PARAMETRIC EVALUATION OF QUANTUM DOT FLUORESCENCE AND INTERMITTENCE

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Abstract

Recent developments in nano science and technology have revealed the possibility of using Quantum dot fluorescence properties for medical imaging aided diagnostics. Quantum dots being one of the novel nano structure that exhibits wide range of quantum phenomena sprawling across optics, electronics and chemistry. This multi domain characterization makes the understanding and further development of any technology based on these devices quite a challenge that needs to be addressed through cross domain experimental and theoretical study.

We present a study of quantum fluorescence property of quantum dots. The emission and absorption rates and energy of the quantum dots are size and environment dependent due to the quantum confinement and discrete energy. We analyze quantum dot emission spectrum response to environmental and structural variations. We consider Bruss energy relation and quantum statistical observations to model the quantum dot fluorescence activity.

Keywords: Quantum dot, Bruss energy, Intermittence, Bohr's exciton.

1. INTRODUCTION

Quantum dots, the nano sized crystal structures are expected to bring a revolution in medical sciences with their potential for probing in fluorescence imaging [1, 2]. The quantum dot's exhibit unique photo physical properties like resistance to photo bleaching, Gaussian emission spectrum and high fluorescent quantum yield due to their quantum confinement structure [3]. These photo physical properties makes them front runner in invivo diagnostics of tumors and cancer cell's compared to other fuorophores [4].

Building applications of the quantum dots in fluorescence imaging requires theoretical and practical understanding of the quantum blinking phenomena. The quantum yield of fluorescence depends on the rate of blinking which consists of radiative and non-radiative phases of exciton recombinations. The long non-radiative phase's limits quantum yield and long term signal monitoring [19]. Quantum dot blinking phenomena in CdSe quantum dots was reported by Nirmal and team in 1996 [20], since then the field of quantum fluorescence has offered a plethora of interesting phenomena. In literature one can find vast practical and theoretical discussions about modeling of the fluorescence intermittency statistics [16,21], possible physics behind the intermittency along with the process and material techniques of improvising quantum yield with efficient fluorescence [22,23].

Most of the models proposed in literature for quantum dot fluorescence and intermittency are focused on time based analysis, characterizing and explaining the occurrence of fluorescence (ON) and intermittent (OFF) states, these early models were based on analysis of experimental results available during their time of study and development, these models still holds good in most of the aspects, but needs to be reworked or updated with the most recent experimental findings and physics. The observations made by Neeleshwar and Chen reveals the size dependent optical properties of the CdSe quantum dots [15], Bullen and Mulvaney have reported about the effects of chemisorptions on the luminescence property of CdSe quantum dots [23], Benjamin Bruhn and team have reported quantum dot system dependent blinking statistics through the study

of CdSe and Zns quantum dots [25]. The quantum fluorescence study conducted by Issac and Cichos has revealed that intermittency statistics depends on dielectric media [26].

In this paper we discuss about a probability and statistics based model of quantum dot fluorescence and intermittence relating the quantum yield to the quantum dot structure and environmental parameters, the model proposed is based on the observations put forth till now. Paper is organized into three sections section 1 is introduction, in section 2 we discuss about the quantum fluorescence model and the conceptual considerations and assumptions made in arriving at the model, section 3 is about the discussion of the model followed by results and conclusion.

2. MODEL

In this model, we consider quantum dot's of spherical structure with radius R encapsulated with ligands as shown in figure 1, immersed in a colloidal suspension. Quantum dots can be made of either group III or IV table element's, we make the following assumptions and consider the facts in deducing the model:

(1) Quantum dots immersed in the colloidal solution are assumed to be stationary and settled.

(2) Colloidal solution is free of charges.

(3) Quantum dots can be capped with different material shells and external cover of the shell is attached with ligands to reduce their poisonous effects.

(4) Quantum dots are chemically stable.

(5) Colloidal solution may contain luminescence accelerators.

