SUPPORTING INFORMATION

All solution processed Low turn-on voltage Near Infrared LEDs based on core-shell PbS/CdS quantum dots with inverted device structure

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Experimental section

Materials. For the QD synthesis: PbO (99.999%), CdO (99.5%), Oleic acid (OLEA, 90%), Trioctylphosphine, (TOP, 90%), 1-octadecene (ODE, 90%) Hexamethyldisilathiane (HMDS, synthesis grade), Anydrous Toluene (99.8%), Isopropanol (99.8%), Acetone (99.5%) were purchased by Sigma Aldrich, Ethanol (99.8%) was purchased by Fluka.

For the device fabrication: FTO substrates (2.5 x 2.5 mm, TEC15), TiO_2 paste (dyesol DSL-90T), $TiCl_4 \cdot (THF)_2$ complex (Sigma-Aldrich), TGA (99%), MPA (99%), EDT (>90%), ETDA (>99.5%), methanol (anhydrous), Octane (anhydrous), P3HT (Luminescence Tech.)

Synthesis of PbS/CdS QDs. Core-shell QDs were prepared by performing Pb to Cd cation exchange process on previously synthesized PbS QDs, adopting some modifications to reported procedures.[17, 18] Briefly, the synthesis of PbS QDs 2.3 nm in diameter was carried out in a three-necked flask connected to a Schlenk line. 0.9 g (4 mmol) of PbO were heated at 150 °C in presence of 2.0 g (7 mmol) of OLEA and 36 ml of ODE, up to the complete decomposition of PbO in Pb-oleate moieties. Such a mixture was degased under vacuum at 150 °C for 30 minutes and then, 3 ml (6.7 mmol) of TOP were injected with a syringe. After 2 minutes the flask was poured under N_2 flow, a solution of 0.420 ml (2 mmol) of HMDS in 4 ml of anhydrous ODE was quickly

injected at 110 °C and the temperature was left to decrease up to 30 °C. The synthesis product was washed with a mixture of ethanol, acetone and isopropanol by means of centrifugation (3000 rpm, 10 minutes), obtaining about 480 mg of PbS QDs, then dispersed in 10 ml of anhydrous toluene in a glove-box. For the synthesis of PbS QDs 3.0 nm in diameter the same procedure was followed, but a larger amount of OLEA (2.7 g – 9.6 mmol) was used.

For CdS shell growth (on PbS QDs 2.3 nm), 0.44 g (3.4 mmol) of CdO, 2.4 g (8.5 mmol) of OLEA and 40 ml of ODE were placed in a three-necked flask. Such a mixture was heated up to 220 °C under air until the complete decomposition of CdO, and then was degassed at 150 °C under vacuum for about 1 hour. At this point the flask was opened to a N_2 flow, and 5 ml of the starting toluene solution of PbS QDs was injected at T= 70 °C. After 5 minutes the synthesis product was cooled with a cold mixture of ethanol, acetone and isopropanol. The QD solution was then precipitated by centrifugation (3000 rpm, 10 minutes), washed 3 times with the same non-solvent mixture, dried under vacuum and dispersed in anhydrous toluene. The same procedure was followed for the CdS shell growth on PbS QDs 3.0 nm in diameter, using different amount of CdO (0.34 g – 2.6 mmol) and OLEA (1.85 g – 6.5 mmol). For this study several batches of PbS/CdS QDs have been prepared and slight differences in the emission maxima wavelength have been observed among batches.

Device fabrication. Pre-patterned FTO substrates (2.5 x 2.5 mm, TEC15) were thoroughly cleaned with aqueous soap and rinsed with MiliQ water. Then, the substrates were immersed in a mixture of acetone:isopropanol (1:1 vv) and sonicated for 15 minutes. Sonicated substrates were rinsed with ethanol and dried with compressed air. Next, a UV/ozone treatment was performed for 20 minutes. A TiO_2 blocking layer (100 nm) was deposited by spraying solution of titanium isopropoxide in acetylacetone and absolute ethanol (1:1:4/3 mass), on the hot substrates (450 ºC). The FTO-TIO_2 electrodes were kept at this temperature for 30 minutes and then cooled down to room temperature. Next, a mesoporous TiO_2 layer was deposited by spin-casting (1500 rpm, 90 s) a solution of the commercial paste DSL-90T (dyesol) diluted in terpineol (1:3 mass). Then the TiO_2 electrodes were heated up to 90 ºC for 15 minutes to evaporate slowly the organic solvents and subsequently calcined at 450 ºC for 30 minutes. The substrates were immersed in a 40 mM aqueous solution of the $TiCl_4 \cdot (THF)_2$ complex (sigma-aldrich) and heated to 70 ºC for 30 minutes. After cooling down to room temperature, the substrates were washed with MiliQ water, rinsed with ethanol and finally dried with compressed air.

