# Förster transfer in coupled colloidal type-II and type-I quantum dots

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## ABSTRACT

We examine theoretically resonant non-radiative exciton (Förster) transfer in the system of colloidal core-shell quantum dots (QDs) of different types. We show that when the type-I QD (acceptor) is coupled with the type-II QD (donor), the electron-hole pair optically excited in the type-II QD can be transferred to the type-I QD non-radiatively, if the recombination time of the former is larger than the time of the exciton transfer. Correspondingly, the time-resolved photoluminescence signal from the type-I QDs would be modified both quantitatively and qualitatively. We also discuss the feasibility to use this effect in a *pathogen detection platform* aimed at a single molecule level. With the QDs functionalized with antibodies to target pathogens, their presence will manifest itself by allowing or disallowing the Förster transfer by either bringing QDs closer to each other or changing electrostatic environmental properties, respectively. This "On-or-Off" scheme can work in both liquids and gases.

***Keywords***: type-II colloidal core-shell quantum dots, time-resolved photoluminescence, Förster transfer

Recently, efficient chemical and biological sensors become extremely important because of their applications in homeland security and environmental control. To protect public and soldiers from chemical/biological attack, food poisoning, or hazardous biological leakage, we need to establish improved diagnostic methods and sampling strategies in order to identify pathogens more rapidly and precisely. In order to satisfy this requirement, improved diagnostic methods are necessary to combine *high specificity*, *sensitivity*, *low power consumption*, and *low unit cost* with ultrahigh throughput and ultrafast detection. One of the most promising directions to build such detectors is the use of the artificial nanoscale structures known as quantum dots (QDs). They have discrete energetic spectra but in the contrast with usual atoms the level spacing can be readily and precisely engineered just through variation of their size [1]. The solubility of colloidal QDs in solution further increased the range of potential applications [2]. For example, their conjugation to biological molecules that can recognize and bind specific types of pathogens represents a great opportunity to perform ultrasensitive biomolecular detections in a readily controllable way. Although those types of bioconjugated QDs have been applied for biomolecular sensors since binding events between biological molecules and QDs can be probed optically due to their distinct change in the emission property, the optical detection by QDs systems in single biological molecule level has not been achieved yet. This ultimate resolution limit will have a significant impact for the improved future sensors. In the present paper, we discuss the physical principles of bioconjugated QDs and the strategy to develop new pathogen sensors with high sensitivity.

The vast majority of investigated QDs are type-I heterojunctioned QDs whose narrower bandgap material is a potential well for both electrons and holes. There exists, however, another group of semiconductor heterojunctions, so-called *type-II systems*, whose band alignment has a staggered character; i.e. the lower potential energy for electrons and the higher energy for holes or vice versa. Thus, electrons and holes are separated in real space, which gives rise to a *longer lifetime of the emission* [3,4]. Moreover, the lifetime can be controlled by optimizing the intensity of excitation, external electric and magnetic fields (see discussions and device examples in Refs. [5-7]). Furthermore, type-II heterostrutures suppress Auger recombination [8,9] that shortens the lifetime of the electron-hall separation and becomes a significant obstacle for successful implementation of nanocrystal-based electronic devices [10,11].

Among various models for sensitive biodetectors, the use of the Förster energy transfer [12] (i.e., the fluorescence resonant energy transfer (FRET) based on the Förster process) between QDs and biomolecules (e.g. Refs. [13,14]) is of special interest. For example, when maltose-binding proteins with dye conjugates were attached to the type-I CdSe-ZnS core-shell QDs, the photoluminescence (PL) signal from the QDs was quenched due to the Förster energy transfer of optical excitation to these proteins. However, once maltose in solution replaced these dye conjugates, PL signal from the QDs was restored and the PL signal amplitude was dependent on the maltose concentration. Method of DNA sensing using Förster energy transfer was proposed in Ref. [15] where the event of coupling of DNA with dye conjugates to QDs can cause

the PL signal quenching. It should be noted that in both these approaches, the signal from FRET donor has been measured.