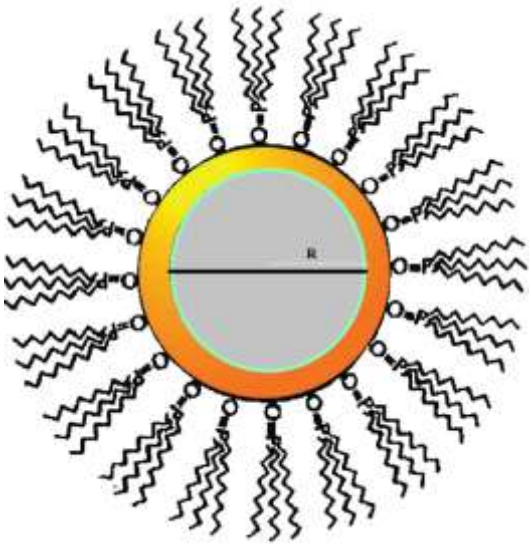


Fig. 1 Quantum dot of radius R with shell and ligands.

The colloidal suspension containing quantum dots is exposed to radiation of frequency ν such that the energy $h\nu$ of the photons corresponds to the energy gap of the Quantum dots, which is given by Brus energy formula as

$$\Delta E = E_{g(Bulk)} + \frac{h^2}{8R^2}\left(\frac{1}{m_{e^*}} + \frac{1}{m_{h^*}}\right) \quad (1)$$

Where $E_{g(Bulk)}$ => Bulk material energy gap, h =>Plank's constant, R =>Quantum dot radius, m_{e^*} =>Effective electron mass and m_{h^*} =>Effective hole mass.

$$\Delta E = h\nu \tag{2}$$

the radiation is considered to be continuous.

We consider the outcome/fact signal of such an experiment conducted by Pavel and Masaru [27] shown in figure 2.

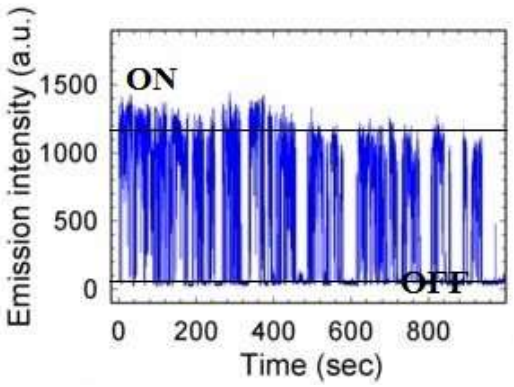


Fig. 2 Emission intensity versus time: Outcome signal of quantum dot continuously illuminated with radiation.

With analysis of the signal one can find out that the intensity is varying between two extreme intensity levels shown with thin black lines in the figure, the extreme high level corresponds to the ON state/fluorescence state of the quantum dot and the extreme low level corresponds to the OFF state/intermittence state of the quantum dot.

The process of ON and OFF is stochastic as the time instance of ON/OFF and duration of ON/OFF is not consistent with respect to time, the signal is the outcome of continuous illumination of the colloidal solution containing quantum dots. We can model this ON/OFF behavior of the quantum dot with parametric and probabilistic model. We consider the behavior to be parametric as stochastic process is found to be function of quantum dot structural and environmental parameters [6].

Let us consider S_{QD} to represent the state of the quantum dot at time t, which can take either ON or OFF state values. The two states are the outcome of interaction of the quantum dot with photons of the radiation. The interaction between the electron in the quantum dot and the photon of the radiation makes the quantum dot to turn ON/glow brightly some times and go blank/OFF other times as illustrated in figure 2, this transition of events/states can be interpreted probabilistically as

$$S_{QD}\,|_t = P_{p\to e} P_{e\to h} \tag{3}$$

Where $P_{p\to e}$ => Probability of photon electron interaction, $P_{e\to h}$ =>Probability of recombination of excited electron in next state and hole in ground state.

