

Surface states and non-FRET photoluminescence quenching in nanoassemblies based on CdSe/ZnS quantum dots and porphyrins

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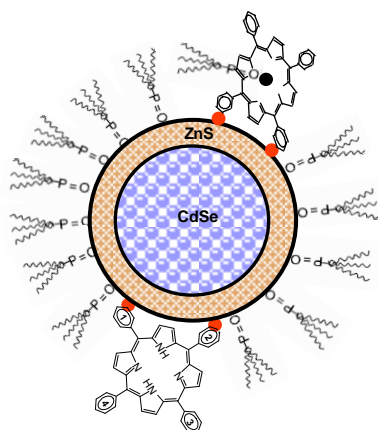
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At the moment, organic-inorganic nanoassemblies based on colloidal semiconductor quantum dots (QDs) in combination with organic molecules are considered and used as perspective nanostructures for using in sensorics, photovoltaics and biomedicine [1]. In this respect, understanding surface/ interface processes in these nanomaterials is a key challenge for those working on applications of hybrid nanomaterials. Methods of optical spectroscopy (including single objects detection) are fundamental to study these processes.



Here, we present a detailed comparison of static and dynamic photoluminescence (PL) quenching for CdSe/ZnS QDs upon self-assembly with tetra-pyridylporphyrins, H₂P, *via* spectral intensities and PL decays, respectively for toluene solutions in a temperature range 77÷295 K. Self-assembly of CdSe/ZnS QDs with H₂P molecules results in a strong quenching of QD PL and a clear shortening of the PL decay, which can be explained by attachment to the QD surface *via* suitable pyridyl anchor groups. For the first time, we were able to quantitatively separate Foerster resonant energy transfer (FRET) and non-FRET processes by a careful comparison of the QD (donor) PL quenching and the dye (acceptor) fluorescence enhancement as a function of the molar ratio [2, 3]. In toluene at 293 K, experimental FRET efficiency is $\Phi_{\text{FRET}} = 12\%$ and is in agreement with the Foerster model calculations. The non-FRET QD PL quenching is related to a replacement of several passivating molecules (TOPO or amines) on the QD surface by the more spacious porphyrin molecules *via* a chemically different bonding. Since the degree of ligand coverage is inhomogeneously distributed across the QD ensemble PL quantum yields vary broadly. The attachment of H₂P molecules occurs

preferentially to those QDs with low ligand coverage. Along with that, nanoassembly formation deviates strongly from Poisson statistics.

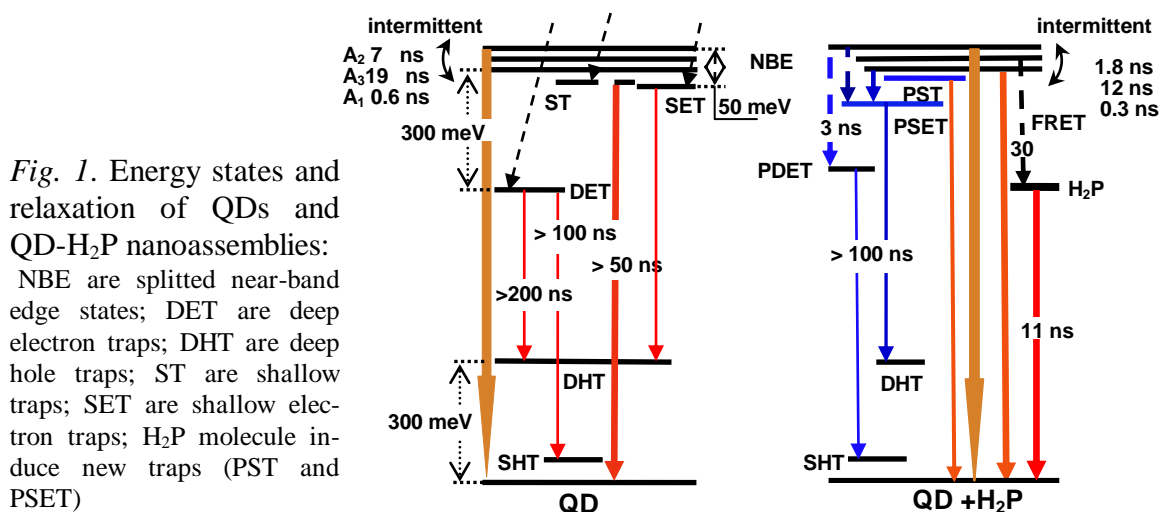


Fig. 1. Energy states and relaxation of QDs and QD-H₂P nanoassemblies: NBE are splitted near-band edge states; DET are deep electron traps; DHT are deep hole traps; ST are shallow traps; SET are shallow electron traps; H₂P molecule induce new traps (PST and PSET)

Based on assembly and single nanoobjects PL measurements (intensities and decays) we have argued that the non-FRET QD PL quenching results in an increase of the relative contribution of only weakly radiative QD states. In terms of single QD detection, H₂P attachment increases the probabilities of “dark” and “dim” states. The modification and/or creation of H₂P induced intra-gap states is due to formation of additional and/or new Cd²⁺ dangling bonds at the QD surface because of dye-induced ligand depletion.

On the basis of the combination of steady-state and time-resolved measurements for bulk and single QD-dye nanoassemblies, it is feasible to follow non-radiative pathways from near-band-edge states to intra-gap states thus investigating microscopic features of surface related energy distributions and decay channels. The realization of non-FRET processes caused by formation of new surface and intra-gap states of various nature should be taken into account for nanodevices based on semiconductor QDs or QD-Dye nanoassemblies operating in complex environments.

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