Fluctuations of electroluminescence intensity of single CdSe nanocrystals excited by scanning tunneling microscope current

I.S. Osad'ko a,⁎, A.S. Trifonov b,c, I.S. Ezubchenko c, I.G. Prokhorova c

a Institute for Spectroscopy, RAS, Fizicheskaya S, Troitsk, Moscow Region 142190, Russia
b Lomonosov Moscow State University, Skobeltsyn Institute of Nuclear Physics, 1(2), Leninskie Gory, GSP-1, Moscow 119991, Russia
c Lomonosov Moscow State University, GSP-1, Leninskie Gory, Moscow 119991, Russia

Abstract

Electroluminescence from single CdSe nanocrystals (NCs) excited by tunneling current of scanning tunneling microscope (STM) has been measured. Two types of samples with low and high concentration of CdSe NCs deposited on the gold substrate have been prepared. Both types of samples had no plasmon emission. It enabled one to detect pure electroluminescence from single CdSe NCs. Samples with low concentration of NCs exhibit an intensive short-term luminescence of NCs for several seconds. Samples with high concentration of NCs exhibit a weak fluctuating long-term luminescence for thousand seconds. Fluctuations of NC electroluminescence differ considerably from those detected recently in photoluminescence of CdSe NCs embedded in polymer films. The difference in fluctuations results from the difference in physical conditions existing in electro- and photoluminescence. The distribution of photons w(N, T) emitted in time interval T has been found from statistical treating of fluctuating luminescence. Due to weakness of the pure signal, we paid a special attention to allowing for photomultiplier tube noise while treating these fluctuations. The photon distribution in pure signal is one of super-Poisson type, i.e. it is broader than Poisson distribution. A dynamical model for an absorber–emitter excited by tunneling current of STM has been offered. The model takes into account the thermal drift of STM tip.

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1. Introduction

Blinking character of photoluminescence consisting of dark-off and bright on-intervals was discovered in the first experiments with single CdSe nanocrystals (NCs) [1]. The first theory for blinking fluorescence of CdSe NCs predicted an exponential distribution $P_{\text{on-off}}(t)$ for dark-off- and bright on-intervals [2]. After power-law $t^{-(1+\alpha)}$ with $0<\alpha<1$ for the distribution functions $P_{\text{on-off}}(t)$ was found in the blinking fluorescence of single semiconductor NCs [3], much attention was attracted to photoluminescence of single semiconductor NCs of various types [4–8]. The reason to this strange power-law distribution was point of interest for many research groups.

The main problem was in the explanation of power-law distribution for on-intervals. For instance, in order to find the explanation for power-law distribution of on-intervals Kuno et al. offered a model with fluctuating boundary of NCs [9]. One year later Osad’ko found that the distribution $P_{\text{off}}(t) \propto t^{-(1+\alpha)}$ can be explained if localized surface states of semiconductor NC core are taken into account [10,11]. Existence of core surface states is able to facilitate the explanation of tunneling mechanism of ionization NCs discussed in Ref. [6]. Phonon assisted direct tunneling from the surface levels of the NC core to the shell traps proposed in Ref. [11] can compete with the Auger ionization in core-shell NCs. Discussion of these details became possible due to measurement of intensity fluctuations in photoluminescence. These details cannot manifest themselves in the absorption and emission optical spectra of NCs.

The following question arises: can we use fluctuations of electroluminescence intensity to clarify the physical phenomena in STM junction? STM is usually used to study the energy structure of single NC deposited on the metal surface in the junction between tip and substrate. The energy structure of NC can be studied with the help of bends in current–voltage characteristics [12] and by means of electroluminescence band shape [13–15]. Value of the energy excitation manifests itself directly in electroluminescence in accordance with the Bohr rule for electronic frequencies.

