Investigations of organic light emitting diodes with CdSe(ZnS) quantum dots

C.W. Lee [a,b], C.H. Chou [b], J.H. Huang [b], C.S. Hsu [b], T.P. Nguyen [a,*]

[a] *Laboratoire de Physique des Matériaux et Nanostructues, Institut des Matériaux Jean Rouxel,*
2 rue de la Houssinière, BP32229, 44322 Nantes, France
[b] *Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan, Republic of China*

Abstract

In this study, we report results on investigation of bilayer light emitting diodes made of organic capped CdSe(ZnS) core/shell type nanocrystals and poly[2-phenyl-3-(9,9-dihexyl-fluoren-2-yl) phenylene vinylene]-co-[2-methoxy-5-(2′-ethylhexyloxy) phenylene vinylene] (FP-PPV-co-MEH-PPV) electroluminescent co-polymer. Light emitting diodes of structure: indium-tin-oxide (ITO)/polyethylene dioxythiophene: polystyrene sulfonate (PEDOT:PSS)/FP-PPV-co-MEH-PPV/Ca/Al devices have been fabricated and studied. The co-polymer device emits a yellow light with a maximum brightness of 3949 cd/m^2 and a maximum external quantum efficiency of 0.27 cd/A at 10 V. Incorporation of CdSe(ZnS) quantum dots into the active polymer film resulted in an increase in device brightness, which reached 8192 cd/m^2 and in external quantum efficiency, which became 1.27 cd/A at 7 V with a lower turn-on voltage. The results indicate that CdSe(ZnS) quantum dots improved significantly the emission of the devices by modifying the injection and transport of the charge carriers. We suggest a non-uniform dispersion of QDs in the co-polymer layer with carrier blocking process by the particles, which produced a balanced charge distribution inside the co-polymer, and thus increased the emission efficiency.

1. Introduction

Conjugated polymers have been extensively studied for potential applications in electroluminescent displays, solar cells, and thin film transistors. Since the first report of an electroluminescence device based on conjugated polymers by Burroughes et al. [1], many conjugated polymers have been synthesized and investigated in order to fabricate efficient devices for industrial applications [2–6]. The science of polymer and organic devices has greatly progressed since then. The development of new materials and device designs has enabled the fabrication of high performance devices: various colors, low turn-on voltage, long lifetime, low energy consumption, and high brightness.

In parallel, nanotechnology science has emerged and is advancing rapidly. In particular, inorganic particles exhibit interesting physical properties as the size approaches nanoscale dimensions. Quantum dots (QDs) are nanomaterials having specific and unique optical properties that can be exploited in display technology. Indeed, the luminescent color of nanocrystals differs from that of the bulk material, and changes with the crystal size due to quantum confinement effects. Several semiconductor QDs exhibit a size-dependent color variation, which covers almost the whole visible range [7,8]. Therefore, QDs have been used in electro-optic devices such as light emitting diodes (LEDs), photovoltaics, and lasers. An obvious advantage of the nanomaterial-based devices is their low production price by using mass production techniques.

The combination of both materials (polymers and QDs) and technologies (LEDs and QDs) is expected to lead to devices of good optical and electronic properties. The adjustable and sharp emission characteristics of these materials make them interesting to be used in light emitting diodes by just varying the particle size because of quantum confinement effects [9–12]. However, the first hybrid organic/inorganic LEDs made with poly(phenylene vinylene) (PPV) and cadmium selenide (CdSe) gave a rather limited performance of light emission, with uncontrolled color

* Corresponding author. Tel.: +33 2 40373976; fax: +33 2 40373991.
E-mail address: nguyen@cnrs-imn.fr (T.P. Nguyen).

light [9]. Furthermore, CdSe showed poor photoluminescence as compared to some conjugated polymers and its stability is strongly influenced by the photo-processes occurring in the luminescent medium. Therefore, a new approach was developed by adding a shell of zinc sulfide (ZnS) to a CdSe particle in order to strengthen its structure and to enhance its emission. The photoluminescence (PL) quantum efficiency of the CdSe/ZnS core–shell QDs can reach more than 50% [13,14]. Further improvements of performance were achieved by the use of new designs of diodes, modifying the spatial distribution of carriers inside the emitter, and favoring their recombination, thereby improving the emission.

