Förster resonance energy transfer enhanced color-conversion using colloidal semiconductor quantum dots for solid state lighting

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In this paper, we present Förster resonance energy transfer (FRET)-enhanced color-conversion using colloidal semiconductor quantum dot nanocrystals (NCs) to make reddish-orange light-emitting diodes for use in ultraefficient solid state lighting. To achieve FRET enhancement at 614 nm, we use an energy gradient hybrid structure made of cyan- and orange-emitting CdSe/ZnS NCs (λ_{PL}=492 and 588 nm in solution, respectively). This enables recycling of trapped excitons using FRET and achieves a relative quantum efficiency enhancement of 15.1% in reddish-orange full color-conversion for the integrated hybrid cyan-orange NC layer with respect to the case of full color-conversion using only orange NCs without FRET. © *2009 American Institute of Physics*. [doi:10.1063/1.3222902]

Today lighting is one of the major energy consumption items in the world. Solid state lighting (SSL) potentially provides substantial energy savings to allow for efficient energy utilization of the limited energy sources and reduction in carbon emission.[1,2] To further increase the energy saving of SSL, a photometric design (named "ultraefficient solid-state lighting") that simultaneously achieves a luminous efficacy of 408 lm/W and a color rendering index (CRI) of 90 at a warm correlated color temperature of 3000 K has been proposed.[3,4] To achieve these photometric properties, it is required to have a set of pure color emission in blue, green, yellow, and orange with the corresponding power levels of 1/8 at 463 nm, 2/8 at 530 nm, 2/8 at 573 nm, and 3/8 at 614 nm, each color having a full width at half maximum (FWHM) of 1 nm.[3,4] In this design, the reddish-orange is the strongest color component with the highest relative power (3/8) and at the longest optical wavelength (at 614 nm), thus with the largest number of photons emitted per unit time among the other color components.

However, the internal quantum efficiency of $In_xGa_{1-x}N$ structures begins to significantly drop as approaching from blue to green color in the visible due to the increased In content in multiquantum wells, though $In_xGa_{1-x}N$ material system has the capability to cover the whole visible. Therefore, it is not possible to obtain reddish-orange emission at 614 nm by using $In_xGa_{1-x}N$ material system.[5–7] Different from the $In_xGa_{1-x}N$ material system, it is possible to achieve reddish-orange emission by using a quaternary alloy $(Al_xGa_{1-x})_{1-y}In_yP$. However, this material system is different from the $In_xGa_{1-x}N$ based material system, which prevents single-chip implementation of $In_xGa_{1-x}N$ based red color emission. The quantum efficiency of $(Al_xGa_{1-x})_{1-y}In_yP$ is also observed to decrease significantly as going from red to the other colors at shorter wavelengths due to the decreasing barrier energy in their quantum well structure. As a possible solution, color-converters can be used for light generation at 614 nm on $In_xGa_{1-x}N$ material system for reddish-orange emission. Although phosphors are the most commonly used color converters on InGaN/GaN light-emitting diodes (LEDs), they are not suitable for generating pure red/orange emission efficiently (e.g., at 614 nm of ultraefficient SSL), as simulated using Refs. 8 and 9 (and also shown in Fig. 1), due to their wide FWHM (of about 100 nm), which undesirably causes the luminous efficacy to drop significantly (down to around 64 lm/W). Therefore, the hybrid use of a relatively narrow color-converter is important to enable the use of $In_xGa_{1-x}N$ LEDs at such long wavelengths.

To achieve this reddish-orange emission needed for ultraefficient SSL, semiconductor colloidal quantum dot nanocrystals (NCs) exhibit favorable optical properties with their narrow and symmetric photoluminescence, which is also widely and precisely tunable across the visible using quantum confinement effect for the targeted peak emission wavelengths.[10,11] In the previous works of our group and the others, a wide range of studies on NC-integrated LEDs, Förster resonance energy transfer (FRET) in NCs, and the

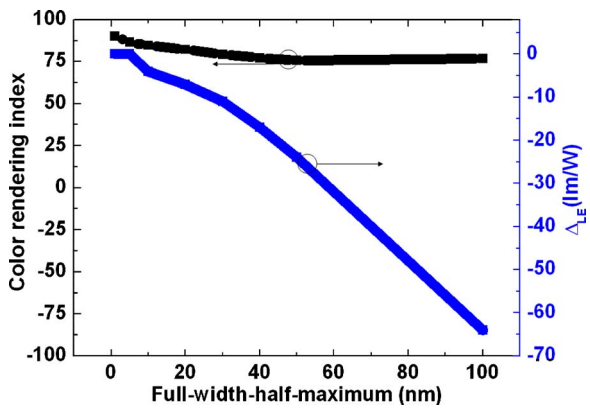

FIG. 1. (Color online) Investigation of FWHM-dependent CRI and luminous efficacy change in optical radiation (Δ_{LE}) with respect to the case of 1 nm FWHM for ultraefficient SSL (with power levels of 1/8 at 463 nm, 2/8 at 530 nm, 2/8 at 573 nm, and 3/8 at 614 nm).