The probability of photon electron interaction represents the physical phenomena of electron photon wave function overlapping which is time and position dependent, it approaches a maximum value of 1 if the two wave functions overlap in time and position without any positional displacement and time delay, in all other cases where the two wave functions will not overlap perfectly in time and position the probability takes a

value less than 1. Whenever the photon electron interaction probability takes value less than 1, the electron absorbs the photon energy which can make electron to move into other energy levels corresponding to traps or vibrons. These probabilities of energy transitions can be shown through Jablonski energy diagram as shown in figure 3.

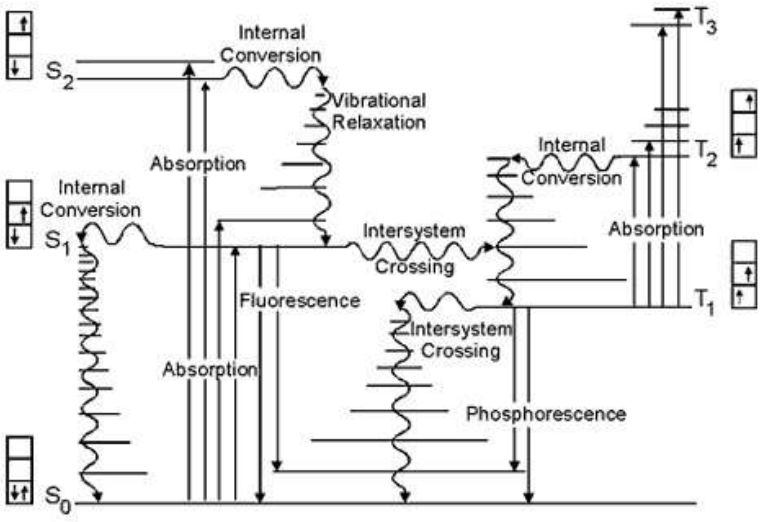


Fig. 3 Quantum dot energy transition Jablonski Diagram.

These probabilities are state and parameter dependent. The probability of electron entering next state depends on the distribution and number of traps, the probability of electron hole recombination again depends on traps and also on vibrational energy states, the probability of electron absorbing complete energy and moving to next state depends on the cross sectional area of quantum dot and shell along with the ligands attached.

The probability of photon electron interaction can be computed with the overlapping integration as

$$P_{p\to e} = \frac{Tf(n_t, \mathrm{d}_t)}{r_1 - r_2} \int_{-\infty}^{T} \psi_p(\tau)\psi_e(t-\tau)d\tau \tag{4}$$

Where $r_1 - r_2$ => Positional overlapping of photon and electron wave functions, T =>Interaction time, $\psi_p(\tau)$ => Photon wave function , $\psi_e(\mathrm{t})$ => Electron wave function and $f(n_t, \mathrm{d}_t)$ =>Function of number of traps and their distribution. The amount of overlapping implies energy consumed by the electron, which in turn is the decision maker for the next state of electron, i.e. maximum/exact overlapping electron absorbs photon and moves to the next energy state, in other cases electron may absorb portion of photon and may enter into vibration state or trap state. This interaction is applicable for electron in any state.

The probability of electron hole recombination or exciton recombination can be computed as [17], considering consider sphere of radius R

$$P_{e\to h} = \frac{f(n_t, d_t)}{4\pi\varepsilon n_e n_h} \int dr_e \int_{r_e - \frac{R}{2}}^{r_e + \frac{R}{2}} \rho_{eh}(\mathrm{r_e}, \mathrm{r_h})d_{rh} \tag{5}$$

n_e => number of electrons, n_h => number of holes, ε => dielectric constant, r_e =>electron position, r_h =>hole position $\rho_{eh}(\mathrm{r}_e, \mathrm{r}_h)$ =>electron hole pair or exciton density. $P_{e\to h}$ can be calculated using the electron-hole explicitly correlated Hartree-Fock method (eh-XCHF) [18].

