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Complete Inorganic Colour Converter Based on Quantum-Dot-Embedded Silicate Glasses for White Light-Emitting-Diodes

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A complete inorganic quantum dot color converter for a white LED is achieved using silicate-based quantum-dot-embedded glasses (QDEGs). The white LED exhibits a high CRI of 90 and highly improved thermal stability up to 200°C, demonstrating its robustness and practicality. The CdSe/CdS core/shell structure within the silicate glass is expected to enhance the colour converting efficiency.

The comparable external quantum efficiency of various QDs to conventional inorganic phosphors along with their color purity has facilitated the preparation of white LEDs (wLEDs) composed of blue LEDs and QDs as a colour converter.[1-5] All previous studies have employed colloidal QDs (CQDs), which are synthesized using a solution-based process. However, CQDs inevitably contain organic passivation layers and solutions to prevent the agglomeration of QDs. Along with the weak chemical and thermal stability of the passivation layers, atmospheric moisture and gases can permeate the organic matrices and easily deteriorate QDs, thus seriously reducing the long-term stability and hindering the practical applications of QDs despite their beneficial optical properties.[5-8] An attempt to improve the long-term stability of CQDs for LEDs was made using a silica monolith embedded with CdSe/CdS/ZnS core-shell structured QDs, which were fabricated using a sol-gel driven silica matrix, thus retaining the drawbacks of organic materials.[4,5] Organic resins, which are used to embed ceramic phosphors in conventional wLEDs, also suffer from weak chemical and thermal stability and restrict the lifetime of the resulting products.[9,10] The recent increase in demand for high-power wLEDs has spurred the replacement of organic materials with complete inorganic color converters such as phosphor ceramic plates or phosphor-in-glass.[11-13]

The elimination of the organic layers and passivation of QDs consisting of a complete inorganic matrix can thus solve the problems associated with CQDs; this task can be accomplished with the introduction of a glass matrix. In this regard, we propose a complete inorganic QD colour converter based on a glass matrix and demonstrate a wLED with controllable chromaticity composed of a blue LED and a QD embedded glass (QDEG). Various semiconductor-based QDs, such as CdSe, CdS, PbSe, and PbS, can be formed within the glass matrix using a conventional melt-quenching method followed by characteristic nucleation and growth under proper heat-treatment (HT) conditions.[14-17] Rearrangement and migration of ions within glass matrix with the supplied thermal energy can form the QDs. The possible application of CdSe QDEG as a LED colour converter has recently been demonstrated; however, its chromaticity was limited due to the poor conversion efficiency.[18] Surface traps of CdSe QDs were believed to be responsible for the poor efficiency, which CQDs have overcome with proper modification of the QD structure by introducing other inorganic layers and constructing core/shell structures such as CdSe/ZnS or CdSe/CdS.[19-21] Gradient multilayered shells have been also suggested to further improve their stability and quantum efficiency.[5,7,8] Complicated multiple fabrication processes along with careful adjustment of various chemicals are required for the production of stable core-shell-structured CQDs, whereas QDEG involves the facile synthesis process of melt-quenching followed by heat treatment. We therefore aim not only to improve the conversion efficiency of QDEG via the modification of CdSe QDs within the glass matrix using the conventional melt-quenching method but also to create a color-tunable wLED with an enhanced colour rendering index (CRI) and practical robustness. As silicate glass melted with CdO and ZnSe as raw materials gives CdSe QD upon HT while CdO and ZnS gives CdS QD,[15,17,18] the modification of CdSe QD was thus implemented via the introduction ZnS as raw materials along with ZnSe.

The nominal composition of the host glass was 65 SiO_2–25 Na_2O–5 BaO–5 ZnO (in mol%). Various additions of ZnS (x mol%) and ZnSe (y mol%) were additionally introduced while the CdO content was fixed at 0.5 mol%. The mixed powders

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were melted at 1350°C for 1 h in an alumina crucible and the melts were quenched on a brass mould to form a glass followed by thermal annealing at 350°C for 1 h. The glasses were then heat-treated at various temperatures for various durations to control the QD formation within the glass.