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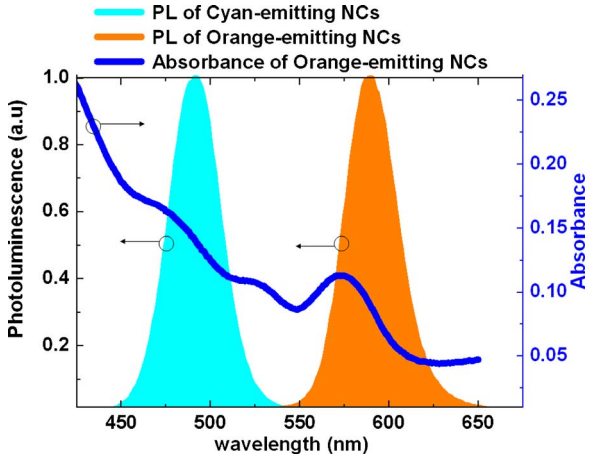

FIG. 2. (Color online) Emission/absorption spectra of orange-emitting CdSe/ZnS core/shell NCs (acceptors) and emission of cyan-emitting CdSe/ZnS core/shell NCs (donors).

use of NCs in white and green/yellow LEDs have already been reported.[12–17] However, FRET-enhanced color-conversion at long wavelengths critically important for ultra-efficient SSL has not been investigated to date. For that, in this paper we present NC-based orange color-conversion at long wavelengths (614 nm) that utilizes FRET in full color-conversion on $In_xGa_{1-x}N$ LEDs for enhanced efficiency. To enable FRET in NCs, we establish an energy gradient hybrid film that embeds a custom-design assembly of cyan- and orange-emitting CdSe/ZnS core/shell NCs. By using this energy gradient, the trapped excitons are recycled into NCs rather than losing them through nonradiative recombination in trap centers. As a result, we achieve a relative quantum efficiency enhancement of 15.1% in full color-conversion for this hybrid cyan-orange NC film with respect to the full color-conversion layer of only orange NCs without FRET.

Figure 1 presents the CRI and luminous efficacy of optical radiation both decreasing as a function of increasing FWHM of 614 nm emission used in SSL as described above. Despite exhibiting FWHM linewidths larger than 1 nm (e.g., 30–40 nm), we find out that the resulting CRI of these NC color-converters is reduced only slightly by 11–13 units, and their luminous efficacy, only by 11–17 lm/W, compared to the case of 1 nm wide FWHM as illustrated in Fig. 1. Thus, this shows that it is possible to achieve reddish-orange emission at 614 nm by using NCs with sufficiently high CRI and high luminous efficacy as required for ultraefficient SSL.

To establish energy gradient, we employ cyan- and orange-emitting CdSe/ZnS core/shell NCs with photoluminescence peaks at 493 and 588 nm in solution, respectively, as depicted in Fig. 2. Our cyan- and orange-emitting NCs have concentrations of 171 and 70 nmol/ml in the toluene solution and molecular weights of 85 and 200 μg/nmol, respectively. Their respective radius is around 3.2 and 4.4 nm, both with a size dispersion of $<5\%$, and they exhibit a quantum efficiency of $>50\%$ in solution.[18] To achieve full color-conversion, we further integrate closely packed NCs in film with just sufficient amounts on the near-UV InGaN LEDs. To accomplish ultraefficient photometric properties in SSL, we reach our desired operating point around 614 nm by using the redshift of these NCs when cast into a solid film due to the resonant coupling and environmental changes. Here in operation the electroluminescence of the near-UV LED excites this integrated NC film and these NCs make photoluminescence so that the desired reddish-orange light at around 614 nm is generated. (The growth, fabrication, and characterization of these near-UV LEDs are explained in detail in Ref. 15.)

For FRET enhancement in color-conversion using NCs, we integrate a carefully designed assembly of 5.6 nmol cyan-emitting donor NCs and 5.6 nmol orange-emitting acceptor NCs, for which the maximum quantum efficiency enhancement is observed at a donor-acceptor ratio of 1:1.[19] These are the minimum NC amounts that lead to full color-conversion in the reddish-orange, while keeping the 1:1 ratio between the cyan and orange NCs. By using this hybrid assembly of NCs, we establish a sufficient energy gradient for nonradiative energy transfer on the near-UV LED. This mixture of NCs further enhance the overall quantum efficiency of the integrated NC film, while fully converting the incident UV photons to reddish-orange photons (with no UV or green photons coming off the hybrid film). Here the quantum efficiency increase comes from recycling of trapped excitonic energy in defect states of donor NCs into acceptor NCs through FRET, as also discussed in Refs. 14, 19, and 20. When the incoming near-UV light is absorbed by these NCs for color-conversion, electron-hole pairs are generated. These photogenerated electron and hole pairs then relax to their respective conduction and valence bands. Some portion of these electron-hole pairs get trapped in the defect states and typically make nonradiative recombination. This decreases the quantum efficiency of the NC film. Using FRET, some of these trapped excitons are further transferred to the orange-emitting NCs that behave as acceptors for these defect states. Therefore, rather than losing the trapped excitons in defect states, a part of the transferred excitons contributes to the emission by radiative recombination.

