Dual-color emitting quantum-dot-quantum-well CdSe-ZnS heteronanocrystals hybridized on InGaN/GaN light emitting diodes for high-quality white light generation

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We report white light generation by hybridizing green-red emitting (CdSe)ZnS/CdSe (core)shell/shell quantum-dot-quantum-well heteronanocrystals on blue InGaN/GaN light emitting diodes with the photometric properties of tristimulus coordinates $(x,y)=(0.36,0.30)$, luminous efficacy of optical radiation LE=278 lm/W, correlated color temperature CCT=3929 K, and color-rendering index CRI=75.1. We present the photometric analysis and the quantum mechanical design of these dual-color emitting heteronanocrystals synthesized to achieve high-quality white light when hybridized on light emitting diodes. Using such multicolor emitting heteronanocrystals facilitates simple device implementation while providing good photometric properties. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2898892]

In the world, approximately 20% of the global electricity production is currently consumed for lighting, and solid-state-based light sources potentially offer 50% reduction in the global electricity consumption for illumination.[1] Today in solid state lighting, yttrium aluminum garnet phosphor-based white light emitting diodes (WLEDs) suffer from comparatively low color rendering index typically of about 70 and difficulties in largely modifying the emission spectrum of phosphor.[2] On the other hand, semiconductor nanocrystals (NCs) exhibit favorable optical properties for lighting applications. NCs feature conveniently tuneable emission using the quantum size effect,[3] allowing for application-specific spectral content, and show large quantum yields and high photostability.[4]

To date, various NC device applications have been demonstrated including sensors, scintillators, and lasers.[5–8] Among them, NC-based WLEDs have achieved significant progress. White light generation using single-color emitting (CdSe)ZnS (core)shell NCs of multiple combinations hybridized on blue-emitting InGaN/GaN LEDs has been demonstrated.[9,10] Also, dual hybridization of NCs and fluorescent polymers has been realized to generate white light.[11] Utilization of a blue/green dual-wavelength InGaN/GaN LED integrated with a single type of red NCs has been reported.[12] Furthermore, white LEDs have been fabricated using CdSeS NC mixture and layer-by-layer assembly of (CdSe)ZnS NCs on UV LEDs.[13–15] However, these WLEDs are all based on the use of monocolor emitting NCs or of their multiple combinations. Recently, complex NC structures that achieve multicolor emission have been investigated.[16] Using a quantum-dot-quantum-well structure in the CdSe–ZnS material system, dual emission in the visible has been accomplished by Battaglia *et al.*[17] Such a heteronanocrystal consists of a quantum dot core made of CdSe, then a ZnS shell barrier surrounding the core, and finally a CdSe shell quantum well surrounding the barrier. Sapra *et al.* has also previously demonstrated white light emitting heteronanocrystals in solution by using dual-color emission in cyan and red;[18] however, only these cyan and red color emitting heteronanocrystals in solution are not sufficient for lighting applications, e.g., due to their low color rendering index.

In this work, we present high-quality white light generation by hybridizing dual-color heteronanocrystals made of (CdSe)ZnS/CdSe in (core)shell/shell structure emitting in red from the CdSe cores and green from the CdSe shells on blue InGaN/GaN LEDs. Employing these onionlike heteronanocrystals, we achieve the photometric properties of tristimulus coordinates $(x,y)=(0.36,0.30)$, luminous efficacy of optical radiation (the ratio of emitted luminous flux to radiant flux as lumens per optical power) LE=278 lm/W, correlated color temperature CCT=3929 K, and color rendering index CRI=75.1, with the emission spectrum, as shown in Fig. 1. We also report the quantum mechanical design and the photometric analysis of these dual-color emitting quantum-dot-quantum-well heteronanocrystals integrated on LEDs to obtain high-quality white light.

