Composition-Tunable Optical Properties of Zn$_x$Cd$_{1-x}$S Quantum Dot–Carboxymethylcellulose Conjugates: Towards One-Pot Green Synthesis of Multifunctional Nanoplatforms for Biomedical and Environmental Applications

Alexandra A. P. Mansur 1, Herman S. Mansur 1,3*, Anderson J. Caires 1, Rafael L. Mansur 1 and Luiz C. Oliveira 2

Abstract

Quantum dots (QDs) are colloidal semiconductor nanocrystals with unique properties that can be engineered by controlling the nanoparticle size and chemical composition by doping and alloying strategies. However, due to their potential toxicity, augmenting their biocompatibility is yet a challenge for expanding to several biomedical and environmentally friendly applications. Thus, the main goal of this study was to develop composition-tunable and biocompatible Zn$_x$Cd$_{1-x}$S QDs using carboxymethylcellulose polysaccharide as direct capping ligand via green colloidal aqueous route at neutral pH and at room temperature for potential biomedical and environmental applications. The ternary alloyed QDs were extensively characterized using UV–vis spectroscopy, photoluminescence spectroscopy (PL), transmission electron microscopy (TEM), X-ray diffraction (XRD), electron energy loss spectroscopy (EELS), and X-ray photoelectrons spectroscopy (XPS). The results indicated that Zn$_x$Cd$_{1-x}$S QDs were surface stabilized by carboxymethylcellulose biopolymer with spherical morphology for all composition of alloys and narrow sizes distributions ranging from 4 to 5 nm. The XRD results indicated that monophasic ternary alloyed Zn$_x$Cd$_{1-x}$S nanocrystals were produced with homogenous composition of the core as evidenced by EELS and XPS analyses. In addition, the absorption and emission optical properties of Zn$_x$Cd$_{1-x}$S QDs were red shifted with increasing the amount of Cd$^{2+}$ in the alloyed nanocrystals, which have also increased the quantum yield compared to pure CdS and ZnS nanoparticles. These properties of alloyed nanomaterials were interpreted based on empirical model of Vegard’s law and chemical bond model (CBM). As a proof of concept, these alloyed-QD conjugates were tested for biomedical and environmental applications. The results demonstrated that they were non-toxic and effective fluorophores for bioimaging live HEK293T cells (human embryonic kidney cells) using confocal laser scanning fluorescence microscopy. Moreover, these conjugates presented photocatalytic activity for photodegradation of methylene blue used as model (Continued on next page)
organic industrial pollutant in water. Hence, composition-tunable optical properties of ternary Zn$_x$Cd$_{1-x}$S $(x = 0–1)$ fluorescent alloyed QDs was achieved using a facile eco-friendly aqueous processing route, which can offer promising alternatives for developing innovative nanomaterials for applications in nanomedicine and environmental science and technology.

**Keywords:** Semiconductor quantum dot nanoparticles, Nanomaterials, Semiconductor-biopolymer interfaces, Nanophotocatalyst, Core-shell nanostructures

---

**Background**

Traditionally, alloys have been used for several centuries to create new materials with improved mechanical, structural, thermal, electrical properties leading to the development of high-performance materials, which cannot be achieved with each component separately. However, only very recently the interest in nanoalloys (also referred to as alloy nanoclusters or alloy nanoparticles) arises, as they constitute a new type of advanced nanoscale materials, which can have unique properties very distinct from those of individual atoms and molecules or original bulk matter [1–4]. One of the major reasons for interest in alloy nanoparticles is the fact that their chemical and physical properties may be tuned by varying the composition and atomic ordering as well as the dimension of the clusters [4, 5]. Besides the metal-based nanomaterial alloys, nano-sized semiconductor nanocrystals (referred to as quantum dots, QDs) have increasingly called the attention of the scientists, researchers, and manufacturers because of their broad range of potential applications in electronics, optics, magnetic, sensors, biosensors, and biomedical fields [6–11]. In that sense, quantum dots based on metal chalcogenide alloys, mostly of group II–VI semiconductors (type MX, M = Cd, Zn, Pb; X = Te, Se, S), are currently under intensive study in many research fields such as in optoelectronics, high-density memory, quantum-dot lasers, and lately for biosensing and biolabeling because they exhibit tunable optical properties (i.e., bandgap energy structure) by adjusting the chemical composition and size [5, 7, 12–15]. Since the bandgap engineering of ternary and quaternary alloyed QDs can be achieved via controlling their composition (relative constituent stoichiometry) in addition to their sizes and internal structures, it is therefore feasible to design and tune their optical properties, which are not readily viable to binary QDs [16–19]. This can be achieved by creating a solid solution (i.e., an alloy) of two semiconductors with different energy gaps, where an increase in the bandgap energy is generally observed with increasing the concentration of the wider bandgap semiconductor, either with cation (i.e., metal constituent) or anion (i.e., chalcogenide constituent) alloyed QDs [20, 21]. Nonetheless, the development of QDs based on Zn–Cd–S alloys using one-pot “greener” aqueous processes with biocompatible ligands are narrowly reported in the literature, where the large majority of studies report the production of QDs at high temperatures by organometallic routes, microwave-assisted synthesis, and using toxic organic solvents [15, 17, 18, 21–25]. High-temperature decomposition methods based on trioctylphosphine oxide (TOPO), commonly used as capping ligand for improved quantum yields, results in hydrophobic QDs insoluble in aqueous medium. However, biological and medical applications require QDs that are water-soluble at physiological conditions, biocompatible, and functionalized with biomolecules for targeting purposes. Hence, the development of novel strategies of surface functionalization and bioconjugation remains an important challenge. Yet, no report was found in the consulted literature addressing the synthesis of Zn$_x$Cd$_{1-x}$S QDs functionalized with biopolymer ligands based on cellulose derivatives for multiple potential purposes, including cell bioimaging and photocatalytic activity for the degradation of organic dye pollutants.

Thus, herein, we report the synthesis and comprehensive characterization of novel ternary alloyed Zn$_x$Cd$_{1-x}$S QDs $(x = 0–1)$ with composition-tunable optical properties using carboxymethylcellulose as a biocompatible and eco-friendly capping ligand produced directly by means of a single-step green colloidal process in aqueous media at room temperature. They proved to be suitable nanoplatforms for live cell bioimaging or heterogeneous photocatalysis of methylene blue organic dye.

**Methods**

**Materials**

All of the reagents and precursors, including zinc chloride (Sigma-Aldrich, USA, ≥98%, ZnCl$_2$), cadmium perchlorate hydrate (Aldrich, USA, Cd(ClO$_4$)$_2$·6H$_2$O), and sodium sulfide hydrate (Synth, Brazil, >98%, Na$_2$S·9H$_2$O) were used as received. Carboxymethylcellulose sodium salt (CMCel, Fluka Chemical, USA), degree of substitution (DS) 0.84 and medium viscosity (870 mPa s, 2% in H$_2$O) were used as capping ligand. Deionized water (DI water, Millipore SimplicityTM) with a resistivity of 18 MΩ cm was used to prepare the solutions and the procedures were performed at room temperature (RT, 23 ± 2 °C), unless specified otherwise.
Synthesis of Quantum Dot Conjugates—Zn_xCd_{1-x}S/CMCen

CMCen solution (1% w/v) was prepared by adding sodium carboxymethylcellulose powder (0.5 g) to a 50 mL of water and stirring at room temperature until complete solubilization occurred. For controlling the molar ratios of cations, premixed Zn^{2+} and Cd^{2+} solutions were prepared from the individual stock solutions (ZnCl_2 and Cd(ClO_4)_{2·6H_2O}) at 1 × 10^{-3} mol L^{-1} total cation concentration (M) but with Zn^{2+}:Cd^{2+} molar ratios of 100:0 (x = 1.0), 75:25 (x = 0.75), 50:50 (x = 0.50), 25:75 (x = 0.25), and 0:100 (x = 0).