In contrast to pure photoluminescence from single NC embedded in an organic film [3–8], the electroluminescence from STM junction is a complex phenomenon because tunneling electron is able to excite both NC and plasmons in substrate. Therefore, the physics of electroluminescence from junction is rather complicated. For instance, by measuring spectral shape of electroluminescence from STM junction, Romero and Langemaat discuss three possible mechanisms for creation of NC luminescence from the junction with plasmons in substrate [14]. If we want to measure fluctuations of integrated luminescence intensity we must exclude ambiguity connected with presence of plasmon emission. It is done in the present work.
metals were deposited in Ar discharge at pressure (1.2×10^{-2} mbar) and then a layer with 60 nm thickness was deposited below using RF-magnetron technique. In order to improve the adhesion, the additional titanium layer with 60 nm thickness was deposited below using RF-magnetron technique in a LEYBOLD-HERAEUS system Z400. Both metals were deposited in Ar discharge at pressure (1.2×10^{-2} mbar; gold, at 50 W; Ti, at 400 W). The experimental diagram is shown in Fig. 1.

Before precipitation the NCs solution was placed into the ultrasonic bath for 10 minutes in order to prevent the particle adhesion. The control of NCs precipitation on the surface of gold was made by measuring the sample topology in the scanning electron microscope (SEM) Carl Zeiss Supra 40. The precipitation of NC to the substrate was accomplished by two methods.

Spin coating method (method (1)) was used for creating the samples with relatively low surface density of NCs (Fig. 2a). The initial NC solution was dripped with a drop volume of 7 μl to the gold substrate and spin coating (rotation speed 3000 rpm with the initial acceleration 2500 rpm² and rotation time 30 s) was carried out. This method allowed to prepare samples in which the main part of NCs is concentrated on the edges of the substrate due to the action of centrifugal forces. NC density was about (2.0±0.5)×10^{10} particles/μm² in the center of the substrate. The NC precipitation method (method (2)) of drying from solution was used for the preparation of the samples with the density packing of NC (Fig. 2b). Dilute solutions of NC were prepared (10 μl of initial solution on 10 ml of toluene). The substrate was immersed into the prepared solution, heated up to 60 °C for 40 minutes. Then, the substrate was placed into vacuum chamber at 10^{-6} mbar for the rest toluene desorption. The holding time of the substrate in the vacuum was 24 h. The CdSe NCs were evenly distributed over the gold surface with the average concentration of (1.5±0.3)×10^{8} particles/μm². Using this procedure, the samples with low and high surface density of NCs were prepared. The topography of samples of both types is presented in Fig. 2.

In accordance with Fig. 1, the CdSe NCs in STM tunnel junction, could be excited by STM tunnel current under various conditions (tunnel voltage: from ±2 to ±5.5 V, tunnel current: from 500 to 3000 pA). Photons emitted by NCs could be recorded by our homemade optical setup. The STM “Nanoscope” (Digital Instruments Inc) with the home-made control electronics and software was used. The setup enabled us to make measurements at room temperature and ambient conditions. In all measurements, we utilized the Pt-Ir tips sharpened by mechanical cutting. This cutting method provided existence of monoatomic bristles on the tip. The longest of them served as the probe (see Fig. 1). All measurements were carried out in the constant current mode at natural thermal drift of the tip, which was approximately 1 nm/s.

The apparatus of the registration of optical signal included the system of lenses, optical fiber with an input diameter of 2.5 mm, highly sensitive photomultiplier tube (PMT, model R636P, HAMAMATSU photonics K.K., dark current 12 cps) and counter (maximum counting rate 2×10^{4} cps). The system of lenses collected light from tunnel junction and converted it into the parallel beam of light, which was focused to optical fiber and was directed to the PMT input. The light collection efficiency of the whole optical system was about 6%. The most part of signal losses occurs on the first lens (d=26 mm, f=30 mm) because of the small angular aperture. However, it was possible to displace the third lens along the optical axis. Due to this special feature of the optical setup configuration (hemisphere) we...
were able to control the phenomenon of the dispersion of light on the first two lenses. Therefore, we could regulate the degree of the parallelism of output beam for different wavelengths of signal since the NCs of various sizes had got different wavelengths of fluorescence. The PMT integration time was of 500 or 1000 ms.

