

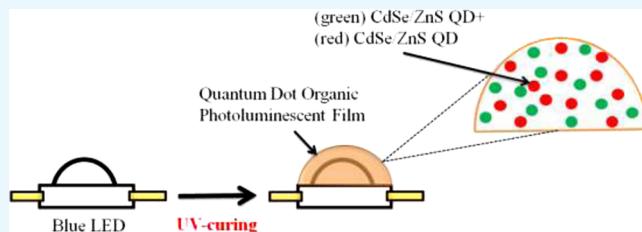
Quantum Dot–Acrylic Acrylate Oligomer Hybrid Films for Stable White Light-Emitting Diodes

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 Supporting Information

ABSTRACT: White light-emitting diodes (LEDs) have been achieved using photopolymerization. Red and green CdSe/ZnS core–shell quantum dots (QDs) are dispersed in photopolymerized aliphatic acrylic acrylate resins, cured by using 36 W UV light for 1.5 min producing QD–acrylate nanocomposites, and then a hybrid LED device is achieved using the QD–acrylate nanocomposite with two emission wavelengths excited by using a blue InGaN LED chip. The cured QD–acrylate nanocomposite films are characterized by using ultraviolet–visible, fluorescence, scanning electron microscopy, atomic force microscopy, and thermogravimetric analysis measurements. Photopolymerization is conveniently employed to adjust several parameters of the CIE-1931 coordinate (x, y), color temperature, and color rendering index (CRI). Good white balance of the red-green hybrid device achieves a luminance of 7976 lm/m² at a 30 mA working current. The light emission efficiency, CRI, and color temperature of 14%, 47, and 11 204 K, respectively, are attained at this working current.



INTRODUCTION

Efficient white light-emitting diodes (LEDs) have attracted considerable attention in solid-state illumination recently. Several methods are developed to fabricate white light LEDs, the phosphor-converted emission is the most commonly used technique.¹ Up to now, various materials such as inorganic phosphors,¹ organic dyes,² and quantum dots (QDs)³ have been employed to test the possibility to replace the common phosphors in white LEDs. In these materials, QD is an innovative material because it has advantages over the commonly used phosphors. The emission wavelength adjustment of the QDs is generally completed by controlling the size of the crystal or varying the chemical composition. In addition, the scattering effects of QDs are rarely observed because the size of QD particles is relatively small compared to inorganic phosphors. Compared to organic dyes, QDs are not easily bleached, demonstrating a longer lifetime and a wider absorption range. A QD-based white LED is generally fabricated using a spin-coating technique, in which QDs are mixed with epoxy resins and are then coated on the excited chips.³ However, an alternative photoactive packaging (PAP) method has also been used to fabricate the white LEDs.⁴ In the PAP method, a bare blue LED chip was covered with a red and green QD-dispersed photosensitive resin film to make the white LED illuminate when the current is passed through the blue LED chip. This packaging method eliminates the additional facilities that are used to package LEDs in the present process. Here, the white balance of this hybrid LED was achieved by mixing red and green QDs in the photosensitive resins.

Quantum dots possess some characteristics such as a size-tunable energy bandgap, high quantum efficiency of photoluminescence (PL), solution processing, and adjustable absorption and emission wavelength.⁵ QDs have been widely used in photoelectronic devices of solar cells^{6–8} and light-emitting diodes.⁹ Encapsulation of quantum dots (QDs) into polymers can improve the photoluminescence stability and device performance of optoelectronic and light-emitting diodes (LEDs).^{10,11} In the fabrication of LEDs, the dispersion and quantum efficiency of QDs in the polymer matrix are the most important factors. The optical properties of QDs are affected by several factors, such as the QD size, the type of ligand molecule, and the type of matrix. The structure and interaction of organic compounds on the surface of the QD affect the fluorescence of the QD. Green's group¹² has reviewed the properties of capped ligands such as trioctylphosphine oxide, amines, carboxylic acids, or thiols on the surface of the QDs. The defects on the surface of the QDs can work as the hole of electrons or holes. Therefore, surface passivation of quantum dots can reduce their recombination leading to the enhancement of fluorescence. A common method of surface passivation of CdSe-QDs is made using a thin shell of a wider bandgap material such as ZnS for surface protection,¹³ thereby forming a core–shell structure.¹⁴ The shell forms a more passivated surface, resulting in the reduction in nonradiative pathways with an effective increase in quantum efficiency. One-step synthesis has been employed to

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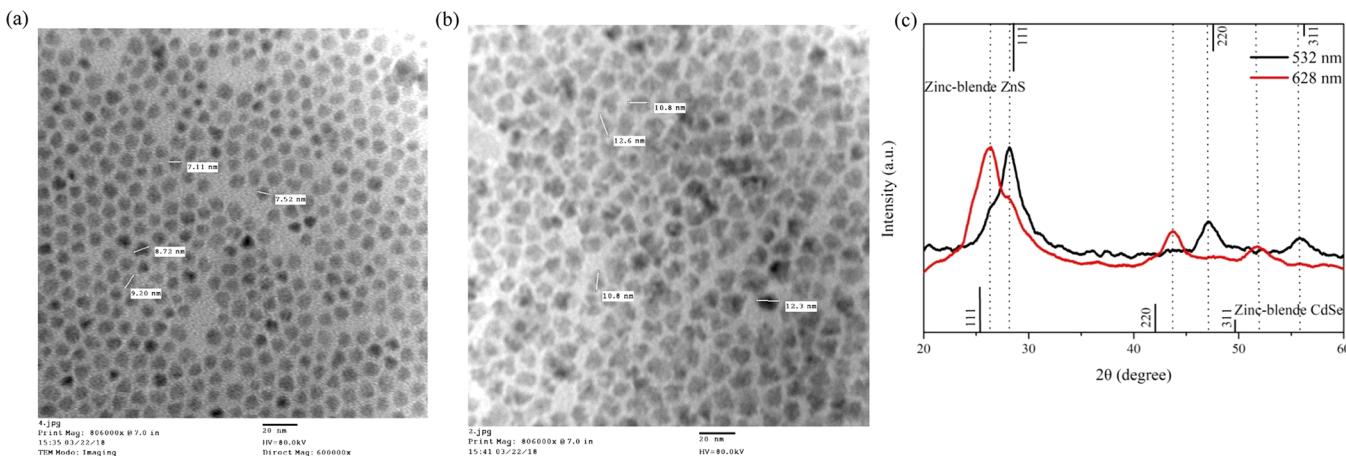


Figure 1. TEM images of red CdSe/ZnS quantum dots (a) and green CdSe/ZnS quantum dots (b). X-ray diffraction of green and red-mixed CdSe/ZnS quantum dots (c).

