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ARTICLE

Fabrication of wafer-scale free-standing quantum dot/polymer nanohybrid films for white-light-emitting diodes using electrospray method

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Wafer-scale free-standing quantum dot (QD)/polymer nanohybrid (NHB) based down-conversion (DC) phosphor films for remote-type white-light-emitting diodes (W-LEDs) are developed. Organic-soluble and nontoxic dodecanethiol-capped $AgIn_5S_8$/ZnS QDs and a thermoplastic polymer, poly(methyl methacrylate) (PMMA), are used as a DC material and a matrix respectively. The NHB based DC films are successfully fabricated by electrospray (e-spray) method and the extraordinarily high concentration of QDs are able to be loaded in the resulting e-sprayed NHB films. The wafer-scale free-standing NHB films are also achieved by using a delamination method with which the e-sprayed films on a thin interlayer of a water-soluble polymer are detached from the substrates. Finally, the free-standing e-sprayed QD/polymer NHB films are successfully applied on top of conventional blue LED for remote-type W-LEDs. The W-LED shows the luminous efficacy of 49 lm/W and color rendering index (CRI) of 64 with an applied current of 60 mA.

Introduction

White-light-emitting diodes (W-LEDs) are an attractive technology for next-generation lighting sources with distinct advantages such as a high luminous efficacy, low power consumption, long lifetime, and slim size. For these reasons, W-LEDs can be used in many types of lighting, signal, and display applications.[1,2] In particular, the commercialization of W-LEDs as light sources replacing incandescent and/or fluorescent bulbs to reduce energy consumption and environmental pollution is the most essential target. Even with current technology, solid-state lighting with W-LEDs can outperform traditional incandescent bulbs in terms of cost and energy, and further development of materials and processing techniques to enhance their efficiency and lifetime will soon lead to their commercialization. Recently, the use of conventional blue-emitting (or UV-emitting) LED chips combined with yellow-emitting down-conversion (DC) phosphor layers has become the most attractive approach for W-LED applications, because it uses a simple structure that is applicable for mass production.[3,4] Therefore, the development of high-performance DC layers (with high luminous efficacy and quality) is a critical issue in the field of W-LEDs, and great efforts have been made to prepare effective DC phosphor layers.

Quantum dots (QDs) have been considered as emerging DC phosphor materials for W-LEDs because they exhibit high luminescence quantum yields (QYs), broad absorption spectra, tunable emission, few scattering effects, and high environmental stability.[5-7] Attempts to utilize the QDs as a direct replacement for conventional rare-earth-based DC

materials[4] or as emission-modifying agents[8] have recently expanded very rapidly. There has also been a report that QD-based phosphors are superior both photometrically and electrically to conventional phosphors when state-of-the-art QDs are used.[9] The progress of wet-chemistry-adaptable synthetic methods to yield high-quality colloidal QDs in large scales could further support the commercial applicability of QDs. These colloidal QD-based DC materials for W-LEDs were typically prepared by dispersing the QDs in other supporting matrixes such as polymers. The host polymers can provide mechanical integrity for device applications and can often protect the QDs from heating and photodegradation. There has even been a report that the luminescent properties of the QD layers are improved if the QDs are properly embedded in an optically transparent polymer matrix.[10]

In DC phosphors based on QD/polymer hybrids, the effective dispersion of QDs in the polymer matrixes is the most critical factor determining their performance. The aggregation of QDs can significantly lower their QY through luminescence quenching or light-scattering.[11] However, the complete dispersion of QDs in the supporting matrixes has been challenging. The QD solutions typically only can afford colloidal stability by the help of ligand molecules tethered on the surfaces of the QDs. Upon the addition of polymers, depletion flocculation occurs easily because the miscibility between QDs (or the surface ligands) and polymers is usually not high.[7]The practical dispersion of QDs has been obtained only under particular conditions, and the loading levels of QDs in the polymer matrixes has been limited to <10 %.[12-14] The nature of the polymer, the surface ligands of the QDs, and their solubility in the desired solvents govern the degree of

flocculation, and various approaches to enhance the dispersibility of the QD in the polymer matrix have been reported.[14-16] The complete dispersion of QDs in polymers at high loading levels will enable the development of highly efficient DC phosphors for W-LEDs. For this reason, the development of effective strategies that can alleviate the flocculation problem will provide an opportunity for the utilization of the hybrids for various optoelectronic devices including W-LEDs.

