Investigation of photoluminescence kinetics CuInS$_2$/ZnS quantum dots

A A Lazareva*, I A Reznik, A Yu Dubavik, A V Veniaminov and A O Orlova
ITMO University, St. Petersburg, 197101 Russia
*e-mail: lazareva.a.a@mail.ru

Abstract. The kinetics of photoluminescence of CuInS$_2$/ZnS quantum dots at room temperature has been studied. We show that the parameters of the photoluminescence band of our quantum dots, i.e. its position and FWHM, do not depend on the delay time after the excitation laser pulse. These may suggest the spectral diffusion of photoluminescence of CuInS$_2$/ZnS quantum dots due to hole localization at different Cu sites.

1. Introduction
CuInS$_2$/ZnS quantum dots (QDs) are luminescent nanocrystals used in various fields of analysis [1], in the production of solar cells [2], LEDs [3], in bioimaging applications [4]. I-III-VI$_2$ quantum dots such as AgInS$_2$ and CuInS$_2$ are being studied as potential alternatives to replace toxic QDs such as CdSe and PbS [6]. I-III-VI chalcogenides have an adjustable bandgap, which varies both depending on the size and shape of particles [7] and on the composition of QDs [8]. CuInS$_2$/ZnS QDs have a number of attractive characteristics [5], such as high photostability, broad absorption band, as well as their tunable bandgap. Also, CuInS$_2$/ZnS have a high optical absorption coefficient and a high probability of radiative recombination, which makes QDs attractive to researchers and developers. Such broad bands contribute to the universality of the energy donor, since a larger number of acceptors with different absorption bands are blocked by the donor radiation. In addition, the photoluminescence (PL) lifetimes of ternary QDs have average values of the order of hundreds of nanoseconds.

However, despite extensive studies, the optical properties of I-III-VI$_2$ are not fully understood, since nanoparticles usually exhibit broad absorption and luminescence spectra with a large Stokes shift [9]. Some researchers associate the broad PL band with the donor-acceptor (defect, DA) radiative recombination model [10]. This model is based on the fact that one of the charge carriers is captured by deep traps, which are structural defects in nanocrystals, whose energy levels lie in the bandgap. Alternatively, the experiments with single quantum dots discussed in the articles [11, 12] also show that the inhomogeneity of dopants inside the nanocrystal determines the wide width of the PL band of CuInS$_2$ nanomaterials. This indicates the electron-phonon interaction, which, along with long PL lifetimes, is consistent with the localization of holes prior to radiative recombination. Also, in spite of the rather narrow QD size distribution, some authors indicate the main reason for the width of the PL line of the ensemble could be the inhomogeneity of the sample [12]. This leads to large variations in the contribution of the electron-hole Coulomb interaction to the PL energy. Raevskaya et. al [13-14] state that at least one of the charge carriers participating in radiative recombination is free. Such conclusions were made when analyzing the position of the maximum of the luminescence bands of AIS and CIS QDs, depending on the QD composition [13, 14]. The model given by Stijnet al. [15] gives the assumption that only one electronic transition exists in CuInS$_2$/ZnS quantum dots. In this theory, luminescence in CuInS$_2$/ZnS QDs may occur via two different radiative recombination routes. Firstly, it is a recombination of
delocalized electron and localized hole at any Cu\(^+\) ion. Secondly, it is a recombination of delocalized electron and localized hole on a specific Cu site. This may be a consequence of the presence of a nearby defect [12] or electrostatic interactions with the QD surface [16]. The first model leads to multiexponential decay due to different overlap between electron-hole wave functions. The second model leads to one-exponential decay of the PL of single QDs, since the overlap of electrons and holes and, hence, the rate of radiative decay is the same. It is the one-exponential nature of the PL decay curves of a single QD that means that one specific Cu site (or at most several) is active in the CuInS\(_2\)/ZnS QD at any time and that the hole does not move between Cu sites on the emission time scale. In consideration of QD’s ensemble measurements both this model would appear the same and indistinguishable from each other.

Thus, there are many theories about the reason for wide photoluminescence band of ternary quantum dots. Further detailed study of the photoluminescent properties is very important since there is still no consensus on the nature of their photoluminescence. Understanding the physical processes occurring in quantum dots helps to more accurately select the field of application of CuInS\(_2\)/ZnS.

2. Methods and Materials

2.1. Chemicals

1-Dodecanthiol (DDT, 98%) was purchased from Acros Organics (USA), indium (III) acetate (In(OAc)\(_3\), 99.99%), sodium hydroxide (NaOH, 98%), copper(I) iodide (CuI, 99.5%), zinc chloride (ZnCl\(_2\), 98%), zinc acetate (Zn(OAc)\(_2\)·2H\(_2\)O, 99%), 4,4,4”-tris(carbazol-9-yl) triphenylamine (TCTA) were all purchased from Sigma-Aldrich (USA). Solvents: Isopropanol (99.8%), acetone (99.75%), and chloroform (99.9%) were purchased from Vekton (Saint-Petersburg, Russian Federation). All chemicals were used as received without further purification.