prepare CdSe/ZnS quantum dots.⁴ The one-step synthesis method is much faster than the two-step in the manufacturing process, which is in favor of mass production in the future. Because the quantum confinement effect and the core–shell structure existed in the QDs having few defects on the crystal surface, the light-emitting efficiency of photoexcitation is extremely high. Another approach uses a dangling bond formed by a suitable surface passivation ligand to reduce surface traps.¹⁵ There are two challenges in the incorporation of QDs into the polymer matrix, that is, QD aggregation and fluorescence quenching. QDs can be incorporated into the polymeric matrix by a number of methods, including the in situ synthesis of QDs in the polymer,¹⁶ the direct incorporation of QDs into the polymer,¹⁷ and the in situ polymerization of monomer-containing QDs forming a cured resin hybrid.^{18,19} The structure and molecular polarity of the polymer matrix have obvious interactions with the capping ligands on the surface of QDs. It needs to select the molecular structure and molecular polarity to be completely miscible with the prepared quantum dots, forming a uniformly transparent precursor solution. After curing, the coating of the precursor solution generates a hybrid film of the light-emitting diode with good light transmittance. Recently, the incorporation of phosphine ligand-coupled CdSe and CdSe/ZnS QDs into poly(methyl methacrylate) demonstrated no phase separation during polymerization.²⁰ Without modification of the surface of the QDs, a stable and bright green photoluminescent CdSe/poly(butyl acrylate) nanocomposite was obtained by in-situ miniemulsion polymerization.²¹ Wang et al. dispersed CdSe/ZnS QDs in photosensitive epoxy resin to produce a white LED by means of an active packaging method.⁴ On the other hand, the incorporation of CdSe/ZnS QDs into poly(2-methoxy-5(2-ethylhexyloxy)) to produce organic LEDs can significantly improve the performance of this hybrid device.²² Organic silicone resins have good transparency, flexibility, stress relief, thermal stability, moisture resistance, and high gas permeability, which have been widely used in packaging CdSe/ZnS QD LEDs.^{11,23} The quantum dots are directly dispersed in the organic resin and mounted on the surface of the semiconductor chip to emit white light.²⁴ The CdSe/ZnS core–shell QDs are encapsulated in the polymer matrix of cyanoacrylate and epoxy resin, resulting in the loss or increase of QD light emission in these polymers.¹⁰ The QD light-emitting film was commonly prepared by adding the

solution of quantum dots into the polymer, coating on the substrate, and then heating to remove the solvent. This process often takes much time to perform the polymerization/curing reaction at relatively high temperatures (~ 120 – 150 °C), leading to a decline in QDs. Alternatively, in 2008, an epoxy acrylate monomer using photopolymerization has been employed to make QD light-emitting films achieve a white LED.²⁵ This epoxy resin system having benzene rings in the polymer chains would result in the yellowing phenomenon by extending the use time, leading to a decline of the light-emitting efficiency.²⁵

Because the photopolymerization of the acrylic system is easier to control compared to the epoxy system, we employed the photopolymerization process using an aliphatic acrylic acrylate oligomer and an acrylic monomer to prepare red and green QDs involving the aliphatic polymer film in this study, avoiding yellowing of the polymer matrix. In this work, we directly dispersed tri-*n*-octylphosphine (TOP)-capped CdSe/ZnS QDs into an acrylic acrylate oligomer using the solution mixing method, followed by solvent removal, and then coating this mixture on a blue LED chip and curing by UV light to achieve a QD–acrylate hybrid LED device. In addition, we report the optical, morphological, topological, and thermal properties of UV-cured acrylate resin-CdSe/ZnS QD nanocomposites in this work. These fluorescent nanocomposites consisted of a small number of quantum dots exhibiting optical features and thermal stability, so these processes and materials are worth promoting in LED applications.

RESULTS AND DISCUSSION

One-Step Synthesis of CdSe/ZnS Core–Shell QDs.

Figure 1a,b present the transmission electron microscope (TEM) images of the synthesized red and green quantum dots, respectively. Although the chemical composition gradient of red and green quantum dots is different, both QDs had a spherical shape and a narrow size ranging from 7 to 9 nm. In our experimental conditions, the QDs exhibited a stable size distribution of 7–9 nm corresponding to a shell (ZnS) thickness of about 1.5 nm.²⁵ Figure 1c shows the X-ray diffraction (XRD) of CdSe/ZnS quantum dots. The standard XRD patterns of CdSe and ZnS are labeled at the bottom and top of Figure 1, respectively. The indicated diffraction signals (2θ) of 26.3, 42.6, and 51.9° at the bottom represent the respective (111), (220), and (311).

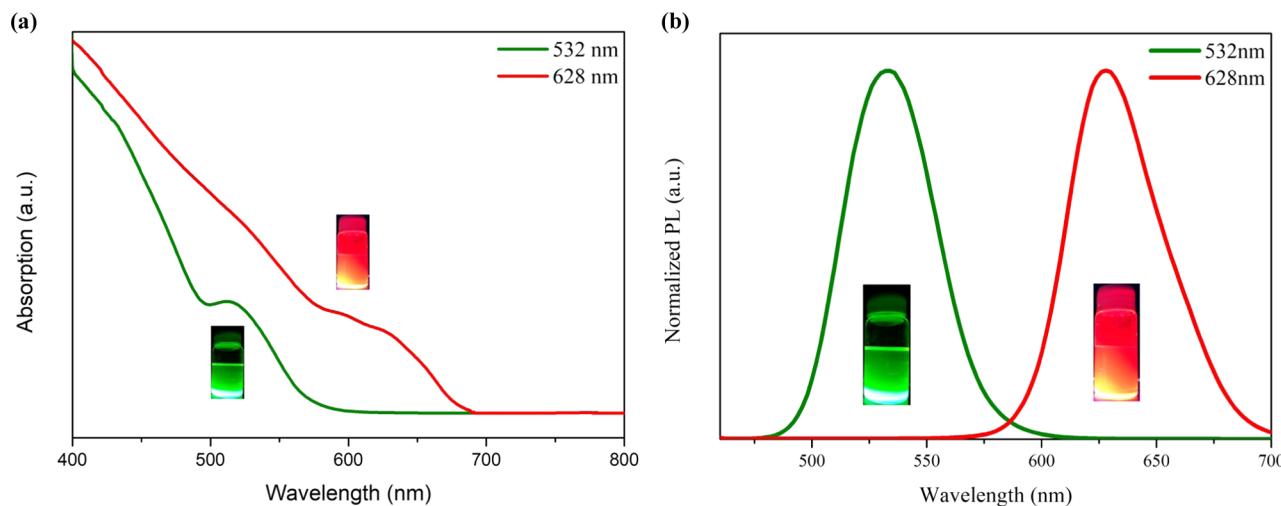


Figure 2. UV-visible spectra (a) and PL spectra of CdSe/ZnS quantum dots (b).