Herein, we introduce a novel strategy for fabricating free-standing films of QD/polymer nanohybrids (NHBs) that can be used as high-performance DC phosphors for W-LEDs. To prepare the NHBs, dodecanethiol (DDT)-capped $AgIn_5S_8$/ZnS QDs (QY: ~60 %)[17] were mixed with a common thermoplastic polymer, poly(methyl methacrylate) (PMMA), in organic media at a range of concentrations (QD/PMMA ratios from 10/100 to 150/100, w/w). From these dispersions, we successfully produced NHB-DC phosphor films containing well-dispersed QDs in the polymer at very high concentrations (~50 wt%) using the electrospray (e-spray) method. The e-spray method is a unique and crucial technique that enables the preparation of high QD loaded NHB films because the film deposition occurred using highly diluted colloidal solutions of the NHBs, in which the flocculation of QDs can be minimized. The QDs could be uniformly dispersed in the polymer matrixes at concentrations up to 100 parts QDs per 100 parts PMMA by weight (i.e., 50 wt% QDs in PMMA) in the resulting e-sprayed films, as confirmed by transmission electron microscopy (TEM) images and optical analysis results. Furthermore, nearly scattering-free large-area (10 cm x 10 cm) free-standing NHB films were readily fabricated by a delamination method, with which the e-sprayed films were detached from a water-soluble polymer interlayer. W-LEDs combining the e-sprayed NHB DC phosphor layers and an InGaN blue LED showed luminous efficacies of 49 lm/W with a color rendering index (CRI) of 64 at a forward current of 60 mA.
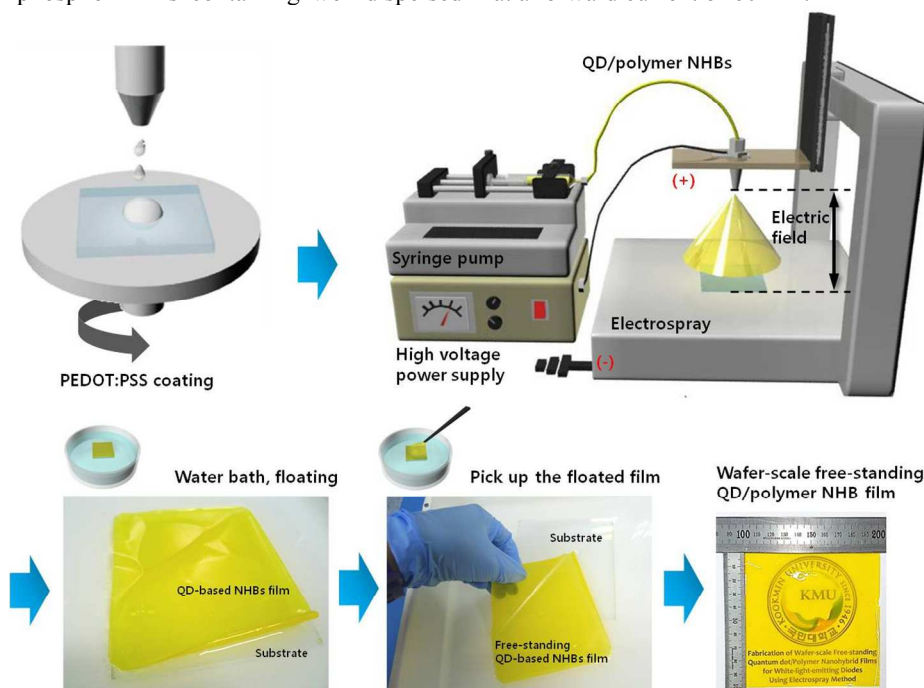

Figure 1. Schematic illustration of fabrication process for wafer-scale free-standing QD/polymer-NHB based DC phosphor films.