Absorption spectra were recorded using a UV/VIS spectrophotometer (Lambda 750, Perkin-Elmer, Waltham, MA), and emission spectra were monitored using a 0.25-m monochromator (MS257, Oriel, Stratford, CT) and lock-in amplifier (MerlinTM, Oriel, Stratford, CT) equipped with a photomultiplier tube. A 455-nm LED source (M455L3, Thorlabs, Newton, NJ) was used to pump the samples for PL measurements with a 475-nm cut-off filter, and a 455-nm blue LED with 3528 package was used to mount the QDEGs. The QY was measured using a calibrated integrating sphere (C9920-02, Hamamatsu, Tokyo, Japan). The QD formation was examined using X-ray diffraction (XRD; D/MAX-2500U, Rigaku, Tokyo, Japan) and Raman spectroscopy (SPEX 1403, HORIBA, Jobin-Yvon Ltd., Germany) using an Ar laser with a centre wavelength of 514 nm for excitation. A field-emission transmission electron microscope (FE-TEM; JEM-2100F, JEOL, Tokyo, Japan) was used to conduct electron energy loss spectroscopy (EELS) analysis and obtain high resolution (HR)-TEM images for QD analysis. All the measurements were performed at room temperature.

After compositional study to find proper ZnS and ZnSe content for controllable QD modification, optimal ZnS and ZnSe contents of 1.0 mol% and 0.5 mol%, respectively, were determined when the CdO content was fixed at 0.5 mol%, yielding a clear glass that exhibited proper colour change with HT (Figure S1a). The glass exhibited characteristic colour and absorption edge changes due to QD growth when the time at the fixed HT temperature of 520°C increased (Figure S1b). X-ray diffraction (XRD) analysis of the inspected glass after HT revealed no apparent crystalline peaks implying nano-sized change of the glass was observed (Figure S1c). The formation

of QDs after HT was clearly observed via TEM, and their size was estimated to be 3.68±0.73 nm (Figure S2). As demonstrated in Figure 1, when mounted on blue LED chip, the modified QDEG (mCdSe) exhibited a highly improved colour-converted photoluminescence (PL) spectrum compared with the glasses containing only CdS or CdSe QDs prepared using the same HT condition and thickness as reported previously.[18] The Commission internationale de l'eclairage (CIE) colour coordinates and actual photos of the LEDs containing QDEG more clearly demonstrated the enhanced colour conversion property of the present system. It should be noted that the colour coordinate of the LED with the present QDEG is near those for white colour, demonstrating the possible realization of wLEDs.