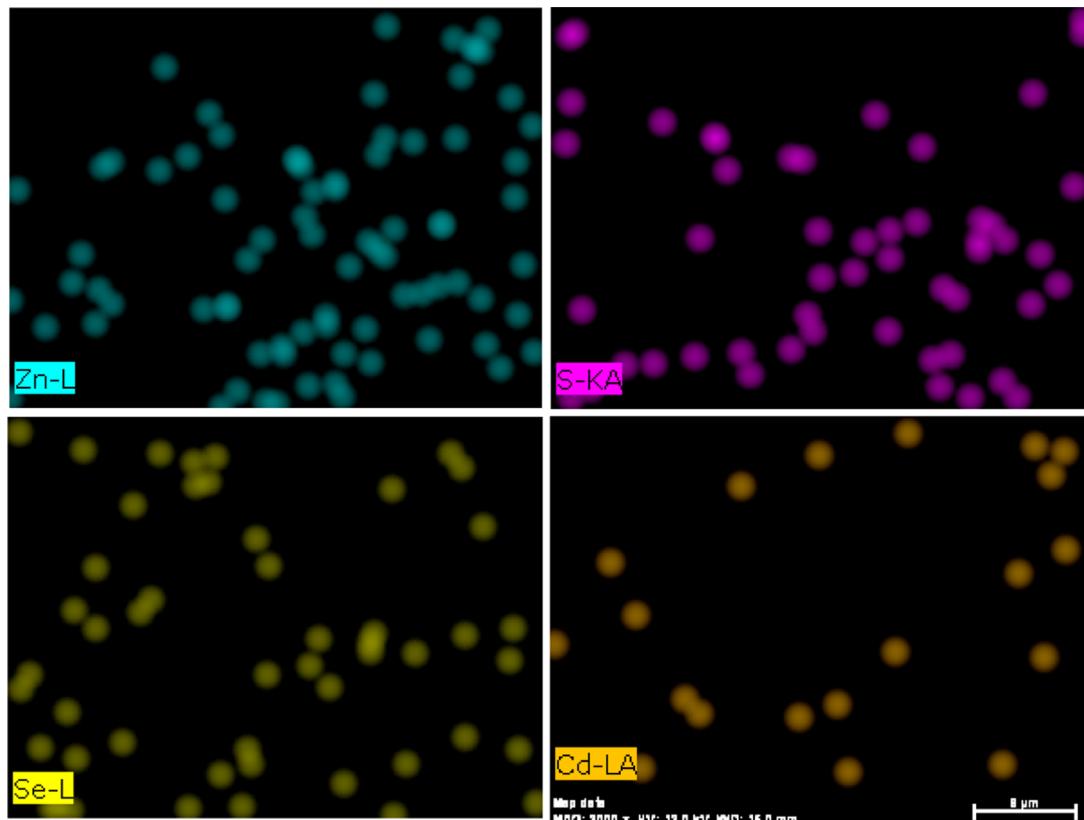


Figure 3. Cross-sectional EDS mapping of the green and red-mixed CdSe/ZnS (0.1 wt %) quantum dot–polymer hybrid light-emitting films. Scale bar: 8 μm .

and (311) crystal planes (JCPDS 19-0191) of the zinc blende cubic crystal structure of CdSe. The indicated diffraction signals of 28.5, 47.515, and 56.28° at the top represent the respective (111), (220), and (311) crystal planes (JCPDS 05-0566) of the zinc blende cubic crystal structure of ZnS. Note that the diffraction signals of the quantum dots prepared in this work are present at 28.14, 47.13, and 55.78°, respectively. Compared with the standard diffraction signals of CdSe and ZnS, the CdSe/ZnS diffraction peaks slightly shifted from smaller angles (corresponding to the CdSe crystal) to larger angles (corresponding to the ZnS crystal). This implies that the synthesized quantum dots have a core–shell structure.²⁵

Figure 2 demonstrates a picture of synthesized quantum dots irradiated by sun light and green (532 nm) and red (628 nm) light emission excited by ultraviolet light. As shown in **Figure 2a**, UV-visible spectra were measured using toluene as the background and then the synthesized quantum dots were diluted in toluene to measure the corresponding absorption spectra. **Figure 2b** shows the fluorescence spectra of the synthesized CdSe/ZnS excited at a wavelength of 440 nm, exhibiting that the peak positions of CdSe/ZnS are present at 532 and 628 nm with full width at half maximum (FWHM) of 28, respectively, corresponding to green and red emitting light. Note that a plurality of exciton peaks appears in the UV-vis

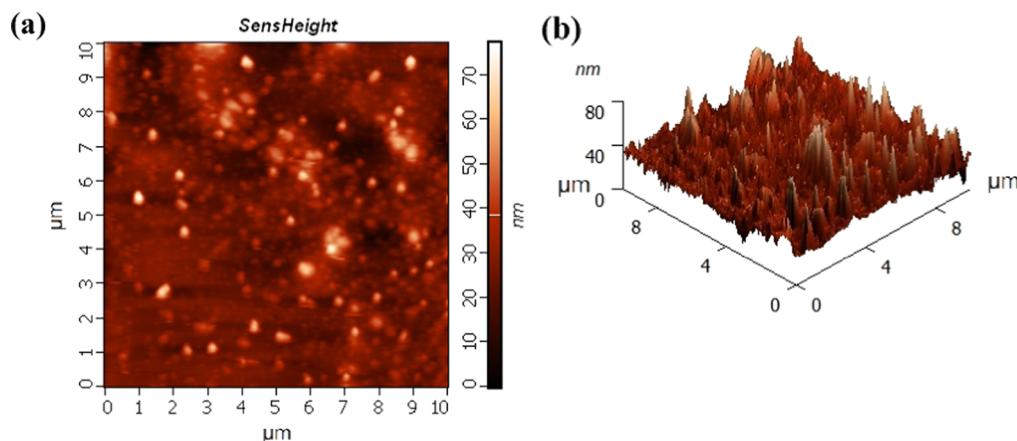


Figure 4. (a) Topographical AFM image and (b) a three-dimensional surface profile image of the green and red-mixed CdSe/ZnS QD (0.1 wt %) polymer hybrid light-emitting films.

