GaN phosphors converted white light-emitting diodes for high luminous efficacy and improved thermal stability

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Abstract: This study analysed GaN nanophosphors based white light-emitting diodes (WLEDs) with ultraviolet (UV) excitation. Graphene quantum dots (GQDs) used as a charge transfer medium to enhance the performance in terms of luminous efficacy and colour quality. The improvement in colour rendering and colour temperature has been observed with the increase in injection current. The luminous efficacy of radiation also gets improved with injection current and maximises up to 255 lm/W at 260 mA along with 90 colour rendering index and 7100 K correlated colour temperature. Mapping of higher surface temperature for GQD-based devices shows a better thermal stability, indicating the good heat dissipation capability of GQDs because of excellent thermal conductivity. Therefore, proposed WLEDs were found more competent with improved thermal quenching of phosphors for rare-earth-free solid-state lighting as compared to the blue chip-excited yellow phosphors.

1 Introduction

Phosphor-converted (pc) white solid-state lighting has an inevitable role in our life with emission close to standard white light because of extraordinary foreseen advantages over the conventional lamps. Out of all the methods to generate white light, the method involving ultraviolet (UV) excitation of phosphors is found to be most suitable from technological and physical point of view for maintaining stable colour rendering index (CRI) and high luminous efficacy (luminous efficacy of radiation (LER)) over time along with uniform excitation for every visible band [1]. Additionally, to resolve the energy crisis and to address the environmental concerns, rare-earth-free solid-state lighting is also in demand with different types of nanostructures [2–7]. YAG based and single-crystalline phosphors might be able to fulfill the criteria, however, these alternatives have a limitation of low CRI and complex growth process, respectively [8, 9]. The blending of different phosphors for UV-excited RGB LEDs also exhibits some critical problems. Therefore, III-nitride based semiconductors have been proposed to fulfill this gap with high luminous efficacy to compete with the present technology of white light-emitting diodes (WLEDs).

In this context, GaN nanoparticles and quantum dots have been explored for generating visible light using a complex process by doping of rare-earth elements and surface modifications, respectively [10, 11]. Recently, our earlier study demonstrated an easy process to initiate white-light emission from intrinsic GaN nanoparticles by carbothermal nitridation of GaN and GQDs simultaneously with broad signatures for GQDs and fine intense for GaN as shown in Figs. 1 a and b, respectively. Hereafter, present work focuses on the investigation of pc WLED that uses GaN nanoparticles as phosphors and GQDs as charge-transfer medium with the above-discussed advantages for the device performance. For this purpose, a composite of the solution processed GQDs and GaN nanoparticles have been prepared. Further, the molded GaN–GQDs film is excited using a UV LED chip. The effect of the GQD concentration on the GaN pc WLED has been examined by photoluminescence measurement of the molded film along with the electroluminescence spectra of LEDs.

2 Experimental details

White light-emitting GaN nanoparticles were synthesised by the methodology proposed in our earlier work by tuning the mid-gap states through a variety of different experimental processes [3]. Synthesis of GQDs performed by the microwave-assisted hydrothermal method through the dehydration of glucose [12]. Nitrogen is also doped in this process by using ammonia water. GQDs’s Homo and Lumo level energy were evaluated together by Tau’s plot analysis and cyclic voltammetry measurement (Supplementary Fig. S1). GaN–GQDs composite was prepared by dissolving different amounts of GaN into the GQDs solution and kept stirring for 24 h at 50°C. After this, the GaN–GQDs composites were collected by centrifugation at 10,000 rpm for 30 min, followed by drying at 70°C for 24 h. The composite film was prepared by first dissolving 0.5 g composite, 1 mL silane coupling agent, 1 g polyvinyl alcohol in 40 mL deionised water and 10 mL ethanol, using magnetic stirring at 80°C for 5 h until the solution became homogeneous and then it was drop-casted into a Teflon mold. The coated film was thermally cured at 50°C for 24 h and finally peeled off. For white light LEDs design, the excitation of the composite film has taken place by UV LED chip of 1 × 1 mm² and was found to be operating at 4 V with 365 nm peak wavelengths.

3 Results and discussion

The XRD pattern and Raman spectra of the GaN–GQDs composite for optimum composition (100/0.75) show the signatures for both GaN and GQDs simultaneously with broad signatures for GQDs and fine intense for GaN as shown in Figs. 1 a and b, respectively. The TEM analysis shown in Figs. 1 c–f for GaN–GQDs shows the quasi-core-shell structure. An enlarged view from high-resolution transmission electron microscopy (HRTEM) reveals that the interplanar spacing of (002) plane of the hexagonal GaN is 0.26...
The emission mechanism in proposed LED occurs typically in a deep donor–acceptor pair band or the variation of the luminescence process. A GaN-based pc-LED was also subjected to the test for EL measurement, which also shows the consistent increment in the visible emission with the injection current (Supplementary Fig. S2).