Once the substrates were prepared, the core-shell PbS/CdS nanocrystals (50 mg/ml in toluene) were deposited on the top of the TiO_2 electrodes by layer-by-layer deposition using a solution of TGA, MPA, ETDA or EDT in methanol (1.3 M) as linker. One spin-coating cycle consists on depositing the PbS/CdS solution on the substrate (2500 rpm, 10 s), performing the exchange ligand (2500 rpm, 10 s) and finally washing, firstly with pure methanol and secondly with pure octane (2500 rpm, 10s, respectively). The optimum amount of nanocrystals was optimized for each batch of QDs (generally 3-6

cycles). For L2-type devices a polymeric layer of P3HT was deposited prior to the metal contact evaporation, which consisted on the spin-casting of a 15 mg/ml solution of P3HT in 1,2-dichlorobenze (500 rpm, 60 s and 1500 rpm, 60 s). Finally, 60 nm of gold were evaporated under ultra-high vacuum using a shadow mask to pattern five independent contacts of 0.224 cm^2 per device (3x10^{-6} mbar, at a rate of 0.7Å/s during the first 10 nm and at 2 Å/s for the last 50 nm).

Device characterization. Characterization was conducted under air atmosphere. The absorption and PL spectra of the electrodes were registered by using a spectrophotometer based on a CCD (Andor i-DUS DV420A-OE) coupled with a spectrograph as diffraction grating (Newport 77400). For the photoemission measurements, a commercial red laser diode (650 nm, 319 mW·cm^{-2}) was used, whose power was adjusted by means of a mechanical pinhole. The *J/V* curves were registered using a potentiostat (Gamry Reference 3000) in dark conditions. The electroluminescence measurements were carried out using the previously detailed spectrophotometer equipment synchronized with the potentiostat. The combination of both apparatus allowed registering optical variations (absorbance, transmittance, light emission, etc.) while applying an external electrical stimulus (voltage or current) with a maximum time resolution in the milliseconds scale. The EQE measurements were performed by calibrating the optical equipment with a commercial GaAs infrared LED (model EL-23G, peak emission centered at λ_{max}= 940 nm, 28.3 W·sr^{-1}·m^{-2}). The cross section SEM images and the energy-dispersive X-ray analysis were registered using a JEOL JSM-7000F FEG-SEM system. The TEM images of QDs have been registered using a 100kV JEOL JEM 1400 Transmission Electron Microscope. TR-PL measurements have been performed by the time-correlated single photon counting (TCSPC) technique, with a FluoroHub (HORIBA Scientific, Jobin-Yvon), exciting at 375 nm by a laser diode (NanoLED 375L, HORIBA Scientific, Jobin-Yvon) emitting τ ≈ 80 ps pulses at a 100KHz repetition rate. The PL signals have been dispersed by a double grating monochromator and detected by a photon counter (TBX ps Photon Detection Module, HORIBA Scientific, Jobin-Yvon). The temporal resolution of the experimental set up was ~200 ps.