Experimental

Preparation of free-standing QD/polymer hybrid films

To synthesize the $AgIn_5S_8$/ZnS-QDs, silver nitrate ($AgNO_3$, 0.10 mmol), indium(III) acetylacetonate (In(acac)$_3$, 0.50 mmol), oleic acid (OA, 1.50 mmol), and 1-octadecene (ODE, 25 mmol) were loaded in a three-necked round bottom flask and purged with N_2 gas for 20 minutes. After the N_2 gas purging, the reaction solution was heated and DDT (4.0 mmol) was injected into the reaction solution at 90℃. Next, sulfur (S, 0.8 mmol) was dissolved in oleylamine (OLA, 4.0 mmol) and quickly injected into to the reaction solution at 120℃. After 3 minutes, the shell precursors (zinc stearate (0.4 mmol) and S (0.4 mmol) dissolved in trioctylphosphine (TOP, 4 mmol)) were injected at 180℃ and reacted for 2 hours. The final solution was purified by centrifugation and dissolved in toluene.[17] Detailed information on the materials and the characteristics of the $AgIn_5S_8$/ZnS-QDs are provided in Figure S1 For the preparation of QD/polymer NHB solutions with a range of concentrations (QD/PMMA ratios from 10/100 to 150/100 (w/w)), $AgIn_5S_8$/ZnS QDs were added into a 1 wt% PMMA solution in a mixed organic solvent (dimethyl-formamide/toluene, 33.3 vol%).

Indium tin oxide (ITO)-coated glass was cleaned and treated under UV irradiation and ozone for 20 min, and polystyrene sulfonic acid, PEDOT/PSS (Baytron AI 4083, Bayer), was mixed with the same volume of methanol. The PEDOT/PSS solution was spin-coated at 4000 rpm for 35 s on the ITO/glass. A 30 ml syringe containing the well-dispersed QD/polymer solution was loaded into a syringe pump and connected to a high-voltage power supply (205B, Bertan). The QD/polymer solution was injected at 40–60 µL•min^{-1}. For e-

spraying, an electric field of 14–15 kV•cm^{-1} was applied between the PEDOT/PSS-coated ITO/glass substrate and the needle, which were held at a distance of 20 cm. After the e-spraying, the QD/polymer NHB film was treated with chloroform vapor for 2 s. To fabricate free-standing films, the e-sprayed QD/polymer NHB film on the substrate was immersed in distilled water to separate the film from the substrate by dissolving the PEDOT/PSS. After the e-sprayed QD/polymer NHB film floated to the water surface, the film was scooped with a mesh or picked up with tweezers.

Fabrication of W-LEDs

For the fabrication of W-LEDs, the free-standing e-sprayed QD/polymer NHB film was placed and fixed on the blue LED package with polymer glue. The InGaN blue LED (λ_{max} = 445 nm, Dongbu LED, Inc.) was used as an excitation source for the QD/polymer NHB film and as a blue light source.

Characterization of free-standing QD/polymer NHB films and W-LEDs

The morphologies, lattice structures, and sizes of the samples were analyzed by making transmission electron microscopy (TEM) (JEM-4010, 400 kV) observations. The thickness of the films was measured using field-emission scanning electron microscopy (SEM, JSM-7401F, JEOL) to measure the cross section of the film. The transmittance of the films was observed by a UV-visible spectrophotometer (S-3100, SCINCO). The optical properties of the films were measured using a He–Cd laser, Xe-lamp, and spectrophotometer (Darsa, PSI Co. Ltd). The emission spectra of the forward emissions of the W-LEDs were measured in an integrated sphere using a spectrophotometer (Darsapro-5000, PSI Co. Ltd) under an applied current of 60 mA.

