

Bridging Energetics and Dynamics of Exciton Trapping in Core-Shell Quantum Dots

Marcello Righetto⁺, Alessandro Minotto⁺ and Renato Bozio^{+,}*

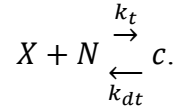
⁺ Department of Chemical Science and U.R. INSTM, University of Padova, Via Marzolo 1, I-35131, Padova (Italy)

SUPPORTING INFORMATION

Contents:	page
• Discussion on QY phenomenological modeling	S2
• Likelihood of sequential absorption	S5
• Table S1. QY absolute values	S6
• Figure S2: Photoluminescence spectra	S8

QY phenomenological modeling

The phenomenological kinetic model used in Ref. ¹ is a reduced form of the model presented by Scholes, et al.² These models aim to describe the photoluminescence dynamics of QDs ensembles, and fit the decay curves measured by TCSPC introducing trapping and de-trapping processes. The complex multi-exponential behavior of photoluminescence decay is reproduced in terms of a combination of trapping and de-trapping events. The fitting procedure results in estimating trapping (k_t) and de-trapping (k_{dt}) rate constants at room temperature. Here, we present a refined phenomenological model in which exciton trapping is described as a chemical process:



The reaction between a bound exciton (X) and a neutral trap site (N) produces a charged trap species (c) with a rate constant (k_t). In turn, the charged trap can regenerate the bound exciton with de-trapping constant (k_{dt}). It is worth to note that the formation of an isolated charge in the core region is not considered, but is granted by charge conservation.

The resulting rate equation system reads:

$$\begin{cases} \frac{d\rho_X}{dt} = -k_t\rho_X\rho_N - (k_r + k_{nr})\rho_X + k_{dt}\rho_c \\ \frac{d\rho_N}{dt} = -k_t\rho_X\rho_N + k_{dt}\rho_c \\ \frac{d\rho_c}{dt} = k_t\rho_X\rho_N - k_{dt}\rho_c \end{cases} \quad (\text{S.1})$$

Where the first equation describes the bound exciton population ρ_X , depleted by trapping (first term on RHS), radiative and other non-radiative recombinations while augmented by de-trapping. The second and third equation describe respectively neutral (ρ_N) and charged (ρ_c) trap

sites population. Their evolution is symmetrical, with trapping depleting neutral trap population while de-trapping increasing it and vice versa for charged trap population.

When steady state conditions are imposed to the above rate equations, one obtains the obvious conditions that the trapping and de-trapping velocities equal each other, namely:

$$v_t = k_t \rho_x \rho_N = v_{dt} = k_{dt} \rho_c. \quad (\text{S.2})$$

Since ρ_x is also constant, we get:

$$\frac{v_{dt}}{v_t} \propto \frac{k_{dt}}{k_t} = R_{DT}. \quad (\text{S.3})$$

From a physical point of view, we seek a correlation between PLQY and the ratio between de-trapping and trapping rate constants simply expressed by R_{DT} .

The outcome of this comparison is reported in Figure 3 of the main text where the trends of PLQY for core/shell QDs with increasing number of shell monolayers is compared with R_{DT} values. An inherent limitation of this comparison derives from the fact that, while the density of trapping and de-trapping centers is constant in steady-state, it is prone to possible changes as the number of shell monolayers increases.

	$k_t[\text{MHz}]$	$k_d[\text{MHz}]$	$k_{dt}[\text{MHz}]$	R_{dt}
CdSe/CdS 1ML	2.4	1.1	115.2	104.7
CdSe/CdS 2ML	8.6	0.9	119.1	132.3
CdSe/CdS 3ML	8,6	0,7	138.6	198.0
CdSe/CdS 4ML	12.7	0.5	78.9	157.8
CdSe/CdS 5ML	10.8	0.4	84.8	212.0
CdSe/CdS 6ML	22.6	0.2	38.1	190.5
CdSe/CdZnS 1ML	11.4	0.3	68.0	215.9
CdSe/CdZnS 2ML	14.4	0.2	51.9	241.4
CdSe/CdZnS 3ML	12.0	0.2	43.7	208.1
CdSe/CdZnS 4ML	9.1	0.2	43.8	203.7
CdSe/CdZnS 5ML	8.6	0.2	47.6	217.4

