Synthetic Metals 211 (2016) 155–160

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Far-field and hole injection enhancement by noble metal nanoparticles in organic light emitting devices

P. Justin Jesuraj[a], K. Jeganathan[a,*], M. Navaneethan[b], Y. Hayakawa[b]

[a] Centre for Nanoscience and Nanotechnology, School of Physics, Bharathidasan University, Tiruchirappalli, Tamil Nadu 620 024, India
[b] Research Institute of Electronics, Shizuoka University, 3-5-1 Johoku, Naka-Ku, Hamamatsu, Shizuoka 432-8011, Japan

ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form 16 November 2015
Accepted 21 November 2015
Available online 7 December 2015

Keywords:
Gold nanoparticles
Silver nanoparticles
Hole injection
Far-field plasmons
OLEDs
Enhanced brightness

ABSTRACT

We report the combined effect of plasmonic far-field and improved hole injection towards enhancing the performance of OLEDs by the incorporation of gold and silver (Au and Ag) nanoparticles at the interface of anode/hole transport layer (HTL). The metal nanoparticles incorporated devices facilitate improved hole injection into HTL owing to the shift in vacuum level of anode resulting in three fold enhancement of current density in OLEDs. Hole only devices made with Au and Ag nanoparticles at anodes offer meliorated hole injection than the reference anode due to the reduced injection barrier. X-ray photoelectron spectroscopy analysis further corroborates the alteration of work function of metal nanoparticles infused ITO by exhibiting an abrupt shift in In 3d and Sn 3d photoelectron energy levels. In addition, time resolved photoluminescence spectra reveal that the interaction of far-field plasmons with the device emission accelerates the luminescence of OLEDs further.

1. Introduction

Surface plasmons (SPs) of metal nanostructures have received a great attention in the past decade due to its proficiency in enhancing the performance of optoelectronic devices [1–5]. Surface plasmon modes exhibit higher momentum ($\hbar k_{SP}$) compared to free space photon ($\hbar k_0$) which provides a way to achieve superior performance in photovoltaic [6,7] and light emitting devices [8]. Organic light emitting devices (OLEDs) have earned great interest in the commercial applications owing to their high brightness, large fields of view and more flexibility [9,10]. Nevertheless, improving the OLED efficiency still needs to be realized for expanding the applications. Among the factors affecting the efficiency, the hole injection barrier at the anode/hole transport layer (HTL) interface is one of the primary hitch that must be reduced. The interface modification with the suitable hole injection layers such as graphene oxide [11], molybdenum trioxide [12,13], PEDOT: PSS [poly (3,4-ethylene dioxythiophene): poly (styrenesulphonate)] [14] and tungsten trioxide [15] are found to improve the device efficiency by reducing the injection barrier.

Metal nanoparticles incorporated in OLEDs found to increase the efficiency via plasmonic [16–20] and hole injection enhancement [21–24]. The metal nanoparticles forms a dipole like electric double layer on anode which indeed alter the vacuum level [21] to ameliorate the hole injection. Further, localized surface plasmons associated with metal nanoparticles offer an effective channel to induce enhanced decay of molecular excited state to cultivate more photons from the device. The localized surface plasmon resonance (LSPR) enhancement could be effective if the distance (spacer thickness) between nanoparticles to emissive layer is limited to 5–15 nm. However, Kümmerlen et al. [25] have reported another kind of intensity enhancement is also possible at higher spacer thickness of around 60 nm. This enhancement is typically termed as far-field enhancement in which radiative rate of photons increased by the mirror type substrate constructed through group of metal nanoparticles [26]. It is effective when the metal to fluorophores distance is equal or greater than $\lambda/10$. Hence, the application of metal nanoparticles in OLED is capable of cultivating the impact of both improved hole injection and plasmonic enhancement strategies.

In the present study, we employed gold and silver nanoparticles embedded anode (ITO/AgNPs and ITO/AuNPs) to investigate charge transport and luminescence enhancement in OLEDs. The incorporation of metal nanoparticles at anode/HTL interface with sufficient coverage enhances the current density more than two times with significant improvement in brightness. The hole injection capabilities of metal nanoparticles and the plasmonic interaction between fluorophores to metal have been discussed in detail towards achieving better device performance.

