Electroluminescence efficiency enhancement of OLEDs by doping with Co nanoparticles

R. Gómez-Aguilar [1], D. Ramirez-Rosales [2], J. Ortíz-López [2], J. Angeles-Islas [1]

[1]Depto. de Ciencias Básicas, UPIITA, Instituto Politécnico Nacional, Av. Acueducto s/n, Barrio la Laguna, Col. Ticomán, 07340, México, DF., México.

[2] Depto. de Física Avanzada, ESFM, Instituto Politécnico Nacional, Av. IPN s/n, Col. Lindavista, 07738, México, DF.,México.

Abstract

This work shows the results of doping single layer "organic light emitting diode" (OLED) synthesized by spin coating. The injector layers of holes and emissive are deposited over ITO substrates and are doped with Co magnetic nanoparticles (size ≈10 nm), the electroluminescence intensity enhances 21% in these devices. For OLED preparation, were mixed with poly-para-phenylenevinylene (PPV) and derivative poly-2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-henyle-nevinylene, (MDMO-PPV) dissolved in chloroform and tetrahidrofuran (5%wt). This technique allows obtaining uniform films on smaller areas than 1[inches^2] and uniform thickness between 80 and 200 nm. The terminated device emits light with wavelength around 590nm. The doped OLEDs was characterized by conventional optical techniques such as optical absorption, photo and electroluminescence determined with a spectrofluorimeter -Horiba JobinNanoLog and Keithley-2400-, additionally magnetic characterization by EPR and VSM is included.

1.-Introduction

Actively has been researched luminous efficiency in organic light emitting devices "OLED", according to roadmaps by Konica Minolta, is expected to reach 120lm/W by 2015, which is close to the efficiency LED lighting (around 140 lm/W) [1].The effort of improving efficiency has been seen in different parts of the world like the Europe or North America, in contrast to what is observed in other parts of the world, where the focus is on expanding capacity for existing OLED, without significant work on performance improvement.

The development of devices Organic Light-Emitting Diode (OLED´s), based on organic compounds such as polymers, have been developed successfully for some decades.

Conjugated polymers having a wealth of unpaired electrons, and thus, p_z-orbitals of successive carbon atoms form delocalized π and π^* orbitals along the structure. Then, conjugated polymers exhibit metallic properties [2,3] or semi-conducting. Differents PPV derivatives are widely used for photovoltaic and OLED applications because of their unique photophysical and electroluminescent features. Effective transport of excitons in conjugated polymers is very important for performances of OLED based on conjugated polymers and show relatively low power efficiencies since the injection of holes is much more favorable than injection of electrons [4]. In this way, to enhance the performances of these devices, the electron and hole injection into the emitting layer should be balanced [3]. In several researches, addition of conductor or semiconductor NPs into the organic layers has been explored as an alternative to the hole or electron transport/blocking layers [5,6].

Recently, the inclusions of new technologies based on nanotechnology have promoted recent studies that suggest the possibility of significant improvements in OLEDs devices when they are doped with metal nanoparticles (M-nPs). The main advantage over non-polymeric organic semiconductors is that form functional and adaptable structures to different applications and designs.

In previous studies Cheng-Jun Sun, et.al [7] demonstrated that it is possible to improve efficiency of OLED with CoFe nanoparticles with an average size of 10 nm approximately; Magnetic nanoparticles of CoFe are used as dopants to enhance the quantum efficiency

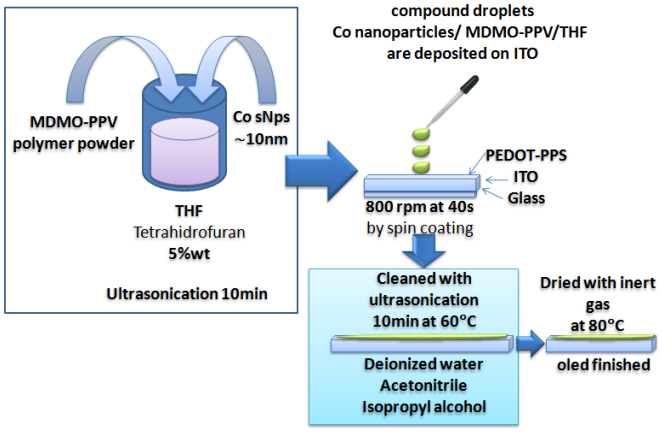
of electroluminance in a single layer organic light emitting device.
In this work, we concentrate particularly on the synthesis and characterization of OLED with Co nanoparticles below 10nm. We report the enhancement of electroluminescent efficiency (proportional to quantum efficiency) with Co nanoparticles and external magnetic field. The Co nPs are easier to develop with lower cost compared to FeCo nPs.
The significance from recent research in this direction is due to various reasons, among which stands out the clear improvement in these devices with greater electroluminescent efficiency and low cost, and also its involvement in developing new electroluminescent technology on 2D.

