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Hybrid colloidal nanocrystal-organics based light emitting diodes

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1. Introduction

In the last few years a new and promising field of research defined “nanoscience” has attracted an increasing interest. This new field involves the capability to manipulate, fabricate and characterize the material structure at a nanometer scale. Research dedicated to this field has an interdisciplinary character and covers physics, engineering, chemistry, material science and, molecular biology. The recent possibility to manipulate the matter with nanoscopic resolution revealed novel physical and chemical properties of low dimensional structures in between bulk materials and atomic sizes. Among all the nanostructured materials, semiconductor quantum dots (QDs) or nanocrystals have been used in a wide array of fields such as electronic and optoelectronic devices. The most recent techniques in the preparation of nanocrystals are the chemical methods and in particular the colloidal nanocrystals synthesis. These techniques allow for the growth of semiconductor nanocrystals in solution and consequently their integration in the organic electronic technology. The most effective technique is the synthesis by thermal decomposition of precursors in hot coordinating solvents. This allows the growth of semiconductor (II-VI, III-V), (Murray et al., 1993; Murray et al., 2001) metal (Murray et al., 2001; Sun et al., 1999) and metal oxide nanocrystals with high quality, (Rockenberger et al., 1999) almost free from defects and narrow size distribution (less than 5%).

In particular the mostly used material in optoelectronic application synthesized by this technique is the luminescent CdSe QDs. Usually the CdSe cores are surrounded by a wider band gap semiconductor (such as ZnS) that passivates the surface states of nanocrystals with a consequent increase in the photoluminescence. In order to ensure the solubility, the QDs are covered by an organic capping group.

These structures are smaller in size than the diameter of a Bohr exciton in a bulk crystal of the same material. By reducing the size of the nanocrystals core, the quantum confinement of the electron, hole and exciton is increased, with a consequent increase in the exciton energy. For instance in CdSe nanocrystals, the quantum confinement increases the exciton energy from a bulk bandgap of 1.7 eV ($\lambda=730\text{nm}$ red edge of visible spectrum) to any value up to 2.7 eV ($\lambda=450\text{nm}$ blue luminescence). The spectral tunability can access almost all the visible range with a single material set. Moreover the saturated color emission (linewidths of $<35\text{nm}$ Full Width at Half Maximum), the high luminous efficiency even in the blue region,

the possibility to tailor the external chemistry without affecting the emitting core as well as the inorganic nature make these structures ideal candidates in the fabrication of hybrid organic/inorganic light emitting diodes (LEDs) potentially more stable and with a longer lifetime with respect to the fully organic counterpart.

In recent years, indeed the development of organic light emitting diode (OLED) showed several basic physical problems that are very difficult to overcome. One is the relatively short lifetime if compared with other electroluminescent devices. Lifetime have been extended using new chemistry to prevent crystallization and sophisticated packaging schemes to avoid the degradation of the organic emitting molecules by water and oxygen. The chemistry optimization must be repeated for each emitter and differences in the aging time of different molecules emitting in the red, green and blue region poses problems in the OLED color stability. Inorganic QDs are robust and high luminescence lumophores but they present poor charge conduction properties. Recently many efforts have been devoted in the successful integration of these nanocrystalline materials in OLED technology. However the studies on photocurrent and injection in thin disordered films of nanocrystals between metal electrodes revealed that transport and injection in these films cannot be described in the framework of the band model of semiconductor (Ginger et al., 2000; Leatherdale et al., 2000). Nanocrystals are particles separated one to each other by organic surfactant. The high degree of disorder in these films suggests that hopping and tunneling between localized states are the principal mechanism for the charge transport (Ginger et al., 2000). The hopping model is similar to the one described for the organic semiconductors, but in the case of nanocrystals the energetic disorder arises from the size distribution of the particles and the geometric disorder comes from their spatial separation, also induced by the surfactant. Moreover colloidal nanocrystals have poor charge transport properties especially in the case of thick multilayer films. To avoid the problem of poor charge conduction in LED fabrication, colloidal nanocrystals have to be merged with organic semiconductor hole and electron transporting/injection materials. In the last few years several hybrid device structures based on colloidal QDs and organic materials have been reported.

In this chapter, the recent development in the fabrication of Hybrid organic/QD-LEDs will be reviewed; In particular the diverse approaches to fabricate multilayer devices and white light emitting devices will be discussed in details.

2. Hybrid Light Emitting Diodes based on Polymer/QDs

The first work on colloidal semiconductors nanocrystal LEDs demonstrated a device structure in which five monolayer of CdSe quantum dots were deposited on the top of spin coated and thermal converted semiconducting p-paraphenylene vinylene (PPV) layer. Nanocrystal layers were bound on the polymer with hexane dithiol functionalization (Colvin et al. 1994). The light emission arises from the recombination of holes injected into the PPV polymer layer with electrons injected into the multilayer film of CdSe nanocrystals. The low external quantum efficiency of the devices (between 0.001 and 0.1%) can be attributed either to the low photoluminescence (PL) efficiency of the CdSe core QDs, or to the poor electron conduction through the five layer thick QD film (Morgan et al., 2002). Moreover, the use of the hexane dithiol for the device fabrication adds impurities that can trap the charges and quenching the QD excitons.

Subsequently electroluminescence has been obtained by incorporating CdSe QDs into a thin film (100 nm) of polyvinylcarbazole (PVK), a photostable hole conducting polymer, and an oxadiazole derivative (t-Bu-PBD), an electron transport species (Dabbousi, 1995). Three devices with different size of QDs ($\sim 32\text{\AA}$, $\sim 40\text{\AA}$, $\sim 60\text{\AA}$ diameter) have been fabricated by spin coating nanocrystals with the mixture of PVK and t-Bu-PBD as an emitting layer (Figure 1). The maximum external quantum efficiency in air and at room temperature of these devices is quite low ($\sim 0.0005\%$) and it decreases with decreasing of the QD size.

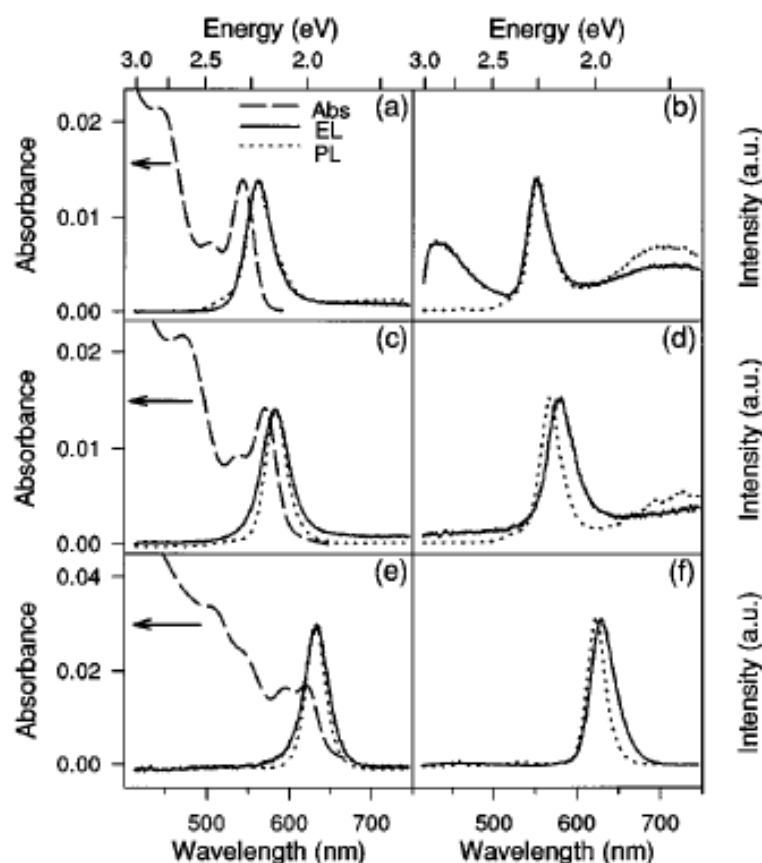


Fig. 1. Absorption (dashed lines), photoluminescence (exc. 457.9 nm) (dotted Lines), and electroluminescence (solid lines) spectra for 32 Å (a),(b), 40 Å (c),(d), and 60 Å (e),(f) diameter CdSe nanocrystallite/PVK/PBD devices at room temperature (a), (c), (e) and at 77 K (b), (d), (f). (Reprinted with permission, Dabbousi et al., 1995. Copyright 1995, American Institute of Physics).

