

# Electrospun polymer/quantum dot composite fibers as down conversion phosphor layers for white light-emitting diodes†

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Color control without severe photoluminescence (PL) quenching is one of main issues in white light emission technology. White light emission was successfully achieved using phosphor layers made of electrospun quantum dot (QD) embedded polymer fibers as color down-conversion layers of blue light-emitting diodes (LEDs). Down-conversion from blue to longer wavelength was characterized by fluorescence microscopy and photoluminescence (PL) spectroscopy. Using orange QD-embedded fiber-based phosphor layers, a broad spectrum of white-light was demonstrated with the CIE coordination of (0.367, 0.367). The QDs in the polymer fiber matrix did not show the aggregation of QDs unlike the QDs in a thin film matrix. Furthermore, from Time-Correlated Single Photon Counting (TCSPC) analysis, the QDs in fiber mats have longer PL lifetime (~3.95 ns) than that in a thin film matrix (~3.20 ns) due to the lower aggregation-induced luminescence concentration quenching. Our results suggest that the simple electrospinning method may be a very good method to obtain uniform and bright QD phosphors for white LEDs which can be used for solid-state illumination sources and lighting devices.

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## Introduction

White light-emitting diodes (WLEDs) have attracted much attention as alternative solid-state illumination sources for general lighting as well as backlighting in full-color liquid crystal displays because they are environmentally friendly, energy efficient, and cost-effective.<sup>1,2</sup>

There are two major approaches to realize WLEDs.<sup>1-14</sup> First of all, WLEDs can be fabricated by simple mixing of three primary colors of red, green, blue LEDs.<sup>1,2</sup> However, the emission power exponentially decays with increasing temperature, which causes substantial change in color stability. The second method is the

coating of an one-color LED (mostly blue LED) with down-conversion phosphors to produce white light.<sup>3-14</sup> Until now, this phosphor-based method is still the most popular for manufacturing high intensity WLEDs because they have the advantages of easy control of colours and cheap manufacturing cost. Phosphor-based WLEDs are classified by the types of emitting materials such as inorganic phosphors,<sup>3-9</sup> organic phosphors,<sup>6</sup> organic-inorganic hybrid phosphors,<sup>7</sup> and colloidal semiconducting nanocrystals or quantum dots (QDs).<sup>8-14</sup> Although WLEDs using inorganic phosphors have high brightness, color control is difficult and color quenching effect occurs as temperature change. In the case of organic phosphors, the color control is relatively simple because of their facile and large-scale synthesis, and molecular and electronic tunability by molecular design but requires precise control of phosphor concentration in multi-component phosphor systems in order to suppress the resonance energy transfer among phosphors.

Recently, WLEDs using colloidal semiconducting QDs are emerging as a completely new technology platform for solid-state lighting and flat-panel displays because of high efficiency and long lifetime.<sup>2,8-12</sup> QDs are expected to very suitable phosphor for WLEDs because of its broad absorption and narrow emission spectrum characteristics. However, self-absorption and red-shift of PL emission peak occurs, because absorption region was overlapped with PL emission spectrum. Besides, QDs phosphor layer is usually consisted of embedding QDs in a

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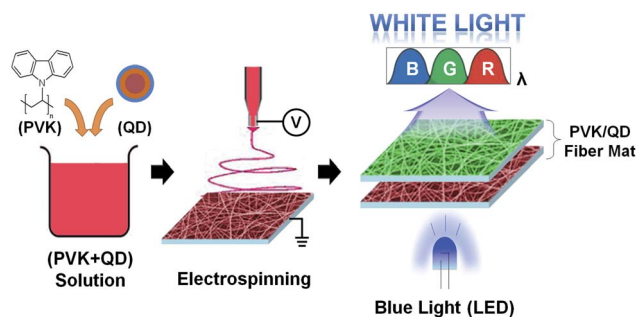


Fig. 1 Process scheme for realization of white-light emitting system using PVK/QDs composite fiber.