Despite the progress in performance of devices, the physical processes in the hybrid materials, especially the specific role of the QDs, have not been fully understood. In some combinations, these particles emit their characteristic light in addition to that of the polymer, and in others, only light from the polymer was obtained with an improved efficiency. In the Section 2, we shall briefly review the different aspects of devices making use of hybrid organic/QDs as active materials in LEDs.

2. Semiconductor quantum dots/polymer hybrid materials

Because of their small size, QDs increase the band gap of a semiconductor as compared to the bulk material according to basic equations of energy in quantum mechanics. In addition, spatial confinement of electrons or holes favors their recombination, and increases the light emission of the material. Techniques for obtaining size controlled QDs have been well known and described [15,16]. In these techniques, factors such as the concentrations of precursor solution, temperature, and reaction duration can be adjusted to provide the desired particle diameter. For CdSe, the size of QDs can vary from 2 to 6 nm, and the emitted colors cover a wide range from blue to red. This particular property has enabled incorporation of QDs in functional polymers to fabricate composites, which are used as an emitter in OLEDs. In earlier work, CdSe QDs were used as chromophores in a polymer matrix [9]. Such diodes could emit light from either the active polymer or the nanoparticles depending on the value of the applied voltage. However, the efficiency of these diodes is low, and they presented little practical interest. A new design of OLED structure using a single layer of QDs, which was sandwiched between two organic layers, gave an external quantum efficiency exceeding 0.4% [10]. In these diodes, the QDs were mixed with an organic material in solution and were deposited by spin coating. After drying, phase segregation occurred, giving a single and self-assembled QD layer, which was formed on the top of the organic film. In this configuration, the QDs act as chromophores, generating excitons either from direct charge injection or by exciton energy transfer from organic molecules (Förster energy transfer). It is expected that QDs act as trapping centers for electrons [10], and capture the injected carriers from the cathode. Subsequently, holes coming from the anode to the vicinity of the particles combine with trapped electrons to form excitons, which decay radiatively. Similar structures have been realized with different sizes of nanoparticles to make white light

emitting devices [17,18]. Another approach used a single QD layer deposited by spin coating of the aqueous solution forming trilayer-emitting diodes [19]. The efficiency is improved as compared to diodes without QDs, and the devices emitted light from both QDs and the organic materials. In order to obtain the light emission directly from the organic material with enhanced performance by QDs, it was suggested to uniformly disperse the particles in the polymer matrix [20,21]. This dispersion can be obtained by using core–shell QDs such as CdSe(ZnS) added to polymer to favor the charge transport in the active layer. A large number of carriers will pass from an electrode to the other without encountering a QD, and excitons will be formed inside the polymer matrix, giving light from the polymer. The role of QDs in carrier transport process in devices has not been clearly established, however. Some results lead to the conclusion that the dots are not involved in transport in hybrid materials, since the current–voltage characteristics are similar for devices containing QDs or not [16]. In devices with a QD monolayer formed on the top of the polymer film, the current density is lower than that measured in similar diodes without QDs [10], suggesting a trapping of charge carriers by the particles. In devices containing well-dispersed dots, the current density is higher as compared to pristine polymer, with improved emission performance.

In this work, we have investigated a hybrid material obtained by mixing a co-polymer of PPV derivatives with QDs. We used CdSe(ZnS) core/shell dots in order to obtain well dispersed nanoparticles in the polymer matrix. By determining the electro-optical characteristics of OLEDs using the material as an active layer, we discuss the role of QDs in the transport and emission processes.