SI1.- Time resolved photoluminescence decays:

The best fit for time resolved photoluminescence decays were obtained for a tri-exponential function for both PbS and PbS@CdS QDs using the following equation:

$$PL = A1\, e^{(-\frac{t}{\tau1})} + A2\, e^{(-\frac{t}{\tau2})} + A3\, e^{(-\frac{t}{\tau3})}$$

(S1)

where τ_x are lifetime and Ax pre-exponential factors. Fitting results are plotted in Table S1. PL decay is mainly governed by long decay times and average lifetime, τ_{av}, is practically coincident with τ_3. τ_{av} has been calculated using equation:[1]

$$t_{av} = \frac{A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2}{A_1\tau_1 + A_2\tau_2 + A_3\tau_3} \qquad (S2)$$

Comparing average lifetimes for PbS and PbS/CdS QDs, a slower decay is detected for PbS/CdS QDs due to suppression of non-radiative decay processes arising from an effective passivation of the surface defects. As a consequence, while the PL decay of PbS QDs results in an average excited-state lifetime of 424 ns, the decay of PbS/CdS QDs has an average lifetime of 742 ns see Table S1.

Supplementary Table 1: Fitted parameters of PL decay, Fig. 1d, using equations S1 and S2. Pre-exponential factors are weighed in %. Fitting X_{sq} values are added to reflect the goodness of the fitting.

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	$A_1\%$	$A_2\%$	$A_3\%$	$\tau_{av.}$ (ns)	X_{sq}
PbS	0.25	10.4	424.3	3.54	2.07	94.38	424.07	1.060
PbS/CdS	0.55	20.5	742	18.23	0.81	80.97	741.68	1.153

SI2.- Energy-dispersive X-ray analysis (EDX) of a QD-LED:

Even though the EDX analysis shows a well differentiated compositional distribution of the layers, the QDs seem to penetrate partially into the TiO_2 nanostructure.
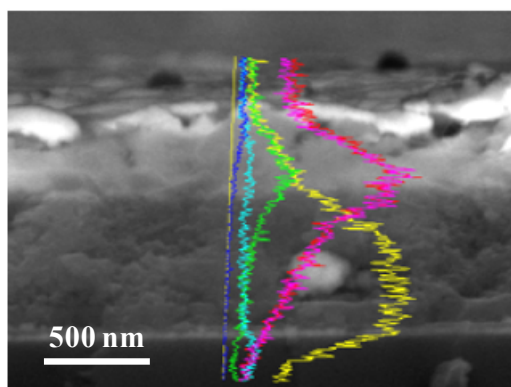
Figure S2.- Compositional analysis (EDX) of a QD-LED. Ti (yellow), Pb (magenta), Cd (green), S (red), Au (blue), Sn (light blue).

SI3.- Photoluminescence vs. Electroluminescence of the prepared QD-LEDs:

The photoluminescence (λ_{exc}= 532 nm) and electroluminescence (bias= 3V) are compared in Fig. S3. Both emission spectra show a similar emission band centered at λ_{max}= 900 nm corresponding to the QD luminescence. Additionally, the PL spectrum shows an emission signal below 800 nm which is ascribed to the presence of the P3HT layer, however the electro-luminescence spectrum does not show this signal, which corroborates that the light generation only takes place at the QD layer instead of emerging from the hole transport layer (P3HT).
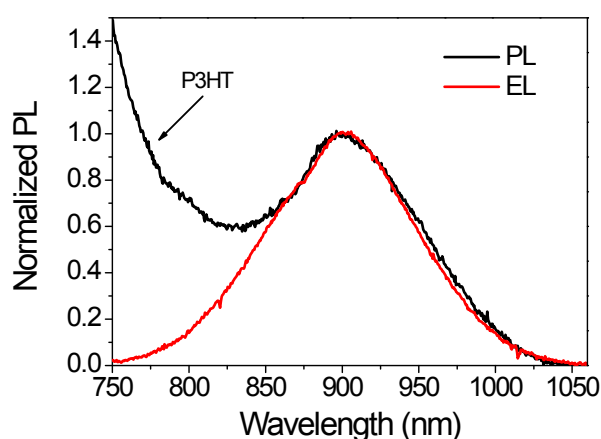

Figure S3.- Photoluminescence and electroluminescence of a complete QD-LED device. Photoluminescence (λ_{exc}= 532 nm) and electroluminescence (bias= 3V) of the complete devices using P3HT as HTM.