Quantum dots CIS\(_2\)/ZnS are synthesized in the laboratory of our scientific center by hot injection method [17]. The synthesis of quantum dot cores included heating the metal precursors, typically, copper(I) iodide, indium (III) acetate, and 1-dodecanethiol. Injecting the chalcogen precursors, lowering the temperature, all these processes took place in a three-headed flask. To improve the stability and fluorescence properties, CuInS\(_2\) cores need to be coated by ZnS shell [18]. When the synthesis of the core QDs was completed, the zinc precursor solution was dropwise added into the core solution. The zinc precursor was prepared by mixing zinc chloride, zinc oxide, and 1-dodecanethiol at room temperature and sonicated until forming a transparent solution [17].

2.2. Sample preparation

A solution of CuInS\(_2\)/ZnS QDs in toluene was created. Quartz cuvette was used to measure various spectra.

2.3. Methods for Studying the Optical Properties of Solution

The UV3600 Probe spectrophotometer (Shimadzu, Japan) was used to measure the absorption spectra of the toluene solution of CuInS\(_2\)/ZnS QDs. The Fluorescence Spectrophotometer (Cary Eclipse, USA) was used to measure the photoluminescence spectra of CuInS\(_2\)/ZnS QDs. The time-resolved confocal microscope (Picoquant, Germany) was used to study PL kinetics of CuInS\(_2\)/ZnS QDs. To excite the photoluminescence of the samples, we used sequences of short laser pulses with a certain repetition rate. The setup used a semiconductor laser (10 MHz frequency, 409 nm wavelength, 80 ps pulse duration). During the measurement of the PL kinetics, interference filters with an FWHM of 10 nm were used to
select some spectral regions into PL band of CuInS$_2$/ZnS QDs ensemble. To analyze the PL kinetics of the whole QD ensemble, the PL decay curve of samples was measured using a standard HQ430 filter, which allows recording a PL signal in 430-800 nm spectral range.

The time-resolved PL spectra of CuInS$_2$/ZnS quantum dots were extracted from a set of PL decay curves of CuInS$_2$/ZnS quantum dots, measured using a set of interference filters.

3. Results and discussion

Figure 1 shows the absorption and PL spectra of CuInS$_2$/ZnS quantum dots solution in toluene in a quartz cell.

![Figure 1. Absorption and PL spectrum of CuInS$_2$/ZnS QD's solution, PL excitation wavelength is 405 nm](image)

The absorption and PL spectra of our quantum dots manifests the important sample features. The absorption spectrum without clear peaks corresponds to a typical spectrum for CIS QDs. This can be explained by either one or the combined factors of wide size distribution of QDs in the ensemble, an uneven distribution of their chemical composition, or a unique electronic property of CuInS$_2$/ZnS quantum dots.

The PL band peak of the CuInS$_2$/ZnS QDs is observed at 610 nm. The emission mechanism of CuInS$_2$/ZnS QDs has not been confirmed yet. The CuInS$_2$ quantum dots, as noted earlier, have broad photoluminescence spectra. It could be connected with a model, where PL from CIS QDs arises as a result of radiative recombination of a delocalized electron at the edge of the band and a hole localized at Cu sites [12].

Figure 2 shows the CuInS$_2$/ZnS QDs PL decay curve measured in 430-800 nm spectral range.

The decay curves of the QD luminescence have a pronounced multiexponential character. The PL decay curves were fitted using a three-exponential model:

$$ y = \sum_{i} A_i e^{-\frac{t}{\tau_i}} $$

(1)

where $A_i$ are the amplitudes and $\tau_i$ are the PL decay times of $i^{th}$ component.

We have used the three-exponential model because it provided acceptable fit results ($\chi^2<1.1$) with the smallest possible number of components. The radiative relaxation of CuInS$_2$/ZnS QDs includes one fast- and two slow-decay components. The fitting of experimental data has yielded characteristic decay
times as 15 ns, 210 ns, 586 ns, which are typical for QDs of ternary compounds. Figure 3 shows the normalized PL decay curves measured with a set of interference filters to select some spectral regions into PL band of the ensemble of CuInS$_2$/ZnS QDs.

Figure 2. PL decay curve (black) of ensemble of CuInS$_2$/ZnS QDs in toluene measured in 430-800 nm spectral range and its fitting (red) by $y(t)=51.1\exp(-t/23) + 42.1\exp(-t/116) + 6.8\exp(-t/400)$

Figure 3. PL decay curves measured with a set of interference filters to select some spectral regions into PL band of the ensemble of CuInS$_2$/ZnS QDs

The dependence of the PL decay time of QDs on the recording wavelength (figure 3, table 1) was not observed. Therefore, it allows assuming that PL in our samples of CuInS$_2$/ZnS QDs occurs with the participation of holes localized at different Cu sites. According to [15] it leads to broadening PL band of an individual CIS and CIS/CdS QDs, their multiexponential PL decay, and spectral diffusion of their
PL bands. We suppose that in our CuInS\textsubscript{2}/ZnS QDs, the hole wandering at different Cu sites in a QD can impact on PL properties of our QDs in the same manner.