3. Experimental

CdSe/ZnS core–shell type quantum dots (QDs) passivated with trioctylphosphineoxide (TOPO) caps were prepared following the technique already described [22]. The size of the dots used in this work was 3.8 nm as determined from transmission electron microscopy (TEM). The co-polymer was obtained from two monomers: 1,4-bis(chloromethyl)-2-phenyl-3-(9,9-dihexylfluoren-2-yl)benzene (M1) and 1,4-bis(bromomethyl)-2-methoxy-5-(2′ethylhexoxy)benzene (M2) whose synthesis was previously described in the literature [23,24]. After preparation of a solution having the defined ratio M1/M2 in the THF, a solution of potassium *tert*-butoxide (*tert*-BuOK) in THF was added. The resulting mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. A solution of 2,6-di-*tert*-butylphenol as end-capping agent in THF was then added and stirred for 6 h. The polymer was obtained by pouring the mixture into methanol and filtering. It was purified by dissolving in THF and reprecipitated from methanol twice. After drying under vacuum for 24 h, the polymer was obtained in a yellow-green powder form. QDs and the polymer were dissolved in $CHCl_3$ then mixed together in different volume ratios. The 1/2.5 volume ratio of QDs to polymer was chosen for fabrication of hybrid emitting films.

For the fabrication of devices, ITO-coated glass substrates were cleaned sequentially in ultrasonic baths of detergent,
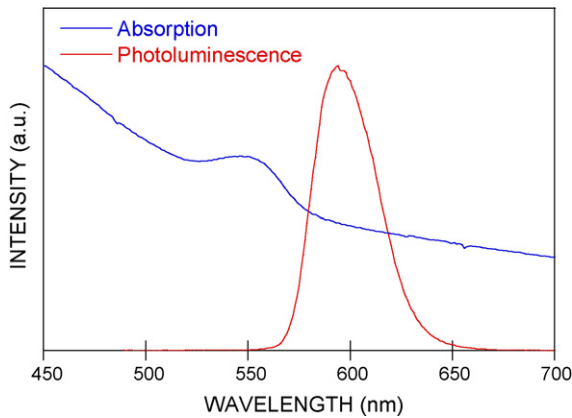
Fig. 1. Absorption and photoluminescence spectra of CdSe/ZnS nanoparticles (3.8 nm).

2-propanol/deionized water (1:1 volume) mixture, toluene, deionized water and acetone. A 50 nm-thick hole injection layer of poly(ethylene-dioxythiophene) (PEDOT) doped with poly(styrenesulfonate) (PSS) was spin-coated on the top of ITO from a 0.7 wt.% dispersion in water and dried at 150 °C for 1 h in vacuum. Thin films of co-polymer were spin-coated from CHCl$_3$ solutions onto the PEDOT layer and dried at 50 °C overnight in vacuum. Finally, 35 nm thick Ca and 100 nm thick Al electrodes were deposited through a shadow mask onto the polymer films by thermal evaporation at base pressures lower than 10^{-6} mbar. The active area of each EL device was 4 mm^2.

4. Results and discussion

4.1. Optical characteristics of materials

Fig. 1 shows the absorption and photoluminescence (PL) spectra of the CdSe(ZnS) QDs in CHCl$_3$. The absorption and emission peaks are located at 550 and 594 nm. In Fig. 2, the PL spectra of co-polymer and composite thin films are shown, together with that of the QDs for comparison. The main emission peak is located at 564 nm with a component at 612 nm. As the emission peak of QDs is close to that of the low energy component in the PL spectrum of the co-polymer, it is not possible
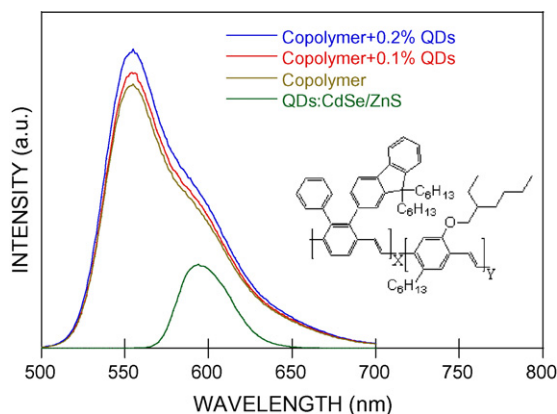
to distinguish between the contribution of QDs and that of the polymer in the spectrum of the composite films. We note an increase of the PL intensity of composite films as compared to pristine polymer. This PL enhancement seems to depend on the QD concentration.

