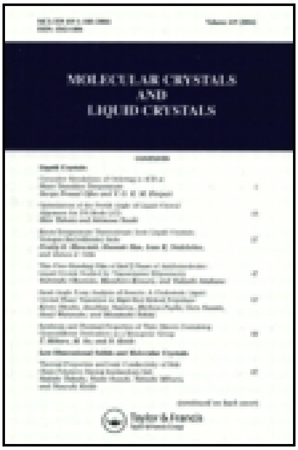

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Facile Preparation of Impurity Doped CdS Nanoparticles in New Polymeric Templates

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Cadmium sulfide nanocrystals (quantum dots) have been prepared using polymer solution as template. The new polymer is a vinyl acetate- maleic anhydride (VAcMA) copolymer obtained by using an original procedure developed in our laboratory.

The influence of composition and concentration of the polymer on the size and the optical properties of the semiconductor nanoparticles has been studied. The influence of the reaction parameter was also investigated in order to obtain a versatile procedure to prepare nanocrystals with tunable optical properties.

The reaction in polymeric matrix could lead to the formation of wide range of particle size (3–8 nm). In addition to modify the emission properties by controlling the particle size, CdS nanocrystals were doped with Zn, Cu and Mn ions. Both blue and red shifts of the maximum emission wavelength were recorded.

QD-polymer composites obtained from CdS nanoparticles prepared in VAcMA matrix have been investigated by UV-VIS, fluorescence and IR spectroscopy, TEM and DLS.

The photophysical properties of the semiconductor nanoparticles obtained in polymer matrix was compared for different QD-polymer composites, according to the obtaining procedure.

Keywords: CdS nanoparticles; photoluminescence; quantum dots-polymer composites

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INTRODUCTION

The semiconductor nanoparticles, known as quantum dots (QD) exhibit specific properties due to the quantum effects, as a consequence of their size in nanometric range: special luminescent properties caused by widening the band gap when the spatial dimension is reduced [1], different colors at different size [2], superior photostability [3]. Based on their unique properties, many industrial applications were developed for quantum dots in the last years in photovoltaics, multicolor LEDs, electronic memory devices, quantum dot based barcodes, chemical sensors. The special optical properties also recommend QDs for important biomedical applications in immunostaining, bioimaging, drug delivery systems, new generation photosensitizers in photodynamic therapy [4–5]. For biomedical applications there are some requirements to be fulfilled for semiconductor nanoparticles, the main important being water dispersability, high stability in biological fluids and biocompatibility.

The main challenge in preparing QD for biomedical application is surface functionalization to ensure water dispersability and reduce the toxicity without losing the photophysical properties.

The usual method to prepare semiconductor nanoparticles is wet chemistry technique, briefly co-precipitation of semiconductor material in homogeneous or nonhomogeneous media. The size and consequently the photophysical properties of QDs can be varied by using different method of preparation and templates: Langmuir-Blodgett films, microemulsions, vesicles, zeolites, glasses, polymers [6–17]. The most usual disperse systems used as heterogeneous medium is W/O microemulsion to be used as nanoreactor for the co-precipitation reaction. The main advantage is to control the size of the nanocrystals obtained by variation in size of the inner water droplets. But this method posses also a disadvantage, the yield is reduced and the semiconductor nanoparticles are difficult to be separated from the microemulsion [18,19].

An alternative to prepare QD with controllable size is to perform the co-precipitation in a polymeric matrix. The well defined polymer chains could play an important role in preventing the agglomeration of QDs during the growth process and also could offer a direct functionalization of the nanocrystal surface in order to passivate the QD surface and improve its optical properties. [20]. Another advantage could be the possibility that the final product could be very easy be casted in thin films, because the QD – polymer composite material imparts favorable bulk mechanical properties to the nanocrystals.

In the last decade, the preparation of inorganic nanoparticles in polymeric matrix has attracted more attention because the organic–inorganic composites containing inorganic particles in polymer provide a simple method to obtain advanced materials integrating properties of both components [21]. Interesting optical properties such as electroluminescence and optical nonlinearity of some quantum dots-polymer composites are examples of the performances of such advanced organic-inorganic hybrid materials.