film-shaped matrix (e.g. epoxy resin)<sup>15–17</sup> and thus this method causes aggregation and subsequent luminescence concentration quenching of the QDs in the matrix.<sup>15–18</sup>

On the other hand, electrospinning is one of the simplest methods to fabricate polymeric nanofibers using viscous polymer solution.<sup>19,20</sup> Polymer is main component of electrospun fiber, but it is also possible to add other components such as metallic or ceramic precursors.<sup>21–23</sup> When QDs are added to polymer solutions, QDs can be uniformly dispersed and aligned along the fiber matrix.<sup>24</sup>

Here, we fabricated the CdSe/CdS/ZnS QD-embedded poly(9-vinylcarbazole) (PVK) fiber mat by using electrospinning and then we used this mat as a down-conversion phosphor layer of a blue LED for achieving white emission (Fig. 1). Photoluminescence (PL) characteristics of QD-embedded polymer fiber mats were investigated. And we found that aggregation of QDs was reduced in polymer fiber mats and thus the PL lifetime increased compared with that of QDs in a film matrix. We present the light-emitting characteristics of WLEDs using QD-based down-conversion phosphor layers.

## Experimental

### Sample preparation

Poly(9-vinylcarbazole) (PVK) ( $M_w \sim 1\,100\,000$ ) was purchased from Aldrich Inc. CdSe/CdS/ZnS QDs were synthesized by previously reported method.<sup>25,26</sup> (10-(2-Benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-[1]-benzopyrano-[6,7,8-*ij*]quinolizin-11-one) (C545T) (Duksan Hi-metal Co., Ltd.) was used as a green-emitting fluorescent dopant. First, QDs were dispersed in styrene and then the QD dispersion was added into PVK solution in styrene ( $0.15\text{ g mL}^{-1}$ ) with 5 : 95 weight ratio. The PVK/QDs solution was injected to a plastic syringe and the flow rate of syringe pump was set to be  $200\text{--}500\text{ nL min}^{-1}$ . Tip-to-collector distance and applied voltage were set to be 7 cm and 4–5 kV (17 kV for PVK-C545T solution), respectively. The glass substrate size is  $6.25\text{ cm}^2$ . Glass substrate was put on the grounded flat-type Al collector. Electrospun PVK/QDs hybrid fibers were collected on the glass substrate for 30 minutes. For concentrated collection of the fiber on the glass substrate, wooden insulating plate was built surrounding the glass substrate. The PVK/QD solution was

diluted to the half of concentration with styrene for preparing thin film sample. Diluted solution was spin-coated on glass substrate at 1000 rpm for 10 s and 3000 rpm for 30 s followed by drying in a vacuum chamber.

### Characterization

Fluorescence image was recorded by Zeiss Axioplan 2 optical microscope. A JEOL JSM-6330F was used for Field-Emission Scanning Electron Microscope (FE-SEM) images. Fiber morphology and chemical mapping were characterized by scanning transmission electron microscopy (STEM) using a JEOL JEM-2200FS (with Image Cs-corrector) (National Institute for Nanomaterials Technology, Korea) at an acceleration voltage of 200 kV without staining. Photoluminescence spectra of thin film and fiber were measured by JASCO FP-6500 and Ocean Optics USB4000-UV-vis spectrophotometer using a 475 nm LED (SU50-RUP501AT475, Seoul Semiconductor Co., LTD) as the excitation source. PL decays of thin film and fiber mat were investigated by the Time-Correlated Single Photon Counting (TCSPC) measurement. The second harmonic (SHG = 400 nm) of a tunable Ti:sapphire laser (Mira900, Coherent) with  $\sim 150\text{ fs}$  pulse width and 76 MHz repetition rate was used as an excitation source. The PL emission was spectrally resolved by using some collection optics and a monochromator (SP-2150i, Acton). The TCSPC module (PicoHarp, PicoQuant) with a MCP-PMT (R3809U-59, Hamamatsu) was used for ultrafast detection. The total instrument response function (IRF) for PL decay was less than 140 ps and the temporal time resolution was less than 10 ps. The deconvolution of actual fluorescence decay and IRF was performed by using a fitting software (FlouFit, PicoQuant) to deduce the time constant associated with each exponential decay. All measurements are performed under ambient conditions.

