### Blinking fluorescence of single semiconductor nanocrystals: basic experimental facts and theoretical models of blinking

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Abstract. Various theoretical models of blinking fluorescence from a single semiconductor core-shell nanocrystal (NC) are discussed from the standpoint of consistency with new experimental data, with most of the emphasis placed on the charging model and the multiple recombination center model. The advantages and disadvantages of each are analyzed, and their recently proposed combination using the advantages of both is examined, which is capable of describing the recently observed properties of A- and B-type NCs (the two types differ by whether the fluorescence quantum yield of a single NC correlates with its fluorescence lifetime). It is shown that the Auger neutralization of the NC core results in an anticorrelation of the off-interval duration and the grey emission lifetime in the offinterval. It is also shown that the exponent in the  $t^m$  power-law distribution of on- and off-intervals in the fluorescence of single NCs characterizes the concentration of traps and localized NC core excitations at the core-shell interface.

Keywords: single semiconductor nanocrystal, blinking fluorescence

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#### 1. Introduction

The study of low-dimensional semiconducting samples began in the 1970s. The transition from three-dimensional semiconductors to lower-dimensional systems led at the beginning of the 1990s to investigations of zero-dimensional systems, now known as quantum dots (QDs) or semiconductor nanocrystals (NCs) [1-3]. Obviously, quantum states of an NC consisting, for example, of a thousand atoms would drastically differ from the band-type states inherent in three-dimensional crystals. The concepts of the electron or hole quasimomentum and dispersion law lose their meaning, and we now have to deal with a thousand electron and hole states in a volume of several cubic nanometers, and therefore the NC now looks more like a macromolecule.

Of course, first investigations of nanocrystal luminescence were performed for an ensemble of NCs incorporated, for example, into glass. Scientists were studying NC ionization by light from an external source and recorded the dependence of the ionization time on the NC size. The ionization time turned out to strongly depend on the NC size. As the NC size was decreased from 3 to 1 nm, the ionization time decreased from  $10^3$  to 10 s [2]. This fact was explained by the Auger mechanism of NC ionization.

The interest in nanocrystals significantly increased after it became possible to manufacture and investigate single NCs. The first investigation of single NC fluorescence was performed for a CdSe NC surrounded by several layers of wide-band gap ZnS semiconductor (core-shell NC) [4]. These experiments have shown that the fluorescence of such NCs



Figure 1. Fluorescence trace of a single NC [4]. The CdSe QD radius is 22 Å, the excitation power is  $0.64 \text{ kW cm}^{-2}$ .

blinks during continuous excitation by light, which means that the fluorescence alternates between periods of bright fluorescence (on-periods) and weak fluorescence (off-periods). This is shown in Fig. 1.

The effect of blinking fluorescence is inherent only in single NCs. In the case of an NC ensemble, the blinking radiation is integrated over many emitters. Because the durations of on/off-periods are random values, the blinking of fluorescence is not observed for a sum of several fluorescence traces.

# 2. Bright and dark periods of blinking fluorescence

#### 2.1 Charging model of blinking fluorescence

Already a year after the publication of paper [4] in *Nature*, Efros and Rosen suggested an explanation for the blinking fluorescence effect observed for single NCs consisting of a core and a wide-band gap shell [5]. According to their theory, of single NC fluorescence is suppressed due to the effect of NC core ionization. The authors chose the Auger ionization as the ionization mechanism, which is realized by two excitons produced in the NC core by external light. One exciton annihilates and gives its energy to the other one. The electron (hole) of the second exciton gains the energy of the disappeared exciton, is ejected from the core, and reaches the trap in the shell. The NC core becomes charged and stops emitting light, although excitation by laser light continues. As soon as the electron (hole) returns from the shell trap into the core, the core recovers its neutrality and starts producing bright fluorescence. This process of Auger ionization is characterized by the only ionization time of this NC,  $t_A$ , which determines the exponential distribution of on-periods in the NC fluorescence. The Efros-Rosen model is now known as the charging model.

#### 2.2 Power law of the on/off-period duration distribution

Already three years later, however, Nesbitt's group at the University of Colorado [6–8] discovered that the distribution of both on- and off-periods is not exponential and can be described by a power law  $t^{-m}$  with  $1 \le m \le 2$ . This result was also confirmed by other groups [9–11], which studied the fluorescence of single NCs with other chemical compositions.

Figure 2 shows the off-period distribution measured by Nesbitt's group [7]. Dashed lines show how the exponential distributions look on the plot in a double logarithmic scale used in Fig. 2. We can clearly see that the measured power-law distribution can be described by a sum of three exponential distributions for off-periods with the decay constant  $\tau$  varying within a wide range.



Figure 2. Off-period distribution in the CdSe/ZnS NC fluorescence trace.



**Figure 3.** Distribution of on-periods in the CdSe/ZnS NC fluorescence trace, which follows the power law  $t^{-m}$  [8].

The duration of the off-period is determined by the neutralization rate  $1/\tau$  of the core by an electron (hole) trapped in the NC shell. Obviously, the existence of three exponents indicated in Fig. 2 by dashed lines can be explained by the existence of three different trap types with different trapping times. However, the power-law of the on-period distribution [7, 8], which was measured by the same group and is shown in Fig. 3, means that there should be several core ionization times in the NC. But the Auger ionization mechanism proposed by Efros and Rosen [4] was based on the existence of two excitons in the core and could not therefore explain the existence of many ionization times.

The authors of [4] tried to explain the power law by fluctuations of a potential barrier. They assumed that the core is separated from the shell by a potential barrier with alternating penetrability. This assumption led to a series of unsolved problems. For example, what is the reason for barrier penetrability fluctuations? Which fluctuations would lead to the power law of the on-period distribution? These questions were not even mentioned in [7]. Therefore, the physical mechanism leading to the power law of the onperiod distribution remained unknown.

