Super-Stable Quantum Dots for Low-Cost, Barrier-Free Components

Regina Qiu, David Olmeijer, Shihai Kan, Chris Sunderland, Austin Smith, Ashavani Kumar, Jason Tillman, Annie Chow, Michael Niemeyer, Jay Yamanaga, Mark Bokchtein, Kevin Wang, ZhongSheng Luo, Jeff Yurek

rqiu@nanosys.com
[1]Nanosys, Inc., 233 S. Hillview Drive, Milpitas, CA 95035
Keywords: Quantum Dot, LCD, environmentally stable, film

ABSTRACT

Nanosys invented the QDEF™ quantum dot film technology[1] for LCDs and has had great success in the premium LCD TV segment with more than 40 million quantum dot (QD) displays shipped worldwide since 2013. A typical QDEF component contains a layer of QD sandwiched between two layers of optically transparent barrier films (typically PET films with specialized thin-film coatings designed to protect QD from oxygen and moisture). In recent years the optical performance including efficiency, color gamut and reliability of QDEF has improved while costs for the QD component have come down approximately 30% per year on average year-over-year. Today, the cost of the QD used in QDEF is less than the cost of the barrier film[2]. Continuing this rapid pace of innovation and cost reduction demands a revolutionary new quantum dot that requires no barrier.

Here, we discuss new types of super-stable QDs and introduce examples of new, "barrier-free" QD display components enabled by such QDs.

1 Introduction

Eliminating the "barrier" films from QDEF components has two primary benefits 1) cost reduction through elimination of a subcomponent with little to no value-added and, 2) a reduction in the total thickness of the QD enabled functional film(s). Since the barrier film in a QDEF component was designed to minimize the performance degradation of QD-containing polymer films under oxygen rich atmospheric environment, the fundamental challenge in removing the barrier film is in how to take the control of the QD degradation process to enable manufacturing of environmentally stable QDs that are robust even when operating in the presence of oxygen, i.e., in air.

1.1 QD Degradation

A particular challenge is performance degradation of QDs operating in environments containing oxygen. While the full mechanism of degradation is a very complex topic, evidence suggests that a significant degradation mechanism involves the generation of reactive oxygen species by QDs in the excited state. The electrons from the QDs can be transferred to molecular oxygen and form a variety of harmful reactive oxygen species (ROS), such as: $•O_2^-$, H_2O_2, HO•, HOO•, $^1O_2$, etc[3]. Once generated, these species can participate in a wide range of harmful chemical reactions[4], resulting oxidative degradation of the ligands, resin or QD itself; and finally, at the macro level, degradation of optical efficiency and stability of the QDs.

1.2 Thermal Stability Considerations

Most current implementations of barrier-free QDEF films involve high temperature thermal processing by various thermoplastic melt conditions, such as extrusion and injection molding methods. Typical melt processing temperatures for common thermoplastics are between 190°C ~290°C (190°C for PP/Polypropylene, 240°C for PMMA /Polymethyl methacrylate, and 290°C for PETs respectively). The thermal stability of barrier-free QDs must meet these manufacturing process conditions, which are significantly higher temperatures than the those seen by traditional QDEF components in manufacturing or end use.

High temperature processing conditions can negatively impact the stability of QDs through chemical rearrangement of atoms on the surface, or through annealing or alloying phenomena which can occur between different layers in a QD's core/shell structure.

2 Super-Stable QDs

2.1 Design Concept for Super-Stable QD

To build a super-stable QD that is able to operate in the presence of oxygen, we designed a QD with layered and gradient core/shell structures. These structures help to confine the electrons to the core, minimizing their potential to interact with molecular oxygen. In addition, we have optimized processing conditions to enable the formation of thick shells, further minimizing the potential of the QD to be damaged by the environment. Lastly, we passivated the QD surface to minimize traps which can leave the QD vulnerable to degradation.

3 Testing Methodology and Results

In order to properly assess the stability of these super-stable QD, we evaluated the QDs in the following formats: 1) QD solution; 2) QD in a freestanding coating layer and 3) QD in an extruded layer. For the QD solution, thermal cycling tests were conducted and for the freestanding and extruded film, accelerated storage and flux operating tests were conducted.

3.1 Thermal Stability Study of QD solution

Table 1 shows typical optical data for the super-stable QDs Nanosys has developed to withstand significant environmental stress such as high temperature and high oxygen level.

