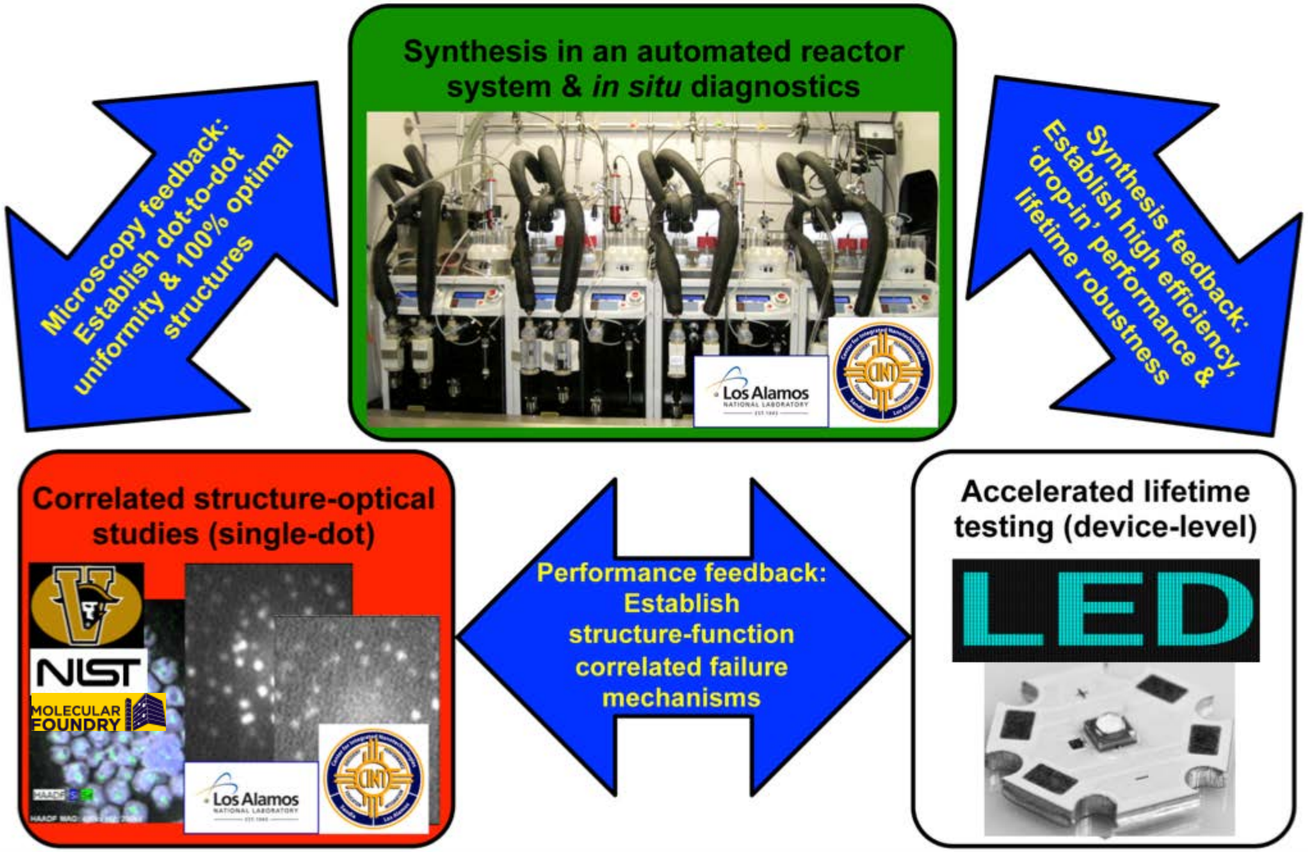
Next-generation "giant" quantum dots: Performance-engineered for solid-state lighting

2017 Building Technologies Office Peer Review



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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Project Summary

Timeline:

