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Fabrication of highly transparent and luminescent quantum dot/polymer nanocomposite for light emitting diode using amphiphilic polymer-modified quantum dots

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HIGHLIGHTS

- CdSe@ZnS/ZnS core/shell QDs were encapsulated by an amphiphilic polymer.
- QD/PDMS nanocomposite was fabricated by using encapsulated QDs as a crosslinker.
- Nanocomposite with uniform QD dispersion could be obtained even at high QD loading.
- Synthesized nanocomposite showed high transparency due to uniform QD dispersion.
- LED with the synthesized nanocomposite exhibited excellent luminous efficacy.

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ABSTRACT

Herein we present the fabrication of a highly transparent and luminescent quantum dot (QD)/polymer nanocomposite for application in optoelectronic devices. First, we encapsulated CdSe@ZnS/ZnS core/shell QDs with an amphiphilic polymer, i.e., poly(styrene-co-maleic anhydride) (PSMA). By encapsulating QDs with PSMA instead of ligand exchange, the photoluminescence intensity of the QDs could be preserved even after surface modification. Next, the PSMA-modified QDs were used as crosslinkers for the aminopropyl-terminated polydimethylsiloxane (PDMS) resin in a ring-opening reaction between the maleic anhydride of the QDs and the diamines of the PDMS, producing polymer networks at a low curing temperature. This method afforded a nanocomposite with uniform dispersion of QDs even at high QD concentrations (~30 wt%) and superior optical properties compared to a nanocomposite prepared from unmodified QDs and commercial resin. Owing to these enhanced properties, the nanocomposite was used to fabricate a light emitting diode (LED) device, and the luminous efficacy was found to be highest at 1 wt%.

1. Introduction

Fluorescent semiconductor nanocrystals, or quantum dots (QDs), have attracted great interest for the development of next-generation devices, such as light emitting diodes, solar cells, and luminescent solar concentrators, due to their excellent optical properties [1–9]. In particular, high color purity, photoluminescence quantum yield (PLQY), and photochemical stability of QDs make them suitable for alternative phosphors in light emitting diodes (LEDs) [3,6]. In white LED applications, for instance, QDs are used as color converters

to convert blue light from an LED chip into green and red colors, thereby generating white light [3,5]. In these applications, QDs are usually in the form of a polymer nanocomposite consisting of QDs embedded in a polymer matrix, which protects them from harsh environments [10–13]. Among the various types of polymers used in LED applications, silicone-based polymers are frequently used because they exhibit excellent transmittance in visible light, thermal stability, and light-extraction efficiency [14–17]. When a silicone-based polymer is used as a matrix, however, it is difficult to fabricate highly transparent and luminescent nanocomposites due to the aggregation of QDs and

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the high curing temperature [18,19]. Aggregation of QDs in a polymer matrix is usually accompanied by serious degradation of the optical properties because of light scattering by QD aggregates and luminescence quenching by Förster resonance energy transfer (FRET) between nearby QDs [20–22]. In addition, the high curing temperature of silicone polymer can damage the QD surface by detaching surface ligands and creating trap states, which reduce the quantum yield (QY) of individual QDs [14,23].

To improve the dispersion of QDs within the silicone matrix, various studies have been conducted [24–26]. For instance, surface ligands on QDs were replaced by ligands that were more compatible with the matrix. In our previous work, the dispersion of QDs in a poly(dimethylsiloxane) (PDMS) matrix was improved by modifying the surface of the QDs with the hydrophobic ligands containing a thiol anchoring group, but the increase in quantum efficiency (QE) of the nanocomposites was not significant [24]. Tao et al. fabricated a transparent QD/PDMS nanocomposite using bimodal PDMS-grafted QDs, but the concentration of QDs in the nanocomposite was low (< 1 wt%) and the QY of the PDMS-grafted QDs significantly decreased (~50%) after ligand exchange [25]. Both methods utilized the ligand exchange reaction that adversely affected surface passivation of the QDs, resulting in the reduction of QY. To circumvent this problem, encapsulation of QDs with amphiphilic polymer has been developed [26–28]. Instead of exchanging ligands on the QD surface, an amphiphilic polymer bearing both hydrophobic and hydrophilic groups was added to modify the surface. In this approach, the hydrophobic portion of the polymer intercalated with the surface ligands of the QD by hydrophobic interaction, thus retaining the original surface ligands and preserving their QY even after surface modification. But, most studies on modification of QDs with amphiphilic polymers have been focused on aqueous dispersion of QDs for biological applications [27,28].