4.2. Electrical characteristics of devices

Fig. 3 shows the current density–voltage characteristics of ITO-PEDOT:PSS-co-polymer/QD-Ca/Al and ITO-PEDOT:PSS-co-polymer-Ca/Al devices at $T = 300$ K. The turn-on voltage of both diodes is ∼4 V. The electroluminescence (EL) spectra of the devices, shown in inset of Fig. 3, are similar with the maximum emission intensity located at about 560 nm. A slight red shift of the composite-based diodes is observed; however, there are no significant differences in the spectral line shape, implying that the fluorescence mechanism is due to the polymer in both devices. The shift of the EL spectrum combined with the overlap of the emission and the absorption spectra of both materials may suggest an energy transfer between the host co-polymer and the guest QDs as previously observed in hybrid systems [10,16]. However, in the studied systems, the QDs dominated the EL, and the emission obtained from particles was assumed to be from the Förster energy transfer of excitons formed in the organic host. A very convincing demonstration was given in trilayer hybrid systems where the efficiency of the devices was found to increase with the shell (ZnS) thickness, without significant change of the emission wavelength [11]. In our devices, there is no such evidence for the emission of the devices. In fact, the EL comes mainly from the co-polymer as can be seen in Fig. 3. In the hybrid device, the 594 nm peak corresponding to the QD emission has a negligible intensity compared to that of the co-polymer. Therefore, an energy transfer from the organic material to the nanoparticles, if any, is negligible. The red shift of the emission spectra in the hybrid device may result from aggregation of polymer chains, which could be induced by incorporation of QDs into the matrix. On the other hand, the current density of this device is lower than that measured in the device using the co-polymer. The difference in current density between the devices is noticeable at high voltages. We note
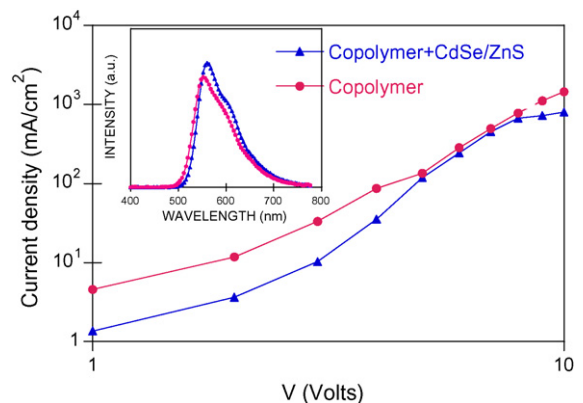

Fig. 2. PL spectra of pure co-polymer, co-polymer/QDs thin films and QDs in solution. Inset shows the chemical structure of the co-polymer.

Fig. 3. Current density–voltage characteristic of ITO-PEDOT:PSS-co-polymer/QD-Ca/Al and ITO-PEDOT:PSS-co-polymer-Ca/Al devices at $T = 300$ K. (Inset) Electroluminescent spectra of the devices.
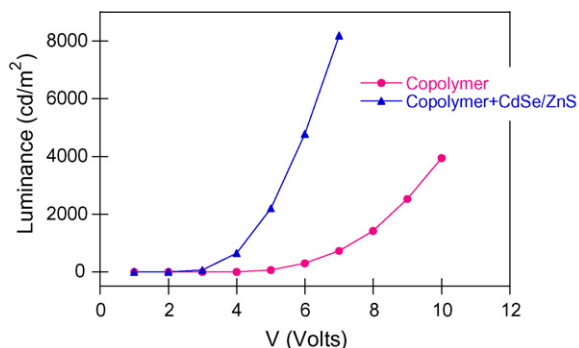
Fig. 4. Luminance–voltage characteristic of ITO-PEDOT:PSS-co-polymer/QD-Ca/Al and ITO-PEDOT:PSS-co-polymer-Ca/Al devices at $T = 300$ K.

that the co-polymer-based diode exhibits space charge limited conduction (SCLC) behavior. In contrast, the composite-based diode shows a strong deviation from the SCLC at high fields. Additional current–voltage measurements have been performed on hole-only (ITO-PEDOT:PSS-co-polymer/QD-Au and) and electron-only devices (ITO-Al-co-polymer/QD-Ca/Al) showing a strong decrease in the current density in the hole-only diode but practically unchanged characteristic in the electron-only diode.

