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Procedures for Controlling the Size, Structure and Optical Properties of CdS Quantum Dots during Synthesis in Aqueous Solution

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Abstract We report an easy approach for the synthesis of CdS Quantum Dots (CdS QDs) with high luminescence and temporal stability through the reaction of Cd^{2+} and S^{2-} in the presence of mercaptoacetic acid (MAA) as a capping reagent in aqueous medium, under normal pressure and room temperature. The influence of several experimental variables, including temperature, pH, the Cd/S ratio and the Cd/MAA ratio, on the optical properties of the QDs obtained was studied systematically. The experimental results indicate that these variables play an important role in determining the size and state of the surface of the nanoparticles, and hence their luminescent properties and temporal stability. The general aspects of nanocrystal nucleation and growth in the synthesis of nanocrystals were studied. The best conditions for the synthesis of nanoparticles of high quality are also reported. The CdS nanocrystals obtained exhibited a narrow PL band, with reproducible room-temperature quantum yields.

Keywords CdS quantum dots, Nanoparticles · Synthesis · Quantum yield · Photoluminescence enhancement

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Introduction

Semiconductor Quantum Dots (QDs) are of outstanding importance owing to their extraordinary optical and electronic properties [1, 2]. Their composition and small size afford these dots extraordinary optical properties (high emission quantum yields, size-tuneable emission profiles, and narrow spectral bands) [3] that can be readily controlled by changing the size or composition of the dots in the synthesis procedure [4–7]. In addition, they possess excellent photostability (many orders of magnitude larger than conventional organic fluorophores) [8] and long fluorescence lifetimes (>10 ns).

Alivisatos and Nie simultaneously demonstrated that semiconductor QDs can be rendered water-soluble and can be conjugated with biological molecules. Those prepared at high temperatures do not have intrinsic aqueous solubility and hence their transfer to the aqueous phase requires the functionalization of their surface with certain ligands, which in turn serve as anchorage sites for biomolecules [9]. Thus, a broad range of methods for bioconjugating colloidal quantum dots has been developed [10–15] in diverse areas of application: cell labelling [16], cell tracking [17, 18], in vivo imaging [19], DNA detection [20, 21], and multiplexed beads [22].

Among the different semiconductor nanocrystals, CdS QDs have been widely studied owing to their size-dependent photoluminescence [23], the advances gained in the procedures used to prepare them [24–31], and their important fields of application in different areas such as nanomedicine, optoelectronics, solar energy, etc. With proper surface modification, core-shell CdS nanoparticles can be obtained with enhanced luminescence properties.

Despite the above, the lack of suitable synthesis methods for the production of the desired amount of high-quality QDs remained bottlenecked in this field [32]. Soumitra et al. [33] have shown that the nature of the solvent and the temperature and source of the CdS used play an important role in determining the morphology and size of CdS nanocrystals.

The synthesis in solution of these nanocrystals normally uses organic stabilizers to cover the surface atoms of the nanoparticles in order to control their rate of growth, but this method has some limitations because the QDs thus prepared cannot be used in biological applications owing to their hydrophobic nature. They must therefore be linked to hydrophilic molecules to render them water-soluble and hence biocompatible.

Parallel to the success in organic synthesis pathways, some alternatives have been developed for the preparation of CdS QDs using aqueous media [34]. In comparison with their synthesis in non-aqueous media, aqueous synthesis is more reproducible, less costly and the samples prepared in this way are soluble in water and, at the same time, biocompatible.

As may be seen from the above, there is currently great interest in proposing new advances in procedures aimed at the synthesis of high-quality CdS QDs. To date, most methods using aqueous media have resulted in low-quantum-yield products [35, 36]. Also, in many such procedures, there are gaps in in-depth studies of the characteristics of the nanoparticles obtained, the basis of later processes of covering and functionalization, and in the importance afforded to the effect of different variables involved in the process as regards their maintenance with time (an important aim for their manufacture and commercialization). Thus, in view of the broad sphere of possible applications this field is of great importance and involves multiple interests.

Here we report an easy preparation of water-soluble and high-quantum-yield CdS quantum dots in aqueous solution at room temperature. The mean diameter of the QDs synthesized depended on the experimental conditions under which they were collected and on the time elapsed since their synthesis. In the original solutions where they were synthesized they were live particles; they continued to evolve over time, altering not only their size but also the state of their surface and their stability as a dispersed phase. It was observed that their formation at low temperatures (4 °C) showed slow kinetics, such that the size of the QDs remained almost constant at 2 nm for 2 months.

The intensity of fluorescence emission of QDs synthesized in aqueous medium depended on their size and the state of their surface. Regarding the latter characteristic, it appears that the presence of a nanocortex of Cd(OH)$_2$ on the surface was very important, as reported in the experimental part. This fluorescence intensity is sufficiently long-lasting for the CQDs obtained to be used as tracers of species, both organic and inorganic, interacting with them. Quantum efficiency values higher than those reported in the literature for different synthesis procedures, in both aqueous and organic medium, were obtained

The QDs obtained were characterized by absorption spectrophotometry, fluorescence, X-ray and transmission electron microscopy studies, controlling all the variables affecting their size and properties in aqueous solution with a view to using them as biological markers and in other applications of interest. The results obtained allowed us to elucidate behavioral aspects in different media that could be attributed to the QDs themselves or other concurrent processes. In aqueous medium, it is possible to make CdS QDs of interest for any given specific application, follow their evolution under different conditions, know their manner of degradation in order to eliminate its or enhance it, depending on the aims pursued, and tailor-mold them to each specific bioconjugation application. All these aspects are crucial in the processes of applying QDs, among others in the rapidly emerging field of nanomedicine.

