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Improvement of the luminescent properties of cadmium sulfide quantum dots by a post-synthesis modification

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ABSTRACT

Here the improvement of the luminescent properties of CdS quantum dots by a post-synthesis modification with aqueous solutions of NaOH at different concentrations is presented. The CdS quantum dots were synthesized by a microwave-assisted method using citrate ions as stabilizer. The addition of the hydroxide ions increased the intensity of the orange-red emission by about 80%. Besides, a violet-blue emission was achieved by means of this post-synthesis modification. The hydroxide ions control the precipitation equilibria of the CdS and $Cd(OH)_2$, dissolving and precipitating the surface of the quantum dots. The NaOH treatment increases the number of traps, which produces less band-edge and more deep-trap emission, which explains the decrease and increase in the intensity of the violet-blue and orange-red emissions, respectively.

1. Introduction

In recent years, the nanomaterials have attracted attention due to their unique chemical and physical properties. The nanometric semiconductors highlight, not only because their quantum confinement effects, but also because they can be incorporated in optoelectronic devices [1], photocatalytic processes [2], biological systems [3] and solar cells [4]. The II–VI semiconductors offer wide band gaps, which confers them great potential for a variety of applications [5]. Among the most studied II–VI compounds, cadmium sulfide (CdS) was shown to have large quantum confinement effects [6]. The CdS has three polymorphs: hexagonal wurtzite, cubic zinc blend and high pressure rock-salt phase [7]. Among these crystalline structures, hexagonal phase is the most stable in both bulk and nanometric systems while cubic and rock-salt phases are only present in nanometric systems [8]. This semiconductor exhibits a direct-band transition with band gap energy (E_g), for the bulk, of 2.53 eV [9].

Many reports have been published on the synthesis of CdS nanoparticles such as solvothermal process [10–12], sol-gel method [13–15], chemical vapor deposition [16–18], spray-pyrolysis [19–21], reverse micelle method [22–24] and biosynthesis [25–27]. Furthermore, the microwave-assisted synthesis is a facile and inexpensive alternative to produce CdS quantum dots with a narrow size distribution [9,28–30]. In general, the microwave-assisted methods offer advantages like high energy efficiency and short reactions times [31].

There are many reports focused on increasing the quantum yields of luminescent quantum dots. However, most of these studies involve modifications to the synthetic route, which restricts its application. On the other hand, if the improvement of the luminescent properties of quantum dots is carried out by a modification after the synthesis process, this modification can be applied to quantum dots regardless of the synthetic route used. In this way, Mićić et al. [32] and Talapin et al. [33] improved the photoluminescent properties of quantum dots by a treatment with HF; however, this material is difficult to handle safely.

The effect of the pH value before the synthetic process of CdS quantum dots was reported by Henglein et al. in 1987 [34]. They studied the effect of alkaline pH values on the intensity of luminescence of CdS quantum dots obtained by precipitation. The authors observed an increase in the orange-red broad emission of CdS quantum dots by about 50% and changed the color of the narrow emission from green (500 nm) to turquoise (490 nm) and blue (470 nm). Based on the above report, the NaOH is a safer alternative to improving the photoluminescent properties of the quantum dots.

In this work, we report the improvement of the luminescent properties of CdS quantum dots by a modification with aqueous solutions of NaOH at different concentrations after the synthetic process.

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2. Materials and methods

2.1. Materials and instrumentation

All the reactants and solvents used in this work were of analytical grade and used without any further purification. The different dispersions of CdS quantum dots were characterized by means of UV–vis spectroscopy, using a Perkin Elmer Lambda 12 spectrophotometer. Luminescence analyses were carried out in a Perkin Elmer LS 55 spectrophotometer. X-ray diffraction (XRD) pattern was carried out in a Siemens D5000 ($\lambda = 1.5418$ Å). The Fourier-transform infrared (FT-IR) analysis was carried out in a Perkin Elmer Spectrum One spectrometer. A Thermo Scientific iCE 3000 AA spectrometer was employed for the atomic absorption (AA) spectrometry.

2.2. Synthesis of cadmium sulfide quantum dots

Aqueous solutions of thioacetamide and cadmium chloride, both at a concentration of 30 mM, were prepared. These aqueous solutions were mixed in stoichiometric ratio, and the resulting solution was diluted to 50 mL with a 2.0 mM sodium citrate solution. The pH value was fixed at 8.0 with a NaOH solution. Finally, the reaction mixture was heated in a conventional microwave oven LG-intelowave at 1650 W for 60 s.

2.3. Post-synthesis modification of the cadmium sulfide quantum dots

The NaOH treatment is based on our previous report [9]. Firstly, 4 mL of a NaOH solution was added into 4 mL of colloidal dispersion of CdS quantum dots under vigorous stirring. The NaOH solutions were prepared in six different concentrations from 0.0050% to 1.0% w/v in NaOH. The percent of removed CdS quantum dots was calculated by means of AA spectrometry.