Figs. 4 and 5 show the luminance and yield of the devices as a function of the applied voltage. A maximum luminescence of $3949 \, cd/m^2$ and maximum external quantum efficiency of $0.27 \, cd/A$ are obtained at 10 V in the co-polymer-based diode. In the composite-based device, a luminance as high as $8192 \, cd/m^2$ with a maximum external quantum efficiency of $1.27 \, cd/A$ at 7 V is obtained. Adding QDs to the emitting co-polymer significantly improves the diode efficiency, even if there is no evidence for energy transfer from the guest particles to the host co-polymer.

The effects of QDs on the physical processes in the composite device are manifold. First, as EL activities in both materials are identical, the increase in luminescence indicates that the number of created excitons is higher in the composite than in the co-polymer, and they originate essentially from the polymer. The excess excitons may result from two processes. The first process is an increase of recombinations resulting from a better balance of charge carriers inside the polymer. Incorporation
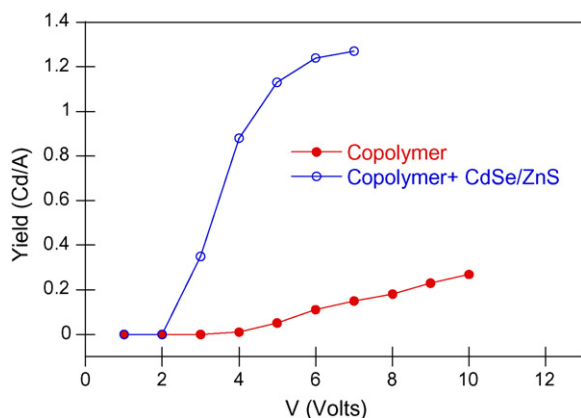
of QDs may create a pathway, improving the mobility of electrons or slowing down that of holes. The second process is the decrease of the number of exciton quenching centers that can be found in the interfacial region between the polymer and the cathode. QDs may be intercalated between the emitter and the metal electrode, preventing a direct contact between the materials. In this case, there would be a phase segregation of the deposited composite film, and QDs would be formed on the top of the polymer film. Considering the *I–V* characteristic of diodes, we note that the current density decreased when QDs are added to the polymer. This observation is an agreement with the phase segregation hypothesis. However, the EL spectra do not show strong evidence of emission arising from QDs, and instead, the emitted light is essentially due to recombination in the polymer. Based on this analysis, we suggest that the QDs are not uniformly dispersed in the polymer matrix but are partially aggregated at the cathode-polymer interface, forming dispersed small islands. The remaining QDs would be distributed in the bulk of the polymer. These dots modify the transport of the injected carriers by affecting their mobility. From the *I–V* characteristic in hole-only devices, we suggest that the QDs in the bulk of the polymer film act as hole blockers, which balance the charge injection and then improve the light emission in the co-polymer.

5. Conclusion

In this work, we have investigated light emitting diodes whose emitter is a hybrid material made by incorporating CdSe(ZnS) into a PPV derivative co-polymer. Compared to diodes using pristine co-polymer, the studied devices have higher brightness and improved efficiency with no significant changes in the emission spectrum. However, the transport process in the diode is affected by a decrease in current density. We suggest a non-uniform dispersion of the QDs with formation of small islands of particles on the polymer layer, resulting from a phase segregation of the composite. Furthermore, the dots distributed in the bulk of the film modify carrier mobilities, especially the hole mobility, leading to a charge balance and improving the performance of the devices.