Experimental

Reagents and Solutions

All chemicals used were of analytical grade and were prepared with ultra-high quality deionized water.

Mercaptoacetic acid, HSCH$_2$COOH, 98% (Acros Organics). Aqueous solutions of the following reagents, prepared by direct weighing of the species indicated and dissolution in water until the desired concentration was reached: CdCl$_2$, (99%, Acros Organics), Na$_2$S, (90%, Acros Organics), NaOH (Scharlau), sodium hexametaphosphate (HMP), 0.022 M Na-(NaPO$_3$)$_n$-ONa (Scharlau). Polyethylenimine (PEI), 50%, M$_w$ 1300 (Sigma-Aldrich). Quinine sulphate, 10^{-5} M solution in 0.5 M H$_2$SO$_4$.

Instrumentation

Fluorescence spectra were measured using a Shimadzu Model RF-5000 spectrofluorophotometer, with a Model DR-15 controller unit and a 150 W Xenon lamp as a light source. The UV-visible absorption measurements of the samples were performed on a Shimadzu UV/Vis-160 spectrophotometer. The pH value of the solutions was measured with a Crison 501 pHmeter. Transmission electron microscopy (TEM) was performed on a ZEISS EM-900 device. X-ray powder diffraction (XRD) patterns were recorded on a Siemens D500 X-ray powder diffractometer equipped with graphite monochromatized high-

intensity Cu-Kα radiation ($\lambda=154.050$ pm). The refraction index of the samples was determined with an Abbé refractometer.

Synthesis of CdS Quantum Dots in Aqueous Medium

The general procedure for the synthesis of CdS nano-particles in aqueous medium was as follows: The starting volume was always 100 mL of a solution containing the Cd^{2+} ions at the desired concentration, prepared by weighing $CdCl_2$ dissolved in distilled water. This mixture was placed in a round three-necked topaz flask subjected to stirring, and the desired microliter amounts of a solution of 1.14 M mercaptoacetic acid were added. The pH of the resulting solution was in the 2.8–3.0 range (depending on the amount of acid added, $K_1=2.1\times10^{-4}$).

The pH of the solution was adjusted with 1 M NaOH. At that time, nitrogen was bubbled through the solution, maintaining this throughout the experiment, and temperature was adjusted. Under stirring conditions, 50 mL of Na_2S was added at the desired concentration. The time of addition of the sulphide ranged between 8 and 10 min, considering this moment as $t=0$ for the kinetic studies. The final pH was checked to control possible modifications. After slow addition of Na_2S no appreciable change in the solution was observed, whereas after 4.5 h the solution, apparently transparent, changed to a green colour, indicating that the process of nanoparticle formation, under the conditions used, exhibited slow kinetics even though the conditions were supersaturating. The MAA bound to the CdS nuclei prevents their growth, the nucleation rate predominating over the growth rate.

Periodically, the absorption spectra and the fluorescence excitation and emission spectra were recorded.

Results and Discussion

Absorption Spectrum

Figure 1 shows the absorption spectrum of the yellowish-green solution at 4.5 h after reagent addition.

The appearance of a band at 370 nm was due to the presence of CdS nanoparticles in which the electrons were confined quantically, being able to absorb electromagnetic waves of a given energy to carry out the electronic transitions through the empty bands of the semiconductor.

In the synthesis of QDs, the maximum of the absorption band is seen to better defined as their amount in solution increases and the distribution of the particle size around its mean size decreases. The value of the absorbance at 370 nm, $A=0.732$, is proportional, at that wavelength, to the amount or concentration of CdS nanoparticles, although
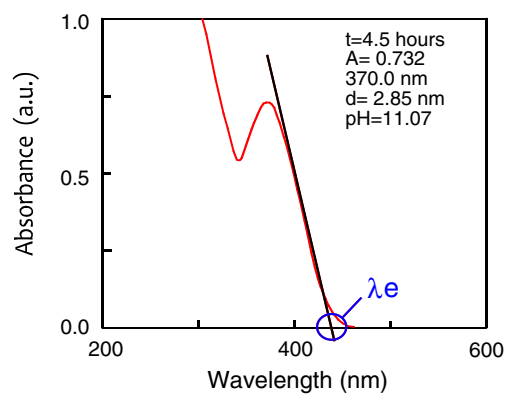

Fig. 1 Absorption spectra of the CdS QDs at 4.5 h after the collection process

the absorption coefficient depends on particle diameter. For wavelengths shorter than 360–370 nm, a non-specific band was seen, due to more energetic electronic transitions.

It is possible to obtain the mean value of the diameter of the QDs without using diffractograms by applying the HENGLEIN equation [37, 38], which relates it to the extrapolated wavelength, λ_e, and is obtained by tracing the tangent to the absorption curve on the ascending segment and is clearly differentiated from the zero absorbance value (Fig. 1):

$$2R = d = \frac{0.1}{(0.138 - 0.0002345\lambda e)}$$

In the present case the value of d obtained was 2.85 nm.

Fluorescence Spectra

Figure 2 shows the excitation spectra of the CdS QDs at 4.5 h after synthesizing them at the optimum λ_{em} (528 nm). An excitation band, not excessively broad, with a maximum at 392 nm was obtained.

Once the optimum λ_{ex}, determined experimentally at 392 nm, had been obtained, the emission spectrum was recorded (Fig. 2); this determines the maximum emission intensity at 521.6 nm (optimum λ_{em}). As seen in ensuing experiments, the emission wavelength depended on nanoparticle diameter, on the intensity of the emission process, and on the state of the NP surface.

