FRET-LEDs involving colloidal quantum dot nanophosphors

S. Nizamoglu, E. Sari, J.-H. Baek, I.-H. Lee, X. W. Sun and H. V. Demir

***Abstract*— Semiconductor nanocrystal quantum dots (NQD) with their narrow and tuneable emission are promising candidates to serve as color convertors integrated on light-emitting diodes (LEDs). The use of nonradiative energy transfer, also known as Förster-type resonance energy transfer (FRET), in such NQD nanophosphors provides additional benefits for color-conversion in solid state lighting. In this paper we discuss these NQD-integrated FRET-LEDs for lighting applications.**

***Index Terms*— Förster resonance energy transfer, light emitting diode, nanocrystal quantum dot, exciton**

I. Introduction

Solid state lighting (SSL) exhibits significant benefits in terms of energy saving and carbon dioxide emission reduction [1]. By extrapolating from current rates of technological progress in SSL, it is expected that the cost of SSL will catch the traditional lighting costs including that of compact fluorescent lamps in 2012 [2]. For SSL both single-colored and white light emitting diodes (LEDs) are needed. As single-colored light sources, LEDs also present a flexible option in various applications of artificial lighting. For example, for greenhouse lighting, during photosynthesis, plants need illumination at around the absorption peaks of chlorophylls a and b molecules (at 662 nm and 642 nm, respectively) [3]. Thus, single-colored LEDs having luminescence close to those absorption lines are good candidates for agricultural applications.

White light emitting diodes (WLEDs) are required for indoor and outdoor illumination. Today one of the most common approaches used for making WLEDs is the integration of broadly emitting visible phosphors as the color converting layer on blue InGaN/GaN light emitting diodes. However, as reported by Sandia National Laboratories (SNL), instead, combinations of narrow emitters, e.g., those with full-width-at-half-maximum (FWHM) as narrow as 1 nm (at the emission wavelengths of 463, 530, 573 and 614 nm) are required to achieve white light generation with color rendering index of 90 and luminous efficacy of 408 lm/W at a correlated color temperature of 3000 K [4]. But FWHMs of traditional luminophores are significantly wider. For example, conventional rare earth ion based phosphors, whose peak emissions can be tuned by changing the chemical composition from yellow to red, have a substantially broad emission covering most of the whole visible. This decreases the luminous efficacy significantly when used as a color convertor, e.g., for warm white LED.

On the other hand, colloidal semiconductor nanocrystal quantum dots (NQDs) exhibit significantly narrower emission linewidths (around 30-40 nm) with respect to conventional phosphors to be used both for single-colored and white LEDs [5]. They exhibit tuneable and controllable emission by controlling their size and structure. Their emission can be adjusted from blue to mid-infrared, varying size in different material systems. Furthermore, they can be easily integrated on LEDs as color converters, and their photostability and photobleaching thresholds are high; more recently high quantum efficiencies have also been shown. Because of these important benefits and continuing development in their colloidal synthesis, they are strong candidates for use in color-conversion LEDs.

NQDs are also capable of facilitating nonradiative Förster-type resonance energy transfer (FRET) between themselves and with other specifies, if the required conditions are set right. FRET is a fast, directional and nonradiative transfer of the excitonic energy (e.g., from donor NQDs to acceptor NQDs). The spectral tunability of NQDs with quantum confinement effect allows us to engineer and control FRET-mediated excitonic energy flow. To date FRET mechanism has been extensively studied by various groups [6]-[10]. Previously Franzl *et al.* demonstrated fast energy

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transfer in layer-by-layer deposited NQDs [9]. Afterward, they showed a cascaded energy transfer structure consisting of subsequent layers comprising green-, yellow-, orange-, red-, orange-, yellow-, and green-emitting NQDs resulting in a funnel-like band gap energy profile. In this structure they observed a four-fold increased photoluminenscence in the cascaded structure with respect to the reference structure consisting of seven layers of all red-emitting NQDs. This emission enhancement stems from the recycling of trapped excitons because of strong FRET [10].