Start date: July 31, 2015

Planned end date: August 31, 2017

Key Milestones

1. Milestone 1.2.1; **M12**: Synthetic and/or advanced separations method realized to achieve very high QY gQD red emitters – *Ensemble QYs >80%; Single-gQD QYs to 100%.*
2. Milestone 2.1.1; **M12**: Determine underlying structural properties responsible for sub-optimal QYs in non-blinking/bleaching gQDs – Orfield et al. *ACS Nano* **2016**, 10, 1960 showed QY heterogeneity from gQD charging.
3. Milestone 3.1.2; **M12**: gQD-LED with demonstrated <20% QY drop after 500 h HTOL testing – *17% after 500 h.*
4. Milestone 2.1.2; **M18**: Mechanistic understanding of gQD failure under high heat/flux stress: *Revealed processes/structure correlations responsible for either resisting or succumbing to photobleaching.*

Budget:

Total Project $ to Date:

- DOE: $583K through FY17 Q1
- Cost Share: $135K through FY17 Q1

Total Project $:

- DOE: $1000K
- Cost Share: $250K

Key Partners:

"U.S. Lighting Manufacturer"
Vanderbilt Un.
National Center for Electron Microscopy (LBNL)
NIST

Project Outcome:

The primary objective is develop the science basis for advancing the **"giant" quantum dot (gQD)** technology to meet or exceed rigorous performance metrics for a new narrowband-red down-conversion material as an alternative to conventional red phosphors and other QD materials. High efficiency (>80% QY) must be paired with stability in direct-on-chip applications for LEDs operated at high-power (1-5 W/mm^2). Mechanistic understanding of QY and failure processes under flux/heat/humidity stress will be established. The final performance milestone is a color-optimized warm-white gQD-LED demonstrating <15% luminous flux decay and <0.007 du'v' color point shift after 3,000 h (M24).

Purpose and Objectives

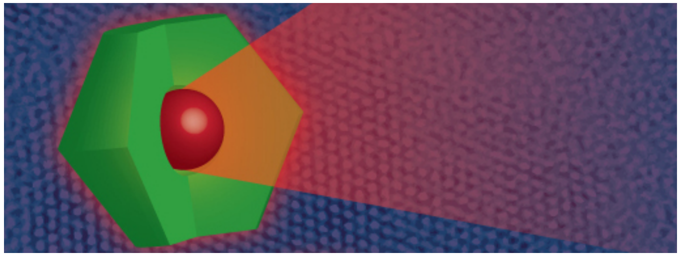
Problem Statement: To support more rapid adoption of SSL in the market place, warm-white LEDs are needed. The technical challenge is to realize **'warm-white' without compromising LER (>400 lm/W)**. For this, narrowband red-emitting down-conversion materials are required. Moreover, these must be **compatible with direct-on-chip use**, i.e., in stark contrast with display-technology applications that tolerate material requirements for low-flux/low-temperature operation and for protection from air and moisture. Rare-earth and other dopant phosphors suffer from poor absorption properties (Eu^{3+} 'line' emitters), poor emission properties (Eu^{2+} broadband emitters), or stability/saturation limits at high-flux (Mn^{4+} fluorides). QDs suffer from self-reabsorption and instability (unless in hermetically sealed remote elements). Our effort aims to **address knowledge gaps in understanding of the processes leading to flux/heat/air/humidity instability of QDs** and to **take advantage of gQD properties of non-self-reabsorption and single-QD photostability** to design/demonstrate new gQD materials for SSL.

Purpose and Objectives

Target Market and Audience: An advanced gQD technology would have an immediate impact on the SSL Phosphor Grand Challenge for narrowband red-emitters, enabling spectral efficiency and precise color quality coupled with minimal flux-density saturation and facile excitation.

Impact of Project: An effective, low-cost, drop-in gQD phosphor replacement

1. Project's outputs are (a) mechanistic-level understanding of processes responsible for gQD/QD failure over time under high flux/temperature/humidity conditions paired with a knowledge of the precise aspects of gQD structure responsible for failure, (b) design strategy for new gQDs that address failure mechanisms, and (c) demonstration of high QY/high stability at single-QD and LED levels.
2. Final product: High-performance gQD-LED – color-optimized warm-white LED demonstrating <15% luminous flux decay and <0.007 du'v' color point shift after 3,000 h.
3. If successful: Rapid adoption in nearly all LED product lines as 'drop-in' replacements for existing red phosphors (1-2 years after the 24 month program)



LANL basis technology for advancing QDs for SSL: Non-blinking "Giant" QD (gQD)

Approach

Approach: 3 Integrated Tasks (LANL-centered: 1&2; Industry partner-centered: 3)