Zn_xCd_{1-x}S nanoparticles were synthesized via an aqueous route at room temperature as follows: 2 mL of CMCen solution and 45 mL of deionized water were added to a flask. The pH was measured and it was close to neutral (pH~7.0). Under magnetic stirring, 20.0 mL of the metal precursor solution (1 × 10^{-3} mol L^{-1}) at the Zn^{2+}:Cd^{2+} different molar ratios and 4.0 mL of the sulfide source solution (Na_2S·9H_2O, 1.0 × 10^{-2} mol L^{-1}) were added to the flask (the S^{2−}:M^{2+} molar ratio was kept at 2:1, i.e., excess of sulfide) and stirred for 10 min. The QDs colloidal dispersions produced were stable and homogeneous. ZnS dispersion was colorless while CdS dispersion was light yellow. The dispersions of ternary Zn_xCd_{1-x}S nanoparticles exhibit colors between clear and light yellow with continuous color gradient as a function of the Zn^{2+}:Cd^{2+} molar ratio.

These colloidal dispersions were concentrated and purified using an Amicon Ultra Filter (Millipore) with a 100,000 molecular mass (M_W) cut-off cellulose membrane. After centrifugation, the samples were stored at RT until further use.

Physicochemical Characterization of Quantum Dot Conjugates

Ultraviolet–visible (UV–vis) spectroscopy measurements were performed using Perkin-Elmer, Inc. (USA) equipment (Lambda EZ-210) in transmission mode with samples in a quartz cuvette over a wavelength range between 600 and 190 nm. All of the experiments were conducted in triplicate (n = 3) unless specified, and the data were presented as the mean ± standard deviation.

The photoluminescence spectroscopy (PL) of the Zn_xCd_{1-x}S/CMCen conjugates was performed based on spectra acquired at RT using a violet diode laser module at λ_{exc} = 405 nm (150-mW, Roithner LaserTechnik, Germany) coupled to a USB4000 VIS-NIR spectrophotometer (Ocean Optics, Inc., USA). All of the tests were performed using a minimum of four repetitions (n ≥ 4). Quantum yield (QY) was measured according to the procedure using Rhodamine 6G (Sigma, USA) in ethanol as the standard at λ_{exc} = 405 nm [26]. Nanostructural characterization of the QDs was based on the images and electron diffraction patterns (ED) using Tecnai G2-20-FEI (FEI Company, USA) transmission electron microscope (TEM) at an accelerating voltage of 200 kV. In all of the TEM analyses, the samples were prepared by placing a drop of a dilute QD suspension onto carbon-coated copper grids (Electron Microscopy Sciences, USA) and allowing them to dry at room temperature overnight. The QD size and size-distribution data were obtained based on the TEM images by measuring at least 150 randomly selected nanoparticles using image processing program (ImageJ, version 1.50, public domain, National Institutes of Health) [27].

X-ray diffraction (XRD) patterns were recorded using PANalytical (UK) Empyrean diffractometer (Cu–Kα radiation with λ = 1.5406 Å). Measurements were performed in the 2θ range from 3° to 70° with steps of 0.06°. For the sample preparation, concentrated colloidal QD dispersions were dropped onto glass slides and oven dried at 40 ± 1 °C for 12 h.

Energy-filtered transmission electron microscopy (EFTEM) with low-loss electron energy-loss spectroscopy (EELS) was performed by using Tecnai G20 TEM operating at 200 kV accelerating voltage and equipped with GATAN GIF energy imaging filter. The cadmium composition map was obtained using the Cd M edge at 404 eV, and the Zn composition map was obtained using the Zn L edge at 1020 eV, using similar sample preparation procedure of TEM analysis.

X-ray photoelectron spectroscopy (XPS) analysis was performed using Mg–Kα as the excitation source (Amicus spectrometer, Shimadzu, Japan). All peak positions were corrected based on C 1s binding energy (284.6 eV). For sample preparation, concentrated QD colloidal medium was dropped onto glass slides and dried in a vacuum desiccator at RT for 48 h.

Dynamic light scattering (DLS) and zeta potential (ZP) analyses were performed using ZetaPlus instrument (Brookhaven Instruments Corporation, 35-mW red diode laser light, wavelength λ = 660 nm) with a minimum of ten replicates. The ZP measurements were performed at 25.0 °C ± 2 °C under the Smoluchowski approximation method. For the DLS measurements, the colloidal solutions of QDs were filtered three times through a 0.45-µm aqueous syringe filter (Milllex LCR 25 mm, Millipore).

Biological Characterization of QD Conjugates

Evaluation of Cytotoxicity by MTT Cell Viability Assay

MTT (3-(4,5-dimethylthiazol-2-yl) 2,5-diphenyl tetrazolium bromide) experiments were performed to evaluate the toxicity of QDs dispersions. MTT assays were conducted according to ISO 10993-5:2009 (Biological evaluation of medical devices: Tests for in vitro cytotoxicity)
using kidney cell line of a human embryonic culture (HEK293T). HEK293T cells were kindly provided by Prof. M.F Leite (Department of Physiology and Biophysics, UFMG), and they were cultured in DMEM with 10% FBS, penicillin G sodium (10 units mL\(^{-1}\)), streptomycin sulfate (10 mg mL\(^{-1}\)), and amphotericin-b (0.025 mg mL\(^{-1}\)), all from Gibco BRL (NY, USA), in a humidified atmosphere of 5% CO\(_2\) at 37 °C.

HEK293T cells on passage 68 were plated (3 × 10^4 cells/well) in 96-well plates. Cell populations were synchronized in serum-free media for 24 h. After that, the media volume was suctioned and replaced with DMEM media containing 10% FBS for 24 h. The samples of CdS, ZnS, and Zn\(_{0.50}\)Cd\(_{0.50}\)S QDs colloidal solutions were added to individual wells at final concentrations of 10 nM. For MTT assay, control samples were designed as follows: control group (cell culture with DMEM medium); positive control (1.0% Triton X-100, Sigma-Aldrich, USA); and negative control (chips of sterile polypropylene Eppendorf, 1 mg mL\(^{-1}\), Eppendorf, Germany). After 120 h, all media were aspirated and replaced with 60 μL of culture media containing serum to each well. MTT (5 mg mL\(^{-1}\), Sigma-Aldrich, USA) solution/4% HCl was placed in each well and incubated for 4 h in an oven at 37 °C and 5% CO\(_2\). Next, 40 μL of each conjugate catalyst under mechanic stirring (330 rpm) and a mercury lamp radiation source (15 W, at \(\lambda = 254\) nm). At certain time intervals, an aliquot of the material was collected and analyzed by UV–vis spectroscopy (Shimadzu-UV-1601 PC) to detect the dye concentration based on Beer–Lambert curves established to correlate the absorbance with the dye concentration at the characteristic maximum absorption wavelength (\(\lambda = 664\) nm). The degradation efficiency was calculated using Eq. 2 where “\(C_0\)” is the initial concentration of the dye (\(t = 0\)) and “\(C\)” is the concentration of MB at a given time of radiation exposure (\(t\)). A control experiment was performed without the presence of the catalytic conjugates.