A significant improvement over the previous devices has been obtained by using CdSe(CdS) core/shell QDs (Schlamp et al., 1997). These core/shell nanocrystals consist in a CdSe core surrounded by a shell of epitaxially grown CdS. The core and shell energy levels alignment confines the holes in the core while electrons are delocalized in throughout the structure. This results in a higher PL quantum yield ($> 50\%$ in solution at room temperature) and photo-oxidative stability of the CdSe(CdS) compared with the CdSe core samples. The active nanocrystal multilayer has been deposited on a thermal converted PPV polymer (Figure 2).

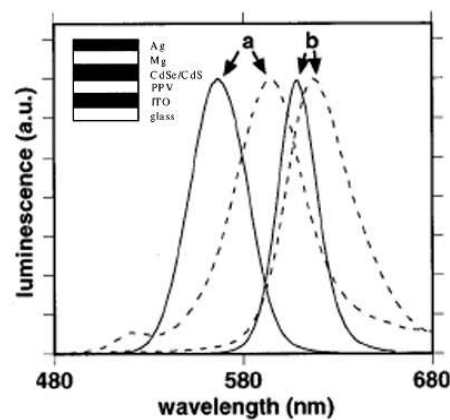


Fig. 2. PL (solid lines) and EL (dashed) of samples of (25, 5) CdSe(CdS) (a) and (34, 7) CdSe(CdS) (b) nanocrystals. The PL was collected in solution at room temperature. Inset: device configuration. (Reprinted with permission, Schlamp et al., 1997. Copyright 1997, American Institute of Physics).

The devices emit from red to green with external quantum efficiency of 0.22% at a brightness of 600 cd/m² and a current density of 1 A/cm². Despite the potential advantages of using QDs as emitters, all these QD-LED structures have efficiencies that are far below of the all organic LED technology ones.

The most limiting factor in the QD devices performances is the poor conductivity of the colloidal nanocrystals compared to semiconductor materials (Leatherdale et al., 2000) and in all the structures reported above the QDs act both as emitters and electron transport species. A multilayer device configuration can allow an independent optimization of materials for charge injection, transport and, emission.

3. High efficiency hybrid LED insulating QD layer function

3.1 QD-LED by phase segregated nanocrystal monolayer

In 2002 an innovative QD-LED structure incorporating a monolayer of CdSe/ZnS core/shell QDs sandwiched between hole and electron transporting organic layers was proposed (Coe et al., 2002). In this device structure colloidal QDs act only as a lumophores and they do not participate to the charge conduction process. The organic layers transport charge carriers to the vicinity of the QD monolayer from which the luminescence originates. In this way the problem of QD poor charge conductivity due to the insulating layer of surfactant, that coat their surface, was overcome. For the device fabrication a solution of QDs and organic small molecule material is spin coated on an Indium Tin Oxide anode. During the spin-coating process the QDs, covered by an aliphatic capping layer, phase separate from the aromatic small molecules, such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), and form a layer on the organic surface.

The thickness and the coverage of the nanocrystals layer depends on the QD concentration in the solution. For the device fabrication the QD concentration is optimized in order to obtain a single close packed monolayer. By exploiting the phase segregation technique they fabricated high luminance devices with emission in the red-green region achieving a maximum external quantum efficiency >2%. (Coe et al., 2002, Coe-Sullivan et al., 2003; Coe-Sullivan et al., 2005) (Fig. 3).

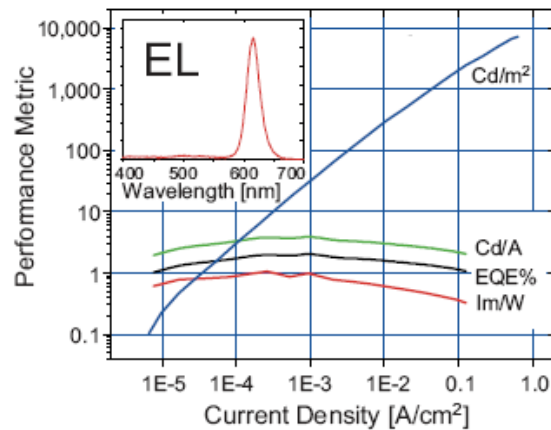


Fig. 3. Performance metrics of the QD-LED, with external quantum efficiency of in excess of 2% and a maximum luminescence over 7,000cd/m². Inset: EL spectrum with a saturated color red emission peaking at 615nm, and full width at half maximum of 27nm (Coe-Sullivan et al., 2005. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

3.2 Multilayer devices by cross-linked hole transporting layer

Recently an alternative strategy for QD-LED fabrication by spin-coating CdSe/ZnS QDs onto a thermally cross-linked hole transporting layer, polystyrene (PS)-N,N'-diphenyl-N,N'-bis(4-n-butylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD)-perfluorocyclobutane (PFCB) was reported (Zhao, 2006). Following the deposition of the QD layer, the electron transporting layer, 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI), was deposited by thermal evaporation. EL spectrum and device structure are reported in fig. 4.

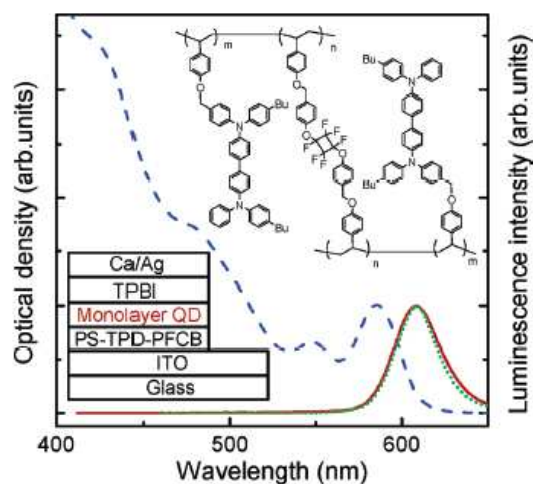


Fig. 4. Absorption (dashed line), photoluminescence (dotted line), and electroluminescence spectra (solid line) for CdSe/CdS QD-LEDs with a structure ITO/PS-TPD-PFCB (30 nm)/CdSe QDs/ TPBI (40 nm)/Ca (30 nm)/Ag (120 nm) at a voltage of 6.0 V. Structures of the multilayered CdSe/CdS QD-LEDs and cross-linked PS-TPD-PFCB are shown in the inset of the figure. (Reprinted with permission, Zhao et al., 2006. Copyright 2006, American Chemical Society).

The maximum external quantum efficiency of these devices was 0.8% at 100 cd/m² and a maximum brightness in excess of 1000 cd/m².

The same group improved the performance of these devices structure by using thermal annealing of the quantum dot layer reaching an external quantum efficiency of 1.6% at a brightness of 100 cd/m² (Niu et al., 2007).

Although QD-LEDs with QDs monolayer have the advantages of higher efficiency and lower turn-on voltages, their output power, maximum luminance and color purity are limited owing to the low chromophore quantity and the poor confinement of excitons in the active QD region.

Recently high-performance red, orange, yellow and green QD-LEDs based on QDs with a CdSe core and a ZnS or CdS/ZnS shell have been reported (Sun et al., 2007). Their maximum luminance reached 9,064, 3,200, 4,470 and 3,700cd/m² (Fig. 5).