#### 2.3 Modified charging model

A solution of the problem of power-law distribution of onperiods in single NC fluorescence was proposed three years



Figure 4. (Color online.) The process of NC core ionization in the modified charging model with surface levels *j* in the core and a trap *k* in the shell.

later in [12, 13]. The Efros–Rosen model was modified in the following way. Figure 4 shows the energy schematic that corresponds to a single NC with a wide-band gap shell. After production of a free electron–hole pair by a quantum of light (shown in blue), the pair starts losing its energy, falling to the bottom of the well that corresponds to the NC core. This pair has two options. First, after losing its energy, it can bind into an exciton, which is then added to the *N* excitons that already exist in the NC. Second, this pair can hop into the quantum state *j* localized in the atom on the core surface.

The crystal lattice inside the NC is ideal; therefore, the wave functions of the excited states of these atoms are delocalized over the whole core. But this homogeneity is broken for atoms on the surface of the core. These atoms have adjacent atoms of the shell of different natures and with higher excitation energies. Both core and shell lattices can have defects at the interface. These factors lead to the localization of the wave function of atoms located on the surface of the core. A level *j* corresponds to the electron/hole excitation of atoms located in the core at the core–shell interface.

Obviously, if the energy of the exciton that disappeared during the Auger ionization is transferred to the electron (hole) in the state *j*, then this electron (hole) is thrown out of the core into the shell with the rate  $1/t_{Aj}$ , which characterizes the electron (hole) doorway from the *j*th core atom into the NC shell. Consequently, there are several ionization times  $t_{Aj}$ , where *j* corresponds to an atom whose electron (hole) exits in the core. This leads to different durations of on-periods, which was observed in experiment.

Figure 5 shows the on-periods with two different durations. According to Fig. 5, the on-period with the duration of about 500 s contains short off-periods and consists of onperiods with the duration of several dozen seconds. We see in what follows that the modified charging model agrees with many experimental facts. Unfortunately, this model was not known to the authors of the review on NC fluorescence published in 2008 in *Nature Physics* [14] (private communication from one of the authors).

#### 2.4 Multiple recombination center model

We note that NC fluorescence traces strongly vary for different samples and papers. Most often, the traces indeed have the form shown in Fig. 1, looking like a random telegraph signal (RTS). However, other types of traces can sometimes be observed, shown in Fig. 6. Paper [15], where such traces were studied, is called "Continuous Distribution of Emission States from Single CdSe/ZnS Quantum Dots." The authors believe that this type of fluorescence trace can hardly be explained by the charging model, and another model is therefore needed.



Figure 5. Short and long on-periods in the CdSe/ZnS NC fluorescence trace [9].



Figure 6. Fluorescence trace of a single CdSe/ZnS NC with on-periods of different types [15].

Tang and Marcus made the first attempt to avoid the charging model [16]. They modeled some stochastic processes occurring in the energy configuration space and represented the interaction of quantum dots with the environment. Their theory led to a  $t^{-3/2}$  law of the on- and off-period distribution in the actual range  $10^{-4} - 10$  s.

In the same year of 2005, Frantsuzov and Marcus [17] suggested another model for describing blinking fluorescence, similar to the one shown in Fig. 6. This model suggested an explanation for the blinking fluorescence of a quantum dot without using the hypothesis of long-lived trap levels. According to [17], fluctuations of the 1p-1s electron energy gap lead to nonradiative transition fluctuations and consequently to the blinking of the fluorescence intensity. The idea of nonradiative transition fluctuations being the source of blinking fluorescence was later developed in [18] and was named the multiple recombination center model (MRC) by the authors of that study.

Obviously, fluctuations of the fluorescence quantum yield

$$Q = \frac{\gamma_{\rm em}}{\gamma_{\rm em} + \Gamma_{\rm nr}} \,, \tag{1}$$

which leads to fluorescence intensity fluctuations, can be a consequence of fluctuations of either the light emission rate  $\gamma_{em}$  or the nonradiative transition rate  $\Gamma_{nr}$ . Fluorescence suppression in the Efros–Rosen model [5] was related to nonradiative Auger recombination quenching in an ionized NC. In the MRC model, the intensity fluctuations are connected with fluctuations of the nonradiative transition rate  $\Gamma_{nr}$ . These nonradiative transitions are realized through a number of recombination centers, which, as the authors of [18] assume, exist in the NC. This mechanism is considered to be universal [18, 19] and unconnected with the core ionization/neutralization processes. In this case, expression (1) for the quantum yield has the form

$$Q(i) = \frac{\gamma_{\rm em}}{\gamma_{\rm em} + \Gamma_{\rm nr}(i)}, \qquad (2)$$

where the rate  $\Gamma_{nr}(i)$  of the nonradiative recombination can randomly take a number of values.

### 2.5 On/off-period distribution according to the modified charging model

As we have mentioned, the Efros–Rosen charging model [5] could not describe the power-law distribution of on/offperiods. We now discuss how the modified charging model can describe such distributions.

Figure 7 shows the schematic of an NC in the modified charging model. We can see a core and a shell with a number of electron doorway states *j* in the core and a number of traps *k* in the shell [12, 13, 20]. The processes of ionization/ neutralization were discussed in [13] with the scheme shown in Fig. 8. Here,  $P_0(N)$  is the probability that the NC core contains *N* excitons,  $P_j(N+1)$  is the probability that the core contains *N* excitons together with an electron and a hole in the *j*th atom localized on the core surface,  $P_{jk}(N-1)$  is the probability that the core (hole) after the *j*th hole (electron) was trapped in the *k*th shell trap,  $G_{jk}$  is the Auger ionization rate, and  $g_k$  is the core neutralization rate.



Figure 7. Arrangement of shell traps k and core atoms j whose electrons (holes) leave the core.



Figure 8. Ionization/neutralization setup in the modified charging model [13].

