Hybrid GaN/Organic white light emitters with aggregation induced emission organic molecule

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Abstract: We demonstrate hybrid white light emitters by employing Gallium Nitride (GaN)-based light-emitting diodes (LEDs) as blue emitters and aggregation-induced emission (AIE) organic molecule 4,7-Bis[4-(1,2,2-triphenylvinyl)phenyl]benzo-2,1,3-thiadiazole (BTPETD) as down-converted yellow emitters. The fabricated device shows CIE coordinates of (0.32, 0.33) and 45.4% optical extraction efficiency from BTPETD layer with pump leakage of 17.3%. At driving current of 30 mA, the highest luminous efficacy of 123.8 lm/W was obtained for the hybrid devices which corresponded a luminance of 1.4×10^5 cd/m^2. Our work indicates that formation of aggregates from AIE materials such as BTPETD is able to greatly enhance the device extraction efficiency and improve the hybrid white LED performance.

OCIS codes: (230.3670) Light-emitting diodes; (160.4890) Organic materials; (250.5230) Photoluminescence.

References and links

1. H. B. Wu, L. Ying, W. Yang, and Y. Cao, "Progress and perspective of polymer white light-emitting devices and materials," Chem. Soc. Rev. **38**(12), 3391–3400 (2009).
2. R. D. Dupuis and M. R. Krames, "History, development, and applications of high-brightness visible light-emitting diodes," J. Lightwave Technol. **26**(9), 1154–1171 (2008).
3. S. Nakamura, "Current Status of GaN-Based Solid-State Lighting," MRS Bull. **34**(02), 101–107 (2009).
4. A. R. Buckley, M. D. Rahn, J. Hill, J. Cabanillas-Gonzalez, A. M. Fox, and D. D. C. Bradley, "Energy transfer dynamics in polyfluorene-based polymer blends," Chem. Phys. Lett. **339**(5-6), 331–336 (2001).
5. G. Itskos, C. R. Belton, G. Heliotis, I. M. Watson, M. D. Dawson, R. Murray, and D. D. C. Bradley, "White light emission via cascade Förster energy transfer in (Ga, In)N quantum well/polymer blend hybrid structures," Nanotechnology **20**(27), 275207 (2009).
6. S. Guha, R. A. Haight, N. A. Bojarczuk, and D. W. Kisker, "Hybrid organic–inorganic semiconductor-based light-emitting diodes," J. Appl. Phys. **82**(8), 4126–4128 (1997).
7. M. Wu, Z. Gong, A. J. C. Kuehne, A. L. Kanibolotsky, Y. J. Chen, I. F. Perepichka, A. R. Mackintosh, E. Gu, P. J. Skabara, R. A. Pethrick, and M. D. Dawson, "Hybrid GaN/organic microstructured light-emitting devices via ink-jet printing," Opt. Express **17**(19), 16436–16443 (2009).
8. P. Schlotter, R. Schmidt, and J. Schneider, "Luminescence conversion of blue light emitting diodes," Appl. Phys., A Mater. Sci. Process. **64**(4), 417–418 (1997).
9. M. R. Krames, O. B. Shchekin, R. Mueller-Mach, G. Mueller, L. Zhou, G. Harbers, and M. G. Craford, "Status and Future of High-Power Light-Emitting Diodes for Solid-State Lighting," J. Display Technol. **3**(2), 160–175 (2007).
10. S. Nishiura, S. Tanabe, K. Fujioka, and Y. Fujimoto, "Properties of transparent Ce:YAG ceramic phosphors for white LED," Opt. Mater. **33**(5), 688–691 (2011).
11. F. Hide, P. Kozodoy, S. P. DenBaars, and A. J. Heeger, "White light from InGaN/conjugated polymer hybrid light-emitting diodes," Appl. Phys. Lett. **70**(20), 2664–2666 (1997).
12. G. Heliotis, E. Gu, C. Griffin, C. W. Jeon, P. N. Stavrinou, M. D. Dawson, and D. D. C. Bradley, "Wavelength-tunable and white-light emission from polymer-converted micropixellated InGaN ultraviolet light-emitting diodes," J. Opt. Soc. A: Pure Appl. Opt. **8**(7), S445–S449 (2006).
13. C. R. Belton, G. Itskos, G. Heliotis, P. N. Stavrinou, P. G. Lagoudakis, J. Lupton, S. Pereira, E. Gu, C. Griffin, B. Guilhabert, I. M. Watson, A. R. Mackintosh, R. A. Pethrick, J. Feldmann, R. Murray, M. D. Dawson, and D.