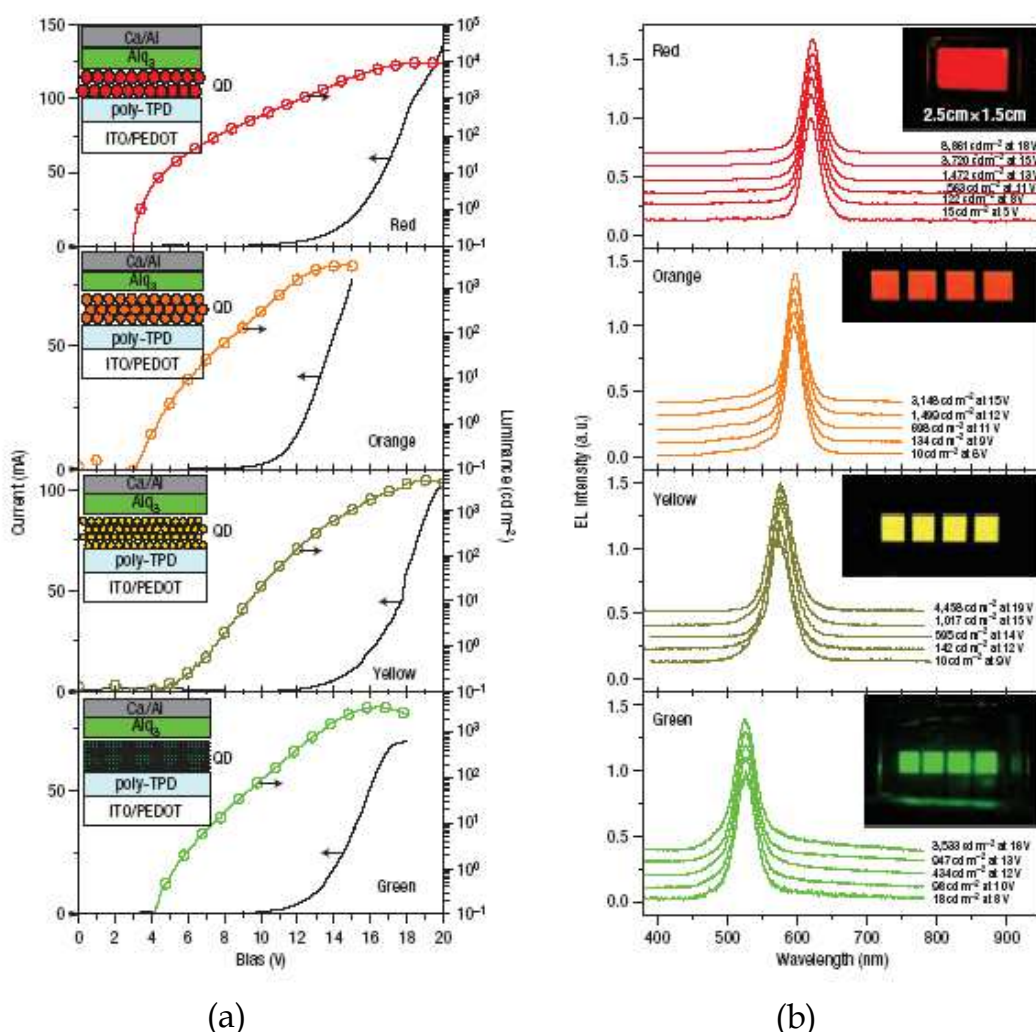


Fig. 5. (a) Current/voltage and luminance/voltage characteristics of red-, orange-, yellow- and green-emitting QD-LEDs. The insets show schematic device configurations of the corresponding QD-LEDs. (b) EL spectra of the red-, orange-, yellow- and green-emitting QD-LEDs operating at different luminances voltages. The insets show images of the devices under operation. (Reprinted with permission, Sun et al., 2007. Copyright 2007, Nature Publishing Group).

The superior performances of the QD-LEDs arise from the careful preparation of highly purified, uniform and monodispersed colloidal core-shell QDs, and optimization of the thicknesses of the polymer HTL, the QD layer and the ETL. Indeed, for use in QD-LEDs, all the QDs were subjected to a multistep purification process to remove the organic ligands. After purification, the red, orange and yellow QDs were in solid powder form with a quantum yield (QY) higher than 30% in toluene, whereas the green QDs were still in liquid solution, with a QY of 10% in toluene, owing to their smaller size. During the purification process, the removal of organic ligands from the QDs produces surface defects that may trap charges.

A trilayer structure of indium tin-oxide(ITO)/poly(ethylenedioxythiophene):polystyrene sulphonate (PEDOT:PSS) (25 nm)/HTL (45 nm)/QDs (15–20 nm)/ETL (35 nm)/Ca (15 nm)/Al (150 nm) was used in the fabrication of the QD-LEDs, with ITO/PEDOT:PSS as the anode, poly(N,N0-bis(4-butylphenyl)-N,N0-bis(phenyl) benzidine) (poly-TPD) spin-coated from its chlorobenzene solution as HTL, QD layers spin-coated from their toluene solutions as emissive layers, tris(8-(hydroxyl-quinoline) aluminium (Alq₃) as ETL, and Ca/Al as the cathode. In the QD-LEDs, the HTL and ETL thicknesses were both optimized to confine the injected electrons and holes to recombine predominantly within the QD layer and provide optimal hole and electron transportation.

3.3 QD-light emitting diodes with metal oxides charge transport layers

For practical device application it is fundamental to improve the shelf-life robustness. Recently the use of sputtered amorphous inorganic semiconductors as robust charge transport layers was reported (Caruge, 2008). In particular 20nm thick film of NiO is deposited by radiofrequency (RF)-sputtering on the ITO electrode; the active layer consists of ZnCdSe alloyed QDs, deposited by spin-coating, with red emission peak at 638nm. The electron transporting layer is an optically transparent film of alloyed ZnO and SnO₂. NiO and ZnO:SnO₂ are p-type and n-type semiconductors respectively (Fig. 6).

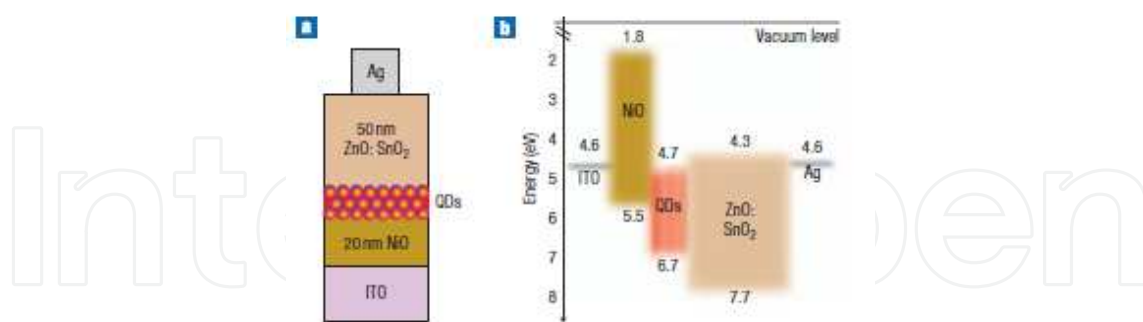


Fig. 6. (a) Device configuration: the Ni is used as hole transporting layer, the QD as active luminescent layer, the ZnO:SnO₂ as electron transporting layer. (b) Band diagram determined from UV photoemission spectroscopy and optical absorption measurements. (Reprinted with permission, Caruge et al., 2008. Copyright 2008, Nature Publishing Group).

A maximum EQE of nearly 0.1% was demonstrated, the peak brightness was measured to be 1950 cd m⁻² at 19.5 V and 3.73 Acm⁻². Comparable brightness and J-V characteristics is claimed when the devices were tested after being stored for four days, in contrast to unpackaged organic QD-LEDs, which cannot withstand prolonged atmospheric exposure.

Recently high efficiency QD-LEDs by using a sol gel TiO_2 electron transporting layer was reported (Cho et al., 2009); the TiO_2 layer is deposited by spin-coating, enabling the QD-LED to be fabricated by means of an all-solution process (Fig. 7). The emissive layer is made of a crosslinked QD layer directly spin-coated on a poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,40-(N-(4-sec-butylphenyl)) diphenylamine)] (TFB) hole transporting layer. The linker molecule, 1,7-diaminoheptane, is attached to the QD through exchange with the pre-existing surfactants or by binding to empty sites on the QD surface. The crosslinking is obtained by a post-deposition thermal treatment. The crosslinking of the QD layer greatly improves the luminance and luminous efficiency.

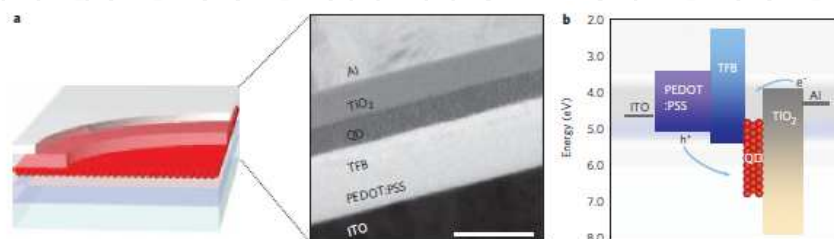


Fig. 7. (a) Device structure (left) and cross-sectional TEM image (right) of the QD-LED. TFB, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,40-(N-(4-sec-butylphenyl))diphenylamine)]. Scale bar, 100 nm. (b) Energy band diagram. (Reprinted with permission, Cho et al., 2009. Copyright 2009, Nature Publishing Group).