The dynamics of a system under the action of a pump L can be described by the set of equations

$$P_{j}(N+1) = -(\Gamma + G_{j}) P_{j}(N+1) + LP_{0}(N) ,$$
  

$$\dot{P}_{0}(N) = \Gamma P_{j}(N+1) - LP_{0}(N) + \sum_{k} g_{k} P_{jk}(N-1) ,$$
(3)  

$$\dot{P}_{jk}(N-1) = -g_{k} P_{jk}(N-1) + G_{jk} P_{j}(N+1) ,$$

where  $G_j = \sum_k G_{jk}$ . These equations allow calculating both the photon distribution and the on/off-period distribution in NC fluorescence.

Before calculating the fluorescence photon distribution, we show that Eqns (3) indeed describe a power-law distribution of on/off-periods.

Obviously, the sums of probabilities  $P_j^{\text{on}} = P_j + P_0$  and  $P_k^{\text{off}} = \sum_j P_{jk}$  describe the probabilities of the emitter being in the respective on- and off-states. The probability that the emitter is in the on- or off-state should tend to zero as the time increases. Therefore, the equations for these probabilities can be obtained from (3) as we now describe.

**On-periods.** To find the function that describes the onperiod distribution, we ignore the term  $\sum_k g_k P_{jk}$  in the second equation in (3). This term describes the transition into a state without fluorescence (dark state). The second equation then becomes independent of the third and the first two equations can be combined into the system

$$P_{j} = -(\Gamma + G_{j}) P_{j} + LP_{0},$$

$$\dot{P}_{0} = \Gamma P_{j} - LP_{0}.$$
(4)

Obviously, the probability that the system is in the on-state,  $P_j^{\text{on}} = P_0 + P_j$ , decreases with time via the *j*th surface state. Equations (4) contain fast dynamics characterized by the constant  $\Gamma$  and slow dynamics characterized by other constants. The slow dynamics can be studied by assuming that the fast relaxation has already occurred,  $\dot{P}_j = 0$ . In this approximation, we can use the first equation to find a relation between the probabilities,

$$P_j = \frac{L}{\Gamma + G_j} P_0 \,. \tag{5}$$

Adding the two equations of system (4) and taking relation (5) into account, we obtain the equation for the probability of observing the on-state

$$\dot{P}_j^{\rm on} = -L_j P_j^{\rm on} \,, \tag{6}$$

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$$L_j = L \frac{G_j}{\Gamma + G_j + L} = \frac{1}{\tau_{\text{on}}^j} \tag{7}$$

is the on-state decay rate through the *j*th doorway. The solution of Eqn (6) is  $L_j \exp(-L_j t)$ , which determines the distribution of on-periods associated with the ionization via the *j*th doorway state. Summing over all ionization channels, we obtain the expression

$$w_{\rm on}(t) = \frac{1}{N_0} \sum_{j=1}^{N_0} L_j \exp\left(-L_j t\right)$$
(8)

for the on-period distribution in NC fluorescence. Here,  $N_0$  is the number of doorway states. If the on-period distribution follows the power law at scales that, for example, include three orders of magnitude, then the constants  $L_j$  should also have three orders of magnitude.

**Off-periods.** To find equations for the off-period distribution, we ignore the term  $G_{jk}P_j$  in the third equation in (3). This term describes the transition into the NC on-state, that is, the decay of the off-state. In this case, the third equation takes the form

$$\dot{P}_{jk} = -g_k P_{jk} \,. \tag{9}$$

Solving Eqn (9) and summing all solutions over *j*, we obtain the probability  $P_k^{\text{off}} = \sum_{j=1}^{N_0} P_{jk}$  of an NC being in the ionized state *k*. After normalization, we obtain the following expression for the distribution function of the off-periods associated with the charge transition in the *k*th shell state:

$$w_k^{\text{off}} = g_k \exp\left(-g_k t\right). \tag{10}$$

The complete distribution function for off-periods of all types is

$$w_{\text{off}}(t) = \frac{1}{N_{\text{t}}} \sum_{k=1}^{N_{\text{t}}} g_k \exp\left(-g_k t\right),$$
(11)

where  $N_t$  is the total number of NC shell traps that can be occupied with the charge from the NC core. Equations (8) and (11) allow theoretically calculating the on- and off-period distribution.

We assume that the subscript k = 1, 2, 3 indicates three types of traps and the subscript j = 1, 2, 3 indicates three types of ionization channels. Consequently, there are three NC core ionization rates  $(g_1, g_2, g_3)$  and three NC core neutralization rates. Strictly speaking, the number of surface levels j and traps k at the NC interface can be significantly larger than 3, which means that the numbers  $N_0$  and  $N_t$  in (8) and (11) are much greater than 3. Therefore, Eqns (8) and (11) can be written in the form

$$w_{\rm on}(t) = \sum_{j=1}^{3} u_j L_j \exp\left(-L_j t\right), \qquad (12)$$

$$w_{\text{off}}(t) = \sum_{k=1}^{3} v_k g_k \exp(-g_k t) \,. \tag{13}$$

Obviously,  $u_j$  is the probability of observing the ionization channel with the rate  $L_j$  and  $v_k$  is the probability of observing the neutralization channel with the rate  $g_k$ . These probabilities must satisfy the conditions  $u_1 + u_2 + u_3 =$  $v_1 + v_2 + v_3 = 1$ . Simple equations (12) and (13) can describe



the power laws that were observed in the on- and off-period distributions.

According to expressions (12) and (13), the calculation of on- and off-period distributions is performed in the same way. For example, we consider the off-period distribution for different values of the probabilities  $v_k$ . The result is shown in Fig. 9. We can see from Fig. 9 that the slope of the power-law distribution increases together with the concentration of traps with a high neutralization rate near the core-shell interface. It is reasonable to assume that the highest neutralization rate is observed in those traps that are closest to the core, and the lowest neutralization rate in traps that are located more deeply in the shell. If this assumption is correct, the slope of the power-law dependences in Fig. 9 characterizes the degree of trap localization near the interface: the higher the concentration of traps near the interface is, the steeper the distribution [12, 13, 20]. Similar reasoning can be applied to the rates  $L_i$  of the ionization channels *j* and the concentration  $u_i$  of these channels near the core-shell interface.

