Two-Step-Enhanced Stability of Quantum Dots via Silica and Siloxane Encapsulation for the Long-Term Operation of Light-Emitting Diodes

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Supporting Information

ABSTRACT: Despite innovative optical properties of quantum dots (QDs) for QD-converted light-emitting diodes (QD-LEDs), the vulnerability of the QDs against heat and moisture, has been a critical issue for commercialization and long-term use. To overcome the instabilities, we fabricated a thermally and photostable QDs-embedded silica/siloxane (S-QD/siloxane) film by embedding QDs in silica and siloxane encapsulation through a two-step sol–gel reaction. S-QDs were stably dispersed in the oligo-siloxane resin with even a QD concentration of 5 wt % without aggregation. The two-step physical barriers of silica and siloxane acted to decrease the toxicity of QDs and improve the stability against heat and moisture [85 °C/5% relative humidity (RH), 85 °C/85% RH, and 120 °C/5% RH], light (50 and 100 mA), and chemicals (ethanol, HCl, and NaOH). Our S-QD/siloxane film was applied as a color-conversion material on a blue LED chip without additional solidification and encapsulation processes for red and white QD-LEDs, exhibiting a wider color gamut (107% in CIE 1931) compared to NTSC. These enhancements indicate that our S-QD/siloxane film is a suitable material for long-term operation of QD-enhanced films and QD-LEDs in next-generation displays.

KEYWORDS: quantum dots, sol–gel reaction, white light-emitting diodes, thermal and photostability, long-term operation

1. INTRODUCTION

White light-emitting diodes (WLEDs) are promising solid-state lighting devices to replace conventional light sources such as fluorescent lamps and incandescent bulbs because of their high efficiency and long lifetime.1,2 To commercially fabricate the WLED, Y3Al5O12:Ce3+ (YAG:Ce3+) phosphor, which is a yellow phosphor particle, on a blue LED chip is a general choice.3 Despite the cost-effective YAG:Ce3+ phosphor, the low color-rendering index and broad full width at half-maximum (FWHM) (50–100 nm) of the phosphors make the WLED show a large overlap in blue-green and green-red peaks.4 In addition, grain boundary light scattering and high sintering temperature (more than 1500 °C) are also the reasons for replacing the phosphor particles.5

Semiconductor-based colloidal quantum dots (QDs)—polymer composites have aroused considerable interest for the color-converting materials as on-chip-type LED encapsulants and on-surface-type QD enhancement films.6–9 This is because QDs exhibit a wider color gamut, higher photoluminescence quantum yield (PL QY), narrower FWHM, and size-dependent color emission, compared to phosphors.10–12 However, to commercialize the QDs-converted LEDs (QD-LEDs), some critical issues should be solved during device fabrication. First, the QDs are dispersed in a polymer matrix with a solvent.13 Therefore, a solidification process is a prerequisite before combination of QDs—polymer composites on an LED chip. During the solidification process, hydrophobic long-chain alkyl ligands on QDs surface give rise to agglomeration of QDs and poor compatibility of QDs in the polymer matrix.14 Second, an encapsulation process is essential after the combination step because QDs are vulnerable against heat, moisture, and chemicals.15–17 Generally, ligands are easily detached from the surface of QDs during device fabrication and long-term use, that is, defects form and aggregation occurs. The defects cause PL quenching and oxidation, and the aggregation leads to reabsorption and degradation of quantum efficiency.18,19 Enhancing the reliability and lifetime of QD-LEDs is a challenge for long-term operation.