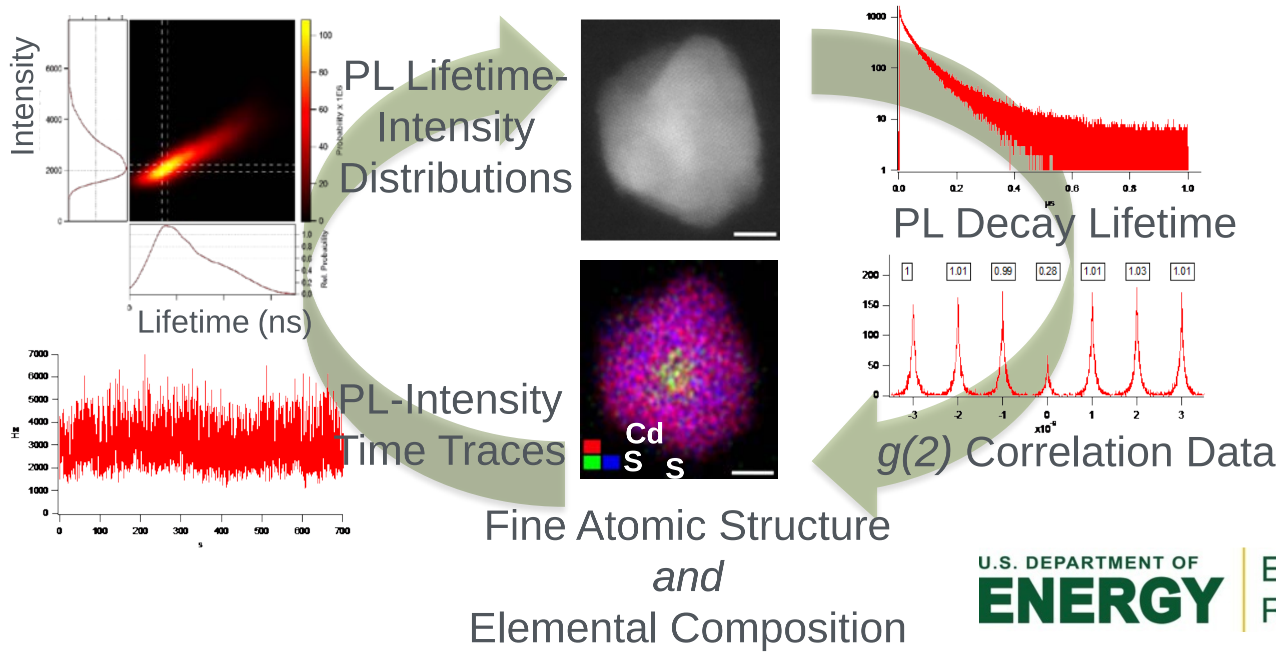
Task 1.0: Synthesize next-generation red-emitting gQD down-converters

Task 2.0: Reveal failure mechanism structure-function relationships through correlated single-dot optical and electron microscopies

Task 3.0: Validate advanced gQD technology in accelerated lifetime testing and performance benchmarking

Key Issues: High stability and high QY are anti-correlated.

Distinctive Characteristics: (a) Our technology basis is LANL-patented gQD down-conversion material, and (b) We have developed a unique single-QD "stress test" that affords novel correlative data for understanding QD (or other phosphor!) device-level failure mechanisms.



Progress and Accomplishments

Accomplishments: Meeting project milestones, e.g.:

Milestone 1.2.1 (M12): Synthetic and/or advanced separations method realized to achieve very high QY gQD red emitters – *Ensemble QYs >80%; Single-gQD QYs to 100%*.

Milestone 2.1.1 (M12): Determine underlying structural properties responsible for sub-optimal QYs in non-blinking/bleaching gQDs – *Orfield et al. ACS Nano 2016, 10, 1960 showed QY heterogeneity from gQD charging and revealed no intrinsic limit to QY.*

Milestone 3.1.2 (M12): gQD-LED with demonstrated <20% QY drop after 500 h HTOL testing – *17% after 500 h*.