\[
\text{Degradation efficiency (\%)} = \left(\frac{[C_0 - C]}{C_0}\right) \times 100\% \quad (2)
\]

**Results and Discussion**

**Physicochemical Characterization of Quantum Dot Conjugates**

Figure 1A shows de UV–vis spectra for Zn\(_x\)Cd\(_{1-x}\)S (\(x = 1.0, 0.75, 0.50, 0.25, \text{ and } 0\)) series. ZnS nanoparticles (Fig. 1A(a)) presents a sharp absorption edge at approximately 290 nm associated with the first excitonic transition indicating nucleation and growth of ZnS (\(x = 1\)) nanoparticles, blue shifted from the bulk value at 343 nm [28] due to the “quantum confinement regime.” Analogously, CdS (\(x = 0\)) colloidal suspension (Fig. 1A(e)) presented a broad absorption band from 430 to 470 nm, blue shifted when compared with the original bulk value (\(\lambda = 512\) nm, [28]) indicating the formation of CdS QDs. The optical absorption spectra of Zn\(_x\)Cd\(_{1-x}\)S ternary systems show a systematic red shift associated with the changes in the absorption onset of the S\(_0\)→S\(_1\) transitions as the Cd content increases which originates from the wider bandgap ZnS (\(E_g = \) for 30 min, washed three times with PBS, and cover slips were mounted with Hydromount (Fisher Scientific Ltd., UK) for posterior analysis in confocal laser scanning fluorescence microscopy (Zeiss LSM Meta 510, Carl Zeiss; excitation 488 nm argon laser; emission filter 505–530 nm). For the control, cells were incubated with only in the original medium with 10% FBS (autofluorescence).
3.61 eV) relative to the narrower bandgap CdS ($E_g = 2.42$ eV) [28].

Bandgap values for the prepared metal sulfide QDs ($E_{QD}$) at different proportions of [Zn,Cd]:S were extracted from the UV–vis absorbance curves using the “Tauc relation” (Fig. 1B). The estimated $E_{QD}$ values are 3.90, 3.20, 2.85, 2.61, and 2.57 eV for ZnS, Zn$_{0.75}$Cd$_{0.25}$S, Zn$_{0.50}$Cd$_{0.50}$S, Zn$_{0.25}$Cd$_{0.75}$S, and CdS, respectively. Therefore, the tunable bandgap effect was indeed verified, as the excitonic transitions for the Zn$_x$Cd$_{1-x}$S ternary solid solutions (Fig. 1A (b–d)) continuously red shifted (i.e., shifted to lower energy) with increasing the amount of Cd$^{2+}$, which demonstrated the formation of Zn$_x$Cd$_{1-x}$S nanoalloys.

Typical room-temperature PL spectra of the Zn$_x$Cd$_{1-x}$S nanoparticles stabilized by CMCd are presented in Fig. 2A. The Zn$_x$Cd$_{1-x}$S QDs showed multi-colored light emissions arising predominantly from defect activated photoluminescence. That means, lattice point defects (vacancies, V, and interstitials atoms, I) act as efficient traps for electrons, holes, and exciton charge carriers, leading to radiative recombination at energies lower than the band-to-band optical transition (i.e., offering non-radiative pathways) [29, 30]. As previously reported [31, 32], due to the small size of QDs and the intrinsic lattice point defects introduced by the synthesis at room temperature and aqueous routes, band edge (excitonic) luminescence was not observed and

![Fig. 1 UV–visible and optical absorption spectroscopy of conjugates. a UV–vis absorption spectra and b optical absorption spectra (relation) for ZnS (a), Zn$_{0.75}$Cd$_{0.25}$S (b), Zn$_{0.50}$Cd$_{0.50}$S (c), Zn$_{0.25}$Cd$_{0.75}$S (d), and CdS (e).](image)
The QYs were typically ≤2.0% (1.0% for ZnS; 1.8% for Zn_{0.50}Cd_{0.50}S; 0.2% for CdS).

The occurrence, population, and depths of the traps determine the pathway that the electron–hole pairs (i.e., exciton, $e^−/h^+$) generated by irradiation will follow during emission. Considering the synthesis process developed in this work, using the stoichiometric molar ratio of $M^{2+} : S^{2−} = 1:2$ (i.e., higher sulfide to cation ratio), the occurrence of vacancies of metals ($V_M$: $V_{Cd}$ or $V_{Zn}$) and sulfur at interstitial sites at lattice ($I_S$) are expected. Moreover, the strong interaction between the metallic cations and the anionic carboxylate species from CMCel, which are fully deprotonated at the pH of synthesis ($pK_a = 4.8$, $R−COOH → R−COO^−$) can cause the formation of vacancies of sulfur ($V_S$) at the QD surface. Thus, considering the combination of the types of point defects ($V_M$, $V_{Cd}$, $V_{Zn}$, and $I_S$) and the similarity of the emission curves for $Zn_xCd_{1−x}S$, three main radiative emissions were observed in the nanoparticles, which were assigned to the energy band diagram depicted in Fig. 2B and summarized in Table 1, supported by the literature [33–37].

First, there is a non-radiative pathway from valence band and energy level of $V_S$ due to shallow trap states. In the sequence, the emission E1 can be associated with transitions involving sulfur vacancies ($V_S$) and valence band ($V_{M}$). Emission E2 can be assigned to the recombination of trapped electrons at $V_S$ and holes trapped at interstitial metal ($I_S$) point defects and E3 is attributed to the recombination between vacancy trap states ($V_S−V_M$). The minor emission bands at higher wavelengths can be assigned to surface defects [33, 35]. Despite the nature of the emission, peaks in the PL spectra shifted to lower energy with the increase of Cd molar ratio in the QDs demonstrated the composition-tunable emission effect of nanoalloys. These values of red shift observed in the PL spectroscopy support the results of previous sections, and they are further strong evidence of the formation of alloyed nanocrystals.

![Fig. 2 Photoluminescence spectroscopy of conjugates. a PL emission spectra for $Zn_xCd_{1−x}S$ ($x = 1.0$ (a), 0.75 (b), 0.50 (c), 0.25 (d), and 0 (e). b The energy band structure suggested for three main emissions of alloyed $Zn_xCd_{1−x}S$ quantum dots](image-url)
The diffraction peaks observed in the XRD pattern of ZnS QDs (Fig. 3a) at 2θ at 28.6 ± 0.1°, 47.8 ± 0.1°, and 56.5 ± 0.1° can be assigned to the planes (111), (220), and (311) of ZnS cubic lattice structure (Zinc blend also referred to as sphalerite, JCPDS 05-0566). Analogously, the peaks at 2θ values of 26.6 ± 0.1°, 43.9 ± 0.1°, and 52.2 ± 0.1° (Fig. 3c) can be indexed to the planes (111), (220), and (311) of the cubic structure CdS (ICCD 89-0440), respectively. The Zn0.50Cd0.50S sample (Fig. 3b) also has a cubic crystal phase with diffraction peaks shifted relative to the two binary systems and located at an intermediary value between ZnS and CdS. As the ionic radius of Zn2+ is smaller than that of Cd2+, the addition of Cd atoms to ZnS structure caused diffraction peaks to shift to lower angles with a correspondent increase of the unit cell volume of the Zn0.50Cd0.50S sample in comparison with ZnS. Thus, it evidenced that a homogeneous alloyed solid solution has been achieved by controlling the stoichiometric ratio of Zn:Cd. In addition, the broad band present at 2θ ~ 21.8° (Fig. 3d) is characteristic of the CMCel polymer used for the chemical stabilization of the metal sulfide QDs [38].