The encapsulation of quantum dots in polymeric shells is a common method to ensure the biocompatibility of the semiconductor nanoparticles, which are highly toxic in the pure form.

The aim of the present work is to obtain CdS QD by using a facile method of preparation in polymeric matrix. A simple method to prepare CdS nanocrystals with biocompatible surface is proposed, using a new polymer as a template. The optical properties of quantum dots were tuned by changing the size of nanoparticles and by using Zn and Cu as doping material.

EXPERIMENTAL

Materials

All inorganic reactants and solvents were analytical grade and used without further purification. $Cd(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 4H_2O$, $Na_2S \cdot 9H_2O$ were from Sigma. All solutions used in the preparation of semiconductor nanoparticles were freshly prepared and filtered through 0.45 μm pore size membrane before the experiments. The water used was double distilled, filtered with a 0.45 μm membrane filter (Millipore) and deaerated.

The vinyl acetate-maleic anhydride copolymer (VAcMA) was prepared as laboratory sample using an original procedure (data unpublished). The polymer was used in acidic form. The polymer is stored as 35% aqueous solution (stock solution).

Preparation of CdS and Doped CdS Nanoparticles

The method to prepared quantum dots was the wet chemistry route using the co-precipitation of Cd^{2+} and S^{2-} precursors in aqueous solution of the polymer. Polymeric solutions were prepared at different concentrations of VAcMA from the stock solution mentioned above.

Different amount of Cd^{2+} and S^{2-} precursors were dissolved in VAcMA solutions, under magnetic stirring at room temperature, in order to obtain reactants dispersed in polymeric matrix. The polymer solution with S^{2-} precursor was added into the Cd^{2+} solution under continuous stirring using magnetic stirring (900 rpm, 5 minutes) or sonication (Cole Parmer ultrasonic homogenizer 750 W with microtip, 5 minutes). The maturation of CdS nanoparticles was achieved by keeping the QD-polymeric dispersion 1 h under constant stirring rate. For some experiment stoichiometric amounts of Cd^{2+} and S^{2-} precursors were used in order to achieve a Cd/S ratio 1:1. To ensure the increase of the photoluminescence, a Cd/S molar ratio of 1.5:1 was used by increasing the quantity of Cd^{2+} solution and keeping the same quantity of S^{2-} solution.

To evaluate the influence of the polymer concentration different polymer solutions were prepared from the stock solution, in the range 0.1–5% (w/v). To investigate the influence of the reactant concentration suitable amount of Cd^{2+} and S^{2-} precursors were mixed in polymeric matrix to ensure reactant concentrations in the range $1{\cdot}10^{-5}$–$1{\cdot}10^{-3}$ M.

The mixed semiconductor nanoparticles $Cd_xM_{1-x}S$ (M = Zn, Cu) were synthesized in the same manner as the pure CdS nanoparticles. Zinc, and copper salts were added to the polymeric solution containing Cd^{2+} precursor, in the desired molar ratio, before the addition of the sulfide. Layered nanocrystals were intend to be prepared by adding Zn precursor in the dispersion containing CdS nanoparticles after 12 hours of aging, followed by the addition of suitable amount of S^{2-} precursor to complete the reaction.

Characterization of Nanoparticles

The dimensions of the nanocrystals obtained were determined by using TEM, DLS measurements and evaluation from the UV spectra.

The emission spectra of QD-polymer composites were recorded with a Jena spectrofluorometer equipped with two monochromators and a 450 W Xenon lamp as the excitation source. It is not necessary any correction of the spectra, due to the fact that VAcMA polymer does not emit excited at $\lambda = 350$ nm, the value used for the excitation of CdS nanoparticles. The absorption spectra in the range of 300–800 nm were measured using a Perkin Elmer UV-VIS spectrometer (Lambda 16 model).

TEM measurements were performed on a JEOL JEM 2010 transmission electron microscope operated at 200 kV. The sample were prepared by spreading a drop of diluted quantum dots-polymer solution on holley carbon covered 200 mesh copper grids and left to dry at room temperature. This procedure provides good sample coverage and very little nanocrystal agglomeration on the grid.