It is demonstrated that the energy band offset between the QD and the HTL was reduced from 1.5 to 0.9 eV that leads to an increase by over a factor of 10 in the maximum luminous efficiency because of more efficient hole injection and enhanced charge balance. Moreover the metal oxide TiO_2 layer shows an improved electron injection superior if compared with the standard organic Alq_3 ; this is a consequence of the lower band offset (0.4 eV) for Al/TiO_2 compared to that for Al/Alq_3 (1.2 eV). And higher electron mobility of the sol-gel TiO_2 ($1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) compared to that for Alq_3 ($\sim 1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The turn-on voltage in the TiO_2 -based QD-LED also significantly decreased to 1.9 V, which is smaller than the QD bandgap of 2.1 eV and much lower than that observed for the Alq_3 -based device (~ 4.0 V). The overall device performances are improved, in particular the luminance reach the value of 12380 cd m^{-2} and a maximum power efficiency of 2.41 lm W^{-1} .

4. White Hybrid Light Emitting Devices

To obtain white light, all the three primary colors (red, green and blue) have to be produced simultaneously. Since it is difficult to obtain all primary emissions from a single molecule, excitation of more than one organic species is often necessary, thus introducing color stability problems. Due to the different degradation rates of the employed organic compounds, the emission color of the device can, in fact, changes with time. The CdSe semiconductor QDs exhibit a size-dependent color variation due to quantum confinement effect, which covers almost whole the visible range (Suzuki et al., 1996; Ginger et al., 2000; Coe-Sullivan et al., 2005). Additionally, the fluorescence efficiency and, in particular the stability of the nanocrystals, can be greatly improved by modifying the particle surface. These characteristics can be merged with peculiar properties of organic materials, such as

flexibility and ease of processing, to give rise to a novel class of low cost hybrid white-LEDs with improved lifetime and color stability. We proposed two different white emitting device structures based on colloidal semiconductor QDs. In the first structure, red emitting CdSe/ZnS QDs are blended in a blue emitting polyfluorene (Li et al., 2005). The matrix polymer provides a simple device preparation process due to its high processability and a blue emitting component in the device emission. The function of green component in the white emission spectrum is given to a green emitting electron transporting material evaporated on top of the polymer/QDs film. In the second structure (Li et al., 2006), three different size of CdSe/ZnS QD samples emitting at wavelength of 490nm, 540nm, 620nm are dispersed in a high mobility hole organic matrix. White bright electroluminescence is obtained from the ternary nanocrystal composites.

4.1 Organic-Inorganic Hybrid White LEDs Based on Polymer and QDs

Host-guest systems are typically employed to obtain white light emission by exploiting two mechanisms, namely, Förster energy transfer (Förster, 1959; Lakowicz, 1983) and charge transfer (Utsugi et al., 1992; Suzuki et al., 1996). All these processes have to be accurately controlled in order to obtain white EL. We demonstrated that a balanced white emission is obtained in hybrid system poly[(9,9-dihexylfluoren-2,7-diyl)-alt-co-(2-methoxy-5-(2-ethylhexyloxy) phenylene-1,4-diyl)](PFH-MEH):QDs/Alq₃ when Förster energy transfer in the guest-host system is accomplished by charge transfer from PFH-MEH and Alq₃ to QDs during the electrical excitation (Li et al., 2005). The absorption and PL spectra of all components and possible energy/charge-transfer pathways were shown in fig. 8.

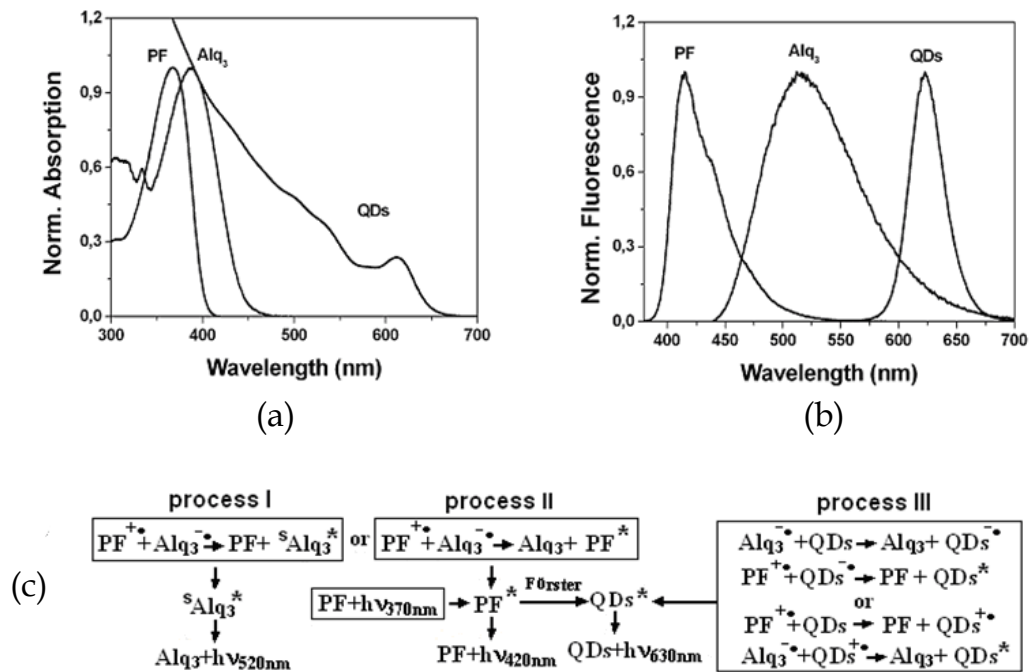


Fig. 8. (a) Absorption and (b) Photoluminescence (PL) spectra of device components. (c) Possible pathways leading to emissive states in device ITO//PEDOT-PSS//PFH-MEH (PF):CdSe/ZnS//Alq₃//Ca/Al. (Reprinted with permission, Li et al., 2005. Copyright 2005, American Institute of Physics).

Electroluminescence measurements have been carried out on ITO//PEDOT-PSS//PFH-MEH:CdSe/ZnS//Alq₃//Ca/Al structures. In fig. 9 the EL spectra for different PFH-MEH:CdSe/ZnS concentration ratios are reported.

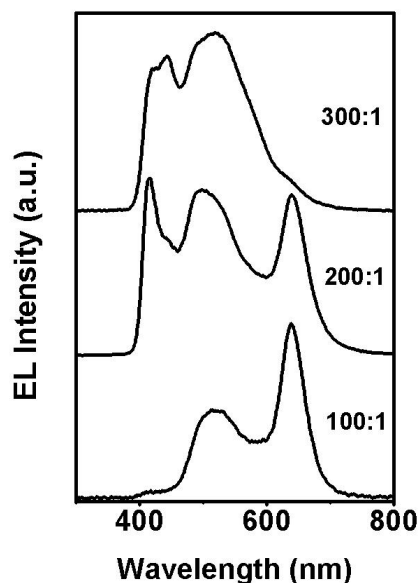


Fig. 9. EL spectra for the device ITO//PEDOT-PSS//PFH-MEH:CdSe/ZnS//Alq₃//Ca/Al with different ratio (PFH-MEH:CdSe/ZnS, c%) (Reprinted with permission, Li et al., 2005. Copyright 2005, American Institute of Physics).