## Results and discussion

### Fiber morphology characterization

Fig. 1 shows the scheme of experimental processes to fabricate the electrospun PVK/QD fibers and realize the white-emission using a blue LED source (475 nm). The 5 wt% QDs were incorporated in the PVK matrix (95 : 5, w/w). PVK is a very good spinnable polymer and is expected as the suitable matrix for emission center, because PVK is excited at 345 nm and emits ultraviolet (UV) light centered at  $\sim 406\text{ nm}$  which overlaps the excitation wavelengths of QDs. When the PVK/QD fibers are excited by a blue LED, the PVK mainly acts as a dispersion medium. PVK has a high glass transition temperature ( $\sim 200\text{ }^\circ\text{C}$ ) and does not undergo any chemical change below  $300\text{ }^\circ\text{C}$ ,<sup>27</sup> so that the PVK/QD fiber mats can be thermally stable.

Fig. 2a shows the electrospun PVK/QDs fiber on glass substrate. To collect the fibers only on the glass substrate, we shielded the conductive collector region outside the glass substrate with a wooden insulating plate thicker than the glass substrate (thickness  $\sim 1\text{ mm}$ ). PVK/QDs fibers were continuously collected only on the glass substrate despite the insulating characteristic of the glass because the surrounding thick

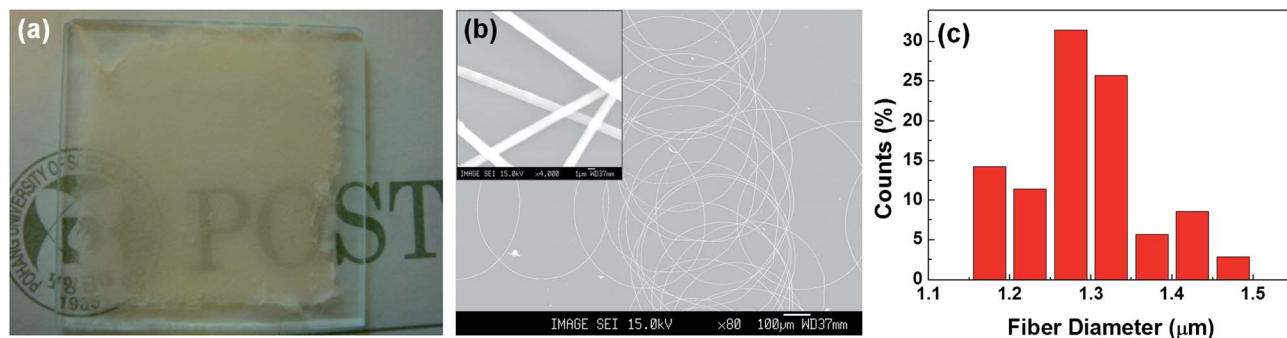


Fig. 2 PVK/QDs fiber mat. (a) Electrospun PVK/QDs fiber mat on glass substrate. (b) SEM image of PVK/QDs fiber. (c) Distribution of fiber diameter (average diameter =  $1.29 \pm 0.07 \mu\text{m}$ ).

wooden insulating plate effectively shielded the electric field outside the glass region. Fig. 2b and c show the morphology and diameter of PVK/QDs fibers: fibers have bead-less and smooth shape and their average diameter was  $1.29 \pm 0.07 \mu\text{m}$ .

### Photoluminescence characterization

We prepared the orange (diameter  $\sim 3.7 \text{ nm}$ ) and red ( $\sim 4.2 \text{ nm}$ ) QDs. And we successfully fabricated the PVK/QDs fibers embedded with QDs of different sizes. When PVK/QDs fibers were excited with a UV light source (350 nm), they emit the characteristic fluorescence of QDs embedded in polymer fibers (Fig. 3a and b).

