From Flasks to Applications: Combinatorial Chemistry and High-Throughput Synthesis of High-Performance Complex Nanomaterials using Automated Synthesis

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ABSTRACT

Highly emissive nanoparticles are extremely attractive options for a variety of applications, including, but not limited to, solid state lighting [1,2], optoelectronics [3], and sensing [4]. However, to utilize these and other nanoparticle materials on a commercially viable scale to meet demand, the design, synthesis, optimization, and scale up of the material must be extremely efficient and consistent across batches. It has been suggested that from development of design to optimized production, more than 100 reactions may need to be completed before the material can be used, which requires time and manpower [5]. We present our Fully Automated Batch Reactor System (FABRS) which drastically cuts down on the time required for both materials discovery and optimization.

Keywords: automation, nanoparticles, synthesis, multi-step processes

1 FABRS FOR NANOPARTICLE SYNTHESIS

Quantum Dots (QDs) have been an attractive option for a variety of applications requiring highly absorptive (solar cells) or emissive (light emitting diodes) "building blocks," but the stability of these materials, particularly in solid state and at the single dot level has inhibited their widespread integration into commercial products [6,7]. Standard core / thin shell QDs, for example, at the single dot level experience fluorescence intermittancy (blinking) and significant photobleaching under prolonged photoexcitation. Additionally, due to significant absorption and emission overlap, when the materials are packed densely into polymers, emission intensities and quantum yields are low compared to that in the solution phase due to self reabsorption and energy transfer [2]. We have previously developed thick-shell "giant" QDs (gQDs) that are extremely stable both in the ensemble and at the single dot level [6,7]. As an example, the cadmium selenide/cadmium sulfide (CdSe/CdS) core/shell gQD with 16 monolayers (ML) of shell is non-blinking for long observation times, and does not photobleach under prolonged excitation at room temperature. In addition to improved environmental and optical stability, the thick shell affords a quasi-type two bandstructure, in which a majority of light is now absorbed in the shell, yet the recombination of the exciton, and thus the emission, is from the core [6,7]. The resulting "effective" Stokes shift drastically reduces the amount of energy transfer and self-reabsorption when the material is packed densely into a solid-state film or monolith. As a result, these materials are good candidates for alternative phosphors for solid-state lighting, as they, unlike thin-shell QD counterparts, have downconversion efficiencies that track with solution quantum yield [2]. We have previously shown (Figure 1) that the gQD materials packed densely into polymers are effective downconverters when placed directly on a blue LED chip, and therefore could be integrated with other commercial yellow-emitting phosphor materials to generate white light [2].
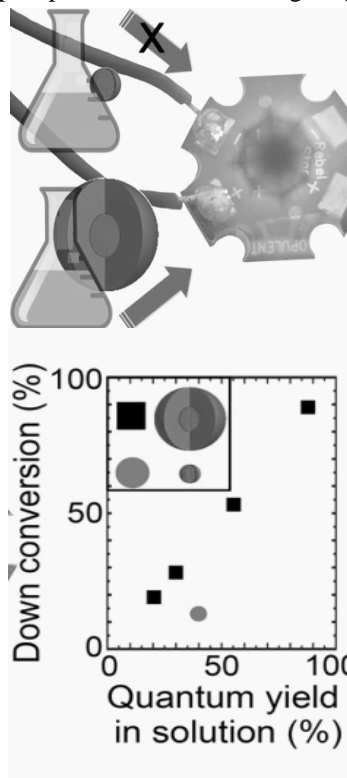

Figure 1: gQDs used as downconverters on standard blue LED chip. Downconversion efficiency matches quantum yield, unlike standard QDs that suffer large photon losses due to self reabsorption and energy transfer