In this study, we report the fabrication of highly luminescent and transparent QD/PDMS nanocomposite films using QDs modified with an amphiphilic polymer. We used poly(styrene-co-maleic anhydride) (PSMA) to encapsulate QDs through hydrophobic interaction. The PSMA acted as a crosslinker for the matrix polymer in a ring-opening reaction between the maleic anhydride on the QDs and the amine end group of PDMS. This enhanced compatibility between the QDs and the PDMS matrix as well as improved the dispersion of the QDs. Using this method, we could fabricate a transparent QD-PSMA/PDMS nanocomposite film with uniform dispersion of QDs at high concentration (up to 30 wt%) without a high-temperature curing step. Finally, the luminous efficacy of this method was compared with the conventional QD-PDMS nanocomposite in LED applications.

2. Experimental

2.1. Materials

Cadmium acetate ($\text{Cd}(\text{OAc})_2$, 99.99%), cadmium oxide (CdO , 99.99%), zinc acetate ($\text{Zn}(\text{OAc})_2$, 99.99%) oleic acid (OA, 90%), trioctylphosphine (TOP, 90%), 1-octadecene (1-ODE), propylene glycol monomethyl ether acetate (PGMEA, 99.5%), 1-dodecanethiol (1-DDT, 98%), poly(styrene-co-maleic anhydride) cumene terminated (PSMA, M_n : ~1900 by GPC), and bis(3-aminopropyl) terminated poly(dimethylsiloxane) ($\text{H}_2\text{N-PDMS-NH}_2$, M_n : ~27,000) were purchased from Aldrich. Selenium (99.999%, powder) and sulfur (99.5%, powder) were purchased from Alfa Aesar. Ethyl alcohol (99.99%), acetone (99.99%), n-hexane (95.0%), and chloroform (99.99%) were purchased from Duksan Chemical. All the chemicals were used without further purification.

2.2. Synthesis of green- and red-emitting QDs

Highly luminescent and stable green-emitting CdSe@ZnS/ZnS core/ shell QDs were synthesized by the previously reported method [29]. In a 50-mL three-neck flask, 0.14 mmol $\text{Cd}(\text{OAc})_2$, 3.41 mmol $\text{Zn}(\text{OAc})_2$, and 7 mL OA were added and degassed at 150 °C under vacuum until the vacuum level

reached 100 mTorr. Temperature was then lowered to 100 °C and 15 mL of 1-ODE was injected into the flask, followed by degassing for 30 min. After degassing, the temperature was elevated to 310 °C to obtain a transparent solution of $\text{Cd}(\text{OAc})_2$ and $\text{Zn}(\text{OAc})_2$, while maintaining Ar purging. Following this step, 2 mL TOPSeS, which was prepared by dissolving 5 mmol Se and 5 mmol S in 5 mL TOP, was rapidly injected into the flask at 310 °C and allowed to react for 10 min for the growth of a CdSe@ZnS alloy core. For higher stability, the CdSe@ZnS core was overcoated with a ZnS shell, by injecting 2.4 mL S source (3.2 mmol S in 4.8 mL 1-ODE) into the suspension of CdSe@ZnS cores. After 12 min, the 5 mL Zn source (4.92 mmol $\text{Zn}(\text{OAc})_2$ in 2 mL OA and 8 mL ODE) was injected into the suspension. Then, 5 mL S precursor (19.3 mmol S in 10 mL TOP) was added into the reaction bath dropwise at a rate of 0.5 mL/min, and allowed to react for 20 min. To complete the reaction, the reactor was quickly cooled to room temperature. The resulting QDs were precipitated by the addition of 4 mL hexane and 50 mL acetone, followed by centrifugation at 9000 rpm for 10 min and redispersion in chloroform. The purification step was repeated three times, after which the QDs were dispersed in the chloroform for further use.