References

[1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burns, A.B. Holmes, Nature 347 (1990) 539–541.
[2] M. Beggren, O. Inganäs, G. Gustafsson, J. Rasmusson, M.R. Andersson, T. Hjertberg, O. Wennerstrom, Nature 372 (1994) 444–446.
[3] M.T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, Adv. Mater. 12 (2000) 1737–1750.
[4] Z. Peng, Z. Bao, M.E. Galvin, Adv. Mater. 10 (1998) 680–684.
[5] J.H. Park, K.J. Lee, O.O. Park, J.W. Yu, Y.C. Kim, J.K. Kim, Chem. Phys. Lett. 386 (2004) 101–104.
[6] D. Sainova, D. Neher, E. Dobruchowska, B. Luszczynska, I. Glowacki, J. Ulanski, H.G. Nothofer, U. Scherf, Chem. Phys. Lett. 371 (2003) 15–22.
[7] X.G. Peng, M.C. Schlamp, A.V. Kadavanich, A.P. Alivisatos, J. Am. Chem. Soc. 119 (1997) 7019–7029.
[8] Y. Tian, T. Newton, N.A. Kotov, J. Phys. Chem. B 100 (1996) 8927–8939.
[9] V.L. Colvin, M.C. Schlamp, A.P. Alivisatos, Nature 370 (1994) 354–357.
[10] S. Coe, W.K. Woo, M. Bawendi, V. Bulovic, Nature 420 (2002) 800–803.
[11] B.O. Dabbousi, M.G. Bawendi, O. Onitsuka, M.F. Rubner, Appl. Phys. Lett. 66 (1995) 1316–1318.

Fig. 5. Luminance–voltage characteristic of ITO-PEDOT:PSS-co-polymer/QD-Ca/Al and ITO-PEDOT:PSS-co-polymer-Ca/Al devices at $T = 300$ K.

[12] A.D. Yoffe, Adv. Phys. 50 (2001) 1–208.

[13] M.A. Hines, P. Guyot-Sionnest, J. Phys. Chem. 100 (1996) 468–471.

[14] B.O. Dabbousi, J. Rodrigez-Viejo, F.V. Mikulec, J.R. Heine, H. Mattoussi, R. Ober, K.J. Jensen, M.G. Bawendi, J. Phys. Chem. B 101 (1997) 9463–9475.

[15] R.A.M. Hikmel, D.V. Talapin, H. Weller, J. Appl. Phys. 93 (2003) 3509–3514.

[16] S.H. Choi, H. Song, I.K. Park, J.H. Yum, S.S. Kim, S. Lee, Y.E. Sung, J. Photochem. Photobiol. A 179 (2006) 135–141.

[17] H. Sun, J. Zhang, H. Zhang, Y. Xuan, C. Wang, M. Li, Y. Ning, D. Ma, B. Yang, Z.Y. Wang, Chem. Phys. Chem. 7 (2006) 2492–2496.

[18] Y. Li, A. Rizzo, R. Cingolani, G. Gigli, Adv. Mater. 18 (2006) 2545–2548.

[19] S. Chaudhary, M. Ozkan, W.C.W. Chan, Appl. Phys. Lett. 84 (2004) 2925–2927.

[20] J.H. Park, S.I. Park, T.H. Kim, O.O. Park, Thin Solid Films 515 (2007) 3085–3089.

[21] J. Zhao, J. Zhang, C. Jiang, J. Bohnenberger, T. Basché, A. Mews, J. Appl. Phys. 96 (2004) 3206–3210.

[22] H.W. Liu, I.R. Laskar, C.P. Huang, J.A. Cheng, S.S. Cheng, L.Y. Luo, H.R. Wang, T.M. Chen, Thin Solid Films 489 (2005) 296–302.

[23] J.P. Neef, C.J. Ferraris, Macromolecules 33 (2000) 2311–2314.

[24] K.B. Chen, H.C. Li, C.K. Chen, S.H. Yang, B.R. Hsieh, C.S. Hsu, Macromolecules 38 (2005) 8617–8624.