The completely symmetrical shape of the emission spectrum indicated that the losses of energy due to non-radiant processes were independent of the emission wavelength in that range, showing that the surface of the QDs was very homogeneous, with no large imperfections, at least during this period of the life-time of the NP.

The width of the emission spectrum at half the maximum value of the intensity of fluorescence emission (to If=244 u.f.), called Δ, had a value of 104 nm. This value is indicative of the greater or lesser size distribution of the NPs around the mean
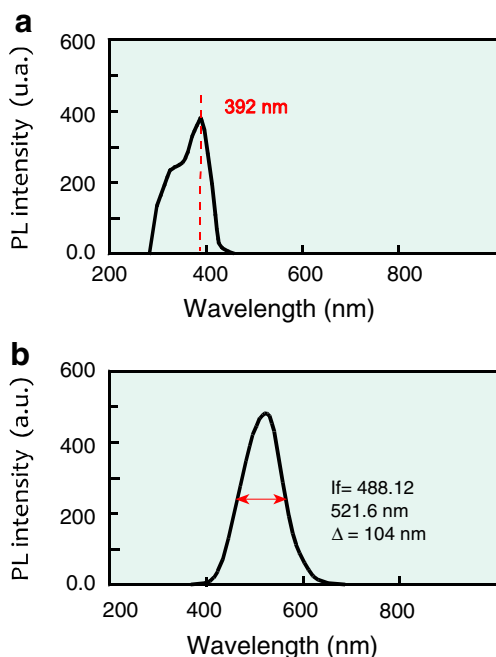
Fig. 2 Photoluminescence behaviour of the CdS QDs at 4.5 h after collection Rex=Rem=5 nm. **a** Excitation spectrum setting λem at 528 nm. **b** Emission spectrum setting λex at 390 nm

diameter. The smaller it is (a narrower emission band), the smaller to size distribution (Gaussian, with a smaller standard deviation), indicating that the particles were more uniform as regards size.

This value, Δ, allowed a comparison to be made of the size distribution under the different experimental conditions and in the different phases of the lifetimes of the QDs. It should be mentioned that the value of Δ for the QDs obtained in organic medium ranged between 50 and 90 nm [39]

Effect of different variables on the size and photoluminescence properties of the QDs synthesized

Evolution of the QDs with time

When stirring of the QDs had been completed, 4.5 h after the end of the process of synthesizing them at laboratory temperature they were allowed to evolve with time in the absence of irradiation with light (topaz flask) and no stirring. Under these conditions, the CdS QDs stabilized with mercaptoacetic acid were dispersed in a solution containing S^{2-}, and mainly Cd^{2+}, ions, because the latter were initially in excess and moved according to their diffusion coefficient and could (theoretically) interact with one another to generate more precipitation nuclei or join those already formed to increase the size of the crystals.

Additionally, the Cd^{2+} ions may participate in other parasitic reactions different from the formation of QDs, such as (at the initial pH of 11) the formation of hydrated

oxides. When these appear, they are deposited on the surface of the QDs, since no turbidity was observed in the solution, and hence there was no precipitation of cadmium hydroxide, $Cd(OH)_2$, in the solution.

It should not be forgotten that CdS QDs are not static but dynamic, in the sense that they are involved in the balance with the species in solution in the processes of solubilization and growth of particle size.

The absorption spectra of the CdS QDs were obtained at different times of evolution, observing that the maximum of the absorption bands with time was increasingly less pronounced, with a flat shoulder between 350 and 370 nm. This cannot be attributed to the decrease in the amount of QDs in solution because the absorbance value in the zone of the maximum remained almost constant, with small variations between 0.695 (at 28 days) and 0.732 (at 4.5 h).

Moreover, the mean diameter of the QDs, d, obtained with the method described above only increased slightly from 2.85 nm to 3.0 nm, which is consistent with the fact that the wavelength of the absorption band maximum was not modified appreciably.

The phenomena addressed up to this point were accompanied by a decrease in the pH of the solution from 11.07 to 8.40, which persisted until day 21. This suggests the consumption of OH^- ions by the Cd^{2+} ions of the solution, to form hydrated oxides on the surface of the QDs, although at such pH values it is not possible to rule out the transformation of such hydrated oxides from the surface into hydroxylated species (an example would be $Cd(OH)_3^-$) or the solubilization of Cd^{2+} ions from the nanocrystals to mainly $CdOH^+$. The adsorption or co-precipitation processes occurring on the CdS surface could be of slow kinetics and could even cover the nanocrystal, forming a crust (nanocortex) of $Cd(OH)_2$.

Regarding the emission spectra of the aqueous solution containing the CdS QDs, their evolution was studied over 50 days. Initially, up to 44 h the intensity of fluorescence emission decreased slightly, not because the amount of QDs decreased—since the absorbance value remained constant-but because this phenomenon could be due to physical and chemical processes occurring on the surface of the QDs, modifying their morphology.

This alteration to the surface elicited an increase in the non-radiant emission such that the intensity of the fluorescent light emitted decreased. Also, this surface alteration was not homogeneous for all of the QDs; it seemed to depend on their size, since the width of the emission spectrum at half height, Δ, increased with time, size distribution with respect to the mean value, d (which remained almost constant), also increasing. As from 44 h, the smallest QDs increased in size, the larger ones becoming solubilized, such that the size distribution was reduced to values close to 104 nm. This was accompanied by a gradual and slow modification the surface of the QDs, leading the intensity of

fluorescence emission to increase considerably as time progressed up to day 24, after which a slight decrease was seen, accompanied by an increase in mean particle size up to 3.0 nm. However, this increase in size was so small that it did not alter the luminescence properties of the QDs since the emission maximum remained constant at 524.8 nm.