For the white LED experiment, red-emitting CdSe/CdZnS/ZnS QDs were synthesized using the previously reported method [30] with a modification. In a 250-mL three-neck flask, 4 mmol CdO , 8 mmol $\text{Zn}(\text{OAc})_2$, and 20 mL OA were mixed and degassed at 150 °C under vacuum (100 mTorr). After 1 h, temperature was set to 50 °C and 100 mL 1-ODE was added to the mixture, followed by degassing at 100 °C for 1 h. The mixture was then heated up to 300 °C with Ar purging, and 0.8 mL TOPSe, which was prepared by dissolving 1 mmol Se in 1 mL TOP, was rapidly injected to the mixture. After 1 min, 1.2 mL 1-DDT was added dropwise at the rate of 1 mL/min. After 20 min, 4 mL TOP dissolving 4.67 mmol S was injected to passivate CdSe/CdZnS QDs with ZnS shell for 10 min. The temperature of reactor was lowered to room temperature, and QDs were precipitated with hexane/acetone, followed by centrifugation and redispersion in chloroform. The as-synthesized red-emitting QDs were dispersed in chloroform for white LED experiments.

2.3. Surface modification by amphiphilic polymer and preparation of QD-PSMA/PDMS nanocomposite

Surface modification of the QDs with amphiphilic polymer (PSMA) was conducted using a hydrophobic interaction between the surface ligands of the QDs and the PSMA. Different amounts of PSMA were added to a 2-mL QD suspension in chloroform. The QD/polymer suspension was stirred for 6 h, leading to a dissolution of PSMA and formation of PSMA-modified QDs (QD-PSMA).

To fabricate the QD-PSMA/PDMS nanocomposite, amine terminated-PDMS ($\text{H}_2\text{N-PDMS-NH}_2$) was mixed with the QD-PSMA suspension at room temperature, enabling a crosslinking reaction between PDMS and the amphiphilic polymer on the QDs. For comparison, nanocomposite was also prepared by using commercially available PDMS polymer (Sylgard-184, Dow Corning), where the QDs or QD-PSMA were mixed with 1 g base polymer and 0.1 g curing agent. The mixture was vacuum-dried for 1 h at room temperature to remove the solvent and air bubbles, and cured in a convection oven at 150 °C for 2 h, resulting in the QD/Sylgard or QD-PSMA/Sylgard nanocomposite.

2.4. LED applications

For LED experiments, the green-emitting QD-PSMA/PDMS mixture was placed on a blue LED chip (Dae-Kwang Illumination, $\lambda_{\text{ex}} = 450$ nm) surface mount device (SMD), followed by curing at 150 °C. For comparison, LEDs were prepared using the QD/Sylgard nanocomposite. White LED device was also fabricated using the QDPSMA/PDMS containing CdSe@ZnS/ZnS green QDs and CdSe/CdZnS/ZnS red QDs at the weight ratio of 10:1. The luminous properties of the LEDs were then measured by the integrating sphere equipped with the LED test apparatus.

For a thermal stability test, luminous efficacy of the fabricated QDPSMA/PDMS LED device was measured in a convection oven at 100 °C for 15 days.

2.5. Characterization

The size and morphology of the QDs were determined using transmission electron microscopy (TEM, JEM-2100, JEOL) and quasi-elastic light scattering (QELS, Nano-ZS, Malvern). The UV–Vis absorption spectra of the QDs and transmittance of the nanocomposite films were obtained using a spectrophotometer (V-730, JASCO). The emission spectra were obtained using a Perkin-Elmer LS-55 photoluminescence (PL) spectrometer. The dispersion states of QD-PSMA/PDMS and QD/ Sylgard nanocomposites were observed with a confocal microscope (LSM-880, ZEISS). The quantum yield was measured with a spectrofluorometer (FP-8500, JASCO) and an integrating sphere (ILF-835, JASCO). The luminous and color conversion efficiencies of the LEDs were estimated using an integrating sphere with a 450-nm Xe laser as an excitation energy source (QE-1000, Otsuka Electronics).

