Glasses are widely used in display applications, as substrates for thin film transistor arrays and color filters or cover windows. In addition, glasses and glass-ceramics now also are being considered as active materials for manipulating the primary colors of light sources, further expanding their potential application in display technologies.

Current cutting-edge systems, such as liquid crystal displays (LCD) using quantum dots (QDs) and organic light emitting diodes (OLED), rely on organic materials or QDs synthesized by wet-chemistry to produce and control the primary colors of lights, such as red, green, and blue (RGB). It is well known that organic materials suffer from inherently weak chemical and thermal stabilities and complicated synthesis process, while inorganic glasses or glass-ceramics possess high chemical and thermal stability. These properties give glasses durability as well as long-term stability, and their relatively easy fabrication process reduces production cost. These advantages are opening new opportunities for glass-based materials as light generating materials, replacing conventional QDs.

In this overview, the recent use of conventional QDs in displays is reviewed, and the development and current status of quantum dots and nanocrystal-embedded glasses for display applications are discussed, along with their challenges and future prospects.

Color gamut of displays

The current high demand and fast-growing market for more realistic images and vivid motion pictures is driving the need for high-quality picture displays, which rely on several key features,
including resolution, brightness, high dynamic range, and color gamut. Color gamut, which represents the range of color reproduction within the visible color space, is especially important as displays with ultrahigh-definition (UHD) resolution (3840 × 2160 in pixels) become more popular in the market. The color gamut of a display is defined by a triangle area enclosing the primary RGB colors.

The standard color gamut for cathode-ray tubes was defined by the National Television Systems Committee (NTSC) within the CIE 1931 chromaticity diagram in 1953. With the development of new display technologies since the 1990s, such as plasma displays and LCDs, the International Telecommunication Union Radio communication organization recommended a new color gamut for high-definition TVs (HDTV) with 1920 × 1080 resolution, which is known as Rec. 709 (or BT. 709), as found in the chromaticity diagram of Figure 1c.

The International Electrotechnical Commission announced standard RGB (sRGB) for computer displays, and it has a color reproduction range similar to Rec. 709. Adobe and Digital Cinema Initiatives, LLC also suggested definitions for color gamut, those being Adobe RGB and DCI-P3 for digital cinema colors, respectively. Thanks to technological advances in the display industry, a new standard was required for the UHDTV environment, and thus the International Telecommunication Union Radio suggested a wider color range, which is known as Rec. 2020 (or BT. 2020), whose area corresponds to 150% of the NTSC area.

It should be noted that the HDTV color gamut corresponds to about 72% of NTSC, which most conventional LCD-based HDTVs provide. Rec. 2020 for UHD was defined by monochromatic 630, 532, and 467 nm lights for red, green, and blue, respectively. Accordingly, to realize UHD color gamut, it is highly important to adjust the peak emission wavelengths of the RGB colors and reduce their emission bandwidth or full width at half maximum for high color saturation (or color purity).

The RGB colors of conventional LCDs are determined by a combination of color filters and the emission spectra of a white LED, which is comprised of a blue LED with green and red ceramic phosphors (RG-LED). βSi₃AlON₉:Eu²⁺ and CaAlSiN₃:Eu²⁺ (CASN:Eu²⁺) were mostly used in commercial RG-LEDs as the green and red phosphors, respectively. However, because of their broad emission bands, the LCD with RG-LED have broad emission spectra, as drawn in Figure 1a. This emission spectra results in a color gamut of about 75% of NTSC.

Scientists achieved significant improvement of the color gamut using QDs, which have narrow emission bandwidth and tunable emission peak wavelengths. As schematically illustrated in Figure 1, when QDs are used as color converting phosphors, well separated emission spectra can be obtained, providing a wide color gamut higher than 100% NTSC. QDs thus were applied by major panel makers such as Samsung in advanced LCD displays known as QLED-TVs.