To investigate the level of efficiency enhancement in this hybrid NC film, we also prepare a negative control group using only orange-emitting NCs. For that, we integrate 7 nmol orange-emitting CdSe/ZnS NCs on our near-UV LED, which is the minimum amount that also achieves full color-conversion in the reddish-orange color. Here for the power measurements to compare quantum efficiencies, we use an integrating sphere (Newport). Initially, we measure the optical output power and the quantum efficiency of the near-UV LEDs; afterward, we measure those of the NC-integrated LEDs. Then, we obtain the quantum efficiency of the NC color-converters extracted from these two sets of data, separately for the cases of using hybrid NC film and control NC film. In both cases, it is made sure that it is full photon conversion to the reddish-orange for fair comparison between them.

Figure 3 shows the time-resolved spectroscopy measurements of the integrated NCs at 614 nm. For time-resolved spectroscopy measurements, we use a FluoTime 200 spectrometer (PicoQuant) with a time-correlated single photon counting system of PicoHarp 300. The system has a calibrated time resolution of 32 ps. We pump our NCs using a laser head at an emission wavelength of 375 nm with light pulses as short as 70 ps. We use a photon multiplier tube as the detector. With an output monochromator, we characterize all of the prepared NC solids at 614 nm, corresponding to the approximate peak emission wavelengths of these NC solids. In Fig. 3 the energy rising component (i.e., the exponential increase) in the photoluminescence kinetics of the hybrid

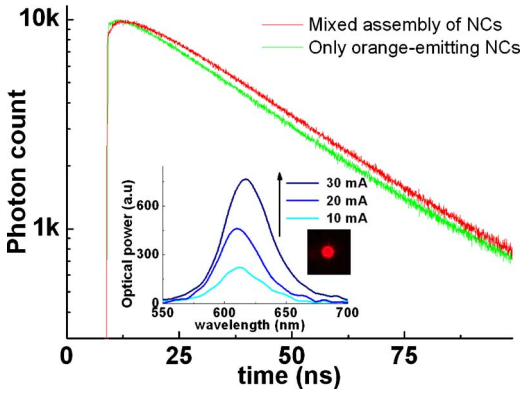

FIG. 3. (Color online) Time-resolved spectroscopy measurements of the integrated orange-emitting CdSe/ZnS core/shell NCs (λ_{PL}=588 nm) and hybrid cyan- and orange-emitting CdSe/ZnS core/shell NCs (λ_{PL}=492 and 588 nm, respectively) on near-UV LED (λ_{EL}=379 nm) along with the emission spectra at different levels of current injection at room temperature and picture of the hybrid NC-LED when electrically driven.

film of these mixed cyan-orange NCs is more dominant compared to the case of the control NC film, because of the strong exciton migration to the orange-emitting NCs in the hybrid film. This manifests itself as a slower photoluminescence decay at shorter times for the hybrid NC film. At longer times, the slope of the decay is almost the same for the hybrid film as that of the control film because their interband recombination lifetimes are similar on the order of tens of nanoseconds.[21]

By using the FRET-enhanced color-conversion, we obtain the resulting luminescence of the hybrid device changing from 612 to 616 nm with the increasing current injection level as shown in the inset of Fig. 3. This NC-based reddish-orange LED leads to a luminous efficacy of optical radiation at 278.7 lm/W and its energy gradient hybrid NC film achieves a quantum efficiency of 16.92% in full color-conversion of UV to reddish-orange. On the other hand, the control NC film without using FRET shows a lower quantum efficiency of 14.7%, again in the full color-conversion on the near-UV LED. As a result, the relative quantum efficiency enhancement in the hybrid cyan-orange NC film is 15.1% in full color-conversion in reddish-orange (with respect to the only orange NCs without FRET). Here it is important again to note that, because of the strong nonradiative energy transfer, cyan-emitting NCs are fully quenched by transferring their energy to orange-emitting NCs in the hybrid film; therefore, the hybrid film only provides orange emission. This proof-of-concept demonstration shows that NC-based LEDs enable us to reach the desired operating wavelength important for ultraefficient SSL without making major sacrifices in color rendering and luminous efficiency because of their relatively narrow emission linewidths.

In conclusion, we presented FRET-enhanced reddish-orange LEDs in which we integrated colloidal semiconductor NCs as color converters on near-UV InGaN/GaN LEDs. For that, we made a hybrid assembly of cyan- and orange-emitting CdSe/ZnS core/shell NCs to enhance the efficiency of hybrid NC LED. By recycling of the trapped excitons into NCs, we achieved a relative quantum efficiency enhancement of 15.1% in full color-conversion with respect to the negative control group without FRET.

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