Here we propose a novel Förster transfer-based sensing system where the detection is not made by the Förster transfer between the QD and an attached biomolecule but rather between *two colloidal QDs* coupled by the pathogen. Since those QDs conjugate antibodies to target the pathogen, the pathogen binding to the antibodies bridges two QDs, which induces the Förster transfer between these QDs. The major advantage over the previous schemes [13,14] is that our approach is not limited to detect molecules which must work as the quenching centers for the QD PL. Our sensing system allows one to detect *any molecule* in the "ON-or-OFF" manner because the Förster transfer signal between two QDs is observed only when the target pathogen exists in solution and bridges these QDs. Another advantage over approaches proposed in Refs. [13-15] is that we plan to study the PL signal from FRET *donors* whose life-time is larger and Förster energy transfer leads not only to quantitative changes of the signal, but to the modified *shape* of the time-resolved PL as well.

The physical origin of the Förster transfer is the electron-hole Coulomb interaction and the matrix element of such transfer (in resonant conditions) is given by

$$V = -\langle 2|U_c|1\rangle \sim \frac{1}{\varepsilon \cdot r_{12}^3} \qquad (1)$$

where |1> and |2> are the exciton wavefunctions in the first and second dots, respectively; $r_{12}$ is the distance between the dots, and $\varepsilon$ is the environmental dielectric constant. The corresponding transfer time, $\tau_{FRET}$, is inversely proportional to the matrix element squared, and thus is linear function of the dielectric constant squared and the sixth power of the interdot distance.

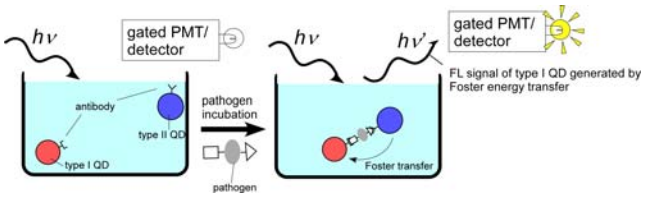


Figure 1: Proposed pathogen sensing platform in solution; Antibody-conjugated quantum dots are coupled in solution via the pathogen bridging under detection.

In our scheme, when the type-I QD (acceptor) is coupled with the type-II QD (donor), the electron-hole pair optically excited in the type-II QD can be transferred to the type-I QD non-radiatively if the recombination time of the former is larger than $\tau_{FRET}$. Due to the long PL decay time of type-II QDs, the binding event between targeted agents and QDs is detected by the characteristically delayed PL signals from the type-I QDs after the Förster transfer occurs (i.e., "On state"). If there is no target agent in the solution, the dots are far from each other and the Förster transfer, which is extremely sensitive to the distance between the donor and the acceptor, is impossible (i.e., "Off state"). When the dots are functionalized to the specific antibodies for the target pathogen, these QDs are coupled by this pathogen into QD-pathogen-QD system, in which these QDs are close enough to facilitate the exciton transfer (see Fig. 1).

Indeed, assuming for the simplicity [16] an exponential decay for donors and acceptors, the rate equation for the acceptors is

$$\frac{dN_A}{dt} = -\frac{N_A}{\tau_A} + \frac{N_D^0}{\tau_{FRET}} \exp\left[-\left(\tau_{FRET}^{-1} + \tau_D^{-1}\right)\cdot t\right] \qquad (2)$$

with the solution

$$N_A(t) = N_A^0 \exp\left[-\frac{t}{\tau_A}\right] + \frac{1}{\tau_A^{-1} - (\tau_{FRET}^{-1} + \tau_D^{-1})} \times \frac{N_D^0}{\tau_{FRET}} \left( \exp\left[-(\tau_{FRET}^{-1} + \tau_D^{-1})\cdot t\right] - \exp\left[-\frac{t}{\tau_A}\right] \right). \qquad (3)$$

Here, $N_A(t)$ is the number of excited acceptors at the time moment, $t$, (this number determines acceptor PL intensity); $N_A{}^0$ and $N_D{}^0$ are the numbers of acceptors and donors at the maximum of the laser pulse ($t$ = 0), respectively; $\tau_D$ and $\tau_A$ are the PL lifetime of donors and acceptors, respectively. In Eq (3), in addition to usual exponential decay expressed by the first term, there is the second term that could increase the number of excitons in the acceptors due to the Förster transfer of excitations from the donors. It should be noted that this term is more pronounced if the number of donors is larger than the number of acceptors.