Milestone 2.1.2 (M18): Mechanistic understanding of gQD failure under high heat/flux stress: *Revealed processes/structure correlations responsible for either resisting or succumbing to photobleaching, i.e., including unexpected QY-stability anticorrelation.*

Progress and Accomplishments

Market Impact: Largely N/A at this phase of effort; Focus is applied R&D for *Topic Area 1 – LED Core Technology.* R&D results shared at and well received by SSL community via panel talk and poster at the 2017 SSL R&D Workshop:

(a) Helping SSL community understand key processes underlying down-conversion material performance
(b) Developing single-phosphor "stress test" for rapid assessment of lifetime stability and unprecedented insight into causative factors influencing stability; benchmarking with 'Company Partner' device testing
(c) Establishing method for scaling-up synthesis of complex nanomaterial phosphors via automation

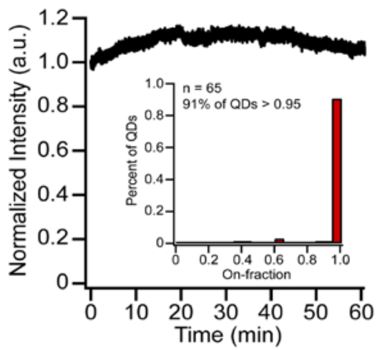
Awards/Recognition: PI named LANL Laboratory Fellow (2016) in part for "discovery and elaboration" of gQD technology.

Lessons Learned: Unexpected QY-stability anticorrelation (see next slide).

Progress and Accomplishments: Revealing & Understanding the 'Quantum-yield/Stability Conundrum'

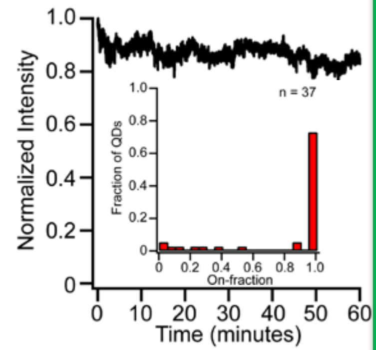
Alternative synthesis

Different structures



Moderate QY

Alternative synthesis



High QY

Similar room-T photobleaching and blinking

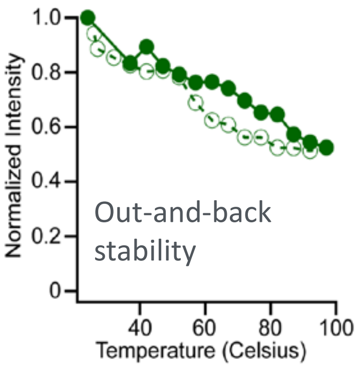
But, different responses to <u>device</u> lifetime stress testing

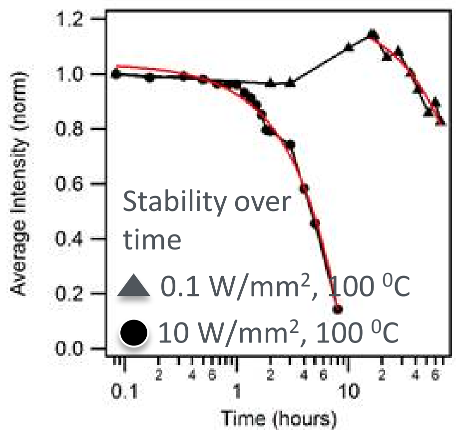
Mod-QY gQD	0 h Cured QY (T_0)	168 h QY (T/T_0)	336 h QY (T/T_0)
Soln QY (40%)	36% (1.0)	41% (1.14)	37% (1.03)

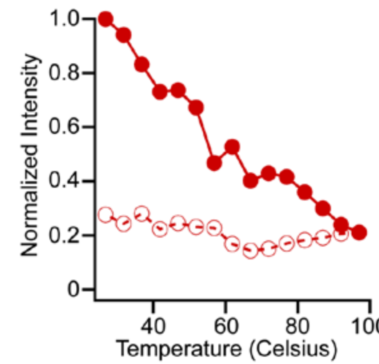
Hi-QY gQD	0 h Cured QY (T_0)	168 h QY (T/T_0)	336 h QY (T/T_0)
Soln QY (85%)	57% (1.0)	NA	34% (0.60)

Progress and Accomplishments: Revealing & Understanding the ‘Quantum-yield/Stability Conundrum’