The on/off-period distribution follows the power law over the time range of several orders of magnitude. Figure 9 shows that the distribution curves diverge from the power law outside the time interval that can be written in the form max  $\tau^{\text{on,off}}$ -min  $\tau^{\text{on,off}}$ . The transition from a power law to an exponential one has been observed for large time scales in many studies [9, 21, 22]. This means that the modified charging model not only can successfully explain the powerlaw distributions of on/off- periods but also gives a simple physical meaning to the slope of the line. If we assume that the rate of the trap deactivation depends on how close this trap is to the interface, then a higher slope corresponds to a higher degree of trap concentration and doorway states near the NC interface.

### 2.6 On/off-period distribution according to the multiple recombination center model

The MRC model was proposed to explain the fluorescence fluctuations when the on- and off-periods are difficult to





Figure 10. Example of a fluorescence trace with more or less pronounced on/off-periods [18].

distinguish. In these cases, the charging model loses its applicability. But without the core charge fluctuations, which lead to the existence of quite clear on- and offperiods, the MRC model can hardly explain the power-law distributions of on/off-periods when the on- and off-periods can be clearly seen and identified in the fluorescence trace. At the same time, there are numerous studies where such traces have been observed.

An analysis of a large number of fluorescence traces with poorly pronounced on- and off-periods was performed in [18]. Figure 10 shows an example of the fluorescence trace with more or less pronounced on- and off-periods. Such traces, as well as ones with less pronounced on/off-periods, were analyzed in [18] in order to find the on/off-period distributions.

It was found that the exponent of the distribution  $t^{-m}$  strongly depends on the choice of the threshold intensity that determines whether the period corresponds to the off- or on-type. The result of processing a large number of fluorescence traces is presented in Fig. 11. Unfortunately, the authors of [18] do not demonstrate the distributions themselves, and it is unclear whether they are similar to the power-law distributions shown in Figs 2, 3 or to the distributions shown in Fig. 9, referring to the modified charging model. However, one conclusion is clear: the MRC model, unlike the modified charging model, does not relate the



Figure 11. Exponent of the power-law dependence versus the threshold intensity that separates the on-period from the off-period [18].

slope of on/off-period distributions to any physical value, but connects it only with the method of fluorescence trace processing.

# 2.7 Important role of the interface between the nanocrystal core and shell

According to the modified charging model, shown in Figs 4 and 7, the atoms localized at the core–shell interface play a decisive role in the core ionization processes and, consequently, in the processes involving off-states, which, in turn, lead to the blinking of the core fluorescence. We can assume that these states at the core–shell interface are also responsible for the delayed fluorescence observed in nanocrystals [23–26]. Recently, new experimental data was presented in [26], and they are in very good agreement with the predictions of the modified charging model.

The authors of [26] studied delayed fluorescence of a single multilayer CdSe NC (1.7 nm CdSe/6 layers of CdS/1 monolayer of CdZnS/1 monolayer of ZnS). The observed blinking fluorescence intensity had three levels: high (4000 –  $1500 \text{ s}^{-1}$ ), medium ( $1500-200 \text{ s}^{-1}$ ), and small ( $< 200 \text{ s}^{-1}$ , off-period). Figure 12a shows the extinction of these three emissions on the scale of 100 ns during pulsed excitation. The lifetime of an excitation in atoms giving intensive fluorescence (excitons) was 21 ns, while the lifetime of atoms that produce medium-intensity fluorescence is 5 times longer (96 ns). This delayed fluorescence was attributed to NC centers with charge separation.

The measured distributions of on-periods in fast (highintensity) and delayed (medium-intensity) fluorescence were similar to each other. The spectral line shapes of fast and delayed fluorescence were also similar, and therefore both cases correspond to the exciton decay. However, the delayed fluorescence line had a slight red shift with respect to the normal exciton line.

These are the facts. We now discuss how well these facts agree with the modified charging model. Within this model, there are states j localized at the core–shell interface (see Fig. 4). The electron and the hole that form a state j have localized wave functions and cannot recombine as fast as the electron and hole in the exciton delocalized over the whole nanocrystal. Therefore, the electron and hole forming a state j live longer than a normal NC exciton, i.e., their conversion into a photon is delayed. The state j is the source of delayed fluorescence.

After losing their energy, the electron and hole eventually fall on the bottom of the potential well and annihilate with the same probability of light emission as in the case of an ordinary exciton. Therefore, the spectral line shapes of ordinary and delayed fluorescence are similar. The red shift of the delayed fluorescence line is apparently connected with the fact that the delayed exciton was not formed in the NC in a normal way, but was created via the state *j*.

The fact that measured distributions of on-periods are similar for normal and delayed fluorescence is consistent with the modified charging model, because the NC core ionization, that is, the transition from the on-state to the off-state, is also realized via the states j, which are also responsible for the existence of delayed fluorescence. The integral intensity of delayed fluorescence amounts to 10% of the total fluorescence, which means that the probability of electron-hole relaxation via the state j is approximately one tenth the probability of the relaxation via all other channels leading to the formation of a normal exciton.



Figure 12. (a) Relaxation of three types of fluorescence over a short time interval and (b) high-intensity fluorescence extinction over a long time interval. The lifetime of the delayed fluorescence is 96 ns [26].



Figure 13. (a) Fluorescence trace of a CdSe/ZnS single NC. (b) Fluorescence extinction curves obtained using the TCSP method in different parts of the trace. (c) Extinction curves measured at time intervals indicated on the trace [30].

The blinking of NC fluorescence is an unwanted phenomenon that lowers the NC efficiency in practical applications. Therefore, a great deal of effort has been made to obtain an NC without blinking fluorescence. Because it was believed that the charge transition from the core to the shell is the main reason for off-periods, the greatest effort has been focused on suppressing these transitions.