In this paper, we study the donor-acceptor ratios to determine the operating point for quantum efficiency enhancement and demonstrate color-conversion NQD integrated LEDs that are enhanced via FRET by recycling of trapped excitons in the integrated color-conversion layer. Specifically, for greenhouse illumination, the emission wavelength range of NQD color-converting layer is shown around 650 nm to enable strong optical absorption in chlorophylls. Additionally, for indoors/outdoors applications the emission wavelengths of the integrated NQD layer is adjusted to provide color-conversion at the specific wavelengths of 573 and 614 nm, which are important for achieving white light generation with high performance as described by SNL [2].

II. MATERIALS USED FOR NANOCRYSTAL QUANTUM DOT HYBRIDIZED LEDS

For FRET-enhanced hybrid LEDs we use cyan-, green-, orange and red-emitting CdSe/ZnS core/shell NQDs. Fig. 1 shows the emission and absorption of these NQDs. The advantages of using such a ZnS shell structure surrounding the CdSe core is that the shell increases the quantum efficiency and photostability of the NQDs and that it fully confines the wavefunctions of the photogenerated charges in the nanocrystal. In our research work presented in this paper the NQDs films are made by close-packed film formation. This hybrid NQD layers are integrated on different InGaN/GaN blue and n-UV LEDs. Such one packaged LED integrated with NQDs is shown as an example in the inset of Fig. 1. The growth and fabrication details of LEDs are explained elsewhere (e.g., see [11]). The turn-on voltage of these blue and n-UV LEDs is around 2.8 and 3.0 V, respectively and their emission wavelengths are 454 and 379 nm, respectively.

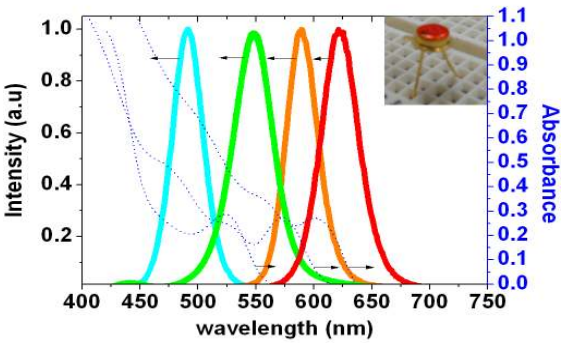

Fig. 1. Emission and absorption of CdSe/ZnS core/shell semiconductor nanocrystal quantum dots used for color-conversion LEDs. Inset shows the photograph of a color-conversion LED integrated with nanocrystal quantum dot nanophosphors.

III. EXCITON RECYCLING VIA FRET

The process of the exciton recycling is important for quantum efficiency enhancement of these integrated NQD nanophosphors layers. The process takes place as follows: The incoming photon is absorbed by the donor NQD and an exciton is generated, and the electron-hole pair then relaxes to their respective conduction and valance bands. This exciton at the interband level can, however, be coupled to the trap states due to the defects and make possibly nonradiative recombination therein. By putting an acceptor NQD in the vicinity of the donor NQD, an energy gradient structure is generated and FRET process from donor to acceptor NQDs occurs. Via FRET this trapped exciton can be transferred to the nearby NQD so that a fraction of the migrated excitons from trapped states can contribute to the acceptor luminescence by radiative recombination. This leads to enhancement in the overall emission [12]. To study the optimum point for the exciton recycling process, we vary the donor/acceptor NQD ratio. For this investigation we use cyan- and green-emitting CdSe/ZnS core/shell NQDs that generate the necessary energy gradient for FRET process. Fig. 2 shows the change of the relative quantum efficiency enhancement for different donor/acceptor ratios. In this figure, the reference points at the edges that are represented with 10^{-4} and 10^{4} are the only acceptor and only donor cases, respectively. As we integrate more donor NQDs in the hybrid layer, more of the trapped excitons start to be transferred to the acceptors and the efficiency of the hybrid layer begins to increase. However, after a certain optimum point, there are not enough acceptors nearby to the collect the trapped excitons via FRET and the enhancement drops. In our experiments, the optimum point for the donor:acceptor ratio is found to be ~1:1 for this hybrid system. Thus, to achieve the highest possible quantum efficiency enhancement, the integrated layer needs to have roughly equal number of donors and acceptors in our case.

