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Fabrication and characterization of red-emitting electroluminescent devices based on thiol-stabilized semiconductor nanocrystals

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Abstract

Thiol-capped CdTe nanocrystals were used to fabricate light-emitting diodes, consisting of an emissive nanocrystal multilayer deposited via layer-by-layer, sandwiched between indium-tin-oxide and aluminum electrodes. The emissive and electrical properties of devices with different numbers of nanocrystal layers were studied. The improved structural homogeneity of the nanocrystal multilayer allowed for stable and repeatable current- and electroluminescence-voltage characteristics. These indicate that both current and electroluminescence are electric-field dependent. Devices were operated under ambient conditions and a clear red-light was detected. The best-performing device shows a peak external efficiency of 0.51% and was measured at 0.35mA/cm^2 and 3.3V.

A recent approach to the fabrication of electroluminescent devices has emerged from the development of colloidal semiconductor nanocrystalline quantum dots - here also termed nanocrystals or nanoparticles. Semiconductor nanocrystals are inorganic nanoparticles that can be synthesized in organic solvents[1] or water[2] and are surrounded by an organic capping layer. The optical and electronic properties are determined by the quantum confinement effect[3]. As their size is reduced below the bulk Bohr exciton diameter, the color of emission can be tuned by varying the size of the nanocrystals while the narrow size distribution allows for photoluminescence peaks with full-width-at-half-maximum (FWHM) of 25-35nm[4].

The use of semiconductor nanocrystals as a light-emitting material has been investigated by several groups worldwide. To date, a number of different structures was produced which combine different organic materials and narrow-band luminescent nanocrystals into light-emitting diodes (LEDs) [5-16]. The emissive properties depend on the type of colloidal nanoparticles used as well as on the additional layers (typically, organic polymers) inserted to promote the electrons and holes injection and transport.

External efficiencies as high as 1.1% have been achieved with hybrid organic/inorganic devices employing CdSe(ZnS) core/shell semiconductor nanoparticles as the emissive material[11]. However, in these structures the nanocrystals do not play an active role in the charge transport and the electrical conduction is determined by the polymer layers. Alternatively, Gao et al.[13] reported a device based on self-assembled CdTe nanocrystals, in which the conduction mechanisms depended on the nanocrystals` electrical properties and arrangement. The nanocrystals were deposited through a layer-by-layer technique. Polyethyleneimine (PEI) and poly-(diallyldimethylammonium) (PDDA) were used to functionalize the substrate and acted exclusively as embedding dielectric matrix for the quantum-dots. The authors propose a field-driven current while the electroluminescence dependency with voltage/field is not discussed. Devices were fabricated using nanocrystals of different sizes. The electroluminescence turn-on spread between 2.5 and 3.5V with the size. This was attributed to a lower injection efficiency of electrons for smaller particles due to the shift of the electron energy levels to higher values as the particle size is decreased. External quantum efficiencies up to 0.1% were achieved.

Here we report results pertaining to the development of a red-emitting electroluminescent device based on thiol-capped CdTe nanocrystals characterized to have 30-40% photoluminescence quantum yield[17]. The device

structure consists of an emissive CdTe nanocrystal multilayer sandwiched between indium-tin-oxide and a thermally evaporated aluminum electrode. To study the emissive and electrical properties of the nanocrystal multilayer, the conductive polymers used in hybrid polymer/nanocrystal LEDs were eliminated, as in reference[13]. Results show that the quality and uniformity of the emissive multilayer was crucial to achieve better efficiencies while the electrical characterization proves that current and electroluminescence are electric-field dependent.

CdTe nanocrystals synthesized in aqueous solution represent a natural core-shell system[2,17,18]. The inorganic core is surrounded by a ligand shell which creates a surface charge on the nanocrystals so that they can be deposited by the self-assembly method to build nanoparticle thin-films[19,20].

Multilayers were manufactured using the layer-by-layer technique under standard laboratory conditions. As reported previously in reference[21], the self-assembly process was simplified by using only one polyelectrolyte – namely, PDDA, to functionalize the substrate in the adsorption process. This was beneficial in terms of the overall uniformity and smoothness of the emissive multilayer together with good reproducibility of the film thickness and quality. The analysis of the device cross-section allowed estimating that each PDDA/CdTe bi-layer is around 3nm in accordance with the mean size of the CdTe nanocrystals used, as derived from their absorption spectra.

