

Heat- and water-proof quantum dot/siloxane composite film: Effect of quantum dot–siloxane linkage

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Abstract — We report on the effect of linkage between quantum dot (QD) and siloxane matrix by preparing two different QD/siloxane films. One has chemical linkages between QD and siloxane matrix, and the other has no chemical linkages between QD and siloxane matrix. The QD/siloxane (methacryl) film, which has the chemical linkages, exhibits no degradation of photoluminescence (PL) quantum yield (QY) under heat or moisture condition for over 1 month, while the QD/siloxane (epoxy) film, which has no linkages, shows drastic decreased of PL QY. The chemical linkages between QD and siloxane matrix that makes effective siloxane passivation layer intact on the surface of QDs in QD/siloxane (methacryl) film. Given its exceptional stability with the help of linkages between QD and siloxane matrix, we expect that the QD/siloxane (methacryl) film is best fitted in PL-type down-conversion layer for display applications.

Keywords — quantum dots, siloxane, cross-linking, surface passivation, photoluminescence quantum yield, thermal stability.

DOI # 10.1002/jsid.542

1 Introduction

Quantum dots (QDs) have attracted a tremendous amount of attention because of their unique optical properties, such as tunable energy band gap, narrow emission bandwidth, and high photoluminescence (PL) quantum yield (QY).^{1–3} In order to utilize unique optical properties of QD, QD/polymer composites, in which QDs are physically dispersed in polymer matrices, have been studied for down-conversion of light from solid-state light emitting diodes (LEDs) for display devices.^{4–6}

Despite enormous research efforts, the fabrication of QD/polymer composites faces two formidable obstacles. First, poor compatibility between QDs and polymer matrices that leads aggregation of QDs from polymer matrices.^{7,8} To solve this problem, ligand exchange processes that change organic ligands where surface of QDs into matrix compatible molecules, such as phosphines, amines, and thiols, were introduced.^{9–11} However, inevitable fall-off in optical properties of QDs is unavoidable during the ligand exchange processes.^{12,13} In addition to the aggregation of QDs from polymer matrices, the PL QY of the QD/polymer composite decreases, when the composite is exposed to oxygen, heat, or moisture.^{14,15} In fact, the recent commercialization of QD-based products was possible because of adopting

barrier films that protect QD/polymer film from oxygen and moisture.^{16,17} One obvious problem is that the barrier films are relatively expensive; therefore, the commercially available QD-based products can lose edge from the price perspective. Consequently, demand for development of barrier-film-free QD/polymer composite, which maintains its optical properties under harsh conditions, is growing.

A siloxane-based film, which is synthesized via sol-gel condensation reaction of silane precursors, has been widely studied for encapsulating molecules, e.g., catalysts, enzymes, and fluorescent dyes, by formation of chemical linkages between molecules and siloxane matrices.^{18–20} Recently, we reported a QD–siloxane composite film which shows long-term PL QY stability under heat or moisture conditions with the aid of thermally stable Si—O bonds and cross-linked bonds between ligand of QD and siloxane matrix, compared with a hydrocarbon-based QD composite film.²¹

In this study, we investigate stability of QD composite films using CdSe/ZnS core/shell QDs surrounded by oleic acid embedded in two different siloxane films. One is QD/siloxane (methacryl) film, which has chemical linkages between QD and siloxane matrix, and the other is QD/siloxane (epoxy) film, which has no linkages between QD and siloxane matrix. The QD/siloxane (methacryl) film and the QD/siloxane (epoxy) film are fabricated via UV-

Received 02/13/17; accepted 03/07/17.

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induced free radical addition reaction and the epoxy ring opening cationic reaction, respectively. We analyzed the PL QY stability of two different QD/siloxane films under harsh heat or moisture conditions; 85°C/5% relative humidity (RH) and 85°C/85% RH, as well as dispersibility of the QDs in both siloxane films.

2 Experimental

2.1 Chemicals

3-Methacryloxypropyltrimethoxysilane (MPTS) (ShinEtsu, Japan), 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS) (ShinEtsu, Japan), diphenylsilanediol (DPSD) (Gelest, USA), barium hydroxide monohydrate (Sigma-Aldrich, USA), 2,2-dimethoxy-2-phenylacetophenone (Sigma-Aldrich, USA), triarylsulfonium hexafluoroantimonate salts (Sigma-Aldrich, USA), octadecyltrichlorosilane (Sigma-Aldrich, USA), and QD (CdSe/ZnS) (Nanodot-HE-series) passivated by oleic acids (Ecoflux, Korea) were purchased and used as received.

2.2 Synthesis of quantum dot/oligosiloxane (methacryl) resin

QD/oligosiloxane (methacryl) resin was synthesized via sol-gel condensation reaction between MPTS (1 mol) and DPSD (1.25 mol) in the presence of QDs (0.5 wt%). 3-Methacryloxypropyltrimethoxysilane, DPSD, and QDs were mixed in a two-neck flask by magnetic stirrer for a few minutes. After the mixing, barium hydroxide monohydrate was added as a catalyst to promote sol-gel condensation reaction under 80°C with nitrogen gas purging for a few hours. After the sol-gel condensation reaction, 2,2-dimethoxy-2-phenylacetophenone was added to the QD/oligosiloxane (methacryl) resin for UV-induced free radical addition reaction to fabricate solid-state film.