Results and Discussion

Figure 1 shows a schematic illustration of the fabrication process for the free-standing QD/polymer NHB based DC phosphor films. First, the QD/polymer NHB films were prepared by e-spray method onto various substrates on which PEDOT:PSS, a popular water processable polymer, interlayers are coated. The e-spray method is a simple and efficient film deposition technique that produces films with low thickness variations, reducing material consumption.[18,19] Using the e-spray technique, our group have successfully fabricated films of various nanomaterials such as carbon nanotubes,[18] polymers,[19] metal oxides,[20,21] and grapheme.[22] In those studies, the e-sprayed films exhibited superior properties as the active and/or electrode materials for organic photovoltaics or dye-sensitized solar cells, as compared to films obtained using other solution-based deposition methods such as spin-coating, doctor blading, or drop casting. The e-spray technique has unique advantages over these other deposition methods for nanomaterials and/or nanohybrids for the following reasons. (i) The deposition process is performed using a highly diluted solution (>10 times more dilute than that in other solution methods) of nanomaterials; therefore, the dispersion of nanomaterials that would therwise be easily flocculated in the solution can be considerably improved. (ii) The atomization is induced by an electric field between the solution and the depositing substrates, so the spraying mist particles have identical charges and therefore self-disperse in the deposition space. As a result, the aggregation of nanomaterials before the deposition is minimized. For successful e-spray deposition, a homogeneous

dispersion of both the QDs and the polymer in the solution is the most important prerequisite. However, the uniform dispersion of QDs in polymer solutions without aggregation has been a very challenging task because of the poor compatibility between QD and polymers. The QDs have often aggregated in the resulting NHBs, impairing their quantum efficiency and transparency. Therefore, there have been significant efforts to enhance the miscibility between QDs and polymers through surface modification of QDs by ligand exchange with compatible molecules[15] or in situ polymerization from the monomers within the solutions.[16] Nevertheless, flocculation of QDs often occurred in the solutions when the polymer matrixes were added in concentrations appropriate for common coating methods such as spin-coating or doctor blading. In this study, we used organic-soluble DDT-capped AgIn$_5$S$_8$/ZnS-QDs as the DC materials (detailed synthetic procedures are in our previous report),[17] because they are nontoxic possessing broad-spectrum emissions, and PMMA was chosen as the matrix polymer because it is relatively transparent and has reasonable mechanical strength along with a high compatibility with DDT. The QD/PMMA solutions in the mixture of toluene and dimethylformamide (DMF) (2/1 by vol/vol) were used for the e-spray. The Hildebrand solubility parameter (δ), which is a general criterion to determining miscibility among materials, is 19.0 MPa$^{1/2}$ for PMMA, while those for DDT and toluene are 17 and 18.3 MPa$^{1/2}$, respectively. This fact indicates that all components for the hybridization are highly compatible with one another. Homogeneous QD/PMMA-NHB solutions could be obtained in toluene at a range of concentrations, and the QD/PMMA ratio (w/w) could be easily controlled from 10/100 to 150/100. For the sake of e-spraying the NHB solution, DMF was added because the high polarity of DMF helps to accommodate sufficient charges for the stable droplets. In this solvent system (toluene/DMF; 2/1 by vol/vol), the stability of the NHB solutions was successfully maintained although the value for DMF was 24.7 MPa$^{1/2}$.
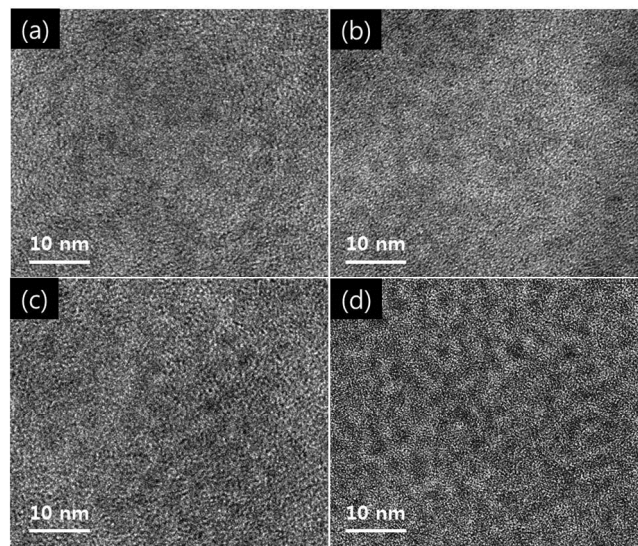

Figure 2. HR-TEM images of NHB films containing different QD loadings: (a) 10 parts, (b) 75 parts, (c) 100 parts, and (d) 150 parts QDs per 100 parts PMMA by weight.