In order to achieve white EL emission, the different color components have to be accurately balanced by controlling both the Förster energy transfer and charge transfer mechanisms. To this aim we fabricated devices with different PFH-MEH:QDs concentration ratios, namely 200:1 and 300:1. At low QDs concentration (300:1), the possible pathways are process I and II. Process I involves the transfer of a hole from a PFH-MEH cation radical (PF^{•+}) to an Alq₃ anion radical (Alq₃^{•-}). Process II involves the transfer of an electron from an Alq₃ anion radical (Alq₃^{•-}) to a PFH-MEH cation radical (PF^{•+}). Both the mechanisms result in excited Alq₃ and PFH-MEH molecules which can decay radiatively, originating blue and green EL emission. Negligible red emission is instead originated from the low amount of QDs. By increasing the concentration of CdSe/ZnS QDs (concentration ratio 200:1), the possible pathway are process I, II and III. A relevant additional role is assumed by the following processes: Förster energy transfer to QDs from excited PFH-MEH and Alq₃ molecules, sequential charge transfer of a hole from PFH-MEH followed by transfer of an electron from Alq₃ or charge transfer of an electron from Alq₃ followed by transfer of a hole charge from PFH-MEH (processes III). Efficient electroluminescence at the three primary colors is thus obtained from PFH-MEH, Alq₃ and QDs with a balanced white spectrum with CIE (0.30,0.33). Maximum External Quantum Efficiency of 0.24% is measured at 1mAcm⁻² and 11V. In these QDs based white-LEDs, holes are considered to be injected from the ITO electrode through PEDOT:PSS layer into the polymer hole conductor and are eventually transported to the QDs. Similarly, the electrons are considered to be injected from Ca/Al cathode into the Alq₃ and are eventually transported to the QDs. Since the high electron affinity of QDs the electrons are better confined within the surface PFH-MEH:QDs/Alq₃, thus enhancing the balance between opposite carriers in the region where more efficient radiative

exciton recombination can occur. In particular, charge transfer processes to CdSe /ZnS core-shell quantum dots are found to be the key element for well balanced white emission.

4.2 Bright White LEDs from Ternary Nanocrystals Composites

To obtain a high performance hybrid device in which QDs act as lumophores is the occurrence of efficient exciton recombination in the inorganic nanocrystals. This is usually inhibited by the poor electron conduction of the inorganic species which limits exciton formation (Leatherdale et al., 2000). Therefore low EL efficiency is observed in QDs/polymers blend based devices. (Colvin et al., 1994; Dabbousi et al., 1995; Schlamp et al., 1997). The phase-segregation technique proposed by Coe et al. allows for the fabrication of high efficiency hybrid monochromatic emission devices, but it involves a narrow QDs size distribution to form high-coverage monolayers, which is compatible only with monochromatic emitting QD-LEDs (Coe et al., 2002; Coe-Sullivan et al., 2003; Coe-Sullivan et al., 2005). To date, efficient QD-LEDs that emit white light only from nanocrystals are still a challenge due to the lack of proper fabrication techniques.

In order to obtain efficient simultaneous emission from different sizes of QDs composites, we proposed a novel device structures in which exciton formation in the inorganic QDs is not exclusively obtained by direct charge injection but by the accurate control of the energy/charge transfer mechanisms from the organic host (Li et al., 2006). We demonstrate the first efficient hybrid light-emitting device, with near white emission from chemically and optically stable ternary nanocrystal composites dispersed in an organic matrix. White bright emission is obtained from homogenous blends, without phase segregation between the active ternary QDs composites and the organic matrix 4,4,N,N-diphenylcarbazole (CBP), exploiting the energy transfer and charge-trapping properties of the different species. The proposed approach is a new general method for the fabrication of potential long operating lifetime, high efficiency white light-emitting devices. The emission mechanisms and the structure of the devices and are shown in the fig. 10a, 10b. In fig. 10c the Photoluminescence (PL) spectra corresponding to isolated lake blue, green and red quantum dots in solid state are shown. The EL spectrum at 13V is shown in fig. 11a. Spectral peaks at wavelengths of 490nm, 540nm and 618nm are attributed to the emission of lake blue, green and red quantum dots, respectively, in agreement with the PL spectra in the solid state (see fig. 10c). A complete quenching of the CBP band is observed in the EL spectrum, resulting in efficient emission at the three primary colors from the QDs, giving rise to a balanced near white overall emission [CIE (0.32,0.45)] at 13V. Furthermore, the color coordinates do not remarkably change with increasing the operating voltage in the range 10V-28V. Possible pathways leading to emissive states are shown in fig. 10a. In our device, holes are injected from the ITO contact through the PEDOT:PSS layer into the CBP host matrix, and are transported towards the QDs. Similarly, electrons are injected from the Ca/Al cathode into the Alq₃ and are transported to the QDs. Then exciton generation on QDs occurs via two parallel processes: (I) charge-trapping and (II) Förster energy transfer from CBP and Alq₃. In the former process, electrons may be trapped in the QDs owing to the relative energy alignment of the LUMO levels of CBP, Alq₃ and QDs, thus, efficient exciton formation on the QDs can occur after recombination with high mobility holes. In the latter process, excitons form on organic molecules CBP (IIa) and Alq₃ (IIb), then undergo Förster energy transfer to the lower-energy QDs sites, where they can recombine radiatively.

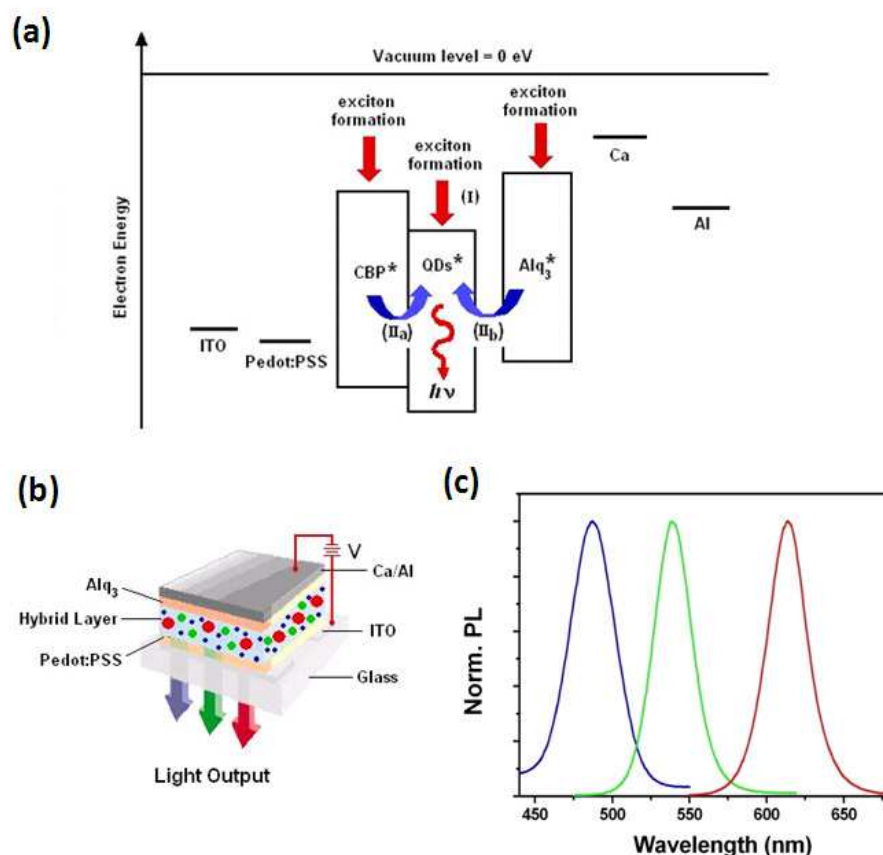


Fig. 10. (a) Proposed simplified energy level diagram of devices and possible exciton creation mechanisms on the QDs: (I) charge-trapping and (II) Förster energy transfer. (b) The structure of the device. (c) PL spectra corresponding to isolated lake blue, green and red quantum dots, measured in solid state. (Li et al. , 2006. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