2.3 Synthesis of quantum dot/oligosiloxane (epoxy) resin

QD/oligosiloxane (epoxy) resin was synthesized via sol-gel condensation reaction between ECTS (1 mol) and DPSD (1.25 mol) in the presence of QDs (0.5 wt%). 2-(3,4-Epoxycyclohexyl)ethyltrimethoxysilane, DPSD, and QDs were mixed in a two-neck flask by magnetic stirrer for a few minutes. After the mixing, barium hydroxide monohydrate was added as a catalyst to promote sol-gel condensation reaction under 80°C with nitrogen gas purging for a few hours. After the sol-gel condensation reaction, triarylsulfonium hexafluoroantimonate salt was added to the QD/oligosiloxane (epoxy) resin for UV-induced epoxy opening cationic reaction to fabricate solid-state film.

2.4 Fabrication of quantum dot/siloxane (methacryl) and quantum dot/siloxane (epoxy) films

The QD/oligosiloxane (methacryl) and QD/siloxane (epoxy) resins were molded separately in stainless steel frame (1 mm of thickness, 40 mm of diameter) with both sides covered by glass plates. Glass plates were surface-treated by octadecyltrichlorosilane to facilitate separation of films from glass plates after UV ($\lambda = 365$ nm)-induced solidification process.

2.5 Aging condition of quantum dot/siloxane (methacryl) and quantum dot/siloxane (epoxy) films

QD/siloxane (methacryl) and QD/siloxane (epoxy) films were aged under 85°C/5% relative humidity (RH) and 85°C/85% RH without exposing films to light.

2.6 Characterization

Photoluminescence QY values were obtained from an absolute PL QY spectrometer, Quantaaurus-QY C11347 series (Hamamatsu Photovics K.K., Japan) using a Xenon light source (150 W). Photoluminescence decay curves were collected by a fluorescence lifetime spectrometer, FL920 (Edinburgh Instruments, England), using 470-nm laser as an excitation source. ^{29}Si nuclear magnetic resonance (^{29}Si NMR) spectra were collected by a DMX600 FT 600 MHz (Bruker Biospin, Australia). The Fourier-transform infrared (FT-IR) spectra were obtained from an FT-IR 680 plus (JASCO, USA). Thermogravimetric analysis (TGA) profiles were collected using a TGA Q50 (TA Instruments, USA) with a ramp of 10°C min^{-1} under nitrogen environment. Absorbance spectra were collected by a UV-vis-NIR spectrometer, SolidSpec-3700 (Shimadzu, Japan). Photoluminescence spectra were obtained from a DARSA PRO 5100 PL system (PSI Trading Co., Ltd., Korea) using a Xenon light source (500 W) as an incident beam. Delta transmission spectra were recorded by the Turbiscan (Formulation, France) using monochromatic light ($\lambda = 880$ nm). The transmission electron microscopy (TEM) samples were prepared by a focused ion beam (FIB) instrument, Nova-200 (FEI Company, Netherlands). Transmission electron microscopy images were obtained from a JEM-ARM200F (JEOL, Japan).

3 Results and discussion

We fabricated the QD/siloxane (methacryl) film via UV-induced cross-linking of free radical addition reaction to solidify the CdSe/ZnS QDs in oligosiloxane (methacryl) resin

(concentration of QDs: 0.5 wt%) which was synthesized by sol-gel condensation reaction between silane precursors of MPTS and DPSD.²² Similarly, the QD/siloxane (epoxy) film was fabricated via UV-induced cross-linking of epoxy ring opening cationic reaction to solidify the same batch of CdSe/ZnS QDs in oligosiloxane (epoxy) resin which was synthesized by sol-gel condensation reaction between silane precursors of ECTS and DPSD.²³ Figure 1a shows traces of PL QY of QD/siloxane (methacryl) film and QD/siloxane (epoxy) film observed for 40 days of aging in air at 85°C and 5% RH for 40 days. The QD/siloxane (methacryl) film retains the initial PL QY (~61%), while the QD/siloxane (epoxy) film exhibits severe decrease of PL QY from ~61 to ~9%, during aging for 40 days.

We also measured PL decay dynamics to characterize the optical properties of QD/siloxane (methacryl) film and QD/siloxane (epoxy) film before and after aging in air at 85°C and 5% RH (Fig. 1b). We define the PL lifetime (τ)