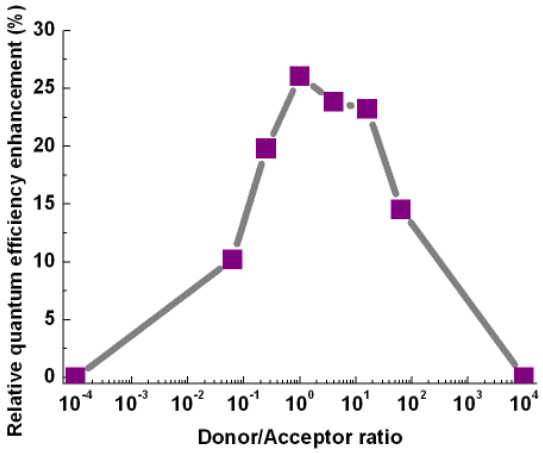

Fig. 2. Relative quantum efficiency enhancement change of the nanocrystal quantum dot layers by recycling of trapped excitons via FRET for various donor/acceptor ratios.

IV. NANOCRYSTAL QUANTUM DOT HYBRIDIZED LEDS FOR GREENHOUSE APPLICATION

To accomplish NQD integrated LED for artificial greenhouse lighting we need emission at around 650 nm so that we can pump the chlorophylls a and b together whose absorption peaks are at 642 and 662 nm. For that on blue LED we integrate a mixture of cyan- and red-emitting NQDs (consisting of the same amount of ca. 5 nmol for maximum quantum efficiency enhancement in the integrated layer) to recycle the trapped excitons. Using these amounts of NQD, all of the blue radiation from LED is fully down-converted to red by the integrated color-conversion NQD layer and we obtain the resulting emission spectra as shown in Fig. 3. The luminescence peak wavelength shifts from 640 nm to 646 nm due to the heat generated by the LED. This hybrid LED achieves an optical power of 0.187 mW at 19 mA (on the other hand, only blue LED generates an optical power of 1.179 mW at 19 mA). Thus, the quantum efficiency of this integrated layer corresponds to 22.4%. As the reference color-conversion layer we also hybridize only red-emitting CdSe/ZnS core/shell NQDs on top of the blue LED. Now at 19 mA this hybrid LED achieves an optical power of 0.142 mW and the quantum efficiency of this integrated layer corresponds to only 17.0%. Thus, the quantum efficiency enhancement for the mixed assembly of NQDs is 31%, which is also close to the results revealed in Fig. 2.

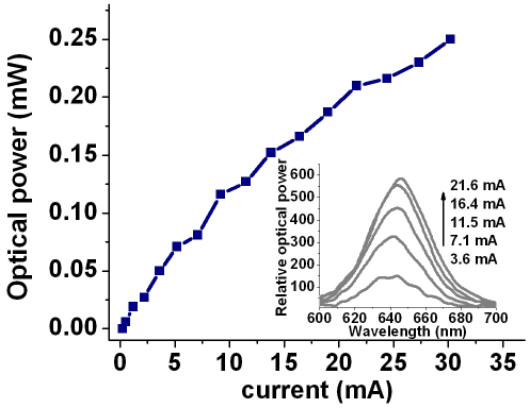

Fig. 3. Optical output power of NQD integrated LEDs for greenhouse application. Inset shows on the emission spectra at different current injection levels at room temperature.

Furthermore, for time-resolved measurements, we use a laser diode at 375 nm to pump the NQDs and a photon multiplier tube (PMT) as the detector. A time-resolution of 4 ps can be achieved in this system. Fig. 4 indicates the time-resolved spectroscopy measurements of the hybrid layers of mixed cyan- and red-emitting NQDs and that of only red-emitting NQDs at the acceptor emission wavelength. The mixed NQD sample shows a slower photoluminescence decay with respect to the only red-emitting NQDs because these acceptor NQDs are fed with the transferred energy from the donor NQDs. To clearly observe FRET in the acceptor emission, in the inset the subtracted dynamics of the hybrid layers of mixed cyan- and red-emitting NQDs from the only red-emitting NQDs is shown.