One of the recent attempts to improve the incompatibility problem is ligand exchange; this process uses affinity differences between the ligand and the surface of QDs.20 Functionalized phenyl groups and oleic acid ligands on QDs surface improved solubility in pyridine and poly(methyl methacrylate).21,22 However, ligand exchange has problems that it changes the optical properties of the original QDs, causing a drop in the PL QY.23–25 In addition, in terms of stability, ligand-exchanged QDs still suffer from ligand...
detachment and are vulnerable to oxygen and moisture due to the lack of encapsulation with a physical barrier. Shell coating with oxide materials (SiO$_2$, Al$_2$O$_3$, and In$_2$O$_3$) on individual QDs, embedding of QDs in silica (SiO$_2$), and ligand exchange have improved the long-term thermal stability and photostability. Among oxide materials, which protect the surface of QDs from oxidation and decrease exposure of inside toxic heavy metals, amorphous silica has been most investigated due to its high optical transparency, precise control of thickness, and hydrophilicity. However, the individual thick silica shell has critical limitations of high QD concentration in the QD–polymer composite and initial PL degradation. QDs-embedded silica, produced by ligand exchange and hydrolysis of tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS), has been widely studied, and improvements to photostability have been reported. To prepare QDs-embedded silica, the ligands on the surface of the QDs should be replaced by those having hydroxyl or alkoxy (Si–OCH$_3$) groups, which can react with hydrolyzed TEOS or TMOS. For example, 3-mercaptopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 5-aminopentanol, and 6-mercaptohexanol (6-MHOH) have been used as the exchange ligands. A stably dispersed QDs-silica monolith was reported using 6-MHOH, and the QDs-silica monolith was compatible with siloxane resin. Despite the enhancement of stability, the QDs-embedded silica has the problems of precipitation when stored for a long time after physical dispersion in resin. In addition, studies about thermal quenching problems over 100 °C, which is a temperature under high driving current, are still limited due to the instability of QDs against heat and moisture.

In this report, we present QDs-embedded silica/siloxane (S-QD/siloxane) films along with silica growth and siloxane encapsulation using a simple sol–gel reaction. The QDs were fixed in amorphous silica and chemically dispersed in siloxane resin, which solves aggregation problems in long-term storage. In addition, no solidification process was needed due to the solvent-free composite. The dual improved S-QD/siloxane film, compared to the reported OA-QD/siloxane film, showed superior long-term operation under harsh heat (120 °C) and moisture [85% relative humidity (RH)] conditions, chemicals (ethanol), and current bias (100 mA) without an additional encapsulation layer. The S-QD/siloxane composite was then fabricated as a color-conversion material into white QD-LEDs, which exhibit a wider color gamut compared to NTSC. This two-step-enhanced S-QD/siloxane proves to be an appropriate candidate for QD-LEDs.

2. RESULTS AND DISCUSSION

The fabrication process of an S-QD/siloxane film, as a color-conversion material, is shown in Figure 1 and the Experimental Section in the Supporting Information. We purchased CdSe/CdZnS (core/shell) QDs passivated by oleic acid and used them without further purification. First, we synthesized S-QD by ligand exchange from oleic acid to 3-mercaptopropyltrimethoxysilane (MPMDMS) and sol–gel reaction with TEOS (Figure 1a). To prepare QDs-embedded silica, the ligands on the surface of the QDs should be replaced by those having hydroxyl or alkoxy (Si–OCH$_3$) groups, which can react with hydrolyzed TEOS or TMOS. For example, 3-mercaptopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 5-aminopentanol, and 6-mercaptopentanol (6-MHOH) have been used as the exchange ligands. A stably dispersed QDs-silica monolith was reported using 6-MHOH, and the QDs-silica monolith was compatible with siloxane resin. Despite the enhancement of stability, the QDs-embedded silica has the problems of precipitation when stored for a long time after physical dispersion in resin. In addition, studies about thermal quenching problems over 100 °C, which is a temperature under high driving current, are still limited due to the instability of QDs against heat and moisture.
Figure S1 shows three different samples in chloroform solvent: (a) without MPMDMS, (b) without MPTMS, and (c) synthesized S-QD. The modified QDs without MPMDMS are not enclosed in silica (Figure S1a) because oleic acid has no reaction site with hydrolyzed TEOS. The un-methacrylate-functionalized QDs-embedded silica (without MPTMS) is incompatible with chloroform due to its hydrophilicity (Figure S1b). However, the methacrylate-functionalized S-QD is well dispersed in chloroform, that is, MPTMS plays an important role in increasing the hydrophobicity of S-QD (Figure S1c).