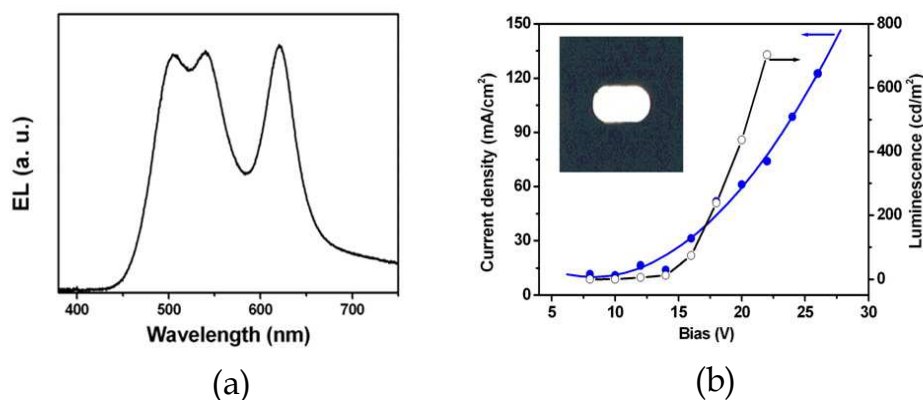


Fig. 11. Electroluminescence (EL) spectra and characteristics of the ternary QDs device. (a) EL spectrum for the device: ITO//PEDOT:PSS//CBP:QDs (B,G,R:18,2,1) //Alq₃//Ca/Al. (b) V-I (dot), V-L (circle) characteristics of the device. Inset: A photo taken from the working device. (Li et al. , 2006. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

Possible pathways leading to emissive states are shown in fig. 10a. In our device, holes are injected from the ITO contact through the PEDOT:PSS layer into the CBP host matrix, and are transported towards the QDs. Similarly, electrons are injected from the Ca/Al cathode into the Alq₃ and are transported to the QDs. Then exciton generation on QDs occurs via two parallel processes: (I) charge-trapping and (II) Förster energy transfer from CBP and Alq₃. In the former process, electrons may be trapped in the QDs owing to the relative energy alignment of the LUMO levels of CBP, Alq₃ and QDs, thus, efficient exciton formation on the QDs can occur after recombination with high mobility holes. In the latter process, excitons form on organic molecules CBP (IIa) and Alq₃ (IIb), then undergo Förster energy transfer to the lower-energy QDs sites, where they can recombine radiatively. The maximum brightness of the device is 1050 cd m⁻² at 58 mA cm⁻², which corresponds to a current efficiency of 1.8 cd A⁻¹, and a turn-on voltage of 6V are measured in air atmosphere fig. 11b. To our knowledge, this is the highest efficiency hybrid device with white emission only from ternary QDs composites, whose luminance satisfies lighting application requirements (i.e. 1000 cd m⁻²).

5. Hybrid Light Emitting Diodes by Micro-Contact Printing

In previous sections different approaches for hybrid LEDs fabrication have been reported. All these device structures are limited by the chemical properties of the employed materials and by the deposition techniques. The main consequence is a restriction of the organic materials choice, especially for the holes transporting and injection layers, which is crucial for the optimization of the device emission. In fact, unlike organic small molecules, QDs cannot be deposited by thermal evaporation because of their high molecular weight and only wet deposition techniques, such as spin-coating and drop-casting are available. Consequently, the separation of the QD active layer from the organic transport layers and the fabrication of multilayer organic/inorganic structures are still challenging. The lack of an appropriate QD deposition technique strongly limits the implementation of Hybrid LEDs in the heterojunction devices technology. This technology could result in an improvement of the devices efficiency and lifetime.

In this frame we developed two totally dry, simple, and inexpensive deposition techniques to transfer colloidal semiconductor QDs onto organic substrates (Rizzo et al., 2008a; Rizzo et al., 2008b). These innovative techniques are modification of the standard microcontact printing (μ CP). In the standard μ CP, a poly(dimethylsiloxane) (PDMS) stamp is inked by the material which is then transferred onto the solid substrate by conformal contact of the elastomeric stamp and the substrate. However this technique cannot be used for the deposition of colloidal semiconductor nanocrystals. PDMS stamp, indeed, can be readily swelled by a number of non polar solvents such as toluene and chloroform, in which nanocrystals for optoelectronic applications are usually dispersed in.

The first technique we developed is named μ CP-Double Transfer because it consists in a two step process. First the nanocrystals are deposited from a toluene solution on a float glass substrate, when the solvent is dried, the PDMS stamp pad is brought in conformal contact with the nanocrystal film, then the PDMS stamp is peeled away and the nanocrystals are transferred to the surface of the stamp. Finally, QDs are deposited by single step microcontact printing from the PDMS stamp to the surface of previously evaporated organic thin films. (Rizzo et al., 2008a).

The second technique consists in protecting the PDMS stamp pad with a SU-8 photoresist layer deposited by spin coating and cross linked in order to make it insoluble to toluene. (Rizzo et al., 2008b). The two techniques that we propose avoided the swelling of the PDMS stamp and combined the ease of wet deposition processes with the possibility to grow a heterojunction QDs-LED using thermal evaporation. White and red electroluminescence from colloidal QDs has been obtained demonstrating that these deposition techniques are fully compatible with OLED technology.

5.1 Hybrid Light-Emitting Diodes from μ -CP Double-Transfer of Colloidal Semiconductor CdSe/ZnS Quantum Dots onto Organic Layers

The sketch of the Double Transfer technique is reported in fig. 12. Drop-casting is the simplest technique for the deposition of a QDs solution on the glass substrate. The degree of order in the resulting assembly is mainly determined by the rate of solvent evaporation: slowing down the evaporation of solvent, in our case toluene, and preventing it from a rapid dewetting is crucial for a successful double transfer. A slow evaporation allows nanocrystals to diffuse and self assemble into large periodical (long range order) structures with fewer defects. In order to slow down the evaporation after the drop deposition, the substrates were placed in an over-saturated environment of toluene vapour.

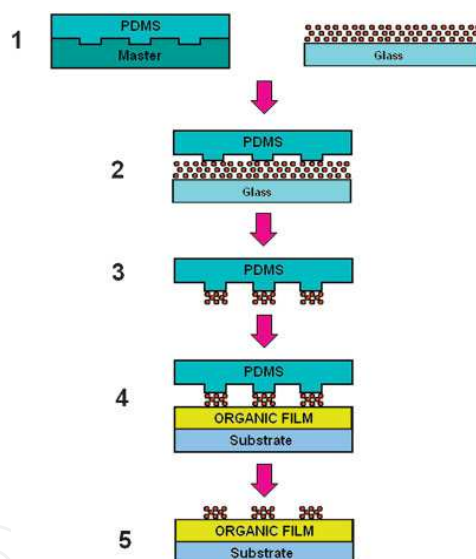


Fig. 12. A schematic illustration of the procedure used to transfer colloidal nanocrystals on organic thin films. 1. Colloidal QDs are deposited from toluene solution on a cleaned float glass substrate; 2. when the solvent is dried, a PDMS stamp pad is brought in conformal contact with the surface of the nanocrystals film; 3. The PDMS stamp is then peeled away and the nanocrystals are transferred to the surface of the stamp; 4. QDs are deposited by single step microcontact printing from the PDMS stamp to the surface of previously evaporated organic thin films; 5. Nanocrystals are transferred on the organic substrate (Rizzo et al., 2008a. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

The quality of the drop-casted films was verified by Transmission Electron Microscope (TEM) measurements. In fig. 13a and 13b we compare two samples realized depositing 20 μ L of the same colloidal solution on a TEM grid in over-saturated environment (fig. 13a) and

under ambient condition (fig. 13b). After a slow dewetting of the solvent, (about 30 minutes) the nanocrystals form a compact layer on a scale of several microns. For a fast solvent evaporation (less than 5 min) the film presents the formation of multilayer domains and microscopic voids. Deposition of a uniform QDs layer on the top of the organic layers has a paramount importance for the correct functioning of the hybrid LED devices. The layer quality of QDs formed on the surface of PDMS reflects the morphology of the QD film on the glass substrate, i.e. it depends on the concentration of the nanocrystals solution and on their assembling on the glass surface.

