Nano-engineering Core/Shell Quantum Dots for Ultimate Utility in Light-emission Applications

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ABSTRACT

We aim to accelerate the development of a new functional class of semiconductor quantum dot (QD) – the "giant" QD (gQD) – as a replacement for rare-earth phosphor down-conversion materials. Doing so will enable high-efficiency/high-power warm-white light-emitting diodes (w-LEDs) for next-generation solid-state lighting (SSL). We are addressing outstanding challenges to the adoption of QDs as drop-in replacements for conventioanl phosphors: (1) high efficiency, (2) lifetime performance, which requires the down-conversion material to be used directly on-chip where it can experience high temperatures and high photon flux, and (3) material reproducibility/scale-up. Here, we describe the science basis for the unique characteristics of gQDs that make these nanoconstructs inherently more stable and less apt to succumb to self-reabsorption losses compared to conventional QDs. We further discuss novel methods for the characterization of gQDs (and applicable to other competing phosphor materials) that enable direct correlation of nanoscale structure with function, affording new insight into the structural and/or electronic origins of quantum yield (QY) and the mechanisms for reversible and permanent photobleaching.

Keywords: giant quantum dot, non-blinking, non-photobleaching, bleaching mechanism

1 INTRODUCTION

The drive toward SSL for domestic and commercial use is propelled by the high energy costs associated with conventional lighting – i.e., ~20% of all electricity generated is used for lighting [1]. After 130 and 70 years of development, respectively, incandescent and fluorescent bulb efficiencies (as overall luminous efficacy, or "wall-plug efficacy," in lm/W) have plateaued, with the former reaching a modest 10-17 and the latter 40-70 lm/W [2]. In contrast, SSL approaches (first commercialized in 1996) already meet or exceed the efficiencies of the best compact fluorescent bulbs (40-100 lm/W), and prototypes have recently reached the theoretical efficiency predicted for white LEDs (w-LEDs) fabricated from phosphor-down-converted blue LEDs – 260-300 lm/W at high-power operation for high luminous flux (current densities >350 mA) [3].

Although overall luminous efficacy of record devices is high, prototype and commercial w-LEDs remain deficient with respect to luminous efficacy of radiation (LER: match to human-eye re-sponse; low LER is "wasted photons") and the quality of the white light. Namely, most commercial w-LEDs depend on partially down-converting a blue LED with a broadband yellow phosphor. The resulting mixture of blue/yellow gives the appearance of white light. Although the phosphor, YAG:Ce^{3+} [4,5], is renowned for its high QY, alone it cannot provide a high color-rendering index (CRI; ability to render colors faithfully) or even 'warmer-white' color temperatures [6,7]. To dramatically improve consumer acceptance of w-LEDs, addition of a red phosphor is required to fill the spectral gap left by YAG:Ce^{3+}[8,9]. A key technical challenge is the lack of a narrowband, efficient, robust and cost-effective red phosphor, and, ultimately, a wider array of similar emitters across the visible spectrum.

QDs comprise a possible answer to this technological challenge due to their now well-known size-depentdent semiconductor bandgap and ensuing color-tunable broadband absorption and narrowband emission characteristics. More specifically, particle-size or 'quantum-confinement' effects have been used for decades to tune semiconductor opto-electronic properties. More recently, particle size control as the primary means for properties control has been succeeded 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. These changes can involve enhancements to the well-known size-induced properties as well as development of unexpected or 'emergent' behaviors. A common structural motif entails enveloping a spherical semiconductor nanocrystal, i.e., the colloidal 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.

Why is all this control necessary? Such enhanced nanoscale engineering can lead to the very properties (or at least closer to them) needed for challenging technological applications, such as SSL.