S-QD was chemically and physically dispersed in methacrylate-phenyl oligo-siloxane resin in situ during sol−gel condensation (Figure 1b)36 and then stably dispersed in the oligo-siloxane resin for 30 days. After that, we fabricated an S-QD/siloxane film with the desired shape through UV radiation using molds, without an additional binder (Figure 1c). The methacrylate-phenyl siloxane hybrid material has been used as an LED encapsulant and passivation layer in LCD-TFT because it exhibits high thermal decomposition temperature, high refractive index, and low WVTR compared to conventional polymers.37−39 To elucidate the improvement of the dispersion, thermal, chemical, and photostability of the S-QD/siloxane film, oleic acid-capped QDs/siloxane (OA-QD/siloxane) films were fabricated according to the method in a previous paper.40

Figure 2 shows representative data for the synthesis and luminescence properties of S-QD. The synthesized S-QD is stably dispersed in chloroform and can be stored in a powder state; it emits a bright red light under 365 nm UV light (Figure 2a). Figure 2b provides an SEM image of S-QD; it is amorphous silica by sol−gel reaction of TEOS and its average size is about 300 nm (Figure S2). Transmission electron microscopy (TEM) and energy-dispersive spectroscopy (EDS) analysis confirm the homogenous isolation of QDs in silica at high density (Figure 2c). The EDS analysis shows that the silica matrix (Si: yellow and O: blue) is formed by sol−gel reaction, and the QDs (Cd: green, Zn: violet, and Se: cyan) are dispersed without aggregation in the silica matrix. As shown in Figure 2d, Fourier transform infrared (FT-IR) analysis was carried out to confirm the synthesis and surface chemistry of S-QD. After ligand exchange with MPMDMS silane (before insertion of TEOS), the two carboxyl carbon peaks (COO−, 1550 and 1471 cm−1), ascribed to the oleic acid ligand, significantly decreased and the Si−CH3 peak (1078 cm−1) was observed. The Si−CH3 peak is equivalent to the Si−CH3 of neat MPMDMS silane. The oleic acid was exchanged with MPMDMS with stirring for 1 day. After formation of S-QD by sol−gel reaction, the amorphous silica peak (1100−1000 cm−1) was observed. In addition, hydroxyl (−OH, 3500−3000 cm−1) and double carbon (C=C, 1638 cm−1) groups were formed. The peaks of −OH and C=C groups indicate that the surface of S-QD is composed of hydroxyl and methacrylate groups. Figure 2e displays the photoluminescence (PL) and absorption spectra of QDs dispersed in chloroform. No PL peak shift and degradation of absorption were observed after embedding QDs in silica. No PL peak shift and degradation of absorption were observed after embedding QDs in silica. However, the PL QY was gradually decreased from 84 to 73%, as QDs were embedded in silica (Table S1). We measured traces of PL QY of S-QD powder at room temperature and 85 °C/5% RH condition (Figure 2f). This is because storage in the powder state has a big advantage in terms of volume and transportation as compared with the dispersion state in a solvent. The PL QY of S-QD powder decreases 6% at room temperature and 13% at 85 °C/5% RH condition for 30 days. S-QD is quite stable and can be stored in a powder state at room temperature.
Figure S3a shows the $^{29}$Si NMR spectra of S-QD/oligo-siloxane resin, which confirm synthesis of methacrylate-phenyl oligo-siloxane resin with a degree of condensation of 85.3%. The highly condensed resin, via simple sol−gel condensation for only 4 h, could be used as a matrix having thermal stability. Despite sol−gel condensation, PL QY of S-QD/siloxane resin was the same as that of S-QD, that is, siloxane encapsulation maintained the optical property of S-QD. To improve the color purity and color-conversion ability of the QD/polymer composite, the high-concentration dispersion of QDs in the polymer matrix is essential.41 Figure 3a shows OA-QD and S-QD/oligo-siloxane resins with a concentration of 3 wt %. In the case of OA-QD/oligo-siloxane resin, precipitation of QDs is observed due to long alkyl chains of oleic acid and only physical dispersion of QDs in oligo-siloxane resin. In contrast, S-QD maintains uniform dispersion in oligo-siloxane resin for 30 days by chemical bonding between oligo-siloxane molecules and hydroxyl groups of S-QD during sol−gel condensation. This phenomenon is visualized by confocal microscopy, shown in Figure 3b. S-QD/oligo-siloxane resin (right) shows uniform dispersion of QDs, whereas QDs in OA-QD/oligo-siloxane resin (left) are highly aggregated at 3 wt % QD concentration.

