Influence of 3D aggregation on the photoluminescence dynamics of CdSe quantum dot films

T. Alejo [a], Pedro M.R. Paulo [b], M.D. Merchán [a], Emilio Garcia-Fernandez [b,1], Sílvia M.B. Costa [b], M.M. Velázquez [a,*]

[a] Departamento de Química Física, Facultad de Ciencias Químicas, Universidad de Salamanca, E-37008 Salamanca, Spain
[b] Centro de Química Estrutural, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais 1, 1049-001 Lisboa, Portugal

ABSTRACT

Thin films of semiconductor CdSe quantum dots, QDs, directly deposited onto quartz as well as onto a Langmuir-Blodgett film of the Gemini surfactant ethyl-bis (dimethyl octadecyl ammonium bromide have been prepared and their photoluminescence properties were characterized by confocal fluorescence lifetime microscopy. 3D aggregates of QDs were observed in QD films directly deposited onto the solid while the Gemini surfactant film avoids the 3D aggregation. The photoluminescence decay analysis was performed by a phenomenological model previously proposed by us which considers that the luminescence dynamics is affected by energy transport and trapping processes and the relative contribution of these processes depends on film morphology. Thus, in the non-aggregated and more homogeneous QD films, QDs deposited onto the surfactant, the relative contribution of the energy transport process increases with trap concentration while 3D aggregation favors the energy transport even at low density of energy traps.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Semiconductor nanocrystals have a huge potential for application in biological research, photonic studies, and optoelectronic devices [1–4]. One of its most important classes is colloidal nanocrystals, such as CdTe and CdSe. Due to quantum confinement, these nanocrystals possess discrete electron and hole energy levels [5,6] and as a consequence, optical absorption occurs at discrete energies which are determined by the size and the shape of nanocrystals [2]. At low excitation density, light emission is due to decay of the lowest exciton state to the ground state. The possibility of tuning the exciton emission energy by the nanocrystal size or shape has led to a worldwide interest in light-emitting semiconductor nanocrystals. It is well established that the optoelectronic properties of quantum dots depend on the surface defects. [7] Moreover, in devices employing QDs deposited onto solids, surface defects play a dominant role in the photoluminescence properties. In this situation, the surface defects depend not only on the value of the surface area but also on the morphology of QD assemblies. In previous work we have analyzed the photoluminescence of CdSe QDs and styrene maleic

anhydride polymer films prepared by the Langmuir-Blodgett methodology [8]. We have chosen the Langmuir-Blodgett deposition methodology because it has provided good quality nanoparticle thin films [9–11] and offers the possibility of preparing reproducible films with control of the interparticle distance. Our results demonstrated that the photoluminescence dynamics are strongly affected by excitation energy transport and trapping processes and the efficiency of each process depends on the interdot distance and on the surface density of traps, which were related with QD clustering or surface defects. The results also pointed out that the photoluminescence of QDs should be increased by a homogeneous distribution of QDs in films and by minimizing the surface defects [8]. To confirm these assumptions, in the current work we compare the photoluminescence properties of homogeneously distributed QDs films with heterogeneous films of QDs directly deposited onto the solid substrate. To prepare homogeneous films, we transferred QDs from the air-water interface to a Langmuir-Blodgett film of the Gemini surfactant ethyl-bis (dimethyl octadecylammonium bromide). We use this deposition methodology since the surfactant film avoids the 3D aggregation of QDs which is obtained when nanocrystals are directly deposited onto the substrate [12–16]. In addition, the surfactant renders an almost continuous film of QDs distributed in an ideal hexagonal array [14].

---

* Corresponding autor.
E-mail address: mvsal@usal.es (M.M. Velázquez).
[1] Present address: Department of Physical Chemistry, Faculty of Pharmacy, University of Granada, Campus Cartuja, 18071 Granada, Spain

2. Experimental

2.1. Materials and methods

CdSe QDs capped with trioctylphosphine oxide (TOPO) were synthesized by the method reported by Yu and Peng [17] and described in more detail by Tomczak [18]. QDs were collected as power by precipitation and centrifugation with acetone. Centrifugation with acetone was used to wash the QDs in order to remove free capping ligands and other molecules of the synthesis medium. The process was repeated at least three times to remove all free ligand and molecules. All these molecules were separated of QDs power because they can be dissolved in acetone. The QDs thus obtained were dried under vacuum and the diameter $(3.55 \pm 0.05 \text{ nm})$ was calculated from the maximum position of the visible spectrum of QDs dispersed in chloroform and the extinction coefficient per mole of nanocrystals at the first excitonic absorption peak [19]. UV–vis absorption spectra of nanocrystal solutions were recorded on a Shimadzu UV-2401PC spectrometer. The stabilizer ligand (TOPO) remains attached to the QD surface after the purification and precipitation processes [20–22].

Gemini surfactant ethyl-bis(dimethyl octadecylammonium bromide), $(M_r=783.02)$ was synthesized using the method described by Zana et al. [23]. We introduced some modifications in the purification procedure to improve the product purity [12]. The degree of purity obtained by mass spectrometry was > 99.9%.