Figure 2 shows the TEM images of the NHB films containing various QD loadings. The thickness of the films for the TEM analysis was 100 ~ 150 nm. In the images, the increased numbers of QD particles in the PMMA matrix were identified at higher QD loaded NHBs (from Figure 2(a) to 2(d)). The QDs were reasonably well-dispersed in the PMMA matrix without significant aggregation up to 100 parts of QD loading. The size of the individual QD was ~3 nm, which is in good accordance with the values from optical analysis (optical band-gap). Because the thickness of the NHB films were 100 ~ 150 nm, further obtaining clearer TEM images of NHB films had a limitation. In order to further reveal the aggregation of QDs in the NHB films, the optical properties of the NHBs were performed.

The transmittance spectra and photoluminescence (PL) spectra of NHB films with various QD loadings are shown in Figure 3. The SEM images of NHB films were shown in Figure S2. For the PL intensity analysis result, we normalized the film thickness as 1.2 μm which we thought intermediate thickness.

The transmittance decreased almost linearly as the QD loading increased, which indicates the absence of significant aggregation up to a QD:PMMA of 1:1 by weight. When 150 parts of QDs were loaded per 100 parts PMMA by weight, the transmittance dropped considerably, implying QD aggregation. Figure 3(b) and Figure 3(c) showed that the PL intensity of the NHB films was also enhanced as the QD loading increased. In particular, it increased nearly linearly up to 100 parts of QDs per 100 parts PMMA by weight (QD:PMMA = 1:1 by weight), then decreased at a QD loading of 150 parts per 100 parts PMMA, which confirms that there is no discernible QD aggregation in the NHB films up to 50 wt% QDs. The increased numbers of QDs in PMMA matrix were identified at higher QD loaded NHBs, and the aggregation-free dispersion of QDs in PMMA up to 50 wt% was confirmed in accordance with the

optical characterizations. Because of their high transmittance (88 % at 500 nm) and strong PL intensity, the NHB films containing 75 parts of QDs per 100 parts PMMA were chosen for further studies on the properties as DC phosphor films.

Based on the aforementioned analysis, we confirmed the NHB films in which the QDs are uniformly dispersed in the PMMA matrix at a high concentration (50 wt% QDs in the NHBs) using the e-spray method. In this work, the QD concentrations of the NHB films are extraordinarily high compared to those in other reported QD/polymer composites. To the best of our knowledge, the QD loading in typical QD/polymer composite phosphor materials has been <10 wt%,[12-15] and the highest reported loading level obtained by optimizing the compatibility between QD and matrix polymers was 18 %.[5] In those reports, further increases in the QD concentration induced significant aggregation because of the limited compatibility between the inorganic QDs and the organic polymers. However, in our NHBs, further increases in QD loading were successfully achieved with the help of the e-spray method.

In order to further confirm the uniqueness of the e-spray method, we fabricated identical NHB films using a conventional spin-coating method. Figure S3 in SI shows the schematic description of the fabrication process of the NHB films by spin-coating method. As shown in Figure S3(b) and S3(c), the NHB films by spin-coating displayed the highest PL intensity at 50 parts of QD containing NHBs that were a 1/2 loading level compared to e-sprayed NHB films. This result confirmed the more facilitated QD aggregation in the NHB films by conventional spin-coating method. Furthermore, the overall PL intensity was much higher in the NHB films that were e-spray coated than those that were spin-coated (Figure S4). This result also revealed that there was no significant QD degradation during the e-spray.
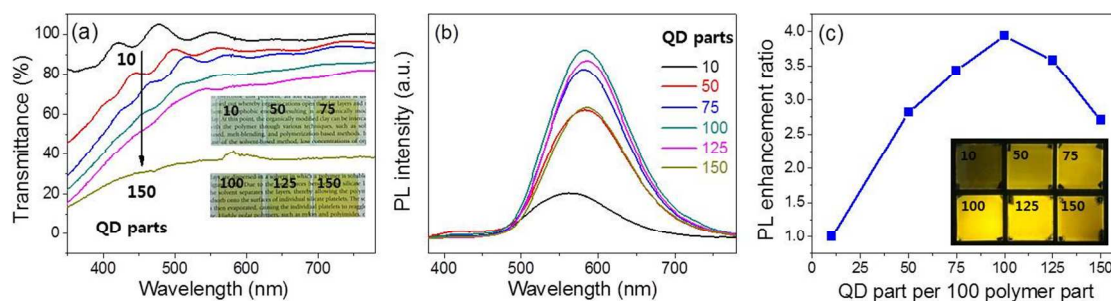