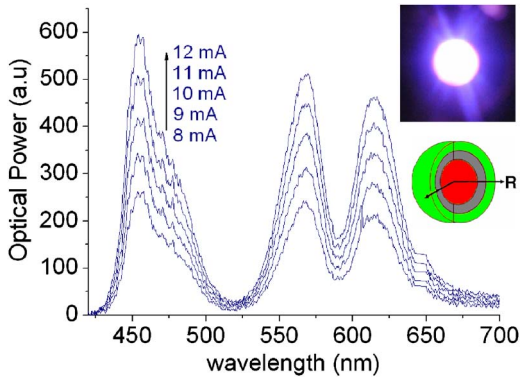

FIG. 1. (Color online) Luminescence spectra of onionlike (CdSe)ZnS/CdSe (core)shell/shell heteronanocrystals hybridized on a blue light emitting diode driven at different levels of current injection at room temperature, along with a schematic structure of the heteronanocrystals and a picture of the resulting hybrid NC-WLED while generating white light.

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TABLE I. Material parameters of CdSe and ZnS.

Material	m_e^*	m_h^*	Monolayer (nm)	Band discontinuity (eV)
CdSe	0.13	0.45	0.56	···
ZnS	0.28	0.49	0.49	1.75 (with respect to CdSe)

In operation, the single color electroluminescence from-LED and the resuling dual-color photoluminescence from the NC emitters contribute to the white light generation. However, to achieve such white light generation with high-quality photometric properties, these NC emitters along with their integrating LEDs need to be very carefully analyzed and designed. For that purpose, in our photometric analysis, by taking into account the possible emission ranges of our heteronanocrystals and LEDs for white light generation, as in the case of conventional red-green-blue WLEDs, we consider a peak emission wavelength of 450 nm in the blue region to be provided by the InGaN/GaN LED, and two peak wavelengths of 550 nm in the green and 620 nm in the red region to be provided by the heteronanocrystals. For feasible implementation, we take the emission in each color with identical peak levels and with a typical variance of 20 nm (corresponding to a full width at half maximum of 33 nm). The photometric analysis of these design parameters leads to white light generation with the optical properties of $(x,y)=(0.34,0.30)$, LE=315 lm/W, CCT=4979 K, and CRI=75.5. This shows in principle that the use of such green-red emitting heteronanocrystals on blue LED enables achieving high-quality WLEDs, if properly designed. To obtain green and red emission from our heteronanocrystals at the targeted wavelengths when cast into solid thin films, we also consider a typical in-film redshift of approximately 20 nm with respect to in-solution emission (due to the interactions[19] between the NCs when in film, e.g., reabsorption, dipole-dipole interaction, energy transfer, etc.). This means that the red emission from the CdSe core must be at around 600 nm in solution. This requires a quantum dot radius of approximately 2.22 nm.[20] Surrounding the core, we then need to add 2 ML of ZnS, which provides a sufficiently high potential barrier. Finally, surrounding the ZnS shell, we need to add the CdSe shell to obtain the green emission as desired.

TABLE II. Electron and hole wave function overlaps ($\langle\psi_{\text{electron}}(r)|\psi_{\text{hole}}(r)\rangle$), their overlap squares ($\langle\psi_{\text{electron}}(r)|\psi_{\text{hole}}(r)\rangle^2$), the exciton binding energy due to their Coulomb interaction, and the resulting optical transition energies for the ground states ($n=1$) and for the first excited states ($n=2$).