3. Results and discussion

3.1. Characterization of the as-synthesized and surface-modified QDs

Highly luminescent green-emitting CdSe@ZnS/ZnS QDs capped with OA and TOP were synthesized by the previously reported method [29], and their surfaces were modified with the PSMA to produce QDPSMA. PL spectra in Fig.

1(a) show that the PL intensity and λ_{max} of the QD-PSMA remained virtually constant even after surface modification. It has been reported that PL intensity of QDs usually decreases after ligand exchange due to detachment of the original surface ligands. Coating amphiphilic polymers on the QD surface, however, retained the original ligands on the surface and hence preserved the PL intensity and λ_{max} . After surface modification with PSMA, the average hydrodynamic diameter of QDs from the QELS, slightly increased from 18.5 ± 2.7 nm to 23.26 ± 4.2 nm, while the TEM did not show a noticeable size change (Fig. 1(b)). The discrepancy between the QELS and TEM sizes suggests that the increase in the hydrodynamic diameter can be attributed to the encapsulation by PSMA. Moreover, when a polar solvent such as PGMEA was added to the as-synthesized QD suspension, aggregation of QDs occurred because of the hydrophobic nature of the QD surfaces. However, PSMA-capped QDs remained colloidally stable in the PGMEA solution, supporting successful modification with the PSMA as shown in Fig. 1(c).

3.2. Preparation of the QD-PSMA/PDMS nanocomposites

QD-PSMA/PDMS nanocomposite was prepared by mixing QD-PSMA and amine terminated-PDMS polymer. The mixture gelled within 2 h, which was caused by the crosslinking reaction between the MA group on the QD surface and the amine group of the PDMS. Note that the QDPSMA acted as a crosslinker for the PDMS polymer (Fig. 2).

To understand the effect of the PSMA amount on the crosslinking reaction, molar ratios of the MA on the QD-PSMA to the NH_2 of the PDMS were varied from 0.1 to 14.8 while the QD concentration was

Fig. 1. Properties of the as-synthesized QDs and QD-PSMA: (a) PL intensity, (b) TEM images, and (c) colloidal stability in PGMEA.

Fig. 2. Schematic representation of crosslinking mechanism between the surface-modified QDs and the amine-terminated PDMS.

kept constant at 1 wt%. Fig. S1 shows that gelation did not occur when the MA/ NH_2 ratio was lower than 0.4 or greater than 3.7, indicating an optimal amount of PSMA for gelation. If the MA/ NH_2 ratio was either too low or too high, the extent of the crosslinking reaction in the PDMS network was not high enough for gelation, resulting in a fluidic mixture. From the above results, the molar ratio of MA/ NH_2 was set to 2.2, and QD-PSMA/PDMS nanocomposite films were fabricated by coating a mixture of QD-PSMA and PDMS on a glass substrate, followed by solvent evaporation. For comparison, nanocomposite film was also prepared using the unmodified QDs and commercial polymer (QD/Sylgard).

3.3. Optical properties of QD-PSMA/PDMS nanocomposites

We compared optical properties of the QD-PSMA/PDMS and the QD/Sylgard nanocomposite films. Fig. 3 shows that transparent QDPSMA/PDMS films could be obtained with a wide range of QD concentrations (0.1–30 wt%). However, the QD/Sylgard film was translucent even at the QD concentration of 1 wt%. Generally, a reduction in transparency of the nanoparticle-based nanocomposite is attributed to the aggregation phenomenon, which is known to cause light scattering and a redshift of λ_{max} in the emission spectrum. The QD-PSMA/PDMS films remained transparent even when the QD concentration was very high (30 wt%), and only a slight redshift was observed as the QD concentration increased (Fig. 4(a)). Alternatively, the QD/Sylgard film was translucent, due to light scattering, and the redshift was evident even at 1 wt%. These results suggest that QDs were distributed in the form of aggregates in the QD/Sylgard film.