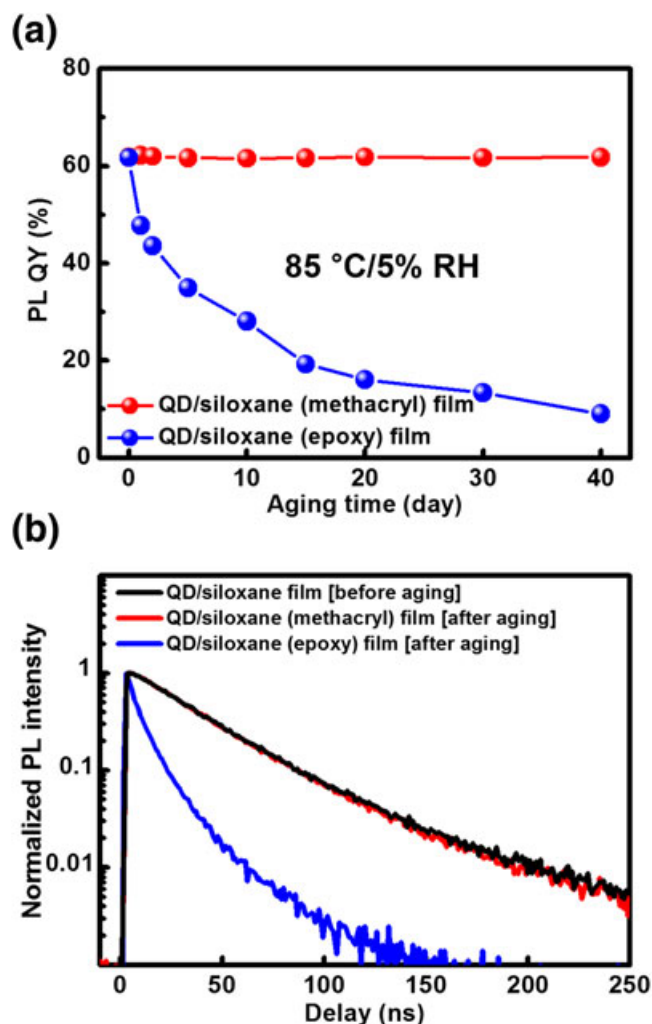


FIGURE 1 — (a) Traces of photoluminescence (PL) quantum yield (QY) of quantum dot (QD)/siloxane (methacryl) film (red) and QD/siloxane (epoxy) film (blue) observed over 40 days of aging in air at 85°C and 5% relative humidity (RH). (b) PL decay dynamics of QD/siloxane films before (black) and after (red: QD/siloxane (methacryl) film; and blue: QD/siloxane (epoxy) film) aging for 40 days.

to be the time at which PL intensity from the film is 1/e times the initial intensity (i.e., 1/e lifetime). The QD/siloxane (methacryl) film maintains the initial PL lifetime (34.3 ns), while the QD/siloxane (epoxy) film shows intense diminish of PL lifetime from 34.3 to 6.8 ns, implying the oxidation of QDs in the QD/siloxane (epoxy) film during the aging. Fitting of PL decay curves to either single-exponential or multiexponential decay is carried out to establish a proposition on the radiative and nonradiative recombination components. The PL decay dynamics of both QD/siloxane films before the aging are fitted with biexponential decay with two recombination components; τ_1 : 34.3 ns (98.4%) and τ_2 : 192.1 ns (1.3%), where percentage in parentheses indicates population of the component. The faster decay component (20–40 ns) is assigned to radiative recombination component, and the slower to delayed recombination component beyond time scale of 100 ns.²⁴ The delayed recombination component indicates the existence of long-lived trap states developed in the surrounding of QD:siloxane matrix. Biexponential fitting

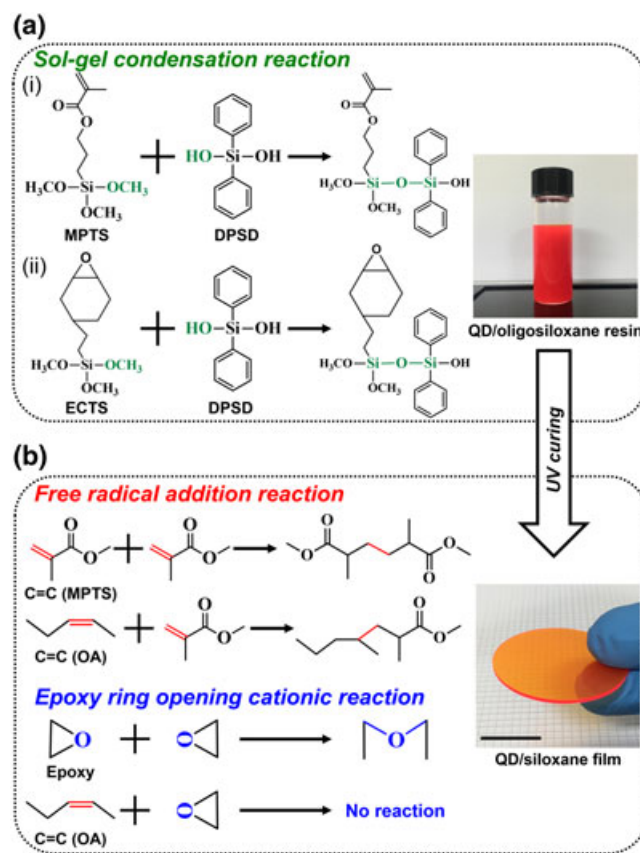


FIGURE 2 — Schematic illustration of fabrication process of QD/siloxane films. (a) Sol-gel condensation reaction between (i) 3-Methacryloxypropyltrimethoxysilane (MPTS) and diphenylsilanediol (DPSD) and (ii) 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECTS) and DPSD. Inset shows photographs of QD/oligosiloxane (methacryl or epoxy) resin under room light. (b) Free radical addition reactions among carbon double bonds of methacryl functional groups and oleic acids of QD/siloxane (methacryl) film, and epoxy ring opening cationic reaction between epoxy groups of QD/siloxane (epoxy) film. Inset shows photographs of QD/siloxane (methacryl or epoxy) film under room light. Scale bar is 20 mm.

of the PL decay for the aged QD/siloxane (methacryl) film yields similar values of radiative (τ_1 : 33.5 ns, 98.1%) and delayed recombination lifetimes (τ_d : 157.4 ns, 1.9%). However, the fitting from the aged QD/siloxane (epoxy) film gives rise to two new fast, nonradiative (τ_1 : 4.0 ns, 53.3%), (τ_2 : 12.0 ns, 44.5%), and slow, radiative (τ_3 : 46.9 ns, 2.2%) recombination components. The new fast decay components and decreased population of radiative recombination component of the QD/siloxane (epoxy) film indicate that new trap states are formed during the aging. We conjecture that formation of new trap states accelerates nonradiative recombination and effectively restrains radiative recombination. Therefore, formation of the new nonradiative recombination components is responsible for decreased PL QY of the aged QD/siloxane (epoxy) film. On the contrary, unchanged PL decay dynamics of the aged QD/siloxane (methacryl) film correspond with the retained PL QY during the aging. We attribute the long-term PL QY stability of QD/siloxane (methacryl) film to uniform passivation of QDs by siloxane matrix.