Dynamic light scattering measurements were performed with a Malvern instrument Zetasizer Nano ZS.

RESULTS AND DISCUSSION

The method proposed to obtain CdS nanoparticles for biomedical applications is based on the co-precipitation reaction in an aqueous solution of vinyl acetate-maleic anhydride copolymer (VAcMA). The chemical structures of the original copolymer and the acidic form used in the present study are presented in Figure 1.

One can presume more advantages of the proposed one-pot method for QD synthesis in polymeric matrix:

- Polymeric chains could prevent the agglomeration of QDs during the growth process.
- direct functionalization of the nanocrystal surface in order to passivate the QD surface and improve its optical properties.

The orderly sited $-COO^-$ groups provided a major contribution to the well dispersed ions from the precursors. We suppose that both molecular chain and electrostatic repulsions are acting to prevent the aggregation of the nanoparticles during their growth. The presence of polymeric chains allows the obtaining of stable QD-polymer composite material.

Particles with different size and consequently different optical properties were obtained modifying the parameters of the preparing procedure.

The dimensions of the obtained nanoparticles were checked by using TEM, DLS measurements and theoretical evaluation from UV spectra.

The TEM image of CdS-VAcMA polymer composite show nanoparticles with size in the range 3–6 nm according to the specific condition of fabrication (Fig. 2 is an example of CdS nanoparticles prepared in 1% VAcMA polymeric solution, at $1 \cdot 10^{-4}$ M concentration of precursors, magnetic stirring procedure).

The dimensions determined from TEM images are consistent with the results of those calculated from the UV spectra.

The specific band in the CdS spectrum centred around 340 nm is due to the first (1s–1s) transition band and it is characterized by the

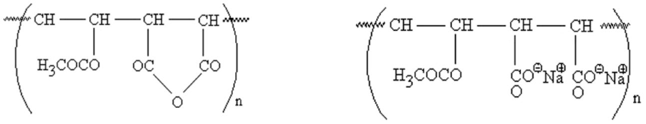
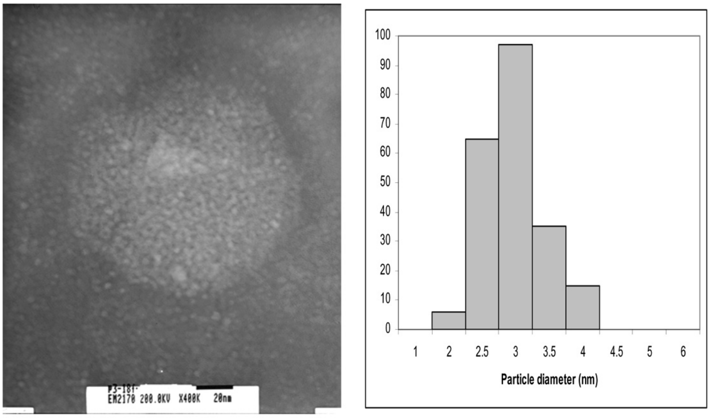


FIGURE 1 Chemical structure of anhydride and acid form of VAcMA copolymer used.



(a) (b)

FIGURE 2 TEM image of CdS – VAcMA polymer composite (a) Histogram of the particle size distribution corresponding to the micrograph (b) Concentration of the polymeric solution 1%, concentration of Cd^{2+} and S^{2-} precursors $1 \cdot 10^{-4}$ M. Cd/S molar ratio = 1:1.

threshold wavelength or absorption onset λ_s. Estimation of the CdS nanoparticle size from UV spectra was made using the well-known relation between the threshold wavelength λ_s and the nanoparticle size [22–25]. For a better evaluation of the value of threshold wavelength λ_s the UV-VIS spectra are analysed by representing them according to the equation:

$$(A/\lambda)^2 = K(1/\lambda - 1/\lambda_s) \qquad (1)$$

where A is absorbance and λ is the wavelength. K is an empirical constant [25]. From the graphical representation $(A/\lambda)^2$ versus $1/\lambda$ the value of λ_s is obtained from the intersection of the tangent drawn to inflection point with the baseline.