SI4.- Response time of the QD-LED depending on the frequency of the sinusoidal A/C electric signal:

The response time of the devices were measured by applying a sinusoidal signal (10 Volts amplitude) at different frequencies. The electroluminescence signal was monitored by using a Si photodiode connected to an oscilloscope. The amplitude of the electroluminescence signal was divided by the amplitude of the input sinusoid in order to calculate the relative amplitude. The cut-off frequency ($\nu_{cut-off}$= 444 Hz) was calculated as the frequency at which the relative amplitude is the 30% of the maximum value (A_{max}). The response time (2.3 ms) was calculated as the inverse of the cut-off frequency.
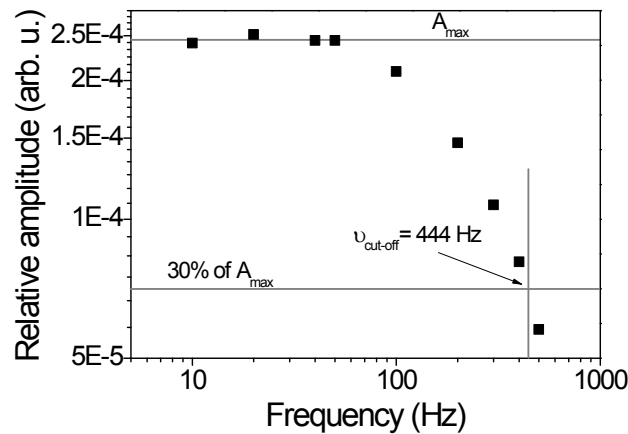

Figure S4.- Relative amplitude of the sine wave vs the electric signal frequency. The electric input signal corresponds to a sine wave of 10 Volts of amplitude.

SI5.- Normalized electroluminescence intensity (EL) at different orientation angles of the QD-LED with respect to the detector:

The electroluminescence intensity of the QD-LED was measured at different angles. The angle $\theta/2$, *i.e.* the angle at which the electroluminescence is the 50% of the signal at $\pi/2$ rad, was estimated to be $2\pi/9$ rad. The solid angle (Ω= 1.47 rad) of the light output was calculated according to the equation:

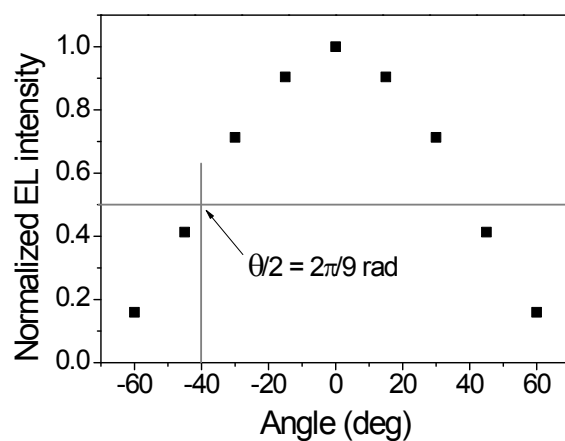$$\Omega = 2\pi \left(1 - \cos\left(\theta/2\right)\right) \qquad\qquad S4$$

Figure S5.- Normalized electroluminescence intensity (EL) depending on the orientation angle of the QD-LED. The calculated value of the solid angle was $\Omega = 1.47$ rad.

SI6.- Evolution over time of the electroluminescence of devices without and with HTM (P3HT):
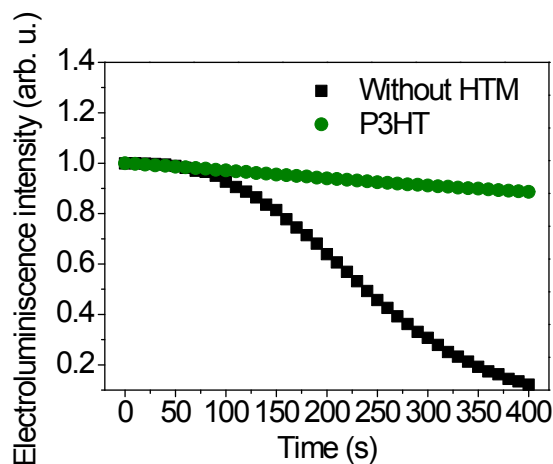

Figure S6.- Influence of the HTM on the electroluminescence of the devices over the operation time. Electroluminescence (bias= 3V) of the complete devices without HTM (black squares) and using P3HT (green dots).