#198371 - $15.00 USD Received 30 Sep 2013; accepted 7 Oct 2013; published 17 Oct 2013

D. C. Bradley, "New light from hybrid inorganic–organic emitters," J. Phys. D Appl. Phys. **41**(9), 094006 (2008).
14. Y. Hong, J. W. Y. Lam, and B. Z. Tang, "Aggregation-induced emission: phenomenon, mechanism and applications," Chem. Commun. (Camb.) (29): 4332–4353 (2009).
15. S. Chen and H.-S. Kwok, "Top-emitting white organic light-emitting diodes with a color conversion cap layer," Org. Electron. **12**(4), 677–681 (2011).
16. Y. Hong, J. W. Y. Lam, and B. Z. Tang, "Aggregation-induced emission," Chem. Soc. Rev. **40**(11), 5361–5388 (2011).
17. Z. Zhao, J. W. Y. Lam, and B. Zhong Tang, "Aggregation-Induced Emission of Tetraarylethene Luminogens," Curr. Org. Chem. **14**, 2109–2132 (2010).
18. J. Liu, J. Y. Lam, and B. Tang, "Aggregation-induced Emission of Silole Molecules and Polymers: Fundamental and Applications," J. Inorg. Organomet. Polym. **19**(3), 249–285 (2009).
19. Z. Zhao, C. Deng, S. Chen, J. W. Y. Lam, W. Qin, P. Lu, Z. Wang, H. S. Kwok, Y. Ma, H. Qiu, and B. Z. Tang, "Full emission color tuning in luminogens constructed from tetraphenylethene, benzo-2,1,3-thiadiazole and thiophene building blocks," Chem. Commun. (Camb.) **47**(31), 8847–8849 (2011).

1. Introduction

New light sources with high efficiency are always desirable since lighting applications consume about 20% of global energy [1]. The light-emitting diodes (LEDs), which can convert electrical energy directly to light, are considered to be the ultimate lamp, because of their high electroluminescence (EL) efficiencies [2]. Among these LEDs, Gallium nitride (GaN)-based LEDs are almost ideal devices for next-generation white light sources due to their customized direct band-gaps in the ultraviolet to visible spectral range [3]. By coating with a yellow emitting overlayer, the GaN-based LEDs can achieve white light emission by mixing the original blue emission with secondary (yellow) luminescence generated from the overlayer.

The energy transfer from LEDs to the overlayer can be either non-radiative (Forster Resonance Energy Transfer) [4, 5] or radiative [6, 7]. In the scheme of white light emitters with radiative energy transfer, inorganic phosphor "YAG" is the most commonly used down conversion material [8–10], to convert the blue emission from the LEDs to yellow emission. The power efficiencies of these LED pumped phosphor-based white lights are all higher than most conventional light sources, because of relatively high external quantum efficiencies of both LEDs and phosphors. However, higher prices and shortage of phosphors are expected as demand for solid state lighting grows. Thus, search for alternative materials for white light emitting is important. Organic conjugated polymers with high photoluminescence (PL) yield have also been studied to generate white light as well [11–13]. Other than conjugated polymers, aggregation-induced emission (AIE) organic molecules are another group of organic materials with very high PL quantum efficiencies (normally exceed 50%) [14,15].As their name suggests, the aggregation of AIE molecules induces the light emission rather than quenches the emission, which means they can be used in high concentration, and makes them good candidates for the hybrid white light emitters. In general, AIE molecules have very high PL quantum efficiencies (i.e., many close to 100%) and quite stable in air, furthermore one can modify their molecular structures by molecular engineering endeavor to give new luminophors with different emission colors [16–18]. Thus, AIE molecules are excellent candidate for display device applications.