	Overlap	Overlap square	Coulomb interaction (meV)	Transition energy (eV)
Ground states ($n=1$)	0.9390	0.8817	99.1	2.0622
First excited states ($n=2$)	0.9505	0.9035	25.8	2.3913

For the quantum mechanical analysis of our dual-color emitting heteronanocrystals, we consider only *s*-symmetry states (with zero angular momentum) in which the wave function depends on the radial part $R_{n,1=0}(r)$. The material parameters used in our design are summarized in Table I.[21–25] After solving for the energy levels (eigenvalues) and wave functions (eigenfunctions) assuming the effective mass approximation,[26] we calculate the energy difference in each transition by adding the respective hole and electron energy eigenvalues, and the Coulomb interaction as a first-order perturbation.[27] As a result, the emission from the CdSe core is computed to be at 602 nm as expected for a radius of 2.22 nm, and the green emission from the CdSe shell is obtained at 518 nm when 2 ML of CdSe shell is used. (Since in our simulation, the last ZnS barrier is taken to be infinitely thick to find bounded solutions, we further expect to have a redshift for this 518 nm peak because of the reduced confinement of the electrons and holes due to the finite barrier in the implementation.) The probability distribution and the spatial product of the electron and hole wave functions for this heteronanocrystal structure are presented in Figs. 2(a) and 2(b) for the ground states ($n=1$) and for the first excited states ($n=2$), respectively. Also, the wave function overlaps and overlap squares (oscillator strength), the exciton binding energy due to the Coulomb interaction, and the resulting optical transition energies are listed in Table II. In both $n=1$ and $n=2$ transition energies, our analysis predicts that the oscillator strengths are near to 1, showing that the transition probability is high, and that the ground state excitons are localized in the core for the red emission and the first excited state excitons are mainly localized in the CdSe shell for the green luminescence possibly to lead to dual-color emis-

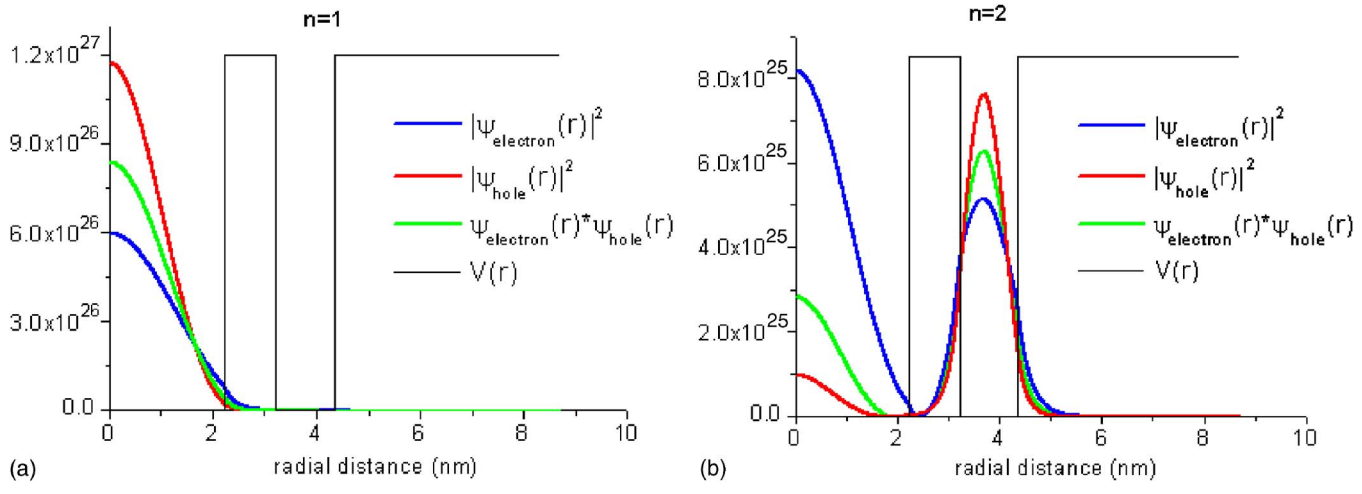

FIG. 2. (Color online) $|\psi_{\text{electron}}(r)|^2$ (in blue) and $|\psi_{\text{hole}}(r)|^2$ (in red) show the probability distribution of electron and holes in the (CdSe)ZnS/CdSe (core)shell/shell heteronanocrystals, respectively, while $\psi_{\text{electron}}(r)^*\ \psi_{\text{hole}}(r)$ (in green) indicates the relative spatial localization of excitons, with respect to the potential profile (in black): (a) for the ground states ($n=1$) and (b) for the first excited states ($n=2$).