We fabricated the QD/siloxane films using only QD/oligo-siloxane resins by radiating UV light. The QD/siloxane films could be obtained with various shapes and thicknesses using the molds, which is a key advantage of the material for manufacturing. Figure S3b indicates FT-IR spectra of the S-QD/oligo-siloxane resin and S-QD/siloxane film. The double carbon-bond (C=C, 1637 cm$^{-1}$) decreases by polymerization;42 the methacrylate groups in oligo-siloxane resin and S-QD were chemically cross-linked by free-radical polymerization. The highly condensed oligo-siloxane resin and cross-linked methacrylate-siloxane co-networks bring about rigid bulks and superior thermal and mechanical properties.
uniform dispersion of S-QD is maintained after polymerization in siloxane hybrid material, confirmed by 2D images of the emission wavelength in the area of 100 μm² (Figure 3c). Because of reabsorption from aggregation of OA-QD in oligo-siloxane resin, a large red shift (13 nm) is obtained when the concentration of OA-QD is only 3 wt % (Figure 3e). Especially, 5 wt % OA-QD/oligo-siloxane resin could not be synthesized due to agglomeration of QDs during sol–gel condensation. However, the PL spectrum of the S-QD/siloxane hybrid material shows only a slight red shift (<3 nm) even when QD concentration is as high as 5 wt % (Figure 3f). Due to the agglomeration problem of OA-QD when its concentration is more than 3 wt %, we compared stabilities using samples with 3 wt %.

To evaluate the enhancement of the thermal stability by embedding QDs in silica, we monitored the optical properties of QD/siloxane films under harsh conditions (85 °C and 120 °C/5% RH, and 85 °C/85% RH). Figure 4a shows the photographs of QD/siloxane films under 120 °C/5% RH conditions during 30 days. The S-QD/siloxane film maintains its red color, but the OA-QD/siloxane film turns from red to dark-brown as the time passes. The degradation of PL under UV light is also observed (Figure S4). The bright red emission of OA-QD/siloxane is changed to no emission after 30 days aging. Figure 4b indicates traces of PL QY during thermal stability tests for 30 days. In a previous paper, the PL QY of the 1 wt % OA-QD/siloxane film was maintained to its initial value under 85 °C/5% RH and increased under 85 °C/85% RH conditions by passivating trap states with water molecules. Siloxane encapsulation was effective for the long-term thermal stability of QDs, compared to commercial polymers. However, when the QD concentration becomes 3 wt %, degradation of PL QY is observed under the same conditions. On the other hand, the S-QD/siloxane film shows long-term thermal stability under conditions of 85 °C/5% RH and enhancement of PL QY under 85 °C/85% RH. The S-QD/siloxane film is still stable against heat and moisture at an even higher QDs concentration. Especially, the improvement of thermal stability is observed to be at its best under the condition of 120 °C/5% RH. After thermal stability tests for 30 days, PL decay dynamics of films was measured (Figure 4c). The PL decay curves of all samples after 30 days aging were fitted using a single- or bi-exponential decay function to calculate average lifetimes (τave) and decay time components. The initial OA-QD and S-QD/siloxane films show the same PL decay curves and lifetimes, that is, silica formation, by hydrolytic sol–gel reaction of TEOS, maintains the optical properties of OA-QD. Among all curves after thermal aging, a dramatic drop of the PL decay curves is observed in the OA-QD/siloxane film under the condition of 120 °C/5% RH and τave decreased from 64.5 to 13.2 ns (τ1 = 38.47 ns, A1 = 12.2%, τ2 = 11.67, and A2 = 87.8%). The new nonradiative (τ2) recombination pathway of the OA-QD/siloxane film indicates an increase of recombination due to the interaction between excitons and generated surface defects. However, no τ2 is obtained and only a slight decrease of radiative recombination (τ1) is found in the S-QD/siloxane film. Results about the superior thermal stability of the S-QD/siloxane film agree well with the traces of PL QY. This thermal stability may be derived from short silane ligands (lower organic portion) compared to oleic acid and fixed QDs in the silica. In addition, using thermogravimetric analysis, the S-QD/siloxane film is found to have delayed thermal decomposition compared to that of neat methacrylate-phenyl siloxane hybrid material (Figure S3c). Additional cross-linkage