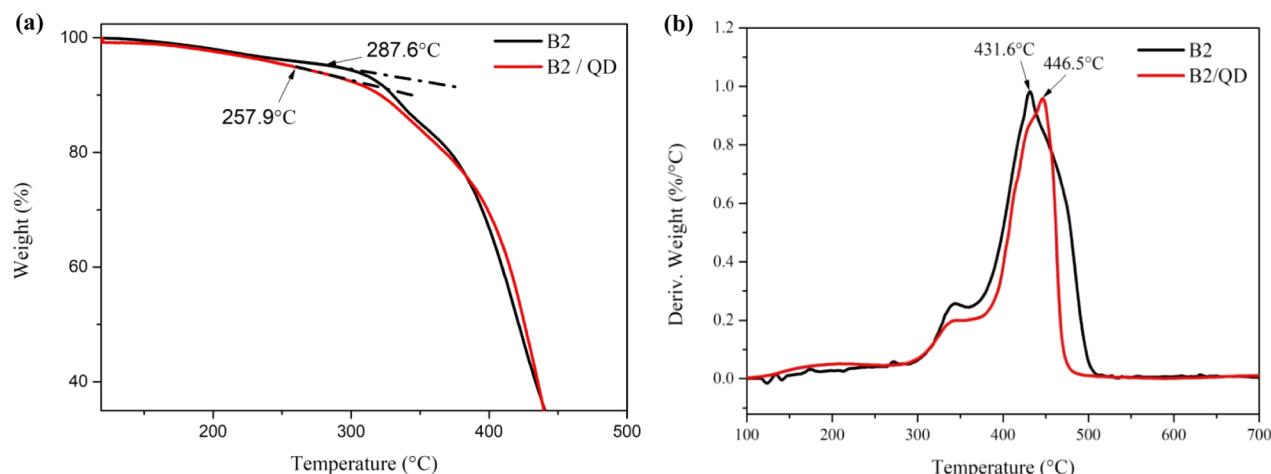


Figure 5. Green and red-mixed CdSe/ZnS (0.1 wt %) quantum dot–polymer hybrid light-emitting films: (a) TGA and (b) DTG analysis. B2: UV-cured polymer; B2/QD: quantum dot–polymer hybrid film.

absorption spectrum and the luminescence spectrum shows a single narrow Gaussian PL peak having a FWHM of less than 35 nm. This implies that the synthesized QD is uniform in size and shape, so it can be inferred that the chemical composition of these QDs is also uniform. This result is consistent with TEM results with uniform size and shape.

Quantum Dot–Polyacrylate Hybrid Light-Emitting Films. Figure 3 demonstrates the cross-sectional energy dispersive spectrometer (EDS) mapping of CdSe/ZnS (0.1 wt %) quantum dot–polymer hybrid light-emitting films. To identify the dispersibility of quantum dots in the polymer matrix, the cross-section of the QD–polymer hybrid light-emitting film was characterized by EDS. The elements of Zn, S, and Se are uniformly distributed in the polymer matrix, suggesting that the quantum dots are well-dispersed in the B2 polymer. But, the signal of Cd is less obvious, presumably because Cd has a higher bind energy.

Figure 4 shows a topographic atomic force microscopy (AFM) image and a three-dimensional surface profile of the CdSe/ZnS-B2 polymer nanocomposite film prepared by spin-coating and UV curing. In Figure 4a, the bright spots correspond to the QD particles and the dark areas correspond to the B2 polymer matrix. The examination of Figure 4a reveals that the spherical aggregates have a relatively uniform spot distribution due to the QD aggregates separated within the polymer domain.

The particle size distribution at about 33 nm corresponds to a QD cluster comprising several individual QDs (diameter 7–10 nm, see Figure 1a,b), indicating that the oleic acid (OA)-capped QDs tend to aggregate generating QD clusters, but these QDs are relatively uniformly distributed in the cured polymer matrix. In addition, some small hillocks are relatively uniformly distributed in the three-dimensional image of the nano-composite film as shown in Figure 4b, corresponding to an average roughness of about ~6 nm.

Figure 5 shows the results of thermal thermogravimetric analysis (TGA) and differential thermogravimetry (DTG). It can be seen from Figure 5a that the 5% decomposition temperature of the CdSe/ZnS QD–polymer hybrid film and the neat polymer film presented at 257.9 and 287.6 °C, respectively, indicative of the significant ligands of TOP/oleic acid-capped QDs. Our result is similar to the previous study of TGA followed by Fourier transform infrared analysis.²⁸ In Figure 5b, the maximum decomposition temperature (446.5 °C) of the CdSe/ZnS QD–polymer hybrid film was slightly higher than that (431.6 °C) of the neat polymer, reflecting that the involvement of inorganic CdSe/ZnS QDs in the polymer matrix would increase the maximum decomposition temperature. Consequently, the thermal stability can be improved in CdSe/ZnS QD–polymer hybrid films.

