

PHOTOENHANCEMENT OF QUANTUM DOT NANOCOMPOSITE VIA UV ANNEALING AND ITS APPLICATION TO WHITE LED

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1 Introduction

Colloidal semiconductor quantum dots (QDs) have attracted a great deal of attention due to their unique physical characteristics such as nanometer scale size, size-tunable optical properties, high photostability, and wide absorption spectrum. Various QD applications such as biological imaging, photovoltaic device, light-emitting diode (LED), and memory have been widely studied in science and engineering. It is important to obtain the desired optical properties from a QD ensemble while maintaining high luminescence efficiency. The effects of thermal annealing and photoactivation on the intrinsic properties of QDs have been the subject of thorough investigation in previous studies. In a polymer matrix, high-temperature thermal annealing changes the interaction between the polymer and the QDs and is useful for enhancing the PL. Under ordinary circumstances, the photoluminescence (PL) of QD ensembles is a reversible function of the temperature. As the temperature increases, the PL intensity decreases, the spectral wavelength shifts toward red, and the QDs shrink. Likewise, reversible enhancement of photo-induced fluorescence in QDs has been studied under various conditions. These changes depend on the irradiated light intensity and wavelength as well as environmental conditions such as the presence of various gases. In this paper, we have firstly reported the irreversible PL enhancement that occurs due to ultraviolet (UV) annealing of a QD nanocomposite, which is a mixture of thermo-curable polymer and core-multishell QDs. We found that the UV

irradiation of a QD nanocomposite after thermal curing caused a permanent change in the PL intensity without changing the QD band energy. The most significant factors were the exposure time and the UV irradiation intensity. We added phosphor to this nanocomposite to create a color converting material, which we then applied to a white LED. The conversion of blue light to white and the performance of the white LED demonstrated more efficient color rendering and better luminance than that without UV annealing.

2 Experimental Results: QD material and Film

Figure 1(a) shows 10-nm synthesized core-multishell QDs (CdSe/CdS/CdZnS/ZnS) composed of Cd, Se, Zn, and S. The first absorption peak was at 586 nm and the band edge of the emission wavelength was 599 nm. The high-resolution transmission electron microscopy (HR-TEM) image in the inset of Fig. 1(a) clearly shows the lattice structure of the QDs. The measured quantum yield of synthesized QDs in solution was about 50% with a FWHM of 35 nm. We prepared a QD-polymer nanocomposite and studied the luminescence properties associated with photo-annealing. To study the effect of the dispersed matrix, we prepared three samples: QDs as a powder, QDs in solution, and QDs in a polymer after thermal curing. We placed the samples into a chamber in which they were illuminated by 365-nm UV light from above. No change in PL intensity of the QD solution was observed even after a long period of UV irradiation. QDs as

powder experienced a decreased PL intensity proportional to the UV irradiation time as shown in Fig. 2(a). This indicates that UV irradiation damaged the surface of QDs by photo-oxidation as previously reported. In particular, QDs in the powder state seem to have many more defects than QDs in any other matrix. Washing out the QD ligands during the transformation into the powder state could increase the generation of surface defects, which may contribute to more QD surface damage by UV irradiation. For the sake of comparison with core-multishell QDs, we synthesized core-shell QDs using a method similar to that used to prepare core-multishell QDs. Figures 2(b) and 2(c) show the PL change of core-shell and core-multishell QDs, respectively, after 96 hr of 365-nm UV irradiation. The PL intensity increased to 230% for core-shell QDs and 180% for core-multishell QDs. The enhancement ratio of the core-shell QD nanocomposite was greater than that of the core-multishell QD nanocomposite. The effect on the core-shell QD is likely more pronounced due to the greater number of interactive sites on the surface of the QDs. In spite of greater PL enhancement, the core-shell QDs intrinsically exhibited lower photostability than the core-multishell QDs. We exposed QDs in air to natural light conditions for several days. The PL intensity of core-shell QDs degraded significantly while the core-multishell QDs experienced little decrease in PL intensity. Therefore, we used mainly core-multishell QDs for our experiments because of their excellent photostability. Figure 2(d) shows the color brightness of the QD nanocomposites before and after UV annealing. After UV annealing, the color of the QD nanocomposite was much brighter.

Figure 3(a) shows the time responses of the nanocomposite for core-multishell and core-shell QDs in the UV chamber. The two samples experienced a great increase in PL intensity after 24 hr. After that, the rate of increase decreased gradually until the PL reached a

saturated value. After 96 hr of UV irradiation, the UV lamp was turned off and we exposed the sample to open air without any treatment.