Table 1. Typical Properties of Super-Stable QDs

	PWL	FWHM
Super Stable QD Green	531 - 535	19 - 23
Super Stable QD Red	622 - 626	22 - 32

We thermal cycled the green and red super-stable QDs, measuring their quantum yield and optical properties. Such tests enabled us to quickly identify QD formulations which were more robust against photooxidative degradation; and, consequently, to determine the impacts of multiple variables, such as core structure, processing conditions and shell composition on the stability of the QDs.

Table 2 shows that there is very little change in these values compared with that from control samples at room temperature. This result confirms that these QDs stay very stable at thermal cycles up to 290°C.

Table 2. QD property vs. processing temperature

	Green Super-QDs			Red Super-Stable QDs		
Compared to Control at RT	Δ QY	Δ PWL	Δ FWHM	Δ QY	Δ PWL	Δ FWHM
Cycled to 240°C	+ 1%	n.c.	n.c.	- 1 %	n.c.	n.c.
Cycled to 290°C	+ 2%	</+ 0.5%	</-1%	- 2 %	n.c.	</+ 0.5%

3.2 Stability Study of QD in Freestanding coating Layer

The super-stable QDs are designed to be used in coating or extruded format. To properly evaluate their stability in each intended application format, we have conducted accelerated storage and flux operating tests on coated and extruded components made using super stable QDs.

One of the main reasons to evaluate in the freestanding format is to accelerate the oxygen and water that can diffuse to the QDs. We also limit the thickness of the film to about 100µm to further increase the stress level through the film. In addition, we use elevated temperature (80°C) to accelerate the oxygen diffusion in the film.

Since green QDs usually exhibit lower stability than the red QDs, we compared the flux stability of the super-stable green QDs with standard green QDs in production today. As shown in Figure 1, the conventional production QDs under flux and at elevated temperature lost over 40% of power in less than 500 hours while the new super-stable green QDs only lost a few percent of power in over 1500 hours of accelerated testing. The improvement under this test condition is over 1000x.

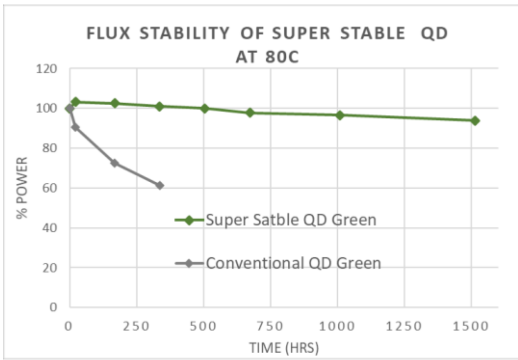

Fig. 1 Flux Stability of Super Stable QD at 80°C

Figure 2 (a) shows the behavior of green and red super-stable QDs in the freestanding white film under flux and 80°C condition.

It can be seen from the chart that both green and red are stable under the test conditions with little to no power degradation in over 1500 hours under test.

Similar performance can also be seen in the high temperature high humidity environment, as shown in Figure 2 (b) below.

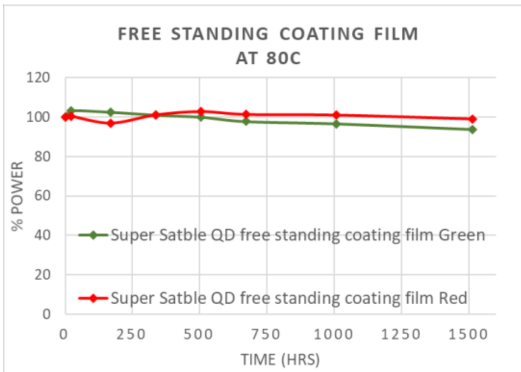

Fig. 2 (a). Stability of freestanding film under flux at 80°C

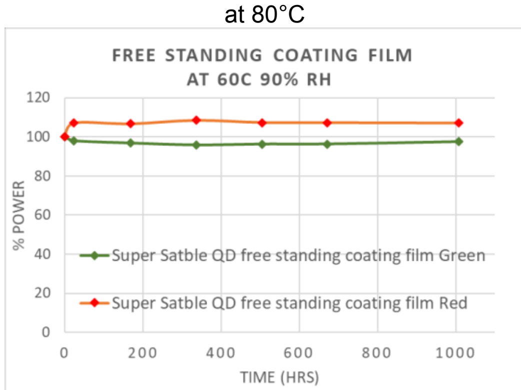

Fig. 2 (b). Stability of freestanding film under flux at 60°C and 90% high humidity condition

3.3 Stability Study of QD in Extruded Layer

In addition to the conventional coating technology, the display industry has long wanted to incorporate QDs into an extruded product to reduce cost and display manufacturing complexity. One of the key challenges in developing an extruded QD component is to maintain high QY after going through a high temperature extrusion process which is roughly 250°C for polymethyl methacrylate (PMMA) or 290°C for polyethylene terephthalate (PET). Once you pass the temperature test, the next big challenge is to maintain good stability under storage and operating condition required by a display product.