The particle size determined from DLS measurements show slightly higher values compared with those obtained from TEM images, due to the presence of the polymeric shell surrounding the semiconductor nanoparticles. From the histogram it is concluded that nearly monodisperse CdS nanoparticles are obtained, the same conclusion from the TEM images.

The VAcMA copolymer exhibit polycationic structure with –COOH groups regularly disposed on the macromolecular chain. The idea of the proposed obtaining procedure is to use the polymer as a template for the formation of the CdS nanoparticles and simultaneously capping the surface of QD with VAcMA. This allows the remained negative

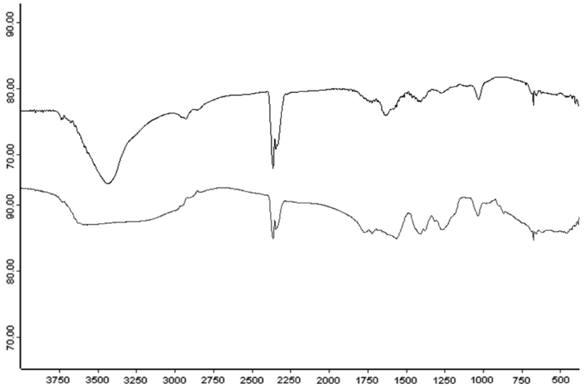


FIGURE 3 FTIR spectra of pure VAcMA copolymer (bottom) and CdS nanoparticles separated from the VAcMA polymeric template used for the reaction (up).

carboxyl groups to functionalize the surface and ensure the stability of the semiconductor nanoparticles.

The presence of the VAcMA copolymer on the surface of the CdS nanoparticles was checked on samples obtained by vigorously washing the QD-polymer composite. FTIR spectrum of CdS nanoparticles separated from the polymeric matrix (Fig. 3) is compared with the spectrum of pure VAcMA copolymer.

Specific signals for polymer are present. The peaks corresponding to the vinyl acetate region of the polymer are practically unmodified. The specific signals for maleic acid region, consisting in the peak at 3667 cm^{-1} (enlarged), corresponding to vibration of OH hydroxyl group exhibiting hydrogen bonds, become sharper and is shifted in QD-polymer, indicating the absence of the hydrogen bonds and an interaction with QD in this region.

Also the stretching vibration of carboxylate group, reflected as a peak at 1558 cm^{-1} in the pure polymer is shifted in QD-polymer composite. The changes in the FTIR spectra of CdS-polymer composite suggest that the location of CdS nanocrystals into the VAcMA polymer matrix is in the near proximity of carboxyl group.

The Influence of the Reaction Parameters on the Size and Optical Properties of the CdS Nanoparticles

The presence of the VAcMA copolymer, with a highly ordered structure of –COOH groups regularly disposed on the macromolecular chain it is presumed to act as a dispersing agent for the reactants, preventing the aggregation of CdS nanoparticles. Increasing the concentration of the polymer in the aqueous solution used as reaction media, while keeping the same concentration of the reactants results in a decrease in the size of the obtained nanoparticles, as it is shown in Figure 4.

The CdS nanoparticles prepared in VAcMA polymer matrix in concentrations greater than 0.5% are stable for 2 month under normal storage conditions (room temperature, dark).

To prepare CdS nanoparticle S^{2-} precursor solution in polymer was add into the polymeric solution containing Cd^{2+} precursor, under rapid mixing to ensure the homogenization of the reactants in the polymer matrix. Magnetic stirring or sonication with ultrasound homogenizer was used as mixing procedure, in both cases small CdS nanocrystals were obtained. Although, some differences in their size were observed when prepared at the same reactant concentrations (Table 1).

The optical properties of pure CdS nanoparticles prepared in VAcMA polymeric matrix depends on the size of the nanoparticles. In Figure 5, the absorption spectra of CdS nanoparticles prepared in VAcMA polymeric solutions are shown for various concentration of polymer.