The densities of NCs in the center of the substrate were approximately identical in all samples and are equal to \(2 \times 10^3\) particles/\(\mu\)m\(^2\) for samples prepared by method (1) and \(1.5 \times 10^4\) particles/\(\mu\)m\(^2\) for samples prepared by method (2). Therefore, the STM tip was positioned in the random place of the sample center and each measurement was carried out in the randomly selected region.

3. Experimental results

Fig. 3 shows the typical dependence of the intensity of the optical emission appeared from STM tunnel junction, on the time scale at fixed tunnel voltage and tunnel current (method (1), CdSe NCs, size: 6.3 ± 1.0 nm). We controlled tunnel current during optical measurements to be sure that there were no sudden jumps in tunnel current. There are two peaks of the electroluminescence with duration of 2 and 5 s. These peaks can be related to the emission of photons from the different single NCs. Temporal behavior of the electroluminescence is connected with existence of the thermal drift of STM tip along the sample plane (usually drift rate was about 1 nm/s). Such drift did not allow us to retain the STM tip above the chosen single NC for a long time. Taking into account the duration of emission peaks and the average size of NC, we ascribed measured peak to emission from the single CdSe NC, randomly fallen into the STM junction.

Fig. 4 shows the dependences of the intensity of the luminescence peaks on the tunnel voltage and the tunnel current. The intensity of peaks nonlinearly depends on voltage. Similar dependence was also observed recently [15]. Existence of the tunnel voltage threshold for luminescence is clearly seen in Fig. 4a. Indeed, the light is absent if voltages of voltage are less than 1.9 V for the NC with the size of 6.3 nm. The voltage threshold is connected with the fact that tunnel electron can create an electron–hole pair in NC if energy of tunneling electron exceeds value of the energy needed for creation of an electron–hole pair.

Indeed, in accordance with Quantum Mechanics [20] values of electronic level in the box can be found from the following equation:

\[
\tan \left( \frac{2mEa}{\hbar} \right) = \frac{(U-E)}{E}. \tag{1}
\]

Here \(m\) is the electron mass, and \(U\) and \(a\) are the height and the width of the box. For the lowest level we have \(?E_0 \ll U\) and \(\tan \to \infty\). Therefore

\[
E_0 = \frac{\pi^2 \hbar^2}{2ma^2}. \tag{2}
\]

is the energy of the lowest electronic level in the box. The energy of the hole can be found in similar fashion. Electron–hole pair cannot be created if the energy of tunneling electron is less than the energy \(E_g + 2E_0\) of electron–hole pair creation. Here \(E_g\) is forbidden gap in bulk CdSe. Expression \(E_g + 2E_0\) explains threshold character of NCs excitation and Eq. (2) with equation \(h\omega = E_g + 2E_0\) explains dependence of the luminescence color on NC diameter \(a\). The less diameter \(a\) of a NC the more shift to the blue of luminescence.

The dependence of this threshold on the size of NC was found in our experiments. Threshold value increases with the decrease of sizes of NC (Table 1) in agreement with the effect of size quantization described by Eq. (2).

Optical radiation disappears at tunnel voltage larger than 6 V. This fact is connected with the effect of the ejection of the CdSe NC from the STM junction due to the large electric field existing in tunnel junction.

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Increase of NC luminescence with the increase of tunnel current was observed as well. This increase of the luminescence intensity is determined by the increase of the number of electrons passing through the NC.

Quantum efficiency of electroluminescence (taking into account the efficiency of our optical system) for such samples was ranged from $5 \times 10^{-8}$ to $7 \times 10^{-6}$. Dispersion of this value is explained by the various shapes of STM tip in the various measurements, small dispersion of sizes of NC, and also by the different mutual arrangement of STM tip and excited NC. Apparently, the quantum efficiency of electroluminescence of NCs is considerably less than the quantum efficiency of its photoluminescence.

For the samples with the high density of NCs (precipitation method (2)), the dependence of luminescence intensity on the time differs considerably from electroluminescence shown in Fig. 3. The short peaks of large intensity were not registered; however, fluctuating signal for a long time was recorded. The signal was several times larger of PMT noise (Fig. 5). The quantum efficiency of electroluminescence decreased and became $\sim 10^{-7}$.