Displays based on active-matrix OLEDs (AMOLED) also can supply RGB colors with narrower emission bands than conventional RG-LEDs and provide a high color gamut. However, for large sized panels, AMOLEDs are used with a combination of white OLED and color filters to produce RGB colors, and accordingly have a limited color gamut following behind QD-based LCDs in terms of brightness and color reproduction range.

QDs for displays

QDs are semiconductor nanocrystals with diameters (typically < 10 nm) smaller than their Bohr radius, and they include group II-VI (e.g., CdS, CdSe, CdTe) and III-V (e.g., InP) compounds. Since their first discovery by Alexey Ekimov in the 1980s, researchers extensively investigated QDs and made several observations. For example, QDs have a high theoretical quantum efficiency, up to 100%, and narrow emission bandwidth of less than 50 nm, thanks to their strong quantum confinement effect. Their emission peak wavelength can be easily tuned from ultraviolet to infrared by varying their shape, size, or chemical composition, as shown in Figure 2. QDs are normally synthesized in a colloidal form by wet chemical approaches using chemical reactors, such as batch reactors and continuous reactors. Among batch reactors, hot injection organometallic synthesis is most widely used to obtain monodisperse colloidal QDs (cQDs).
Quantum dots and nanocrystal-embedded glasses for display applications

which are obtained by the pyrolysis of organometallic precursors rapidly injected into a hot organic coordination solvent at a temperature of 120–360°C.4

To improve batch-to-batch reproducibility, a one-pot noninjection colloidal synthesis method at low temperature was also suggested for various QDs.4 An aqueous synthesis method, in which QDs are directly synthesized within a water-based solvent, also was suggested for biological and clinical applications. Synthesis approaches in continuous reactors, which provide more controlled reactions in large scale production, include QD synthesis in microfluidics, high-gravity technique, and thermospray synthesis.4

Monodispersed cQDs with large specific surface area are highly vulnerable to environmental factors, which can degrade their luminescence conversion efficiency via the nonradiative recombination of excitons.5,6 To protect cQDs from external environmental conditions and reduce nonradiative recombination, researchers developed core/shell structured QDs, including CdSe/ZnSe and CdSe/ZnS with an encapsulation layer and wider band gap energy.

The core/shell structured QDs successfully demonstrated improved chemical stability and photoluminescence quantum yield (PLQY). Multishell cQDs (e.g., CdSe/ZnSe/ZnS) or ternary/quaternary alloyed cQDs (e.g., CdS_{1−y}Zn_{y}Se, Zn_{1−x}Cd_{x}Se, or Zn_{1−x}Cd_{x}S_{1−y}Se) demonstrated significant enhancement of PLQY, up to 80–100%, by successfully decreasing defects caused by lattice mismatch.5,6 Although cadmium-based QDs with core/shell structure showed highest QY, cadmium-free or heavy metal-free QDs were required due to the European Union’s Restriction of Hazardous Substances regulations.

Among various alternative QDs, including copper indium sulfide (CIS) QDs, carbon nanodots, and InP-based QDs (e.g., InP or InZnP/ZnSe and InP or InZnP/ZnSe/ZnS core/shell QDs), InP-based QDs showed wide color tunability, high quantum yield, and narrow emission bandwidth.7 Accordingly, they are currently used in commercial QLED-TVs, in spite of their complicated synthesis process and relatively inferior emission properties, which are lower than cadmium-based QDs.

When QDs are used in LCD backlight units within conventional QLED-TVs, the green and red QDs are typically embedded within a polyethylene terephthalate film to form a QD enhance-
QDs, and to facilitate dispersion within various organic solvents.\textsuperscript{1,9}

Due to the weak chemical and thermal stability of the organic ligands, it is highly important to prevent the permeation of air and moisture. Accordingly, conventional cQDs including QD enhancement films require multiple encapsulation layers, resulting in additional production cost. Moreover, due to the ionic bond nature of PNCs, they are vulnerable to exposure to light and heat as well as oxygen and moisture, and thus require various encapsulation strategies to improve stability. These strategies include inorganic or polymer encapsulation, perovskite shell engineering, ligand, and defect engineering.\textsuperscript{8}

**QD embedded glasses (QDEG) for displays**

To improve the long-term stability of QDs, it is essential to avoid the use of organic ligands. This feat can be accomplished by using an inorganic glass matrix as an alternative.