We characterized the PL spectra of PVK and PVK/red QD fibers (Fig. 3d). When pure PVK is excited at a wavelength of UV region (345 nm), the PL peak emission occurs at 406 nm, edge of blue region. However, when PVK/red QD fibers are excited at the same wavelength, the PL peak emission occurs at 602 nm but

the original PL emission peak of PVK disappeared. The PL emission spectrum of pure PVK is well overlapped with PL excitation spectrum of pure QD. Therefore, excitation energy transfer occurs from the PVK to QDs when the fibers are excited with a UV light that PVK can absorb. However, judging from the PL excitation spectra (Fig. 3d), only the QDs in the fibers were excited by the blue LED and PVK play a role as the solid dispersion medium.

On the other hand, we fabricated the PVK/QDs thin film in order to compare with PVK/QDs fiber system. QD-embedded spin-cast PVK thin film showed the aggregation of QDs occurs in long range, and fluorescence is not uniform through the film (Fig. 4a). Thin film (thickness  $\sim 430 \text{ nm}$ ) had much lower PL emission intensity than that of fiber mat (Fig. 4b). However, from these PL measurements, we cannot conclude that the fluorescent quantum yield of the fiber mat is better than that of the film because of the different QD densities in each sample. Therefore, we performed Time-Correlated Single Photon Counting (TCSPC) measurement in order to investigate the effect of aggregation of QDs in films compared with the QDs in the fiber mats (Fig. 4c). The PL decay profiles of the PVK/QDs film and the PVK/QDs fiber mat were fitted by a bi-exponential decay fitting, which suggests that the PL excitons decay of the PVK/QDs film and the PVK/QDs fiber mat took place through two relaxation pathways. Table 1 summarizes the PL lifetime results of the PVK/QDs film and the PVK/QDs fiber mat. The PVK/QDs film and the PVK/QDs fiber mat showed the two lifetimes of long and short-lived excited species. It is expected that the short-lived excited species are aggregated QDs in the polymer matrix which cause the luminescence concentration quenching.<sup>15</sup> On the other hand, the long-lived excited species are aggregation free or less-aggregated QDs. The PVK/QDs fiber mat showed the large fraction of long-lived excited species and longer exciton lifetime than those of the PVK/QDs film. From above results, it is concluded that QDs can be uniformly dispersed in fiber morphology. The large fraction of long-lived excitons also increases average PL lifetimes of the PVK/QDs fiber, indicative of avoiding the luminescence concentration quenching, and is well matched with results of the steady-state PL emission. These results are consistent with the STEM image and elemental analysis results (Fig. S1, ESI†). As using the QDs-embedded fiber mat system, we can get the uniform quality of

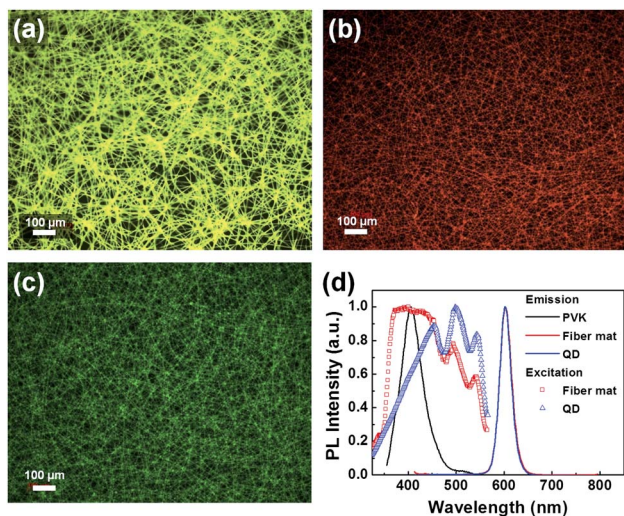


Fig. 3 PL emission characteristics of PVK/QDs fiber mats. Fluorescence microscope image of electrospun (a) PVK/orange QDs, (b) PVK/red QDs and (c) PVK/C545T fiber mats under UV light source (350 nm). (d) PL emission spectra of PVK in styrene (black solid line), PVK/red QDs fiber (red solid line) and QD dispersion in styrene (blue solid line) and excitation spectra of PVK/red QDs fiber (red square) and QD dispersion in styrene (blue triangle).

