Tetrachromatic hybrid white light-emitting diodes and the energy transfer between conjugated polymers and CdSe/ZnS quantum dots

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We have demonstrated the fabrication and characterization of high efficacy tetrachromatic white light-emitting diodes (LEDs) based on polymer and colloidal quantum dots. With a certain amount of green-emitting 2,3-dibutoxy-1,4-poly(phenylene vinylene) (DBPPV) and red-emitting CdSe/ZnS QD composite attached on an InGaN blue chip, stable and pure white light with CIE-1931 chromaticity coordinates of (0.325, 0.342), a correlated color temperature (CCT) of 5800 K, and a color rendering index (CRI) of 75 can be obtained. The luminous flux and efficacy of the device operated at 20 mA are 0.55 lm and 330 lm/W, respectively. In this device configuration, the emission of QDs is not only due to the radiative energy transfer from InGaN QWs and DBPPV, but also the Förster energy transfer of excitons in adjacent DBPPV chains. Based on a theoretical calculation, high efficiency up to 32% is possible.

The chemically-synthesized colloidal semiconductor quantum dots (QDs), or nanocrystals, have attracted considerable attention for their biomedical, electronic, and optoelectronic applications. Their foremost advantages include high chemical and optical stabilities, easy tuning of the saturated color emission across the visible-NIR range, and easy processability in hybridizing with organic and inorganic materials. Nowadays, several safer and easier methods have been proposed to synthesize high quality QDs with different core/shell materials and aspects. In this study, both the CdSe/ZnS QDs and DBPPV (from Eternal Chemical Co., Ltd.) are firstly monodispersed in toluene. Figure 1 shows the normalized UV/Vis absorption and photoluminescence (PL) spectra of QD and DBPPV solutions with concentrations of 2.5 and 6 mg/ml, respectively. The first absorption/PL peaks of DBPPV and QDs are at 462/538 and 598/634 nm, respectively. As shown, here the DBPPV is adopted because of its double-peaked yellowish green emission with a broader spectrum (50~100 nm) for higher CRIs. The QYs of QDs and DBPPV are estimated to be 35 and 82%, respectively, by comparing with a fluorescent standard (Rhodamine 6G in ethanol, QY=95%).
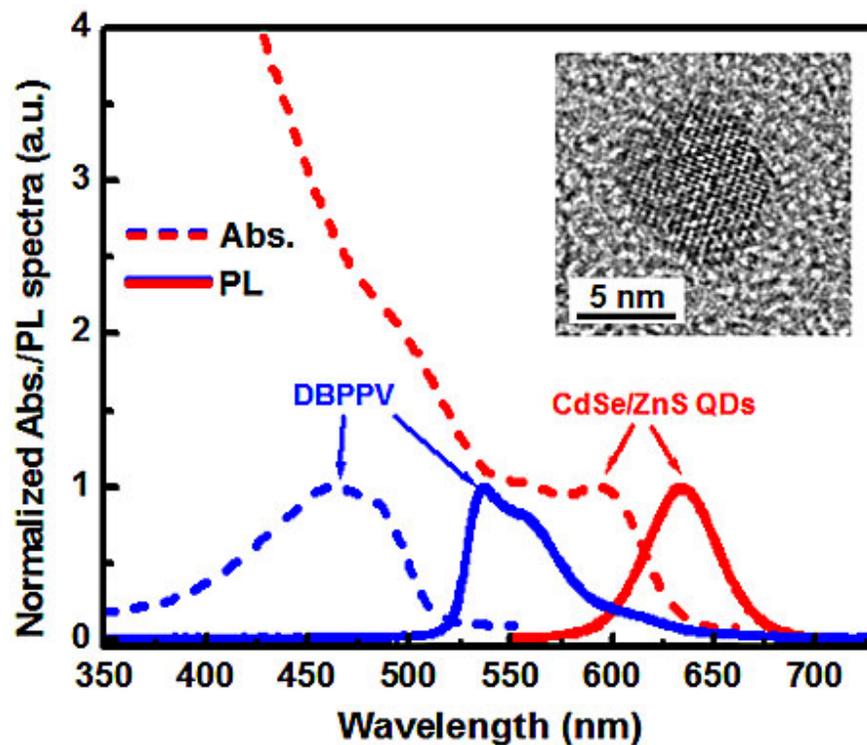
Fig. 1 Room temperature normalized UV/Vis absorption and PL spectra of CdSe/ZnS QD and DBPPV solutions. The inset shows the HRTEM image of a single QD.
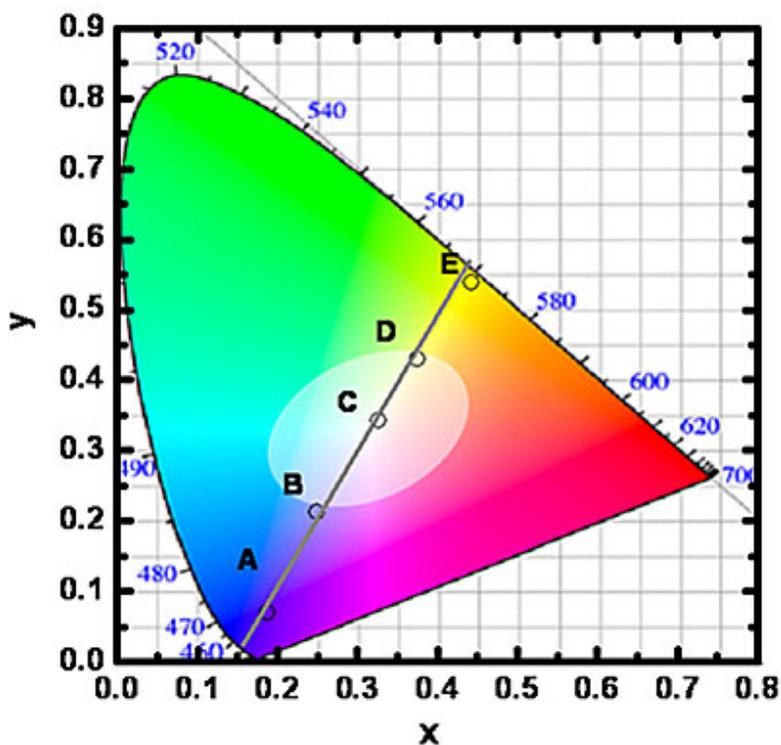