To reveal the difference of the PL QY stability of QD/siloxane (methacryl) film and QD/siloxane (epoxy) film, the molecular difference of both films needs to be dissected. Both films are fabricated via three steps. First, QDs are dispersed in the mixture of silane precursors, which are MPTS/DPSD and ECTS/DPSD, separately, forgoing ligand-exchange of QDs.²¹ During this step, hydrophobic interaction between oleic acid (OA, surface ligand on QDs) and functional groups of the silane precursors triggers encapsulation of the QDs.^{21,25,26} In the second step, the siloxane bonds of the siloxane network are formed by sol-gel condensation reaction between methoxy groups of MPTS and hydroxyl groups of DPSD, resulting QD/oligosiloxane (methacryl) resin (i of Fig. 2a), and between methoxy groups of ECTS and hydroxyl groups of DPSD, resulting QD/oligosiloxane (epoxy) resin (ii of Fig. 2a), at the vicinity of QDs, separately. The resulting viscous QD/oligosiloxane (methacryl or epoxy) resin shows no flocculation, and PL QY remains the same (the inset images of Fig. 2a and Table 1). Finally, a QD/siloxane (methacryl or epoxy) film was fabricated by exposing UV light onto the QD/oligosiloxane (methacryl or epoxy) resin (see the inset images of Fig. 2b). As shown in Fig. 2b, the free radical addition reaction of the QD/oligosiloxane (methacryl) resin results in the formation of carbon single bonds by two cross-linking reaction pathways: the one is the reaction between C=C bonds of methacryl groups of siloxane matrix (i.e., cross-linked bonds between

siloxane matrix), and another is the reaction between C=C bonds of the methacryl group and OA (i.e., cross-linked bonds between QD and siloxane matrix).^{21,22,27} While, the epoxy ring opening cationic reaction of the QD/oligosiloxane (epoxy) resin results in the formation of only ether bonds of between epoxy groups of siloxane matrix.²³ Therefore, the long-term PL QY stability of the QD/siloxane (methacryl) film attributed to cross-linked bonding forms between QD and siloxane matrix responsible for robust encapsulation of QDs, whereas the QD/siloxane (epoxy) film has no bonding forms between QD and siloxane matrix.

Formation of siloxane bonds via sol-gel condensation reaction is verified by the ²⁹Si NMR analysis on QD/oligosiloxane (methacryl) and QD/oligosiloxane (epoxy) resins (Fig. 3a and b, respectively). As shown in the chemical formulas in inset of Fig. 3a and b, the mono-, di-, and trimeric species of Si atoms in siloxane bonds exist

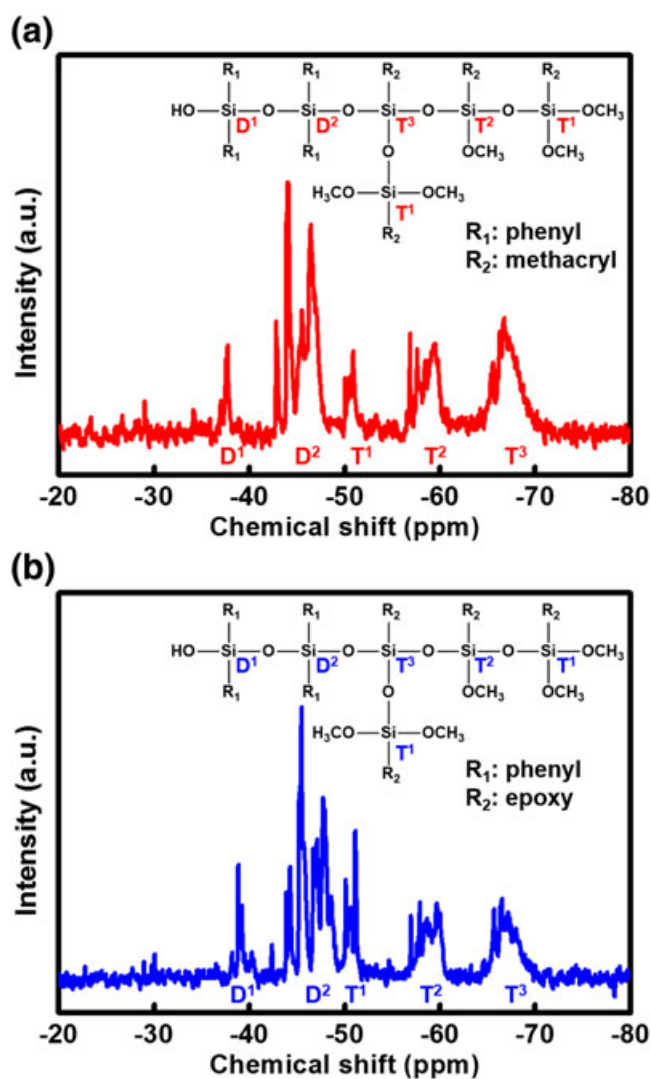


FIGURE 3 — ²⁹Si nuclear magnetic resonance (NMR) spectra of (a) QD/oligosiloxane (methacryl) resin and (b) QD/oligosiloxane (epoxy) resin. (Inset) Chemical structure of both QD/oligosiloxane resins representing Si atoms with different bond states.

TABLE 1 — Photoluminescence (PL) quantum yield (QY) of diluted [to eliminate reabsorption among quantum dots (QDs)] samples of QD/chloroform solution and QD/oligosiloxane (methacryl or epoxy) resin.