3. Results and discussion

3.1. Cadmium sulfide quantum dots

UV–vis absorption spectrum of the aqueous dispersion of CdS quantum dots is shown in Fig. 1. The value of the wavelength of the threshold of absorption is 447 nm, which corresponds to 2.77 eV, the E_g of the quantum dots. In comparison with the E_g value reported for the bulk, the decrement of this value indicates that the size of the CdS nanocrystals is less than twice the exciton Bohr radius (r_a) [35]. Quantum-size effects of Wannier excitons in semiconductor nanocrystals are manifest at different sizes for each semiconductor depending on their r_a value. In the case of CdS crystals, the reported r_a value is 2.9 nm [36]; nanocrystals smaller than this threshold size are considered quantum dots.

The Brus model [37] is a theoretical model based on quantum mechanics known as the effective mass approximation. The model expresses a relationship between the shift of the E_g (ΔE) and the crystal radius (r) described by the following expression:

$$\Delta E = (\hbar^2\pi^2/2r^2)(1/m_e + 1/m_h) - (1.8e^2/r\varepsilon) \quad (1)$$

where e is the charge of the electron, $\hbar$ is the reduced Planck's constant, ε is the dielectric constant and, m_e and m_h are the reduced masses of the electron and hole, respectively. The CdS nanocrystal radius was estimated at 2.3 nm, which is smaller than the CdS r_a value confirming the synthesis of CdS quantum dots. Besides, electron microscopic inspections of the CdS quantum dots have revealed that the aqueous colloid formed at values of pH around 8 had the most narrow size distribution [34].

The XRD pattern of the CdS quantum dots shows broad peaks, characteristics of very fine crystallite size phases, as shown in Fig. 2. The XRD pattern corresponds to the cubic structure of the CdS (JCPDS 10–454). The (111), (220) and (311) planes were observed at 26.3°, 43.8° and 51.9°, respectively.

Fig. 3 shows the luminescence spectrum of the CdS quantum dots recorded at 380 nm. The quantum yield of the CdS quantum dots is 0.014, this low value is due to the presence of traps. The highest emission intensity for the violet-blue and orange-red emissions is achieved at an excitation wavelength of 360 and 390 nm, respectively.

3.2. Improved cadmium sulfide quantum dots

The addition of the NaOH solutions into the colloidal dispersions of CdS quantum dots increases their intensity of luminescence. However, we found that some of these dispersions were unstable and precipitated. In order to quantify the removal percentage of CdS quantum dots, an AA analysis of the colloidal dispersions was performed. In this analysis we determined the amount of cadmium in the decanted after centrifuging the dispersions at 3000 rpm for 30 min. Fig. 4 shows a bar graph of the removal percentages of the CdS quantum dots in terms of the concentration of the different NaOH solutions; also a picture of the different colloidal dispersions of

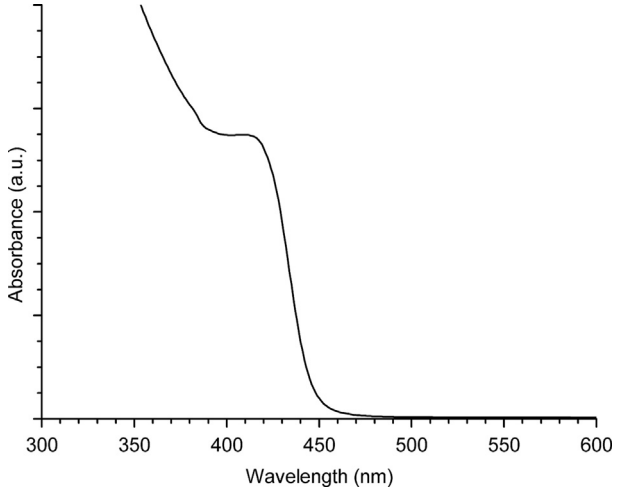

Fig. 1. UV–vis spectrum of the aqueous dispersion of CdS quantum dots.

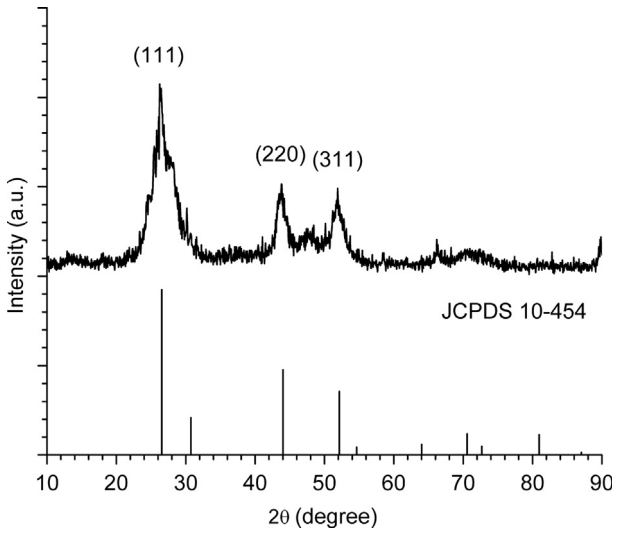

Fig. 2. XRD pattern of the powder obtained from the dispersion of CdS quantum dots.