation of electrons and holes, reducing the recombination rate [56].

QD-0.3 ML mixed with Hg^{2+} produces shorter average fluorescence lifetimes, corroborating the effect of these cations to PL detriment. Similar sensing systems have also reported shorter FL lifetimes, accompanied by FL quenching in presence of metal ions [58–60]. As we explained, FL quenching by Hg^{2+} is derived by the metal cation exchange reaction with Cd^{2+} (from core) or Zn^{2+} (from shell), generating HgSe and HgS particles that quench FL. In addition, the underpassivated S^{2-} species in the QD-0.3 ML sample bind to Hg^{2+} , producing HgS and HgSe .

Effect of other metal ions

The effect of other metal transition cations on the fluorescence of CdSe/ZnS quantum dots (QD-0.3 ML, QD-0.7 ML, and QD-1 ML) was performed in homogeneous mixtures. A solution of QDs in chloroform/ethanol (1/1 v/v) was mixed with aqueous solutions of metal chloride salts (Co^{2+} , Mn^{2+} , Ni^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+}) (**Figure 10**). For QD-0.3 ML sample, the reduction of fluorescence intensity was observed with all the evaluated cations; however, Hg^{2+} reduced 100% fluorescence quenching. This result could be explained by the cation exchange reaction between Hg^{2+} ions and Se^{2-} and S^{2-} anions. Based on the K_{sp} values of HgSe (4.0×10^{-59}) and HgS (1.6×10^{-52}), which are lower than other ions [16, 38], a better ability of Hg^{2+} to PL quench is expected.

In the QD-0.7 ML and QD-1 ML samples, all the evaluated ions produce fluorescence *turn-on* (**Figure 10**). However, the turn-on effect of Hg^{2+} induced is higher [16, 38]. The role of the shell is essential to protect the core and avoid cation exchange reactions with foreign metal ions. We demonstrated that cations can passivate the surface of the QDs, eliminating some trapping sites and thus increasing the photoluminescence.

Conclusions

Three samples of oleic acid-capped CdSe/ZnS QDs with different shell thicknesses ranging between 0.3 ML and 1.0 ML were obtained by varying the [S]/[Zn] molar ratio of shell precursors. Characterization measurements of their optical and structural properties (UV-Vis, PL, fluorescence decay, XRD, HR-TEM, XPS, FT-IR) revealed differences in chemical speciation (i.e., underpassivated Zn²⁺ and S²⁻ species), which were correlated with the thickness of the shell. Underpassivated S²⁻ were formed mainly in the thinner sample, while Zn²⁺ species were primarily formed in the thicker sample. These species act as electron/hole trapping sites that affect PL differently.

The ability of CdSe/ZnS QDs samples to detect Hg²⁺ by PL measurements was studied. Fluorescence could be quenched and enhanced when Hg²⁺ ions were present. These opposite mechanisms could be tuned due to changes in the thickness and chemical speciation in core/shell QDs. A thicker shell protects the core of the unwanted cation exchange reaction with Hg²⁺, which deteriorates PL. In addition, the Hg²⁺ could passivate the surface defects, producing longer fluorescence lifetimes and better PL. Obtaining a thicker shell to protect the core produced a lower LOD (8.98 nM). However, other foreign cations also achieved increased PL; therefore, the selectivity is affected. Results show that core/shell QDs are promising for detecting Hg²⁺ ions and tuning shell properties is a determinant factor in the sensitivity and selectivity of the application.

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