Various semiconductor-based QDs can be formed within conventional oxide glasses via conventional nucleation and growth mechanisms, although so far they mostly are used as saturation filters or studied for infrared (IR) applications.\textsuperscript{10} The potential feasibility of QD embedded glasses (QDEGs) as a white light source was only recently demonstrated, by the successful fabrication of CdSe/CdS core/shell structured QDs within silicate glasses.\textsuperscript{11}

For example, silicate glass with a SiO$_2$-Na$_2$O-BaO-ZnO composition including CdO, ZnSe, and ZnS was prepared using a conventional melting and quenching method at 1,350°C and then heat treated at 520°C to form QDs within the glass. High-resolution transmission electron microscope (HR-TEM) and Raman spectroscopy revealed the successful formation of CdSe/CdS core/shell structured QDs. Thanks to the encapsulation of defect traps by the CdS shell, PLQY was significantly improved, from 3% without the CdS shell to 20%.

As seen in Figure 3, adjusting the heat treatment condition can change the QD size and the color of the glass as well as the emission peak wavelength. When the QDEG was mounted on top of a blue LED as a color converter, the resultant color coordination of the LEDs could thus be tuned by changing the heat treatment condition and thickness of the QDEGs. Because the QDEG is comprised of completely inorganic materials, it showed highly improved thermal stability compared with cQDs and maintained its emission intensity up to 200°C. No meaningful degradation in photoluminescence intensity was observed even after almost two years in ambient atmosphere conditions, under which cQDs cannot survive without proper passivation layers.\textsuperscript{11}

When the color gamut of a LED with a CdSe/CdS QDEG was inspected for display application after adjusting the heat treatment duration time and thickness of the QDEG, the QDEG-LED covered 74% of NTSC, which corresponds to the HD color range of conventional RG-LEDs (Figure 4). This performance demonstrated its practical feasibility as a color converting material for display applications.\textsuperscript{12} However, the color gamut was limited due to a broad single emission band centered at about 530 nm. To improve the color gamut, the fabrication of the QDEG should produce separated green and red emission bands.

Unlike cQDs, it is hard to form QDs of two different sizes within the glass matrix under the same heat treatment condition. Thus, to obtain dual emission bands, two QDEGs with different thermal history were prepared and bonded with each other to form a pattern structured QDEG. A QDEG for red emission was pre-heat treated and aligned with a second QDEG that was not heat treated. Bonding of the two QDEGs by viscous flow and QD formation within the QDEGs took place during the heat treat-

---

**Figure 3.** (a) Absorption (dashed lines) and photoluminescence (solid lines) spectra of QDEG, and actual photographs (inset figures) with varying heat treatment duration times. (b) Comparison of thermal stability of QDEG, cQD, and various color converting materials. (c) Schematic diagram of a QDEG mounted blue LED chip and changes in its color coordinate depending on the heat treatment duration time and the thickness of the QDEGs along with their actual photographs (right). (Reprinted with permission from Ref. 11. Copyright 2016 The Royal Society of Chemistry.)

**Figure 4.** Color gamut of RG-LED, single QDEG, and pattern structured QDEG (pQDEG). The inset figures represent actual photographs of QDEGs and LEDs mounted with them.
Quantum dots and nanocrystal-embedded glasses for display applications

Fig. 5. (a) Absorption, photoluminescence, and photoluminescence excitation spectra of CsPbBr3 PNEG. (b) Comparison of photostability of CsPbBr3 PNEG and PNCs. (c) Electroluminescence and photoluminescence (EL+PL) spectra. (d) Color gamut of a wLED with CsPbBr3 PNEG stacked with Cs2SiF6:Mn4+ phosphor in glass (PiG) as a red emitting converter. (Reprinted with permission from Ref. 20. Copyright 2019 The Royal Society of Chemistry.)