The first solution was to decrease the number of traps in the shell by surface passivation. This was demonstrated in [27]. The second solution was to grow the NC with a very thick shell [28, 29]. The idea was to create a broad potential barrier for the charge leaving the NC core. But these attempts did not solve the problem of obtaining a single NC with continuous fluorescence.

### 3. Fluorescence lifetime fluctuations

### 3.1 Correlation between quantum yield fluctuations and fluorescence lifetime fluctuations

Important physical information was obtained in the experiments by Bawendi's group [30], where the fluorescence lifetime was measured in different parts of the blinking fluorescence trace. Figure 13 shows the experimental results obtained in [30] using the time-correlated single-photon (TCSP) counting technique.

We can see from the data presented in Fig. 13 that the NC fluorescence lifetime is larger in the parts of the trace with a higher intensity. This result can be written in the mathematical form

$$Q(i) = \gamma_{\rm em} t_i \,, \tag{14}$$

which relates the fluorescence quantum yield to the fluorescence lifetime. Parts of the trace corresponding to three different i are indicated by rectangles in Fig. 13a. Dependence (14) was also observed in paper [15], which was discussed in Section 2.4.

#### 3.2 A- and B-type nanocrystals

Recently published results of experiments [31] on the blinking fluorescence lifetime are similar to the ones described in Section 3.2. These results show that chemically identical NCs with identical core-shell pairs can have either a



Figure 14. (Color online.) Fluorescence intensity fluctuations (black lines) and fluorescence lifetime fluctuations (red lines) [31].

fluctuating or constant fluorescence lifetime. This situation is illustrated in Fig. 14. Nanocrystals with the fluorescence lifetime fluctuating in phase with the fluorescence intensity fluctuations were attributed to the A type, while NCs with a constant lifetime and fluctuating intensity were attributed to the B type. Obviously, the nanocrystals studied in [30] by Bawendi's group with the results shown in Fig. 13 correspond to the A type.

# 3.3 Modified charging model for the fluorescence of A- and B-type nanocrystals

The discovery of A- and B-type NCs raised the question of whether the discussed models (modified charging model and multiple recombination center model) can explain the experimental facts, as shown in Fig. 14. This problem has not been solved yet for the MRC model. At the same time, the results shown in Fig. 14 can be explained in the framework of the modified charging model. We recently demonstrated this in [32] in the following way.

Because both the modified charging model and the MRC model have their advantages and shortcomings, the model in [32] used the strong sides of both these models, i.e., a combination of these models with some additional elements. This model was therefore called the combined model [32].

The combined model is based on the modified charging model. The NC core contains excitons together with electrons and holes in a state j, localized in the core near the interface and playing an important role in Auger ionization of the NC core. The pump schematic for these quantum states is shown in Fig. 15. According to Fig. 15a, hot electron-hole pairs produced by laser radiation in the NC lose energy and either bind into an exciton (ex) or make a transition into j states localized at the interface. This means that the exciton level and the j level are pumped with intensities that can be written in the form

$$L_{\text{ex}} = L \frac{\gamma_{\text{ex}}}{\gamma_{\text{ex}} + \sum_{j} \gamma_{j}}, \quad L_{j} = L \frac{\gamma_{j}}{\gamma_{\text{ex}} + \sum_{j} \gamma_{j}}.$$
 (15)

Therefore, the diagram in Fig. 15a can be replaced with the effective setup shown in Fig. 15b.

Using the effective pumping scheme, we consider the structure of the lowest NC core levels and transitions between them. This scheme can be represented as shown in Fig. 16. The left-hand part of the diagram shows the lowest levels of the neutral NC core. The right-hand part shows the lowest levels of the ionized NC core.

We separately discuss the question of the sign of the charge that leaves the NC core during its ionization. Figure 4 shows two possible processes: an electron leaves the core or a hole leaves the core. If the core loses an electron [33], the



Figure 15. Transition to the effective scheme for pumping exciton levels (ex) and levels (j) of atoms located in the NC core at the interface.



Figure 16. (Color online.) Schematic of the lowest levels and transitions between them in a neutral and ionized NC core. Dark (red) and bright slanted arrows indicate processes of NC core ionization and neutralization.

exciton in the ionized core (trion) is charged positively; if a hole leaves the core [34], it is charged negatively. Recent measurements of polarization-resolved photoluminescence in a strong magnetic field led the authors of [34] to the conclusion that the trion is negatively charged. This means that a hole leaves the core during Auger ionization. We use this result in what follows.

We now specify the notation for levels in Fig. 16. Here, ex is the exciton state in the neutral core, j is the state of the jth atom on the surface of the neutral core, and ex + j is the exciton produced by the pumping radiation plus the excited jth atom in the neutral core (i.e., ex + j is two-particle excitation in the neutral core).

The right-hand part of the diagram shows the lowest electron states of the ionized core plus hole in the *k*th shell trap. Here, *k* is the ground state of the ionized core with a hole in the *k*th trap and ex + *k* is the exciton (trion) in the ionized core. The state j + k is not important for the ionization process discussed below, and we omit it.

The core can be neutralized in two ways. The dark (red) arrow illustrates the Auger neutralization with the rate  $g_k^A$ , during which an electron located in the charged core (trion) vanishes and its energy is transferred to the hole in trap k. After gaining this energy, the hole jumps from trap k into the core and neutralizes it. The white arrow stands for the neutralization with a rate  $g_k$ , which is realized by tunneling of the hole from trap k into the NC core. The scheme shown in Fig. 16 describes both A- and B-type NCs.



Figure 17. Two possible locations of the hole that left the NC core relative to the electron that was created in the NC core.

