

Excitation resolved color conversion of CdSe/ZnS core/shell quantum dot solids for hybrid white light emitting diodes

Sedat Nizamoglu and Hilmi Volkan Demir^{a)}

Department of Electrical and Electronics Engineering, Department of Physics, Nanotechnology Research Center, and Institute of Materials Science and Nanotechnology, Bilkent University, Ankara TR-06800, Turkey

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In this paper, for their use as nanoluminophors on color-conversion white light emitting diodes (LEDs), we present spectrally resolved relative quantum efficiency and relative color (photon) conversion efficiency of CdSe/ZnS core/shell nanocrystal (NC) emitters in the solid-state film. We observe that both the averaged relative quantum efficiency and the averaged relative photon conversion efficiency of these NC solids increase with the increasing photon pump energy. Therefore, the excitation LED platform emitting at shorter wavelengths facilitates such NC luminophor solids to be more efficiently pumped optically. Furthermore, we investigate the spectral time-resolved spectroscopy of NCs in solution and in film with 0.4–2.4 nmol integrated number of NCs in the spectral range of 610–660 nm. We observe that the average lifetime of NCs increases toward longer wavelengths as the number of in-film NCs increases. With the increased amount of NCs, the average lifetime increases even further and the emission of NCs is shifted further toward red. This is attributed to the enhanced nonradiative energy transfer between these NCs due to the inhomogeneous size distribution. Thus, in principle, for fine tuning of the collective color of NCs for color-conversion LEDs, it is important to control the energy transfer by changing the integrated number of NCs. © 2009 American Institute of Physics. [DOI: 10.1063/1.3109151]

White light emitting diodes (WLEDs) offer significant technological and economical benefits including energy saving and long lifetime.¹ They are currently used in various applications such as architectural lighting, flashlights, and backlighting of displays.² They are expected to find large-volume applications such as vehicle front/rear lighting, street lighting, and indoor lighting.³ For white light generation, phosphor based color conversion approach has already been commercialized and is most commonly used today.^{4–6} However, there are problems related to the use of phosphors: e.g., undesirably low color rendering index (CRI) and uncontrolled changes in the optical properties of the generated white light. Also, phosphor based luminophors inconveniently lack the capability to provide widely tunable optical emission. But such an ability to tune and control emission spectrum is particularly important for wide-scale use of WLEDs in large-volume spectrum-specific applications including scotopic street lighting, greenhouse lighting, and high-CRI warm white lighting. These applications require precise spectral engineering of the emission content for illumination. Therefore, alternatively hybrid WLEDs integrated with combinations of semiconductor nanocrystal (NC) luminophors have attracted great attention with recent significant progress and important proof-of-concept demonstrations as reported in recent years.^{7–18}

Such nanoluminophors made of semiconductor NC quantum dots feature attractive optical properties including widely tunable emission using quantum size effect.¹⁹ Fur-

thermore, the ability to make their uniform films using common deposition techniques (spin casting, dip coating, etc.) is an important motivation for their use in solid-state devices. Because of these advantages, NCs have recently been investigated in further applications such as photovoltaics, detectors, scintillators, etc.^{19–24} For WLEDs and other device applications, although there exist ample choices of NCs including CdSe/CdS, CdS/HgS, and CdS/ZnSe core/shell heterostructures to be possibly utilized in these devices, CdSe/ZnS NCs are the most commonly used ones in device research. This is particularly because of their good electronic isolation coming from ZnS shells and the resulting high quantum efficiency (QE) (i.e., >50% in solution).²⁵

However, when these NCs are cast into the solid film, their in-film QE undesirably drops despite their high QE in solution. Thus, this also substantially limits the overall efficiency of the integrating devices that incorporate them.²⁶ To date the characteristics of such CdSe/ZnS NC solids have not been sufficiently studied and their relative behavior of in-film color (photon) conversion and quantum efficiencies have not been thoroughly explored. Until date, only for CdSe core NCs, Gindele *et al.*²⁷ reported the dependence of QE on excitation wavelength and temperature, but these CdSe NCs do not make a strong candidate for use in WLEDs because they exhibit weak electronic isolation and much lower QE compared to CdSe/ZnS core/shell NCs. Furthermore, Biju *et al.*²⁸ investigated quantum efficiencies of CdSe NCs under photoactivation in different chemical environments including polymer solutions and solvent systems. Also, for CdSe/ZnS core/shell NCs, the radiative quantum efficiencies in different solvents such as polymethyl methacrylate, chloroform,