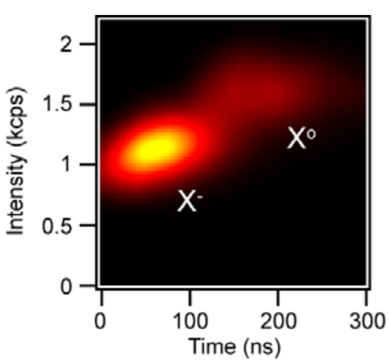
And, different responses to <u>single-dot</u> lifetime stress testing







Key insight: Both – differences in device and single-dot stability – result from differences in photobleaching mechanism for the differently synthesized gQDs

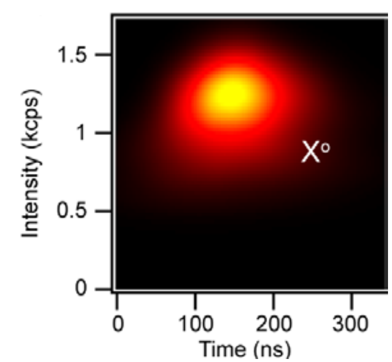


(1) Mod-QY gQDs → “A-Type”

Bleaching via increased dot charging; Never completely bleach, but neutral (brighter) exciton ceases to contribute over time, such that emission only from charged states

(2) Hi-QY gQDs → “B-Type”

Bleaching via increased surface trapping; Neutral exciton dominates PL, but fails catastrophically



Project Integration and Collaboration

Project Integration: Project is a partnership with a large 'U.S. Lighting Manufacturer.' As new gQDs are synthesized and tested at the single-dot level, they are shipped to our partner for device-level lifetime testing (HTOL and WHTOL to date). ***The criteria (temperature, flux, humidity) used for device-level tests inform the criteria we use for single-dot level tests.*** Also, QDs or other alternative phosphors provided to the company by third parties for device testing are provided to us for blind testing of single-QD/phosphor properties. Our data are then given to the company to enable a comprehensive assessment of performance and benchmarking of all materials.

Partners, Subcontractors, and Collaborators: Project further involves collaborations with university (Vanderbilt Un.) and other national lab (NIST, LBNL) partners. These are unfunded collaborations of mutual benefit coordinated through the LANL CINT User Program, as well as the User Programs of the the partner national labs (NIST, LBNL). These coordinated efforts are allowing for the first time a **comprehensive chemistry-structure-function correlation** to be established, which is enabling more rapid development of the gQD down-conversion materials for SSL.

Communications: 2016 SSL R&D Workshop (poster), 2017 SSL R&D Workshop (poster & talk), BES/EERE Roundtable on SSL 2015 and 2016, NIST Advancing Nanoparticle Manufacturing Workshop, seminars (Un. Washington, Seattle; Wayne St. Un.), conference talks (SPIE Optics + Photonics 2016).

Next Steps and Future Plans

Next Steps and Future Plans:

(1) Implement new understanding of gQD synthesis/structure and QY/stability correlations into design of optimal gQD to either: (a) take advantage of a "charge reservoir" effect to stabilize gQDS from photobleaching or (b) eliminate surface trapping pathways to stabilize gQDS from photobleaching. *Determine: Does this mean a "barrier layer"?*

(2) Demonstrate key milestones pertaining to **efficiency/stability requirements for device performance** to match *MYPP Goals per A.1.3 Down-Converters Table* & culminating in a gQD device meeting color-shifting target of <0.007 over 3000 h (MS 3.4.3), which is set by our industry partner and approaches MYPP 2020 goal of $\Delta u'v'$ <0.002 "over life."

(3) Demonstrate key milestones for **gQD scale-up** using one-of-its-kind automated reactor system for complex, multi-step nanomaterials syntheses.

Automated parallel reactor system

…designed for multi-step synthetic processes

REFERENCE SLIDES

Project Budget

Project Budget: Budget Period 1 (BP1) corresponds to partial Q4 of FY15 and FY16 to end August. BP2 corresponds to partial Q4 of FY16 and FY17 to end August.
Variances: Project end date has been shifted by ~1 month to account for initial slow spending as a result of having to assemble the team – 2 postdoc hires at LANL.
Cost to Date: DOE: $583K through FY17 Q1; Cost Share: $135K through FY17 Q1.
Additional Funding: None for this effort.

