

Multi-layered CdSe/ZnS/CdSe heteronanocrystals to generate and tune white light

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Till date different types of white light emitting diodes (WLEDs) including multi-chip WLEDs, monolithic WLEDs, and color-conversion WLEDs have been investigated [1-3]. Among them, color-conversion WLEDs have been the most widely investigated thus far and are commercially used today [4]. For WLEDs applications, recently semiconductor quantum dot nanocrystals (NCs) have also attracted great attention because of their tunable photoluminescence, high photoluminescence quantum yields, high photostability, and easy handling. Nanocrystals have been exploited in several WLED implementations to date [5-10]. However, in all of these NC based WLEDs mono-color emitting nanocrystals or their multiple combinations have been used as the luminophors. Only recently multi-color emitting semiconductor heteronanocrystals (hetero-NCs) have been introduced by synthesizing a quantum-dot-quantum-well (QDQW) structure in CdSe-ZnS material system [11]. In this heterostructure, first a CdSe core (quantum well), then a surrounding ZnS shell (quantum barrier), and finally a CdSe shell (quantum well) are synthesized one after the other. By using these multi-layered CdSe-ZnS hetero-NCs in solution, white light generation with multi-color emission from their CdSe cores (in yellow-orange) and from their CdSe shells (in cyan) has been shown [12]. However, for white light generation, using these heteronanocrystals in solution is not sufficient for the potential application in solid state lighting. Therefore, optical properties of such heteronanocrystal luminophors in the solid form need to be carefully analyzed to understand and control the photometric properties of the generated white light.

In this study, we present tuneable white light generation by controlling CdSe/ZnS/CdSe core/shell/shell heteronanocrystals integrated on InGaN/GaN light emitting diodes [13-15]. These multi-layered quantum dots, also known as onion-like heterostructures, are designed and synthesized to emit in red (around 600 nm) from the CdSe core and in green (around 550 nm) from the CdSe shell. By designing and hybridizing these red-green emitting heterostructures on blue emitting LEDs, we demonstrate integrated WLEDs on a single chip. By controlling the number of integrated heteronanocrystals, their (x,y) tristimulus coordinates are tuned from (0.26,0.23) to (0.37,0.36) as shown in figure 1(a), along with their corresponding correlated color temperature tuned from 27413 K to 4192 K and the luminous efficacy of their optical radiation (the ratio of the emitted luminous flux to the radiant flux) tuned from 258 lm/W to 375 lm/W. We further investigate the change of in-film optical properties of these heteronanocrystals with respect to their in-solution emission. This plays a significant role in the use of these structures in hybrid LED applications.

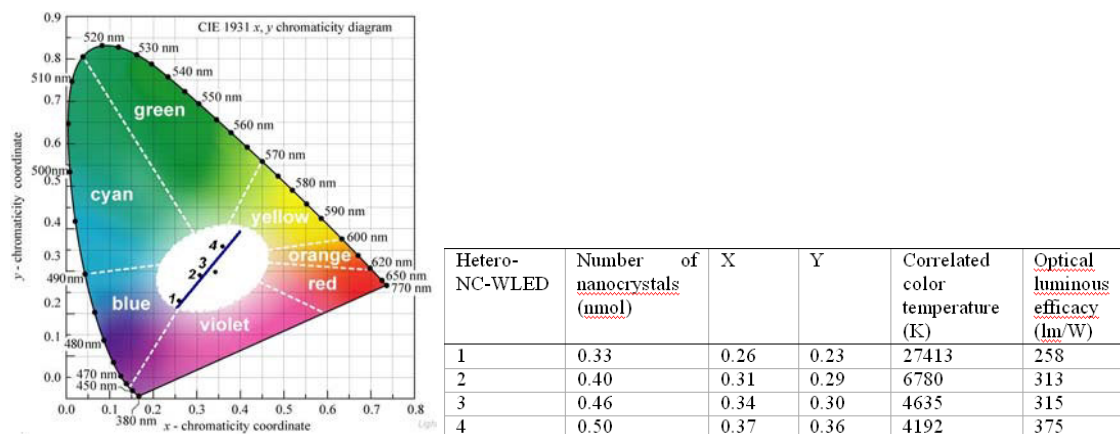


Figure 1. (a) Tuning shades of the generated white light across CIE (1931) chromaticity diagram, and (b) photometric characteristics of our hybrid white hetero-NC-WLEDs (1-4).