Influence of Temperature

The relationship between temperature, supersaturation and solubility is well known. Accordingly, a study was performed to determine the influence of this variable on the characteristics of the CdS QDs obtained. Seven solutions were prepared following the general procedure, allowing the solution to reach the desired temperature, When this temperature had been reached, and under nitrogen bubbling, 50 mL of a solution containing 0.075 millimoles of Na_2S were added. After a stirring time of 15 h, the absorption and luminescence spectra were recorded to compare the results obtained. Between measurements, the solutions were kept at 4 °C in a refrigerator.

Under these conditions it was possible to obtain information about the QDs collected upon maintaining the solutions used in the collection procedure at different temperatures; in all cases, the later evolution of the NP solutions occurred at 4 °C in the refrigerator, with no stirring. The fluorescence intensity at maximum emission initially increased with temperature up to 35 °C (Fig. 3), thereafter decreasing with the fall in temperature; all for the same time of evolution. This indicates that the shape and state of the surface is strongly influenced by the temperature of the solution, the latter affecting not only the kinetic aspects of the nucleation and growth but also the possible formation of a nanoshell of $Cd(OH)_2$ on the nanoparticle. Thus, there must be an optimum size of this nanoshell related to the radiant and non-radiant emission processes.
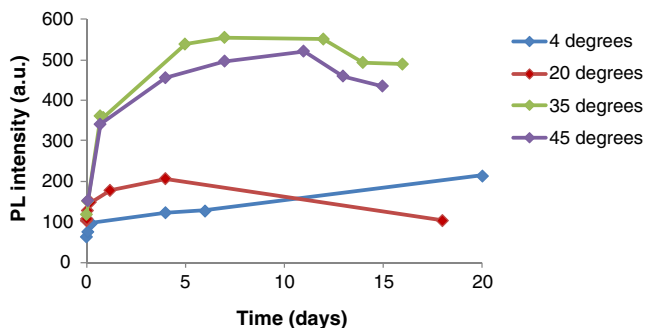

Fig. 3 Influence of temperature. Temporal evolution of PL intensity of CdS QDs synthesized at different temperatures (in degrees centigrade). The concentrations of reagents in the final solution were: $[Cd^{2+}]_f=1.0\times10^{-3}$ M; $[S^{2-}]_f=0.5\times10^{-3}$ M; $[MAA]_f=0.9\times10^{-3}$ M. The f subindex indicates the final concentration of each species
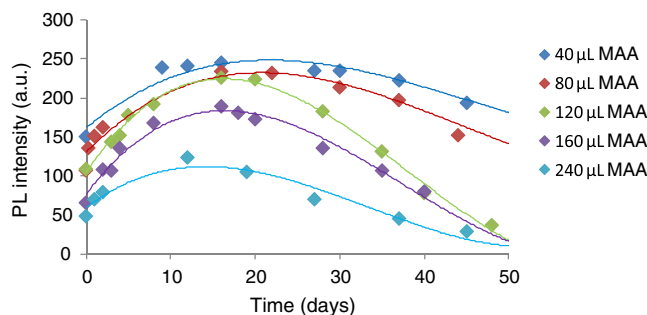

Fig. 4 Influence of the Cd/MAA ratio. Temporal evolution of PL intensity of CdS QDs synthesized with different Cd/MAA ratios

At temperatures higher than those shown in Fig. 3, according to the fluorescence spectra it was observed that the particles evolved rapidly in both size and their surface characteristics, such that their stability was low. It could not be ruled out that 90 °C some of the MAA (in the form of mercaptoacetate) could have been vaporized, leaving the nanoparticle surface with a lower amount of dispersant.

Regarding the maximum intensity of fluorescence and the stability of that parameter, the best results were obtained at 35 °C. Additionally, on controlling the temperature in the collection method and the time of evolution of the QDs it was possible to obtain nanoparticles of different sizes and with different luminescence properties.

Regarding the size distribution of the QDs with respect to the mean diameter, only at 70 and 90 °C was this clearly observed to increase, in agreement with the notion of the existence of aggregation processes.

Influence of the Molar Cd^{2+}/S^{2-} and Cd^{2+}/MAA Ratios

Since Cd^{2+}, S^{2-}, and MAA are the three main species involved in the formation of CdS nanoparticles and in their stability or dispersion, it is necessary to have knowledge of the influence of their molar ratios on the characteristics of the QDs. The influence was studied in two types of experiments:
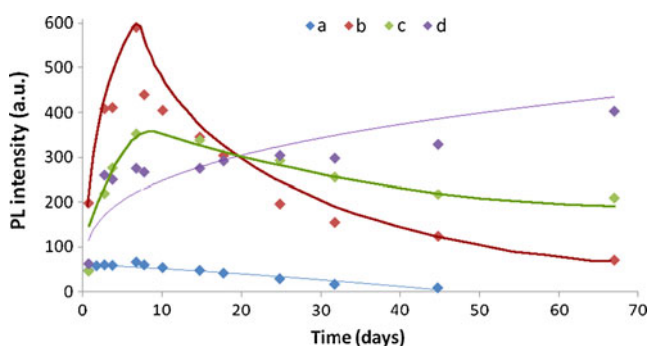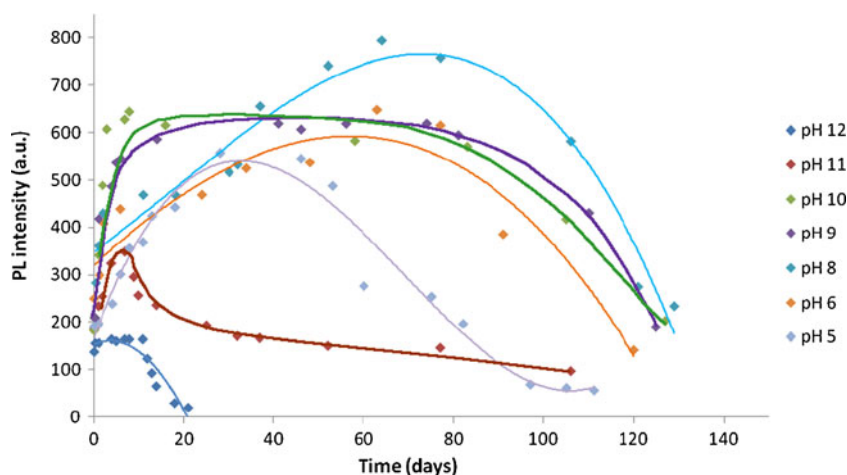