Table 1 Summary of types and energies of Zn_xCd_{1-x}S QD emissions

| Emission Type            | ZnS          | Zn_{0.75}Cd_{0.25}S | Zn_{0.50}Cd_{0.50}S | Zn_{0.25}Cd_{0.75}S | CdS          |
|--------------------------|--------------|---------------------|---------------------|---------------------|--------------|
| Excitonic emission       |              |                     |                     |                     |              |
| Defect activated emission (eV) |              |                     |                     |                     |              |
| E1 (ν_S—V_B)             | 2.56         | 2.42                | 2.21                | 2.02                | 2.03         |
| E2 (ν_S—V_M)             | 2.42 green   | 2.24 green          | 2.07 yellow         | 1.91 red            | 1.90 red     |
| E3 (ν_S—V_M)             | 2.27         | 2.07                | 1.89                | 1.71                | 1.71         |

Italicized values indicate the maximum PL intensity and visible emission color.

In order to access the morphological features and the sizes of the Zn_xCd_{1-x}S systems (x = 1.0, 0.50, and 0), TEM analysis was performed and the typical images are showed in Fig. 4A (ZnS), Fig. 4B (Cd_{0.50}Zn_{0.50}S), and Fig. 4C (CdS). TEM images confirm the formation of QDs with reasonable spherical shape and similar sizes (average diameter ± standard deviation) of 4.9 ± 0.5 nm for CdS, 4.3 ± 0.3 nm for ZnS, and 4.3 ± 0.5 nm for Zn_{0.50}Cd_{0.50}S. The clear two-dimensional crystal lattice stripes obtained by selected area electron diffraction (SAED patterns) in the TEM images demonstrate the crystalline nature of the QDs and indicate the formation of nanocrystals with cubic structure and lattice parameters consistent with the 2θ diffraction angles obtained by XRD.

From the materials science perspective, the properties of the semiconductor nanoalloys produced were interpreted considering empirical and semi-empirical models. Therefore, Vegard’s law empirical rule widely used in metallurgy to predict the physical and optical properties of materials was used to validate the relationship that the lattice constant and bandgap energy would be changed depending on the concentration of
the constituents [18, 39, 40]. Therefore, by the combination of wide-bandgap (ZnS, $E_g = 3.61$ eV) with medium-bandgap (CdS, $E_g = 2.42$ eV) semiconductors [28], it was predicted a linear reduction of the energy of absorption of the alloyed metal sulfide system as the concentration of Cd$^{2+}$ was increased, following the Vegard’s law, Eq. 3.

$$E_g^{\text{alloy}}(Zn_xCd_{1-x}S) = x E_g(ZnS) + (1 - x) E_g(CdS), \quad 1.0 < x < 0$$

However, it can be observed in Fig. 5a that the experimental results of bandgap energies and PL emission of the Zn$_x$Cd$_{1-x}$S ternary nanoalloys presented a deviation
to lower values as a general trend from the Vegard’s law
plot (dotted line), except for pure QDs (i.e., ZnS or
CdS), which were used as reference for constructing this
equation. Both optical properties, absorption and emis-
sion, were significantly affected by the composition of
the Zn$_x$Cd$_{1-x}$S alloys but with distinct energies from the
predicted linear behavior of Vegard’s law. In general,
similar to Vegard’s law [39], other models are used for
calculating the correlation of optical properties with the
size and composition of semiconductor nanocrystals,
such as effective mass approximation (EMA) [41], semi-
empirical tight-binding model (TBM) [42], and chemical
bond model (CBM) [43–45]. Nonetheless, they usually
overestimate the bandgap energies under the quantum
confinement of the exciton mainly because of simplified
assumptions such as by considering a spherical volume
of the nanocrystallite, minimizing the complexity and re-
ducing the parameters involved [42, 44]. Although not
accurate and valid for all ternary and quaternary alloyed
QDs, the chemical bond model (CBM) [43–45], which is
not a linear function, is suggested as more adequate for
correlating the effect of quantum dependence of optical
properties (bandgap energy) with the concentration of
alloyed QDs such as Zn$_x$Cd$_{1-x}$S (dashed line). It can be
noted that the CBM plot from the literature [45] with
the similar system but with different surface ligand and
alloy compositions (Zn$_x$Cd$_{1-x}$S, x = 0 to 0.42, and QD
size of 4.4 nm) presented overestimated values of ap-
proximately ~200 meV compared to our experimental
data. However, the shape of the curve resemble more
similarly than linear Vegard’s law, due to the combination
of parameters related to quantum confinement (inner

Fig. 5 Empirical and semi-empirical models of semiconductor nanowires. a Non-linear relationship of $E_{QD}$ (squares) and PL wavelength (circles) as a function of the molar content of Zn$^{2+}$. Dotted line indicates Vegard’s law (calculated) and dashed line, the expected values based on Chemical Bond Theory (from reference [45]). b Linear relationship of lattice parameters as a function of the concentration of Zn$^{2+}$ in the material (data from ED analysis).
QD) and chemical interactions with ligands at the surface (outermost layer of QD) in the CBM model [44, 45].

It is worth mentioning that the red shift of the emission with respect to absorption spectra (known as Stokes shift) increased with raising the Zn$^{2+}$ concentration in the $Zn_{x}Cd_{1-x}S$, from $x=0$ to 1.0 (Fig. 5a) due to the complex mechanism of separation and recombination of charges in the nanoalloys. Essentially, based on Brus’ equation [41], who developed the first theoretical calculation for semiconductor nanoparticles named EMA model (Eq. 4), an exciton is considered to be confined to a spherical volume of the nanocrystallite and the mass of electron and hole is replaced with effective masses ($m_e$ and $m_h$) to define the wave function. Hence, the higher reduced mass of exciton (Eq. 5, $1/\mu = 1/m_e^* + 1/m_h^*$) increased its relative blue shift by approximately 6% ($\Delta E_g$, Eq. 6, where $h$ is the Planck’s constant) associated with the quantum confinement, which was indeed verified by increasing the concentration of Zn$^{2+}$ in the alloyed QDs of $Zn_{x}Cd_{1-x}S$.

$$E_{QD} = E_g + \Delta E_g$$

$$1/\mu = 1/m_e^* + 1/m_h^*$$

$$\Delta E_g \approx h^2/8\mu R^2$$

Nonetheless, a distinct behavior was observed for the physical properties (e.g., interplanar distances), where a linear correlation was observed by varying the ternary alloy composition in agreement with the literature [20]. Figure 5b shows the lattice spacing for (111) and (220) planes calculated from ED patterns (TEM images). The interplanar distances exhibit a linear behavior upon changing the $x$ values according to Vegard’s law evidencing that the $Zn_{0.30}Cd_{0.70}S$ system is an alloyed QD instead of a mixture of CdS and ZnS nanocrystals.