2.-Experimental

Co nanoparticles (Nps)~10nm, were prepared by mechano-chemical reaction

$$CoCl_2+2Na \Rightarrow (Co)_{Nps}+2NaCl$$

following the method of J. Ding [8,9] with mechanical alloying Co Nps, are cleaned in anhydrous methanol to dissolve the excess NaCl and are recovered directly from the powder precipitates at the bottom. Then Co nPs are deposited in tetrahidrofuran+ MDMO-PPV solution, to obtain composite MDMO-PPV/THF/Co sNps-0.05Co%wt, and then drops of resultant suspension are deposited in substrate of ITO.
The 120nm thick light emitting films were prepared by spin coating from the composite solutions on ITO substrates (2.5cmx2.5cm), with 800 rpm for 40s. Obtained a single layer OLED composed of Co nanoparticles/ MDMO-PPV/THF-0.5%Wt.
Device is build with architecture ITO/PEDOT:PSS/composite/Ga-In by use of contacts made with an Ga-In alloy (Figure 1). The electroluminescence (EL) has been measured with a Horiba JobinNanoLog-spectrofluorimeter at room temperature. More details [10].
The studied sample was prepared from luminescent polymer powders MDMO-PPV (made by Sigma Adrich™ , Num. Cat. 536512).
Deposited compounds of MDMO-PPV+Co sNps in ITO are cleaned under ultrasonication in deionized water, acetonitrile and isopropyl alcohol in periods of 10 min at 60°C and dried with inert gas.
See manufacturing diagram.



Manufacturing diagram

The characteristic line: current density *I* vs voltage *V* (i.e.*I* vs *V*), has been measured with a Keithley-2400(-100V:100V-500mA), digital oscilloscope-Rigol DS 1102E with two channels (100 MHz) and voltmeter - Fluke 8846A (6 ½), in 0-20 V and 0-40 mA
The design outline is shown in Figure 1

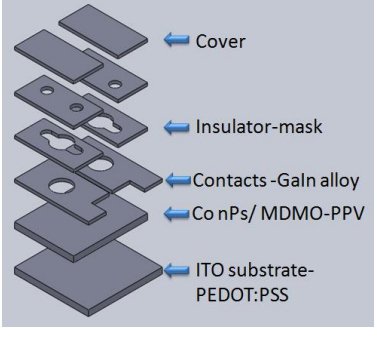


Figure 1.- Design outline of OLED

3.-Results and discussion

Figure 2 shows comparatively electroluminescence (left vertical scale) and current (right vertical scale) versus operating voltage in the doped and undoped system. There substantial increase in the electroluminescence and current in the doped system. Additionally registers a small increase in both parameters by applying an external magnetic field H of 0.7 Tesla in the doped systems.

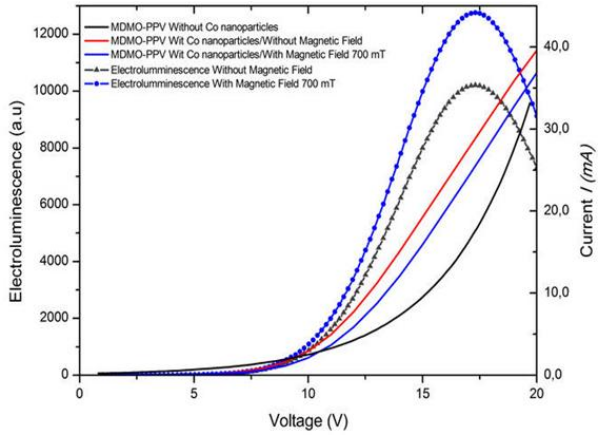


Figure 2.-EL vs V, and I vs V properties of devices doped and undoped with Co nPs, and with/without magnetic field.