Fig. 5 Influence of the Cd/S ratio. Temporal evolution of PL intensity of CdS QDs solutions with different Cd/S ratios. a) Cd/S=1.3; b) Cd/S=2.0; c) Cd/S=2.7; d) Cd/S=4.0

Influence of the Concentration of Mercaptoacetic Acid. $Cd^2{}^+/S^{2-}$ Constant; Cd^{2+}/MAA Variable

Six solutions were prepared whose final concentrations of MAA varied between 0.2×10^{-3} M and 1.5×10^{-3} M ($Cd^{2+}/$MAA ratios between 4 and 0.3). The solution with the lowest concentration of MAA did not generate a fluorescence signal. A ratio of $[Cd^{2+}]_f/[MAA]_f=4$ was insufficient for the collection of fluorescent QDs.

In all cases, for each solution the emission intensity of fluorescence emission at its optimum excitation wavelength increased with the time of evolution until a constant value was reached (Fig. 4); this persisted for a few days (more days with increasing $[Cd^{2+}]/[MAA]$ ratios, because the MAA concentration was lower), thereafter decreasing progressively faster as the concentration of MAA was increased. This, together with the evolution of the mean diameter of the QDs over time, shows that at the same time as the CdS increased in size, losing quantum efficiency,

their shape and surface were also modified, contributing to such a decrease in quantum efficiency.

From a practical point of view, the best results concerning the fluorescence values and the time during which the QDs maintained such fluorescence were obtained for a $[Cd^{2+}]/[MAA]$ ratio between 1 and 2.

Influence of the Concentration Ratios of the Formers of Nanoparticles, with Cd^{2+}/MAA Constant and Cd^{2+}/S^{2-} Variable

For these experiments, we kept the $[Cd^{2+}]_f/[MAA]_f$ ratio constant and almost equal to 1 in all the solutions, varying the $[Cd^{2+}]_f/[S^{2-}]_f$ ratio between 0.7 and 4. The f subindex indicates the final concentration of each species.

The nanoparticles obtained under the conditions in which there was no excess of Cd^{2+} ($[Cd^{2+}]_f/[MAA]_f=0.7$ and 1) were large -between 3.9 and 4.0 nm- and were not fluorescent, which confirms the hypothesis that there must

Fig. 7 Influence of the change in the pH value on the already synthesized nanoparticles. Temporal evolution of PL intensity at different pH values
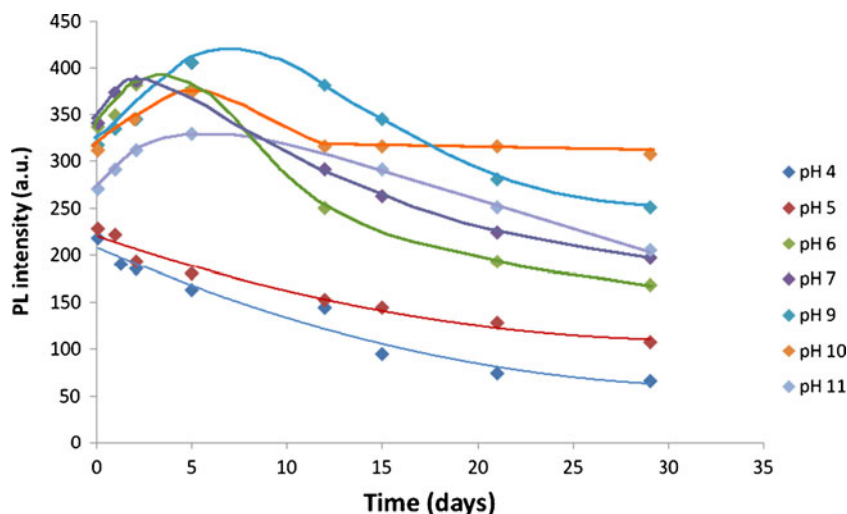
be a relationship between fluorescence and the Cd(OH)$_2$ nanoshell of a given size deposited on their surface. The maximum intensity of fluorescence (Fig. 5) was attained for an optimum relationship between the thickness of the nanoshell and the mean diameter of the QDs. If the nanoshell is a very thin deposit as compared with the mean diameter, only the transfer of electrons through it is improved, the quantum efficiency in the excitation-emission process being altered only slightly. When the nanoshell is thick in comparison with the particle diameter, the transfer of electrons through it in the excitation process increases, but in the process of the emission of radiation the non-energetic, non-radiant fraction increases. The intermediate situation—an optimum ratio between the thickness of the nanoshell and mean diameter- afforded the highest quantum efficiency.