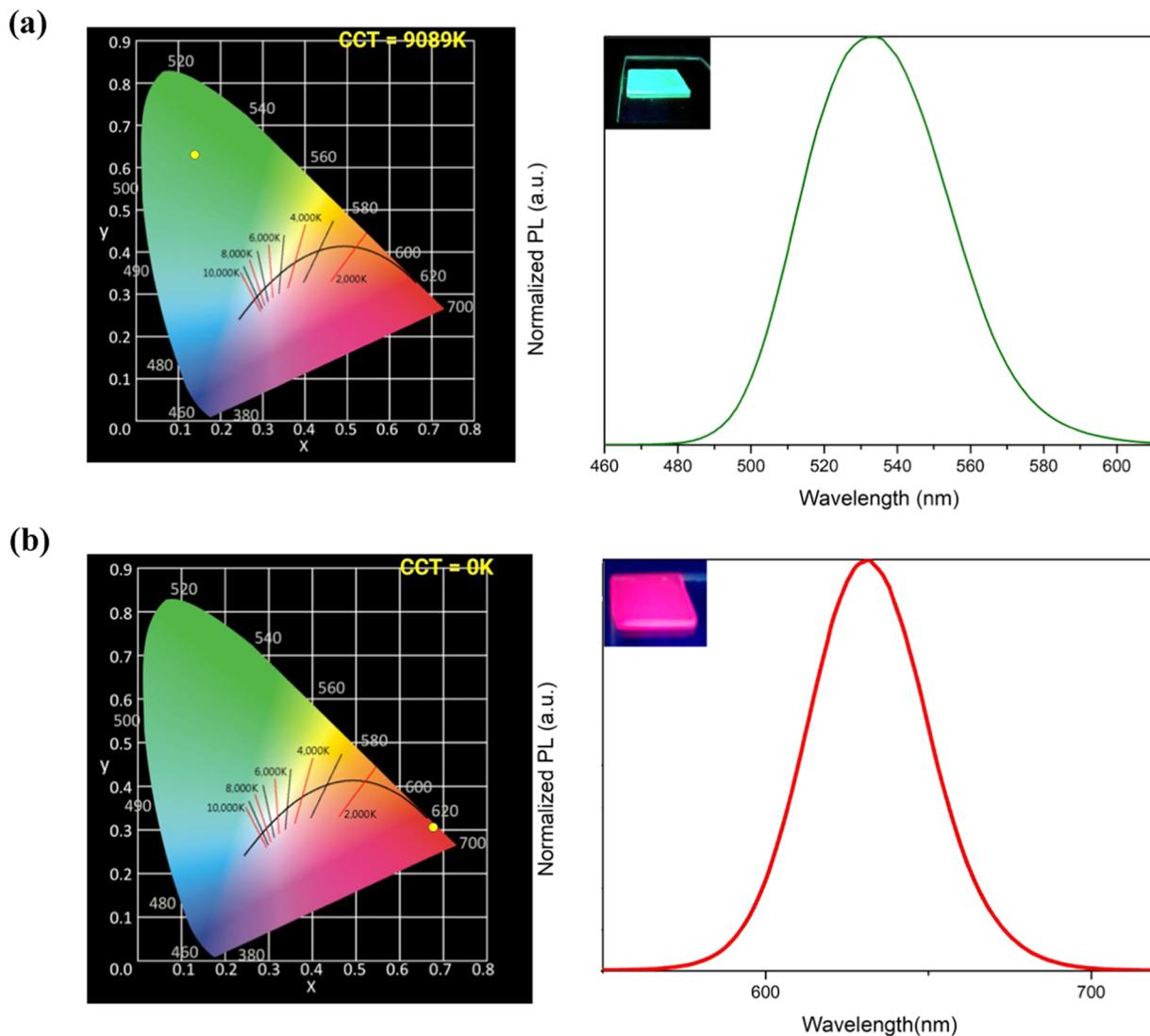


Figure 6. CIE coordinates and PL spectra of CdSe/ZnS QD–polymer hybrid light-emitting films (~1 mm thickness), emission wavelength: (a) 532 nm and (b) 628 nm.

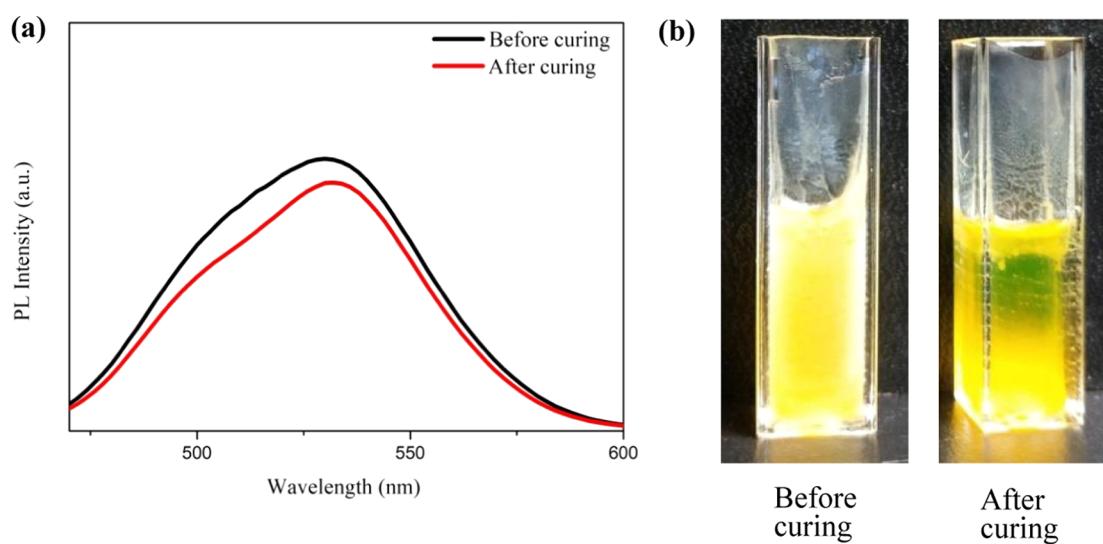


Figure 7. Green CdSe/ZnS (0.1 wt %) quantum dot–polymer hybrid light-emitting films. (a) PL spectra and (b) samples of before and after photopolymerization.

In this study, photopolymerization was used to rapidly prepare a smooth surface of QD–polymer hybrid light-emitting films. In order to increase compatibility, the functional groups of the oligomers in the above hybrid films should match well with the polarity of the ligands on quantum dots. Then, the photoinitiator was added to the mixture of quantum dots and oligomer and uniformly mixed. The above mixture was spin-coated on a glass substrate and then subjected to ultraviolet light irradiation. A single-color QD–polymer hybrid light-emitting film can be obtained using this photopolymerization. Figure 6 shows the CIE-1931 coordinates and PL spectra of the green and red quantum dot–polymer hybrid light-emitting films. It can be seen that the quantum dots are well-dispersed in the B2 polymer. This is evidenced by the fact that the emission wavelength (green at 532 nm and red at 628 nm, respectively) of QD–polymer hybrid films is almost the same as that of the quantum dots dispersed in toluene, which ensures that the quantum dots are well compatible with the B2 polymer leading to no suspicion on the emission wavelength shift in subsequent applications. The CIE-1931 coordinates of green and red QD–polymer hybrid films located at (0.13, 0.64) and (0.67, 0.32) corresponds to the wavelength of 532 and 628 nm, respectively.

In general, the PL emission intensity of quantum dots decreases with increasing temperature. Because heating makes the ligands peel off the surface of the quantum dot, resulting in agglomeration of the quantum dots, and thus reducing their luminous intensity. In addition, thermal energy also affects electronic transitions, especially the recombination of electron–holes, which in turn leads to a significant drop in the luminous intensity. This fluorescence heat quenching of quantum dots presents in a silicone package using the conventional thermal curing process.^{29–33} To reduce the above disadvantages of fluorescence heat quenching, we have tried to employ a photopolymerization process. In Figure 7, the emission intensity of green quantum dots in the B2 polymer matrix after photopolymerization retains about 90% intensity before photopolymerization. Compared with a silicone package using the conventional thermal curing process, this result fully demonstrates that the use of photopolymerization has a major advantage of emission stability over the thermal curing process. It can be explained that the preparation of the QD–polymer hybrid light-emitting film by the photopolymerization method not only has a fast process speed but can also reduce the damage to the materials of quantum dots. Red quantum dots have a similar result to that of green quantum dots.

Red and green quantum dots are added with an appropriate ratio to the mixture of oligomer, monomer, and photoinitiator. The well-mixed dispersion was spin-coated on the surface of the blue LED chip and subjected to ultraviolet light irradiation to complete a white light LED device. In lighting the blue chip, the emitted blue light excited the mixed QDs to emit green and red lights, whereas the blue light, green light, and red light are mixed together to obtain white light emitting LED (as shown in Figure 8). Figure 8 also shows the PL spectra and the CIE-1931 coordinate of the white LED. PL spectra exhibit blue, green, and red peaks corresponding to the blue chip, green QD, and red QD emission, respectively. The above three primary colors are mixed to obtain white light located at CIE-1931 coordinate of 0.3339 and 0.3192 in the present study.