^{a)}Electronic mail: volkan@bilkent.edu.tr. Tel.: [+90](312) 290-1021. FAX: [+90](312) 290-1015.

toluene, and tetrahydrofuran were previously studied.²⁹ However, their spectrally resolved in-film QE (i.e., the ratio of the number of photons emitted by the NC film to the number of photons absorbed in the NC film) and their photon conversion efficiency (i.e., the ratio of the number of photons emitted by the NC film to the number of photons incident to the NC film) have not been fully investigated. These are fundamentally important to investigate the optimal condition of excitation source platform and amount of integrated NCs in the film for hybrid WLEDs.

In this paper, we present the spectrally resolved relative QE and spectrally resolved relative color conversion efficiency of CdSe/ZnS core/shell NC solids to understand the optimal conditions of excitation source platform for WLEDs. For that, we investigate the optical absorbance, photoluminescence, spectral relative QE, and spectral relative photon conversion efficiency of red-emitting CdSe/ZnS core/shell NCs of 0.4–2.4 nmol integrated in the film. We observe that both the averaged relative QE and the averaged relative photon conversion efficiency of the NC film increase with the increasing photon energy incident onto the NC solids. However, we cannot see a direct correlation between the hybrid NC film efficiency and number of NCs in this NC amount regime. Furthermore, we investigate the time dependent emission characteristics of these NCs and take time-resolved spectroscopy of their films. As the number of in-film NCs increases, the average lifetime of these NC solids increases toward longer wavelengths.

To investigate the optical properties, we use monodispersed red-emitting core/shell CdSe/ZnS NCs acquired from Evident Technologies. These NCs exhibit a photoluminescence peak at 622 nm in solution with a concentration of 15.85 nmol/ml in toluene. The diameters of these quantum dots are around 5.8 nm with a size distribution of <5%, as specified by the manufacturer. Their transmission electron microscopy (TEM) images are illustrated in Fig. 1. For film formation we make closely packed NC film on quartz substrates. For that, after drop casting the NC-toluene solution on quartz, we evaporate the toluene solution of NCs by baking the samples around 70 °C. We hybridize a total of 0.4, 0.8, 1.6, and 2.4 nmol NCs on separate diced quartz substrates, each with an area of 7 × 7 mm².

For absorbance, we measure our samples using a Varian spectrophotometer. For QE measurements, we use a xenon halogen lamp with a monochromator as the excitation light source with a full width at half maximum of 20 nm and a Newport integrating sphere for collecting the total emission from the NC solids. We calculate QE by dividing the total number of emitted photons to the total number of absorbed photons of the NC films. The integrating sphere is expected to collect most of the emitted photons. However, if there are those that are not collected (and thus not counted for the efficiency calculation), it means that the actual efficiency level is only possibly slightly larger than the measured one. For time-resolved spectroscopy measurements, we use a FluoTime 200 spectrometer from PicoQuant with a time-correlated single photon counting system of PicoHarp 300 with a calibrated time resolution of 32 ps. For pumping NC solids, we use a laser head at 375 nm with light pulses as