Effect of the pH of the Medium in the Synthesis of CdS QDs

It was decided that this variable should be studied in two types of experiments:

Influence of pH in the Method Used for the Synthesis of CdS Nanoparticles

The procedure and conditions used were as follows: 105 μL of 1.41 M (0.148 mmoles) of MAA was added to a 100 mL solution containing 0.20 mmoles de Cd^{2+} under stirring conditions at 380 rpm. The pH of this solution, which was acid, was adjusted with 0.5 M NaOH in six experiments with a pH range from 5.2 to 11.0. Following this, nitrogen was bubbled through for 15–20 min, after which 50 mL of an Na$_2$S solution (0.075 mmoles) was added slowly. Under these working conditions, the final concentrations of the 6 different species and their molar ratios are shown in Fig. 6. It was observed that the results regarding nanoparticle size and the luminescence properties depended on the pH of the
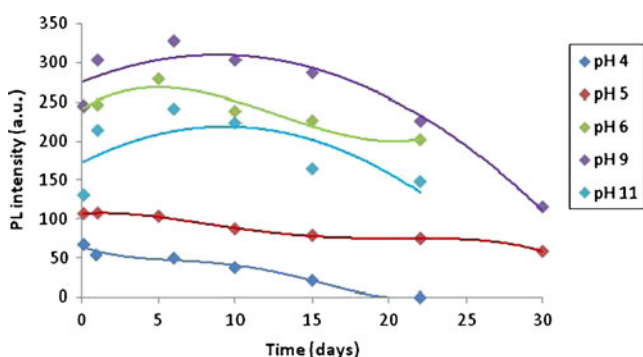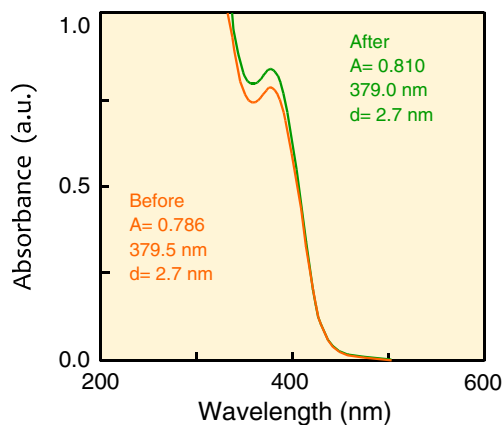
Fig. 9 UV–vis spectra of CdS QDs grown in aqueous medium at pH= 11, before and after the bubbling with oxygen

solution containing Cd^{2+} and MAA before the slow addition of S^{2-}.

There is a point in time at which for each pH value an optimum size ratio between a nanoparticle and the nanoshell is reached, when the joint structure reaches the maximum quantum yield and a maximum of the intensity of fluorescence emission value is attained. Scrutiny of Fig. 6 suggests that the optimum conditions for the formation of QDs with such quantum efficiency (a high intensity of fluorescence emission value) and stable for longer correspond to setting the pH value at 9 or 10.

Influence of the pH of the Medium Once the CdS Nanoparticles have been Formed

In the luminescent properties of CdS nanoparticles, a fundamental influence comes from the state of the surface, not only as regards their physical aspect but also their composition, and the species that are absorbed onto their surface are pH-dependent. As mentioned in the Introduc-

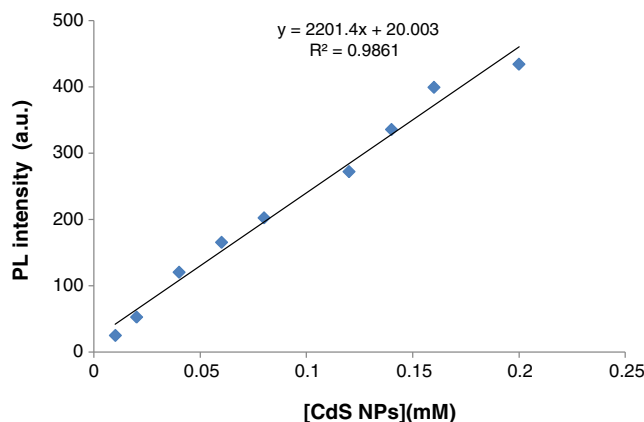**Fig. 8** Temporal evolution of PL intensity at different pH values of the nanoparticles synthesized with the recent CdCl$_2$ solution

Fig. 10 Effect of NP concentration on the PL intensity (λem=592 nm; excitation and emission slit widths: 5 nm)
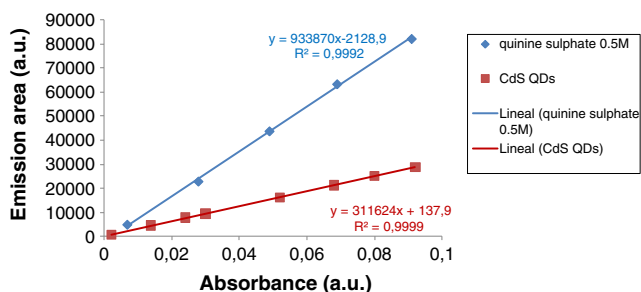
Fig. 11 Values of absorption against the values of integrated areas of the emission fluorescence spectra

tion, one future application is the use of nanoparticles obtained at the laboratory in biological media, which logically have pH values different from the medium used for collecting them.

It is important to know how the CdS nanoparticles obtained at the laboratory at elevated pH values above 10 will evolve when introduced into a medium with a different pH.

