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Authors that wish to refer to this work are advised to cite the full-length version by referring to it's DOI:

[10.1002/jsid.542](https://doi.org/10.1002/jsid.542)

Quantum Dot/Siloxane Composite Film Exceptionally Stable Against Heat and Moisture

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Abstract

We report the siloxane-encapsulated quantum dot (QD) film (QD/siloxane film), whose photoluminescence (PL) quantum yield (QY) remains nearly undegraded under harsh heat or moisture conditions; 85 °C/5% relative humidity (RH) and 85 °C/85% RH for over 1 month.

Author Keywords

Quantum Dots; Siloxane hybrid; Thermal stability; Humid stability; Surface passivation; Photoluminescence quantum yield.

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 PL QY of the QD/polymer composite decreases, when the composite is exposed to oxygen, heat or moisture [7,8]. In fact, the recent commercialization of QD-based products were possible because of adopting barrier films that protect QD/polymer film from oxygen and moisture [9,10]. 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 barrier-film-free QD/polymer composite, which maintains its optical properties under harsh conditions, is growing.

A siloxane-based film, which synthesized *via* sol-gel condensation reaction of silane precursors, has been widely studied for encapsulating molecules by formation of chemical linkages or interactions between molecules and siloxane matrices [11,12]. Recently, we reported a dye-siloxane composite film, which shows long-term stability at high temperatures [12]. The encapsulation of dyes by heat resistive siloxane matrix accounts for the long-term stable fluorescence of dye-siloxane film.

In this study, we investigate stability of QD composite film using CdSe/ZnS QDs surrounded by oleic acid (OA) that dispersed in siloxane matrix (QD/siloxane film). We analyzed the PL QY stability of QD/siloxane film under harsh heat or moisture conditions; 85 °C/5% relative humidity (RH) and 85 °C/85% RH. To compare encapsulating properties of QD/siloxane film, QD/hydrocarbon film which matrix is acrylate functionalized hydrocarbon-based polymer, was selected as a reference matrix because it has acryl functional groups and no siloxane bonds.

2. Results and Discussion

We fabricated the QD/siloxane film *via* UV-induced free radical addition reaction to solidify the CdSe/ZnS QDs in oligosiloxane resin (concentration of QDs: 0.5 wt %) which was synthesized by sol-gel condensation reaction between silane precursors of 3-methacryloxypropyltrimethoxysilane (MPTS) and diphenylsilanediol (DPSD) [13]. Similarly, the QD/hydrocarbon film was fabricated *via* UV-induced free radical addition reaction to solidify the same batch of CdSe/ZnS QDs in acrylate functionalized hydrocarbon-based matrix.

Figure 1A shows traces of PL QY of QD/siloxane film and QD/hydrocarbon film observed for 40 days of aging in air at 85 °C and 5% relative humidity (RH). The QD/siloxane film retains the initial PL QY (~61%), while the QD/hydrocarbon film exhibits severe decrease of PL QY from ~61% to ~19%, during the aging. In order to investigate PL QY stability of both films under heat and moisture condition, we monitored the PL QY of QD/siloxane and QD/hydrocarbon films aged in air at 85 °C and 85% RH for 40 days (Figure 1B). The PL QY of the QD/siloxane film is noticeably enhanced from ~61% to ~74% and it retains its enhanced PL QY. While, QD/hydrocarbon film exhibits significant decrease in PL QY down to ~35%.

To reveal the PL QY stability of QD/siloxane film, the molecular structure of QD/siloxane film need to be dissected. The QD/siloxane film is fabricated *via* three steps. First, QDs are dispersed in the mixture of silane precursors; MPTS and DPSD. During this step, hydrophobic interaction between oleic acid (OA) which is ligand of QD and functional groups of the silane precursors triggers encapsulation of the QDs [14]. In the second step, the siloxane network are formed by sol-gel condensation reaction between methoxy groups of MPTS and hydroxyl groups of DPSD, resulting QD/oligosiloxane resin at the vicinity of QDs (Figure 2A). The resulting viscous QD/oligosiloxane resin shows no flocculation (the inset images of Figure 2A).

Finally, a QD/siloxane film was fabricated by exposing UV light onto the QD/oligosiloxane resin (see the inset image of Figure 2B). As shown in Figure 2B, the free radical addition reaction of the QD/oligosiloxane 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 the other is the reaction between C=C bonds of the methacryl group and OA (*i.e.*, cross-linked bonds between QD and siloxane matrix) [15,16]. Either one of these two cross-linking pathways is responsible for robust encapsulation of QDs by sol-gel derived siloxane matrix.