Figure 3 (a) shows a few pictures of extruded PET, film in various format formats.

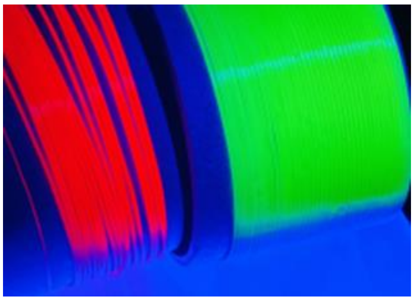

Fig 3 (a) Photos of extruded green and red PET sample, illuminated by UV light

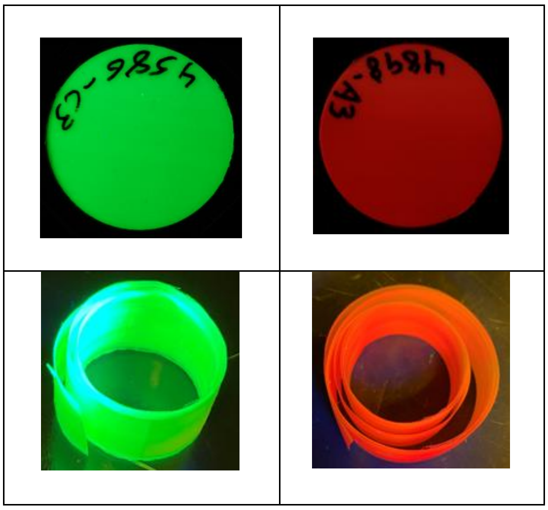

Fig **3** (b) Photos of extruded green and red PMMA samples, illuminated by UV light

In Fig. 3 (b) The super-stable QDs particles are compounded with PMMA with a twin-screw extrusion barrel and extruded into films. Green and red film are shown separately in the picture.

We put a white extruded film under typical high temperature high humidity condition and operating condition to evaluate its stability. The performance of green and red super-stable QDs in the extruded film under operating condition can be seen in Figure 4 (a). It can be seen from the chart that both green and red are very stable under the test conditions to over 4000 hours.

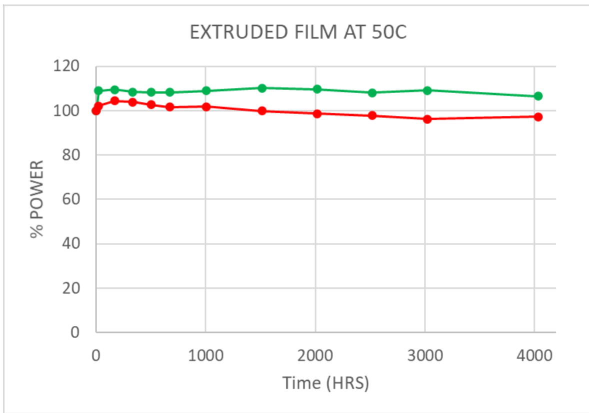

Fig. 4 (a) Operating stability of the extruded film

Similar performance can also be seen in the high temperature high humidity test, both green and red QDs remain almost no change over 1000 hours, as shown in Figure 4 (b).

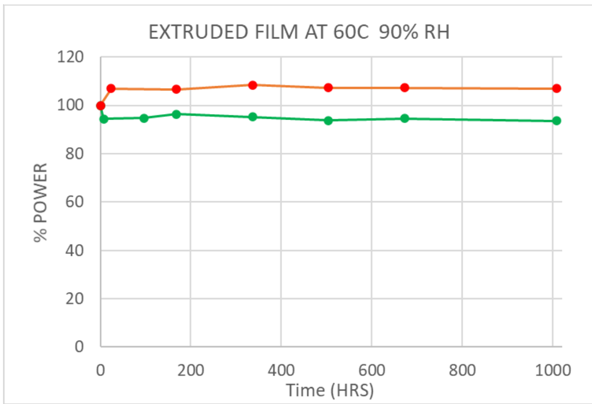

Fig. 4(b) Stability of extruded film under high temperature (60°C) with 90% Humidity.

4 Discussion

We have successfully developed a new class of super-stable QDs that can be used in a wide range of applications from laminated QDEF with pure PET to co-extruded QD diffuser plates to more complex composite implementations. We have now successfully scaled up the synthesis of such class of QDs to large scale manufacturing in >1,000 liter-class reactors with highly satisfactory performance and stability. Further improvements are ongoing, including the expansion of the concept to heavy metal free QDs.