Management of QD size distribution within a glass matrix was observed with rare earth dopants, due to the preferential nucleation of QDs near rare earth oxide clusters.13 Emission bandwidth narrowing by silver ion exchange was reported, after 532 nm continuous wave laser irradiation, producing a CdSe/Cd1−xZnxS structure.

TEM equipped with electron energy loss spectroscopy and local electrode atom probe confirmed the evolution of the Cd1−xZnxSe layer on the surface of the CdSe QDs, which effectively reduced the broad emission band related to surface defects.14 Further increases in the color gamut of the QDEGs can thus be anticipated with proper manipulation of the emission bandwidth.

Considering the high PLQY of cQDs (higher than 90%), the relatively low PLQY of QDEGs (less than 20%) is another obstacle that should also be improved before their practical application. Compositions that form QDs within silicate, such as CdO, ZnSe, and ZnS, were optimized for quantum yield adjustment but showed little increase in quantum yield, up to 25%.15 The formation of CdS/Cd1−xZnxS sandwich structured QDs within silicate glass successfully increased quantum yield up to 57%.16 However, to compete with conventional cQDs, a novel approach to QDEG is required for quantum yield enhancement. This approach may include eliminating nonradiative quenching elements by reducing surface defects on the QDs or by sophisticated control of their size and distribution within the glass matrix.

Although ZnSe QDEGs were recently reported to exhibit visible emission under ultraviolet excitation,11 meaningful color conversion of blue LEDs was only reported with cadmium-based QDs so far. Thus, cadmium-free QDEGs also need to be developed for practical applications.

Perovskite nanocrystal embedded glasses (PNEG) for displays

Like semiconductor-based QDEGs, PNCs or PQDs can be formed within oxide glasses via nucleation and growth. The first report of perovskite nanocrystal embedded glasses (PNEG) in phosphate glass has thus attracted considerable attention.18 Due to the intrinsic insensitivity of PNCs to defects, high PLQYs of up to 80% were achieved in boro-germanate glass with CsPbX3 (X=Cl, Br and I) PNCs.19 Varying the PNC size via heat treatment conditions, such as temperature and duration time, or by the compositional variation of halides such as chlorine, bromine, and iodine can easily manipulate the peak emission wavelength of PNCs, resulting in narrow bandwidths of less than about 30 nm, as shown in Figure 5. Moreover, complete inorganic glass passivation highly improved the stability of PNCs against heat, light, aging, and moisture compared to colloidal PNCs (cPNCs).20

While cPNCs can be easily decomposed after extended exposure by light and heat, the emission intensity of PNEGs can be restored after the external stress is removed, showing reversible properties. They also showed limited decay in emission intensity even after being in water for 45 days.10 The robustness and high potential of PNEGs as a robust color converter were demonstrated by using them to compose a white LED.10 Due to the weak stability of PNEGs with CsPbI3, which can give red emission, CsPbBr3 PNEGs were used as the green phosphor while ceramic phosphors such as CASN:Eu2+ or KSF:Mn4+...
are used as the red phosphor to prepare a white LED. Their color coordinate, color rendering index, and correlated color temperature can be easily tuned by adjusting the green-to-red phosphor ratio.

When CsPbBr$_3$ PNEG powders were mixed with CASN:Eu$^{2+}$ and pasted on a blue LED using organic resin, almost pure white LED with color coordinates of (0.33,0.35), a high color rendering index of about 92, and reasonable luminous efficiency of up to 60 lm/W was obtained.$^{10}$ The wide color gamut of PNEGs for display applications was also successfully demonstrated when the CsPbBr$_3$ PNEG powder was mixed with KSF:Mn$^{4+}$. The narrow emission band of the green PNEG and KSF:Mn$^{4+}$ enabled a color gamut covering 130% of the NTSC, suggesting PNEGs were highly feasible for display applications.