2 GIANT QUANTUM DOTS

We use seemingly simple solution-phase colloidal synthesis to fabricate sophisticated examples of nano-engineered semiconductor nanostructures with novel functionality. In particular, we discovered and elucidated ‘giant’ core/thick-shell QDs (gQDs) [10] that represent a particualar structural design motif: thick shell, type II band alignment and, potentially, alloyed core/shell interface. Due to this synthesized nanoscale structure, gQDs exhibit a range of fundamentally interesting and useful behaviors, including being non-blinking and non-photobleaching [11-15], and remarkably efficient emitters of multiexcitons due to extreme suppression of Auger recombination [16,17]. To date, we have demonstrated this approach across the visible spectrum (green to red) and into the infrared. We have further used shape-tuning to realize dual-color (green and red) multiexcitonic emission [18] – all with strong blinking suppression and enhanced single-nanostructure photostability.

3 TOOLS FOR ADVANCED CHARACTERIZATION AND SYNTHESIS

Subtle structural and electronic variations in the individual QDs of a large ensemble of QDs, e.g., such as the aggregate of nanocrystals forming the phosphor-silicone composite on an LED chip, can give rise to heterogeneity in expressed optical behavior. This dot-to-dot variability impacts overall device performance and ultimate reliability of the w-LED, as individual QDs can respond differently to thermal, flux, oxygen and humidity stressors. To understand more precisely how the structural and electronic chracteristics of individual QDs impact optical properties, new methods for correlating single-dot structure with single-dot function are needed. Working with collaborators at Vanderbilt University, we have previously established a technique for correlating fine atomic structure and chemical composition with time-resolved single-photon PL data for the same individual nanocrystals [19]. Doing so allowed us to expose the underlying cause of sub-unity QYs in non-blinking gQDs, namely, the inhomogeneity in the QYs of single gQDs [19]. In particular, each gQD was shown to possess distinctive single exciton and biexciton QYs that result mainly from variations in the degree of charging, rather than from volume or structure inhomogeneity.

We also showed that there is a very limited “dark” or nonemissive fraction (<2%). For this small subpopulation of gQDs, a clear structural origin was identified - a lack of inorganic passivation, i.e., lack of shell on one side of the QD. However, this was the rare case, with the majority of gQDs always emissive, though to varying degrees. Therefore, unlike conventional QDs, ensemble PL QY in gQDs is principally defined by charging processes. An additional key finding was that there is no limit to gQD QYs, as sub-populations possessing relative unity QYs (presumed to be close, if not reaching, absolute unity QY) were clearly observed. These were the gQDs that emitted almost exclusively from non-charged, purely excitonic states. The task going forward is to identify how to synthetically modify, or otherwise control, gQD charging behavior.

More recently, we have continued to advance our ability to assign structural or electronic origins to key PL properties of the gQD down-conversion materials. In particular, we have developed single-dot “stress tests” akin to the device testing performed in w-LEDs. These entail exposing the phosphor (QD) material to thermal, flux and environmental (air, humidity) stressors to assess impact on lifetime performance reliability. We now apply this strategy at the level of single gQDs and observe impacts on advanced optical and quantum optical properties of the nanocrystal emitters. In this way, we are able to uncover the photobleaching mechanisms that are responsible for both reversible and permanent performance degradation.

With new understanding attained from advanced characterization approaches and tools, new synthesis methods and tools are needed to rapidly modify the gQD structure to address the identified deficiencies. Furthermore, even the basic gQD structure comprises multiple layers of shell material that is applied in numerous sequential steps. Conventional colloidal synthesis techniques are not ammenable to scale-up for mass production in the case of complex, parameters-sensitive, multi-step processes. For this reason, we have pursued synthesis automation to support quasi-combinatorial exploration of parameter phase space (“discovery” period of development) as well as scale-up of optimally designed nanostructures (Fig. 1).

Figure 1: Custom automated reactor system for combinatorial approaches to functional photonic nanomaterials discovery and optimization located in the Center for Integrated Nanotechologies (CINT) Gateway Facility, Los Alamos National Laboratory.

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