We also investigate the variation of the color rendering index (CRI), color temperature (T_c), and light extraction efficiency of the white LEDs operated at different current densities. In Figure 9a, the value of the CRI increases with the increase in the

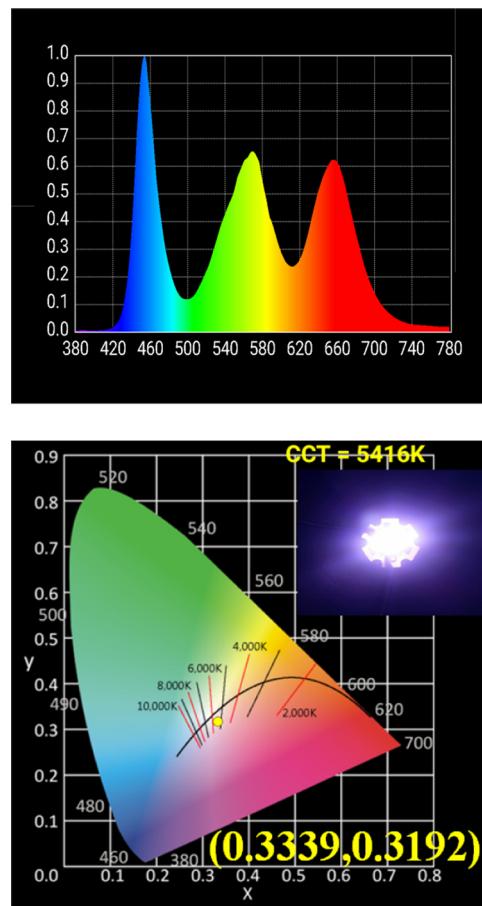


Figure 8. PL spectra and CIE coordinate of white light LED devices derived from red and green CdSe/ZnS QD–polymer hybrid films excited by a blue chip.

operating current density, because the increased operating current density results in an increase of the emission band width which eventually leads to an increase in the CRI value.⁴ Figure 9b shows the corresponding color temperature of the sample operating at different current densities, revealing that the value of T_c decreases with the increase in the operating current density from 14 500 (refer to 10 mA) to 5600 K (refer to 50 mA) corresponding clear sky and blazing sun at noon, respectively. Figure 9c shows the light extraction efficiency of the sample operating at different current densities, revealing that the efficiency reaches a maximum of 14% at a current density of 30 mA, whereas the overall value falls on average around 10–12%. This value is similar to other matrix materials (Scheme 1).

A traditional liquid crystal television using a white light-emitting diode (WLED) as a backlight is called an “LED-TV”, which uses a color filter to generate three colors of RGB light. Therefore, red and green quantum dots can be directly printed between the two poly(ethylene terephthalate) (PET) films to replace the role of the backlight on the panel. High adhesion of the quantum dot–polymer hybrid is required in the real application. The 3-(trimethoxysilyl)propyl methacrylate (TMSPMA) monomer having methoxysilyl groups is generally considered to enhance the adhesion on PET sheets. Furthermore, the light extraction efficiency of the quantum dot–polymer composite films would not be significantly influenced by the addition of TMSPMA lower than 10 wt %. In this work, the TMSPMA monomer was added into the

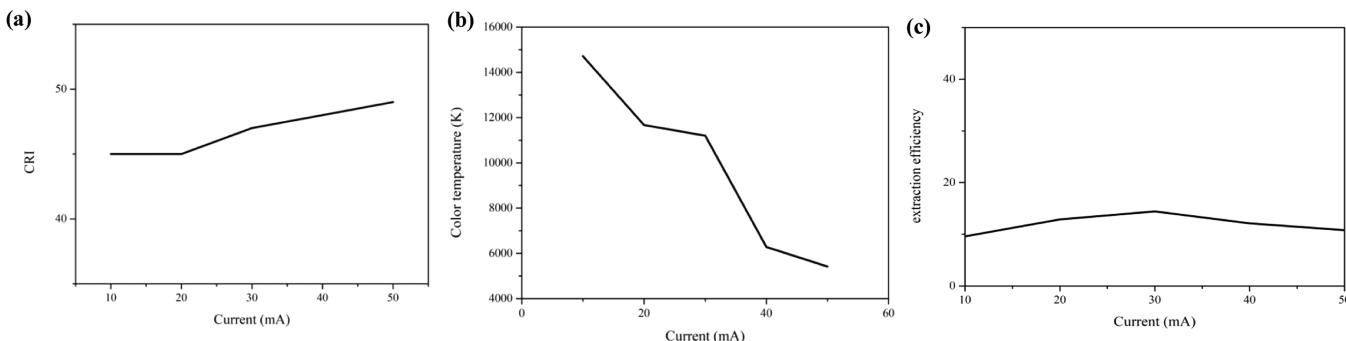
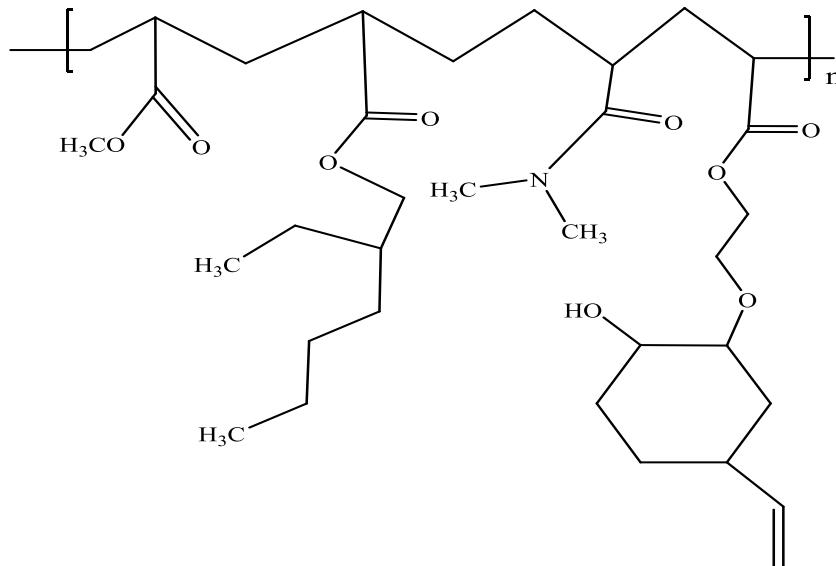


Figure 9. (a) Color rendering index (CRI), (b) color temperature (T_c), and (c) light extraction efficiency of white light LED devices derived from red and green CdSe/ZnS QD–polymer hybrid films at different current densities.