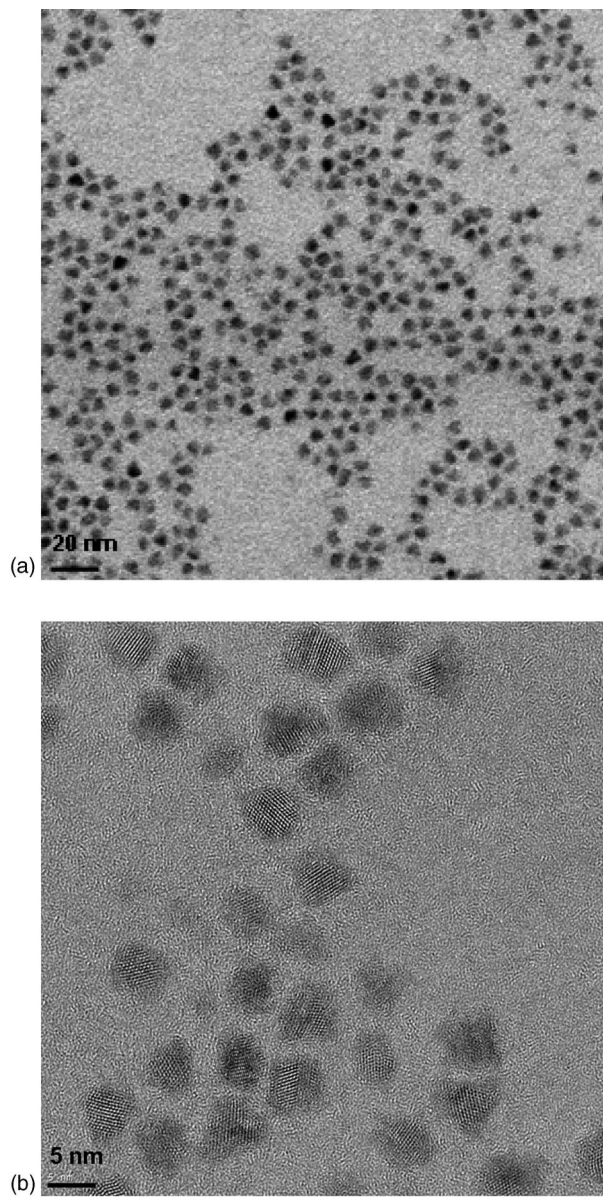
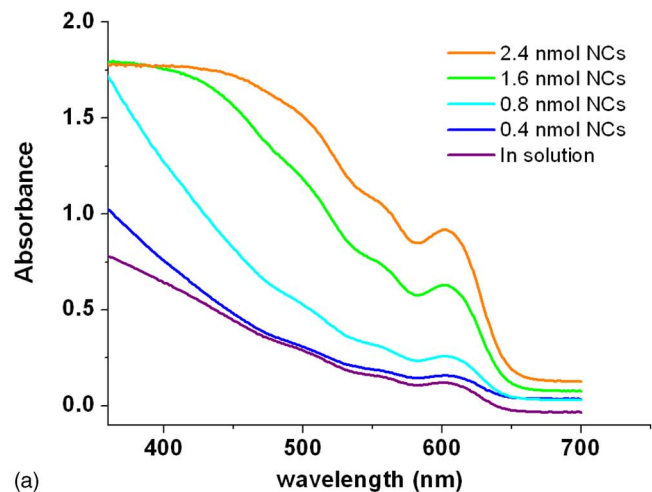


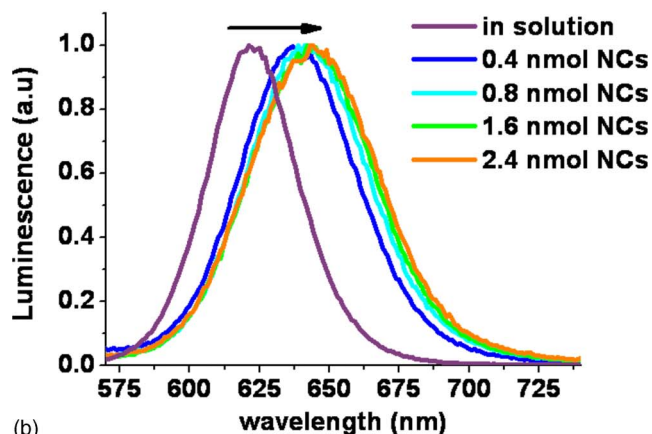
FIG. 1. (a) and (b) show the TEM images of red emitting core/shell CdSe/ZnS NC solid films (λ_{PL} in solution=622 nm) with the scale bars of 20 and 5 nm, respectively.

short as 70 ps and a photon multiplier tube as the detector. We measure the time-resolved emission of NCs from 610 to 660 nm with 10 nm spacing. For the data analysis we use the software FLUOFIT, which also includes the instrumental response function in convolution in the analysis.

