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Delayed exciton emission in CdSe nanocrystals, from 0-D quantum dots to 2-D platelets

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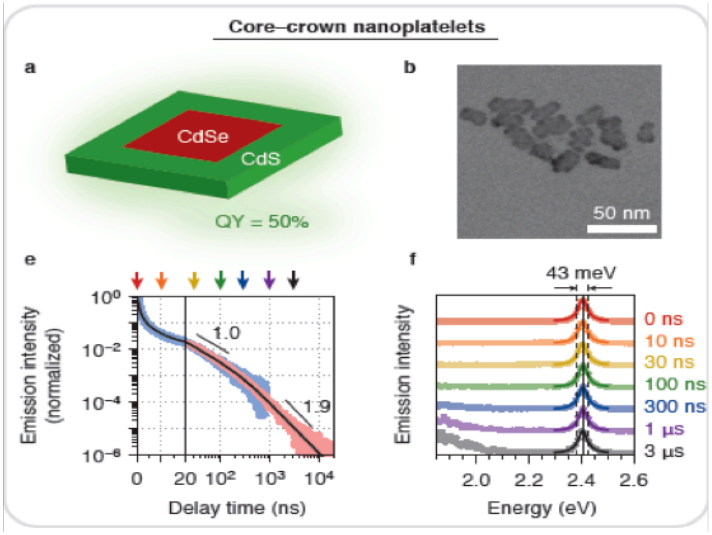
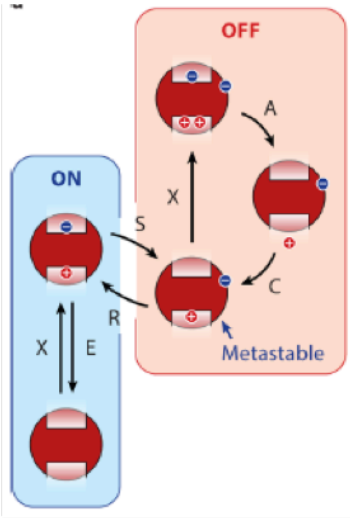
Introduction: Since the 1990's, colloidal nanocrystals of the compound CdSe have known a tremendous development, and 0-D, 1-D and 2-D nanocrystals of this compound can be considered as the workhorses in the field. In 1993 a synthesis method was reported for nearly monodisperse CdSe 0-D nanocrystals; the light emission from the exciton led to nearly monochromatic light with a QY of 10 %. A few years later, the quantum yield could be considerably enhanced (close to 80%) by growing an inorganic shell around the CdSe core. Since then, the optical properties of CdSe nanocrystals have been investigated extensively by various optical and electrical spectroscopic methods. A few landmarks should be named here: the research on the exciton fine structure, the determination of the energy levels of single dots by scanning tunneling microscopy, the dynamics of bi-excitons and charged excitons, the reduction of Auger recombination by soft potential wells, the discovery and basic understanding of fluorescence intermittency, i.e. blinking of individual nanocrystals. All this research has resulted into potential and real applications of these nanocrystals, e.g. as fluorescent labels in biological cell research, in transistors and in opto-electronic devices such as LEDs, LASERs, and solar cells. These developments will be reviewed in a special issue of Chemical Reviews 2016.

Unsolved: Delayed emission and its relation to blinking. The dynamics of the lowest-energy exciton in CdSe nanocrystals has been investigated by time-resolved photoluminescence spectroscopy on the level of a nanocrystal ensemble (i.e. suspension) and single, individual nanocrystals. The photoluminescence decay curves in the first 50 ns after the laser pulse are often (nearly) mono-exponential, resulting in a (radiative) life time of the lowest-energy exciton in the 5-30 ns range, depending on the system. The luminescence intensity after the investigated first period has dropped to a few % of the intensity at time zero, and the regime at longer times has been overlooked. However, by using a sensitive photon detector with low dark-count rate, we found that there is a much slower "delayed" emission spanning over 6 orders of time, from the ns to ms regime. We found that the total number of photons emitted later than the first time period can amount to 15 % of the total for 0-D CdSe quantum dots, and even to 50 % for 2-D nanocrystal platelets. Hence, delayed emission is an important feature of colloidal CdSe nanocrystals that deserves a close watch. In this lecture, I will report our main results.

Our work: General features of the delayed emission in CdSe core (CdS shell) nanocrystals, from 0-D to 2-D: The time-resolved photoluminescence of 0-D[1], 1-D[2], and 2-D[3] CdSe (core)/CdS (shell) nanocrystals show a number of common features: (1) After a short exponential decay in the first tens of ns, the decay follows a power law, i.e. I(t) is proportional to t^{-a}; where **a** is the power-law exponent between 1.5 and 2, depending on the system (see figure above). This power law is valid up to the longest time that we could detect photons with our sensitive detector. (2) The spectrum of the CdSe nanocrystals (0-D, 2-D) does not change over the time range of the delayed emission. (The figure shows the narrow and constant spectrum of CdSe platelets). This indicates that the delayed emission is coming from an unperturbed single exciton. It hence means that the exciton can be "stored" in an optically inactive state over variable periods before transition to the optically active state. (3) We also measured the delayed luminescence on individual 0-D CdSe/CdS

quantum dots and observed that there is delayed emission on the level of a single dot. Moreover, the value for the power-law exponent is similar to those for the on- and off- periods of the blinking statistics of individual CdSe/CdS dots of the same batch. This is a strong indication that there is a single mechanism underlying the delayed emission and blinking. (4) With this 0-D system, we also found that the relative fraction of delayed emission decreases with increasing refractive index, showing that the bifurcation between the delay process and photon emission occurs on the level of the single exciton.





We present a heuristic model (see above, right) in which an exciton can undergo reversible transitions between the emitting and "optically inactive" states (e.g. by trapping/detrapping of one of the carriers). The rates of (de)activation vary over a wide range, essentially from faster than radiative recombination to much slower. Thus, an exciton can switch between "on" and "off" even during bright periods in the blinking characteristic, but can also become inactive (charge-separated) for a longer time (e.g. ms). In the inactive state, a new photon can be absorbed, e.g. leading to a charged (trion) exciton state, subject to Auger recombination. Simulations with this model explain both the blinking trajectories as the delayed emission dynamics. The microscopic nature of the "inactive" state remains elusive.

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