	DOE BP1	Cost Share BP1	Total Value BP1	DOE BP2	Cost Share BP2	Total Value BP2	DOE Total	Cost Share Total	Total Value
LANL	$500k	$0k	$500k	$500k	$0k	$500k	$1,000k	$0k	$1,000k
CREE	$0k	$125k	$125k	$0k	$125k	$125k	$0k	$250k	$250k
Total	$500k	$125k	$625K	$500k	$125k	$625K	$1,000k	$250k	$1250k
CS %		20%			20%			20%	

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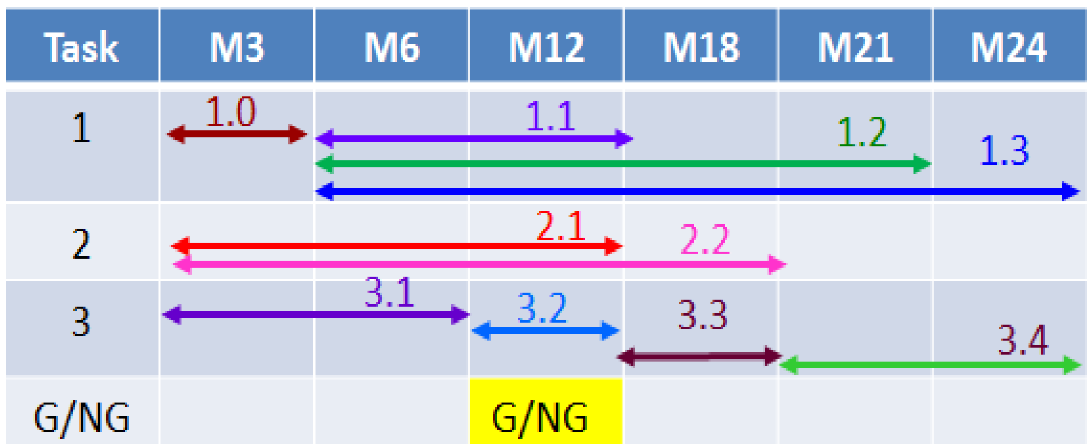
Project Plan and Schedule

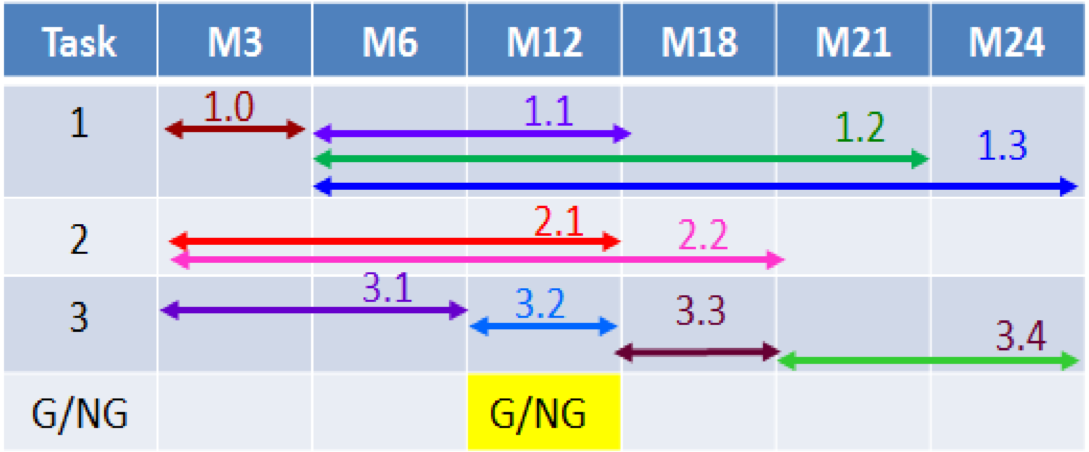
Describe the project plan including:

- Project original initiation date & Project planned completion date
- Schedule and Milestones
- Explanation for slipped milestones and slips in schedule
- Go/no-go decision points
- Current and future work



Project Plan and Schedule

- Project dates: July 31, 2015 – August 31, 2017
- Schedule and Milestones: See next 4 slides
- Hires dates for 2 LANL postdocs did not correspond with start-of-project date, which caused initially slow spending; currently on track
- Next slides explain a postponed milestone and a milestone variance
- Go/no-go decision points: Met in M12 by meeting key milestones – see next slides
- Past, current, future work – see next slides