Figure 3. (a) Transmittance spectra of QD/PMMA NHB films with different concentrations. The inset photograph is of transparent QD/PMMA NHB films coated on ITO substrates. (b) PL spectra and (c) PL enhancement ratio of QD/PMMA NHB films as a function of QD part per 100 polymer part. The inset photograph is of yellow-emitting films under UV irradiation.
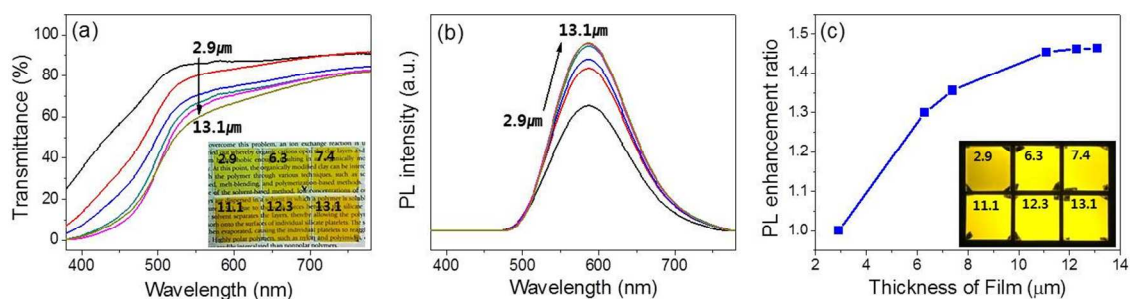
Figure 4. (a) Transmittance spectra of QD/PMMA NHB films with different thicknesses. The inset photograph is of transparent QD/PMMA NHB films coated on ITO substrates. (b) PL spectra and (c) PL enhancement ratio of QD/PMMA NHB films with different thicknesses. The inset photograph is of yellow-emitting films under UV irradiation.

The optical properties of the high QD loaded e-sprayed NHB films (75 parts of QD per 100 parts of PMMA) with respect to thicknesses are shown in Figure 4. The thickness of the DC phosphor films plays a key role in the resulting chromatic coordination and luminous efficacy, because the degree of DC will be altered by the thickness. E-sprayed NHB films with thicknesses ranging from 2.9 to 13.1 μm were readily prepared by changing the e-spraying duration. The films had extremely low thickness variations, as shown in the cross-sectional SEM images (see Figure 4 and Figure S5). In the range of thicknesses used in this study, the general trend (transmittance decrease with PL enhancement) was observed as the films became thicker, which indicates the manipulation capability of the figures of merit for energy efficiency and vision performance, such as the luminous efficacy (lm/W), correlated color temperature (CCT), and color rendering index (CRI).

Wafer-scale free-standing NHB films were fabricated using a delamination method (Figure 1). During this process, an e-sprayed NHB film that were deposited on a thin interlayer of a water processable polymer, PEDOT:PSS, coated on a glass plate was floated on water, and the NHB film was readily delaminated from the substrate by dissolving the interlayer. The uniformity of the NHB films was also confirmed by PL measurement at various areas. The PL intensities were almost identical regardless of the measurement locations of the films (Figure 5).The uniformity of the wafer-scale free-standing NHB films was revealed by performing cross-sectional FE-SEM

