

Abstract

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Synthesis and analysis of kinetic processes in single colloidal quasi-molecules based on two near-field coupled quantum dots

Semiconductor quantum dots (QDs), due to their small size and the quantum size effect responsible for the discretization of energy levels can, to a first approximation, be viewed as artificial atoms. In recent years, the first protocols for the intentional assembly of single QDs into interacting nanostructures have been presented in the literature. Because of the atom-particle analogy and the presence of interactions between the QDs, these nanostructures have come to be known as artificial molecules (QDM, or QDs Molecules). In their simplest form, which is represented by two interacting QDs, they are an analogy for a molecule of hydrogen or sodium chloride depending on the size of the used QDs.

Despite the first attempts to synthesize and characterize them from the experimental and theoretical side, these systems are still little understood. One of the more pronounced differences observed in QDM with respect to isolated QDs is a very pronounced change in the statistics of relaxation processes, which is a direct consequence of the possibility of charge transfer between interacting QDs. A better understanding of the effect of coupling on changes in the statistics of relaxation processes, or the possibility of directional charge transfer within the QDM, is therefore an important problem to solve. This problem takes on broader significance given the complexity of kinetic processes in individual QDs leading to different types of blinking. The research performed in this work aims to answer these questions.

The research performed was both experimental and theoretical. The experimental part focused on obtaining colloidal QDM systems built based on two QDs of different sizes. The work was limited to the use of cadmium selenide QDs in both uncoated and core-shell CdSe/ZnS structures. A proprietary procedure was developed for selective coupling of colloidal QD in solution using surface-modified SiO₂ nanoparticles. The developed method makes it possible to synthesize QDMs with a relatively high 30% - 50% yield. The obtained QDMs were analyzed using a range of methods allowing imaging of the real structure (TEM, AFM), spectral characterization including absorption spectroscopy, emission spectroscopy (photoluminescence and time-resolved luminescence spectroscopy), as well as characterization using single particle emission spectroscopy. The theoretical part includes numerical simulations of the time evolution of kinetic processes in QDM, which were performed using the kinetic Monte Carlo (KMC) method. Due to the possibility of simulating all relaxation processes (not only radiative relaxation), but these methods are also very helpful in interpreting experimentally obtained data.

The results show a number of effects that are not observed for single QDs, i.e., cascade relaxation of excitons taking place in a chain-like manner, which leads to the emission of photon packets with very high intensity, or the emission of photons correlated in time, although the effect was random. The work also succeeded in confirming the possibility of obtaining directional

charge/exciton transfer between interacting QDs. This result may be important if one considers QDMs as nano-systems for information processing, in which the exciton may act as the basic unit of information.

However, the correlation of the strength of coupling with the distance between interacting QDs remains an unresolved issue. When studying colloidal systems that are anchored to each other using organic molecules, this issue is difficult to resolve conclusively.