To perform a more in-depth characterization of $Zn_{0.50}Cd_{0.50}S$ QDs at nanoscale order, EFTEM coupled with EELS and XPS measurements were performed. Energy-filtered transmission electron microscopy (EFTEM) with low-loss electron energy-loss spectroscopy (EELS) yields new possibilities for the investigation of alloyed ternary nanomaterials [46, 47]. Therefore, the elemental distribution of $Zn_{0.50}Cd_{0.50}S$ QDs was assessed using EELS/EFTEM techniques to investigate the distribution of Cd and Zn in the synthesized $Zn_{0.50}Cd_{0.50}S$ QDs, which was selected as a typical alloyed ternary system. Figure 6a shows a zero energy loss image of an isolated QD, and Fig. 6b, c shows the chemical composition maps of Cd and Zn at nanometer resolution. The uniform distribution of the Zn and Cd elements demonstrated the formation of homogeneous alloyed $Zn_{0.50}Cd_{0.50}S$ QDs, supporting the XRD and TEM results. Moreover, the thermodynamics and kinetics favored the formation of homogenous alloyed ternary QDs as the Gibbs free energy of formation of ZnS and CdS are of the same magnitude (~180–200 kJ mol$^{-1}$) and the solubility product constant are very low (ksp$\sim$10$^{-25}$–10$^{-27}$) in the presence of excess of sulfides in the reaction medium at room temperature.

Figure 7a–e shows typical XPS spectra obtained directly at the surface of the conjugate composed of $Zn_{0.50}Cd_{0.50}S$-CMCel. Figures 7a, b shows representative spectra of C 1s and O 1s regions, respectively. Both spectra are showed several peaks that were identified by deconvolution procedure [48]. C 1s spectrum revealed different chemical bonds of carbon atoms: C–H and C–C bonds at binding energy of 284.5 eV; C–O bond at 286.2 eV; one peak at 287.9 eV assigned to C=O and O–C–O bonds; and O=C–OR bonds at 290.6 eV [48, 49]. Peaks of O=C and O–C at 531.7 and 532.9 eV, respectively, were observed in the O 1s region [49]. These XPS spectra are compatible with the chemical structure of CMCEL. In addition, XPS spectra at the surface of the quantum dot–CMCEL conjugates in the regions related to Zn 2p (Fig. 7c), Cd 3d (Fig. 7d), and S 2p (Fig. 7e) indicated no detectable signal from zinc, cadmium, and sulfur, respectively. This result demonstrated the presence of an organic shell of CMCel used as capping agent of QD nanoparticles for controlling the nucleation and limiting the growth of the alloyed nanocrystals just formed in the colloidal media within the quantum confinement regime. Due to the expected repulsion between negatively charged CMC chains associated with carboxylate groups, this organic shell is probably composed of a monolayer surrounding the semiconductor core, which is complex to be precisely measured [50]. Thus, in order to get the distribution of the elements at the surface underneath this CMCel layer, ion bombardment with argon ions (Ar$^+$, 1 cycle, 10 s, emission current 10 mA, and beam voltage 0.5 kV) was applied for removing the organic shell. The corresponding elemental composition of the QD surface obtained by XPS spectroscopy taken for Zn 2p, Cd 3d, and S 2p regions is showed in Fig. 7f–h. First, it can be observed that the three chemical elements of the ternary systems were detected, in agreement with the previous results that indicated the formation of ternary nanoalloy. In Fig. 7f, the peaks at 1021.8 and 1044.8 eV correspond to the Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$ levels, respectively, and are associated with the Zn (2p) transitions in ZnS. The spin-orbit components (Zn 2p$_{3/2}$ and Zn 2p$_{1/2}$) are separated by a binding energy interval of approximately 23.0 eV [49, 51–53]. The two strong peaks in Fig. 7g at 411.7 eV (Cd 3d$_{5/2}$) and 404.9 eV (Cd 3d$_{3/2}$) are generally assigned to Cd–S bonding in CdS. The difference between the binding energies of Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$ is 6.8 eV, in agreement with the literature [30, 49, 53]. The S 2p$_{3/2}$ peak (Fig. 7h)
Fig. 6 EELS and EFTEM analyses of conjugates. EFTEM Elemental maps of Cd and Zn in samples of Zn$_{0.50}$Cd$_{0.50}$S quantum dots. 

- **a** EFTEM zero energy loss image of an individual Zn$_{0.50}$Cd$_{0.50}$S quantum dot.
- **b** EELS signals of Cd forming the composition map (Cd M edge at 404 eV).
- **c** EELS signals of Zn forming the composition map (Zn L edge at 1020 eV).

Fig. 7 X-ray photoelectron spectroscopy of conjugates. XPS spectra of C 1s (a), O 1s (b), Zn 2p (c), Cd 3d (d), and S 2p (e) regions at the surface of Zn$_{0.50}$Cd$_{0.50}$S ternary system and XPS spectra of Zn 2p (f), Cd 3d (g), and S 2p (h) regions after etching.
and S 2p\textsubscript{1/2} peaks were found at 161.3 and 162.5 eV, respectively, \((\Delta = 1.2 \text{ eV})\), which can be assigned to sulfur in metal sulfides \((M–S)\) [49, 51–53]. Elemental analysis data was determined from the integrated area of Cd 3d, Zn 2p, and S 2p signals with appropriate atomic sensitivity factors using the XPS software for data processing (Vision Processing, Kratos).

Despite neglecting effects of spherical particle geometry, small QD size, and preferential sputtering, the outmost surface of the QDs presented atomic concentrations (%) of Zn, Cd, and S of 50 ± 4%, 16 ± 2%, and 33 ± 3%, respectively. As expected, distinct from the homogenous composition of the “inner” portion of the nanocrystals, the XPS results of the surface indicated depletion in sulfur content and, therefore, a metal enriched surface (with \([\text{Zn}^{2+}] > [\text{Cd}^{2+}]\)). This metal-rich outmost layer can be assigned to the formation of complexes at the surface involving the cations (i.e., \(\text{Cd}^{2+}\) and \(\text{Zn}^{2+}\)) and groups of the polymer capping ligands [54–57] that compete with sulfide \((S^2–)\) ions. The relatively higher concentration of \(\text{Zn}^{2+}\) compared to \(\text{Cd}^{2+}\) at the QD surface is attributed to the hardness parameter derived from electronegativity, where \(\text{Zn(II)}\) forms more stable complexes with both oxygen and nitrogen than \(\text{Cd(II)}\). The stability of complexes of divalent ions in the transition metal series with chelators containing oxygen or nitrogen donors often follows the Irving–Williams order [58, 59]. Conversely, the concentration of sulfides at the surface of QDs is decreased by the repulsion of the anionic carboxylate groups of the CMCel polymer ligand. In addition, this ZnS-rich outmost layer may act as an encapsulating coating of wider bandgap over the homogeneous nanocrystalline “core” that physically separates the surface of the optically active core and reduces the number of dangling bonds that can act as non-radiative surface states that quench PL intensity [60, 61]. Hence, the XPS results evidenced that QD conjugates were produced with core-shell nanostructure composed of alloyed ternary \(\text{Zn}_{x}\text{Cd}_{1−x}\text{S}\) inorganic core and carboxymethylcellulose organic shell uniformly dispersed and stabilized in aqueous media as depicted in Fig. 8.