With this in mind, we carried out the synthesis following the general procedure described. The experiment was conducted at room temperature and during the time taken for the measurements temperature was maintained between 20 and 23 °C. Stirring was stopped at the exact moment of completing the addition of the Na_2S solution; the time considered $t=0$ for the studies of evolution. At that time, aliquots of 8 mL were collected and after adjusting pH from 4 to 10 with 0.1 M HCl volume was brought up to 10 mL topaz flasks.

According to the absorption spectra, the nanoparticles obtained under the above experimental conditions can be used in receptor media with pH values between 5 and 11, with only small alterations in their size (mean diameter), and they remain dispersed in the solution for at least 4 months.

Regarding luminescence properties, the nanoparticles obtained under the experimental conditions described, with a half-life of one hour, added to aqueous media with pH values between 4 and 11 did not maintain their capacity for fluorescence emission in the case of the

most acid media (pH=4 and pH=5), while they did in less acid media; the most favourable range was pH=6 and 11 (Fig. 7). In future experimental work addressing the markers of analytes in biological and biochemical media it will be necessary to take this kind of fluorescence behaviour over time into account in order not to commit certain experimental errors.

Influence of the Age of the Reagent Solutions

As indicated in the previous experimental studies, in all cases the Na_2S solution was prepared at the time of use in order to prevent the oxidation of S^{2-}, whereas the $CdCl_2$ solution was prepared and used as a stock solution for later studies lasting months. In order to check how the *age* of the Cd^{2+} solution affected the formation and development of CdS nanoparticles, the above experiment (exploring the influence of the pH of the medium once the CdS QDs had been formed) was performed, repeating all the steps of the procedure except the solution of Cd^{2+}, which was prepared at the same concentration but was used immediately after its preparation, and is the one we shall refer to as the recent solution.

The morphology of those spectra was clearly different; on comparing the same pH values the mean diameter of the QDs obtained with the recent solution was greater than that of those obtained with the older solution. This difference can be attributed to the presence of nanocrystals of $CdCl_2$ not dissolved in the recent solution, which acted as a support for the later growth of CdS nuclei.

The difference in size of the QDs and in their surface characteristics was reflected in differences in the luminescence properties of the nanoparticles obtained with the recent solution. Their fluorescence emission intensity values were lower (Fig. 8), although for each pH value they evolved in a way similar to the QDs obtained with the older solution (Fig. 7).

From this study it was concluded that, from the point of view of size and luminescence properties, in the process of nanoparticle synthesis it is preferable to use $CdCl_2$ solutions prepared some time previously (older solutions).

Table 1 Evolution of the values of Φ for NPs obtained with different Cd^{2+}/S^{2-} ratios

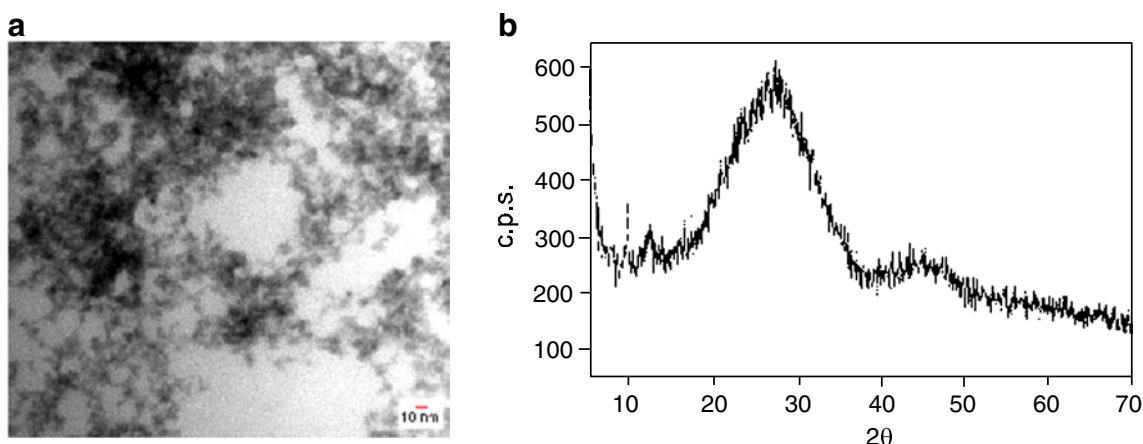| Φ_{CdS}				
t (days)	$Cd^{2+}/S^{2-}=1.33$	$Cd^{2+}/S^{2-}=2.00$	$Cd^{2+}/S^{2-}=2.70$	$Cd^{2+}/S^{2-}=4.00$
1	7.0	19	24.0	29.0
5	8.0	48	31.5	29.5
12	7.5	31	30.0	29.0
20	7.0	22	26.5	28.0
40	4.5	15	21.5	28.0
60	<1	10	17.0	31.0

Fig. 12 **a** TEM image of the as-prepared CdS nanoparticles and **b** Powder XRD pattern of the CdS QDs

Influence of the presence of oxygen in the solutions on the evolution of QDs

Using aliquots of the pH=11 solution, taken at different times of evolution, the effect of the presence of oxygen in the medium was assayed. O_2 was introduced into the solution by bubbling air through it for 30 min, to guarantee its saturation, using a membrane pump.

It may be seen (Fig. 9) that the presence of O_2 (recall that in the solutions there was an excess of Cd^{2+}) did not induce the formation of a nanoshell of $Cd(OH)_2$. Particle size was not altered, even in the presence of vigorous and irregular stirring, as occurs during bubbling. Neither did the surface of the nanoparticles undergo any alteration, since both the excitation and emission spectra and the maximum intensity of fluorescence emission were similar after the bubbling.