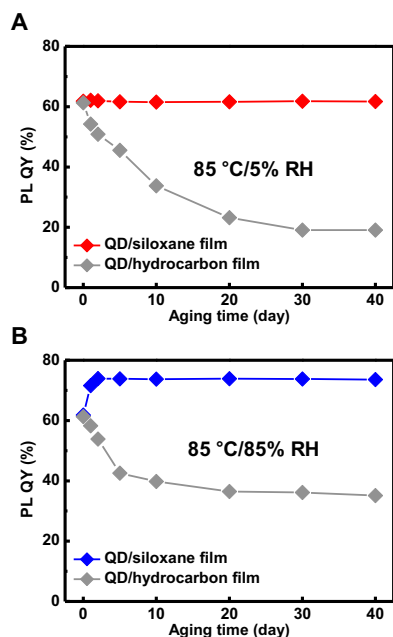


Figure 1. Traces of PL QY of QD/siloxane film (red and blue) and QD/hydrocarbon film (gray) observed over 40 days of aging (A) in air at 85 °C and 5% relative humidity (RH) and (B) in air at 85 °C and 85% RH [15].

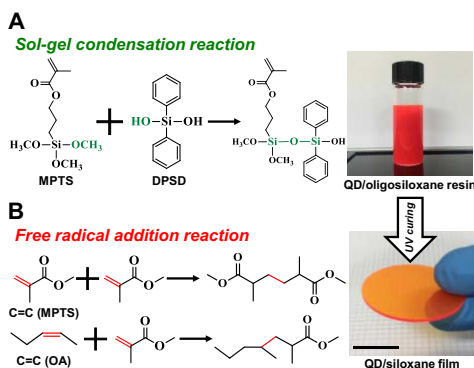


Figure 2. (A) Sol-gel condensation reaction between MPTS and DPSD. Inset shows photograph of QD/oligosiloxane resin under room light. (B) Free radical addition reactions among carbon double bonds of methacryl functional groups and oleic acid (OA). Inset shows photographs of QD/siloxane film under room light. Scale bar is 20 mm [15].

Figure 3 shows Fourier-transform infrared (FT-IR) spectra of QD/oligosiloxane resin and QD/siloxane 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 by sol-gel condensation reaction. Moreover, bands corresponding to the carbon double bond (C=C) at 1000–950 cm^{-1} (=CH out-of-plane deformation) of QD/oligosiloxane resin are detected from methacryl group and OA (Figure 3). Disappearance of the bands corresponding to C=C in the QD/siloxane film indicates that the two cross-linking pathways occurs by free radical addition reaction among carbon double bonds in methacryl group and OA in QD/oligosiloxane resin.

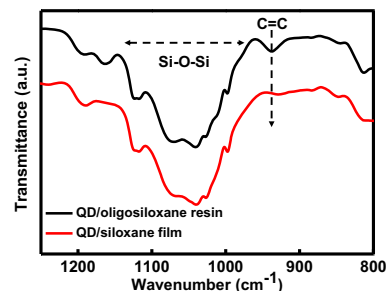


Figure 3. FT-IR spectra of QD/oligosiloxane resin (black) and QD/siloxane film (red).

Figure 4 shows thermogravimetric analysis (TGA) profiles of QD/siloxane film and QD/hydrocarbon film. As shown in Figure 4, the QD/siloxane film exhibits higher thermal stability compared to the QD/hydrocarbon film: the temperatures at which 1% weight loss occurs ($T_{d1\%}$) are 300 and 230 °C for the QD/siloxane film and the QD/hydrocarbon film, respectively. In terms of chemical structure, the QD/siloxane film is mostly composed of Si—O bonds whose bonding energy is 452 kJ/mol, while the QD/acrylate film contains majority part of carbon single bonds whose bonding energy is 346 kJ/mol. These structural differences underlies the long-term PL QY stability of our QD/siloxane film under heat or moisture conditions.

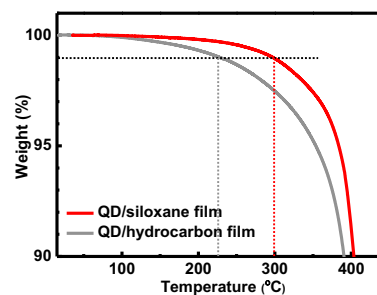


Figure 4. TGA profiles of QD/siloxane film (red) and QD/hydrocarbon film (gray). Ramping rate is 10 °C/min under N_2 .

3. Conclusion

We reported QD encapsulated siloxane film (QD/siloxane film) by sol-gel condensation reaction and free radical addition reaction. The PL QY of QD/siloxane film does not decrease under 85 °C/5% relative humidity (RH) and 85 °C/85% RH, whereas QD/hydrocarbon film shows severe decrease of PL QY. Therefore, we expect that the encapsulate QDs by heat resistive siloxane matrix will advance the envelope of QD/polymer composite films as an organic/inorganic hybrid system.

4. Impact of Research

The QD/siloxane film, which has heat resistive siloxane bonding forms and cross-linked bonding forms between QD and siloxane matrix, whose PL QY undegraded under harsh heat or moisture conditions: 85 °C/5% relative humidity (RH) and 85 °C/85% RH, without applying additional oxygen and moisture barrier layers.

5. Acknowledgements

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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