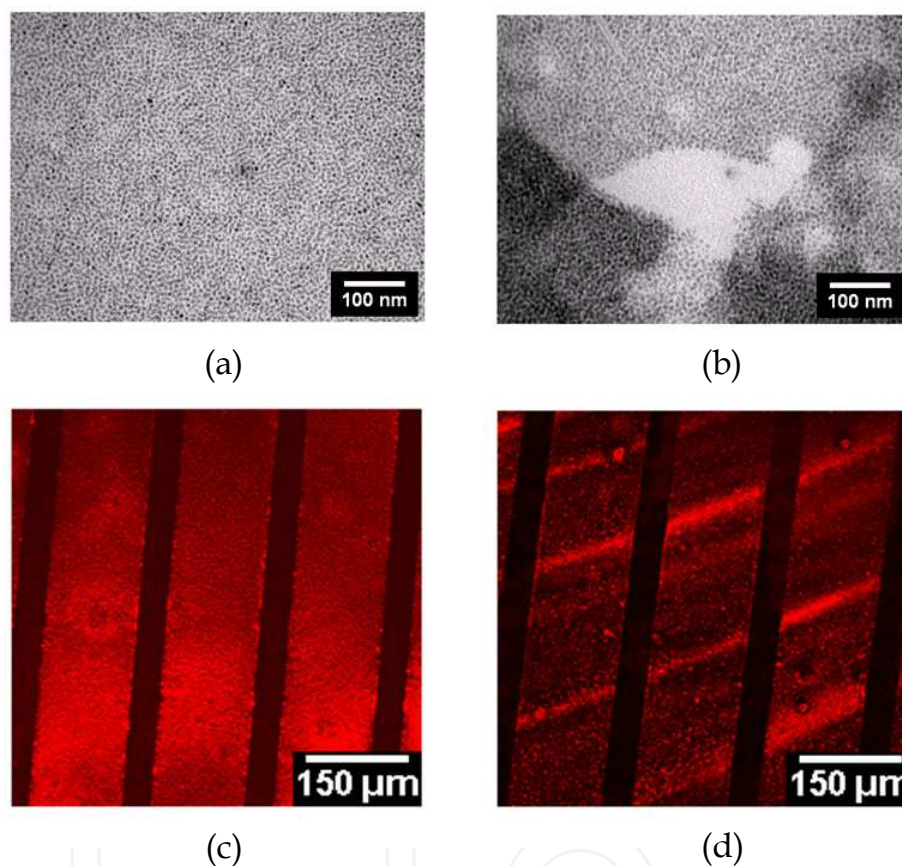


Fig. 13. a) TEM images of nanocrystals deposited by drop-casting on TEM grid after slow evaporation of the solvent and b) fast evaporation of the solvent. c) Confocal microscopy image of QDs transferred by double transfer μ CP onto CBP organic substrates from a glass substrate after slow evaporation of the solvent; d) QDs on CBP transferred from a glass substrate after fast evaporation of the solvent. (Rizzo et al., 2008a. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

In fig. 13c and 13d we show the confocal microscope images of QDs transferred on CBP layer by μ CP Double Transfer from glass substrates after slow (fig. 13c) and fast evaporation (fig. 13d) of the solvent. The morphology of $50 \times 150 \mu\text{m}$ QDs stripes results uniform for samples made after slow evaporation of the solvent and very dishomogeneous for the one made after a fast evaporation of the solvent. This is also a further proof of how effective slower solvent evaporation is in assuring highly homogeneous film of colloidal QDs at the

micrometer scale. Increasing 15 times the concentration of QDs in toluene solution, the thickness of the transferred layer can vary from few layers to more than 100 nm.

The transferring mechanism of QDs from the glass substrate to the stamp can be explained by considering the strong interaction between the PDMS stamp surface and the colloidal nanocrystal hydrophobic surfactant. This can be attributed to the existence of highly mobile hydrophobic oligomers on the PDMS stamp surface. Moreover PDMS has a very low surface energy of 21.6 dyn/cm thus allowing the transfer of the QDs on a higher surface energy substrate, such as the CBP. In this contest the organic material acts as glue for the nanocrystals.

In order to realize a hybrid LED that emits light from nanocrystals alone, a high coverage and compact QDs layer has to be deposited on the top of the organic material. For this reason in the device fabrication we decided to use a flat PDMS pad for the QDs transfer. The device structure (fig. 14a, inset) consists of a thermally evaporated N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (α -NPD) hole injection layer (HIL) doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-quinodimethane (F4-TCNQ) and CBP hole transporting layer (HTL). A QDs active layer of 80 nm is transferred on the organic substrate by the Double Transfer technique reported above. The 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) hole blocking layer (HBL), the Alq₃ electron transporting layer (ETL), and the electrodes are evaporated after the QDs deposition.

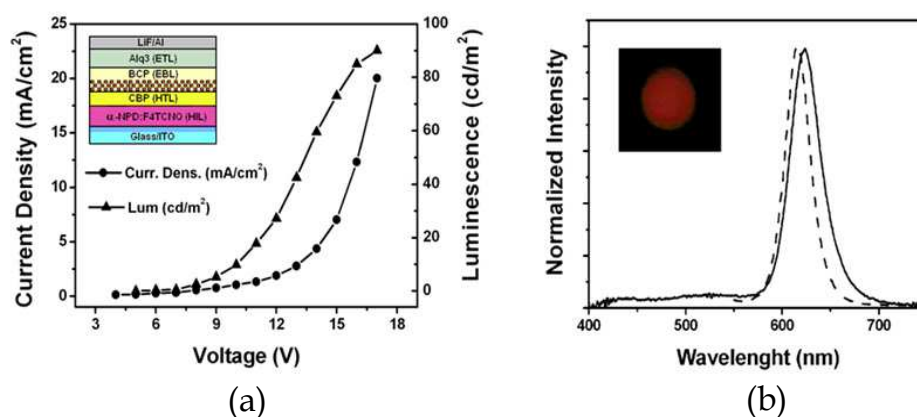


Fig. 14. Structure and performance of a hybrid LED fabricated by μ CP double transfer. a) Current-density-voltage and luminescence-voltage characteristics of the hybrid LED; inset: a schematic illustration of the device structure. b) Electroluminescence (solid line) and PL (dashed line) spectra; the inset shows a picture of a functional 1.5mmx1.5mm area device (Rizzo et al., 2008a. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

In the proposed device the holes and electrons are delivered to the nanocrystals layer through the injection and transport layers. The electroluminescence (EL) spectrum and the picture of the working device in fig. 14b demonstrate that the emission is dominated by QDs band edge emission. Photoluminescence (PL) spectrum of the nanocrystals is reported in dashed line in the same figure.

In fig. 14a a current density versus voltage and luminescence versus voltage characteristics are reported. The maximum brightness of the device is 90 cd m⁻² at 20 mA cm⁻², which corresponds to an external quantum efficiency of 0.15%.

5.2 White Electroluminescence from a μ -CP Deposited CdSe/ZnS Colloidal Quantum Dot Monolayer

In Figure 15 a schematic sketch of the second approach for QD deposition is displayed (Rizzo et al., 2008b).

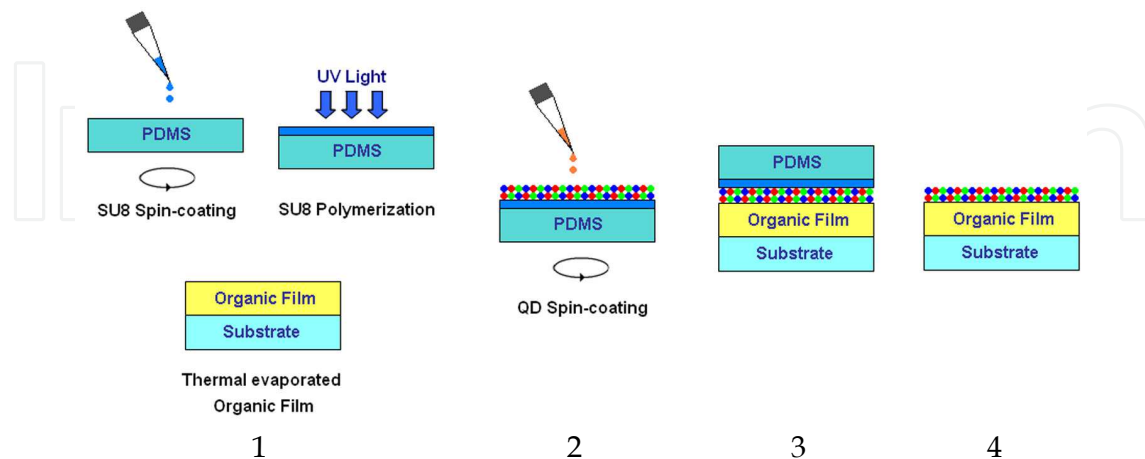


Fig. 15. A schematic sketch of the modified μ CP technique used to deposit colloidal nanocrystals on organic thin films. 1. The SU-8 is spin-coated on the top of a flat PDMS stamp pad, then exposed to UV radiation and subsequently thermally cross-linked in order to make the film insoluble to toluene; 2. a mixed blue, green and red CdSe/ZnS QD solution is spin-coated at on the SU-8 protected PDMS; 3. the inked stamp is then inverted on the surface of a previously evaporated organic thin film and peeled away after 30 second; 4. nanocrystals are transferred on the organic substrate. (Rizzo et al., 2008b. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