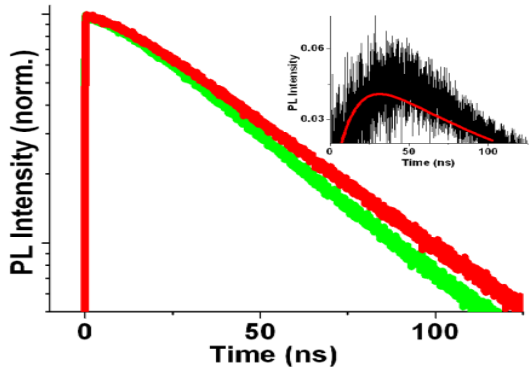

Fig. 4. Time resolved spectroscopy of the mixed cyan- and red-emitting NQDs integrated layer (in red) and only red-emitting NQDs integrated layer (in green). Inset shows the difference of the mixed cyan- and red-emitting NQDs integrated layer dynamics from the only red-emitting NQDs integrated layer (solid black-colored line) and its theoretical fit (dotted red line).

The decay of the NQDs experiencing FRET can be expressed by Eq. (1) [13] and this fitted dynamics is in agreement with the experimental measurements.

$$I(t) \propto \frac{k_{FRET}}{k_A - k_D - k_{FRET}} \left(e^{-(k_D + k_{FRET})t} - e^{-k_A t} \right) \quad \textbf{(1)}$$

V. NANOCRYSTAL QUANTUM DOT HYBRIDIZED LEDS FOR WHITE LIGHT GENERATION

As our color-conversion LED required for high-quality white light generation, we work on hybrid LEDs to achieve greenish yellow emission at 573 nm [11]. For that we hybridize 9.1 nmol green-emitting CdSe/ZnS core/shell NQDs on our n-UV LED. By using this amount of NQDs, all of the incoming n-UV radiation from LED is fully converted to greenish yellow. The emission spectra of the resulting LED are shown in Fig. 5. The emission peak shifts from ca. 550 nm in solution to ca. 573 nm because of the environmental change from solution to solid state and also as a result of FRET between the NQD solids. The FRET process that takes place in this thin film layer is because of the size-distribution of the NQDs; however, since the size-distribution is small (<5%), FRET is not strong. When we increase the current injection level of our hybrid LED, its (x, y) tristimulus coordinates moves from (0.42, 0.54) to (0.46, 0.51) because of heating. At 19.05 mA, our hybrid LED exhibits a luminous efficacy of 425 lm/Wopt and a luminous efficiency of 17 lm/W.

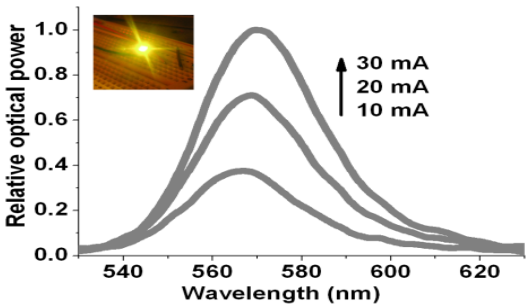

Fig. 5. NQD integrated LEDs emitting at ca. 573 nm under increasing current injection levels at room temperature. Inset shows a photograph of the hybrid LED when it is turned on.

In order to enhance the luminous efficiency of the hybrid LED, an energy gradient layer consisting of cyan- and green-emitting NQDs is integrated on n-UV LED for recycling the trapped excitons. For that 3.4 nmol cyan-emitting NCs and 4.9 nmol green-emitting NQDs are hybridized on n-UV LED. These amounts are chosen to be as close as possible to satisfy 1:1 ratio, but at the same time, they are designed such that the emission of the donor NQDs is fully quenched. As a result, in this hybrid layer cyan-emission is suppressed in its entirety due to strong FRET and the emission spectra of the resulting LED become similar to the previous hybrid LED with only green NQDs as shown in Fig. 5. The relative quantum efficiency enhancement for this hybrid layer with respect to the previous one is 19%, in agreement with Fig. 2. As a result, this hybrid LED reaches a luminous efficiency of ca. 19 lm/W as a result of exciton recycling via FRET, while the luminous efficacy of optical radiation is maintained at 425 lm/W_{opt} at 19.05 mA.

Furthermore, Fig. 6 indicates the time-resolved spectroscopy measurements of the hybrid layers of these mixed cyan- and green-emitting NQDs and that of only green-emitting NQDs at the acceptor emission wavelength. The time-resolved photoluminescence of the mixed NQD sample reveals a slower decay with respect to the only green-emitting NQDs. Here this stems again from the feeding of these acceptor NQDs with the transferred energy from the donor NQDs. In the inset the subtracted dynamics of the hybrid layers of mixed cyan- and green-emitting NQDs from the only green-emitting NQDs is indicated and the fitted dynamics of Eq. (1) is in agreement with the experimental measurements. .