The HRTEM picture of a 5 PDDA/nanocrystal bi-layers deposited layer-by-layer is shown in figure 1. X-ray reflectivity measurements were used to determine the density of nanoparticles. The results gave density figures of 2.3-2.6g/cm^3. Using the density of CdTe (6.2g/cm^3) and PDDA (1.04g/cm^3) the filling factor for CdTe nanoparticles was derived and is of ~27%. From this result and assuming spherical particles, a simple 3D computer model gave a mean inter-particle distance of 2–3Å and 2-D cross-sections consistent with the TEM analysis of figure 1.

A number of samples were produced consisting of 30, 40 and 50 bi-layers. The current-voltage characteristics and the devices light output were measured in normal laboratory conditions (i.e., devices were not sealed or packaged) using a Keithley 6517 electrometer operated as source-meter and a silicon photodiode (OPT-301 from Texas Instruments).

Figure 2 shows current-voltage characteristics for several devices made of 30, 40 and 50 bi-layers. The curves appear distributed in voltage according to the number of layers that determine the thickness of the multilayer. Once plotted versus the electric field (see figure 3), curves corresponding to different number of layers are mixed together, and group within a narrow field range – that is between 2×10^7 to 3×10^7V/m. This clearly indicates an electric-field dependency. The narrow spread of fields is due to variations between samples, caused by interfacial effects – such as, localized thermal damages, oxidation or contaminants, introduced during manufacturing between electrodes and nanocrystal multilayer.

All devices had a $4mm^2$ emissive area. Samples showed stable currents and the light output was recorded at operational current densities in the range of $100\mu A/cm^2$ - two orders of magnitude lower than the figures reported in[13]. The lower levels and stability of currents are due to the improved uniformity and homogeneity of the nanocrystal multilayers. This contributes to reduce the leakage current through structural defects and pin-holes, and to stabilize the device against localized high-field areas prone to electrical breakdowns.

The log-log plot of the electroluminescence (expressed in nW) versus the current for the same set of devices is reported in the inset of figure 3. As can be observed, the electroluminescence is roughly proportional to the squared current indicating that also the electroluminescence is field-dependent.

The efficiency figures for all the devices were compared. The best efficiencies were recorded for the 30 bi-layer devices while as the number of layers increases, higher voltages are required for light emission lowering the efficiency figures. For the 30-bilayer devices, a maximum radiant power of 141nW was measured at current densities of $350\mu A/cm^2$ ($I\approx14.05\mu A$) and 3.3V. The insets (a) and (b) show the emission spectrum centered at 630nm and the device operated on a laboratory bench - emitting a clear red light. Assuming monochromatic emission, the maximum radiant power corresponds to an external quantum efficiency of 0.51% and to luminous efficiencies of 0.8lm/W and 0.4cd/A (see Figure 4), the brightness peaks at $1.42cd/m^2$. This represents a five-fold improvement with respect to reference[13].

In summary, the structural improvement of the nanoparticle multilayer helped removing leakage currents and obtaining repeatable current-voltage characteristics. Under these conditions, it was derived that the

current is field-dependent as well as the electroluminescence, which is proportional to the squared current. It is believed that the efficiency of these devices is limited by the device structure and nanoparticle engineering. Through improving the proportion of light emitted from the device by inserting functional layers to favor carrier injection or by increased particle efficiency a significant improvement in the device performance is anticipated to be achieved.

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Figure captions

Figure 1. HRTEM picture of five bilayers of CdTe nanocrystals/PDDA deposited with the 'layer-by-layer' technique on a TEM copper grid using the same method as for devices giving a realistic impression of the particle packing in a device. The distribution of nanoparticles and their relative distances are in agreement with X-ray reflectivity measurements and the inter-particle distance estimated through modeling of the 3-D nanocrystal packing.

Figure 2. Current-voltage characteristics of 30, 40 and 50 bi-layers devices. The curves span regularly from lower to higher voltages in accordance to the number of layers; this suggests a field-dependency of the current, as the number of layers determines the thickness of the emissive layer. The small change in switch-on voltage for each sub-set of samples is attributed to variations at the multilayer-electrode interface.

Figure 3. Current density versus electric-field for 30, 40 and 50 bi-layer devices. Curves corresponding to different number of layers accumulate within a narrow range of field values, confirming a field dependency of the current. The inset shows the log-log plot of the electroluminescence (expressed in radiant power) versus the current for the same set of devices. As can be seen, the electroluminescence is approximately proportional to the squared current. This indicate that the electroluminescence follows the current and therefore it is electric-field dependent.