The trapping function can be modelled as

$$f(n_t, d_t) = \frac{1}{n_t}\alpha e^{-\alpha r_t} \tag{6}$$

Where is r_t the particle trap distance, α is the decay length associated with the tunneling barrier which is computed with

$$\alpha = \sqrt{\frac{2m_e\Delta V}{h}} \tag{7}$$

In the above expression m_e is the mass of electron, ΔV is the potential difference bewteen the trapping site and the particle being trapped.

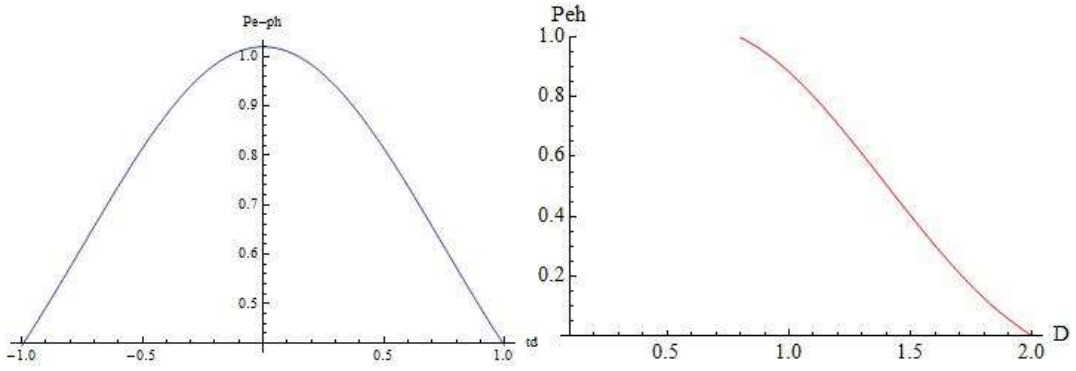
3. DISCUSSION

From equation (3) we can deduce that the state of the quantum dot ON/OFF depends on the electron photon overlapping along with electron hole recombination. With equation (4) we see that overlapping function is probabilistic which depends on time and positional overlapping of electron and photon wave functions along with this it depends on the number of traps and their distribution, equation (5) describes the electron hole recombination as a probability which depends on the density of electron-hole pair, number of electrons and holes, dielectric of the medium and the separation between the electron and hole.

The trapping density and distribution function as defined in equation (6) evolves with time and the dynamics of this function plays a vital role in turning the quantum dot ON or OFF. The state of the quantum dot is a function of squared trap density and distribution, any variations in trap density and distribution brings a multifold change in the state of the quantum dot. The quantum dot will be turned ON when the two probabilities takes maximum value of 1 which is possible only when the electron absorbs the photon and enters into appropriates next state followed by recombination, these two processes depends on the quantum dot material and encapsulating shell.

4. RESULTS

Plots for the two probability functions, from plot (a) we can see that the zero delay and zero positional overlapping leads to the maximum value of 1 for probability of electron-photon interaction i.e. the electron from the ground state will absorb the photon and enter into the next energy level, with increase in delay and positional variance between the electron and the photon wave functions the probability of electron entering next state reduces. Plot (b) shows the variation of exciton recombination probability with respect to the diameter of the quantum dot, where the probability of exciton recombination reduces with the increasing diameter of the quantum dot.



(a) (b)

Fig 4. (a) Probability of Photon electron overlapping as function of position and time, (b) Probability of exciton recombination as a function of quantum dot diameter

CONCLUSION

In this work we have tried to analyze the experimental results of quantum dot fluorescence and intermittency based on the outcome of analysis we have proposed model to explain the quantum dot blinking and its behavioral dependency on quantum dot structural parameters and environment. The model presented is novel idea. The model in itself cannot be expected to be complete as the stochastic process are always subject to observations, with new findings and observations the model can be fine-tuned based on experimental results cross verification. The model can be evaluated with the simulation by considering appropriate environmental parameters and quantum dots. We are in the process of simulating the model and will try to update the results and fine tune the model further in future by comparing the model simulation results with the practical data.

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