measurement at various areas. The thickness of the NHB films at the 9 different areas showed almost constant thickness (Figure 5 and Figure S6). These two results confirm that the free-standing wafer-scale NHB films were uniform in terms of thickness and light conversion capability. Our free-standing NHB films have several desirable properties as DC phosphor layers for W-LEDs. First, we used AgIn$_5$S$_8$/ZnS QDs, which are nontoxic and exhibit well-balanced broad-spectrum emission because of the donor-acceptor recombination that spans the majority of visible spectrum range. Previously, we reported the synthesis of stoichiometric cubic spinel AgIn$_5$S$_8$/ZnS QDs.[17] These QDs showed high QYs with broad emission spectra, which are preferential characteristics to realize the DC phosphor for W-LEDs. This broad emission can produce CRI values better than those of other conventional QDs such as CdSe/ZnS or CdTe/ZnS (FWHM > 30 nm) QDs, which have narrow emission peaks. This allows the complexity of the QD/polymer NHB-type DC phosphor layers to be reduced, simplifying fabrication process, because efficient DC can be achieved using just a single component. Second, the effective dispersion of a high concentration of QDs in the polymer matrix can offer an opportunity to reduce the required DC layer thickness to achieve desired colors. Third, the free-standing NHB thin films can be used in devices with various geometries. They are especially ideal for LED devices containing remote-type phosphor layers (discussed further in later sections), which exhibit superior properties in terms of thermal dissipation and reduced back-scattering compared to conventional dispensing-type devices.[23,24]
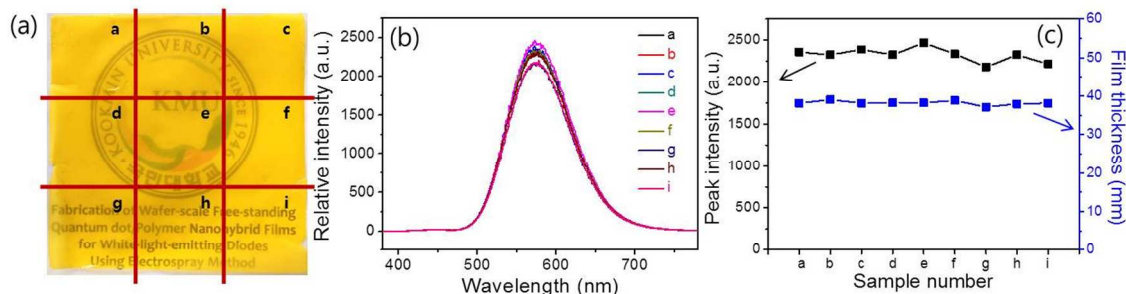

Figure 5. The free-standing films were divided into 9 pieces (a) a photograph, (b) the PL spectrum of each piece and (c) the PL intensity and film thickness of each piece.