We also compared transmittances of QD-PDMS nanocomposite films by UV–Vis spectroscopy. In particle-embedded nanocomposites, several factors can affect transmittance. According to the Rayleigh scattering theory, the loss

of transparency of nanocomposites results from light scattering by spherical nanoparticles with radius r and volume fraction ϕ_p as follows:

$$T = \exp \left[- \frac{32\pi \phi_p x r^3 n_p^3 m^4}{\lambda^4 \left\{ (n_p m)^2 + 2 \right\}} \right] \quad (1)$$

where T is the transmittance of the nanocomposites, λ is the wavelength of light, x is the optical path length, and n_p and n_m are the refractive indices of the nanoparticle and polymer matrix, respectively. In this work, all the parameters were identical except the size of particles in the films. Generally, the particle size should be smaller than approximately one-tenth of the wavelength of light to minimize the loss of transparency by light scattering. Thus, aggregation of QDs can lead to significant light scattering and hence reduce transparency of the nanocomposite film. Fig. 4(b) shows that the QD-PSMA/PDMS films exhibited much higher transmittance than the QD/Sylgard film at all wavelengths regardless of the QD concentration, because aggregation caused significant light scattering and reduction in transmittance in the QD/Sylgard film. In addition, increasing QD concentration decreased the transmittance in the QD-PSMA/PDMS films. Because the light scattering was negligible in the QD-PSMA/PDMS film (Fig. 3), transmittance was mainly governed by absorption by the QDs, decreasing transmittance with the QD concentration.

Using an integrating sphere, we measured QY of QDs after fabrication of QD-PSMA/PDMS nanocomposite, and found that QY decreased from 81% to 55%. There have been several studies that reported a QY drop after incorporation of QDs within polymer composites [31–33]. We suspect that QDs were oxidized during dispersion and curing processes, resulting in luminescence quenching.

Fig. 3. Pictures of QD-PSMA/PDMS nanocomposites with different QD concentrations when MA/NH₂ ratio was 2.2 and QD/Sylgard nanocomposite (QD 1 wt%) on glass substrates.

3.4. Dispersion states of QDs within nanocomposite films

To confirm the relation between the optical properties and dispersion state of the nanocomposite films, we directly observed dispersion states of QDs in QD-PSMA/PDMS and QD/Sylgard films with the confocal microscope and TEM. Fig. 5(a) and (b) show that the distribution of QDs was uniform in the QD-PSMA/PDMS, while in the QD/Sylgard there were mostly micro-sized fluorescent particles and voids (no fluorescence) due to significant aggregation. We also prepared focused ion beam (FIB) samples of QD-PSMA/PDMS for TEM analysis, which showed that QDs existed as isolated nanoparticles without aggregation even at high concentration (Fig. 5(c) and (d)).

The discrepancy in the dispersion states of QDs can be explained as follows. In the QD/Sylgard nanocomposite, van der Waals attraction between QDs was dominant, causing serious aggregation of QDs in the polymer matrix. In the QD-PSMA/PDMS nanocomposite, however, van der Waals attraction between QDs was reduced because the QDs were isolated by the PSMA polymer encapsulation layer, which also provided steric stabilization. Furthermore, the crosslinking reaction of the QDPSMA with the amine-terminated PDMS caused QDs to be enclosed by the PDMS network. Note that the amine-terminated PDMS in this study had a molecular weight of 27,000, which was sufficiently high to act as a spacer to prevent the aggregation of QDs. To determine whether the PSMA encapsulation layer or the crosslinking reaction was more important in uniform dispersion of QDs, the PSMA-modified QDs were dispersed in the commercial PDMS polymer without amine groups (QDPSMA/Sylgard). Fig.

S2 shows that without amine groups, QDs exhibited significant aggregation even at 1 wt%, confirming that the crosslinking reaction played a dominant role in improving dispersion of QDs in the QD-PSMA/PDMS nanocomposite.