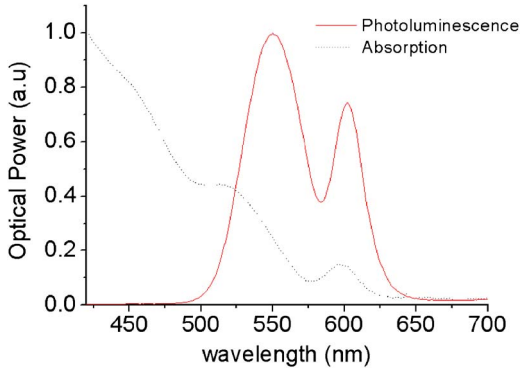

FIG. 3. (Color online) In-solution photoluminescence and absorption spectra of onionlike (CdSe)ZnS/CdSe (core)shell/shell heteronanocrystals.

sion. However, at this juncture, it is also worth mentioning that although the theoretical calculations predict dual emission and these onionlike structures have been shown to exhibit dual emission in the solutions, a further study on a single-particle level needs to be performed to confirm the dual nature of this emission. Nevertheless, the present working parameters for the device will still remain valid whether the single particles exhibit dual emission or not.

To realize our heteronanocrystal design, we synthesize (CdSe)ZnS/CdSe (core)shell/shell NCs by following the procedure given in Ref. 18. The absorption and emission spectra of the resultant NCs are given in Fig. 3. In solution, it is significant to obtain the red peak lower than the green peak, because when the NCs are closely packed in film, the green light emitted by the NC shells is partially reabsorbed by the NC cores that re-emit in red, and as a result, the lower red peak increases. For the blue InGaN/GaN LED, we use a GaN dedicated metal-organic chemical vapor deposition system (Aixtron RF200/4 RF-S). For this LED emitting at 452 nm, similar design, growth, fabrication, and characterization are explained in our previous work.[28–31] For the hybridization of NCs and LED, we make closely packed NC films on the LED platform.

For the hybrid NC-WLED, we use 0.83 nmol of these dual-color emitting heteronanocrystals to achieve white light generation. The resulting luminescence spectra under different current injection levels are given in Fig. 1, which correspond to $(x,y)=(0.36,0.30)$, LE=278 lm/W, CCT=3929 K, and CRI=75.1 at all current levels. These experimental results are in good agreement with our photometric simulation. For example, in our previous research work, white light generation by hybridizing a single combination of yellow NCs (λ_{PL}=580 nm) is obtained with a color rendering index of only 14.6.[8] In another work of ours, even when quadruple combinations of NCs—green (λ_{PL}=540 nm), cyan (λ_{PL}=500 nm), yellow (λ_{PL}=580 nm), and red (λ_{PL}=620 nm)—are hybridized with the blue LED (λ_{EL}=452 nm), the result is a color rendering index of only 71.0.[9] On the other hand, in this work, using only a single type of green-red emitting heteronanocrystals, the color rendering index is 75.1. Thus, the hybrid WLEDs based on such onionlike heteronanocrystals are advantageous because they provide high color rendering index thanks to their tuneable broad emission.

In conclusion, we presented white light generation by hybridizing dual-color green and red emitting heteronanocrystals made of (CdSe)ZnS/CdSe (core)shell/shell on a blue emitting InGaN/GaN LED. We showed the photometric and quantum mechanical analyses of these onionlike heteronanocrystals integrated on blue LEDs to achieve high-quality white light generation. These hybrid WLEDs based on such multicolor emitting heteronanocrystals prove to be beneficial because of simple device hybridization requiring the integration of only a single type of NCs rather than the integration of multiple combinations of various single-color emitting NCs.

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