

OLED Device Review and A Summary of the Plasmonic Enhancement thereof

Guy Francis Mongelli

Department of Chemical Engineering, Case Western Reserve University, 10900 Euclid Ave. A.W. Smith 116, Cleveland, Ohio
Email: gfm12@case.edu

Abstract— Within this work the major breakthroughs in the development of OLED technologies are described. There is a strong emphasis placed upon materials discovery. The basic OLED structure is shown and the plasmonic effect is detailed in the context of OLED technologies.

Keywords— organic light emitting diode (OLED), outcoupling efficiency, plasmonic materials, singlet/triplet emissions.

Air	n=1.0
ITO	n=2.0
Organics	n≈1.7-1.9

Cathode Ideal reflector

Figure 1: The above figure depicts a simplified, planar OLED structure. The cathode is assumed to be an ideal reflector, which the organic layers are directly adjacent to. The ITO hole-injecting contact and air are also shown. Each of these layers corresponds to a significant change of refractive index within the OLED. Furthermore, this is an example of a top-emitting structure.

I. INTRODUCTION

Organic light emitting diodes (OLEDs) are quickly emerging as the next-generation of ambient lighting and information display technology due to their high brightness, high contrast ratios, wide viewing angles, fast switching times, low power consumption, lack of hazardous metals and large color gamut¹. Since their discovery in 1987, scientists and researchers have increased their internal quantum efficiencies to nearly unity^{3,4}. The study of structural, thermal and spectral properties of OLED materials has greatly contributed to our understanding of the device limitations⁵. The emergent and widespread use of OLED-related technologies has led to several books on the subject⁶⁻⁹.

II. DISCUSSION

A simplified OLED structure (Figure 1) is composed of an electron injecting cathode, organic transport and emitting layers, and a hole injecting contact. The ITO typically is in direct contact with air. The organic layers include a doped emissive layer but may also incorporate a hole transport layer and an electron transport layer. These devices have adapted from a single heterostructure to a double heterostructure which increased the theoretical IQE and EQE of 25% and 5%, respectively¹⁰. This relatively low limit is because the dopants utilized were fluorescent/singlet-type; meaning only singlet excitons resulted in radiative recombination. Since singlet-type excitons account for only a quarter of all excitons, only 25% of the total exciton recombinations within these materials resulted in optical emission. To overcome this limitation, triplet/phosphorescent-type materials were newly synthesized and added to OLEDs¹¹.



Fig.2: White OLED device for lighting applications.
Courtesy of OLED Works.

Since the excitons associated with triplets have longer lifetimes and diffusion lengths, more complex OLED structures were required to prevent the excitons from drifting into materials which would result in non-

radiative recombinations. These complex structures possess additional layers for electron¹², hole¹³ and exciton¹⁴ diffusion blocking as well as charge generating¹⁵ layers. Other structures include multiple emitting layers and are termed stacked/tandem OLED devices. ITO is typically chosen as the hole injecting contact because of its transparency in the visible and high conductivity.

One issue common to electronic device manufacturing is functional yield due to structural defects. Typical abnormal device behaviors include unstable I-V characteristics and shorting. Another typical defect is physical damage on the surface of the cathode contact which typically leads to shortened lifetimes. Additionally ITO contacts have been known to be less efficient for hole-injection than the low work-function metal cathodes for electron injection. This results in hole-limited devices and is confirmed in an experiment by Klubek et al¹⁶.

Device lifetimes are limited through degradation mechanisms; most significantly the aggregation of mobile ions, which increase driving voltages and decrease brightness of devices over time¹⁷. Water and air entering the device lead to 'shorting' and the decomposition of organic molecules shorten lifetimes, respectively. Both of these hinder device performance. These can be prevented through the incorporation of an encapsulation layer into the device structure¹⁸.

Several key metrics in evaluating an OLED or other light emitting device are the internal quantum efficiency [$\eta_{IQE}(\lambda)$] (IQE), the external quantum efficiency [$\eta_{EQE}(\lambda)$] (EQE), and the out-coupling factor [$\eta_c(\lambda)$]. Other measures that quantify and characterize involved in the characterization and analysis of the OLED are the wall plug efficiency, the luminous power emitted (lm/W), luminance (cd/Am²), and current efficiency (cd/A). The IQE is defined as the ratio of the total number of photons generated within the device structure to the number of electrons entering the device. In many instances, the IQE is not unity due to absorptions within the device, non-radiative recombination processes and ohmic losses. The EQE is defined as the number of photons that are perceived by the viewer per charge entering the device. Both of these quantities are typically considered on a wavelength-dependent basis because there are many wavelength-dependent optical phenomena at play in the OLED. The relationship between these quantities is the wavelength-dependent out-coupling efficiency, denoted: η_c :

$$\eta_{ext}(\lambda) = \eta_{int}(\lambda) \cdot \eta_c(\lambda) \quad (1)$$

Presently, the out-coupling efficiency and, therefore, external quantum efficiency, of OLEDs (see Figure 2) is limited due to the optical phenomena of total internal

reflection (TIR) at the organic/glass and organic/air interfaces, surface plasmon effects at the metal cathode interface, and micro-cavity effects. Each of these effects reduce the out-coupling factor to some extent. It is the focus of this work to look at one particular method- the incorporation of isotropic scattering media- to increase the out-coupling efficiency of the OLED.