Figures 2(a) and 2(b) show the absorbance and photoluminescence spectra of CdSe/ZnS core/shell NCs in solution and in solid films with an integrated NC number of 0.4, 0.8, 1.6, and 2.4 nmol. In Fig. 2(a) as the number of NCs increases, the absorbance of NC increases expectedly. In Fig. 2(b), the photoluminescence spectra of NCs in film exhibit redshift with respect to the luminescence in solution. Furthermore, as the number of NCs increases, the emission peak continues shifting toward red. One major reason of this spectral change is the dipole-dipole interaction between the NCs, which plays an important role for fine tuning of their collective color.³⁰ In addition, the reabsorption process also affects



(a)

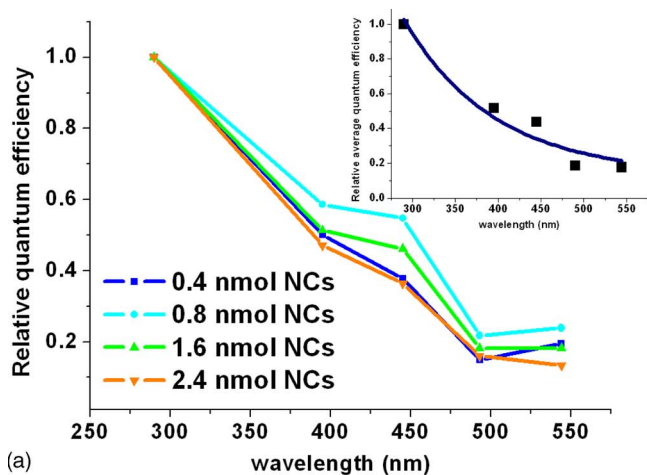


(b)

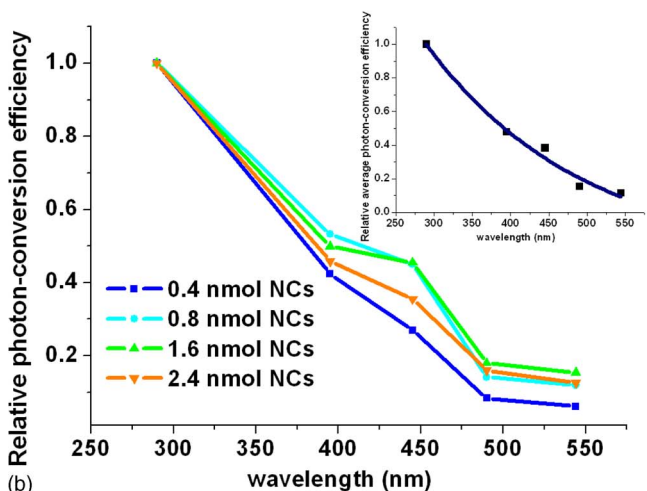
FIG. 2. (Color online) (a) Absorbance and (b) photoluminescence of closely packed red emitting CdSe/ZnS core/shell NC solid films ($\lambda_{\text{PL in solution}} = 622$ nm) parametrized with respect to the number of NCs (0.4, 0.8, 1.6, and 2.4 nmol) compared to those in solution.

the emission of the NC solids, which causes further redshifts. Since the absorbance of the NC emitters is observed to increase especially toward shorter wavelengths, the emission coming from the smaller NCs is more strongly absorbed than the emission from the larger ones. As a result, an asymmetry in photoluminescence profile is observed and this asymmetry is more pronounced as the number of integrated NCs is increased.

In Fig. 3(a) we present the spectral relative QE of the NC films. We observe that the averaged relative QE tends to increase toward shorter excitation wavelengths, as shown in the inset of Fig. 3(a). This result shows that the excitation light emitting diode (LED) platform emitting at shorter wavelengths facilitates such NC luminophor solids to be more efficiently pumped. Although nowadays high-power, short-wavelength LED platforms are not available for pumping the hybridized NCs, near-UV LEDs are expected to reach significantly high optical power levels in the near future (e.g., as announced by Japanese LED maker Nichia for the production of UV LEDs with output optical powers up to 5 W in short term³¹). Furthermore, the number of NCs also tends to affect the film QE as well. Although in our working regime in terms of the number of NCs we cannot observe



(a)



(b)

