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STUDY OF THE INFLUENCE OF MICROWAVE IRRADIATION UNDER CONTROLLED CONDITIONS ON THE OPTICAL AND STRUCTURAL PROPERTIES OF CdTe QUANTUM DOTS SYNTHESIZED BY ONE-POT SYNTHESIS

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We present the results of the systematic study of CdTe quantum dots synthesized in aqueous medium by one-pot technique. Allsamples were heated by microwave irradiation under controlled conditions such as, temperature, heating time, and vapor pression, in order to promote their luminescence. We found that the maximum luminescence was reached in colloids prepared with pH 8 and pH 9. The analysis by transmission electron microscopy exhibited the particular characteristic of thiol-capped CdTe quantum dots and their tendency to form aggregates. The nanocrystal morphology resulted in the truncated tetrahedral shape described by other authors and the mean nanocrystal size resulted between 2 to 5 nm. Analysis by electron diffraction indicated that the crystalline structure of quantum dots corresponds to the face centered cubical (fcc) structure of CdTe. According to optical spectroscopies of absorbance and photoluminescence, the crystalline growth was different for each sample group. Through these techniques, we found that the group of samples synthesized at pH 8 the crystalline growth depends of heating temperature and for the group synthesized at pH 9, the crystalline growth depends of heating time.

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1. Introduction

From the previous works of Ekimov [1], Efros [2] and Brus [3] begins the research field on colloidal quantum dots, also called semiconductor nanocrystals or simply nanocrystals. This meant the feasibility to synthesize semiconductor materials to nanometric scale with quantum confinement properties in solution, by using the precipitation phenomena through organic stabilizers of different lengths and diverse functional groups.

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That is how the research on colloidal quantum dots emerged as a promising area in materials science, with potential applications in light emitter devices [4], bioidentifiers [5], thermoelectric devices [6] and photovoltaics [7]. In the area of renewal energies, the processing of semiconductive nanocrystals offers the potential fabrication of solar cells of multiple excitonicgeneration, which would rise their energy conversion efficiency [8].

In the colloidal chemistry area, the most studied semiconductor material is CdTe. This material has a relatively large exciton Bohr radius (7.3 nm), as well as a band gap of 1.5 eV, which allows it to exhibit a stable and highly efficient luminescence in the visible range (500 ~ 730 nm), depending of the particle size [9]. Additionally, its high absorption coefficient in the visible (10^5 cm^{-1}) and the fact that its optoelectronic properties practically do not depend on synthesis methods, makes the CdTe a potential candidate in applications as bioidentifier [10], light emitting device [4] and photovoltaic cells [11,12].

Really, there is a large number of reports about the synthesis of CdTe in a great variety of organic solvents [13] and also in water [9]. However, due its low boiling point (100^oC), quantum dots synthesized in water were not considered to exhibit the same size dispersion nor the same crystalline quality than those dispersed in organic media [14] where reflux temperatures (200 ~ 400 ^oC) are applied. On the other hand, it should know that during the heating of sample in a traditional reflux system, the colloidal solution is not heated directly, its temperature will rise as the flask is heated up, forming a temperature gradient and consequently a non-uniform growth of nanocrystals. Also, reflux timing is determinant to modulate the nanocrystal size, which it can be too long when CdTe quantum dots have been synthesized in aqueous solution [15]. Due to this; synthesis, dispersion, size control and thermal treatment on quantum dots could be more efficient with a heating under microwave irradiation. However, there are just a few reports, not only of CdTe quantum dots, but any compound in general [16-21]. These works have proven the feasibility to obtain quantum dots with high luminescent efficiency and with a good size-dispersion in aqueous solution; however, we consider that has not yet reported a systematic study in a controlled environment, where a precise correlation between the physiochemical properties of quantum dots with the synthesis conditions and with the parameters of sample heating under microwave irradiation.

The present work has the intention of exhibiting the results of a systematic study about the synthesis, and the structural and the optical characterization of CdTe quantum dots dispersed in aqueous media, using 3-mercaptopropionic acid as a stabilizing agent. The synthesized samples were heated under microwave irradiation with water vapor pressure, temperature and heating time controlled. It was found that it is possible to modulate the nanocrystal size either in function of heating temperature or depending on the heating time. Likewise, the intensity of luminescence is related with the pH of sample.