Figure 4. Efficiency figures for the best performing 30-layer device. The device showed an electroluminescence turn-on at 2.5V and the maximum light output was obtained at 3.3V and 350μA/cm^2, with a peak radiated power of 141nW corresponding to an external quantum efficiency of 0.51%. Taking into account the wavelength of emission (i.e., 630nm), the luminous efficiencies reach 0.4cd/A and 0.8lm/W. The insets show (a) the emission spectrum of a 30 bi-layers device and (b) a view of the emissive area while the device is operated in standard laboratory conditions without sealing or packaging.

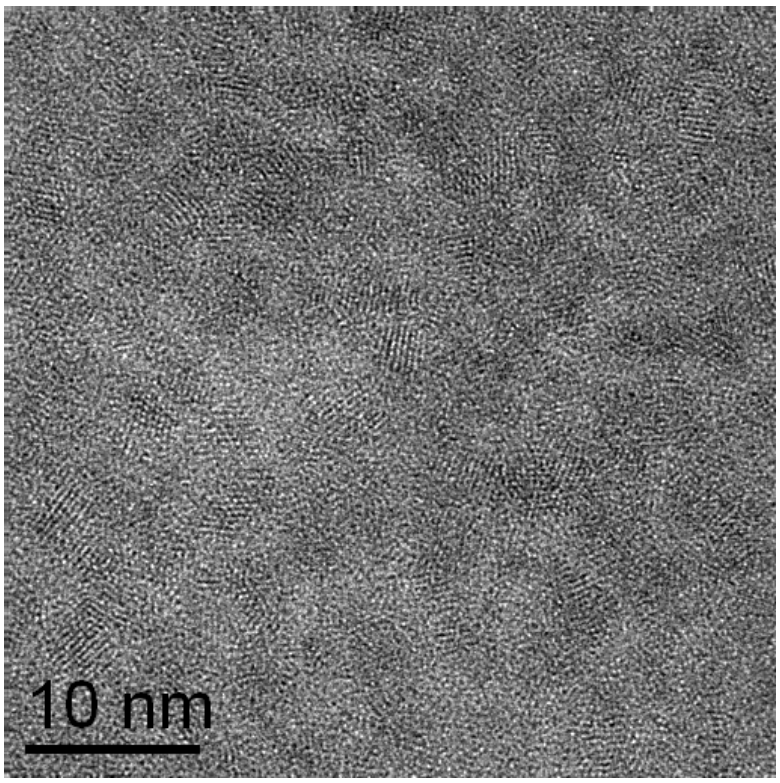

Figure 1

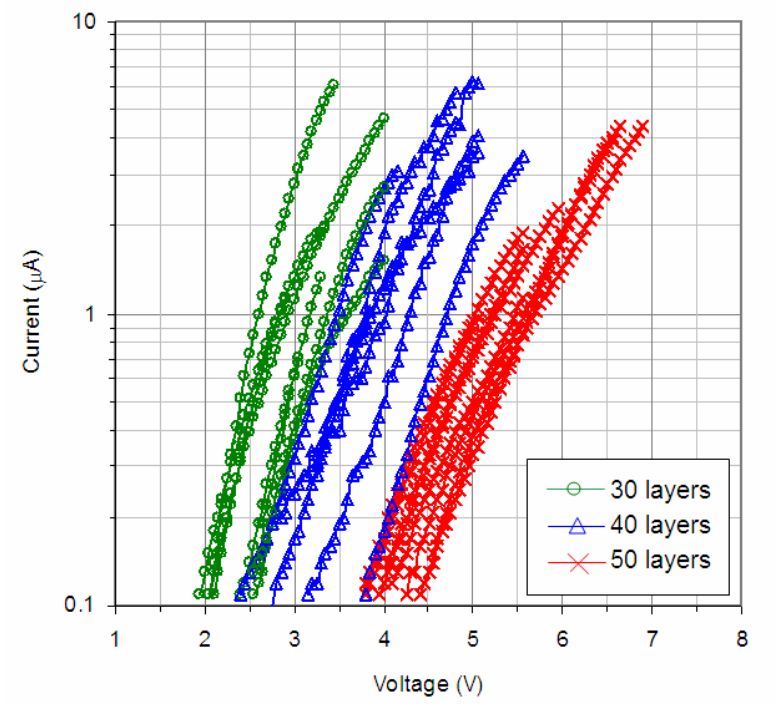

Figure 2

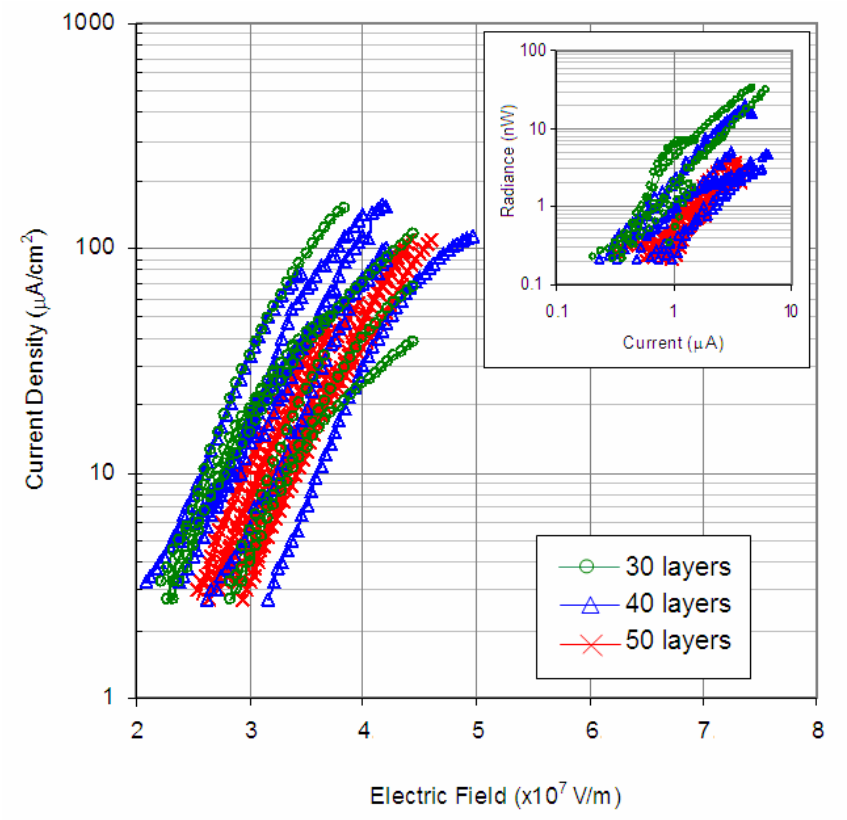

Figure 3

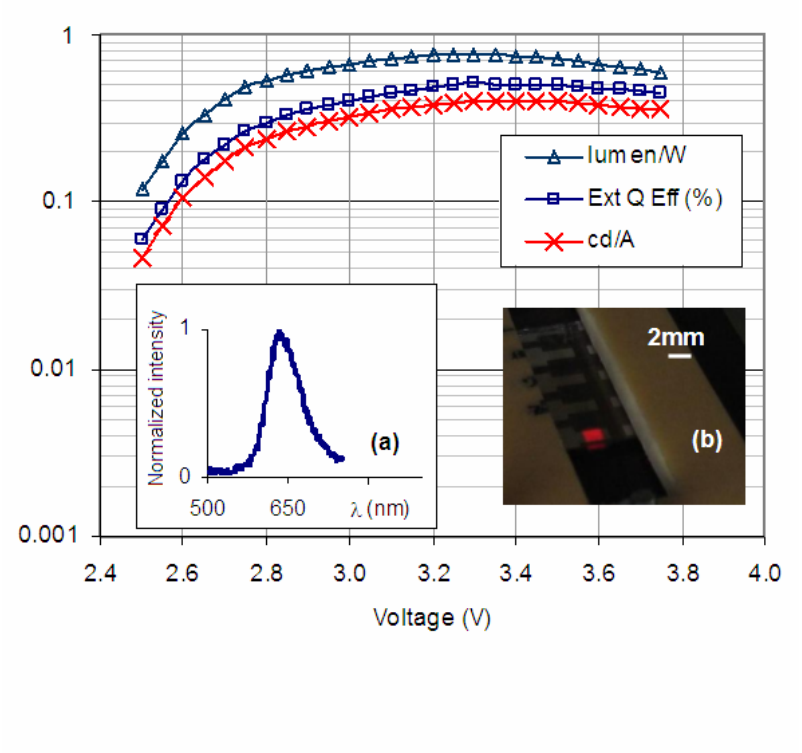

Figure 4