Two-photon photoluminescence of a thin-film hybrid material based on CdSe(core)/ZnS/CdS/ZnS(multishell) semiconductor quantum dots

D V Dyagileva, V A Krivenkov, P S Samokhvalov, I Nabiev, Yu P Rakovich

1 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 115409 Moscow, Russia
2 Laboratoire de Recherche en Nanosciences, LRN-EA4682, Université de Reims Champagne-Ardenne, 51100 Reims, France
3 Centro de Física de Materiales (MPC, CSIC-UPV/EHU) and Donostia International Physics Center, 20018 San Sebastian, Spain
4 IKERBASQUE, Basque Foundation for Science, 48013 Bilbao, Spain

Abstract. Semiconductor quantum dots (QDs) are widely used as components of hybrid materials for development of efficient light emitters and converters. Their unique nonlinear optical properties, such as two-photon absorption and two-photon photoluminescence from biexcitons, make them promising materials for photovoltaic and optoelectronic applications. In this study, thin-film hybrid materials based on the CdSe(core)/ZnS/CdS/ZnS(multishell) QDs have been fabricated, and the two-photon photoluminescence (PL) from the generated biexcitons have been studied. The results show that fabricated thin-film hybrid materials based on the QDs are efficient fluorophores in the one- and two-photon PL regimes for applications in optoelectronics and biosensing.

1. Introduction
Semiconductor quantum dots (QDs) are widely used as the basis of hybrid materials for novel optoelectronic devices [1,2]. Their high photostability [3] and quantum yield (QY) of photoluminescence (PL) reaching 100% [4], allow one to consider these nanocrystals as one of the most attractive material in the fields of nanophotonics, nanomedicine, and nano-biotechnology [5]. An interesting feature is that, unlike traditional molecular fluorophores, single QDs can have two and/or more excited states [6]. Thus, QD can generate two excitons simultaneously [7]. Biexcitons (BX) is a second exciton in the same QD: they are known for the ability to produce two photons as a result of exciton/biexciton cascade recombination. This unique optical process makes QDs a promising material for optoelectronic applications in the field of entangled photons generation [8], which can be used for quantum cryptography [9]. However, the QY of BX in CdSe-core QDs, with traditionally used inorganic ZnS or CdSe shells, is only about 4-5% [10,11]. CdSe-core QDs covered with an improved multicomponent ZnS/CdS/ZnS shell-structure are known for their high quantum yields reaching the values up to 100% [4]. These QDs are characterized by the small diameters of about 5 nm, what distinguishes them from the giant shell QDs with much larger volumes. The improved energy structure of CdSe(core)/ZnS/CdS/ZnS(multishell) QDs can improve the QY of BX, what will expand the QDs application for entangled photons generation for the field of quantum cryptography. Thereunder, the main goal of this study was to investigate the optical properties of excitons and biexcitons in thin-film nanohybrid material based on CdSe(core)/ZnS/CdS/ZnS(multishell) QDs embedded in a polymer matrix.
2. Materials and methods

2.1. Quantum dots

The QDs with a CdSe core and ZnS/CdS/ZnS multishells were synthesized according to the two-stages procedure and dissolved in a hexane solution. The first stage corresponded to the synthesis of QD-cores. The QDs with the wavelength of the maximum of PL band at 560 nm should have a core size of 2.3 nm. The synthesis of QDs cores was carried out according to the method of high-temperature reaction between cadmium hexadecylphosphonic and selenides of trioctylphosphine. The choice of these reagents allows to achieve a high QDs homogeneity in size and shape. The synthesis was carried out in a high boiling non-polar organic solvent 1-octadecene at the injection temperature of 240 °C [14].

The second stage corresponded to the growing of the epitaxial shell with additional intermediate purification, which provided an additional increase in the monodispersity of the QDs ensemble. Further, the purified CdSe-cores with the sizes of 2.3 nm were coated with the multi-component epitaxial shell of ZnS/CdS/ZnS structure by the method of layer-by-layer ionic adsorption and reaction (SILAR) [15]. This method allowed us to control the thickness of the shell by accurately calculating the required amount of reagents. After completion of the reaction, QDs were purified by coagulation and dispersion. After growing the shell, the average size has been estimated from TEM images and was found to be about 5 nm. Figure 1(a) shows the PL and absorption spectra of the synthesized QDs. The PL decay curve recorded from a solution of QDs (Figure 1(b)) showed the average PL lifetime of 30.1 ns. The relative QY of the QDs in hexane was determined by comparison of the QDs PL with a fluorescence of Rhodamine 6G in methanol and was found to be 90%.