Zeta potential (\(\zeta\)) measurements evidenced the interaction of QDs with carboxylate groups at the nanoparticle–polymer interfaces and the role of these groups in the stabilization of the QDs. The measured \(\zeta\)-potentials were all negative values, \(-52 ± 5 \text{ mV (ZnS)}, -53 ± 6 \text{ mV (ZnCdS)}, \) and \(-56 ± 8 \text{ mV (CdS)}, \) lower than \(-72 \text{ mV of CMCel solution, probably because of metal complexes remained at the nanocrystal–polymer interface (QD–CMCel). In addition, these highly negative values (i.e., } \zeta ≤ −50 \text{ mV})\) indicated that the nanoparticles were electrostatically stabilized by CMCel carboxylate functional groups avoiding the growth and agglomeration of the nanocrystals, which is crucial for quantum-size confinement effects. Moreover, the morphological and stability features of these colloidal ZnCdS conjugates in aqueous medium were assessed by DLS analysis. Thus, the DLS results showed that the systems were produced with hydrodynamic diameters \((\text{H}\text{D})\) of 12.5 ± 1.3 nm, 11.8 ± 0.8 nm, and 8.0 ± 0.5 nm for ZnS, ZnCdS, and CdS, respectively. The \(\text{H}\text{D}\) is assigned to the sum of contributions from the inorganic QDs “core” and the CMCel organic “shell” of the conjugates, including the effect of solvation layers and the lateral extension of the capping ligands. The DLS measurements clearly indicated a lower volume of solvation for the CdS that may be associated with the type, extension, and/or stability of the \(\text{Cd}^{2+}\) chelate complex with chemical groups of the carboxymethylcellulose compared to \(\text{Zn}^{2+}\), which probably caused the higher contraction of the polymeric shell around the Cd-based QD inorganic core.

**Biological Characterization of Zn\(_{x}\)Cd\(_{1-x}\)-S QD Conjugates**

**Evaluation of Cytotoxicity by MTT Cell Viability Assay**

MTT (3-[4,5-dimethylthiazol-2-yl]-2,5-diphenyltetrazolium bromide) assay accesses the mitochondrial activity response of cells, which is suitable for evaluating the cell viability and cytotoxicity towards the QD conjugates. The results of MTT assay after 120 h of contact of the cells with ZnS, \(\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}\), and CdS conjugates at concentration of 10 nM are presented in Fig. 9A. It demonstrated that, within the statistical variation, no difference was found in the cell viability after 5 days of incubation with the ZnS and \(\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}\) conjugates when compared to the control condition validating the hypothesis of non-toxicity associated with ZnS and alloyed \(\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}\) conjugates. Conversely, for CdS samples, as previously reported in the literature [62, 63], an adverse reduction of approximately 30% of cell viability response (~70% viability) was verified, which was attributed predominately to the potential cytotoxicity caused by release of \(\text{Cd}^{2+}\). Therefore, it was demonstrated that the CMCel polymer played multiple functions for chemically stabilizing and rendering biocompatible ZnS and \(\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}\) conjugates. Moreover, the Zn-rich outmost surface of \(\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}\) conjugates, besides enhancing the optical properties compared to pure binary QDs (i.e., ZnS and CdS) as discussed in previous section, it may have also played a relevant role for improving the biocompatibility by hindering the contact of the Cd-alloyed core with the water medium and, therefore, impeding the release of \(\text{Cd}^{2+}\).

**Cellular Uptake of Zn\(_{x}\)Cd\(_{1-x}\)-S QD Conjugates by Laser Scanning Confocal Microscopy**

In the present study, as a proof of concept, the uptake process of \(\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}\) and ZnS QD conjugates by live cells was performed by laser scanning confocal microscopy. CdS conjugates were not tested as it has already proved to reduce cell viability by the MTT assay results discussed in the previous section. On the other hand, ZnS QDs have
been reported to be safe and non-toxic for in vitro endocyto-
sis and cellular imaging assays. Thus, for the cellular in-
ternalization assay, HEK293T cells were incubated for 1 h
with Zn$_{0.50}$Cd$_{0.50}$S and ZnS conjugates at final concentra-
tion of 500 nM. After this period of incubation, images
were captured using laser confocal microscopy for the pur-
pose of visualizing the internalization of the developed
surface-biofunctionalized Zn$_0.50$Cd$_0.50$S and Zn$_0.50$Cd$_0.50$S QDs.
Figure 9B shows that the Zn$_{0.50}$Cd$_{0.50}$S (A) and Zn$_0.50$Cd$_0.50$S (B)
conjugates were effectively internalized by HEK293T cells.
Based on these confocal microscopy images, it was verified
that Zn$_{0.50}$Cd$_0.50$S and ZnS conjugates were cytocompatible
as they penetrated through the cell membrane and were
found homogeneously distributed inside the cellular cyto-
plasm. Therefore, these findings combined with MTT
results highlight the suitability of using ZnS and alloyed
Zn$_{0.50}$Cd$_{0.50}$S QDs capped by CMCel ligand as fluorescent
nanoprobes for in vitro cellular imaging and labeling appli-
cations. Although it is a fascinating area of research, a more
in-depth investigation is beyond the scope of this work and
will certainly be subject of future studies.

**Photocatalytic Activity of Zn$_x$Cd$_{1-x}$S QD Conjugates for
environmental Applications**

Photocatalysis is a rapidly expanding technology for
wastewater treatment. For that reason, using a multi-
functional approach, here it is presented as a proof of
concept, preliminary tests using the ZnS and alloyed
Zn$_{0.50}$Cd$_0.50$S conjugates as nano-photocatalysts for the
degradation of methylene blue (MB) used as a model
organic dye pollutant under UV irradiation. The results of degradation efficiency and UV–vis spectra after 4 h of irradiation are summarized in Fig. 10A, B, respectively. Based on Eq. 2, it was found that ZnS conjugates bleached MB relatively faster (first-order rate constant $k = 0.37 \text{h}^{-1}$) than $\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}$ sample ($k = 0.27 \text{h}^{-1}$) within the first 2 h but with similar degradation efficiency ($58\% \pm 2\%$) after 4 h of photocatalytic test (Fig. 10A). As both conjugates presented equivalent QD sizes (i.e., 4.3 nm) and surface areas, the minor difference observed for the catalysis kinetics rate can be associated with the presence of a Zn-rich outmost surface layer in the alloyed QD ($\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}$). It is suggested that the wider bandgap surface layer of ZnS over the narrower bandgap $\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}$ nanocrystal decreased the density of surface defects (i.e., energy trap states) promoting faster excitonic recombination process inside the semiconductor core. Therefore, this diminution of charge carrier separation (i.e., electron–hole pairs) caused the reduction of generated reactive species crucial for the photocatalytic activity to degrade MB molecules.

**Fig. 9** MTT cell viability in vitro assay of conjugates. a MTT cell viability assay of HEK293T cells after 120 h of contact of cells with ZnS, $\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}$, and CdS conjugates. b Confocal microscopy imaging of the internalization of the (a) $\text{Zn}_{0.50}\text{Cd}_{0.50}\text{S}$ and (b) ZnS conjugates in the HEK293T cells (scale bar = 10 $\mu\text{m}$)
Analogously, it can be observed the reduction of absorbance associated with the color of MB at $\lambda = 664$ nm (Fig. 10B) caused by the photo-oxidation of the MB molecule, shifting the absorption peaks to lower wavelength (blue shift). This photodegradation is related to chemical species generated by electron–hole pairs ($\text{QD} + h\nu \rightarrow h^+ + e^-$) from irradiated QDs (i.e., ZnS or Zn$_{0.50}$Cd$_{0.50}$S, Fig. 10A, inset drawing). The oxidation mechanism is primarily governed by the valence band holes ($h^+$), which are powerful oxidants, and they can react with water or surface-bound chemisorbed hydroxyl groups (OH$^-$) producing hydroxyl radicals (OH•). Most organic photodegradation reactions utilize the strong oxidizing power of the holes directly or indirectly produced by excitation of nanomaterials [64–66]. It is reasonable to consider that this degradation of MB may have followed a double-stage process. Initially, the negatively charged CMCell polymer is likely to have attracted MB molecules (i.e., positively charged) leading to the adsorption process, which does not degrade or promote decolorization of MB. In the sequence, the photo-oxidation of the MB dye occurred by the photocatalytic process, which was enhanced by previous adsorption favoring the charge exchange at the conjugate-MB interfaces (i.e., $h^+/e^-$ scavenging).