Figure 3 shows three-dimensional representation between wavelength, voltage and luminescent intensity. Maximum luminescent intensity is observed at V = 17V with wavelength 570nm (blue line).
Figure 4 shows the EL emission spectrum obtained by photo-excitation, red represents the critical voltage in which achieves the maximum photo-excitation, corresponds to V=17V consistent with results obtained in Figure 3. That spectrum shows excitation wavelength value around 540nm, and emission wavelength between 570 and 590nm.
Studies with high concentrations of Co nPs are currently studied by the authors of this work.

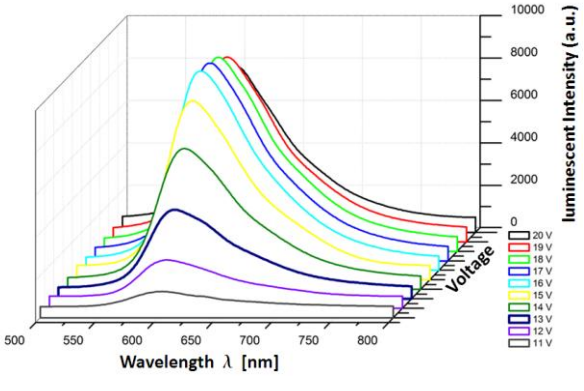


Figure 3.- Three-dimensional Excitation vs Emission spectrum in MDMO-PPV.

We observed a significant enhancement of the electroluminescent efficiency attributable to the increment in the quantum efficiency upon including nPs Co dopant. For case Co dopant, the luminescent efficiency can be further enhanced by applying an external magnetic field of 0.7T.

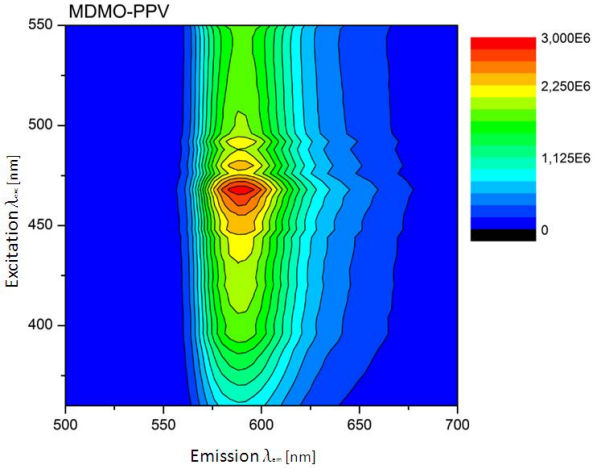


Figure 4.-Three-dimensional Excitation vs Emission spectrum in MDMO-PPV.

An interpretation of this fact is given through on measurements of carrier transport and electroluminance. A simple model is proposed by Cheng [7], suggesting that the density of electron traps increases with the Co NPs dopants. The electron traps balance the currents of holes and electrons in the hole dominant device, resulting in an increase of the critical voltage VC and a significant enhancement of emission intensity. For the device created in this work is 20%.
The authors [7] demonstrated that the nanoparticles can increase EL value via balancing the currents of electrons and holes that have been injected into the MEHPPV, optimizing the combination process.
We believe that such an explanation from the authors about their results, applies equally to the results observed in the present work.
The application of an external magnetic field produces the effect to align the spins of Co nanoparticles, generating the increase in fraction of singlets and therefore the emission EL via a spin-polarized charge transfer process [11].
The explanation for the increased electroluminescence in doped OLED by presence of magnetic field is provided by Toshihiro Shimada[12], suggests that the reactions proceed via intermediate state whose energy could be modified by the magnetic field. As is known, the energy difference is explained by the Zeeman effect on spin triplet state, which does not is valid on the spin singlet state.
In the words of author "the reaction path between the singlet to or from the triplet can modify the reaction rate. For other hand, the Zeeman energy is too small to alter the reaction path in a single molecule.