2. Materials and methods

2.1. Materials

Cadmiun Chloride ($CdCl_2$, anhydrous ≥ 99.0% Fluka), Trisodium Citrate Dihydrate ($Na_3C_6H_5O_7$ $2H_2O$, Sigma-Aldrich), Sodium Tellurite ($NaTeO_3$, −100 mesh, 99% Aldrich), Sodium Borohydride ($NaBH_4$, ≥ 96.0% Aldrich), 3-Mercaptopropionic Acid ($C_3H_6O_2S$, MPA, Merck), Sodium hydroxide (NaOH, Fermon). All chemicals were used as received without further purification.

2.2. Synthesis of CdTe-QDs

The synthesis of CdTe quantum dots (CdTe-QDs) was realized by one-pot method reported elsewhere [22]. On a glass beaker 4 mL of $CdCl_2$ 0.04 mol/L were diluted in 42 mL of ultrapure water, and then trisodium citrate dihydrate (100 mg), Na_2TeO_3 (0.01 mol/L, 4 mL), MPA (119 mg), and $NaBH_4$ (50 mg) were added successively under magnetic stirring. The pH of the solution was adjusted by dropping aliquots of sodium hydroxide solution (1 mol/L) and afterwards, the sample is aged during 48 h. The molar ratio of Cd^{2+}/MPA/Te was 1:7:0.25. An aliquot of 10 mL of the resulting CdTe precursor solution was heated by using a specific vial (30 mL) in an Anton PaarMonowave 300 system, with a maximum power of 800 W. The power required for heating was regulated by the desired temperature. A series of CdTe-QDs were prepared at different temperatures, heating times and pH under microwave irradiation. After microwave irradiation, the mixture was cooled to a lower temperature than 55 °C and the sample was removed. Exhibiting photoluminescence (see Fig. 1).

2.3. CdTe-QDs characterization

Morphology, crystal structure and nanoparticle size of CdTe-QDs, were determined by transmission electron microscopy (TEM) using a FEI Tecnai G^2 F30 microscope, The nanocrystals solution were dropped on 300 mesh Lacey carbon grid and dried under laboratory conditions. The structural analysis was carried out by X-ray diffraction, employing a Panalytical Empyrean (45kV and 40 mA, λ = 1.5406 Å) diffractor. Optical characterization was realized by the techniques of absorbance and photoluminescence of the CdTe colloids at room temperature using a Thermo Fisher Scientific spectrometer, model Evolution 600 (400 - 900 nm) and Horiba Fluoromax 4 system, using a 150 W Xe lamp (200 – 950 nm), respectively.

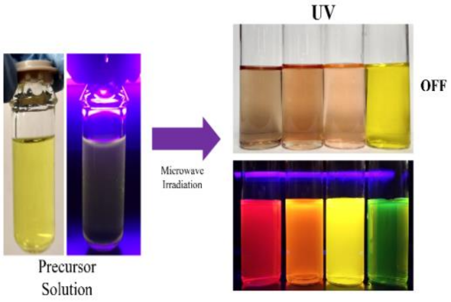

Fig. 1.Schematic procedure of the obtained CdTe-QDs.

3. Results and discussion

The Fig. 2 shows the TEM micrography of CdTe-QDs synthesized under microwave irradiation in the Anton Paar system. We can see that CdTe-QDs have the truncated tetrahedral shape described by Tang *et al.*[23,24], with sizes between 2 to 5 nm. This tetrahedral shape is a particularity of CdTe colloids estabilized in aqueous solutions with thiols [25-27], where the nanocrystals tend to aggregate [26]. On the other hand, it is not difficult to observe the atomic array and the interatomic spacing in the most nanocrystals,a particularity of CdTe, because its physicochemical properties are independent of the synthesis technique. In the same micrography of Fig. 2, we select a nanocrystal to determine its reciprocal lattice via Fast Fourier Transform (FFT), resulting the body centered cubical lattice (bcc) showed in the inset of Fig. 3. This means that the crystal structure of CdTe-QDs is the face centered cubical lattice (fcc), as has been reported in other works [28]. The structural analysis exhibited in Fig. 3 indicates that CdTe nanocrystals have an interplanar distance in [111] direction of 3.69 Å, practically the same result previously reported [29,15].