Super-stable QD has enabled a new generation of low-cost QD components in the market. Figure 5 (a) shows the schematic of a barrier free QDEF implementation in which the QD layer is sandwiched between two 100μm thick PET film. This component is being co-developed with our partner and is expected to be in mass production in Q4 2021. The advantage of this implementation is that it is a direct replacement for existing QDEF, as a result, customers do not need to make any design or manufacturing adjustment to their display products. In addition, due to the maturity of pure PET film and its low cost comparing with barrier film, it can not only significantly reduce the material cost, but also simplify the coating process and improve the production yield.

Another implementation of diffuser plate through a co-extrusion process can be seen in Figure 5 (b). One of the key innovations here is to do co-extrusion such that the outer layers can provide some level of oxygen and water barrier to achieve the best stability. The 3-layer structure also enable new flexibility in tuning scattering performance of diffuser plate. As a result, the product can integrate QD into the diffuser plate while perfectly maintaining the required scattering performance and the excellent optical properties of QDs. Since this implementation has monolithically combined QD and diffuser plate together, it can simplify the backlight assembly process and consequently reduce the manufacturing cost. This product has been in mass production since the first half of 2021. The matrix material currently in use is PMMA.

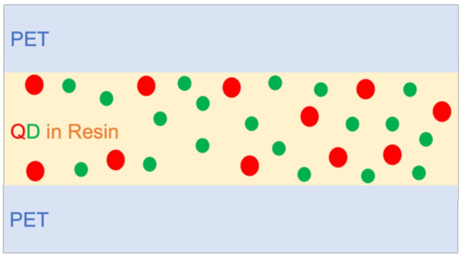

Fig 5 (a) Schematic of barrier-free QDEF implementation with the super-stable QDs

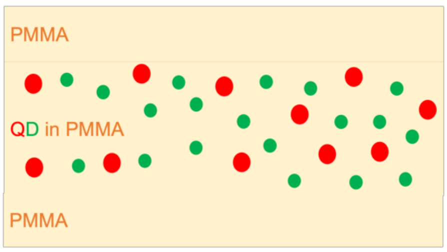

Fig 5 (b) Schematic of QD diffuser plate implantation with the super-stable QDs

There is one other implementation that is still under development, as shown in Figure 6. The ultimate goal is to eliminate all water and oxygen barriers. The implementation can be done via coating or extrusion process.

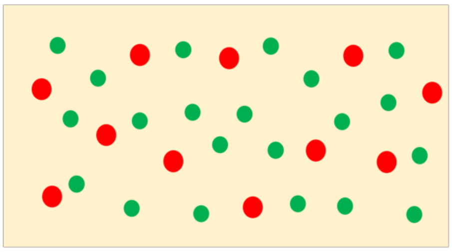

Fig. 6. Schematic of xQDEF

5 Conclusions

Nanosys invented QDEF quantum dot technology and is the first company commercialized this technology for displays.

This current report shows Nanosys constantly strives to successfully meet market demands with its evolutionary products of super-stable QDs while enabling better and thinner form factor of the films, and the testing cost down trend in the mainstream display market.

References

[1] A High-Efficiency Wide-Color-Gamut Solid-State Backlight System for LCDs Using Quantum Dot Enhancement Films. Jian Chen PhD., Veeral Hardev, Jason Hartlove, Jurgen Hofler PhD., Ernie Lee, Nanosys, Inc., Palo Alto, CA

[2] US TV Market: Can the Boom Continue. Baker, Stephen. (May 2021). SID DisplayWeek: DSCC Business Conference, Virtual Event. http://www.displayweek.org/2021/Program/Business-Conference [PowerPoint Presentation].

[3] Cytotoxicity of InP/ZnS quantum dots related to reactive oxygen species generation
Hicham Chibli[a], Lina Carlini[a], Soonhyang Park[b], Nada M. Dimitrijevic[c] and Jay L. Nadeau*[a]
The Royal Society of Chem., Nanoscale, 2011, 3, 2552 www.rsc.org/nanoscale.
[a]McGill University
Lina Carlini
[b]Korean National Defense University
[c]Argonne National Laboratory

[4] Katerina Krumova and Gonzalo Cosa, Chapter 1:Overview of Reactive Oxygen Species , in Singlet Oxygen: Applications in Biosciences and Nanosciences, Volume 1, 2016, pp. 1-21