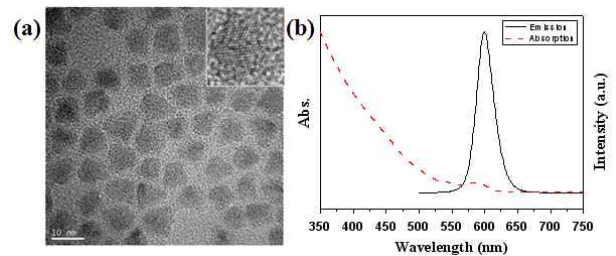


Fig.1. (a) HR-TEM Image and (b) UV-vis absorption and PL emission spectra of core-multishell QD (CdSe/CdS/CdZnS/ZnS)

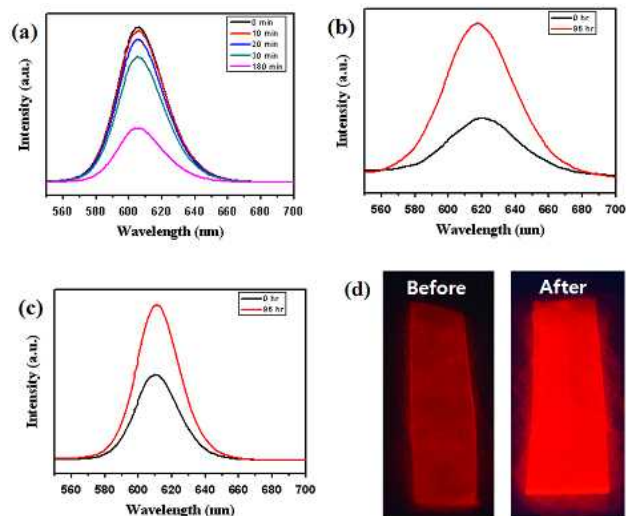


Fig.2. (The PL intensity before and after UV irradiation for (a) core-shell QD (b) core-multishell QD in a polymer matrix (c) core-multishell QD as a powder state, respectively. (d) color of the core-multishell QD nanocomposite before and after UV irradiation.)

As Figure 3(a) shows, the PL intensity of core-multishell QD decreased only slightly after further 48 hr, demonstrating that this effect was irreversible as well as stable. We used an intensity-tunable high-power UV lamp to study the effect of UV intensity. This portable UV lamp with an optical cable was situated close to the PL measurement setup and the UV source irradiated the sample directly so we could obtain

PL information during UV illumination. Figure 3(b) shows the effect of UV intensity for annealing. We compared PL changes of the core-multishell QD nanocomposite as a function of the UV intensity from 30 to 100 W. We observed that the PL enhancement was proportional to UV intensity for values less than 50 W. However, no significant increases of PL were observed for intensities greater than 50 W. The 30 min of irradiation at 100 W even decreased the PL intensity of the QD nanocomposite compared to irradiation of the same duration at 70 W. The maximum rate of PL intensity increase was about 1.6, which is similar to the result of long-term exposure in the vacuum chamber. These experiments indicated that the UV annealing effect was dependent on both the UV intensity and the exposure time, although the PL increase could be saturated under high-power conditions. Irradiating a nanocomposite with UV light caused little change in the FWHM and emission wavelength. This demonstrated that no change in the QDs themselves occurred.

We believe that this phenomenon is closely related to the polymer because photodegradation occurred in the powder state as well as there was no PL change in the solution. We obtained HR-TEM images of the QD nanocomposite before and after UV annealing to study the morphological change in molecule size. As shown in Figure 4, a significant change occurred in the contacting phase between the polymer and the QDs after UV illumination. Before UV illumination, we observed that the QDs were randomly dispersed in clumps throughout the polymer matrix. After UV illumination, the QDs were well dispersed in a regular pattern. Our experimental results suggest two possibilities for the mechanism by which this morphological change triggered the enhancement of QD nanocomposites. The first is the stable photoactivation due to the ordered and individualized dispersion of QDs in the polymer and the second is the passivation of the

defect sites on the QDs. Further detail investigation is required to verify the exact causes.