This is because the energy difference between spin singlet and spin triplet it is very big (0.1~1eV) compared to the Zeeman energy (< 10 meV) under easily attainable magnetic field".
Continues the explanation by Toshihiro Shimada: " therefore it is considered that the intermediate state to which magnetic field can affect is a "radical pair" in which an anion radical and a cation radical are placed closely and about to transfer charges.
Those radicals have unpaired spins and thus spin triplet and spin singlet states exist. The energy difference between the singlet and the triplet is very small because the spin-spin interaction is small due to the large distance belonging to different (but adjacent) atoms (or molecules or ions) and can be comparable with the Zeeman energy. Magnetic field effects on chemical reaction rate come from the radical pairs".
We believe that this explanation is consistent and complements the theory of charge injection. The effect on electroluminescence increasing is explained with both effects simultaneously.
Explanation is equally favourable for the system based on Co nPs/MDMO-PPV presented in this work.
Figure 5 show the hysteresis loops of the Co nPs measured at 300 K indicating the ferromagnetic behaviour of the Co nPs.

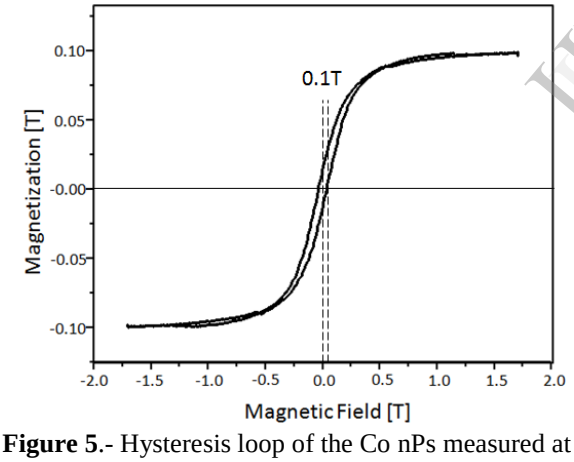


Figure 5.- Hysteresis loop of the Co nPs measured at room temperature (by VSM).

Furthermore, figure 6 shows the microwave absorption dP/dH (where P = absorption-potency and H=Magnetic external field) obtained by conventional EPR characterization in LFA mode (Low Field Absorption [13]). EPR measurements have been carried out at an X-band frequency of 9.4 GHz with a JEOL JES RES 3X spectrometer operating at a 100 kHz field modulation.

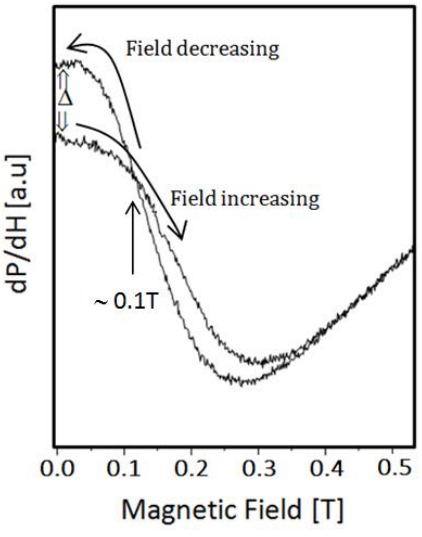


Figure 6.- X-band (9.4 GHz) derivative microwave power absorption (dP/dH) measurements in the Co nPs (by EPR-LFA).

Hysteresis is observed in the microwave absorption cycle, reinforcing the evidence on the magnetic properties in the Co sNp. A notable difference Δ occurs in H=0T, is usually attributed to the high remnant magnetization in Co nPs.
Power line-absorption associated with the magnetization dynamic process is similar to used energy in the magnetization process observed in VSM.
The correlation between the results observed in figures 5 y 6 shows that the particles possess a coercive field around 0.1T, which implies the presence of permanent intrinsic magnetic properties in the Co nPs.

