"Giant" Nanocrystal Quantum Dots: Suppressed Blinking and Auger Recombination Through Solution-Phase Physical and Electronic-Structure Engineering

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Scientific Thrust Area: Nanophotonics and Optical Nanomaterials

Research Achievement:

In many respects, semiconductor nanocrystal quantum dots (NQDs) are near-ideal "building blocks" for light-emission applications. Their optically excited emission is efficient (quantum efficiencies can approach unity), narrow-band ("color-pure"), and particle-size-tunable, i.e., light-output colors are precisely tunable from the ultraviolet through the visible and into the mid-infrared depending on NQD composition and size. Furthermore, NQDs are synthesized using scalable and inexpensive solution-phase approaches, rendering NQDs with "molecule-like" properties and an ability to be chemically processed. Despite these enabling characteristics, conventional NQD optical properties are sensitive to NQD surface chemistry and chemical environment, which has three important results: (1) high NQD solution-phase photoluminescence quantum yields are not maintained in the solid state (e.g., 90% solution-phase QYs can drop to ~10% when the NQDs are deposited into thin-film form), (2) NQDs "bleach" (PL intensity degrades over time), and (3) NQDs at the single-particle level "blink" (exhibit fluorescence intermittency), all limiting total NQD "brightness."

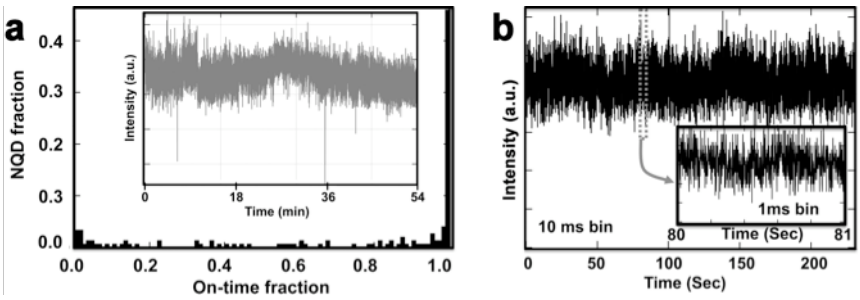

Figure 1. (a) On-time histogram for prototype (CdSe)19CdS g-NQDs. Inset shows fluorescence time trace for a representative g-NQD with an experimental temporal resolution of 200 ms. (b) Fluorescence time trace for representative individual g-NQD with temporal resolutions of 10 ms and 1 ms (inset), revealing that non-blinking behavior is evident at 'all' time-scales.

We recently reported that these key NQD optical properties—quantum yield, photobleaching and blinking—can be rendered independent of NQD surface chemistry and chemical environment by growth of a very thick, defect-free inorganic shell (Chen, et al. *J. Am. Chem. Soc.* 2008). Effectively, we isolated the wavefunction of the NQD core from its surface, creating a colloidal NQD that is structurally more akin to physically grown epitaxial QDs. We named this new functional "class" of NQD the "giant" NQD (g-NQD). Importantly, g-NQDs do not photobleach, are insensitive to changes in surface chemistry, and show markedly improved blinking behavior (Fig. 1). To date, for example, up to 50% of a given sample is "non-blinking," where non-blinking is defined as the NQD being "on" under continuous excitation for >99% of the long observation time of 54 minutes.

Suppressed blinking is a strong indicator of additional "new physics" that is afforded by this new class of NQD. Namely, suppressed blinking is an indicator of suppressed Auger recombination, where Auger recombination is a nonradiative carrier (electron-hole) recombination process that is active (and can outcompete radiative recombination processes) when an NQD is charged or populated with more than one electron-hole pair (Klimov et al. *Science* 2000). Through a random series of surface-related "charging" and "discharging" events, NQDs become alternatingly susceptible to nonradiative Auger recombination and, thus, successively turn "off" then "on," or blink. When Auger recombination is inactive, even a charged NQD should not blink. Therefore, the suppressed blinking behavior observed for g-NQDs is a possible indicator of suppressed Auger recombination.

Recently, we performed ensemble photoluminescence dynamical studies on g-NQDs that revealed more direct evidence for strong suppression of non-radiative Auger recombination – including biexciton lifetimes that are 50 times longer than those obtained for conventional NQDs. Also, we performed low-temperature single-g-NQD photoluminescence studies that revealed unprecedented emission from multiexciton states. In the case of conventional NQDs, multiexciton states cannot participate in emission, while for g-NQDs, multiexciton-state emission is in fact efficient. In this way, it is clear that g-NQDs can afford *new exciton→photon conversion pathways*.

Future Work:

Together, these novel properties have important implications for diverse applications from advanced bioimaging to room-temperature single-photon sources and efficient solid-state lighting. The observed enhanced environmental stability and novel photophysics go a long way toward solving the outstanding issues (e.g., sensitivity to chemical environment, blinking, and efficient nonradiative Auger recombination processes) that have to date limited the utility of these otherwise promising light-emitting nanomaterials. Further, the prototype g-NQDs provide a unique "test bed" for fundamental studies of the effect of nanoscale architecture in semiconductor systems on optical and electronic properties. Future work in the areas of nanomaterials synthesis, atomic-level structural characterization, and advanced spectroscopy will enable the fundamental understanding necessary to generalize these important early results to new g-NQD systems.

Publications

1. Chen, Y., Vela, J., Htoon, H., Casson, J. L., Werder, D. J., Bussian, D. A., Klimov, V. I., and Hollingsworth, J. A.,""Giant" multishell CdSe nanocrystal quantum dots with suppressed blinking," *J. Am. Chem. Soc.* **130**, 5026 (2008).
2. Hollingsworth, J. A., Vela, J., Chen, Y., Htoon, H., Klimov, V. I., and Casson, A. R., "Giant multishell CdSe nanocrystal quantum dots with suppressed blinking: novel fluorescent probes for real-time detection of single-molecule events," *Proc. SPIE* 7189, 718904 (2009).
3. Hollingsworth, J. A.; Chen, Y.; Vela, J.; Htoon, H.; Klimov, V. U.S. Patent Application No. 61/065,077 (Feb. 2009): "Thick-shell Nanocrystal Quantum Dots."