Fig. 2 CIE-1931 chromaticity coordinates of devices biased at 20 mA. As predicated, the connection of the coordinates is almost a straight line.

In our device configuration, the possible energy transfer processes of DBPPV and QDs are discussed as follows. From Fig. 1, one can easily understand that the principal excitation source of DBPPV is the radiative energy transfer from E_{QW}. Besides, for a host-guest system, the rate (K_F) of Förster resonance ET (FRET) is given by

$$K_F = \tau^{-1}(R_F / R)^6 \tag{1}$$

where τ is the lifetime of the donor in the absence of the acceptor, R is the distance between host and guest, R_F is the characteristic Förster radius:

$$R_F = (8.8 \times 10^{23} J K^2 Q_D n^{-4})^{1/6} \tag{2}$$

where K^2 is the orientation factor, J is the spectral overlap integral, Q_D is the PL quantum yield of donor without acceptor, and n is the refractive index of the medium. In our case, $K^2 = 2/3$ for random orientation, Q_D is 0.82 for DBPPV, n is 1.5 for epoxy resin, and J is calculated to be 2.4×10^{-13} M^{-1}cm^3 by the spectral overlap integral method. The FRET efficiency, E_F, is simply given by

$$E_F = \frac{K_F}{K_F + \tau^{-1}} = \frac{R_F^6}{R_F^6 + R^6} \tag{3}$$
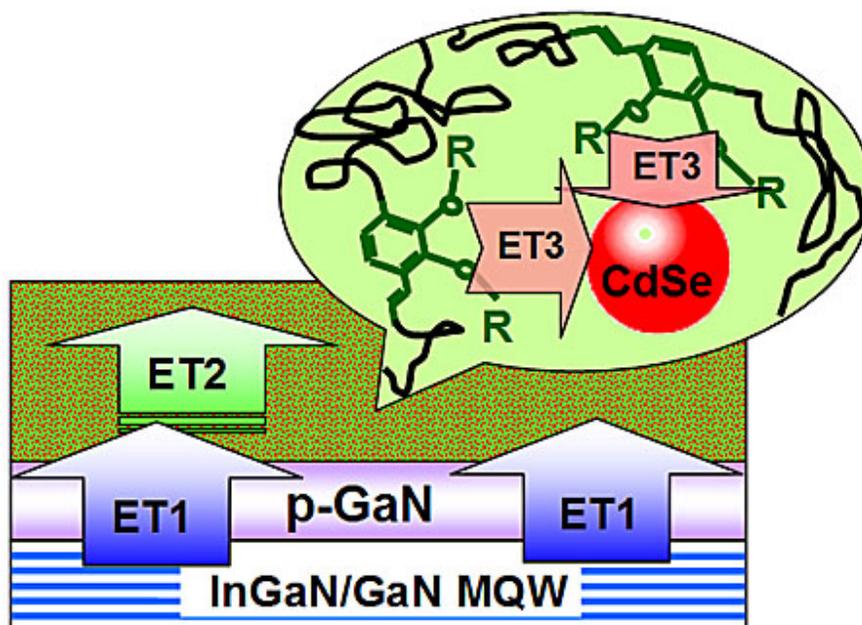
Schematic description of energy transfer routes among InGaN/GaN QWs, DBPPV, and CdSe/ZnS QDs. ET1 is the radiative ET from QWs to DBPPV and QDs, while ET2 and ET3 are the radiative and FRET from DBPPV to QDs, respectively. Zoomed polymer chains with representative characteristic groups adjacent to a QD are shown.

Thereby, R_F is calculated to be 53 Å in the DBPPV-QD system. When the QD's core radius and shell thickness and the length of the surface ligand, trioctylphosphine oxide (TOPO), are taken into account, the distance R is about 60 Å and a FRET efficiency E_F of 32% can be deduced under ideal circumstances from Eq. (3). Further device characterization and analysis such as time-resolved luminescence spectra (FRET tends to shorten the lifetime of the donor emission) are necessary for the sake of precisely evaluating the proportion of these ET mechanisms.