For sample hetero-NC-WLED 1, we integrate 0.33 nmol heteronanocrystals on the blue LED and obtain the tristimulus coordinates of (0.26,0.23) with a color temperature of 27413 K, and a luminous efficacy of the

emitted spectrum of 258 lm/W. This operating point falls in the white region as shown in Figure 1 (a). From hetero-NC based WLED 1 to 4, we gradually increase the integrated number heteronano-crystals on the pumping LED platform. Since the relative emission of the heteronano-crystals increases with respect to the blue LED electroluminescence, the color temperature decreases. In hetero-NC-WLED 4, to obtain a warmer white light, we hybridize 0.50 nmol heteronano-crystals, which yields an operating point with the tristimulus coordinates of (0.50,0.37) in the white region, a correlated color temperature of 4192 K, and a high luminous efficacy of the emitted spectrum of 375 lm/W. Photometric characteristics of our hybrid white hetero-NC-WLEDs are further summarized in Figure 1 (b).

A variety of physical mechanisms including reabsorption, dipole-dipole interaction, energy transfer, and effective dielectric constant change of the environment affect the optical emission properties of these heteronano-crystals. To investigate these luminescence modifications of such heteronano-crystals, we use another set of heteronano-crystals with in-solution luminescence peaks around 613 nm coming from CdSe core and around 558 nm coming from the shell. For investigating in-film luminescence red shift with respect to in-solution luminescence, we prepare four samples of heteronano-crystal films with different heteronano-crystal amounts precisely in integer multiples (1, 2, 4, and 9 multiples) of the starting sample (ca. 1 nmol). Tables 1(a) and 1(b) exhibit the photoluminescence (PL) peak wavelengths and relative peak intensities of these samples (Samples 1-4). These samples are all excited with a He-Cd laser at 325 nm at room temperature. By increasing the number of heteronano-crystals, we observe that both emission peaks shift towards red in the film and that the relative intensities of emission at shorter wavelengths decrease. In this red shift, re-absorption, dipole-dipole interaction, and energy transfer are the three mainly effective processes. However, with respect to the in-solution PL (reference), the core emission in the thin films (Samples 1-3) makes a blue shift as shown in Table 1(a), which is attributed to the effect of the substrate. This effect decreases with increasing number of nano-crystals [16]. Furthermore, for Samples 1-4, it is interesting to note that, although the peak emission from the core makes a red shift of 8.2 nm for Sample 1 to 4, the peak emission from the shell reveals a red shift of 11.0 nm. Thus, the shells exhibit a larger red shift in comparison to the core in the thin films. The additional red shift of shell in comparison with the core is due to delocalization of excitons in the shell over other coupled shells. At this point, it is also worth discussing that, though these onion-like heteronano-crystals have been previously [11] and also in our works [13-15] shown to exhibit multi-color emission in solutions and in films, a further study on a single-nano-crystal level needs to be conducted to verify the multiple nature of this emission from single nano-crystals. However, these present discussions will still remain valid regardless the single heteronano-crystals exhibit multiple color emission or not.

Table 1. (a) Photoluminescence peak wavelengths and **(b)** photoluminescence relative peak intensities of the synthesized onion-like (CdSe)ZnS/CdSe heteronano-crystals in solution and in film (Samples 1-4).

Samples	Peak wavelengths (nm)		Samples	Relative intensity (a.u.)	
	Shell emission peak	Core emission peak		Shell emission peak	Core emission peak
Reference (in solution)	558.42	613.32	Reference (in solution)	0.695	0.156
Sample 1 (in film)	561.75	602.17	Sample 1 (in film)	0.573	0.152
Sample 2 (2 x hetero-NCs in Sample 1)	562.74	604.64	Sample 2 (2 x hetero-NCs in Sample 1)	0.609	0.145
Sample 3 (4 x hetero-NCs in Sample 1)	560.48	612.62	Sample 3 (4 x hetero-NCs in Sample 1)	0.228	0.668
Sample 4 (9 x hetero-NCs in Sample 1)	569.44	621.53	Sample 4 (9 x hetero-NCs in Sample 1)	0.136	0.820

In conclusion, we fabricated hybrid white light emitting diodes by integration of CdSe/ZnS/CdSe core/shell/shell heteronano-crystals on blue emitting InGaN/GaN LEDs. We tuned white light parameters of (x,y) tristimulus coordinates from (0.26,0.23) to (0.37,0.36), correlated color temperature from 27413 to 4192 K, and luminous efficacy of optical radiation from 258 to 375 lm/W by controlling the number of integrated heteronano-crystals. Also, we further investigated modifications of in-film optical properties of these heteronano-crystals with respect to their in-solution emission, which plays an important role in designing solid heteronano-crystal luminophors in solid state lighting.

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