FIG. 3. (Color online) (a) Spectrally resolved relative QE and (b) relative photon conversion efficiency of red emitting CdSe/ZnS core/shell NC films ($\lambda_{\text{PL in solution}} = 622$ nm) with the integrated NC amounts of 0.4, 0.8, 1.6, and 2.4 nmol at the excitation wavelengths of 290, 395, 445, 493, and 544 nm along with the average of relative QE and relative photon conversion efficiency in the insets of (a) and (b), respectively. These relative efficiency levels are normalized to better present the relative change over the optical wavelength.

any direct correlation between NC amount and QE, using fewer numbers of NCs (i.e., <0.4 nmol NCs on an area of 7×7 mm² substrate) may have higher capability of achieving higher QEs because of reduced reabsorption.

Another important figure of merit for hybrid WLED application is the spectrally resolved relative photon conversion efficiency, as shown in Fig. 3(b). The photon conversion efficiency also tends to increase with the increasing excitation energy of the incoming photon in general. However, there are differences between the relative behavior of the photon conversion efficiency and QE. For example, although the sample with 0.4 nmol NCs exhibits the highest QE at 544 nm, the photon conversion efficiency is the lowest because this sample contains the least number of NC emitters that absorb only a portion of the incoming excitation and convert to red emission. However, as the photon energy of the incoming photons increases, the optical absorption gets stronger, as depicted in Fig. 3(b), and more of the incident photons are absorbed and converted to the NC emission with

higher QE. Thus, for color-conversion NC-WLED operation, this experimental characterization demonstrates that it is in principle possible to achieve high color conversion with thin NC films by pumping at a shorter wavelength.

To investigate the time dependent photoluminescence characteristics, we also take time-resolved spectroscopy of our NC films. Their lifetime kinetics in solution and in film with 0.4 and 2.4 nmol of integrated NC number are presented in the emission range of 610–660 nm (with a 10 nm spectral spacing) in Figs. 4(a)–4(c), respectively. In Fig. 4(a), the spectral dynamics of in-solution NCs are shown and in this case the decay curves do not alter significantly from 610 to 660 nm. The average lifetimes (i.e., amplitude averaged lifetimes) change from $\tau=15$ to $\tau=21$ ns (i.e., $\Delta\tau=6$ ns), respectively, as indicated in the inset of Fig. 4(a). However, when the NCs are cast in the solid film with the amount of 0.4 nmol, the time-resolved decay curves become more separated from each other in each 10 nm spectral step and vary much more significantly while scanning from 610 to 660 nm in Fig. 4(b). The modification of lifetime dynamics in 0.4 nmol NC case with respect to in-solution case comes from environmental change from solution to air NC. Furthermore, the interdot separation in solution is more than 100 nm, which is larger than the distance needed for dipole-dipole coupling of NCs (i.e., around <5 nm). Thus, the NCs in solution do not have nonradiative energy transfer. However, in closely packed solid films the dipole-dipole interaction becomes possible. This means that smaller-sized NCs with wider effective bandgap may donate their excitation energy to larger-sized ones with narrower bandgap because of the inhomogeneous size distribution of NCs. Also in 0.4 nmol case the average lifetimes change from $\tau=4$ ns to $\tau=15$ ns (i.e., $\Delta\tau=11$ ns), respectively, as indicated in the inset of Fig. 4(b). When the number of NCs is increased to 2.4 nmol, the transient decay curves become even more separated from each other. The average lifetimes then change from $\tau=4$ ns to $\tau=20$ ns (i.e., $\Delta\tau=16$ ns), respectively, as indicated in the inset of Fig. 4(c). Thus, the separation between the radiative decays at different wavelengths increases from the case of solution to 0.4 nmol NCs in film and finally to 2.4 nmol NCs. As a result, because of the increased energy transfer, the emission of in-film 2.4 nmol NCs is shifted further toward red, as depicted in Fig. 2(b). Therefore, these show that it is possible to tune the emission color of NCs in film for WLED application by changing the integrated number of NCs and modifying the energy transfer among them.