The observed mechanism of photo-induced doping might be helpful for GaN-based light-emitting devices and to make them feasible from performance point of view. Further, EL measurement of pc-LEDs was conducted on the optimum composite film (100/0.75) and shown in Fig. 4. The measurement has been performed within the range of 20–260 mA which reflects the steady rise for every visible band. The increment in the blue band slightly dominates at higher injection which might be a contribution of blue-emitting GQDs. This might be confirmed by comparing with the bare GaN pc-LED EL spectra. Evolution of higher wavelength (towards red band) also perceived with the increase in the injection current in the EL spectrum. Such change occurs typically in a deep donor–acceptor pair band or the variation in the charge state of defects. A GaN-based pc-LED was also subjected to the test for EL measurement, which also shows the consistent increment in the visible emission with the injection current (Supplementary Fig. S2).

The increment of the EL intensity with the injection currents is analysed in Fig. S4. QD-based devices show higher increment rate of EL intensity with injection current because of improved absorption in the UV region. Luminous flux and LER of white light LED are the parameters of standardisation for a LED to show the comparativeness, which defines the brightness of a light source and effectiveness of emissive spectrum against the spectral function of the human eye (P(λ)), respectively. Therefore, both parameters have analysed for GaN–GQDs composite as well as bare GaN pc-LEDs and found to increase with the injection current as shown in Fig. 5a. The steady increment in luminous flux and LER has been observed with the injection current. The GQD-based device outperformed its counterpart. Both parameters also increased in a much higher rate for GQD-based devices as expected because of the same response for EL measurement. The highest luminous flux ~140 lm along with 255 lm/W LER @ 260 mA shows a significant performance in comparison to the commercial YAG-based phosphors-based LEDs [14], which provides further pathways for III–V group based pc-LEDs.

Prolonged operation of LEDs under high injection current is expected to generate huge extent of heat, which adversely affects the performance in terms of colour quality due to the low thermal conductivity of the phosphor. Accumulation of heat may also lead to the degradation of the phosphor, reducing its efficiency. Therefore, it is crucial to develop strategies to manage heat dissipation in LED devices.
damage the LED chip and diminish the efficiency of the phosphors. Thermal management for dissipation of heat is required for proper operation of white lighting. GQDs used in this study are expected to provide such benefits and hence have gone through the mapping of the surface temperature of phosphors film. Thermal imaging of the phosphor surface has been performed and is shown in Fig. 5d. The GQD-based device shows the higher surface temperature from its counterpart because of better thermal conductivity of GQDs (i.e. the derivative of graphene), which acts as good heat dissipater from the phosphor plate. This effect probably shrinks the thermal quenching and reflection in the form of higher luminous flux.

Further, EL spectra are used to examine CCT and CRI corresponding to them and compared with both devices (Supplementary Fig. S3). For GaN pc-WLED, no major CCT and CRI shift with the injection current was observed, which were found to be around 6000 K and 92, respectively. For GaN–GQDs pc-WLED, the CCT varied from 8440 to 7000 K and CRI, from 97 to 92 with the change in examined range of injection current. This decrease in CCT occurred because of the evolution of higher wavelength visible band with the increase in injection current, which made the spectrum warmer. The generation of red band shoulder at a high injection current minimises this effect of blue band intensification by maintaining good CRI of 92 for 220 mA, making the device useful for different lighting applications with enough high CRI.

LER for GaN pc-WLED was found stable at around 225 lm/W within the tested range of injection current. However, GaN–GQD-based device showed consistent increase in LER with the subsequent increment in current, with a maximum value of 255 lm/W at 260 mA. Hence GQD-based device was found to retain a better LER, which might be attributed to the accumulation of emissive power density into the spectral function of $I(\lambda)$. Therefore, the proposed GaN–GQDs pc-WLED was found to be more efficient with 92 CRI and 7100 K CCT along with 250 LER as compared to existing phosphors materials system with the high absorption capability of the excitation source. Further, tuning might be possible with injection current to achieve a varying range of colour temperature from natural to cool white for different lighting applications. Another beauty of proposed GaN phosphors is to tune the CCT towards the lower value by making the composite with efficient red-emitting materials system. Recently, the good luminous efficiency red-emitting GQDs have been reported, which might be a good candidate to achieve lower CCT with this GaN phosphors. This type of GQD is also able to maintain good thermal stability at high exposure with a good heat-dissipating property as discussed above. As a result, findings of the present work can be very useful and timely in progress of the solid-state lighting technology that avoids the potential health risk of currently used WLEDs based on the encapsulation of blue LED with YAG phosphors, which often shows stronger blue emission.

4 Conclusion

The proposed study successfully demonstrated the use of GaN- pc LEDs with GQD as an efficient charge transfer medium to produce cool daylight with high luminous efficacy and UV excitation source, which is free from traditional tricolour rare-earth phosphors. Inclusion of GQDs into the materials system enforces the device in achieving an excellent LER value (255 lm/W). Proposed phosphor with GQDs will definitely support better thermal stability by using composite film in place of direct dispenses of the polymer suspension on UV chip for reducing thermal effect at high-intensity excitation during operation. The proposed white LEDs might be suitable for various high-quality lighting for cool daylight.

5 Acknowledgment

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (No. 2019R1A2C1089080).

6 References

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