CdSe/CdZnS 6ML	12.1	0.2	40.1	211.1
CdSe/ZnS 1ML	0.3	0.9	180.9	201.0
CdSe/ZnS 2ML	1,9	0,7	141,0	201,4
CdSe/ZnS 3ML	2,1	0,5	124,5	247,0
CdSe/ZnS 4ML	2,2	0,4	89,9	256,9

Table SI_1 – Rate constants for radiative recombination (k_r), trapping (k_{dt}), and detrapping (k_{dt}), obtained by applying the revised kinetic model (eq S.1) to TRPL data of Ref.28 for CdSe/CdS, CdSe/CdZnS and CdSe/ZnS series.

Likelihood of sequential absorption of two photons

We quantified the average rate of photon absorption by multiplying the photon flux $\phi \left[\frac{\text{ph}}{\text{s}\cdot\text{cm}^2} \right]$ and the absorption cross section of QDs $\sigma \text{ [cm}^2\text{]}$. We obtain an average rate of absorption on the order of 110 absorbed photons per second per QDs.

Then, we calculated the diffusion coefficient of QDs via Einstein-Stokes equation $D = \frac{k_B T}{6\pi\eta R_h} = 1.8 \times 10^{-6} \frac{\text{cm}^2}{\text{s}}$ (cores). To be conservative, we underestimated the hydrodynamic radius by neglecting the presence of ligand shell, thereby overestimating the diffusion coefficient. The resulting diffusion coefficient is in agreement with literature data³ [Aruda, et al, J. Phys. Chem. Lett. 2015, 6, 2841-2846]. Therefore, with the smaller axis of the excitation beam profile $l_1 = 0.12\text{cm}$, we estimated the average diffusion time to be $\tau_D = 5 \times 10^2\text{s}$. Namely, we can consider a single QD to dwell into excitation volume for the entire duration of the steady state measurement.

Concerning the lifetime of charged states, a recent paper⁴ has reported an investigation of the delayed emission and PL QY of single-QDs with a core/shell structure quite similar to one of the series of QDs reported in our paper. The percentage of intensity emitted at delay times longer than 1 microsecond is estimated to be a few percent. However, long-lived charged QDs are likely in greater amounts because, on steady-state excitation, absorption of a second photon would produce a dark state owing to Auger recombination in a trion.

<i>Exc.Energy (eV)</i>	CdS 1ML	CdS 2ML	CdS 3ML	CdS 4ML	CdS 5ML	CdS 6ML
3.14	2.9±0.4	6.3±0.6	4±0.4	2±0.2	14±1	6.7±0.7
3.1	2.7±0.4	6.6±0.6	4.1±0.4	2.2±0.2	15±1	7.6±0.7
3.06	3.3±0.5	7±0.6	4.3±0.4	2.5±0.2	15±1	8.2±0.8
2.56	4.4±0.5	10±1	7.1±0.7	5.4±0.5	22±1	21±2
2.53	4.3±0.5	11±1	7.3±0.7	5.4±0.5	23±1	22±2
2.51	4.5±0.5	12±1	7.8±0.8	6.2±0.6	22±1	26±2
2.28	3.9±0.5	12±1	8.2±0.8	8±0.8	25±1	36±3
2.25	3.1±0.4	12±1	8.2±0.8	7.8±0.8	25±1	38±4
2.23	3.7±0.5	12±1	8.5±0.8	8.5±0.8	26±1	38±4

<i>Exc.Energy (eV)</i>	CdZnS 1ML	CdZnS 2ML	CdZnS 3ML	CdZnS 4ML	CdZnS 5ML	CdZnS 6ML
3.14	19±2	30±3	31±3	17±1	12±1	44±4
3.1	20±2	31±3	32±3	18±2	13±1	44±4
3.06	21±2	32±3	33±3	19±2	14±1	45±4
2.56	17±2	26±2	30±3	22±2	21±2	30±3
2.53	17±2	27±2	31±3	23±2	23±2	30±3
2.51	19±2	28±2	31±3	24±2	24±2	31±3
2.28	24±2	40±4	44±4	37±3	40±4	48±4
2.25	24±2	40±4	42±4	37±3	39±4	46±4
2.23	26±2	40±4	43±4	38±3	39±4	46±4