A clear shift of the absorption onset is observed with the increasing polymer concentration. The position of the absorption edge for dispersions with CdS nanoparticles prepared in polymer are in the region of 425–460 nm, blue shifted compared to the 515 nm value for bulk CdS material indicating the quantum confinement effect [26]. In Figure 6 the fluorescence spectra of CdS nanoparticles in VAcMA polymer

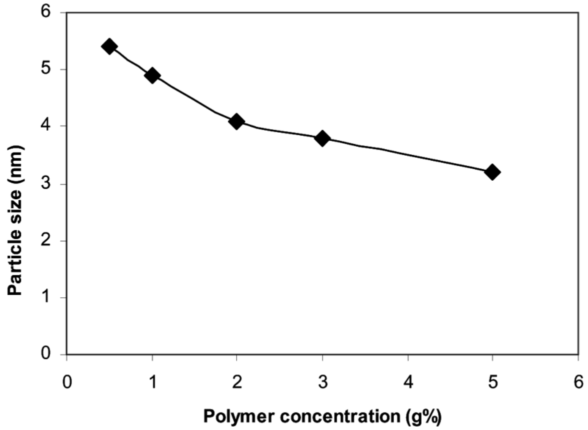


FIGURE 4 Variation of CdS nanoparticle size prepared in VAcMA solutions of various concentrations. Cd^{2+} and S^{2-} $5 \cdot 10^{-4}$ M, sonication method.

TABLE 1 Variation of CdS Nanoparticle Size Prepared in 1% VAcMA Solution Using Different Mixing Methods: (A) Continuous Magnetic Stirring; (B) Sonication = 5 minute Sonication, Growth 1 h Under Magnetic Stirring

Sample homogenization	Final CdS concentration mol/l	Particle size (nm)
A	$1 \cdot 10^{-5}$	3.9
A	$5 \cdot 10^{-5}$	4.7
A	$1 \cdot 10^{-4}$	4.9
B	$1 \cdot 10^{-5}$	2.8
B	$5 \cdot 10^{-5}$	3.3
B	$1 \cdot 10^{-4}$	4.2

solution prepared at various molar ratio of Cd and S precursors are presented.

As is it well known, the emission intensity and the efficiency are very sensitive to the nature of the nanocrystal surface. The surface nonstoichiometry, presence of unsaturated bonds, reflected in the presence of gap surface states lead to drastic changes in fluorescence intensity. The excess of Cd^{2+} ion on the surface leads to the significant increase in the intensity of the luminescence of the QDs obtained.

The use of VAcMA polymer as a capping agent it is presumed to prove an enhancement of the photoluminescent efficiency due to the possibility to reduce the number of dangling bonds on the nanocrystal surface, and to reduce the nonradiative recombination. QDs capped with polymeric chains show significant luminescent properties

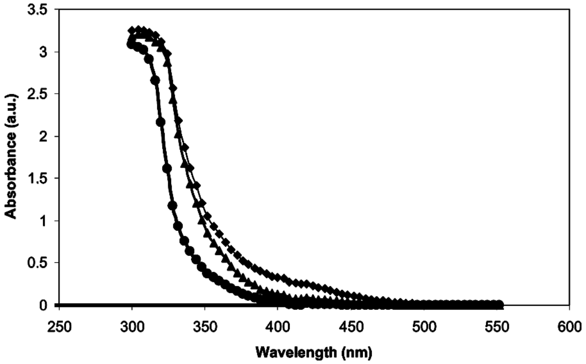


FIGURE 5 Absorption spectra of CdS nanoparticles prepared in VAcMA polymer solution (polymer concentration 5% (●), 2% (▲) and 1% (◆); Cd and S precursor concentrations $1 \cdot 10^{-4}$ M).

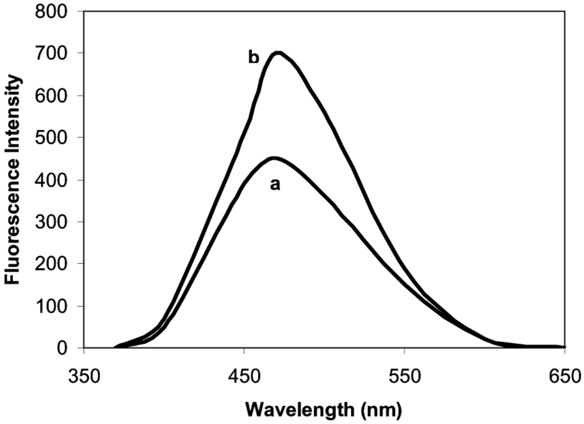


FIGURE 6 Emission spectra of CdS nanocrystals prepared in aqueous solution of VAcMA (10%) ($\lambda_{ex} = 350\,nm$); (a) Cd^{2+}/S^{2-} ratio 1:1; (b) Cd^{2+}/S^{2-} -{}$ratio 1 \cdot 5 : 1$.