Fine tuning of the QD size was accomplished when the modified glasses were heat-treated at 500°C (Figure S3). Variation of the HT duration resulted in glass colours ranging from green to orange as well as modification of the absorption edge due to QD growth, as depicted in Figure 2a. The PL spectra under 455-nm LED excitation also revealed a red shift with increasing HT duration. Excitation PL (PLE) spectra of those QDEGs were monitored at their peak emission wavelength and well matched to their first excitonic absorption peak of absorption spectra. (Figure S4) The QDEGs were then mounted on a blue LED chip to create a wLED; their thicknesses were varied to adjust the chromaticity. As observed in Figure 2b, the colour coordinates of the LEDs were easily controlled by adjusting the HT duration and thickness of the QDEG and almost varied linearly with the thickness. Note that a wLED was successfully prepared using the present mCdSe QDEG. When the thickness was reduced from 2 to 1.2 mm, the CIE colour coordinates could be manipulated to approach those of natural white with a high CRI of 90 and colour correlated temperature (CCT) of 5497 K for the glass heat-treated for 10 h at 500°C (Table S1). The glasses heat-treated for 15 and 20 h could also achieve white light depending on their thickness, as expected from Figure 2b. The quantum yields (QYs) of the QDEGs were estimated by the ratio of photons emitted to photons absorbed using an integrating sphere, and the QDEG undergoing 10-h HT resulted in a wLED with 14 % QY. When we examined the QDEG undergoing 20-hHT after further adjustment of the glass preparation conditions and thickness up to ~0.8 mm to make white light, the QY was estimated to increase up to 20%, which represents a significant improvement compared with the value for CdSe QDEG (~3 %).[18] The QY is even higher than that of the QDEG prepared with CQDs via the sol-gel process, which exhibited a QY of 5–10 %.[22] As the present QD colour converter is a complete inorganic material based on a stable silicate glass, no apparent degradation of the material or spectral properties was observed even after 584 days under ambient atmosphere, unlike for the materials based on CQDs (Figure S5). Moreover, as a practical measure of high-power LED application, the thermal quenching (TQ) property was monitored up to 200°C. As demonstrated in the Figure 2c, the QDEG can withstand temperatures up to 200°C, with its emission intensity up to ~65% of the initial intensity. Although
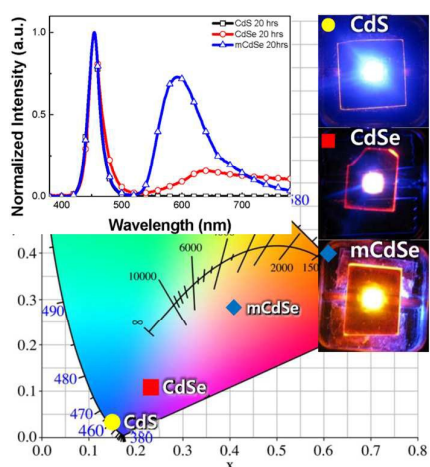

Figure 1. CIE color coordinates of LEDs mounted with CdS, CdSe, and mCdSe QDEGs prepared using the same HT condition of 520°C/20 h and thickness. The inset presents the electro-luminescence (EL) and photo-luminescence (PL) spectra of the LEDs. Actual photos of the LEDs are displayed on the right side.
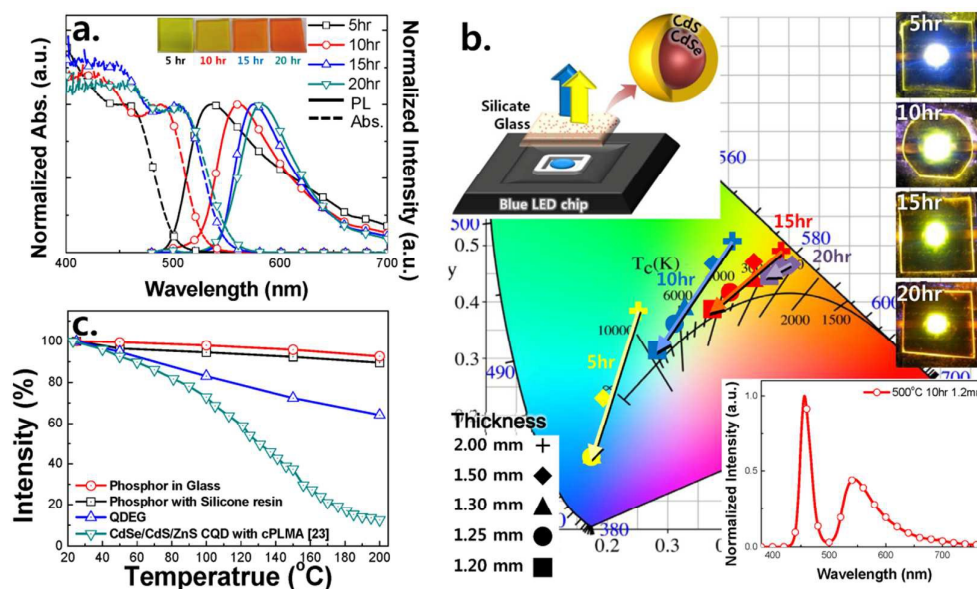
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Figure 2. a. Normalized absorption coefficient (dashed) and PL spectra under 455-nm excitation (solid) of mCdSe QDEGs heat-treated at 500°C for varying duration. Images of the QDEGs are also displayed within the figure. **b.** CIE color coordinates of LEDs mounted with mCdSe QDEGs of various thicknesses heat-treated for 5, 10, 15, and 20 h at 500°C. Lines are drawn as guides for the eye. The inset presents the EL and PL spectra of the wLED, which had coordinates of (0.3277, 0.3458) and a CRI of 90. Actual photos of the LEDs with QDEGs of the same thickness (1.2 mm) with varying HT duration are presented at the right of the figure. **c.** Thermal quenching property of wLED with QDEG compared with other wLEDs with phosphor-in-glass or phosphor with silicone resin employed as the color converter. TQ property of CQD with multi-shells (ref. 23) was also displayed for comparison.