The light trapped in the glass due to the glass-air and organic-glass interfaces are referred to as the glass-air modes. Similarly, the light trapped in the organic layers due to the organic/ITO interface are referred to as the organic-glass modes. The modes associated with the absorption losses at the cathode are referred to as the surface plasmon polariton (SPP) modes. Our work in the near future will assume an ideal back contact and derive an expression for the out-coupling efficiency for scattering enhanced OLEDs. Since the SPP mode losses are much smaller in comparison to the TIR losses, this is acceptable.

The total internal reflection and SPP phenomena prevent approximately 80% of the light emitted from reaching the observer. Methods for addressing these limitations include scattering media, micro-lenses, micro-pyramids, photonic crystals, sandblasting and other surface modifications, and surface plasmon-enhanced effects¹⁹. It is not yet clear which of these will be the best from an engineering and economics standpoints. Recent studies have begun to explore the role of surface plasmonic effects in enhancing the light out-coupling of OLEDs.

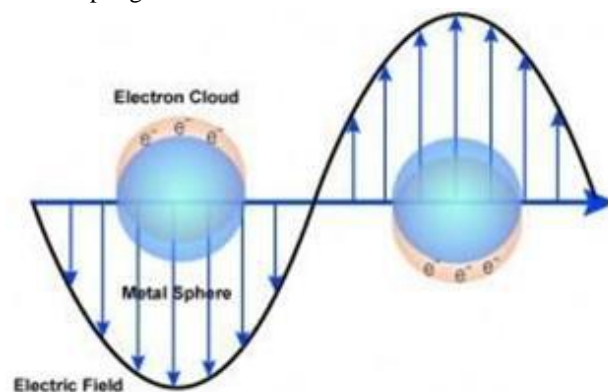


Fig.3: The above image depicts a metallic nanoparticle with an incident linearly polarized light beam

Due to the development of narrow size distribution plasmonic materials, studies of their properties have drawn much attention. Silver is commonly known to be a material with one of the highest scattering capabilities per unit volume. The ability of silver nanoparticles to scatter light is of keen interest as a method to break or suppress total internal reflection. Unfortunately, there is little data that estimates how effective silver is at reorienting and/or

absorbing the light approaching interfaces in materials like those present within OLEDs. This work will address these considerations. Furthermore, since computational simulations have become more prevalent as a method to optimize device fabrication and, specifically, in OLEDs and nanoparticle scattering²⁰, computational electrodynamics seems particularly appropriate as a novel method to evaluate these particles. Additionally, it will be important to benchmark these results with other work OLEDs that incorporate layers with glass scattering media have been shown to increase out-coupling efficiency²¹.

III. SURFACE PLASMON RESONANCE

Metallic nanoparticles are suggested as a prime candidate for incorporation into OLED devices because such particles exhibit the localized surface plasmon resonance (LSPR) effect²² and have been synthesized in readily controllable sizes not previously available.

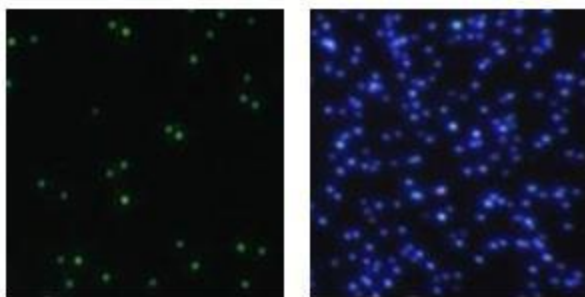


Fig.4: Dark field microscopy of 50 nm Au (left) and 60 nm Ag (right). Image courtesy of Nanocomposix. From these images, it is clear that scattering green and blue light is possible. Dark field microscopy does not offer a method to describe how much light is scattered relative to the intensity of the incident field.

One understanding of the surface plasmon effect is presented here. When a light ray interacts with the metallic nanoparticle and excites the electrons on the surface of the metal. The electric fields of the light are intense enough to induce charge separation along the surface of the sphere (Figure 3). These incident fields shift the electron cloud in the entire particle surface to be outside of the particle when particle size is small compared to the wavelength of light. This collective excitation of the electrons in a metal lattice to similar wave-function states is referred to as a polariton. Therefore, for small particles this is known as the localized surface plasmon resonance effect. Metallic nanoparticles that exhibit this effect are also known as nano-antennas, since the distribution of EM radiation in the near field is similar to that of a dipole Hertz antenna that are used in radios. One key difference is that a complete understanding of LSPR relaxation emissions requires consideration of multi-pole contributions to the

scattered field. Particles that exhibit LSPR effects have also found niches within solar cell technologies and have been shown to enhance their efficiencies²³. Future studies will detail an alternative understanding of the scattering properties of metallic nanoparticles.