<i>Exc.Energy (eV)</i>	ZnS 1ML	ZnS 2ML	ZnS 3ML	ZnS 4ML	ZnS 5ML
3.1	12±1	3±0.5	8±1	14±1	4±0.5
2.53	26±2	17±1	17±1	17±1	16±1
2.48	28±2	18±1	19±2	17±1	16±1
2.43	30±3	19±1	20±2	19±1	18±1
2.38	30±3	20±1	20±2	19±2	18±1
2.34	31±3	21±2	21±2	20±2	19±1
2.3	33±3	22±2	21±2	21±2	20±2

2.25	31±3	22±2	22±2	20±2	19±2
2.21	31±3	21±2	22±2	21±2	20±2
2.18	32±3	23±1	22±2	21±2	19±2

Table SI_2 – PLQY values calculated by excitation energy dependent measurements of PL for CdSe/CdS, CdSe/CdZnS and CdSe/ZnS series. Red values are those values used in normalization of data in Figure 5. Errors are estimated considering PLQY standard uncertainty and error on integrated PL intensity.

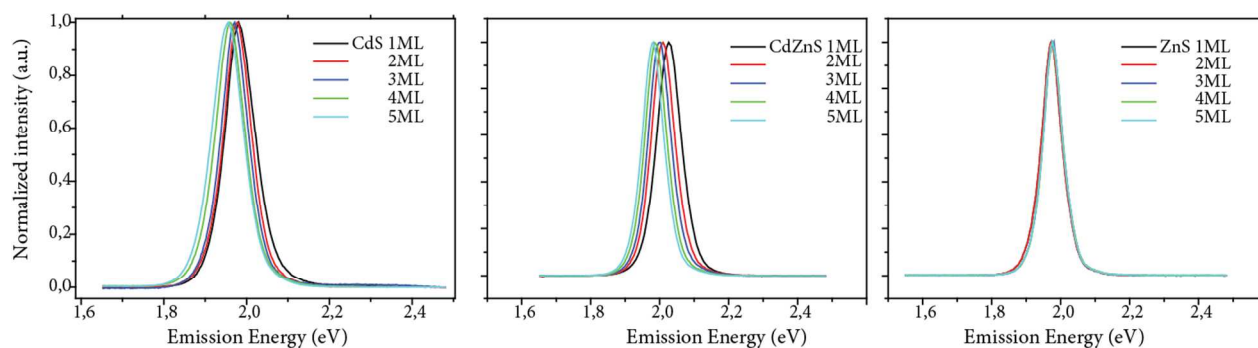


Figure SI_2- Steady state PL spectra recorded under 490nm excitation. PL peak energy shifts, according with absorption spectra, due to reduced confinement. This effect is more pronounced for CdS and CdZnS shell. Any appreciable shift is not observed for ZnS shell.

REFERENCES

- (1) Minotto, A.; Todescato, F.; Fortunati, I.; Signorini, R.; Jasieniak, J. J.; Bozio, R. Role of Core–Shell Interfaces on Exciton Recombination in CdSe–Cd_xZn_{1–x}S Quantum Dots. *The Journal of Physical Chemistry C* **2014**, *118*, 24117-24126.
- (2) Jones, M.; Lo, S. S.; Scholes, G. D. Quantitative Modeling of the Role of Surface Traps in CdSe/CdS/ZnS Nanocrystal Photoluminescence Decay Dynamics. *Proceedings of the National Academy of Sciences* **2009**, *106*, 3011-3016.
- (3) Aruda, K. O.; Bohlmann Kunz, M.; Tagliazucchi, M.; Weiss, E. A. Temperature-Dependent Permeability of the Ligand Shell of PbS Quantum Dots Probed by Electron Transfer to Benzoquinone. *The Journal of Physical Chemistry Letters* **2015**, *6*, 2841-2846.

4. Rabouw, F. T.; Kamp, M.; van Dijk-Moes, R. J. A.; Gamelin, D. R.; Koenderink, A. F.; Meijerink, A.; Vanmaekelbergh, A. Delayed Exciton Emission and Its Relation to Blinking in CdSe Quantum Dots. *Nano Letters* **2015**, *15*, 7718-7725.