CdSe/CdS gQD shells are grown using a Successive Ionic Layer Adsorption and Reaction (SILAR) process to prevent the homogeneous nucleation of particles from the shell-growth precursors and to precisely control the shell thickness [6,7]. In this process the reaction is held at a high temperature (~240 °C) and to a mixture of QD cores and ligands,

quantities of precursor in the amount needed for growth of 1 ML of shell are added. Cation and anion precursors (cadmium and sulfur, respectively, in the case of CdSe/CdS gQDs) are added consecutively following 3 and 1 hour anneal times, respectively. This process is repeated ~15-20 times, resulting in non-blinking/non-bleaching gQDs. Manually, the process takes 1-2 weeks to complete,
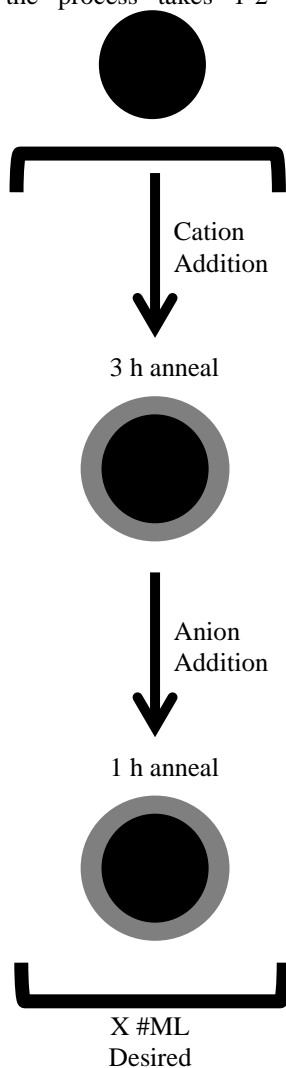

Figure 2: SILAR process for addition of
1 ML of shell. Process is repeated until
desired shell thickness is achieved

challenging materials discovery and materials optimization efforts. (Figure 2)

To enhance the pace of new materials development and optimization, we emply a custom automated reactor system: Fully Automated Batch Reactor System (FABRS), which allows for the optimization and development of current and future complex heterostructured nanomaterials (Figure 3). With FABRS, the many synthesis parameters that influence nanocrystal structure and properties can be more rapidly

screened with significantly less opportunities for "operator-introduced" error. The gQD reactions proceed 300% faster (with no downtime), and multiple variables can be tested in parallel with real-time analysis of reaction progression with *in situ* monitoring. The automated reactors allow us for the first time in a facile manner precisely control the rate of addition of precursors from batch-to-batch, the stirring speed of the reaction and the temperature of both the reagents used as well as the reaction itself. The system comprises 8 indvidual reactor modules run in parallel and is ammenable to gQD synthesis, as well as other complex nano-heterostructures requiring multiple synthetic steps for completion.

Figure 3: FABRS system. With 8 systems total, efficient and reproducible high throughput optimization and scale up of multi-step processes can be achieved.
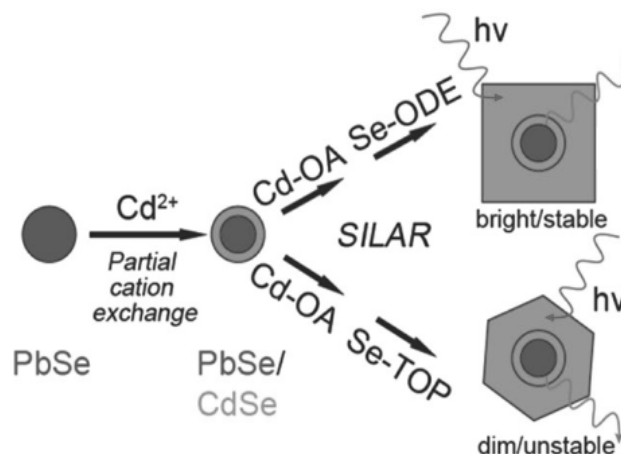

Figure 4: New materials development in our lab[8], gQDs with IR emission. These PbSe/PbS/PbS materials will now undergo further optimization using FABRS.

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