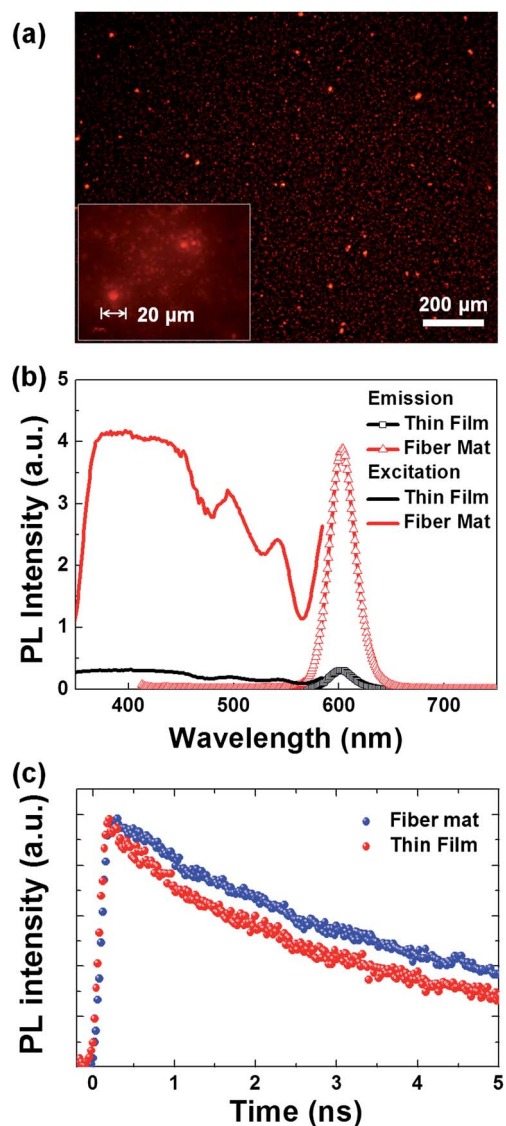


Fig. 4 Comparison of photoluminescence characteristics between PVK/QDs thin film and fiber mat. (a) Fluorescence image of PVK/QDs thin film. Aggregation of QDs occurs in long range. (b) PL emission spectra of PVK/QDs thin film (black square), fiber (red triangle), and excitation spectra of thin film (black solid line), fiber (red solid line). (c) PL decay curves for thin film and fiber.

white light without any severe aggregation. Therefore, the fiber mat system is a more suitable candidate for the phosphor layer to achieve bright white emission.

Table 1 PL lifetimes of PVK/QDs thin film and fiber mat/QDs<sup>a</sup>

	$\tau_1$ [ns] ( $f_1$ )	$\tau_2$ [ns] ( $f_2$ )	$\tau_{avr}$ <sup>b</sup> [ns]
Thin film	4.23 (0.73)	0.36 (0.27)	3.20
Fiber mat	4.85 (0.81)	0.20 (0.19)	3.95

<sup>a</sup> Monitoring wavelength is 602 nm.  $\tau_1$  and  $\tau_2$  are lifetimes (ns),  $f_1$  and  $f_2$  are fractional intensities. <sup>b</sup>  $\tau_{avr}$  is the average lifetime obtained from  $f_1\tau_1 + f_2\tau_2$ .