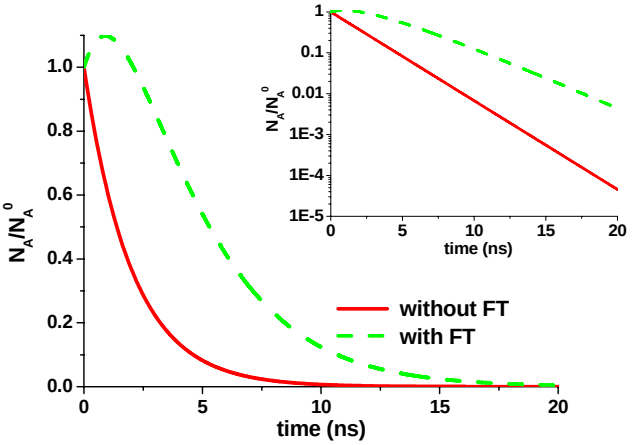


Figure 2: Simulated time dependence of the number of excitons in acceptors. The main panel (linear scale) demonstrates the characteristic increasing of the number of excitons in acceptors when QDs are coupled with the Förster transfer, whereas the inset (in logarithmic scale)

shows the increase of the decay time by orders of magnitude by the Förster transfer.

The time dependence of the number of excited acceptors is shown in Fig. 2 for $\tau_A$ = 2 ns, $\tau_D$ = 10 ns, $\tau_{FRET}$ = 4 ns, and $N_D^0/N_A^0$ = 3. It is evident that the time-resolved PL signal changes both qualitatively and quantitatively when the Förster transfer occurs. As shown in the inset of Figure 2, the characteristic increase of PL intensity is observed in the initial phase under the influence of the Förster transfer and the acceptor is drastically increased as a function of PL decay time due to the extension of the excitonic lifetime of the type II QDs. This result indicates that the Förster transfer-based spectral change by binding the donor QD and the acceptor QD via the pathogen-antibody binding can be applied to sense and assay the targeted pathogens.

The scheme described above makes it possible to detect pathogen agents in solutions. Alternatively, the sensing platform in Fig. 3 can also be used to detect pathogens, which could be convenient for the gaseous environmental sensors. Arrays of type-II and type-I QDs are immobilized on a surface and then QDs are spaced with the distance allowing the Förster transfer. When the pathogen attached to these QDs, the environmental dielectric constant increases and the Förster transfer is strongly suppressed (see Eq. (1)). This binding event can be monitored by the emission from the type I QDs as shown in Figure 2.

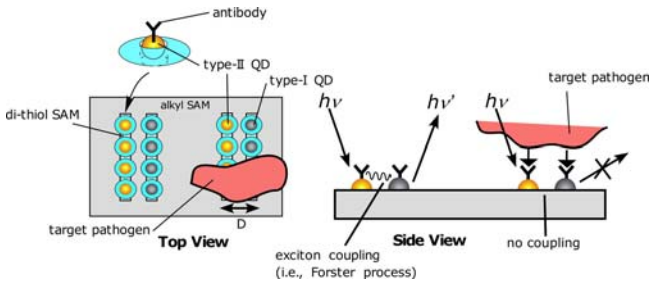


Figure 3: Illustration of the pathogen-sensing platform in gaseous environment.

In conclusion, we proposed a novel method suitable for detection of *any* biomolecules by coupling two heterogeneous QDs, type II and type I, in solution. Since the Förster transfer from the type II QD to the type I QD produces the delayed emission from the type I QDs, this characteristic emission can be applied as the signal for the pathogen sensing. The detection of the Förster transfer induced by the pathogen binding in the time domain makes the proposed scheme inherently more sensitive than other techniques detecting by the quenching of the donor or acceptor PL intensity. In the alternative platform, the array of the acceptor QDs and the donor QDs, already electrostatically coupled, can detect the pathogen by disallowing the Förster transfer via the pathogen binding on these QDs and switching the emission spectra to the non-Förster characteristics.

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16. It is known that time-resolved PL of type-II QDs is usually non-exponential (e.g., Refs. 3, 4 and references therein), whereas that of type-I QDs is often fitted by two exponentials (e.g. Klimov, et al., Phys. Rev. B **60**, R2177 (1999)); however, after a relatively long time, the decay for both QD types can be looked at as a single exponent, and the characteristic times are usually selected after such a delay. The only requirement we have here is that the decay of a type-II QDs be slower than that of type-I QDs.