Sample	PL QY (%)
Diluted QD/chloroform solution	80
Diluted QD/oligosiloxane resin	80

in each QD/oligosiloxane resin and are represented by the terms of D^n and T^n , with the superscript “n” indicating the number of siloxane bonds of the Si atoms. The ^{29}Si NMR spectra of both QD/oligosiloxane resins show formation of siloxane bond network which is confirmed by presence of mono- (D^1 and T^1), di- (D^2 and T^2), and trimeric (T^3) species while absence of precursor species (T^0 and D^0). The degree of siloxane bond condensation (DOC) of QD/oligosiloxane (methacryl) and QD/oligosiloxane (epoxy)

resins is calculated by the peak area of their ^{29}Si NMR spectra (Table 2) and following equation.

$$\text{DOC} = \frac{D^1 + 2D^2 + T^1 + 2T^2 + 3T^3}{2(D^0 + D^1 + D^2) + 3(T^0 + T^1 + T^2 + T^3)} \times 100$$

The calculated DOC values of QD/oligosiloxane (methacryl) resin and QD/oligosiloxane (epoxy) resin are ~85 and ~84%, respectively, which indicate the successful

TABLE 2 — Chemical shift and peak area of Si atoms with different bond states in QD/oligosiloxane (methacryl) resin and QD/oligosiloxane (epoxy) resin.

Species	D^0	D^1	D^2	T^0	T^1	T^2	T^3
Chemical shift (ppm)	-34	-36 ~ -38	-42 ~ -47	-40 ~ -41	-49 ~ -51	-57 ~ -61	-65 ~ -69
Peak area (methacryl)	0	2.618	27.045	0	4.038	12.196	19.098
Peak area (epoxy)	0	4.223	29.355	0	6.905	11.534	16.838

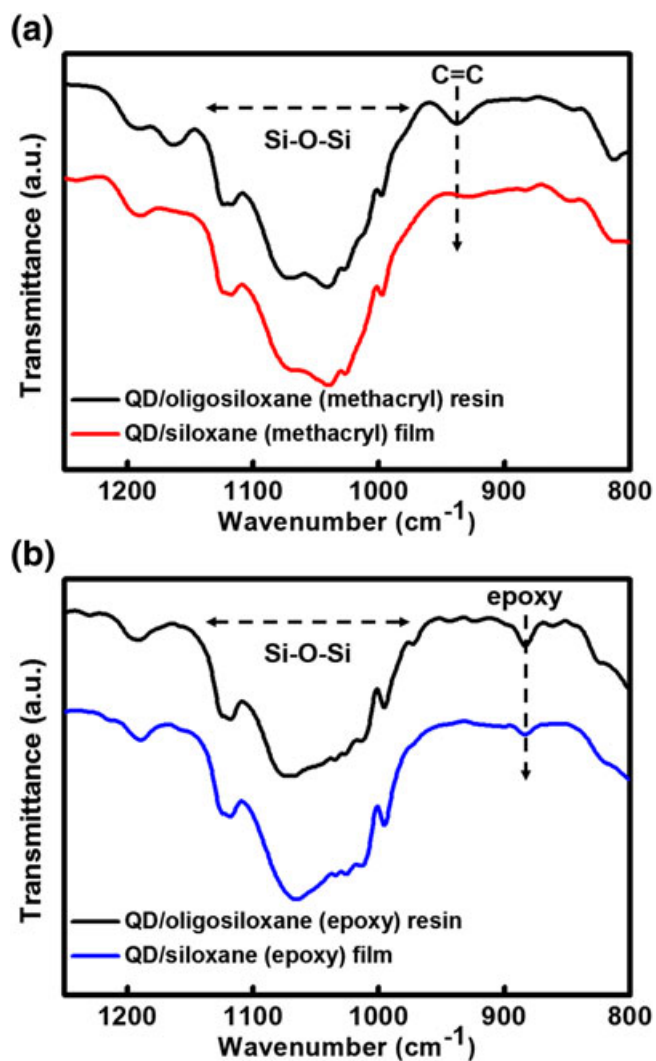


FIGURE 4 — (a) Fourier-transform infrared (FT-IR) spectra of QD/oligosiloxane (methacryl) resin (black) and QD/siloxane (methacryl) film (red). (b) FT-IR spectra of QD/oligosiloxane (epoxy) resin (black) and QD/siloxane (epoxy) film (blue).