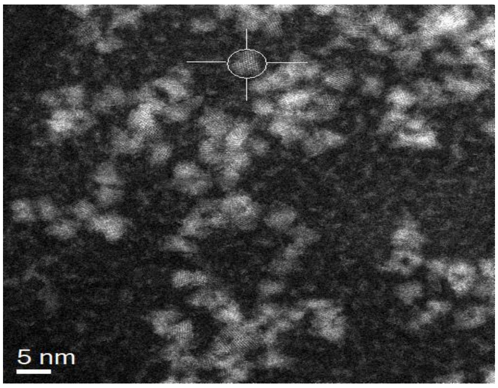

Fig. 2.TEM micrography of CdTe-QDs synthesized under microwave irradiation.

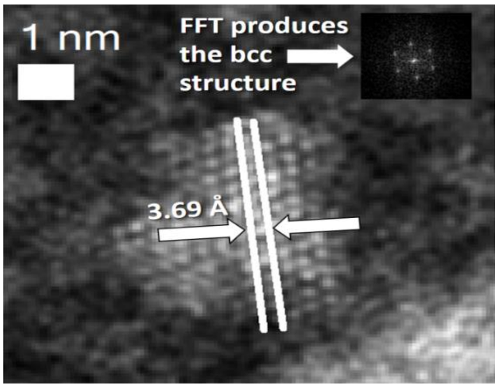

Fig. 3. Structural analysis of a selected nanocrystal showed in Fig. 1.

In order to get the diffraction pattern of CdTe-QDs, we cleaned the colloids using the separation size method [27]. The solid phase was dispersed in a 2 mL volume of deionized water and the CdTe-QDs were dripped on a glass substrate. The sample was characterized until the liquid phase was evaporated. About this process, we can say that nanocrystal manipulation was relatively simple, because only one cleaning process was required as result of the strong stabilization of QDs. Fig. 4 exhibits the x-ray diffraction pattern of CdTe-QDs, where we can observe three well defined peaks at 23.834^o, 44.447^o and 48.429^o corresponding to the (111), (220) and (311) reflections whit a high peak oriented in the (111) direction, revealing the formation of the face-centered cubical CdTe structure (group F-43m), according to the crystallographic JCPDS chart 03-065-8880. This result coincides with that found by TEM analysis, and also, additional phases was not found in the sample. The well defined x-ray pattern exhibited by CdTe-QDs is a consequence of their crystallinity due the thermal treatment under microwave irradiation, since nanocrystals are strongly dispersed. Unlike the traditional method, with the heating under microwave irradiation we can avoid that beaker warms up before the sample, which causes a temperature gradient and non-uniform crystal growth.

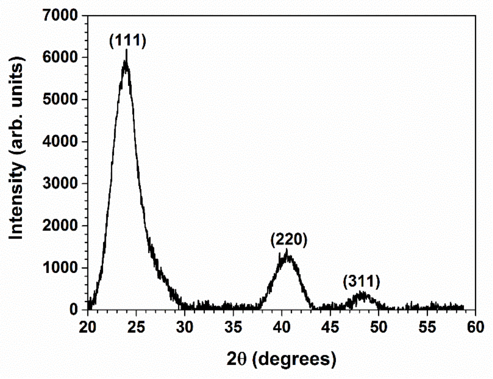

Fig. 4. X-ray diffraction pattern of a dripped CdTe quantum dots on glass substrate.

Precisely through the results of the optical characterization by absorbance and photoluminescence, we could verify that the crystal growth was nearly monodisperse as consequence of the strong stabilization and the optimal thermal treatment provided directly to each nanocrystal. After experimenting with various pH values in the colloidal samples, we found that samples that exhibit the highest luminescence correspond to pH values of 8 and 9, values that differ from those reported for MPA-capped CdTe-QDs, located in the acid range [30,31]. In Fig. 5, e. g., we have the absorbance spectra corresponding to a group of samples synthesized at pH 8. The peaks on Fig. 5 are attributed to the lowest energy exciton transition ($1S_h$–$1S_e$) of CdTe-QDs. [32]. It can observe that the position of excitonic peak is shifted to red as the temperature increases, due to the nanocrystal growth, so we have a correlation between heating temperature and nanocrystal size for samples synthesized at pH 8. The same correlation is observed in the photoluminescence, whose spectra are exhibited also in Fig. 5. Likewise, samples synthesized with pH 9, exhibited a similar behavior, but the redshift of the excitonic peak was based on heating time, (see Fig. 6).