Project Plan and Schedule: Milestone Chart

Milestone Summary Table			
LANL - Next-Generation 'Giant' Quantum Dots: Performance-Engineered for Lighting			
Milestone	**Description**	**Verification Process**	**Anticipated Date (Month)**
Budget Period 1			
1.1.1	Via analysis of gQD photoluminescence (PL) spectra, demonstrate red gQD narrowband emission centered at 610, 615, 620 and 625 nm; FWHM $\leq$35 nm	Spectral data collected on a Horiba Jobin Yvon Nanolog UV-Vis-NIR fluorimeter	3
1.1.2	Via analysis of gQD absorption spectra and relevant LED or laser electroluminescence (EL) spectra, demonstrate gQD absorption overlap with commercial LEDs (UV-A: 365-405 nm; blue: 450-470 nm) and blue laser diode (blue-violet: 405 nm; blue: 440-460 nm)	Comparison of gQD spectral data collected on a Varian Cary 500 UV-Vis-NIR absorption spectrophotometer and EL collected on a Horiba Jobin Yvon Nanolog UV-Vis-NIR fluorimeter outfitted with an integrating sphere	3
1.1.3	Demonstrate absence of flux-density saturation as 'PL intensity versus source power,' including comparison with conventional QDs and commercial red phosphors (line and broad emitters)	Comparison of PL data collected using Horiba Jobin Yvon Nanolog UV-Vis-NIR fluorimeter outfitted with an integrating sphere for different LED pump powers	3
1.1.4	Analysis (calculation) of impact of emitter radiative decay rate, absorption cross-sections on saturation characteristics, flux density, and Auger recombination processes on factors influencing flux saturation behavior	Calculation as described using known values as input variables	3
1.1.5	Assessment of luminous intensity per mass of emitter at a set distance and as a function of LED source power; baseline comparison between gQDs, conventional QDs and commercial red phosphors (line and broad emitters)	Distance-dependent intensities assessed using Konica Minolta CS 2000A spectroradiometer	3
1.2.1	Synthetic and/or advanced separations method realized to achieve very high QY gQD red emitters (QY >90%) and supporting data. High QY gQD product material provided to industrial partner for accelerated lifetime testing, along with data demonstrating QY	QY determined by absolute QY method employing integrating sphere	12

Milestone met

Milestone partially met: >80% ensemble QY; up to 100% individual gQD QYs

Milestone postponed with PM concurrence until near-final gQD emitter is realized for greater relevance and to afford increased focus on Task 2.0 activities, namely, *improved setup built* for investigation of flux/temperature/humidity-dependent single-dot optical performance

Project Plan and Schedule: Milestone Chart

1.3.1	Demonstration of <15% decay in PL QY to 85 °C	QY determined by absolute QY method employing integrating sphere as a function of temperature using Peltier sample heater	6
1.3.2	Demonstration of <10% decay in PL QY to 85 °C; <15% decay in PL QY to 115 °C	QY determined by absolute QY method employing integrating sphere as a function of temperature using Peltier sample heater	12
1.4.1	gQD/ZnO material synthesized and provided for internal analysis as well as to university and industrial partners for single-dot thermal/flux experiments, correlated single-dot optical/structural investigations, and device-level accelerated lifetime tests, respectively, by **M6** and thereafter as needed	Optical properties data [collected using single-dot spectroscopy system integrated with environmental chamber to control temperature (and/or humidity, oxygen/inert gas environment) and coupled to excitation laser sources that are power tunable] correlated with structural data [collected using a high-resolution transmission electron microscope and coupled with elemental data obtained by energy-dispersive x-ray spectroscopy]	6
2.1.1	Mechanistic description for gQD QY and the supporting single-QD optical/electron microscopy data showing the structural properties responsible for sub-optimal QYs	Correlate observations of function (single-dot PL intensity) with structure (high-resolution imaging and elemental mapping at single-dot level)	12
3.1.1	Comparative data from HTOL accelerated lifetime testing of multiple initial batches of gQD-LEDs provided to LANL	Partner supplied comparative study (analysis of spectral shifting and QY changes)	6
3.1.2	gQD-LED with demonstrated <20% gQD QY drop after 500 h HTOL testing	Partner supplied data from HTOL testing	12
3.2.1	Comparative data from WHTOL accelerated lifetime testing of multiple initial batches of gQD-LEDs provided to LANL	Partner supplied comparative study (analysis of spectral shifting and QY changes)	6
3.3.1	Comparative data from HTSL accelerated lifetime testing of multiple initial batches of gQD-LEDs provided to LANL	Partner supplied comparative study (analysis of spectral shifting and QY changes)	6
3.4.1	Comparative data from TS accelerated lifetime testing of multiple initial batches of gQD-LEDs provided to LANL	Partner supplied comparative study (analysis of spectral shifting and QY changes)	6