3.5. LED application of QD/PDMS nanocomposites

LED chips were prepared by curing QD-PSMA/PDMS at various QD concentrations (0.1, 0.5, 1, 5, 10, 15 wt%) and 1 wt% QD/Sylgard nanocomposite on the blue LED SMD chips. Note that it was possible to fabricate an LED chip with the QD-PSMA/PDMS even at high concentration while poor dispersion of QDs in the QD/Sylgard prevented the fabrication of the LED chip at high concentration. We compared luminous efficacies of the LED chips using an integrating sphere (with the LED equipped). When the LEDs were operated at 60 mA, the luminous efficacy of the QD-PSMA/PDMS was higher than that of the 1 wt% QD/Sylgard nanocomposite even at much higher QD concentration (15 wt%, Fig. 6(a)). The luminous efficacy of QD-PSMA/PDMS nanocomposite was highest at 1 wt%. Above 1 wt%, reabsorption of emitted light by QDs and FRET among QDs became significant due to a decrease in the interparticle distance, which decreased the luminous efficacy. In addition, electroluminescence spectra of the LED chips using the QD-PSMA/PDMS and QD/Sylgard nanocomposites at the same QD concentration (1 wt%) were obtained. Fig. 6(b) shows that an LED with the QD-PSMA/PDMS exhibited higher emission intensity than that with the QD/Sylgard even though much more blue light remained, which suggests that the QD-PSMA/PDMS nanocomposite could convert blue light to emitted light more efficiently, leading to higher luminous

Fig. 4. Photoluminescence spectra (a) and transmittance (b) of nanocomposite films (numbers indicate wt%).

Fig. 5. Confocal microscope images of QDs within QD-PSMA/PDMS (a) and QD/Sylgard nanocomposites (b), and TEM images of QD-PSMA/PDMS with different QD emitting QDs. Fig. 7(b) shows that white color could be obtained (color coordinate: $x = 0.363$, $y = 0.3564$) using this method, suggesting its potential for white LED applications.

efficacy. Conversely, an LED with QD/Sylgard exhibited not only lower emission intensity but also a significant redshift in $\lambda_{\max}$ (~8 nm). This result can be explained by aggregation of QDs in the QD/Sylgard nanocomposite that blocked light propagation and generated backscattering and reabsorption, causing a reduction in luminous efficacy and a redshift in $\lambda_{\max}$. The calculated color conversion efficiency of the LED with the QD-PSMA/PDMS was also much higher (17.1%) than that with the QD/Sylgard (5.1%). We also tested a thermal stability of the LED with the QD-PSMA/PDMS, and confirmed that luminous efficacy could be preserved (> 94%) even after an exposure to high temperature (100 °C) for 15 days (Fig. 7(a)). We believe that effective isolation of the PSMA-encapsulated QDs within PDMS resin using the crosslinking reaction could prevent QDs from oxidation at high temperature. Finally, we fabricated a white LED using the QD-PSMA/PDMS with both green and red-

4. Conclusions

To utilize QDs as a new-generation material in optoelectronic devices, meet requirements for various device morphologies, and keep QDs from direct exposure to extreme conditions such as high humidity or temperature, it is necessary to fabricate QD-polymer nanocomposites from colloidal QDs. In this work, we presented a novel method to fabricate a QD-polymer nanocomposite that possesses superior optical properties to those with conventional resins. In particular, QDs were encapsulated with the amphiphilic polymer (PSMA), which then acted

Fig. 6. Luminous efficacy of the LED chips using QD-PSMA/PDMS with different QD concentrations and QD/Sylgard of 1 wt% of QD at a forward bias current of 60 mA (a), and electroluminescence (EL) spectra of the LED chips using QD-PSMA/PDMS 1 wt% and QD/Sylgard at 1 wt% (b).

Fig. 7. Changes in relative luminous efficacy of LED with QD-PSMA/PDMS nanocomposite at 100 °C (a), and electroluminescence spectra of the fabricated white LED with QD-PSMA/PDMS nanocomposite (b).

as a crosslinker for the amine-terminated PDMS polymer to produce a nanocomposite with a uniform dispersion of QDs. The resulting nanocomposite exhibited higher transparency and luminous efficacy than that with unmodified QDs and commercial resin. These results can be used to design a new device that requires high transparency and efficiency at high QD concentration.

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Appendix A. Supplementary data

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