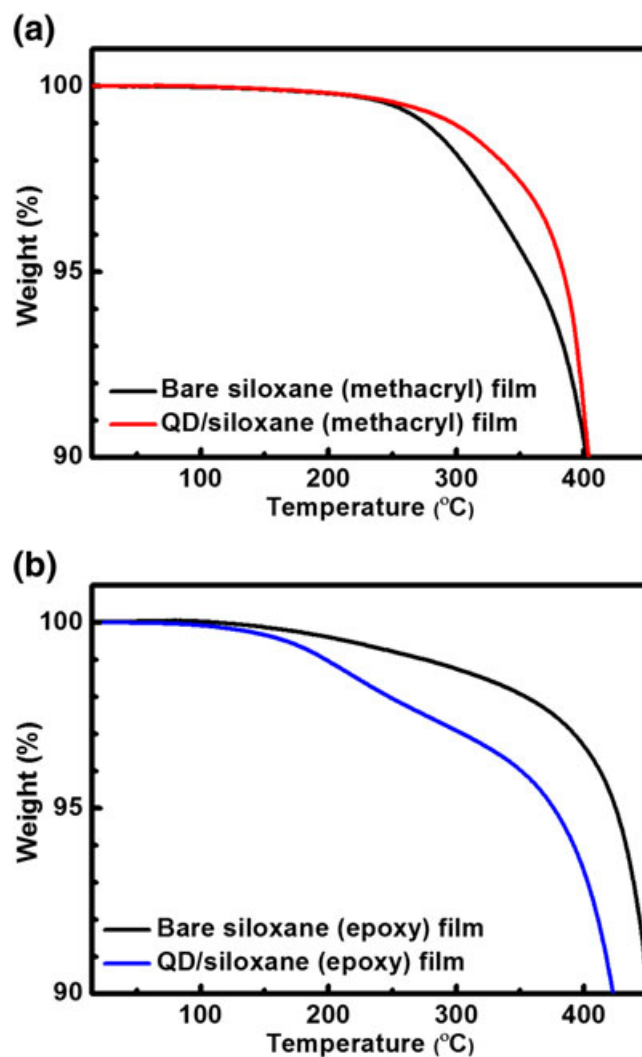


FIGURE 5 — (a) Thermogravimetric analysis (TGA) profiles of bare siloxane (methacryl) film without QDs (black) and QD/siloxane (methacryl) film (red). (b) TGA profiles of bare siloxane (epoxy) film (black) and QD/siloxane (epoxy) film (blue). Ramping rate is 10°C/min under N_2 .

formation of nearly same degree of siloxane networks in both QD/oligosiloxane resins.

Figure 4 shows FT-IR spectra of QD/oligosiloxane (methacryl) resin, QD/siloxane (methacryl) film, QD/oligosiloxane (epoxy) resin, and QD/siloxane (epoxy) film. Bands corresponding to the stretching of siloxane bond (Si—O—Si) at 1100–1000 cm^{-1} are detected in all samples which underpins the formation of siloxane network from the ^{29}Si NMR spectra. Moreover, bands corresponding to the carbon double bond (C=C) at 1000–950 cm^{-1} (=CH out-of-plane deformation) of QD/oligosiloxane (methacryl) resin are detected from methacryl group and oleic acid (Fig. 4a). Disappearance of the bands corresponding to C=C in the QD/siloxane (methacryl) film indicates that the cross-linking occurs by free radical addition reaction among carbon double bonds in methacryl group and oleic acid in QD/oligosiloxane (methacryl) resin. However, bands corresponding to the epoxy at 900–870 cm^{-1} are detected from QD/siloxane (epoxy) film, because of the presence of QDs that block the way of epoxy ring opening cationic reaction among epoxy groups of QD/oligosiloxane (epoxy) resin (Fig. 4b). Note that the cross-linked bondings between ligand (OA) of QD and functional group (methacryl) of siloxane matrix are the key mechanism for the robust encapsulation of the QDs by siloxane matrix.

Another testament to formation of cross-linked bonds between ligand (OA) of QDs and siloxane (methacryl) matrix is also verified by TGA profiles of bare siloxane (methacryl) film without QDs and QD/siloxane (methacryl) film. As shown in Fig. 5a, the QD/siloxane (methacryl) film exhibits the higher thermal stability compared to the bare siloxane

(methacryl) film: the temperatures at which 5% weight loss occurs ($T_{d5\%}$) are 385 and 360°C for the QD/siloxane (methacryl) film and the bare siloxane (methacryl) film, respectively. The additional linkages between ligands and siloxane matrix result in enhanced thermal stability of the QD/siloxane (methacryl) film. While, the QD/siloxane (epoxy) film shows drastic decreased thermal stability compared to bare siloxane (epoxy) film: $T_{d5\%}$ values are 425 and 375°C for the bare siloxane (epoxy) film and the QD/siloxane (epoxy) film, respectively. This reduced thermal stability of the QD/siloxane (epoxy) film corresponds with unreacted residual epoxy groups in the film [FT-IR spectrum of QD/siloxane (epoxy) film in Fig. 4b]. Both results are ascribed to existence of QDs that disturb complete epoxy ring opening cationic reaction in QD/siloxane (epoxy) film. In terms of the molecular structural difference between QD/siloxane (methacryl) film and QD/siloxane (epoxy) film underlies the long-term PL QY stability of QD/siloxane (methacryl) film under highly oxidative environment with the help of linkages between QD and siloxane matrix.

In the view of using the QD/polymer composite film in display devices, uniform dispersion of QDs in the film will be a crucial requirement because uneven dispersion of QDs causes scattering of incident light that results in vague image from final products. We confirmed the uniformity of QD dispersion in the QD/oligosiloxane (methacryl) resin, QD/oligosiloxane (epoxy) resin, QD/siloxane (methacryl) film, and QD/siloxane (epoxy) film using UV/vis spectroscopy, PL spectroscopy, Turbiscan, and TEM (Fig. 6). As shown in Fig. 6a and b, the absorbance and PL spectra of