Scheme 1. Chemical Structure of the B2 Aliphatic Acrylic Acrylate Oligomer



mixture of CdSe/ZnS (0.1 wt %) quantum dot–B2 oligomer hybrid white light-emitting formulation to enhance adhesion between the two PET plastic substrates (2 cm × 2 cm) after photopolymerization. The pull-off strength was measured by a universal material testing machine to obtain the relationship between the TMSPMA content and pull-off strength. As shown in Figure 10, it can be observed that the pull-off strength increases with the increasing TMSPMA addition to reach a maximum value of 8.9 N/cm² at 5 wt % TMSPMA. The enhancement is just 43.5% higher compared to that (6.2 N/cm²) without the addition of TMSPMA. This result arises from the hydrolysis of Si–(OCH₃)₃ forming Si–(OH)₃ as shown in Scheme 2,I, the dehydrated condensation between Si–OH and hydrogen bonding between Si–OH and –OH groups on the surface of the PET substrate is as shown in Scheme 2,II. These sequence reactions can be expressed in Scheme 2.³⁴

However, the amount of TMSPMA added more than 5 wt % TMSPMA, the pull-off strength does not keep rising but decreases from 8.9 to 7.25 N/cm² at 10 wt % TMSPMA. The enhancement is just 16.9% higher compared to that (6.2 N/cm²) without the addition of TMSPMA. This is because TMSPMA is a monofunctional monomer. When the addition of TMSPMA is increased higher than 5 wt %, the polymer chains formed by photopolymerization is not long as that of 5 wt % TMSPMA addition. It is worth noting that the addition of 5 wt % TMSPMA

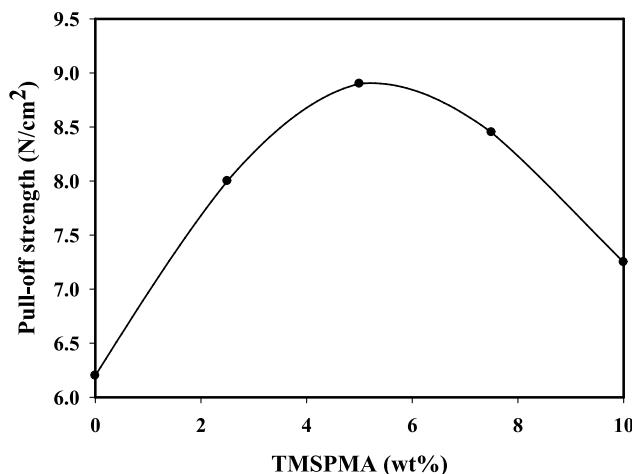
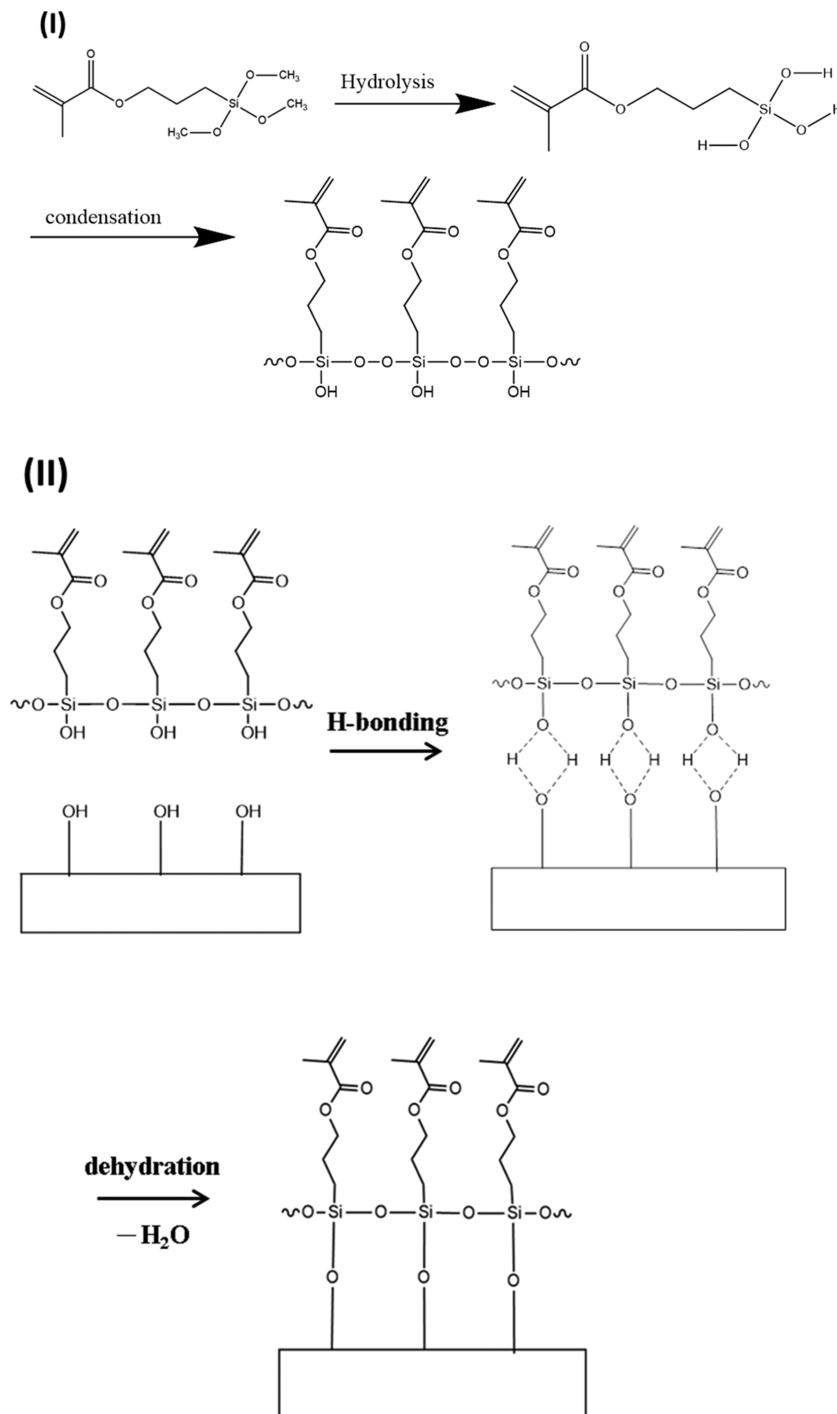


Figure 10. Plot of pull-off strength (adhesion) against 3-(trimethoxysilyl)propyl methacrylate monomer addition in the CdSe/ZnS (0.1 wt %) quantum dot–polymer hybrid white light-emitting layer between the two plasma-pretreated PET films.

has no significant effect on the transparency of the hybrid film and the light extraction efficiency of white LEDs.

Scheme 2. Sequence Reactions between TMSPMA with the Surface of Plasma-Treated PET Films^a

^a(I) The hydrolysis of trimethoxysilyl groups and (II) dehydrated condensation between Si—OH and —OH groups on the surface of the PET substrate.

CONCLUSIONS

In this study, oleic acid-capped CdSe/ZnS core–shell QDs were incorporated into an aliphatic acrylate polymer by the solution mixing method, followed by photopolymerization. The small amounts of QD clusters were uniformly dispersed in the polymer matrix. The prepared nanocomposite consisted of 0.1 wt % of CdSe/ZnS QDs showing stable optical properties, achieving high white LED performance of 7976 lm/m² under a 30 mA working current. The light emission efficiency, CRI, and

the color temperature of 14%, 47, and 11 204 K, were obtained at this current. Meanwhile, the incorporation of a small amount of QDs improved the thermal stability of the polymer matrix. These results are important for the practical application of electroluminescent LED devices using the QD package.