dispersed in water. The maximum wavelength emission is blue shifted according to the size of the obtained CdS nanoparticles.

The photostability of CdS nanoparticles in VAcMA polymeric matrix was investigated in a regular condition stability test. Samples of CdS-polymer composites previous characterized form the point of view of size and fluorescence intensity were let to stand at room temperature, in dark conditions, in sealed vials. The ratio between the intensity of the fluorescence measured at various time and the fluorescence immediately after preparation IF_1/IF_0 was used as the parameter to describe the photostability. The CdS nanoparticles stabilized with VAcMA copolymer exhibits significant stability over a period of up to ten weeks for all precursor concentrations and polymer concentrations used in the present experiment.

Synthesis of Mixed $Cd_x M_{(1-x)}S$ Nanoparticles

To evaluate the possibility to tune the emission color of the QD by doping the CdS nanoparticles with various impurities, mixed nanoparticles were prepared. As dopant metal zinc or copper were used in various proportions to cadmium ions.

The bandgap increases as Zn is added in the composition of nanoparticles. For comparation purposes pure CdS and ZnS nanoparticles were prepared in the same conditions. Pure CdS nanoparticles were generated using magnetic stirring procedure, in VAcMA polymer 3% aqueous solution, Cd^{2+} and S^{2-} precursor concentration $5 \cdot 10^{-4}\,M$, molar ratio Cd/S = 1:1. To prepare mixed nanoparticles the reactant concentration was kept the same, using different ratio between Cd and Zn precursors.

In Figure 7, the emission spectra of pure CdS semiconductor nanoparticles and mixed (CdZn)S nanoparticles with different concentration of the impurity (in the range 0.25–0.75) are presented.

A significant shift of the donor-acceptor band to shorter wavelengths is observed as increase the concentration of zinc derivative added. The size and size distribution of the samples are similar for the sample with mixed nanoparticles and those with pure CdS nanoparticles.

The absorbance spectra indicate a dramatic increase in the absorption strength for the mixed (CdZn)S nanoparticles compared to pure CdS (data not shown) for the same concentration of reactants. Mixed nanoparticles show a continuously tunable energy gap from pure CdS nanoparticles to single ZnS nanoparticles.

The variation of optical properties of CdS nanoparticles prepared in VAcMA polymer can be obtained preparing core-shell nanoparticles with CdS core surrounded by a ZnS layer. The layered QD could be obtained usually by growth of ZnS layer on a previous formed CdS nanoparticles. In the present experiment CdS nanoparticles were prepared in VAcMA polymeric solution at 1% polymer concentration and [Cd]/[S] ratio 1:1 at precursor concentration of $5 \cdot 10^{-4}$ M. The zinc salt was added to this dispersion after 12 hour, and further procedure is used to form the zinc sulfide layer. The zinc precursor concentration was varied in the range 10–30% form total (CdZn) content. For all

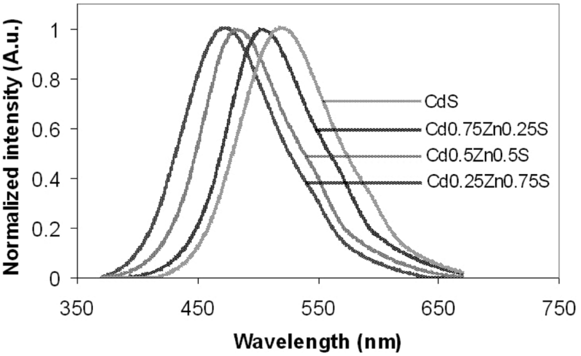


FIGURE 7 Fluorescence spectra ($\lambda_{ex} = 350$ nm) of mixed $Cd_x Zn_{(1-x)}S$ nanoparticles prepared in VAcMA 3%, reactant concentration $1 \cdot 10^{-4}$ M. The zinc precursor was added before the formation of CdS nanoparticles.