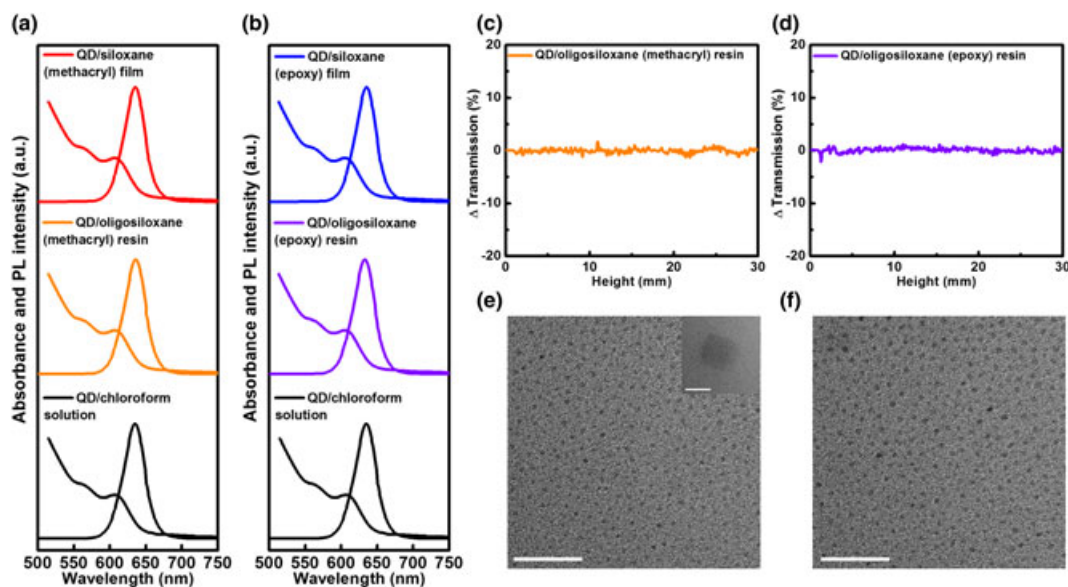


FIGURE 6 — (a–b) Absorbance and PL spectra of QD/chloroform solution (black), QD/oligosiloxane (methacryl) resin (orange), QD/siloxane (methacryl) film (red), QD/oligosiloxane (epoxy) resin (violet), and QD/siloxane (epoxy) film (blue). (c–d) Delta transmission spectra of QD/oligosiloxane (methacryl) resin (orange) and QD/oligosiloxane (epoxy) resin (violet) under ambient condition, respectively. (e–f) Transmission electron microscopy (TEM) images of QD/siloxane (methacryl) film and QD/siloxane (epoxy) film which films were prepared by focused ion beam (FIB) instrument, respectively (scale bars =50 nm). Inset shows magnified TEM image of QD/siloxane (methacryl) film (scale bar =5 nm).

QD/chloroform solution, both QD/oligosiloxane resins and both QD/siloxane films, reveal the uniform dispersion of QDs: the 1S peak wavelength, emission peak wavelength, and full width at half-maximum unchanged throughout the film fabrication processes (Table 3).

More intuitive observation of uniform QD dispersion of both QD/oligosiloxane resins is enabled by Turbiscan, which detects changes of light transmission along the height of sample. Both QD/oligosiloxane (methacryl) resin and QD/oligosiloxane (epoxy) resin exhibit almost no change of light transmission along the height of sample, indicating that uniform dispersion of QDs without aggregation (Fig. 6c and d, respectively). This uniform QD dispersion of both QD/oligosiloxane resins can be ascribed to hydrophobic interaction between high content of functional groups of the two different siloxane matrices and ligand (OA) of QDs.^{25,26}

In addition, structural analysis on both of QD/siloxane films was also examined to verify the dispersion of QDs. For TEM analysis, the QD/siloxane (methacryl) film and the QD/siloxane (epoxy) film were prepared by FIB instrument. As shown in the TEM images of Fig. 6e and f, QDs are evenly dispersed in the QD/siloxane (methacryl) film and the QD/siloxane (epoxy) film, respectively [the inset of Fig. 6e shows magnified TEM image of QD/siloxane (methacryl) film]. The TEM analysis of both QD/siloxane films indicates that aggregation of QDs does not arise through the film fabrication process, which is in accordance with uniform dispersibility of QDs in QD/oligosiloxane resins. Consequently, hydrophobic interaction between ligand of QD and functional groups of siloxane matrix confers the uniform dispersion of QDs in both QD/siloxane films.

In order to emphasize the effect of cross-linked bonding forms between QD and siloxane matrix, we monitored the PL QY of QD/siloxane (methacryl) film and QD/siloxane (epoxy) film aged in air at 85°C and 85% RH for 40 days (Fig. 7a). The PL QY of the QD/siloxane (methacryl) film and QD/siloxane (epoxy) film are noticeably enhanced from ~61 to ~74 and ~70%, respectively, in the first 2 days of aging. After the 2 days of aging, the QD/siloxane (methacryl) film retains its enhanced PL QY of ~74%, whereas QD/siloxane (epoxy) film exhibits significant decrease in PL QY down to ~22%.

The different behaviors of PL QY changes in QD/siloxane (methacryl) film and QD/siloxane (epoxy) film under moisture environment can be explained by PL decay dynamics (Fig. 7b). As we defined earlier, the 1/e lifetime (τ) of the QD/siloxane (methacryl) film increases from 34.3 to 48.2 ns,