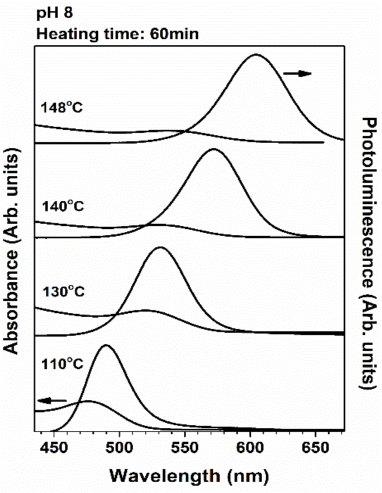

Fig. 5. Absorbance and photoluminescence spectra of CdTe-QDs synthesized with pH 8 and heating time of 60 min.

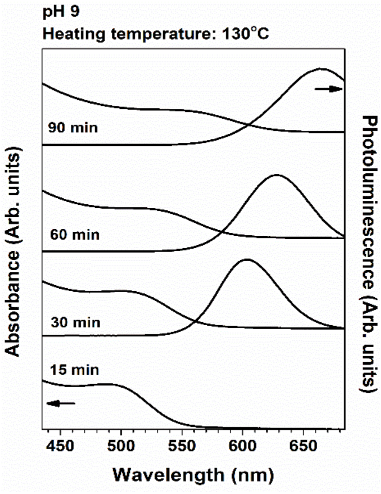

Fig. 6. Absorbance and photoluminescence spectra of CdTe-QDs synthesized with pH 9 and heating temperature of 130°C.

The results of the optical characterization analysis by absorbance and photoluminescence are showed in Table 1. The well-defined peaks observed both in absorbance and photoluminescence for samples with pH 8, exhibit a nearly monodisperse size distribution of CdTe-QDs, e. g., from the photoluminescence spectra, the minor value obtained for FWHM correspond to sample heated at 110°C (37 nm), a closely value to the reported for practically monodispersed CdTe colloids (25 nm - 35 nm) [27], then, this parameter was increased with temperature due to nanocrystal growth [33]. The maximum value matched in 58 nm (148°C). On the other hand, the highest values of FWHM were obtained for the samples synthesized at pH 9, whose excitonic peaks are broadened compared with pH 8 samples.

Table 1. Optical characterization results for the both groups of samples.

pH 8			pH 9		
Heating Temperature (°C)	**FWHM (nm)**	**Stokes Shift (eV)**	**Heating Time (Min)**	**FWHM (nm)**	**Stokes Shift (eV)**
110	37	0.21	30	59	0.27
130	47	0.17	60	65	0.26
140	54	0.16	90	81	0.26
148	58	0.17			

The Stokes shift is an indication of the surface protection of quantum dots, because if the position of the excitonic peak and the position of photoluminescence-maximum are separated, then the registered emission is not due to a band-to-band transition, but to a possible interband-interband transition [34]. The best values correspond to samples synthesized with pH 8, this means that the best surface passivation in nanocrystals is obtained by adjusting the pH solution at 8, therefore, samples with pH 8 are the most luminescent and nearly monodispersed.

4. Conclusions

We have made a systematic study of CdTe quantum dots dispersed in aqueous solution by one-pot synthesis and applying a thermal treatment by microwave irradiation under controlled vapor pressure, temperature, heating time and inert conditions. We found that microwave irradiation promotes the formation of high quality nanocrystals, with a well defined crystal structure and an effective surface protection, since microwave irradiation guarantees the direct heating of nanocrystals. The more quality samples were prepared with pH 8, exhibiting highest luminescence and nearly monodispersity. When it was thought that due to low boiling point (100°C), quantum dots synthesized in water were not considered to exhibit the same size dispersion nor the same crystalline quality than those dispersed in organic media where reflux temperatures (200 ~ 400 $^{\circ}$C) are applied, microwave irradiation under controlled conditions has allowed to obtain nanocrystals with the same structure quality and easily manipulated.

Acknowledgments

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