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Finally, the performance of the free-standing NHB based DC phosphor films were examined by fabricating W-LEDs using a commercial blue LED source. Figure 6(a) shows the electroluminescence (EL) emission spectra of the W-LEDs that used the free-standing NHB-based DC phosphor layers of various thicknesses. As the thicknesses of the NHB films increased, the intensity of the blue emission decreased and that of the yellow-orange emission increased. Figure S7 shows cross-sectional SEM images of the QD/PMMA NHB films used in the remote-type W-LEDs. The CIE (Commission International de l'Eclairage) chromaticity coordinates of the EL spectra of the W-LEDs containing our NHB-based DC layers are shown in Figure 6(b). As the thickness of the QD/PMMA-NHB films increased, the color approached a more orange-yellow region because of the enhanced contribution of the DC effect from the $AgIn_5S_8/ZnS$ QDs. A relatively wide range of colors could be obtained by changing the thickness of the NHB film based on the lever rule. In order to evaluate the performance of the W-LEDs, it is necessary to assess the figures of merit for energy efficiency and vision performance (luminous efficacy, CCT, CRI). To the best of our knowledge, only a few publications report the figures of merit for the vision performance of W-LEDs with remote-type QD films. Herein, we investigate the measurable and meaningful figures of merit of our e-sprayed $AgIn_5S_8/ZnS/PMMA$ NHB free-standing films to assess their practical applicability as remote-type DC films for W-LEDs. The efficient PL properties of the highly dispersed QDs in the free-standing NHB films indicate their potential as high-performance DC layers. Table 1 shows the figures of merit (the chromaticity coordinates (CIEx, CIEy), the luminous efficacy, CCT, and CRI) of the remote-type W-LEDs with QD/polymer NHB films of different thicknesses. The results obtained for the W-LEDs indicate that simple mixing between the blue emission from the blue LED and the yellow-orange emission from the $AgIn_5S_8/ZnS$ QDs provides an opportunity to obtain any type of white light in the 7000–3000 K CCT region (from cold to warm white). As increasing the thickness of the NHB-based DC films, the CCTs were lowered because the blue emission was reduced while the yellow-orange emission increased. As a result, the CRI values of the W-LEDs decreased from 80 to 59. The highest luminous efficacy (LE) was 49 lm/W with a CRI of 64 at a 3800 K CCT under an applied current of 60 mA. While there have been few thorough evaluations of the figures of merit of QD/polymer-based DC phosphor layers, our NHB-based DC films exhibited state-of-the-art performance, to the best of our knowledge. The high concentration of uniformly dispersed, high-QY, broad-emission QDs in the large-area free-standing NHB thin films fabricated using our novel e-spray processing technique yielded high-performance DC materials. Because our QDs are environmentally friendly, this work could have a strong impact on the field of DC materials for W-LEDs by enabling the replacement of the currently commercialized rare-earth phosphor materials.
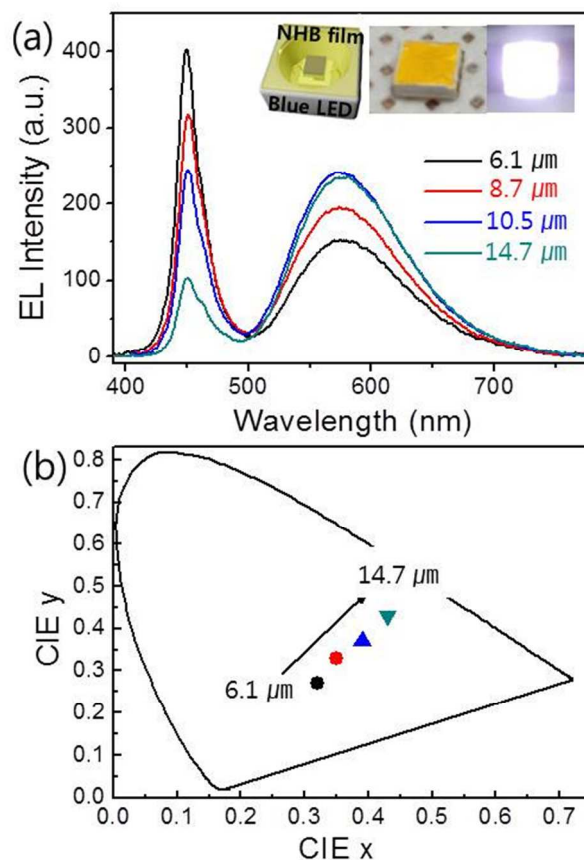

Figure 6. (a) EL spectra of QD/PMMA NHB film converted into remote-type W-LED. The insets are schematic illustration and photographs of remote-type LED (left) and W-LED with applied current 60 mA (right). (b) CIE chromaticity coordinates of W-LEDs with QD/PMMA NHB films for applied current 60 mA.

Table 1. Figures of merit of remote-type W-LEDs with QD/polymer NHB films of different thickness.

	CIE x	CIE y	LE (lm/W)	CCT (K)	CRI (R_a)
6.1 μm	0.32	0.27	32	6857	80
8.7 μm	0.35	0.33	40	4610	71
10.5 μm	0.39	0.37	49	3803	64
14.7 μm	0.43	0.43	46	3258	59

Conclusions

In summary, we have developed high-performance QD/polymer NHB-based DC phosphor materials fabricated from nontoxic QDs using a novel e-spray fabrication method. The unique abilities of the e-spray method played crucial roles in the fabrication of the extraordinary heavily QD-loaded (up to 50 wt%) NHB films, because highly diluted NHB solutions can be used for the deposition. When the e-spray method was coupled with a floating/delamination technique, wafer-scale free-standing QD/polymer NHB films were achievable. The highest luminous efficacy obtained was 49 lm/W with a CRI of 65 at a 3800 K CCT under an applied current of 60 mA. This work demonstrates that the e-spray method is effective for preparing QD/polymer NHB films, and it confirms the potential of the NHB films as efficient DC phosphor materials for W-LEDs that could enable the replacement of the currently commercialized rare-earth phosphor materials.

Acknowledgements

Notes and references

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