Cd/Zn molar ratio, the same blue shift of the absorption and emission band was obtained compared to the pure CdS nanoparticles (data not shown). The shift is much smaller than the one obtained for mixed $Cd_xZn_{(1-x)}S$ nanoparticles prepared by mixing cadmium and zinc precursor in the same polymer solution, before the sulfide derivative addition. The fact the absorption and emission band are also shifted to the higher energies suggests that using this procedure no ZnS layer can be deposited onto the CdS nanoparticles, so the obtained QDs does not have core-shell morphology. The exchange of Cd and Zn ions during the aging process after the zinc precursor is added could be the explanation of the morphology of the particles obtained.

An opposite shift that one obtained using zinc as dopant can be achieved by preparing CdS nanocrystals with copper impurities [27,28].

In Figure 8, the variation of the emission spectra produced by the presence of Cu in the mixed (CdCu)S nanoparticles is presented.

The absorption and emission spectra of mixed CdS particles containing copper impurities are red shifted, according to the content of Cu. It is reported in the literature [28] that the actual content of copper inside the mixed nanoparticles is significantly lower than the [Cd]/[Cu] molar ratio in the polymeric solution used in the preparation (the molar ratio depicted in the graphical representation of spectra). The absorption spectra (data not shown) indicate that the absorption onset is not significantly influenced by the presence of the copper in the mixed (CdCu)S nanoparticles, as expected, but in the emission spectra the red shift is observed. It is presumed that

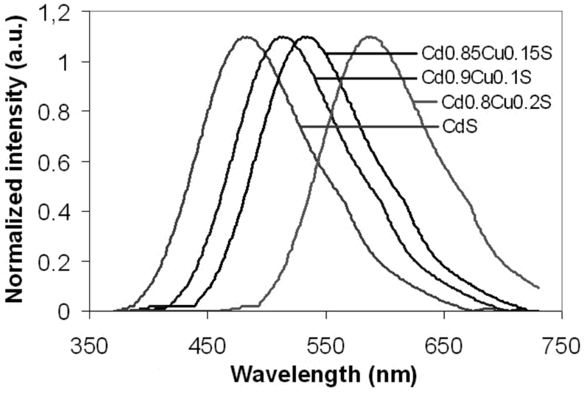


FIGURE 8 Fluorescence spectra of mixed $Cd_xCu_{(1-x)}S$ nanoparticles prepared in VAcMA 5%, reactant concentration $5 \cdot 10^{-5}$ M.

the copper ions incorporated into the CdS nanocrystals act as recombinant centers situated in the bandgap and produce the red shift of the emission.

The fluorescence spectrum of the mixed (CdCu)S nanoparticles prepared with low content of Cu as doping agent is broadened probably due to the presence of the emission of pure, undoped CdS nanoparticles.

CONCLUSIONS

Semiconductor CdS nanoparticles in the nanometric range have been successfully prepared using a new VAcMA copolymer as template. The presence of the polymer was effective in preventing the aggregation of nanoparticles during the growth process. The TEM, DLS and theoretical evaluation of size nanoparticles show that QDs obtained are nanometric sized and nearly monodispersed. The size, stability and luminescent intensity of the QD-polymer nanodispersions were shown to be dependent on the concentration of precursors, polymer concentration and mixing procedure.

The optical properties depend to the size of the CdS nanoparticles. The maximum emission can be shifted by preparing impurities doped CdS nanoparticles. Mixed particles containing Zn and Cu as doping materials were prepared and corresponding blue and red shifts in fluorescence were obtained.

The photoluminescence stability of the QDs in VAcMA polymer is very high and the CdS-polymer composite materials are very stable from the kinetic point of view.

The proposed method offer a simple and reliable way to prepare semiconductor nanoparticles stabilized with polymer, providing biocompatible surface for the nanocrystals, suitable for biomedical applications.

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