

Spectroscopy of single nanocrystals of doped I-III-IV semiconductors and organic-inorganic hybrid nanoparticles

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This contribution covers topics with a common theme of utilizing the unique features of single-molecule spectroscopy in characterization individualities in photophysical properties of nanoparticles that are otherwise inaccessible by ensemble measurements. Ternary I-III-IV semiconductor nanocrystals have been recently explored as non-toxic alternatives to II-VI semiconductors for optoelectronic and sensing applications, but large photoluminescence spectral width and moderate brightness restrict their practical use. We use single-particle photoluminescence spectroscopy on nanocrystals of $(\text{AgIn})_x\text{Zn}_{2(1-x)}\text{S}_2$ to show that the photoluminescence band is inhomogeneously broadened and that size distribution is the dominant factor in the broadening.^[1] The residual homogeneous linewidth of individual nanocrystals reaches up to 75% of the ensemble spectral width. Single nanocrystals undergo spectral diffusion which also contributes to the inhomogeneous band. Excitation with two lasers with energies above and below the bandgap reveals coexistence of two emitting donor-acceptor pairs within one particle. Spectral diffusion in such particles is due to temporal activation and deactivation of one such pair. Filling of a trap state with the lower-energy laser enables optical modulation of photoluminescence intermittency (blinking) and leads to an almost two-fold increase in brightness, as seen in Figure 1. Further, the relative amount of Zn in the particles beyond a particular limit places the radiative recombination centers close to each other, leading to an increase in non-radiative transitions. Proximity between the energy levels of these radiative centers and the conduction band results in non-radiative localized-delocalized transitions, affecting the overall quantum yield.^[2]

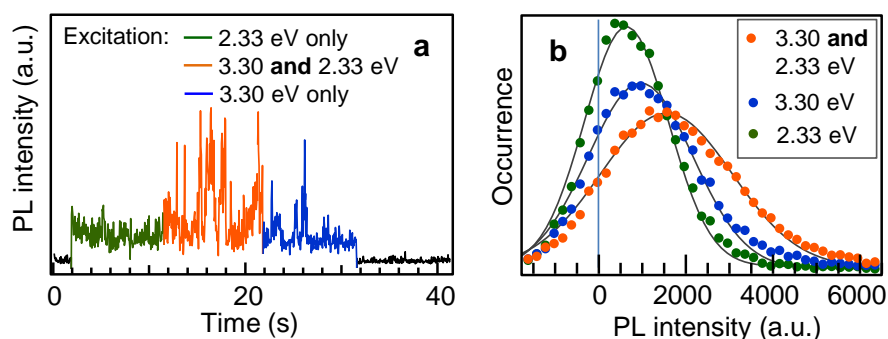


Figure 1. Single-particle blinking of $(\text{AgIn})_x\text{Zn}_{2(1-x)}\text{S}_2$ ($x = 0.3$) nanocrystals. (a) Example of PL intensity trace for a single nanocrystal excited sequentially with 2.33 eV only (green), both 3.30 and 2.33 eV (orange) and 3.30 eV only (blue) lasers. (b) Distributions of single-particle PL counts obtained with the sequential excitations. The solid lines are Gaussian fits.

As a second example, the effect of localized plasmon on the process of Förster energy transfer was studied using hybrid nanoparticles in which donor and acceptor dye molecules are randomly attached to a gold nanorod. Fluorescence spectra of the donor and acceptor molecules excited with light polarized along the long axis of the nanorod show increased intensity from the acceptor as compared to polarization perpendicular to the axis. This observation was attributed to enhancement of the energy transfer by the longitudinal plasmon mode. The emission intensity of the acceptor molecules can thus be controllably and reversibly modulated over a wide range by the polarization angle, enabling a selective turn-on of the Förster energy transfer process and control over the emission color of the hybrid nanostructure.^[3] The spectral response was well reproduced by theoretical simulations which also provided a quantitative extent of the energy transfer enhancement which in terms of energy transfer efficiency was by a factor of 65. These results point to the feasibility of controlling energy transfer by switching on a plasmon mode with proper light polarization.

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References:

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