the TQ property is relatively weak compared with that of commercially used colour converters, such as phosphor-in-glass (PiG) and phosphor with silicone resin using $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) as a phosphor, it is highly improved compared with that of CdSe CQDs with multi-shells, which exhibit intensities of ~10 % at 200°C.[23] This result clearly suggests the practical feasibility of the present QDEG as a robust LED colour converter. Thermally activated carrier trapping is mostly responsible for the temperature dependence of the PL decay.[24,25] The modified structure of the current QDs along with the improved thermal property of the inorganic glass matrix compared with organic materials is believed to effectively enhance the thermal stability.
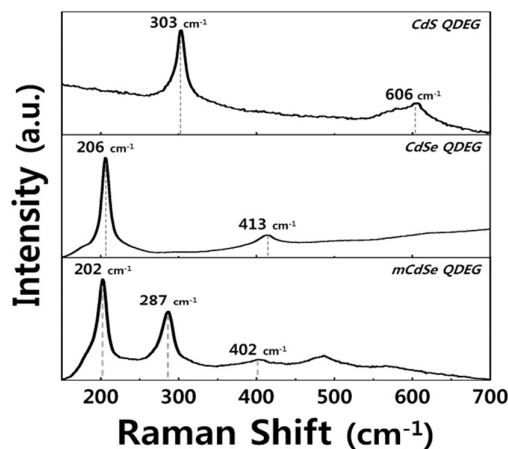

Figure 3. Raman spectra of QDEGs containing CdS, CdSe, and mCdSe QDs.

The enhancement of the quantum efficiency as well as thermal stability was also observed in CQDs when CdSe was encapsulated with inorganic CdS or ZnS layers.[5,7,8,19-21] Similar structural modification can thus be anticipated in the present glass system. However, considering the nucleation and growth mechanism of QDs within the glass matrix upon HT, the formation of alloyed QDs such as CdS_xSe_{1-x} cannot be ruled out. Raman spectroscopy was employed to examine the structure compared with that of glasses prepared only with CdSe and CdS QDs, and the results are presented in Figure 3. The glasses containing CdSe and CdS QDs exhibited their characteristic Raman peaks due to the surface optical (SO) and longitudinal optical (LO) modes of CdSe and CdS QDs, as observed in CQDs.[26,27] Unlike the glasses with single QDs, the present QDEG exhibited Raman peaks at ~ 202, 287, 402, and 487 cm^{-1}. The shift of the peak near 200 cm^{-1} to shorter frequency compared with the CdSe-only glass (~206 cm^{-1}) and the appearance of a peak near 287 cm^{-1} due to the LO mode of alloyed CdS were observed. Similar behaviour was reported when the CdS shell thickness was increased in CdSe/CdS CQDs[26,27] and when the S content was increased in $CdS_{1-x}Se_x$ QDEG.[28] Although it is difficult to determine the structure solely from the Raman spectra, this result clearly supports the conclusion that the current QDEG contains QDs modified with S.