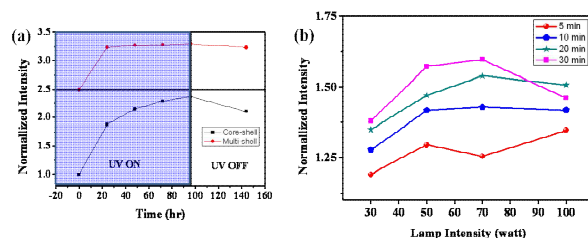


Fig.3. (a) Time response of PL intensity of core-shell QD nanocomposites, and (b) PL enhancement according to the UV intensity for the core-multishell QD nanocomposite

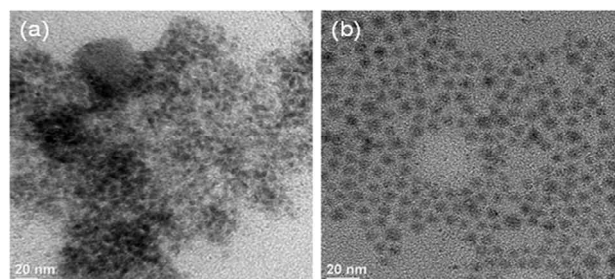


Fig.4. TEM images of QD nanocomposite (a) before and (b) after high power UV illumination for 1 h

3 Experiment Result: LED device

We used UV annealing to fabricate white LEDs with a QD-phosphor nanocomposite. The nanocomposite was prepared using a mixture of yellow phosphors, red core-multishell QDs, and thermocurable polymer. Figure 5(a) shows a diagram of the white LED using a nanocomposite of phosphor, QDs, and polymer. The emitted blue light is transformed into white light as it passes through the nanocomposite. In this experiment, we used the yellow phosphor that is commonly used for white LED fabrication. Figure 5(b) shows the luminance spectrum of the QD-phosphor white LED before and after UV annealing. The luminance flux in the red color region increased

significantly after UV annealing. We observed that the peak wavelength matched the emission wavelength of the QDs closely. The overall luminance was about 110% that of the original LED chip without UV annealing and the correlated color temperature (CCT) changed to warm white. The CRI (Color Rendering Index) was increased from 87.2 to 91. Figures 5(c) and 2(d) show the fabricated LED device and the illumination it produced. The nanocomposite appeared yellow and the emitted light was bright white.[1]

In summary, irreversible PL enhancement of a QD nanocomposite has been achieved by UV annealing. The enhancement ratio was dependent of both the intensity and the exposing time of UV light. As the result, the PL of the core-multishell QD nanocomposite increased 1.8 times after UV annealing. When we applied this UV annealing process to QD nanocomposite before the fabrication of white LED, the optical characteristics of white LED were quite improved in terms of brightness and CRI. This method has great potential for many applications using QD nanocomposite.

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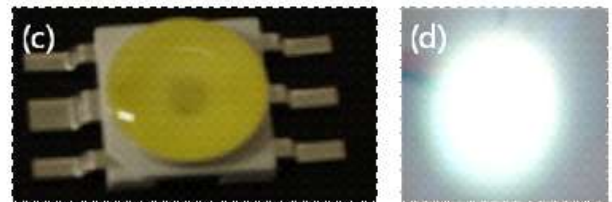
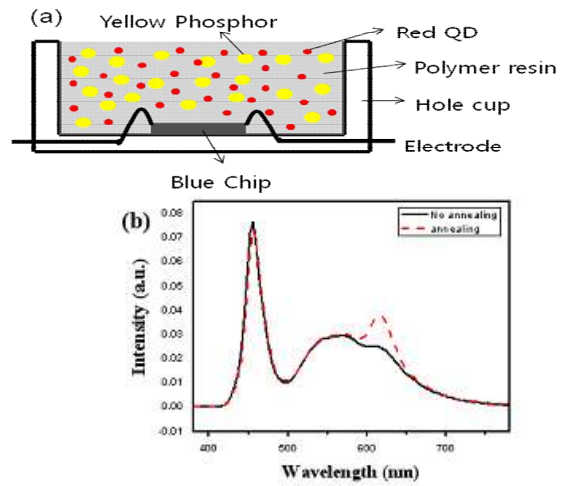


Fig.5. ((a) Schematic view of white LED chip, (b) luminance characteristics of LED before and after UV illumination, (c) the fabricated LED chip with QD-phosphor material, and (d) the emitted white light of the LED device (c). The driving current was 350 mA)

References

[1] K. Kim, J. Y. Woo, S. Jeong and C. -S. Han “Photoenhancement of Quantum Dot Nanocomposite via UV Annealing and Its Application to White LED”. *Adv. Mater.* Online published, 2010.