It was reported that the electric current passing through the conducting surface could create the surface plasmons, which relaxation also could lead to the creation of photons over a wide range of wavelengths. The light emitted by plasmons from the STM junction has already detected [14,21–24]. To convince the fact that in our experiments the light was emitted only by NCs, before the NC precipitation all the gold substrates were checked against the presence of electroluminescence under the same conditions for excitation as for the substrate with NCs. However, in such testing experiments the light was never detected.

We measured the light signal with tunnel voltage of 2 V. Electron–hole pairs cannot be created in NCs at such low voltage. The measured signal is presented in Fig. 5.

Track shown in Fig. 5 was treated statistically for finding the photoelectric pulse distribution function $w(N, T)$. The distribution of PMT pulses in this signal is shown in Fig. 6.

The distribution of the signal pulses is of Poisson type. Maximum at $N = 9.5$ corresponds to the average level of PMT noise. The squares in Fig. 6 describe, in fact, Poisson distribution of PMT noise. Hence, we did not observe the signal from NCs at such low voltage as 2 V.

If voltage increases, the different situation emerges. Electron–hole pairs can be created in NCs at bias of 3 V. Fig. 7 demonstrates a three-fold growth of the signal as compared with the signal shown in Fig. 5.

Track shown in Fig. 7 was treated statistically for finding pulse distribution function $w(N, T)$ for signal acquisition time $T = 1$ s. This distribution of photoelectric pulses is shown in Fig. 8.

The measured distribution is considerably broader as compared with the Poisson distribution. Hence the distribution is of super-Poisson type. Thus it is important to understand why such super-Poisson distribution emerges in our experiment.

4. Discussion of experimental results

We measured 80 tracks like those shown in Figs. 5 and 7 at various values of tip-substrate voltage and tunnel current. These tracks were treated statistically for finding the distribution function $w(N, T)$ of photons emitted in time interval $T$. These distribution functions have to be used for interpretation of physical processes taking place in single NC under excitation by tunnel current.

It should be reminded that photoluminescence of the same core-shell NCs revealed off-intervals in the time scale ranged from 0.1 s to 100 s [3–6]. For instance, off-interval of 10 s could be observed in the track shown in Fig. 7. However, we could not observe any off-intervals in electroluminescence created in the samples shown both in Figs. 2a and b. Obviously, the absence of off-intervals in electroluminescence is due to the difference in physical conditions existing in electro- and photo-luminescence.

Our PMT had shot-noise of $10^{-12}$–$10^{-14}$ cps. Since the average level of the signal shown in Fig. 7 is only three times larger, the noise of PMT contributes considerably to the track shown in Fig. 7. If we intend to measure the distribution of photons created by NC, i.e. a pure signal, the noise must be removed. Unfortunately a simple subtraction of the average noise level $<N_s>$ from signal + noise is incorrect procedure if we are interested in the pulse distribution function. This problem should be considered in more detail.

Let us consider a pure signal of the Poisson type. Pure signal and noise of the Poisson type results in the Poisson distribution for whole signal + noise. It will be shown further. Such signal + noise of the Poisson type is shown schematically in Fig. 9.

In accordance with Fig. 9 the amplitude of fluctuations of signal + noise $<N_{s+n}>$ equals to amplitude of fluctuations in $<N_s>$. However the average values of $N_{s+n}$ and $N_s$ shown by dotted lines differ considerably. The Poisson distribution is characterized by a single parameter, namely by average value $<N>$ of the distribution. The
smaller value of \( <N_s> \) the narrower will be the Poisson distribution. However the distribution of \( N_s \) equals to the distribution of \( N_{s+n} \) whereas \( <N_s> \) is smaller than \( <N_{s+n}> \). Hence, the distribution of values \( N_s \) will be broader as compared with the Poisson distribution with the same value of \( <N_s> \). Therefore, after subtraction of \( <N_s> \) from signal + noise we can obtain a super-Poisson distribution, i.e. we can arrive at false signal distribution. Noise has to be taken into account in another fashion.