Influence of the Amount of QD on Intensity of Fluorescence Emission

The aim of using CdS nanoparticles is based on their luminescent properties as fluorescent tracers in biological media with a view to measuring an analyte after its chemical bonding to such nanoparticles.

In order to check whether there was proportionality between the CdS QDs concentration and their luminescence intensity, CdS nanoparticles were obtained at the laboratory using 100 mL of an old solution of 1.2×10^{-3} M $CdCl_2$, to which 8 μL of 14.1 M MAA was added, then adjusting pH to 11. Under nitrogen bubbling and stirring conditions, 50 mL of 1.5×10^{-3} M Na_2S was slowly added, after which the mixture was left to stand (maintaining the stirring) for 24 h. Exactly 28 h after completing the mixture of the reagents, 10 solutions at different concentrations were prepared by dilution of the original solution, pH=10.89, in which the mean size of the QDs was 2.9 nm.

It may be seen (Fig. 10) that there was direct proportionality between the concentration of QD and fluorescence emission, with a linear regression coefficient of R^2=0.9861 for a 95% confidence interval.

Quantum Yield

Room-temperature PL quantum yields (QYs) were determined by comparing the integrated emission of the QDs samples in water with that of a fluorescent organic molecule (such as quinine).

$$\Phi_x = \Phi_s(K_x/K_s)(\eta_x/\eta_s)^2 \tag{1}$$

In Eq. 1, x is the substance to be measured, s is the fluorescence standard, Φ is the quantum yield in percentage, η is the refraction index of the solvent employed in each solution, and K is the proportionality constant between absorbance and the corrected integrated area of the emission spectrum (its ratio should be linear, such that the constant is the slope, Fig. 11).

A quantum yield of 18% was obtained for the aqueous solutions of CdS QDs. Unlike organic fluorophores, the Φ value in QDs or QDs depends on several variables such as the experimental conditions used to synthesize them, which determine mean size of the QDs and the greater or lesser
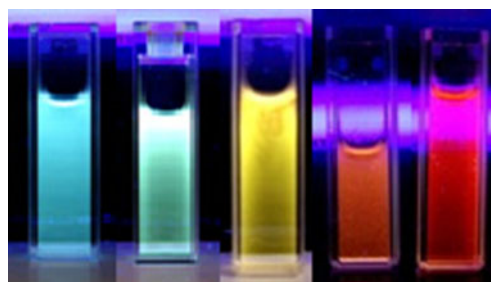

Fig. 13 Fluorescence of the CdS QDs of different sizes (from 2 to 5 nm)

capacity to form the nanocortex of Cd(OH)$_2$,, which in turn governs their luminescence properties. As confirmation of the above, Table 1 shows the values obtained in the calculation of Φ for solutions with different Cd^{2+}/S^{2-} ratios at different times of evolution.

Characterization of the CdS Quantum Dots

The shape of the CdS nanoparticles was studied with Transmission Electron Microscopy (TEM) after evaporating off the solvent (Fig. 12, on the left), and X-ray diffraction was employed to study the morphology of the CdS nanocrystals (Fig. 12, on the right). It was observed that they were β-CdS nanocrystals with a cubic crystalline network.

Conclusions

At room temperature, the mixture of aqueous solutions of CdCl$_2$ and Na$_2$S, in the presence of mercaptoacetic acid as a dispersant leads to the formation of a solution with a pH= 11, oversaturated in CdS, in which -after stirring- first nuclei and then quantum-sized (<10 nm) particles of the CdS semiconductor are obtained.

The QDs obtained, subjected to X-ray diffraction studies, were confirmed to be nanoparticles of β-CdS, with a cubic crystalline network, no other crystalline phases being observed in their structure.

Quantum size (<10 nm) was confirmed not only from the absorption spectra but also by Transmission Electron Microscopy.

At any given moment, the rate of nucleation and the growth rate govern nanoparticle size and also the state of their surface, although the importance of the excess of Cd^{2+} over S^{2-} was observed experimentally.

The size of the nanoparticles, their evolution with time, the state of their surface, and their stability depend on many variables, studied in depth in the present work. The mean diameter of QDs depends on the experimental conditions used to synthesize them. In the original solutions where they were synthesized, they were *live particles* that continued to evolve with time, not only their size but also the state of their surface and their stability as a dispersed phase being modified.

Regarding the fluorescence of the CdS QDs obtained in aqueous medium (Fig. 13), both the emission wavelength (greenish blue light to orange light) and the maximum intensity were found to depend on the mean size of the QDs and on the state of their surface. Concerning this second characteristic, the presence of a nanoshell of Cd(OH)$_2$ deposited on the nanoparticle seems to be very important, favouring the process of electronic excitation up to a maximum value of the nanoshell/nanoparticle size ratio,

above which the processes of the emission of non-dispersive light increases. This optimum size ratio depends on the experimental conditions employed and is reached at a given and variable time of development.

The fluorescence of the CdS QDs obtained in aqueous medium is sufficiently long-lasting for them to be used as tracers of both inorganic and organic species that interact with them.

The CdS QDs obtained under given experimental conditions and with different life-times behave as true analytical reagents, showing linear proportionality between intensity of fluorescence emission and the number of nanoparticles per unit volume.

The quantum yield of the luminescence process depends on the experimental conditions used to synthesize the QDs and their life-times, this being -for the best conditions- between 19 and 29% for a life-time of one day, and between 10 and 31% for 60 days. In general, higher quantum yields were obtained than those indicated in the literature for different procedures for the synthesis of nanoparticles in both aqueous and organic media.

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