Indeed, A-type nanocrystals are characterized by the following relation between the fluorescence quantum yield *Q* and the fluorescence lifetime:

$$Q_{\rm A}^{\rm on,\,off}(k) = \frac{\gamma_{\rm em}}{\gamma_{\rm em} + \Gamma_{\rm nr}^{\rm on,\,off}(k)} = \gamma_{\rm em} t^{\rm on,\,off}(k) \,, \tag{16}$$

where

$$\Gamma_{\rm nr}^{\rm on}(k) = \Gamma_0, \quad \Gamma_{\rm nr}^{\rm off}(k) = \Gamma_0 + g_k^{\rm A}. \tag{17}$$

According to Fig. 16, the relation between the quantum yield and the lifetime in a B-type NC has the form

$$Q_{\rm B}^{\rm on, off}(k) = \frac{\gamma_{\rm em}^{\rm on, off}}{\gamma_{\rm em}^{\rm on, off} + \Gamma_0 + g_k^{\rm A}} \approx \frac{\gamma_{\rm em}^{\rm on, off}}{\Gamma_0} = \gamma_{\rm em}^{\rm on, off} t_0 \,. \tag{18}$$

Consequently, in B-type NCs, the emission rate  $\gamma_{em}^{on, off}$  and the neutralization rate  $g_k^A$  should be significantly smaller than the rate of nonradiative transitions  $\Gamma_0$ .

The key element in Eqn (18) is the fluctuating ability  $\gamma_{em}^{on, off}$  to emit fluorescence photons. This effect was explained in [32] in the following way. We need to know why the emissive ability of the NC in the off-state can be significantly lower than in the on-state. Figure 17 schematically shows NCs of both types in off-states, that is, when a hole left the *j*th atom of the core and an electron was created in the core. During the Auger ionization, the hole gains a large amount of energy and makes a transition to higher

quantum states of the core and shell. After traveling through these delocalized upper states and losing its energy, the hole can descend into a trap that is located either near the electron, as shown in Fig. 17a, or far from the electron (Fig. 17b). In the first case, the Coulomb field induced in the core region due to the electron–hole separation is weak, while in the second case, it is strong. A strong Coulomb field induced by the separated electron and hole prevents the annihilation of electron–hole pairs in the off-state, lowering the core capacity to emit photons in the off-state, compared to the on-state. Consequently, we observe on/off fluctuations of the emissive ability of the B-type NC, according to Eqn (18).

# 3.4 Anticorrelation between the off-period duration and the 'grey' fluorescence lifetime

Obviously, the background fluorescence is always present during the off-periods. However, many experiments have shown that the fluorescence intensity in off-periods significantly exceeds the background, although it is smaller than the fluorescence intensity during on-periods. Therefore, the emission during off-periods was called 'grey' emission.

Investigations of such grey emission have been performed in a number of studies. An unexpected result was obtained by Leone's group [35] (Fig. 18). Figure 18 demonstrates the anticorrelation between the off-period length  $\tau_{\text{off}}$  (it is indicated in the left-hand side of Fig. 18) and the time  $t_k$ , i.e.,

$$\frac{1}{\tau_{\rm off}(k)} \propto t_k \,. \tag{19}$$

Here,  $t_k$  is the lifetime of grey fluorescence described by transitions in the right-hand part of the schematic in Fig. 16.

The modified charging model explains the appearance of relation (19) as follows. We write the set of six balance equations corresponding to the quantum state structure shown in Fig. 16. These equations are given in our paper [32]. Now we can use the method that we used to derive the expressions for on/off-period durations from Eqns (3), and obtain the expressions for  $\tau_{on,off}$  based on the set of six equations corresponding to the schematic in Fig. 16. The result for  $\tau_{off}$ , which we are interested in, has the form

$$\frac{1}{\tau_{\text{off}}^k} \approx g_k + g_k^A \frac{L_{\text{ex}}}{\Gamma_0 + g_k^A} \,. \tag{20}$$



Equation (20) shows that the duration of the kth off-period is determined by the rates of both the tunnel and Auger neutralizations. The latter is realized when the exciton in the charged core (trion) vanishes and transfers its energy to the hole in trap k located in the NC shell, which stimulates the transition of this hole back into the NC core. If the second term in (20) is significantly larger than the first one and Auger neutralization prevails over the tunnel one, then

$$\frac{1}{\tau_{\text{off}}^{k}} \approx g_{k}^{A} \frac{L_{\text{ex}}}{\Gamma_{0} + g_{k}^{A}} = g_{k}^{A} L_{\text{ex}} t_{k} , \qquad (21)$$

which means that in this case we can indeed observe an anticorrelation between the *k*th off-period duration  $\tau_{\text{off}}^k$  and the grey fluorescence lifetime  $t_k$ .

# 3.5 Facts that question the validity of the charging model and their possible explanation

We now discuss whether the modified charging model for NCs, i.e., the schematic shown in Fig. 16, with additional considerations shown in Fig. 17, can agree with the facts that were recently discovered by the authors of [36, 37]. The authors of these studies believe that the results they have obtained do not agree with the charging model.

Bawendi's group studied the blinking fluorescence of a single CdSe/CdZnS NC. They showed in [36] that the quantum yield  $Q_1^{\text{off}}$  of exciton (trion) fluorescence during the off-period is approximately 100 times lower than the quantum yield  $Q_1^{on}$  of the neutral exciton fluorescence during the on-period. Based on the quantum yield of the biexciton measured earlier, the authors of [36] believe that the ratio  $Q_1^{\text{off}}/Q_1^{\text{on}}$  should be at least 10 times larger. However, in addition to this consideration, which involves the value of the biexciton quantum yield, it should be noted that in later paper [38], Bawendi's group showed that there is a significant uncertainty in the value of the biexciton quantum yield. The extremely small value of the trion fluorescence quantum yield is considered by this group to be a phenomenon that cannot be explained in the framework of the charging model, which usually assumes that the light emission rate  $\gamma_{em}$  is the same in on- and off-states. However, the facts discovered a year later in [31] clearly show that in B-type NCs, the light emission rate in off-states is much smaller than in on-states, i.e.  $\gamma_{em}^{off} \ll \gamma_{em}^{on}$ . Unfortunately, it remains unclear which type of NCs were studied in [36]. If we assume that this inequality holds for the NC investigated in [36], then there is no conflict with the charging model.