Since pulses from the noise and the pure signal are statistically independent with each other, the distribution for signal + noise pulses can be described by the following equation:[25]

\[
w_{s+n}(N) = \sum_{m=0}^{N} w_s(m) w_n(N-m)
\]

Here \( w_s(m) \) and \( w_n(N-m) \) are the distribution functions of pure signal and noise for time interval \( T = 1 \) s used in our experiment. If distributions \( w_s(m) \equiv w_s(<N_s>) \) and \( w_n(N-m) \equiv w_n(<N_n>) \) are the distributions of Poisson type, the distribution \( w_{s+n} \) would be also the Poisson type distribution, i.e. \( w_{s+n}(N) = <N_{s+n}>^N e^{-<N_{s+n}>}/N! \), with the average value of counts, \( <N_{s+n}> = <N_s> + <N_n> \). This state can be verified by using Eq. (1). This equation can be also applied to the distribution functions of arbitrary types.

In accordance with Fig. 8, the distribution function of signal + noise is broader as compared with Poisson distribution. In other words the distribution of signal + noise has a super-Poisson type. As Fig. 6 shows, the noise is of Poisson type. Hence, the super-Poisson character of the distribution in signal + noise results from super-Poisson type of the distribution function for pure signal.

The super-Poisson distribution of pure signal results from physical processes in NCs excited by tunneling current of STM. The super-Poisson distribution of pulses in electroluminescence of core-shell CdSe NCs differs considerably from the super-Poisson distribution of photons in photoluminescence of the same NCs [4–8]. The general reason for super-Poisson character of the photon distribution in photoluminescence is existence of “dark” off-intervals in photoluminescence [17,18]. As we have already mentioned there are no off-intervals in electroluminescent signal. If off-intervals are absent what would be the reason to super-Poisson character of the pulse distribution in electroluminescence from STM?

We can suppose that the main reason to appearance of super-Poisson distribution in electroluminescence is a thermal drift of STM tip along substrate plane shown in the left hand side of Fig. 10.

Because of such drift the tip runs over a several NCs, and therefore the tunnel electron excitation slightly varies in time. Each NC is described by two-level scheme. If each NC has the same value of \( k \), the distribution of photons would be of Poisson type despite of thermal drift. However if each NC has its own rate of excitation \( k \) as shown in the left hand side of Fig. 10, the dynamics of such system cannot be described by two-level scheme. The photon distribution will not be of Poisson type.

Main peculiarities of such complicated system are caught by the simplified model shown in the right hand side of Fig. 10. Here, value of \( k \) jumps between two different values \( k_0 \) and \( k_2 \). It is obvious that the transition of the tip to the third NC is equivalent to returning to the first NC. Therefore, the photon statistics in such model can be calculated with the help of the scheme shown in Fig. 11.

This scheme is applied for NCs of “0” type and NCs of “2” types with absorption rates \( k_0 \) and \( k_2 \), respectively. Shape of the distribution function for photons depends on two parameters. Non-dimensional parameter \( k_2/k_0 \) determines the difference in absorption coefficients of NCs of “0” and “2” types. The \( 1/A \) value is the time of excitation of single NC by tunnel current via tip. In such model the photons fluorescence distribution has been recently calculated in Ref. [26] with the help of Monte Carlo method. Here we used the same method to calculate the distribution function \( w_s(N) \) for pure signal.

In accordance with the scheme shown in Fig. 11, the molecule leaves state 0 with rate, \( k_0 + A \), for state 1 or state 2. It gets state 2 with the probability \( A/k_0 + A \), and state 1 with the probability \( k_0/(k_0 + A) \). Leaving state 1, the molecule gets to state 0 with rate \( G \). By leaving state 2 with the rate \( k_2 + A \), the molecule gets to state 0 with the probability \( A/(k_2 + A) \), or state 3 with the probability \( k_0/(k_2 + A) \). Leaving state 3, the molecule gets to state 2 with the rate \( G \) and so on. By considering \( 10^6 \) of such steps, we found the sequence of random events relating to the scheme shown in Fig. 11. Treating sequence of calculated random events statistically, we arrived at the distribution function for pure signal. The calculated function \( w_s(N) \) was inserted to Eq. (3) in which the distribution function \( w_s(N) \) for the noise was taken as Poisson distribution with \( <N_s> = 11 \). The results of our calculation with the help of Eq. (3) for various values of ratio \( k_2/k_0 \) are presented in Fig. 12.