Milestone met

Milestone partially met: Realized in polymer composite but not in solution.

Variance: Industry partner pursued a combination of HTOL and WHTOL reliability tests in lieu of high temperature storage lifetime (HTSL; 3.3.1), which does not have LEDs operating, and thermal shock (TS; 3.4.1). This allowed for characterization of degradation when exposed to both blue light flux and high temperature or temperature with humidity. In the future, HTSL, e.g., will be used to verify storage compatibility of materials (heat/no flux).

Project Plan and Schedule: Ongoing and Future

Budget Period 2			
1.1.6	Demonstrate <10% decay in PL QY to 115 °C; <15% decay in PL QY to 150 °C	QY determined by absolute QY method employing integrating sphere as a function of temperature using Peltier sample heater	18
1.1.7	Demonstrate <10% decay in PL QY to 150 °C	QY determined by absolute QY method employing integrating sphere as a function of temperature using Peltier sample heater	21
1.1.8	Synthetic and/or advanced separations method to achieve PL-intensity stability to 150 °C and PL-intensity and radiative lifetime data that demonstrates optimal thermal stability, with this new gQD material provided to industry partner for accelerated lifetime testing	Temperature-dependent PL data (intensity and radiative rates)	21
1.2.2	Synthetic or separations protocol and resulting gQD material that does not degrade photo-oxidatively under combined thermal and flux stressors in accelerated lifetime testing	Partner supplied study to verify material stability (analysis of spectral shifting and QY changes)	24
1.2.3	Scaling: Demonstration of 5 g optimized g-QD material with minimal variation in peak PL wavelength (± 2.5 nm; to demonstrate uniformity in product)	PL data collected using Horiba Jobin Yvon Nanolog UV-Vis-NIR fluorimeter from random samples from the 5g product (at least 5 samples)	24
✔ 2.1.2	Mechanistic understanding of heat and flux-induced changes to QD QY and structural/chemical integrity; supporting single-QD optical and electron microscopy data showing structural properties responsible for sub-optimal thermal and photo-oxidative stability	Correlate observations of function (single-dot PL intensity) with structure (high-resolution imaging and elemental mapping at single-dot level)	18
3.1.3	Comparative data from HTOL accelerated lifetime testing of multiple optimized batches of gQD-LEDs provided to LANL to aid in down-selection of gQD chemistry	Partner supplied comparative study (analysis of spectral shifting and QY changes)	18

Project Plan and Schedule: Ongoing and Future

3.1.4	gQD-LED with <15% gQD QY drop after 1,000 h HTOL testing	Partner supplied data from HTOL testing	18
3.2.2	Comparative data from WHTOL accelerated lifetime testing of multiple optimized batches of gQD-LEDs provided to LANL to aid in down-selection of gQD chemistry	Partner supplied comparative study (analysis of spectral shifting and QY changes)	18
3.2.3	gQD-LED with <15% gQD QY drop after 1,000 h WHTOL testing	Partner supplied data from WHTOL testing	18
3.3.2	Comparative data from HTSL accelerated lifetime testing of multiple initial batches of gQD-LEDs provided to LANL to aid in down-selection of gQD chemistry	Partner supplied comparative study (analysis of spectral shifting and QY changes)	18
3.4.2	Comparative data from TS accelerated lifetime testing of multiple optimized batches of gQD-LEDs provided to LANL to aid in down-selection of gQD chemistry	Partner supplied comparative study (analysis of spectral shifting and QY changes)	18
3.4.3	Color-optimized warm-white gQD-CREE LED demonstrating <15% luminous flux decay and <0.007 du'v' color point shift after 3,000 h	Partner supplied device data	24