In [37], Rosen's group measured the off-state fluorescence lifetime of CdSe/CdS/ZnS NCs with three different sizes: 3.8, 5, and 8 nm. The fluorescence extinction curve had a fast component with the time constant of about 200 ps and a slow component with the time constant around 1 ns. The time constant of the fast component was independent of the NC size. This led the authors of [37] to the conclusion that the NC core neutralization is not realized via the Auger mechanism and is not therefore described by the rate  $g_k^A$ indicated with a dark (red) arrow in Fig. 16. The authors of [37] considered this fact to be inconsistent with the charging model. But if we take into account that the core neutralization can be realized in the charging model via the tunnel mechanism indicated by a wide white arrow in Fig. 16, then the experimental data in [37] can agree quite well with the charging model.

### 4. Combined model of a nanocrystal

#### 4.1 Spectral line jumps and the two-level system model

The nonradiative recombination  $\Gamma_0$  of an exciton in a neutral core exists even for low intensities of the pumping radiation, when the probability of finding two excitations in the core is small and Auger recombination is impossible. Therefore, there is another reason for nonradiative transitions: interaction of electron degrees of freedom with the motion of atoms in the NC.

There are two types of atomic motion in a condensed medium: atom oscillations around their equilibrium positions (phonons) and hops of atoms from one equilibrium position to another. The second type of motion is realized by tunneling through the potential barrier that separates two equilibrium positions of the atom. It can be described by the so-called two-level system (TLS), already introduced in the 1970s [39, 40]. This tunnel motion of atoms was multiply observed in polymers and glasses at low temperatures [41–44]. Figure 19a shows the manifestation of the TLS in the absorption spectrum of a polyatomic molecule incorporated into a polymer.

Where can we find a TLS in an NC? Atoms that are located inside the NC core form an ideal crystal lattice. However, the ideal structure of the core atom lattice is broken into regions where these atoms have adjacent shell atoms (at the interface). The energy of electronic excitation of an atom located at the interface can fluctuate and take two different values. An atom with two possible excitation energies can be described by the TLS. Obviously, the number of TLSs is significantly smaller than the number of atoms on the interface.

Figure 20a shows an NC with defects at the interface (vacancies). Transitions to these states can be described using the TLS model. The existence of two possible positions of a nonexcited atom means that there are two types of ground electron states in such an NC. These states 0 and 2 are indicated in Fig. 20b.

Why  $\Gamma_{nr}^0 \neq \Gamma_{nr}^2$ ? Nonradiative transition means that the energy  $E_{ex}$  of the electron excitation transforms into the energy of phonons  $\hbar\omega_q$  and the TLS energy  $\varepsilon_i$ , i.e.,

$$E_{\rm ex} = \sum_{q} \hbar \omega_q + \sum_{i} \varepsilon_i(t) \,. \tag{22}$$



**Figure 19.** Spontaneous jumps of spectral lines in the tetra-tert-butylterrylene molecule (TBT), incorporated (a) in the polyisobutylene (PIB) [43] and (b) in the CdSe/ZnS NC (T = 10 K) [45]. Fluorescence traces of a molecule and an NC are similar.



**Figure 20.** (a) NC with a defect (vacancy) and an excited atom *j* at the interface. (b) Energy diagram for an NC with two nonexcited electron states (0, 2) and two excited electron states (1, 3). The rates  $\Gamma_1 = \gamma_{em} + \Gamma_{nr}^0$  and  $\Gamma_3 = \gamma_{em} + \Gamma_{nr}^2$  of total relaxation include the emission rate  $\gamma_{em}$  and the rate  $\Gamma_{nr}^{0,2}$  of nonradiative transitions during the decay of excited electron states.

The probability of a nonradiative transition is maximal when equality (22) is satisfied exactly. If the energy of one TLS changes, we should add or subtract this energy from the right-hand side of (22). Such a fluctuation of energy, which is a term in the right-hand side of (22), leads to fluctuations of the nonradiative transition rate, which means that there is a transition from  $\Gamma_{nr}^0$  to  $\Gamma_{nr}^2$  and vice versa.

Due to the interaction of the electron degrees of freedom with the TLS, the exciton (excited state of the NC) 'feels' which of the two possible positions at the interface is occupied by the atom. Therefore, states 1 and 3 are attributed to two possible exciton states. The populations of states 0 and 2 are described by the functions [44]

$$\rho_0(t) = \frac{A}{R} + \left(\rho_0(0) - \frac{A}{R}\right) \exp\left(-Rt\right),$$

$$\rho_2(t) = \frac{a}{R} + \left(\rho_2(0) - \frac{a}{R}\right) \exp\left(-Rt\right).$$
(23)

Here, R = A + a is the fluctuation rate in the TLS. Equations (23) are dynamical. However, these equations can describe quantum hopping, which looks like a stochastic process. For example, a quantum hop from state 0 to state 2 at t = 0 corresponds to the initial condition  $\rho_0(0) = 0$  and  $\rho_2(0) = 1$ , and a quantum hop from state 2 to state 0, to another initial condition,  $\rho_0(0) = 1$  and  $\rho_2(0) = 0$ . Every quantum hop implies a change in the initial conditions for Eqns (23).