2.2. Fabrication of thin-film hybrid materials

To fabricate thin-film hybrid structures, the method of layer-by-layer spin-coating with the KW-4A Spin Coater has been used. To prevent interaction of QDs with the glass surface, the first layer of PMMA was deposited on a cover glass by spin-coating at a rotation speed of 1000 rpm, from a solution of polymethyl methacrylate (PMMA) in toluene (PMMA molar weight 120 000 Da, weight concentration 0.2 wt %). Further, the next layer of QDs was deposited by spin-coating from a solution in hexane with a molar concentration of 0.1 nmol/l. Then a second layer of PMMA was deposited on the QD-layer from a toluene solution with a weight concentration of 0.4 wt %, to fix the QDs in the PMMA matrix. The thickness of the obtained structure was estimated using the atomic force microscopy (AFM) height profiling method after cutting off a part of the deposited film. The measured thickness of the matrix structure was 6-8 nm, what corresponds to a monolayer of fixed QDs in PMMA matrix.

2.3. Setup and methods of measurement

To study the emission properties of single QDs, a scattering confocal time-resolved fluorescent microscope setup (Micro Time 200, PicoQuant) was used. The optical scheme of the setup is shown in Figure 2. The structure formed was excited by a diode laser with a wavelength \( \lambda = 485 \text{ nm} \) (\( P \leq 0.3 \mu \text{W} \)) in a pulsed mode with a repetition frequency of 5 MHz and a pulse duration of 50 ps. The excitation beam was reflected from dichroic mirror and focused on the sample using UPLSAPO 60XW Plan Apochromat water-immersion objective lens with numerical aperture NA = 1.2. The PL signal was collected by the same lens, passed through a dichroic mirror and 50-μm pinhole and recorded by the avalanche photodiode connected to the photon counting system (HydraHarp 400) with a time resolution of 16 ps.
The PL properties of biexcitons in QDs were studied using photon correlation spectroscopy methods. The second-order cross correlation function $g^{(2)}$ of single QDs was measured by splitting the PL signal into two detectors. This function is calculated by the following equation:

$$g^{(2)}(\tau) = \frac{\langle I_1(t)I_2(t+\tau) \rangle}{\langle I_1(t) \rangle \langle I_2(t+\tau) \rangle}, \quad (1)$$

where $I_1(t)$ is the temporal signal from the first detector, $I_2(t)$ is the signal from the second detector, and $\tau$ is the time delay between them. The equation (1) describes the probability of photon registration by one of two detectors. For a single photon emitter, a typical value of $g^{(2)}(0) = 0$, that means the absence of simultaneous events on the detectors. In contrast, in the case of two-photon PL (biexciton PL), the amplitude of the central peak of the cross-correlation function is not zero. As is known from the literature, at low excitation intensities the area ratio of the central peak to the average side peak is equal to the ratio of the QY of exciton to the QY biexciton [16]:

$$\Phi_{XX} \approx \Phi_X \frac{\int_{-\Delta t}^{\Delta t} g^{(2)}(\tau)d\tau}{\int_{-\Delta t}^{\Delta t} g^{(2)}(\tau)d\tau} = \Phi_X \frac{\text{central peak}}{\text{average side peak}}, \quad (2)$$

where $\Phi_{XX}$ and $\Phi_X$ are the QYs of the BX and single exciton, respectively. The equation (2) was used to estimate QY of the BX in single QD.

PL decay curves recorded from a single QD were approximated by the following equation:

$$I(t) = \sum_i A_i \cdot e^{-t/\tau_i}, \quad (3)$$

where $I$ is the intensity, $t$ is the time, and $\tau_i$ are the PL decay times. To compare the temporal characteristics of the PL in different samples, the parameter $\tau_{awt}$ was used, which is the amplitude-weighted average lifetime and can be expressed as:

$$\tau_{awt} = \frac{\sum_i A_i \tau_i}{\sum_i A_i}. \quad (4)$$

This parameter is proportional to the average value of QY at a condition of a constant rate of radiative relaxation [17].