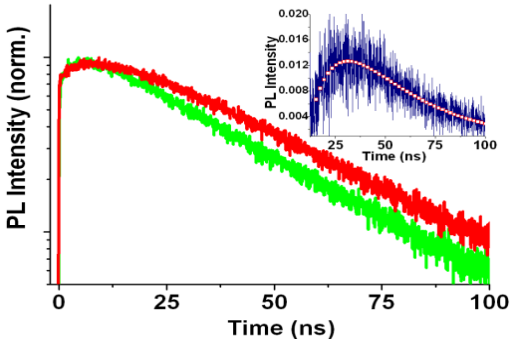

Fig. 6. . Time resolved spectroscopy of the mixed cyan- and green-emitting NQDs integrated layer (in red) and only green-emitting NQDs integrated layer (in green). Inset shows the difference of the mixed cyan- and green-emitting NQDs integrated layer dynamics from the only green-emitting NQDs integrated layer (solid navy-colored line) and its theoretical fit (dotted red line).

Light emitting diodes that exhibit luminescence at 614 nm are also important to achieve high quality white light generation. To achieve the emission at this wavelength we hybridize 5.6 nmol cyan-emitting and 5.6 nmol orange-emitting NQDs. The emission spectra of the resulting NQD hybridized LED are shown in Fig. 7. The emission changes from 612 nm to 616 nm due to heating. The hybrid LED achieves a luminous efficacy of 278.7 lm/W_{opt}. To observe the efficiency enhancement we hybridize only 7 nmol of NQDs and in the mixed hybrid structure the emission is enhanced by 16.92% with respect to the case of only orange-emitting NQDs [14]. As in the previous case, a slower photoluminescence decay for the mixed NQD layer is observed because of the transferred energy from the cyan-emitting donor NQDs as shown in Fig. 8. The inset of Fig. 8 clearly shows the FRET process, for which the fitted dynamics due to the FRET is indicated.

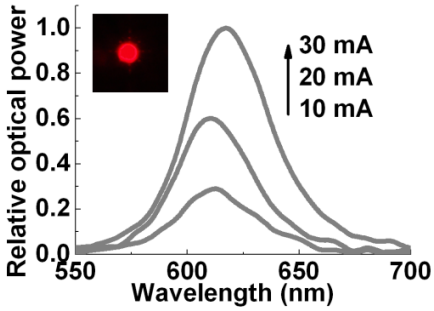

Fig. 7. NQD integrated LEDs emitting at ca. 614 nm for increasing current injection levels at room temperature. Inset shows a photograph of the hybrid LED when it is turned on.

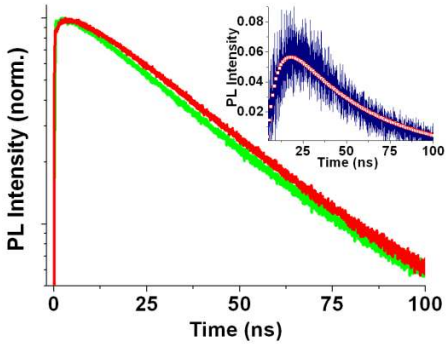

Fig. 8. Time resolved spectroscopy of the mixed cyan- and orange-emitting NQDs integrated layer (in red) and only orange-emitting NQDs integrated layer (in green). Inset shows the difference of the mixed cyan- and orange-emitting NQDs integrated layer dynamics from the only orange-emitting NQDs integrated layer (solid navy-colored line) and the theoretical fit (dotted red line).

In conclusion, we studied the optimum operating point of NQD color-conversion layer for quantum efficiency enhancement by recycling of trapped excitons via FRET. We revealed that FRET-LEDs that exhibit exciton recycling in the hybrid color-converting layer are more efficient than the NQD integrated LEDs with no strong FRET. Furthermore, LEDs operating at specific wavelengths can be obtained by selecting the emission color of NQD, which can further be fine-tuned using size effect, e.g., for greenhouse illumination and indoor/outdoor lighting. These results indicated that such FRET-enhanced NQD nanophosphor integrated LEDs are promising candidates for future SSL applications.

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