and sol−gel condensation between S-QD and oligo-siloxane lead to dense methacrylate-siloxane co-networks, resulting in a delay of thermal decomposition. Figure 5 shows the photostability of QD/siloxane films, directly encapsulated on a blue LED chip, with a QD concentration of 3 wt %. The blue light, emitted from LED chips, is completely converted to red light (Figure S5a). The PL spectra of the S-QD/siloxane-encapsulated LED (S-LED) maintain their emission wavelength and increase the PL intensity at forward bias currents from 10 to 100 mA (Figure S5b). Compared to the OA-QD/siloxane-encapsulated LED (OA-LED) (Figure 5a), according to traces of PL QY, the photostability is considerably enhanced by embedding QDs in silica. As shown in Figure S5b, the emission of OA-LEDs under 50 mA after 30 days, is a violet light that is close to blue. In contrast, the pure red emission of S-QD is maintained after 30 days. Figures 5c and S6 show the Commission Internationale de l’Eclairage (CIE) color coordinates of OA-LEDs under 50 mA after 30 days, exhibiting no change (50 mA) and only a slight shift (100 mA). After photostability tests for 30 days, we measured PL decay dynamics (Figure 5d). In the case of OA-LEDs, short recombination (19.49 ns for 50 mA, 1.65 and 6.31 ns for 100 mA, 30 days) and considerable drops of $\tau_{av}$ are observed from 64.5 to 4.6 ns under 100 mA bias (Figure 5e,f). This photoderived degradation of QDs in OA-LEDs is associated with formation of nonradiative defect states on the surface or interface of the core/shell, referred to photo-oxidation, due to the weak affinity of the oleic acid ligand on QDs surface. In contrast, S-LEDs exhibit superior photostability as a slight decrease of $\tau_{av}$ from 63.5 to 50.8 ns (50 mA, 30 days) and 44.9 ns (100 mA, 30 days); $\tau_1$ shows the same tendency. In particular, color purity, which is an important factor for a color-conversion film, is also drastically reduced at current bias in OA-LEDs (from 99 to 26% at 50 mA and 0.8% at 100 mA), whereas this is not the case in S-LEDs (from 99 to 96% at 50 mA and 74% at 500 mA) (Figures 5f and S7). That is, silica embedding acts as a barrier, enabling long-term preservation of QDs from harsh thermal and photo-operating conditions. In addition, we measured the chemical stability of the S-QD/siloxane film in ethanol and in strong acidic (0.5 N HCl) and strong basic (0.1 N NaOH) aqueous solutions, which cause a significant PL QY drop of QDs; the PL QY of the S-QD/siloxane film is maintained for 30 days (Figure S8). That is, the S-QD/siloxane film is suitable for device manufacturing. To demonstrate our S-QD/siloxane film for white light-emitting diodes (WLEDs), we fabricated the white QD-LEDs using a mixture of red and green colored S-QD/oligo-siloxane resins on a blue LED chip. Each blue, green, and red light shows a narrow emission peak (Figure 6a), and the PL spectra
of the white QD-LEDs maintain the peak position at forward bias from 10 to 70 mA (Figure 6b). Figure 6c shows the fabricated white QD-LED chip and its PL under forward current bias. We could control characteristics of the white QD-LEDs, such as color coordinates and temperature, by changing the ratio of red and green S-QD/oligo-siloxane resins for different CIE coordinates: (1) color coordinates were (0.32, 0.36) (red:green = 1:5.2) for CIE 1931 and (0.24, 0.48) (red:green = 1:6) for CIE 1976. (2) The color temperatures were 6176 K (1:5.2) and 7527 K (1:6), respectively. Individual CIE coordinates of blue, green, and red emissions are indicated in the CIE 1931 (Figure 6d) and CIE 1976 (Figure 6e) color spaces. The color gamut of our white QD-LEDs is 107%, related to the National Television System Committee (NTSC), in CIE 1931 and 139% in CIE 1976.\textsuperscript{38}

3. CONCLUSIONS

In summary, QDs-embedded silica/siloxane (S-QD/siloxane) films have been fabricated through sol−gel reaction of TEOS and sol−gel condensation of MPTMS and DPSD. Silica formation and siloxane encapsulation maintained the initial PL and optical properties of oleic acid-capped QDs (OA-QD). S-QDs were dispersed without aggregation in methacrylate and optical properties of oleic acid-capped QDs (OA-QD). S-QD/siloxane resins for white QD-LEDs: the fabricated white QD-LED chip and its PL under forward light (640 nm). Compared to the OA-QD/siloxane (QY of QDs during silica growth and siloxane encapsulation (PDF)

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.9b06987.

Experimental section including the synthesis and size of S-QD; molecular structure of S-QD/oligo-siloxane resin; optical properties after thermal stability, photostability, and chemical stability tests of the S-QD siloxane film. PL QY of QDs during silica growth and siloxane encapsulation (PDF)

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Notes

The authors declare no competing financial interest.

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