In this study, the properties of hybrid white light emitters with GaN-based LEDs and AIE molecule 4,7-Bis[4-(1,2,2-triphenylvinyl)phenyl]benzo-2,1,3-thiadiazole (BTPETD) are reported. The hybrid devices are also been capped with epoxy to improve the stability. Since the PL quantum efficiency of BTPETD is around 89% in thin film [19], the fabricated devices show a high peak luminous efficacy of 123.8 lm/W at a driving current of 30 mA, and CIE coordinate of (0.32, 0.33). We demonstrated that good performance white light emitting LED can be made in a relatively simple manner by simply capping the commercial blue GaN LED with an efficient yellow emitting AIE organic compound.

2. Experimental

The commercially-sourced InGaN/GaN LED wafers are grown on c-plane sapphire substrate by metal-organic chemical vapor deposition (MOCVD), with embedded multi-quantum wells

#198371 - $15.00 USD Received 30 Sep 2013; accepted 7 Oct 2013; published 17 Oct 2013

designed for emission at around 460 nm. A 200 nm-thick transparent ITO coating is deposited by sputtering as current spreading layer. Photolithographic patterning defines the mesa regions, followed by dry etching to expose the n-GaN layer. Another photolithographic step is performed to define the contact pad regions for metallization. The Ti/Al p-pads and n-pads are deposited by e-beam evaporation and the wafer is subject to rapid thermal annealing at 500°C in an N_2 ambient to form ohmic contacts. The chips are diced by ultraviolet nanosecond laser micro-machining and die-bonded onto TO-headers, followed by Al wire-bonding.

BTPETD was synthesized according to our previous publication [16]. Absorption spectrum was measured on a Milton Roy Spectronic 3000 Array spectrophotometer. Photoluminescence (PL) spectrum was recorded on a Perkin-Elmer LS 55 spectrofluorometer. The hybrid white light emitters were fabricated by dropping BTPETD toluene solution with concentration of 20 mg/mL on top of GaN-based LEDs to form a thin over layer of BTPETD. The thickness of this down conversion layer was carefully adjusted to achieve overall white emission from the hybrid devices through the combination of blue emission from GaN-based LEDs and down converted yellow emission from BTPETD. In addition to the BTPETD down conversion layer, the hybrid devices were later encapsulated with an epoxy coating to improve their stability. The epoxy was chosen to be curable at room temperature in this experiment to avoid any possible degradation of BTPETD at high temperature. The spectra of hybrid devices were measured at 0° viewing angle by an optical fiber of Ocean Optics USB2000 spectrometer. The CIE 1931 chromaticity coordinates were calculated from the collected spectra and verified by a PR-705 SpectraScan System. The luminance intensities were calculated from the spectra calibrated by the PR-705 SpectraScan System. The luminous efficacies at a driving current of 30 mA were measured by an integrating sphere connected to an Ocean Optics USB2000 spectrometer.

3. Results and discussion

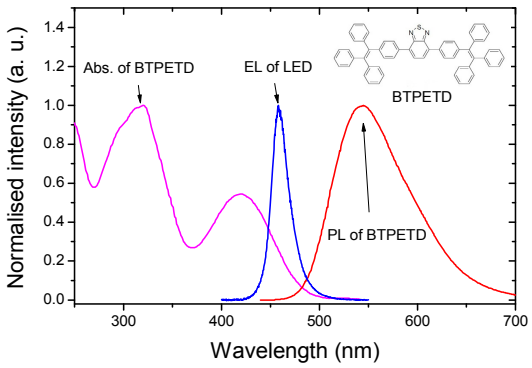

Fig. 1. Normalized absorption and PL spectra of BTPETD in THF solutions and EL spectrum of GaN-based LED. Solution concentration: 10 μM; excitation wavelength: 350 nm. The inset shows the molecular structure of BTPETD.