### Fiber mat down-conversion phosphor layer

When a PVK/orange QD fiber mat was illuminated as a phosphor layer with a blue LED (475 nm), a whitish color was observed with the naked eyes. In order to realize pure white emission, we stacked the fiber mats as shown in inset of Fig. 5a. When we stacked the seven plates of fiber mats, pure white emission was observed with Commission Internationale de l'Eclairage (CIE) coordination of (0.367, 0.367).

We also tried the two colors phosphor system using CdSe/CdS/ZnS QDs (red) and (10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-[1]-benzopyrano-[6,7,8-*ij*]-quinolizin-11-one) (C545T) (green). PVK/C545T (95 : 5, w/w) fibers were also successfully fabricated by electrospinning, and they showed greenish fluorescence under illumination of a UV light (350 nm) as shown in Fig. 3c. And then, we achieved the broad PL emission spectrum using PVK/red QD fiber mats and PVK/C545T fiber mats with excitation of a blue LED (Fig. 5b). The CIE coordination of this system was calculated to (x, y) = (0.344, 0.453). As changing the number and stacking sequence of fiber mats and fiber density in the mat, we can easily control the color coordinate of the emitted light.

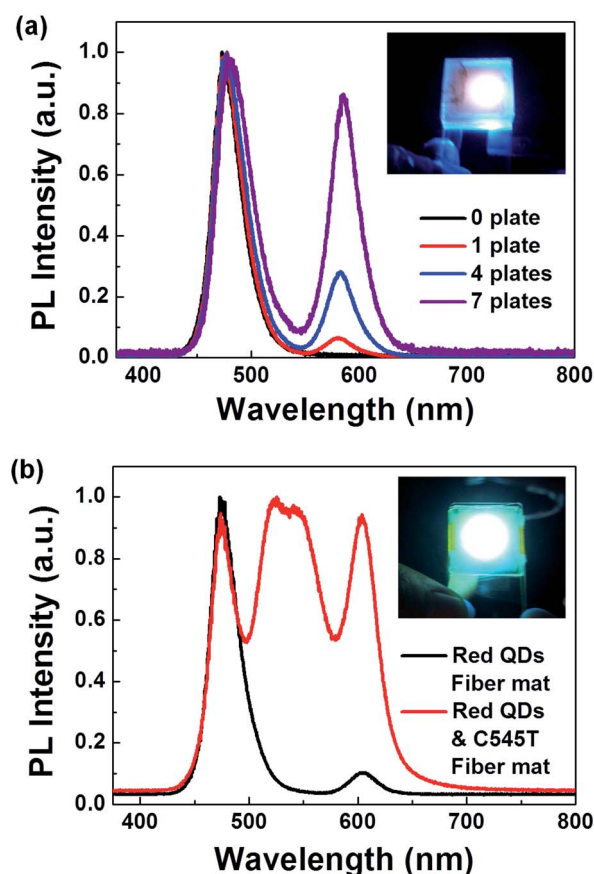


Fig. 5 White emission of PVK/QDs fiber phosphor plates with blue LED source (475 nm). PL spectra of (a) PVK/orange QDs fiber plates and (b) PVK/red QDs-PVK/C545T fiber plates with a blue LED as the excitation source. Inset of (a) and (b) shows PVK/orange QDs fiber plates and PVK/red QDs-PVK/C545T fiber plates with blue LED source, respectively.

## Conclusions

In conclusion, we achieved the white fluorescence emission using electrospun PVK/QDs fiber phosphor layers in front of a blue LED as an excitation source. The down-conversion of photon energy from the blue LED to QDs enables to generate the white fluorescence emission. This method has the advantages of uniform distribution of QDs in a fiber matrix and reduced luminescence quenching compared with the conventional phosphor layer with QDs-embedded thin film structure. In addition, fluorescence emission color can be easily tunable by controlling the size of QDs and the number of fiber mats. These results suggest that simple electrospinning method can be applied to obtain uniform and bright QD phosphor-based WLEDs which can be used for solid-state lighting devices and illumination source for liquid crystal displays.

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