Development of a Highly Stable and Thermally Processable *Sapphire*™ Quantum Dot Polymer Matrix Using a Two-Prong Approach

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Presented at the 26th International Liquid Crystal Conference, July 31 - August 5, 2016, Kent State University

Overview

Semiconductor nanocrystals, also commonly called quantum dots (QDs), are attracting widespread attention because of unique optical properties, including emission wavelengths in the visible range, high quantum efficiency, narrow emission with wide absorption profiles, and compatibility with custom matrix polymers. Dispersion in a custom polymer requires **1.)** modifying the surface of the QDs to isolate them from the degrading effects of oxygen and water vapor, and **2.)** developing a custom host polymer matrix optimized for the QD surface interaction.

Integrating QDs can significantly improve the performance of optoelectronic devices, but the stability of QDs under such high photon flux conditions and in such high temperature environments presents key challenges. Accordingly, Crystalplex, has developed a unique QD that can meet the requirements of optoelectronic applications. Properties include:

- Emission wavelengths tuned by the ratio of two or more semiconductor materials in the core instead of by particle size
- An equilibrium batch process for synthesis that is easily scalable
- High quantum efficiencies (QE) of above 80%
- High stability under robust environmental and high photon flux conditions due to an Al_2O_3 outer coating
- Narrow full width, half-max (FWHM) emission bandwidths of 28-32 nm
- Reduced manufacturing cost due to a batch synthesis process using metals and metal oxides as starting materials instead of more expensive organo-metallic complexes

The efficient dispersion of QDs in a polymer matrix is essential in demanding optoelectronic applications. Crystalplex's proprietary Al_2O_3 outer coating provides both inherent nanocrystal stability (by adding an environmental barrier to each individual crystal) and strong surface binding sites for custom polymers. Interaction between the base polymer and the QD surface is achieved by optimizing the polymer architecture and introducing specific QD-docking sites in a custom homo-polymer. This creates an ideal dispersion environment for the QDs and a highly stable, homogenous QD composite.

Traditional approaches to QD dispersion require the use of small molecule surfactants as additives or functionalized block-copolymers as the matrix, or a combination of both. A number of challenges exist with these systems due to their complexity. Crystalplex polymer-QD composites, developed with Liquid Ion Solutions LLC, can survive thermoplastic injection molding and extrusion conditions without a decrease in quantum efficiency or photostability of the nanocrystals. This opens up new opportunities for high-performance optical components.

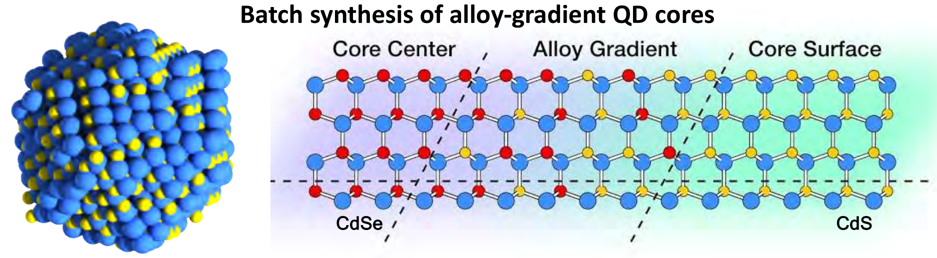
Future directions

Future work includes partnering with leaders in the display and lighting industries to apply these formulations to real world applications, such as:

- Engineered thermoplastic lens components for injection molded remote phosphors
- Engineered thermoplastic extrusions for edge-lit display applications
- QD coated display components, such as mirrors or prism films, potentially eliminating a separate QD film
- Silicone systems with embedded QDs for direct LED encapsulation in low-temperature applications (below 85C)
- Silicone systems with embedded QDs as a printable ink