Figure 1 shows the absorption and PL spectra of BTPETD, as well as the electroluminescence (EL) spectrum of GaN-based LED. For hybrid devices with radiative energy transfer, there are two requirements in the luminescence down-conversion process. One is that there should be spectral overlap between the EL emission spectrum of LED and absorption spectrum of BTPETD. The other one requires the BTPETD molecule to convert absorbed photons into photons at longer wavelengths. The emission spectrum of LED shows a single peak at 460 nm with a narrow linewidth of 20 nm, and its left shoulder coincides with the absorption tail of BTPETD. Although it would be better if the EL spectrum of LED overlapped with the absorption maxima rather than presented absorption tail of the chromophore, the reason why BTPETD is still chosen to be the down-conversion material, is due to the fact that the PL of BTPETD and the blue emission from LED are complementary colors. Thus, by combining the

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blue EL emission and the yellow PL emission, white light emission from the hybrid devices can be achieved.

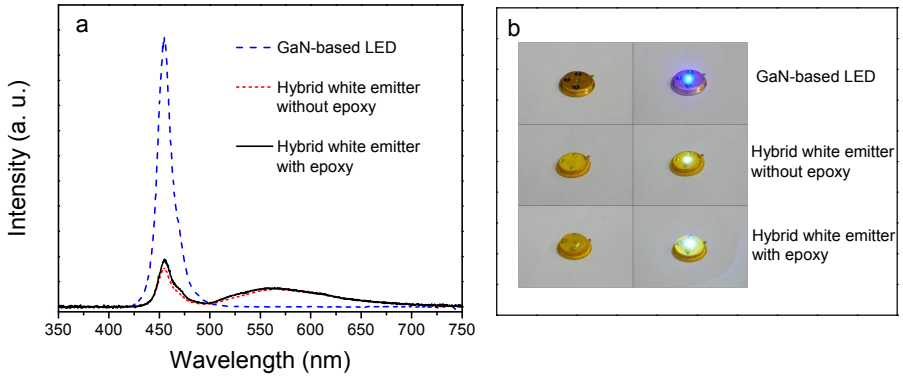

Fig. 2. (a) EL spectra of GaN-based LED and hybrid white light emitter constructed from GaN-based LED and BTPETD without and with epoxy encapsulation. (b) Photos of the fabricated devices taken in the absence (left side) and presence of 2 mA driving current (right side).

By carefully adjust the coating condition of BTPETD toluene solution onto the GaN-based LED Chip, white light emission from the hybrid devices is observed with CIE coordinates of (0.32,0.33), which is close to the ideal white color. The spectra of such devices are shown in Fig. 2(a) along with the EL spectra of GaN-based LED and Fig. 2(b) illustrates the photos of fabricated devices in switch off state or switch on state with driving current I = 2 mA. Bright blue emission can be seen from the top LED device without BTPETD coating, as well as white emission from underlying two hybrid devices. The emission characteristics of these two hybrid white light emitters with or without the epoxy encapsulation layer seems to have no obvious difference according to the emission spectra. However, as suggested by the change in PL intensity of BTPETD with time shown in Fig. 3, the device encapsulated with epoxy layer appears to be more stable under high intensity photon pumping. The epoxy layer well insulates the BTPETD molecules, which prevents them from being oxidized by air. Because the epoxy layer tend to stabilize the hybrid device, in the remaining section of this paper, all hybrid devices presented in the following discussion will be the ones encapsulated with epoxy layer.