Table 1. Luminescence curve approximation data

| Interference filter, nm | \(\tau_1\), ns | \(\tau_2\), ns | \(\tau_3\), ns | \(A_1\), % | \(A_2\), % | \(A_3\), % | \(\bar{\tau}\), nm |
|------------------------|----------------|----------------|----------------|-----------|-----------|-----------|----------------|
| HQ430                  | 23\(\pm\)1.2  | 116\(\pm\)5.8 | 400\(\pm\)20.0 | 51.1\(\pm\)2.6 | 42.1\(\pm\)2.1 | 6.8\(\pm\)0.3 | 32.8\(\pm\)1.6 |
| 550                    | 11\(\pm\)0.6  | 51\(\pm\)2.6  | 310\(\pm\)15.5 | 69.2\(\pm\)3.5 | 28.0\(\pm\)1.4 | 2.8\(\pm\)0.1  | 54.1\(\pm\)2.7 |
| 570                    | 14\(\pm\)0.7  | 66\(\pm\)3.3  | 325\(\pm\)16.3 | 68.1\(\pm\)3.4 | 29.3\(\pm\)1.5 | 2.6\(\pm\)0.1  | 51.2\(\pm\)2.6 |
| 590                    | 14\(\pm\)0.7  | 64\(\pm\)3.2  | 294\(\pm\)14.7 | 62.1\(\pm\)3.1 | 34.5\(\pm\)1.7 | 3.3\(\pm\)0.2  | 76.8\(\pm\)3.8 |
| 610                    | 19\(\pm\)0.9  | 87\(\pm\)4.4  | 325\(\pm\)16.3 | 60.1\(\pm\)3.0 | 36.6\(\pm\)1.8 | 3.3\(\pm\)0.2  | 59.9\(\pm\)3.0 |
| 630                    | 23\(\pm\)1.2  | 87\(\pm\)4.4  | 292\(\pm\)14.6 | 55.8\(\pm\)2.8 | 38.5\(\pm\)1.9 | 5.6\(\pm\)0.3  | 52.3\(\pm\)2.6 |
| 650                    | 19\(\pm\)0.9  | 93\(\pm\)4.7  | 314\(\pm\)15.7 | 51.3\(\pm\)2.6 | 40.8\(\pm\)2.0 | 7.9\(\pm\)0.4  | 48.8\(\pm\)2.4 |

\(\bar{\tau} = \frac{\sum \tau_i^2 A_i}{\sum \tau_i A_i} (2)\)

Table 1 shows that the characteristic times and amplitudes approximately coincide with each other and with the curve recorded with HQ430. It means that at each spectral subrange included in the PL band of the ensemble of CuInS\textsubscript{2}/ZnS QDs (figure 1) photoluminescence is characterized by three-exponential decay with similar characteristic times. Therefore, there are no three sub ensembles of the QDs with different radiative transitions. To confirm this statement, we have analyzed time-resolved PL spectra of the QD ensemble (figure 4), which were extracted from PL decay curves (figure 3) using different delay times after the excitation pulse.

It can be seen that time-resolved spectra appear identical (figure 4 (b)). In Shabaev et al. research [19] the PL decay of each QD ensemble is single-exponential at any time, but it fluctuates so that the time-averaged PL decay of an individual QD is multiexponential. The study [19] suggested that fluctuations in the environment surrounding the quantum dot must play an important role, they can also lead to changes in the quantum yield of fluorescence (QY) of each QD. It is assumed that the QY of an ensemble of dots can represent the average of widely varying QY values from individual quantum dots. The same radiative transition can be characterized by a different quantum yield of luminescence due to the "on/off" mode of the nonradiative channel.
Figure 4. PL time-resolved spectra of CuInS$_2$/ZnS QDs in toluene extracted from PL decay curves measured with the set of interference filters, which are shown in figure 3. (a) is extracted and (b) is normalized by PL maximum. Steady-state PL spectrum of the sample is also presented.

4. Conclusions

We studied the kinetics of photoluminescence of CuInS$_2$/ZnS quantum dot ensemble at room temperature. We found that the position and FWHM of PL spectra do not depend on the delay time after the excitation laser pulse. Also, we did not find any spectral dependence of the PL decay curves recorded using the set of interference filters. We believe that our results perfectly correlate with the model, which suggests hole localization at different Cu sites in a CuInS$_2$/ZnS quantum dot at different times.

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