Curve 1 with two peaks relates to large difference in values of \( k_0 \) and \( k_2 \). Curve 3 is similar to Poisson distribution and corresponds the small difference in values of \( k_0 \) and \( k_2 \). Curve 2 calculated for
$k_2/k_0 = 15/20$ is able to describe the distribution measured in experiment. Time, $1/A = 3$ s, relates to time interval of NC excitation by tip current.

Why did not we see the off-intervals in electroluminescence? We consider at least two reasons to this. The ionization of NC after absorption of light is the main reason of appearance of off-intervals in photoluminescence. In accordance with Ref. [6], there are two processes of NC ionization under CW-laser excitation.

The first process is temperature independent Auger ionization in which one electron–hole pair annihilates and the electron from another electron–hole pair acquires this portion of energy and leaves NC core for a trap in NC shell. Coulomb field between core and shell hampers recombination of other electrons and holes in NC. Therefore, luminescence stops and we watch off-interval. After electron comes back from the trap in NC shell, luminescence is renewed. We watch that at least two electron–hole pairs have to exist simultaneously in NC for Auger ionization. Solely it can exist at strong laser excitation only. The second process of NC ionization can be realized with the help of phonon assisted direct electron tunneling from a surface level of NC core to a trap level of NC shell. This mechanism depends on temperature and was discussed in detail in Ref. [11].

Another situation exists in electroluminescence excited by tunnel current. Kinetic energy of tunneling electron is a reason for electron–hole pair creation. As a result we can see a very weak luminescence. It means that the probability of finding of two or more electron–hole pairs in NC is very small. Therefore, Auger ionization is impossible. Direct tunneling of an electron from electron–hole pair does not lead to core ionization in presence of tunneling electron current from tip. Therefore, NCs excited by tunnel current cannot be ionized and hence their electroluminescence does not stop.

5. Conclusion

It was known that photoluminescence of single CdSe NCs fluctuated [3–8]. Here we successfully investigated the fluctuations of electroluminescence from single CdSe NCs and compared the fluctuations in electroluminescence excited by tunnel current from STM with photoluminescence fluctuations. It was found that photoluminescence and electroluminescence processes were quite different. Since there was not plasmon emission from our samples; whole electroluminescence was created solely by NCs situated in STM junction. This very fact facilitated our theoretical analysis of electroluminescence fluctuations.

In samples with low concentration of NCs, we observed intensive short-term luminescence for several seconds. Luminescence signal certainly was created by single CdSe NC in which electron–hole pair creation provided a threshold character of luminescence. Value of the threshold is in agreement with the effect of size quantization in NC.

In samples with high concentration of NCs, we observed a weak long-term luminescence for thousand seconds. Statistical treating of fluctuations in this long-term luminescence enabled one to find a photon distribution function $w(N, T)$ of super-Poisson type.

We supposed that thermal drift of the STM tip is the main reason of appearance of super-Poisson photon distribution in long-term NC electroluminescence. By applying Monte Carlo method, we calculated three distribution functions for various rates $k_0$ and $k_2$ of electron–hole pair creation. One of these calculations can describe the distribution of electric pulses observed in our experiment.

In contrast to other works in which electroluminescence band shape was measured, for the first time we measured successfully the fluctuations of integrated electroluminescence only. We shown that the analysis of the distribution function $w(N, T)$ measured for photoelectric pulses is the rather effective method for creating a microscopic model of absorber-emitter existing in tunnel junction of STM. By measuring the average intensity of electroluminescence we shall find, in fact, only the first moment of the distribution function in accordance with the equation $<N>/T = (1/T) \sum_{N=0}^{\infty} N w(N, T)$. However the shape of the whole distribution function gives more information about quantum dynamics of the emitter than its first moment. Therefore, the measurement of fluctuations of electroluminescence from STM is the promising method for studying single NCs deposited on a metal surface.

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