Effects of Shape, Crystal Structure and Defect Engineering on Photophysical Properties of Single Inorganic Semiconductor Nanocrystals

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Particle-size or 'quantum-confinement' effects have been used for decades to tune inorganic semiconductor photophysical properties (bandgap and, thereby, photoluminescence color). More recently, particle size control as the primary means for properties control has been superseded by nanoscale hetero-structuring. In this case, the nanosized particle is modified to include internal, nanoscale interfaces, generally defined by compositional variations that induce additional changes to semiconductor properties, including enhancements to the existing properties properties and development of new, 'emergent' behaviors. A common structural motif entails enveloping a spherical semiconductor nanocrystal, i.e., the colloidal quantum dot (QD), within a shell (or multiple shells) of different composition. Greater structural and properties complexity can be achieved by extending the dimension of the shell material(s) to create asymmetric seeded nanorods or "multipods," adding volume and novel shape effects to the mechanisms for tuning fundamental nanoscale photonic processes.

In this talk, I will discuss solution-phase colloidal synthesis as a means for fine-tuning shape, crystal structure and defect composition in engineered semiconductor nanocrystals. I will also correlate these structural properties with resulting photophysical properties as studied in single nanocrystals. As a basis for recent investigations, I will briefly review our experiences with so-called 'giant' core/shell QDs (gQDs),[1] especially CdSe/CdS gQDs, which, due to their internal nanoscale structure (thick shell, type II band alignment and potentially alloyed interface), exhibit a range of fundamentally interesting and useful behaviors, including being non-blinking and non-photobleaching,[2-6] as well as remarkably efficient emitters of multiexcitons due to extreme suppression of Auger recombination.[7,8]

Our current studies follow from these insights and three will be described: (1) shape-tuning CdSe/CdS to realize dual-color multiexcitonic blinking-suppressed emission (Fig. 1),[9] (2) crystal structure control to realize ultra-stable single-dot photoluminescence in the near-infrared from PbSe/CdSe gQDs,[10] and (3) interface and defect engineering to optimize quantum yield and long-term photooxidative stability in CdSe/CdS gQDs exposed to thermal, photon-flux and oxygen/humidity stressors. Overarching, I will emphasize the need for new synthesis and characterization tools to enable the required insights into structure-function relationships for the intelligent design of functional photonic nanostructures. These include correlated optical/structural characterization methodologies,[11] and synthesis automation.

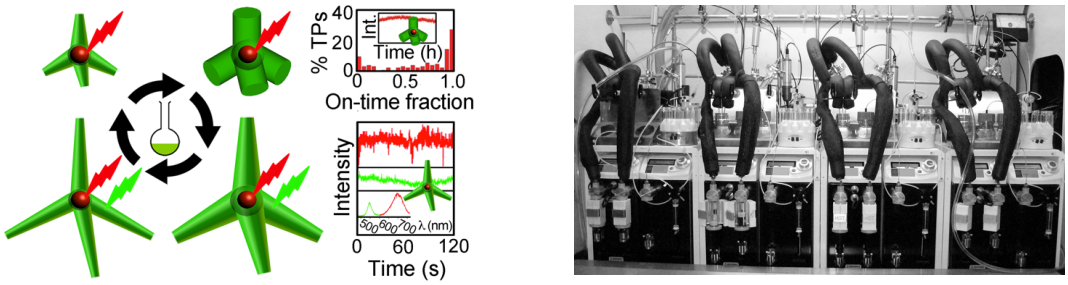

Figure 1. (left) Nano-engineered tetrapod shape series. (right) Automated reactor system for combinatorial approaches to functional photonic nanomaterials discovery and optimization.

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