From Carrier Multiplication and Hot-Electron Transfer to the Mysteries of Nanocrystal Blinking

Victor I. Klimov

Center for Advanced Solar Photophysics, C-PCS, Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA, klimov@lanl.gov, http://quantumdot.lanl.gov

Due to "sub-excitonic" dimensions, nanocrystal quantum dots can produce novel electronic interactions that involve charges residing in intrinsic quantized states as well as species located at nanocrystal surfaces. For example, the interaction of a hot conduction-band electron with valence-band charges can lead to an interesting relaxation regime in which the kinetic energy of a hot carrier is not lost as heat but is used to produce additional electron-hole pairs, a process known as carrier multiplication [1]. Our recent work in this area includes the development of reliable methods for efficient screening of carrier multiplication performance of infra-red emitting nanocrystal quantum dots using photon counting with superconducting nanowire detectors, the studies of the impact of "extraneous" processes on quantitative measurements of this process [2], and the evaluation of the effects of the nanocrystal composition, dimensions, and shape on multiexciton yields. An interesting "byproduct" of these studies has been the observation of high-efficiency hot-carrier transfer that has a significant effect on quantitative measurement of carrier multiplication yields [3]. Surprisingly, we also observe that escape of hot electrons from the nanocrystals has direct relevance to another puzzle in the nanocrystal field – nanocrystal blinking [4]. By conducting measurements of fluorescence intermittency in individual quantum dots, while controlling the degree of their charging via electrochemical means, we detect two distinct blinking regimes. The first is consistent with the traditional concept of charging and discharging of the quantum dot core. In this model a charged state is "dark" due to highly efficient nonradiative Auger recombination. The second mechanism, however, is somewhat a surprise; the majority of the quantum dots display blinking due to the filling and emptying of a trap on the surface of the dot. If not occupied, this trap intercepts a hot electron prior to its relaxation into the emitting state, thus causing a "blink." Importantly blinking can be controlled and even completely suppressed electrochemically by applying an appropriate potential. Finally, I will overview our work on the development of a new generation of quantum dots that in addition to stable blinking-free emission show a significant suppression of nonradiative of Auger recombination [5]. Such dots are promising candidates for applications in future solution processable devices from lasers and light emitting diodes to sources of single photons.

1. Schaller, R.D. and V.I. Klimov, *High efficiency carrier multiplication in PbSe nanocrystals: Implications for solar-energy conversion.* Phys. Rev. Lett., 2004. **92**: p. 186601-1-4.
2. McGuire, J.A., et al., *Apparent Versus True Carrier Multiplication Yields in Semiconductor Nanocrystals.* Nano Letters, 2010. **10**(6): p. 2049-2057.
3. McGuire, J.A., et al., *Spectroscopic Signatures of Photocharging due to Hot-Carrier Transfer in Solutions of Semiconductor Nanocrystals under Low-Intensity Ultraviolet Excitation.* ACS Nano, 2010. **4**(10): p. 6087-6097.
4. Galland, C., et al., *Two types of luminescence blinking revealed by spectroelectrochemistry of single quantum dots.* Nature, 2011. **479** p. 203-207.
5. Garcia-Santamaria, F., et al., *Breakdown of volume scaling in Auger recombination in CdSe/CdS heteronanocrystals: The role of the core-shell interface.* Nano Letters, 2011. **11**(2): p. 687-693.