3. Results and discussion
In order to analyze the PL properties of excitons (EX) in the single QDs, the area of the sample in which there was only one single QD has been found (see inset images in Figure 3). To determine QY of the EX states in the found single QDs, we have used the method based on the comparison of experimentally obtained PL average lifetimes in solution and in PMMA matrix. Using the measured value of QY of QDs
in hexane solution (nearly 90%) and the average PL lifetime of 30.1 ns, one can calculate the radiative lifetime of QDs using the following equation:

\[ QY = \frac{k_r}{k_{r} + k_{nr}} = \frac{\tau_{nr}}{\tau_{nr} + \tau_r}, \]  

(5)

where \( k_{nr} \) is the non-radiative decay rate; \( k_r \) is the radiative decay rate; \( \tau_{nr} \) and \( \tau_r \) are the corresponding lifetimes. The obtained value of the radiative lifetime is 33.3 ns. Then, the average lifetimes of single QDs in the thin-film PMMA matrix were measured. The PL decay curves recorded from six single QDs are presented in Figure 3. The PL decay kinetics of QDs were approximated by equation (3) and the average lifetimes were calculated by equation (4). Using these data, the QYs of EX states in the PMMA matrix were calculated using the following equation, which can be derived from equation (5), assuming the constant radiative decay rate \( k_r \):

\[ \frac{QY_1}{QY_2} = \frac{k_{r1} + k_{nr1}}{k_{r2} + k_{nr2}} = \frac{\tau_{aw1}}{\tau_{aw2}}. \]  

(6)

The obtained results are summarized in the Table 1.

Figure 3. The PL decay curves recorded from six single QDs. Inset figures show the PL images of these QDs.

To determine the QY of BX PL in these six single QDs, their second order cross-correlation functions were measured (Figure 4). In all cases, the amplitude of the central peak of \( g^{(2)} \) was found to be not zero, but lower than 0.5, what confirms that the observation was carried out from a single QD and not from the aggregates of QDs [18]. It’s well known, that the ratio of EX QY to BX QY is equal to the ratio of the area of the central peak from \( g^{(2)} \) to the averaged area of side peaks (Equation 2) [16]. Using the obtained values of EX QY and ratio of \( g^{(2)} \) peaks, the QYs of BX PL in six selected single QDs have been calculated and were found to be in the range from 8% to 16.3%. The results are presented in the Table 1. The obtained values are much higher than the BX QY of QDs with a conventional ZnS or CdS shell structures [9,10] and as high or even higher than the BX QY of QDs with the ultra-thick shells [12]. It is worth mentioning, that the size of our CdSe(core)/ZnS/CdS/ZnS(shell) QDs is much smaller in size than that for QDs with an ultra-thick shell. Our results show that CdSe QDs with ZnS/CdS/ZnS multishell are promising nanomaterials for fabrication of hybrid systems with two-photon (exciton/biexciton cascade) PL properties.
Figure 4. Cross-correlation functions of the single QDs. Panels (a) – (f) show the cross-correlation functions of six different single QDs.

Table 1. Calculated parameters for samples of single QD.

| Sample | $\tau$, ns | QY of EX, % | QY of BX, % |
|--------|------------|-------------|-------------|
| 1 (a)  | 14.6       | 43.6        | 8.3         |
| 2 (b)  | 12.7       | 37.9        | 8.3         |
| 3 (c)  | 13.0       | 38.8        | 16.3        |
| 4 (d)  | 17.4       | 52.0        | 8.8         |
| 5 (e)  | 11.9       | 35.6        | 10.3        |
| 6 (f)  | 18.9       | 56.5        | 9.0         |

4. Conclusions
The purpose of this study was to investigate the two-photon PL properties of QDs with CdSe cores and ZnS/CdS/ZnS multishells, embedded into thin-film PMMA matrix. We have fabricated a thin-film structures to study the EX and BX PL of single QDs. The average lifetimes and QY values of EX PL were measured. To calculate the BX PL QY of the single QDs, we have measured the second order cross-correlation functions $g^{(2)}$ of six single QDs. The results confirm that the measurements were carried out from single QDs. The values of the BX QYs were calculated using the values of EX QY and ratios of the area of $g^{(2)}$ central peak to the averaged area of $g^{(2)}$ side peaks. The obtained biexciton QYs for all fabricated samples were found to be up to 16.3%. These values are much higher than that for the BX QYs of QDs with the traditional ZnS or CdSe shell structures and are as high or higher than the BX QYs of QDs with an ultra-thick shell. The obtained data show that QDs with improved ZnS/CdS/ZnS multishell structures are promising materials for the fabrication of the two-photon PL sources for use in biosensing, quantum cryptography and optical computing.

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