EXPERIMENTAL SECTION

Chemicals. Cadmium oxide (CdO), tri-*n*-octylphosphine (TOP, purity >97%), and 3-(trimethoxysilyl)propyl methacry-

late were purchased from Sigma-Aldrich. Octadecene (ODE, Acros), oleic acid (OA, Showa), selenium (Se, Alfa Aesar), zinc acetate (Riedel-de Haën), and sulfur (purity >99%, Riedel-de Haën) were of reagent grade. Analytic-grade solvents of toluene and ethanol were purchased from Echo. A sample of commercially available acrylic acrylate oligomer (trade mark, B2) was kindly provided by Hopax Company in Taiwan to prepare the QD composites. Diphenyl(2,4,6-trimethylbenzoyl)-phosphine oxide (TPO, Darocur), 1-hydroxy-cyclohexyl-phenyl-ketone (Irgacure 184, Ciba), and 2-methyl-1-[4-(methylthio)phenyl]-2-(4-morpholinyl)-1-propanone (Irgacure 907, Ciba) were used as photoinitiators. All chemicals were used as received without further purification.

Single-Step Synthesis of CdSe/ZnS Quantum Dots with Chemical Composition Gradients. The single-step synthesis method, a typical synthetic procedure to synthesize green QDs,^{25,26} was employed to synthesize CdSe/ZnS quantum dots in this work. In brief, 0.4 mmol of cadmium oxide, 4 mmol of zinc acetate, and 4.971 g (17.6 mmol) of oleic acid (OA) were placed in a 250 mL three-necked flask. The mixture was heated to 150 °C, degassed 0.1 Torr pressure to remove water for 30 min, purged with N₂ gas, and heated to 300 °C and 10 mL of 1-octadecene (ODE) was injected into the reacted mixture forming a clear solution of Cd(OA)₂ and Zn(OA)₂. At 300 °C, 0.4 mmol of selenium and 4 mmol of sulfur powder were dissolved in 3 mL of trioctylphosphine and were rapidly injected into the above reactor. The reaction was set at 300 °C for 10 min to promote the growth of CdSe/ZnS core-shell QDs and the reactor was cooled to room temperature to stop the reaction. These QDs were further purified by the addition of toluene (20 mL) and excess ethanol three times; they were finally redispersed in toluene.

To synthesize red QDs,²⁷ 1 mmol of cadmium oxide, 4 mmol of zinc acetate, and 5 mL of oleic acid were placed in a 250 mL three-necked flask. The mixture was heated to 150 °C, degassed 0.1 Torr pressure to remove water for 30 min, purged with N₂ gas, and heated to 300 °C and 15 mL of 1-octadecene (ODE) was injected into the reacted mixture forming a clear solution of Cd(OA)₂ and Zn(OA)₂. At 300 °C, 0.4 mL of 1 M selenium-dissolved trioctylphosphine solution was added to the above mixture, 4 mmol of sulfur powder was dissolved in 4 mL of trioctylphosphine and were injected into the reactor in 30 s. The reaction was set at 300 °C for 10 min to promote the growth of CdSe/ZnS core-shell QDs, and the reactor was cooled to room temperature to stop the reaction. These QDs were further purified by the addition of toluene (20 mL) and excess ethanol three times; they were finally redispersed in toluene.

Preparation of QD-Polyacrylate Hybrid Light-Emitting Films. A mixed photoinitiator (5 wt % for total mixture, TPO/Irgacure 184/Irgacure 907 = 2:2:1, by weight ratio) was added to the mixture of quantum dots, B2 oligomer (**Scheme 1**, molecular distribution refers to **Supporting Information**), and monomers. The mixture was uniformly mixed and then spin-coated on the glass substrate. The single-color organic light-emitting film was obtained by photopolymerization using 36 W UV light for 1.5 min. The thickness of the organic light-emitting film was controlled at about 1 mm by adjusting the speed of spin-coating.

Fabrication of White LEDs. Red and green quantum dots were blended with an appropriate ratio and added to a mixture of oligomer, monomer, and photoinitiator. This mixture was stirred to obtain a uniform dispersion of QDs and dropped on the surface of a blue LED chip (emitting wavelength at 460 nm)

which was then photopolymerized through irradiation for 90 s on 36 WLED-bulb UV light. When the switch of the QD-hybrid film covered blue chip was turned on, a white light-emitting LED was obtained and the PL spectrum and CIE-1931 coordinates were measured.

Characterization and Measurements. Particle shape and size of the quantum dots were estimated by using a transmission electron microscope (TEM, JEM-1230, JEOL Ltd., Japan) using an acceleration voltage of 80 kV. The film surface morphology was observed on a field emission scanning electron microscope (FESEM, Hitachi, S4800). An energy dispersive spectrometer (EDS, Genesis XM 4i Energy Dispersive X-ray Analysis System, FEI) was used to observe elemental distribution of cross-section in QD-polymer hybrid films, confirming the dispersion of QDs in the polymer matrix. Atomic force microscopy (AFM) images were taken for samples on a NT-MDT Solver PRO-M AFM operated at 200 kV. The crystal structures of CdSe-QDs were measured using an X-ray diffractometer (Bruker D8 ADVANCE X) with Cu radiation. UV-vis absorption and transmittance spectra were measured using a Perkin-Elmer Lambda UV-vis spectrophotometer using toluene as a background. The as-prepared quantum dots were diluted using toluene and placed in a quartz cell for measurement. The as-prepared quantum dots were diluted using toluene and placed in a quartz cell, and the prepared organic light-emitting film was placed on a solid stand. Photoluminescence (PL) spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer exciting at a wavelength of 440 nm to confirm the peak position of the fluorescence emission spectrum of the material. Thermogravimetric analysis (TGA) was measured on a thermogravimetric analyzer (SDT-Q600, TA) scanning from 25 to 800 °C. The analysis was performed at initial temperatures of 25 and 120 °C for 10 min to remove water at a heating rate of 20 °C/min. The CIE coordinates of a white LED device and QD-hybrid light-emitting film were determined on a lighting spectrometer (Model 14-1, Lighting Passport) using a UV light source excited at a wavelength of 365 nm. The fabricated white LEDs were employed to measure the color rendering index (CRI) and color temperature at different current densities from 10 to 50 mA. The luminous flux was measured by different current densities of 10–50 mA for the fabricated white LEDs and the original blue LED chip, respectively. The light extraction efficiency was calculated using the ratio of the above two luminous flux.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acsomega.8b03241](https://doi.org/10.1021/acsomega.8b03241).

Gel permeation chromatography for B2 aliphatic acrylic acrylate; GPC results of B2 aliphatic acrylic acrylate; CdSe/ZnS QDs in a mixture of B2 oligomer, TMSPMA monomer, and photoinitiators; red and green CdSe/ZnS QD/polymer-based WLED ([PDF](#))

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Notes

The authors declare no competing financial interest.

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