When the atom hops from state 0 to state 2 and back, the exciton line jumps from the frequency  $\omega_0$  to the frequency  $\omega_0 + \Delta$  and back. These jumps occur over time, and in the frequency scale they can be described by the spectral function

$$I(\omega, t) = \rho_0(t) \frac{\gamma_{\rm em} + \Gamma_{\rm nr}^0}{(\omega - \omega_0)^2 + (\gamma_{\rm em} + \Gamma_{\rm nr}^0)^2} + \rho_2(t) \frac{\gamma_{\rm em} + \Gamma_{\rm nr}^2}{(\omega - \omega_0 - \Delta)^2 + (\gamma_{\rm em} + \Gamma_{\rm nr}^2)^2},$$
(24)

where  $\gamma_{\rm em}$  is the photon emission rate and  $\Gamma_{\rm nr}^{0,2}$  is the nonradiative transition rate in the NC with the TLS with two states 0 and 2. According to Eqn (24), the nonradiative transition rate fluctuates as

$$\Gamma_{\rm nr}(t) = \frac{1}{\pi} \left[ \Gamma_{\rm nr}^{0} \rho_0(t) + \Gamma_{\rm nr}^2 \rho_2(t) \right].$$
(25)

If  $\Delta = 0$ , we observe only one exciton line. The nonradiative transition rate takes two values,  $\Gamma_{nr}^0$  and  $\Gamma_{nr}^2$ , at random time moments. If there are two TLSs, then the rate of nonradiative transitions takes four values, according to the equation

$$\Gamma_{\rm nr}(t) = \frac{1}{\pi} \left[ \Gamma_{\rm nr}^0 \rho_0(t) + \Gamma_{\rm nr}^2 \rho_2(t) + (\Gamma_{\rm nr}^0)' (\rho_0(t))' + (\Gamma_{\rm nr}^2)' (\rho_2(t))' \right].$$
(26)

Fluctuations of nonradiative transitions due to hopping in the TLS cause additional fluctuations in both on- and off-states. In this regard, the TLS model becomes similar to the MRC model introduced in [18], if we add the recombination center energies to energy balance (22). However, the TLS model is only a part of the combined model that was described by the author in [32]. It is introduced additionally to the modified charging model that determines on/off-fluctuations of large amplitude.

# 4.2 Manifestation of two-level system fluctuations in the photon distribution function

As was shown in [46], TLSs can influence both the fluorescence trace and the photon distribution function. Figure 21 shows the fluorescence trace of a single CdSe/ZnS NC and the distribution of photons in this trace, measured in [46].

The photon distribution has two peaks: one corresponds to small and the other to large values of photocounts N every 10 ms. The peak that corresponds to a large number N of photons is considerably broader than the Poisson distribution, shown by the dashed line. It is known that the Poisson distribution of photons is inherent in fluorescence of a twolevel atom. It is also known that the appearance of off-periods



**Figure 21.** (a) Fluorescence trace of a 5.2 nm single CdSe/ZnS NC, measured at room temperature and for continuous pumping with a 532 nm laser. Signal accumulation time is 10 ms. (b) Histogram of the photon distribution over a period of 10 ms in this fluorescence trace. The dashed line shows the Poisson distribution.



Figure 22. (Color online.) (a) Fluorescence trace and (b) the photon distribution in this trace, calculated in [46] using the Monte Carlo method and a model that takes the influence of the TLS into account.

in fluorescence leads to a distribution that is broader than the Poisson one [47]. However, all the efforts to describe the measured photon distribution by taking the actually existing long and short off-periods into account have had no success. The new result was obtained when a model that used the Monte Carlo method to calculate the fluorescence trace and photon distribution was completed by small-amplitude fluorescence intensity fluctuations, which appear due to the fluctuation of nonradiative transitions in the NC caused by hopping in the TLS described above.

The results of this calculation using the Monte Carlo method for the fluorescence trace and photon distribution function are shown in Fig. 22. First, we see a qualitative agreement between the calculated and measured traces. Second, the photon distribution function measured in the calculated trace (blue solid line in Fig. 22b) is in good agreement with the experimentally measured histogram. This result can be considered more evidence of the existence of TLSs in NCs.

#### 5. Conclusions

The first article [4] where it was observed that single nanocrystals pumped by a continuous laser produce blinking fluorescence was published 20 years ago. During these years, hundreds of papers were published dedicated to the investigation of various aspects of this, as it turned out later, very common phenomenon. The obtained experimental data are very extensive and can hardly be covered in one review.

Aspects such as the influence of the temperature and various chemical additives on the blinking character, features of exciton, biexciton, and triexciton emission spectra, influence of external fields such as electric ones on the blinking fluorescence character and on the radiation spectra, and many others were not considered in this review.

The author joined the research on single NC photoluminescence in 2000 during the Matsumoto Single Quantum Dot Project, which was realized in Tsukuba (Japan). The discovery of power-law distributions for on- and off-periods was made in the same year by Nesbit's group [6, 7]. This was a very intriguing phenomenon, because explaining it required considering a set of ionization and neutralization times in the NC. The existence of multiple neutralization times was not a surprise for the Efros–Rosen theory because it considered a number of traps in the NC shell, each loosing the charge with its one relaxation time. But the existence of multiple ionization times required an explanation because it did not agree with the Efros–Rosen theory, which dealt only with excitons and predicted that a single NC should have a single ionization time. To solve the problem of multiple ionization times, the Efros–Rosen model had to be modified, and this was done in [12, 13]. The basic idea was that the core atoms located at the core–shell interface play a decisive role in the ionization and, consequently, in the blinking effect.

Experiments that have demonstrated a correlation between the blinking of the fluorescence quantum yield and the photoluminescence lifetime, as well as the discovery of A- and B-type NCs, were very important for understanding the physics behind the blinking and for the development of the theoretical blinking model presented in this review. The basis of this combined model, that is, the modified charging model, is shown in the schematic in Fig. 16. This allows interpreting several experimental facts that could not be explained before. First of all, this is the existence of A- and B-type NCs. Of course, this approach is not considered to be universal and it can be improved further if new experiments reveal any discrepancies. New experiments that would verify the obtained results should show whether this model is realistic. This, in turn, will help progress in understanding the physical nature of blinking fluorescence emitted by single semiconductor nanocrystals.

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