As shown by the emission spectrum, the emission from the hybrid device consists of two parts [9]. One is the residual or "leaked" pump light from GaN-based LED, whose output power P_{Leak} can be denoted as $l \cdot P_{LED} \cdot \eta_{opt,LED}$. The other one is PL from BTPETD, its output power is:

$$P_{PL} = (1-l) \cdot P_{LED} \cdot \eta_{QE,BTPETD} \cdot \frac{\overline{E}_{nBTPETD}}{\overline{E}_{nLED}} \cdot \eta_{opt,BTPETD} \qquad (1)$$

Where l is the pump light leakage fraction, P_{LED} is the total output power of LED, $\eta_{QE,BTPETD}$ is the quantum efficiency of BTPETD, $\overline{E}_n$ is the spectral centroid photon energy and η_{opt} is the optical extraction efficiency. Giving the spectral lumen equivalent (LE) of emission from LED and BTPETD respectively, the luminous efficacy of overall emission is then given by dividing $[P_{Leak}*LE_{LED} + P_{PL}*LE_{BTPETD}]$ with P_{LED}:

$$l \cdot \eta_{opt,LED} \cdot LE_{LED} + (1-l) \cdot \eta_{QE,BTPETD} \cdot \frac{\overline{E}_{nBTPETD}}{\overline{E}_{nLED}} \cdot \eta_{opt,BTPETD} \cdot LE_{BTPETD} \qquad (2)$$

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The part of first term $\eta_{opt,LED} \cdot LE_{LED}$ in Eq. (2) can be interpreted as luminous efficacy of GaN-based LED which is 61 lm/W obtained through measurement. In the second term, the quantum efficiency of BTPETD is known as 89%. Other terms besides the optical extraction of PL emission from BTPETD all can be calculated from the emission spectra as shown in Fig. 2(a). The values of these terms are l = 17.3%, $\bar{E}_{nBTPETD}/\bar{E}_{nLED} = E_{n\lambda=585.9nm}/E_{n\lambda=458.0nm}$ = 0.782, and LE_{BTPETD} = 433.6 lm/W. The luminous efficacy of the hybrid device is measured to be 123.8 lm/W, from which we calculate the extraction efficiency of the PL of BTPETD to be 45.4% from Eq. (2). Thus by using this BTPETD molecule which has high optical extraction efficiency along with high internal quantum efficiency of 89%, we fabricated hybrid white light emitters with luminous efficacy of 123.8 lm/W under driving current I = 30 mA.

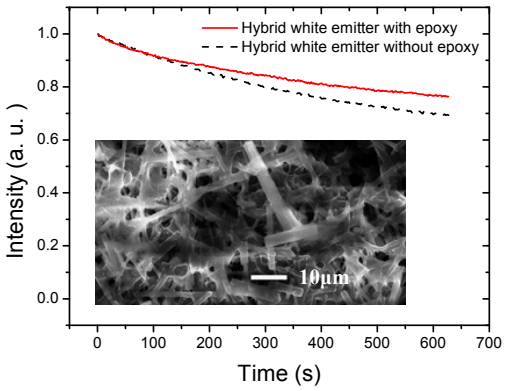

Fig. 3. Change in the PL intensity of BTPETD with time at a driving current of 30 mA. Red solid line represents hybrid white emitter encapsulated with epoxy, while black dash line represents hybrid white emitter without epoxy. The inset shows the SEM image of BTPETD deposited on the LED surface indicating formation of large aggregate/polycrystalline structures which enhance the light scattering in this hybrid white emitter.

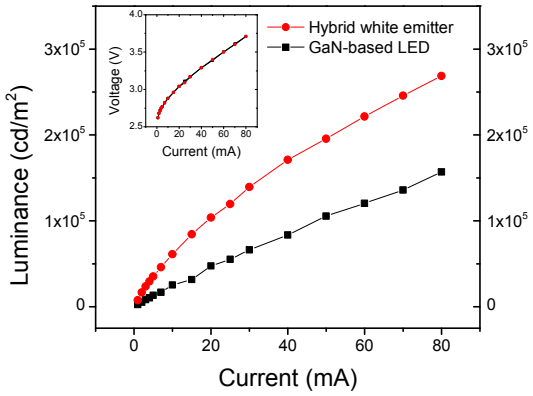

Fig. 4. Dependence of luminance and applied current in the GaN-based LED and hybrid white light emitter. The inset shows the I-V characteristic of the GaN-based LED and hybrid white light emitter.