In fig. 16 we report atomic force microscopy (AFM) images of the same film. Fig. 16a was taken at the interface between the CBP and QDs layer at the edge of a pinhole defect. By the profile (fig. 16b) we can estimate QD film thickness of about 10nm. In fig. 16c, 16d, 16e, and 16f AFM images of the QD film at different resolutions are reported. Pictures in fig. 16a, 16c, 16d, point out the uniform distribution of the QDs on the organic material with an average roughness of about 5nm. Moreover in the higher resolution images in fig. 16e and 16f is possible to discriminate the two phases: QDs from 4-10 nm in diameter on the top and organic CBP as underlayer. The film such prepared was used for the fabrication of white emitting hybrid LED. In Fig. 17 the electroluminescence spectra at different applied voltages are reported, showing an increase of the green and blue components relative to the red one when voltage is increased from 5V to 10V. This is consistent with the larger barrier for holes injection in the smaller QDs. Two dominant QD excitation mechanisms are present in the hybrid device: the Förster energy transfer and the charge trapping. In the charge trapping process the electrons may be trapped in the QD owing to the absence of any energy barrier between the organic Alq₃ and BCP layers and CdSe/ZnS one. For these charged QDs the barrier to holes injection and transfer from the α -NPD/CBP bilayer is reduced. Thus, exciton formation and consequent radiative recombination occur on QD sites upon an acceptance of high mobility holes from CBP. The presence of a α -NPD (420nm) small band emission is due to the presence of pinhole defects, grain boundaries, interstitial spaces in the QD thin layer that allow the formation of exciton on organic sites. The HOMO level alignment of α -NPD/CBP suggests an accumulation of holes in the α -NPD at the HIL/HTL interface.

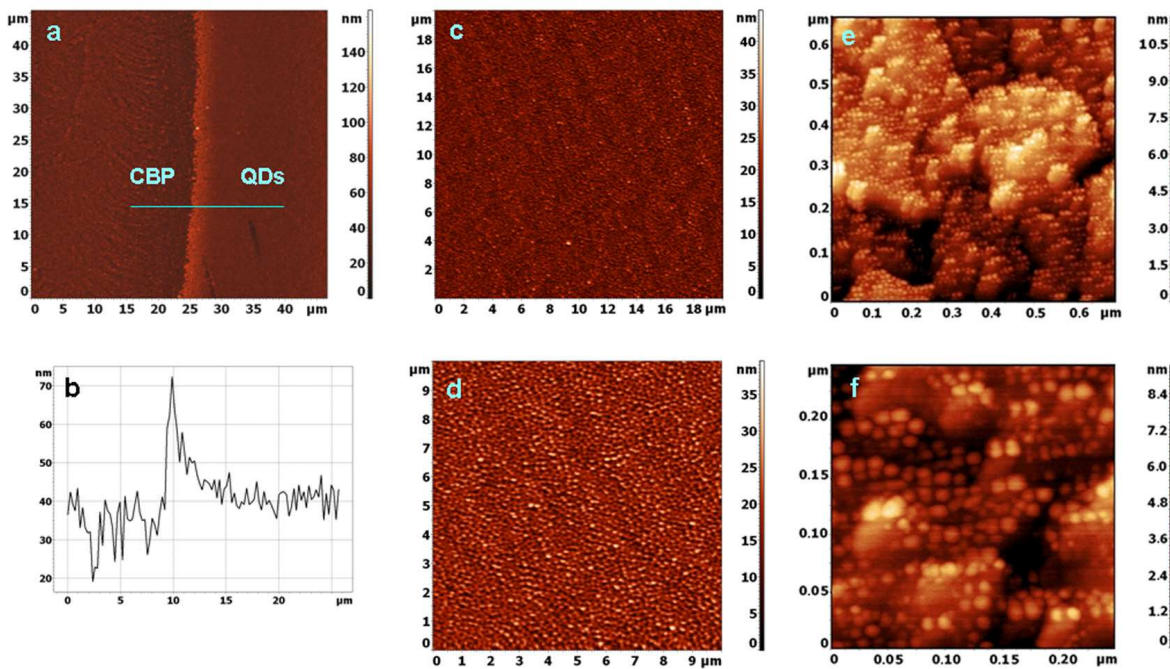


Fig. 16. Atomic force microscopy (AFM) characterization of the transferred nanocrystal layer. a) AFM image of the layer at the edge of a pinhole defect and b) profile corresponding to a); c), d), e), f), AFM images of the QD film at different scanning sizes. (Rizzo et al., 2008b. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

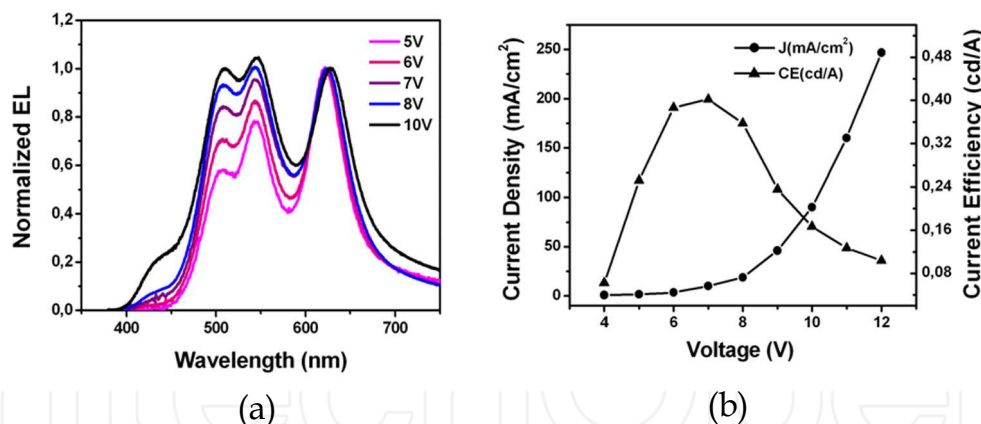


Fig. 17. a) EL spectra of the device at different applied voltages normalized at the red peak. b) Current-Voltage I-V characteristic and current efficiency (CE) for the hybrid device. (Rizzo et al., 2008b. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.).

By increasing the voltage and, consequently the current, the fraction of emission coming from the organic layer increases. The development of these two techniques enables us to separate the deposition of the organic materials from the QDs deposition and the fabrication of multilayer complex device structures without any restriction in the organic material choice. By taking advantage from the independent processing of QD we fabricated red and white emitting multilayer LEDs with a doped holes injection layer.

6. Conclusion

Several approaches have been followed for the incorporation of inorganic colloidal semiconductor nanocrystals in organic light emitting diodes technology. As a results we first reported two methods for the fabrication of white emitting hybrid organic/inorganic LEDs wherein colloidal CdSe/ZnS QDs are blended in a blue emitting polymer or in a high mobility hole transporting organic small molecule. The major breakthrough has been reached with the fabrication of white hybrid LEDs from ternary nanocrystal composites. CdSe/ZnS QDs with different sizes simultaneously emit light at different wavelength (blue, red and green region) to achieve white emission. By accurately controlling the Förster energy transfer and the charge trapping on QDs sites we were able to fabricate the highest efficiency hybrid device with emission only from QD composites. The maximum satisfies the lighting application requirements. Moreover the development of two innovative micro-contact printing techniques allow the fabrication of multilayer hybrid LEDs structure without restrictions in the organic under-layers. These deposition methods permit the integration of colloidal QDs in the promising p-doping organic technology. The recent results demonstrate that the successful integration of colloidal nanocrystals in OLED technology could enable the creation of a new set of promising devices with a possible improvement in the color stability and the device lifetime.

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This book contains a number of latest research developments on nanocrystals. It is a promising new research area that has received a lot of attention in recent years. Here you will find interesting reports on cutting-edge science and technology related to synthesis, morphology control, self-assembly and application of nanocrystals. I hope that the book will lead to systematization of nanocrystal science, creation of new nanocrystal research field and further promotion of nanocrystal technology for the bright future of our children.

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