4.- Concluding Remarks

In summary, we show the increase in the efficiency that involves doping with Co nanoparticles in low concentration, in a single layer OLED (MDMO), we found that voltage-saturation MDMO + Co NPS is accomplished in (10v), this result corresponds well with the voltage in which is reached ohmic linearity. Significant differences occur between the values of the threshold voltage in undoped OLED (17v) (i.e. MDMO-ITO), in contrast, for doped OLED (i.e. MDMO+ConPs-ITO) is obtained 10v. Additionally, the magnetic field reduces the ohmic-voltage. Increasing excitons density in the film (MDMO + Co NPS) is displayed. Finally, the impedance does not show significant dependence with the magnetic field extern H, the effect is significant only with the addition of nanoparticles. However, the EL efficiencies can be further improved by applying an external magnetic

field H of 0.7T in 5% –7%, in this way is obtained a final efficiency of 17%. The enhancement in EL efficiency is attributable to combining the both effects mentioned in the text.

References

[1] Cara Harrington, IDTechEx Printed Electronics Asia (2013) conference Tokyo- Japan. published online Nanotecnology Now. www.PrintedElectronicsAsia.com.
[2] Selin Piravadih Mucur, T. Ash Tumay, Sait Eren San, E. Tekin "Enhancing effects of nanoparticles on polymer-oled performances". J. Nanopart. Res. 14:1214 (2012) Doi 10.1007/s1051-012-1214-9
[3] Zhigang Li, Zhingang Rick Li, Hong Meng, Organic "Light-Emitting Materials and Devices", CRC Press, Taylor and francis group USA -(2010), pp 673
[4] Chung-Chia Chen, Bo-Chao Huang, Ming-Shiang Lin, Yin-Jui Lu, Ting-Yi Cho, Chih-Hao Chang, Kun-Cheng Tien, Su-Hao Liu, Tung-Hui Ke, Chung-Chih Wu, "Impedance spectroscopy and equivalent circuits of conductively doped organic hole-transport materials", Organics Electronics vol.11, issue 12 (2010) pp 1901-1908.
[5] Abhishek P. Kulkarni, Christopher J. Tonzola, Amit Babel, and Samson A. Jenekhe, "Electron Transport Materials for Organic Light-EmittingDiodes", Chem. Mater. (2004), 16, pp 4556-4573
[6] Hu, X.-D.; Jenkins, S. E.; Min, B. G.; Polk, M. B.; Kumar, S. Macromol. Mater. Eng. (2003), pp.288, 823
[7] Cheng-Jun Sun, Yue Wu, Zhihua Xu, Bin Hu, Jianmin Bai, Jian-Ping Wang, Jian Shen, "Enhancement of quantum efficiency of organic light emitting devices by doping magnetic nanoparticles", (2007), Applied Physics Letters 90, 232110.
[8] J. Ding, W. F. Miao, P. G. McCormick and R. Street,"Mechanochemical Synthesis Of Ultrafine Fe Powder". Applied Physics Letters, Volume:67 Issue:25, (1995) pp. 3804 – 3806 doi: 10.1063/1.115389
[9] Angeles Islas J; C. Velazquez; H.A. Calderon "Synthesis and characterization of metallic nanoparticles of Cu, Co and Cu-Co by reactive milling", NSTI Nanotechnology Conference and Trade Show - NSTI Nanotech 2007, Technical Proceedings, 4:273-276. (2007) ISBN 1-4200-6376-6
[10] R. Gómez-Aguilar "Estudio de materiales organicossemiconductors para aplicaciones en optoelectrónica" (2013) PhD thesis (to be published) Instituto Politécnico Nacional - México.
[11] B. Hu, Y. Wu, Z. T. Zhang, S. Dai, and J. Shen, "Effects of Ferromagnetic nanowires on singlet and triplet exciton fractions in fluorescent and phosphorescent organic semiconductors", Appl. Phys. Lett. 88, 022114 (2006) Doi:10.1063/1.2162801
[12] Toshihiro Shimada "Organic Light Emitting Diode - Material, Process and Devices", book edited by Seung Hwan Ko, Chapter 12ISBN 978-953-307-273-9, under CC BY-NC-SA 3.0 license.(2011), pp. 311-322 DOI: 10.5772/2
[13] M.E. Mata-Zamora, H. Montiel, G. Alvarez, J.M. Saniger, R. Zamorano, R. Valenzuela "Microwave non-resonant absorption in fine Cobalt ferrite particles" Journal of Magnetism and Magnetic Materials 316 (2007), e532–e53