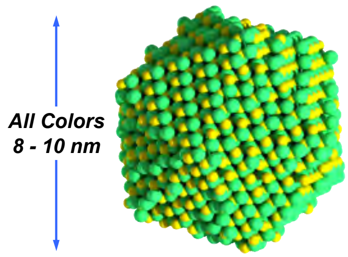
Crystalplex® *Sapphire*™ quantum dots

Batch synthesis of alloy-gradient QD cores



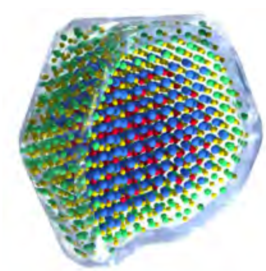
IN A BATCH EQUILIBRIUM PROCESS, REACTANTS ARE MIXED THEN HEATED TO INITIATE CRYSTAL GROWTH. THE HIGHER REACTIVITY OF THE Se PRECURSOR RESULTS IN A Se – S GRADIENT. THIS PROCESS ENABLES PRECISE EMISSION TUNING BY VARYING QD COMPOSITION INSTEAD OF SIZE. SYNTHESIS OF ALLOY-GRADIENT QDs ALSO ELIMINATES CRYSTAL SIZE UNCERTAINTY INHERENT IN THE RAPID QUENCHING PROCESS OF SIZE-DEPENDENT QUANTUM DOTS, SIGNIFICANTLY SIMPLIFYING MANUFACTURING SCALE-UP.

Addition of Zn:S shell and *Sapphire*™ coating for QD stability



Zn:S shell added to alloy-gradient core

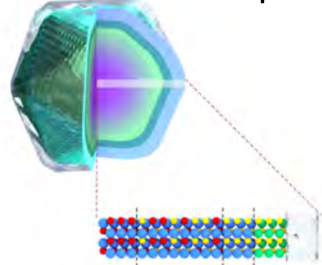
Surface rendering of ~ 5 atom-thick layer of aluminum, prior to oxidation



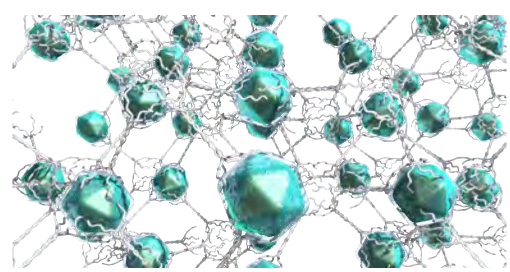
Cutaway view of alloy-gradient QD with Al_2O_3 Sapphire shell following oxidation

THE Zn:S CORE-SHELL STRUCTURE IS PROTECTED FROM THE ENVIRONMENT BY THE *SAPPHIRE*™ COATING, WHILE REMAINING HIGHLY TRANSPARENT TO INCOMING AND OUTGOING PHOTONS

Dispersion in a stabilizing polymer matrix



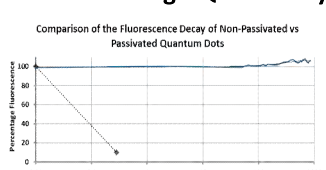
Cutaway view of Crystalplex alloy-gradient QD with Sapphire™ shell



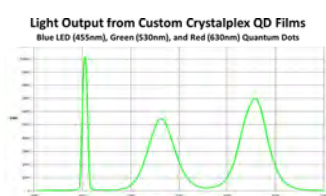
3-D rendering of Sapphire™ coated QDs with matrix dispersion to control reabsorption and maintain efficiency

FOR UTILITY IN OPTOELECTRONICS, QDS MUST BE DISPERSED IN A STABILIZING MATRIX TO MAINTAIN QD SPATIAL SEPARATION. CRYSTALPLEX ACCOMPLISHES THIS USING EITHER A.) A POLYMER-QD COMPOSITE SYSTEM ADDED AS A QD-POLYMER COMPOSITE FOR SOLVENT CASTING, AS A QD CONCENTRATE FOR THERMOPLASTIC EXTRUSION OF ACRYLICS (OVER 200C), OR AS A QD CONCENTRATE FOR THERMOPLASTIC INJECTION MOLDING, OR B.) AN INORGANIC QD COMPOSITE SYSTEM ADDED TO TWO-PART SILICONE THERMOSET POLYMERS OR TWO-PART ACRYLIC THERMOSET POLYMERS

The result: High QD stability and other characteristics essential for OE applications



Effects of Al_2O_3 passivation on QD stability using QDs spun-coated in PMMA on glass exposed to 100C and 100% relative humidity



Fluorometer scan on green/red film for LCD backlight

Lamination of solvent-cast polymer/QD matrix onto carrier film

THE COMBINATION OF *SAPPHIRE*™ COATING AND OPTIMAL QD-MATRIX INTERFACE CHEMISTRY CREATES ALLOY-GRADIENT QDS WITH THE CHARACTERISTICS NECESSARY FOR DEMANDING OPTOELECTRONIC APPLICATIONS. THESE INCLUDE HIGH STABILITY, HIGH QUANTUM EFFICIENCY (>80% FOR ALL COLORS), NARROW EMISSION BANDWIDTH (~ 30NM FWHM FOR ALL COLORS), AND VERY LOW MANUFACTURING COSTS.