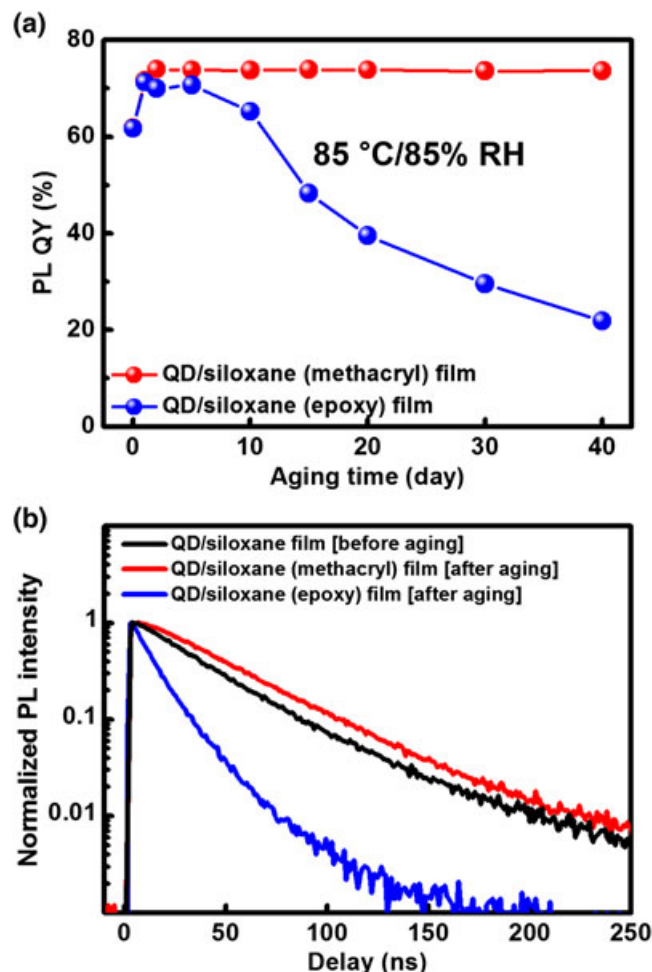


FIGURE 7 — (a) Traces of PL QY of QD/siloxane (methacryl) film (red) and QD/siloxane (epoxy) film (blue) observed over 40 days of aging in air at 85°C and 85% relative humidity (RH). (b) PL decay dynamics of QD/siloxane films before (black) and after (red: QD/siloxane (methacryl) film; and blue: QD/siloxane (epoxy) film) aging for 40 days.

while the QD/siloxane (epoxy) film shows a decrease of τ to 11.7 ns during 40 days of aging. The PL decay curves of QD/siloxane (methacryl) and QD/siloxane (epoxy) films before aging are fitted with biexponential decay with two recombination components of radiative (τ_1 : 34.3 ns, 98.4%) and delayed (τ_2 : 192.1 ns, 1.3%) recombination. After aging, the QD/siloxane (methacryl) film is fitted with single-exponential decay with increased radiative recombination lifetime (τ_1 : 43.1 ns), while the aged QD/siloxane (epoxy) film is fitted on a biexponential decay with new fast, nonradiative (τ_1 : 9.7 ns, 77.6%) and slow, reduced radiative (τ_2 : 23.0 ns, 22.4%) recombination components.

TABLE 3 — 1S peak wavelength, emission peak wavelength, and fwhm of QD/chloroform solution, QD/oligosiloxane (methacryl) resin, QD/oligosiloxane (epoxy) resin, QD/siloxane (methacryl) film and QD/siloxane (epoxy) film.

Sample	1S peak wavelength (nm)	Emission peak wavelength (nm)	fwhm (nm)
QD/chloroform solution	605	635	34
QD/oligosiloxane resin (methacryl/epoxy)	605/605	636/635	34/34
QD/siloxane film (methacryl/epoxy)	605/605	635/635	35/35

Enhanced PL QY of CdSe/ZnS QDs by passivating trap states with the help of adsorbed water molecules has been reported in previous studies.^{21,28} From this standpoint, both increased radiative (from 34.4 to 43.2 ns) and disappeared delayed recombination components of the QD/siloxane (methacryl) film indicate reduced trap states after aging which correspond with its enhanced PL QY. Therefore, we summarize that passivated trap states by water molecules and cross-linked bonding forms between ligand of QD and siloxane matrix contribute the enhanced and long-term PL QY stability of QD/siloxane (methacryl) film in air at 85°C and 85% RH.

4 Conclusions

We reported critical effect of linkages between QD and siloxane matrix by comparing PL QY stabilities of two different QD/siloxane films, one has the linkages and the other has not: QD/siloxane (methacryl) film and QD/siloxane (epoxy) film, respectively. The QD/siloxane (methacryl) film and the QD/siloxane (epoxy) film were fabricated by free radical addition reaction and epoxy ring opening cationic reaction, respectively. Both films show uniform dispersion of QDs via hydrophobic interaction between oleic acid on surface of QD and functional groups of siloxane matrix. More to the point, the PL QY of QD/siloxane (methacryl) film does not decrease under 85°C/5% RH and 85°C/85% RH, whereas QD/siloxane (epoxy) film shows severe decrease of PL QY. Therefore, cross-linked bonding forms between oleic acid and the methacryl group of siloxane matrix, which is the core mechanism to encapsulate QDs by siloxane matrix under harsh oxidative conditions.

The uniform dispersion of QDs in the QD/siloxane (methacryl) film and its stable optical properties under harsh oxidative conditions, e.g., heat and moisture, are the two essential requirements in the down-conversion film in display applications. Therefore, we expect that the approach to encapsulate QDs by forming chemically cross-linked bondings between organic ligand of QD and siloxane matrix will advance research on QD/polymer composite films.

Acknowledgments

This work was supported by the Wearable Platform Materials Technology Center (WMC) funded by the National Research Foundation of Korea (NRF) Grant of the Korean Government (MSIP) (NRF-2016R1A5A1009926 and NRF-2016M3A7B4910618). This research was also supported by a grant from the Korea Evaluation Institute of Industrial Technology (Project 10051337).

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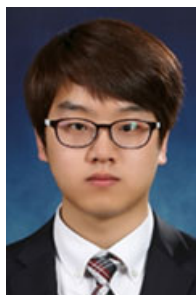
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