Figure 4 shows the dependence of luminance and current in the GaN-based LED and the hybrid white light emitters. There is no difference between two I-V curves of the devices which means the BTPETD coating has no negative effects on the electronic properties of the LED (Fig. 4 inset). The luminance of the GaN-based LED can be up to 1.57×10^5 cd/m^2 with driving current up to 80 mA, and shows no degradation within such range of driving current.

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The luminance of emission from the hybrid devices is higher than the LED due to the overlap between the PL emission and the standard luminosity function, and shows a maximum of 2.69×10^5 cd/m^2 at I = 80 mA. However the BTPETD molecules degrade at intense photon pumping, which leads to the saturation at high driving current.

Figure 5(a) shows the emission spectra at different driving currents which illustrate the degradation of the hybrid white light emitters at high current density. For the blue and yellow components of the spectra, one clearly see that the EL emission from the LED increases linearly with driving current, but the PL emission from BTPETD tends to saturate at high driving current. This results in the shift of CIE chromaticity coordinates of overall emission as shown in Fig. 5(b). Generally speaking, with the increasing of driving current, the CIE coordinates of hybrid devices move away from the central white region to the left bottom corner that is close to the blue emission of the LED.

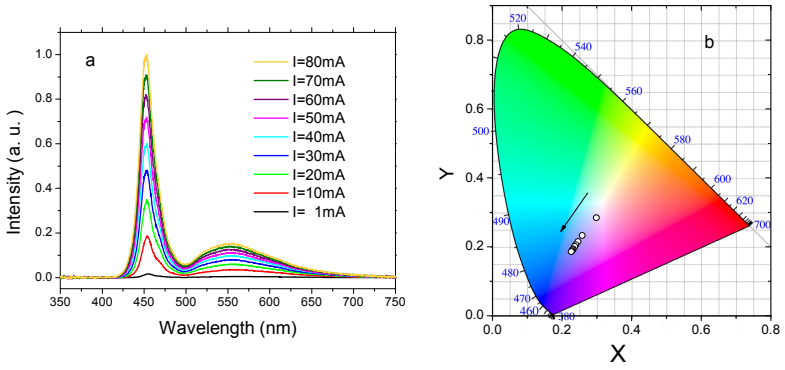

Fig. 5. (a) Emission spectra of the hybrid white light emitter at different driving currents. (b) Dependence of the CIE chromaticity coordinates on the driving current. The arrow shows the direction of driving current.

The 45% extraction efficiency for the BTPETD down conversion layer is very large. Normally for a flat organic or inorganic layer, the extraction efficiency is in the range of 10 to 20% [9]. Unlike normal polymers or other molecules such as polyfluorene or poly(*p*-phenylene-vinylene) which form a smooth film when deposited on a substrate, this AIE molecule BTPETD tends to aggregate forming particles when deposited on a substrate. Thus, this remarkable large extraction efficiency with simple deposition of the BTPETD layer on the GaN-based LED is due to aggregation of the BTPETD molecules producing a rough surface (i.e., see Fig. 3 inset) which enhance light scattering and consequently large extraction efficiency.

4. Conclusions

In summary, hybrid white light emitters constructed with GaN-based LED and AIE molecule BTPETD are demonstrated. The fabricated device shows CIE coordinates of (0.32, 0.33) and optical extraction efficacy of 45.4% with leakage fraction of 17.3%. At a driving current of 30 mA, the hybrid device shows the highest luminous efficacy of 123.8 lm/W. Formation of aggregates in solid state form for the AIE BTPETD molecules greatly enhances the extraction efficiency of the organic/inorganic hybrid white LED.

Acknowledgments

The authors thank Prof. Hoi Sing Kwok for providing PR-705 SpectraScan System for luminance intensity measurements. Financial support from the Research Grants Council of Hong Kong (project # HKUST2/CRF/10 and HKUST2/CRF/11G) and the University Grants Committee of Hong Kong (project # AoE/P-03/08, AoE/P-02/12) is acknowledged.