Furthermore, it is widely known that metals are subject to non-linear optical effects wherein the polarized state of the nanoparticle is not proportional to the electric field strength. This effect is vastly different from transparent, non-metallic nanoparticle scattering that takes place in glassy compounds such as TiO₂ and fused silica glasses. These non-linear optical effects are ignored in this work and assumed insignificant in comparison to the magnitude of the scattered field caused by the SPR effect. Experimental studies can verify that this effect does not predominate.

IV. CONCLUSIONS

This manuscript details several key milestones in the development of OLED devices and materials. It includes a description of advances in material properties, device structure, and goes on to discuss a new approach to the current limitation of device performance: the incorporation of metallic nanoparticles as scattering media.

ACKNOWLEDGEMENTS

This work was supported by the *Department of Energy* under the National Energy Technology Laboratory Grant # DE-EE0005274.

REFERENCES

- [1] S.R. Forrest, "The road to high efficiency organic light emitting devices", *Organic Electronics* 4 (2003) 45-48.
- [2] Tang, C. W., VanSlyke, S. A.; "Organic electroluminescent diodes", *App. Phys. Lett.* (1987), 51(12), 913-15. DOI: 10.1063/1.98799
- [3] Ji Hoon Seo et al.; "White Organic light-emitting diodes showing nearly 100% internal quantum efficiency", *Organic Electronics* 11 (2010) 1759-176.
- [4] L.S. Liao, K. P. Klubek, C. W. Tang; "High-efficiency tandem organic light-emitting diodes", *Appl. Phys. Lett.* Vol 84, No. 2 (Jan. 2004).
- [5] M. Rajeswaran, T.N. Blanton, C.W. Tanget al.; "Structural, thermal and spectral characterization of the different crystalline forms of Alq₃, tris(quinolin-8-olato)aluminium(III), an electroluminescent material in OLED technology"; *Polyhedron* 28 (2009).
- [6] Z. Li, H. Meng; "Organic Light Emitting Materials and Devices" Taylor & Francis, Boca Raton (2006).

- [7] T. Tsujimura, "OLED Display Fundamentals with applications" John Wiley & Sons, New York (2012).
- [8] H. Yersin, "Highly Efficient OLEDs with Phosphorescent Materials", John Wiley & Sons (2007).
- [9] G.E. Jabbour, "The Fundamentals of OLED Fabrication" Intertech, San Francisco (2004). S. Reineke, F. Lindner, G. Schwartz et al.; "White organic light-emitting diodes with fluorescent tube efficiency" Nature (London) 459 (2009).
- [10] M.A. Baldo, M.E. Thompson, S.R. Forrest et al.; "Highly efficient phosphorescent emission from organic electroluminescent devices" Nature 395 (1998) 151.
- [11] J.A. Hagen, W. Li, J. Steckl, J.G. Grote; "Enhanced emission efficiency in organic light-emitting diodes using deoxyribonucleic acid complex as an electron blocking layer" Appl. Phys. Lett. 88, Is. 17 (2006).
- [12] V.I. Admovick et al.; "New charge-carrier blocking materials for high efficiency OLEDs" Organic electronics, Vol. 4, Iss. 2-3, (2003).
- [13] M. Ikai, S. Tokito, T. Taga; "Highly Efficient phosphorescence from organic light-emitting devices with an exciton-block layer" Appl. Phys. Lett. Vol. 79, No. 2 (2001).
- [14] S. Hamwi et al., "The Role of Transition Metal Oxides in Charge-Generation Layers for Stacked Organic Light-Emitting Diodes" Adv. Func. Mat. 20, Is. 11 (2010).
- [15] H. Wang, K. P. Klubek, C.W. Tang; "Current efficiency in organic light-emitting diodes with a hole-injection layer"; Appl. Phys. Lett. 93 (2008).
- [16] W.A. Burrow, P.J. Green, C.W. Tang, et al.; "Degradation mechanisms in organic light emitting diodes"; Synthetic metals 111-112 (2000).
- [17] K.H. Jung, J.Y. Bae, S.J. Park, S. Yoo, B.S. Bae; "High performance organic-inorganic hybrid barrier coating for encapsulation of OLEDs"; J. Mater. Chem. Vol. 21 (2011).
- [18] K. Saxena, V.K. Jain, D.S. Mehta; "A review on the light extraction techniques in organic electroluminescent devices", Optical Materials 32 (2009).
- [19] S.W. Cheong, K.L. Woon; "Modeling of light extraction efficiency of scattering thin film using Mie scattering"; Optica Applicata, Vol. XLI, No. 1 (2011).
- [20] B.Y. Jung et al., "Spectra characteristics of organic light-emitting diodes with (SiO₂/TiO₂) dielectric layers" Journ. Of the Korean Physical Soc. 49, Is. 5 (2006).
- [21] E. Hutten, J.H. Fendler; "Exploitation of Localized Surface Plasmon Resonance" Adv. Mater. 16, Is. 19 (2004).
- [22] S. Pallai et al., "Surface Plasmon Enhanced Solar Cells" J. Appl. Phys. 101, Is. 9 (2007).