Regarding to toxicity, some researchers have raised concerns about the environmental safety related to the use of nanomaterials composed with toxic elements such as Cd-containing QDs motivated by the possibility of photo-oxidation with eventual releasing of hazardous elements in the medium [67, 68]. However, despite the hypothetical possibility, it is not likely to occur in these alloyed conjugates because of the biocompatible organic shell encapsulating the inorganic core, the extremely low concentration of the metallic elements (i.e., from $\mu$m to nM), associated with the very low water solubility of their compounds (e.g., oxides, sulfates, hydroxides) minimizing eventual risk of contamination.
Thus, these results demonstrated that ZnS and Zn$_{0.5}$Cd$_{0.5}$S semiconductor conjugates were surface functionalized by carboxymethylcellulose using a novel green sustainable process, which can offer promising alternatives as nanoplatforms in environmental and biomedical applications.

Conclusions

In this study, it is presented the synthesis and characterization of new ternary alloyed Zn$_{x}$Cd$_{1-x}$S semiconductor QDs using carboxymethylcellulose as a biocompatible polymer capping ligand directly produced via eco-friendly colloidal process in aqueous media and at room temperature. XPS results evidenced the mechanism of stabilization of the Zn$_{x}$Cd$_{1-x}$S nanaolloys dominated by the chemical interactions of metal-rich surface (Zn$^{2+}$ > Cd$^{2+}$ > S$^{2-}$) with the carboxylates and hydroxyls groups of the polymer ligands. The EELS, TEM, XRD, and selected area electron diffraction analyses ruled out the formation of core-shell or multiphasic systems, demonstrating that homogenous Zn$_{x}$Cd$_{1-x}$S nanoalloys were produced with optical absorption and emission dependent on the concentration of Zn$_{x}$. In addition, it was observed that the composition of ternary Zn$_{x0.5}$Cd$_{0.5}$S$_{x}$ alloys improved the luminescence quantum yield compared to the pure binary systems (ZnS and CdS QDs). These optical properties of Zn$_{x}$Cd$_{1-x}$S nanoalloys were studied based on empirical model of Vegard’s law and chemical bond model (CBM), where the differences observed of the values were assigned to the bandgap structure of each system. Moreover, in order to provide insights about potential applications of these alloyed-QD conjugates, they were tested for live cell imaging and for photocatalysis of organic molecules. The results demonstrated that ZnS and Zn$_{0.5}$Cd$_{0.5}$S conjugates were non-toxic and behaved as effective fluorophores for in vitro imaging live human embryonic kidney cells (HEK293T) with confocal fluorescence microscopy. Additionally, these alloyed-QD conjugates presented photocatalytic activity for photodegradation of methylene blue, which was used as model organic industrial pollutant in water. Hence, composition-tunable optical properties of ternary Zn$_{x}$Cd$_{1-x}$S ($x = 0–1.0$) fluorescent alloyed QDs was verified based on a facile eco-friendly process. It is foreseeable that this class of alloyed fluorescent semiconductor nanocrystals offers several possibilities of bandgap engineering for multiple applications such as bioimaging and bioimaging in nanomedicine or as nano-photocatalyst for environmental purposes in water treatment.

Acknowledgements

The authors acknowledge the financial support from the following Brazilian research agencies: CAPES—Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (PRORJ-PRONEX2010-2014), FAPERJ—Fundação do Amparo à Pesquisa do Estado de Minas Gerais (PPM-00202-13:BQN-TEC 30030/ 12), CNPq—Conselho Nacional de Pesquisa (PQ1B—306306/2014-0: UNIVERSAL- 457537/2014-0), and FINEP—Financiadora de Estudos e Projetos (CTINFRA-PRONIFRA 2008/2010/2011). The authors express their gratitude to the staff at the Microscopy Center at UFMG for their assistance with TEM–EFTEM–EELS analysis and Prof. A. Bicalho for XRD experiments. The authors thank the staff at the Center of Nanoscience, Nanotechnology and Innovation-CeNano/CEMUCASi/UFMG for the spectroscopy analyses. Finally, the authors thank Universidade Federal de Minas Gerais—UFMG/PRPq for the financial support for the publication of this study (PRPq—02/2017).

Authors’ contributions

HSM carried out the experimental design and analysis and drafted the manuscript. AAPM carried out the synthesis, physicochemical characterization, and analysis of conjugates and drafted the manuscript. RLM carried out the synthesis, physicochemical characterization, and analysis of conjugates. AJC designed, performed, and analyzed TEM, SAED, EFTEM-EELS experiments. LCO designed, performed, and analyzed the photocatalysis experiments. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Publisher’s Note

Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Author details

1 Center of Nanoscience, Nanotechnology and Innovation – CeNano(2), Department of Metallurgical and Materials Engineering, Universidade Federal de Minas Gerais—UFMG, Belo Horizonte, Brazil. 2 Department of Chemistry, Universidade Federal de Minas Gerais—UFMG, Belo Horizonte, Brazil. 3 Federal University of Minas Gerais, Av. Antônio Carlos, 6627 – Escola de Engenharia, Bloco 2 – Sala 2233, Belo Horizonte, MG 31.270-901, Brazil.

Received: 4 May 2017 Accepted: 25 June 2017

References

1. Farber E (1960) A history of metals. Science 132:887–888
2. An L, Yu Y, Li X, Liu W, Yang H, Wu D, Yang S (2014) Dextran-coated superparamagnetic amorphous Fe–Co nanomagnet for magnetic resonance imaging applications. Mater Res Bull 49:285–290
3. Farle M (2017) Imaging techniques: nanoparticle atoms pinpointed. Nature 542:35–36
4. Ferrando R, Jelinek J, Johnston RL (2008) Nanaolloys: from theory to applications of alloy clusters and nanoparticles. Chem Rev 108:845–910
5. Qin Z, Zhang F (2013) Surface decorated Cd$_{x}$Zn$_{1-x}$S cluster with CdS quantum dot as sensitizer for highly photocatalytic efficiency. Appl Surf Sci 285:912–917
6. Ayleea DW, Suc W, Zhou H, Pan C, Huang B (2014) Composition-controlled optical properties of colloidal CdSe quantum dots. Appl Surf Sci 322:177–184
7. Shen S, Wang Q (2013) Rational tuning the optical properties of metal sulfide nanocrystals and their applications. Chem Mater 25:1166–1178
8. Zhou J, Yang Y, Zhang C-Y (2015) Toward biocompatible semiconductor quantum dots: from biosynthesis and bioconjugation to biomedical application. Chem Rev 115:11669–11717
9. Xu Q, Zhang Y, Tang B, Zhang C-Y (2016) Multicolor quantum dot-based chemical nose for rapid and array-free differentiation of multiple proteins. Anal Chem 88:2051–2058
10. Wang L-J, Ma F, Tang B, Zhang C-Y (2016) Base-excision-repair-induced construction of a single quantum-dot-based sensor for sensitive detection of DNA glycosylase activity. Anal Chem 88:7523–7529
11. Ma F, Li Y, Tang B, Zhang C-Y (2016) Fluorescent biosensors based on single-molecule counting. Acc Chem Res 49:1722–1730
12. Zhou L, Gao C, Xu W (2010) Simultaneous photoluminescence import and mechanical enhancement of polymer films using silica-hybridized quantum dots. J Mater Chem 20:5675–5681
13. Zhou L, Gao C, Hu X, Xu W (2010) One-pot large-scale synthesis of robust ultrathin silica-hybridized CdTe quantum dots. ACS Appl Mater Interfaces 2: 1211–1219
14. Zhou L, Gao C, Xu W, Wang X, Xu Y (2009) Biomacromolecules, enhanced biocompatibility and biostability of CdTe quantum dots by facile surface-initiated dendritic polymerization. Biomacromolecules 10:1865–1874
15. Archana J, Navaneethan M, Hayakawa Y, Ponnusamy S, Muthumadivelvan C (2012) Effects of multiple organic ligands on size uniformity and optical properties of ZnSe quantum dots. Mater Res Bull 47:1892–1897