The detailed structure of the QDs was investigated using EELS and HR-TEM. When elemental mapping was conducted using EELS, as depicted in Figure 4, Cd, S, and Se were observed to be well confined within the QDs, suggesting the possible formation of a $CdS_{1-x}Se_x$ alloyed or CdSe/CdS core-
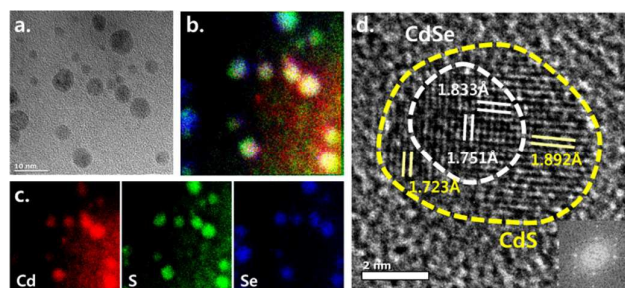
Figure 4. a. Original TEM image of mCdSe QDEG for EELS analysis. **b.** Combined EELS image of Cd, S, and Se elements. **c.** EELS elemental mapping of Cd, S, and Se. d. HR-TEM image of QDEG showing two regions with different lattice parameters.

shell structure. However, upon closely inspecting the lattice parameters, two areas with different lattice parameters were detected. The lattice parameters of the central area were well matched to CdSe (JCPDS #77-2307), whereas those of the outer area were more closely matched to CdS (JCPDS # 77-2306). The $CdS_{1-x}Se_x$ alloyed structures were also compared but hardly matched those of current QDs (Table S2). Thus, it is highly probable that CdSe/CdS core-shell structured QDs were formed within the silicate glass matrix and are responsible for the enhanced QY of the current QDEG. A schematic diagram of the wLED with CdSe/CdS QDEG is presented in Figure 2.b. Note that the core-shell-structured QDEG was obtained via the conventional melt-quenching method followed by HT. It is a facile process compared with that used to prepare CQDs, which requires complicated and elaborate synthesis processes and careful adjustments of various chemicals, thus suggesting another advantage of the current QDEGs. In silicate glasses, ZnSe decomposes to give Se ions during melting and produces Se^{2-} or Se-Se chains which react with Cd^{2+}-ions to form CdSe nuclei upon HT.[29] In the present system, Se and S ions can compete to form QDs. Although the mechanism has not been clearly identified, it can be proposed that CdSe QDs are preferentially formed by first consuming Se ions followed by the selective formation of CdS layers on the surface of CdSe QD, resulting in CdSe/CdS QDs within the glass matrix. However, further study is required to understand the formation mechanism more clearly and improve the QY of the QDEG.

In summary, we successfully fabricated a complete inorganic QD colour converter based on silicate glasses via a facile melt-quenching method and demonstrated colour-tunable wLEDs with high CRI values. Careful adjustment of the composition and HT condition resulted in improvement of the colour conversion efficiency of the QDEG. The chromaticity, CRI, and CCT of the LEDs can be easily varied by modifying the HT conditions and thickness of the QDEG. Unlike CQDs, no practical degradation of the materials or conversion efficiency was observed, and the TQ property was greatly improved from 20 to 65 % at 200°C. The high CRI, up to 90, along with the improved TQ property suggests the practical feasibility of QDEGs as alternative colour converters for high-power wLEDs. EELS and HR-TEM analysis suggested that CdSe/CdS core-shell-structured QDs were formed within the silicate glass and are responsible for the enhanced QY. With further improvement of the QY and TQ properties, we believe that the applications of QDEG can be further expanded, effectively replacing the conventional ceramic phosphors and CQDs currently used for the colour converters of wLEDs and backlight units (BLU) in liquid-crystal displays (LCDs).

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