Filtered Chloroform (PAI) was supplied from Sigma Aldrich and ultra pure water used as subphase to build the Langmuir monolayers were obtained by combination of RiOs and MilliQ systems from Millipore. The solid substrate Quartz was supplied by Ted Pella (US) and prior deposition was cleaned by the RCA process [24] to remove organic residues from quartz substrates [25]. Briefly, the substrate was successively cleaned with acetone (PAI), ethanol (PAI) and water (Milli Q); then, it was submerged in 60 mL of a cleaning solution of MilliQ water, ammonia (25%) (5:1 vol/vol) and 10 mL of hydrogen peroxide (30%). The substrate was maintained during 15 min in the cleaning mixture at 70 °C. Finally, it was rinsed with abundant water (Milli Q) and dried under a stream of nitrogen.

2.2. Film preparation

The QD films were prepared by the Langmuir–Blodgett technique (LB) on a Langmuir standard-trough (KSV2000 System 2, Finland) placed in an antivibration table. QD Langmuir monolayers were prepared by deposition of the spreading solution of QDs (10^{-6} M) onto the water subphase with a Hamilton microsyringe with a precision of 1 μL. The subphase temperature was kept constant at (23.0 ± 0.1) °C by flowing thermostated water through jackets at the bottom of the trough. Monolayers were compressed by symmetric barrier compression until they reach a given surface concentration value with the quartz substrate dipped into the trough. The surface density was controlled by the surface pressure value measured with a Pt-Wilhelmy plate connected to an electrobalance. Films were transferred from the air-water interface to the solid by vertically dipping it upward (5 mm min^{-1}) at surface pressure value constant. Surface pressure–area isotherms of both components, CdSe QDs and Gemini surfactant, agree with those previously reported, [26,13]. The methodology and the experimental conditions employed for the bilayer preparation were previously reported [8,14].

Since it is necessary to eliminate spurious variations in the QDs emission quantum yield caused by solvent or dilution effects on the surface conditions of QDs, [21,27–29], we have used only one batch of synthesized QDs. Accordingly, the spreading solutions were prepared in chloroform with the QD powder obtained from a single extraction. The QD solution concentration was kept constant at 10^{-6} M.

2.3. Confocal Fluorescence Lifetime Microscopy (FLIM)

Surface photoluminescence measurements were recorded in a time-resolved fluorescence microscope (MicroTime 200, PicoQuant GmbH). A detailed description was previously reported [30]. In our measurements, the excitation source was a pulsed diode laser emitting at 482 nm with a repetition rate of 2.5 MHz. We used a water immersion objective 60× magnification with N.A. of 1.2 (UPLSAPO 60XW, Olympus). Samples are scanned with a piezo xy-stage. The emitted fluorescence was cleaned through a dichroic mirror and a bandpass filter with transmission in the interval $550 - 690$ nm. To reject out-of-focus light a pinhole of 30 μm was used. The emitted light was detected with single-photon counting avalanche diodes from Perkin-Elmer and digitized using TimeHarp 200 TCSPC PC board (PicoQuant GmbH). The fwhm of instrument response function was around 1 ns and the time increment was 150 ps/channel.

The experimental conditions were the same to those employed in the previous work [8]. Typically, the image scans cover an area of $80 \times 80 \text{ μm}^2$ and are composed of (256×256) pixels. To prevent photo-enhancement effects in QD emission we use an low integration time per pixel, 2 ms [31,32]. The excitation power remained constant at 108 W/cm^2 to minimize multiexcitonic processes. In this condition these processes do not exceed 3.1% of excitation probability [32,33]. The QD luminescence decay is intrinsically complex; therefore, the total number of detected photons per image amounted to a few million counts. On the other hand, the luminescence decays are integrated over the imaged area and can be retrieved from the photon arrival time histogram of all detected photons. The SymPhoTime software (PicoQuant GmbH) was used to analyze the experimental data with a multi-exponential function. Fits of decay curves to Eq. (1) was carried out on Matlab software [8]. The quality of the fits was evaluated by the χ^2 parameter and weighted residuals.

2.4. Atomic force microscopy (AFM)

AFM images of the LB films deposited on quartz were obtained in constant repulsive force mode by AFM (Nanotec Dulcinea, Spain) with a rectangular microfabricated silicon nitride cantilever (Olympus OMCL-RC800PSA) with a height of 100 μm, a Si pyramidal tip (radius < 20 nm) and a spring constant of 0.73 N m^{-1}. The scanning frequencies were usually in the range between 0.5 and 2.0 Hz per line. The measurements were carried out under ambient laboratory conditions.

3. Results and discussion

The Langmuir monolayers of different QD surface density were transferred from the air-water interface to a LB film of Gemini surfactant at 30 mN m^{-1}. The surface density was controlled by the surface pressure value. To analyze thoroughly the photoluminescence of QD/Gemini films, multiple fluorescence lifetime images were acquired on each film at different macroscopic positions. From a total of 5 images acquired per sample we have selected representative examples in Fig. 1.

Some dark areas are observed in the image of the lowest QD density (5 mN m^{-1}) and correspond to uncovered regions which are likely due to the low QD concentration. Qualitative information can be extracted from images; thus, when the QD surface concentration is increased, the film coverage increases, however, the image brightness related with the luminescence intensity,