In conclusion, we presented an optical study of CdSe/ZnS core/shell NC solids to investigate the optimal condition of excitation source platform for color-conversion WLEDs. We observed that both the averaged relative QE and the averaged relative photon conversion efficiency of the NC film increase with the increasing photon energy incident onto the NC solids. Furthermore, we investigated the spectral time-resolved spectroscopy of these NCs in solution and in film with a 0.4 and 2.4 nmol integrated number of NCs. As the number of in-film NCs increases, the average lifetime of NCs increases toward longer wavelengths. With the in-

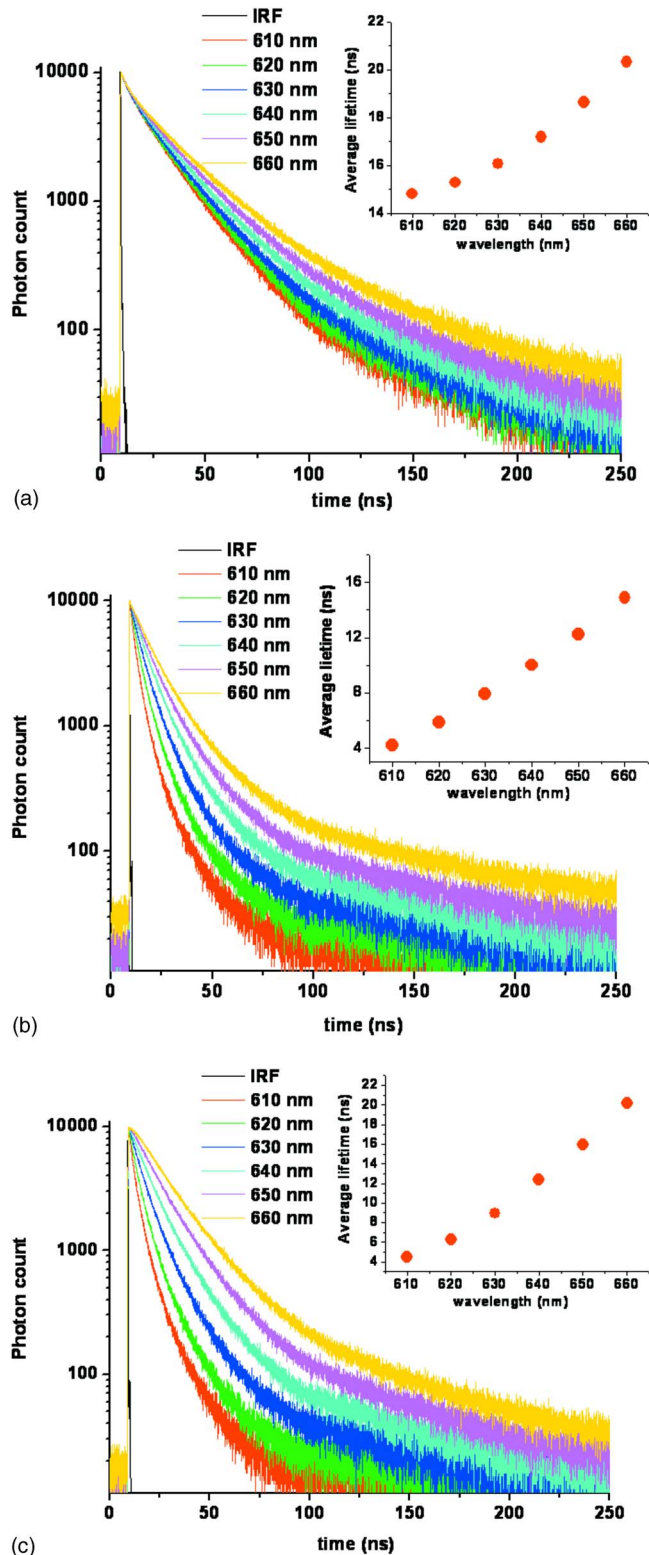


FIG. 4. (Color online) (a) Spectral time-resolved emission spectroscopy in the spectral emission range of 610–660 nm (with a 10 nm spectral spacing) of (a) in-solution NCs and in-film NCs with the amounts of (b) 0.4 and (c) 2.4 nmol.

creased amount of NCs, the average lifetime of emission increases more and the emission of NCs is shifted further toward red. As a result, by changing the integrated number of NCs on LED chip, we can control the energy transfer among NCs and modify the redshift of their emission.

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