To further improve the stability of PNEGs, our group recently introduced various structures, including phosphor in glass and remote phosphor, and investigated other glass matrices, such as borosilicate glasses, to demonstrate their practical feasibility with wide color gamut up to 131%.

**Oxyfluoride glasses for displays**

Oxyfluoride glasses with various fluororods and nanocrystals including CaF$_2$, BaF$_2$, SrF$_2$, PbF$_2$, and LaF$_3$, are reported to improve the visible emission intensity and color conversion efficiency of various doped rare earth ions, including Pr$^{3+}$, Eu$^{3+}$, Tb$^{3+}$, Dy$^{3+}$, and Ho$^{3+}$. Modification of the local environment near the rare earth ions by the formation of fluoride nanocrystals can provide lower phonon energy and increase the quantum efficiency of the doped rare earth ions. Additionally, the parity-forbidden 4f→4f transition of rare earth ions can result in a very narrow emission bandwidth, suitable for high color saturation. However, most of the previous reports used ultraviolet wavelengths or lasers for excitation, and white LEDs with a blue LED chip are not properly demonstrated yet due to the low absorption cross section of the rare earth ions (around 450 nm).

Recently, our group heavily crystallized a Pr$^{3+}$-doped oxyfluoride glass with LaF$_3$ to enhance blue LED absorption via scattering, and it successfully composed a white LED when the glass-ceramic was mounted on top of a blue LED.$^{21}$ Green (Pr$^{3+}$:3P$_0^+$→3P$_1^-$) and red (Pr$^{3+}$:4D$_{1/2}$→4P$_{3/2}$/4P$_{1/2}$) emissions with a narrow emission band were obtained using the single glass-ceramic plate, enabling a color gamut even up to 120% of NTSC, which clearly demonstrated its potential for display application. However, the weak conversion efficiency of the rare earth-doped glass-ceramics resulted in very low luminous efficiency, of less than few lm/W of the wLED, and this property still remains as a big hurdle for their practical employment.

**Challenges and perspectives**

Nanostructured inorganic oxide glasses such as QDEGs or PNEGs have unique strengths, offering high resistance against external factors such as moisture, oxygen, and heat. These properties give them long-term stability, which conventional colloidal-based QDs or PNCs cannot beat, and is crucial for practical display applications. Along with the stability, their relatively easy fabrication process and encapsulation-free characteristics can significantly reduce production costs. Overall, nanostructured glasses are good potential candidates for use in displays, replacing conventional RG-LEDs or cQD-based white light sources.

However, to enter the commercial market, several challenges need to be properly addressed, including their relatively low PLQY under 450 nm excitation, low luminous efficacy, and cadmium or lead-free QDs or PNCs cannot beat, and is crucial for practical display applications. Challenges and possible solutions,” Mater. Today, 24, 69–93, (2019).

Yoon Hee Nam, Hansol Lee, and Woon Jin Chung are master’s student, Ph.D. student, and professor, respectively, in the Institute for Rare Metals and Division of Advanced Materials Engineering at Kongju National University in Cheonan, Republic of Korea. Contact Chung at wjin@kongju.ac.kr.

**References**


**Acknowledgements**

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT). (NRF-2019R1A2C1007621).
Quantum dots and nanocrystal-embedded glasses for display applications

1Quantum dots and nanocrystal-embedded glasses for display applications
Celebrating 100 years


ONLINE TRAINING FOR YOU OR YOUR STAFF

NEW ACerS Learning Center online course
Ceramic Manufacturing Technology
with Carl Frahme Ph.D., FACerS

Starts Feb. 2, 2021
To learn more and to register, visit ceramics.org/learning-center

Celebrating 100 years