16. Yu D, Du K, Zhang J, Wang F, Chen L, Zhao M, Bian J, Feng Y, Jao Y (2014) Composition-tunable nonlinear optical properties of ternary CdSe,Sn,Te (x = 0–1) alloy quantum dots. New J Chem 38:5081–5086

17. Bailey RE, Nie S (2003) Aligned semiconductor quantum dots: tuning the optical properties without changing the particle size. J Am Chem Soc 125:7100–7106

18. Zhong X, Feng Y, Knoll W, Han M (2003) Aligned Cd, Zn, Cd, Se nanocrystals with highly narrow luminescence spectral width. J Am Chem Soc 125:15359–15363

19. Wang L, Cao L, Su G, Liu W, Xia C, Zhou H (2013) Preparation and characterization of water-soluble ZnSe/CdSe/ZnS(core/shell) quantum dots. Appl Surf Sci 259:6703–6708

20. Regulacio MD, Han MY (2010) Composition-tunable aligned semiconductor nanocrystals. Acc Chem Res 43:6261–630

21. Adegoke O, Nyokong T, Forbes PBC (2015) Structural and optical properties of alloyed quaternary CdSe/CdTe core and CdSe/ZnS core-shell quantum dots. J Alloys Compd 615:443–449

22. Takayuki A, Chaaban TB, Aboulaich A, Mahiou R, Balan L, Medjahdi G, Schneider R (2016) Aqueous synthesis of Cu-doped CdZnSe quantum dots with controlled and efficient photoluminescence. J Lumin 175:193–202

23. S. Singh, Y. M. Sabit, D. J. Park, S. P. Selvakannan, A. Nafady, A. Esmaeizadeh-Kandjani, S. K. Bhargava, Easy, one-step synthesis of CdTe quantum dots via microwave irradiation for fingerprinting application, Mater. Res. Bull. (2017), in press.

24. Zhong KH, Han MY, Dong ZL, White TJ, Knoll W (2003) Composition-tunable Zn, Cd, Se nanocrystals with high luminescence and stability. J Am Chem Soc 125:8589–8594

25. Yin Y, Akiyasu AP (2005) Colloidal cadmium nanocrystals and the organic–inorganic interface. Nature 437:664–670

26. Eaton DF (1988) Reference materials for fluorescence measurement. Pure & Appl Chem 60:1107–1114

27. Schneider CA, Rasband WS, Elseeit KU (2012) NIH Image to Image: 25 years of image analysis. Nat Methods 9:671–675

28. Rajeshwar K, de Tacconi NR, Chenthamarakshan CR (2001) Semiconductor-based composite materials: preparation, properties, and performance. Chem Mater 13:2765–2782

29. Tongay S, Suh J, Ataca C, Fan W, Luce A, Kang JS, Liu J, Ko C, Teranishi T, Tachibana Y (2015) Origin of surface trap states in CdS quantum dots via microwaved thermal annealing and UV irradiation effects on structure, morphology, optical and surface properties of CdS, ZnS and CdS/ZnS quantum dots. J Mater Res 20:1696–1711

30. Mansur HS, Mansur AAP, Mansur HS (2013) Surface modified fluorescent quantum dots with neurotransmitter ligands for potential targeting of cell signaling applications. Colloids Surf, B 111:60–70

31. Mansur HS, Mansur AAP, Mansur HS (2013) Surface modified fluorescent quantum dots with neurotransmitter ligands for potential targeting of cell signaling applications. Colloids Surf, B 111:60–70

32. Ramanery FP, Mansur AAP, Mansur HS (2014) Green and facile synthesis of water-soluble ZnS quantum dots nanohybrids using chitosan derivative ligands. J Nanopart Res 16:5204

33. Mansur HS, Mansur AAPM, Curti E, de Almeida MV (2013) Functionalized-chitosan/quantum dots nano-hybrids for nanomedicine applications: towards biolabeling and biosorbing phosphate metabolites. J Mater Chem B 1:1696–1711

34. Mansur HS, Mansur AAPM, Curti E, de Almeida MV (2012) Bisconjugation of quantum dots with chitosan and N, N, N-trimethyl chitosan. Carbohydr Polym 90:189–196

35. Mannori DP, Malay L (1947) Stability constants of internal complexes. Nature 159:370–370

36. Reiss P, Protiere M, Liang L (2009) Core/shell semiconductor nanocrystals. Small 5:154–168

37. Li Y, Zhong H, Li R, Zhou Y, Yang C, Li Y (2006) High-yield fabrication and electrochemical characterization of tetrapodal CdSe, CdTe, and CdSeTe1-x quantum dots. Adv Funct Mater 16:1705–1716

38. Mansur HS, Mansur HS, Mansur AAP, A. S. R. Araujo, Z. P. Lobato, Beyond biocompatibility: an approach for the synthesis of ZnS quantum dot-chitosan nano-immunoconjugates for cancer diagnosis, Green Chem. 17 (2015) 1820–1830

39. Mansur AAP, Mansur HS, de Carvalho SM, Lobato ZP, Guedes MI, Leite MF (2016) Surface biofunctionalized CdS and ZnS quantum dot conjugates for nanomedicine and oncology: To be or not to be nanotoxic? Int J Nanomedicine 11:4669–4690

40. Chen X, Rangaiah GP, Zhao XS (2014) Photocatalytic degradation of methylene blue by titanium dioxide: Experimental and modeling study. Ind Eng Chem Res 53:14641–14649

41. Mansur AAP, Mansur HS, Ramanery FP, Oliveira LC, Souza PP (2014) “Green” colloidal ZnS quantum dots/chitosan nano-photocatalysts for advanced oxidation processes: study of the photodegradation of organic dye pollutants. Appl Catal B 158:159–3297

42. Punnose A, Dodge K, Rasmussen JW, Chess J, Wingett D, Anders C (2014) Cryotoxicity of ZnO nanoparticles can be tailored by modifying their surface structure: a green chemistry approach for safer nanomaterials. ACS Sustainable Chem Eng 2:1666–1673
67. Manner VW, Koposov AY, Szymanski P, Klimov VL, Sykora M (2012) Role of solvent-oxygen ion pairs in photooxidation of CdSe nanocrystal quantum dots. ACS Nano 6:2371–2377
68. W.J.H.M. van Sark, P.L.T.M. Frederix, D.J. Van den Heuvel, H.C. Gerritsen, A.A. Bol, J.N.J. van Lingen, C.M. Donegá, A. Meijerink, Photooxidation and photobleaching of single CdSe/ZnS quantum dots probed by room-temperature time-resolved spectroscopy, J. Phys. Chem. B 105 (2001) 8281–8284.