* Corresponding author. Fax: +91 431 2497 045/2407 020.
E-mail addresses: jagan@physics.bdu.ac.in, kjeganathan@yahoo.com (K. Jeganathan).

http://dx.doi.org/10.1016/j.synthmet.2015.11.024
0379-6779/

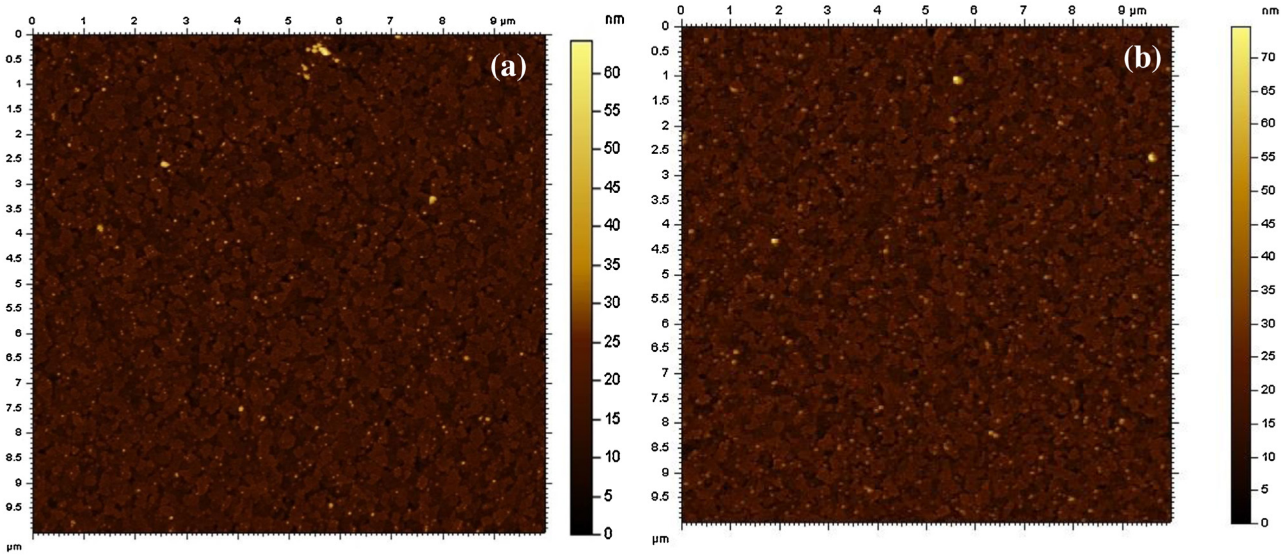

Fig.1. AFM micrograph ($10 \times 10\ \mu m^2$) of (a) Au and (b) Ag nanoparticles dispersed ITO anodes.

2. Experimental methods

Gold and silver nanoparticles have been prepared by standard chemical routes for the application in OLEDs. AuNPs having size around 20 nm have been prepared through Fren's method [27] by reducing the gold (III) chloride. trihydrate [$HAuCl_4 \cdot 3H_2O$] with 1 wt.% trisodium citrate. Whereas, AgNP solution is prepared by reducing the 10 ml of 1.0 mM of silver nitrate with 30 ml of 2.0 mM of sodium borohydride ($NaBH_4$) solution [28]. The resultant clear yellow solution consists of AgNPs with sizes between 30 and 40 nm. The Ultraviolet-visible absorption spectra were recorded to confirm the formation of nanoparticles. Indium tin oxide (ITO) coated corning glass substrate with sheet resistance ~20 Ω/Sq. (Vinkarola Pvt. Ltd, USA) has been used as anode for OLEDs and it is cleansed by ultrasonication with acetone and 2-propanol followed by oxygen plasma treatment. Chemically synthesized Au and Ag nanoparticles with absorption maximum at 530 and 400 nm respectively (Fig. S1, Supplementary data) have been spin coated on to ITO with 3000 RPM for 30 s. To optimize the surface coverage of metal nanoparticles on ITO, concentration of nanoparticles in solution have been adjusted.

A standard OLED structure (Fig. S2, Supplementary data) consists of ITO/N,N′-Di-(1-naphthyl)-N,N′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (α-NPD)/Tris-(8-hydroxyquinoline) aluminum (Alq_3)/Lithium fluoride (LiF)/Aluminum (Al) have been fabricated to understand the effect of metal nanoparticles. Initially, hole injection properties of gold and silver nanoparticles have been extensively investigated with the help of hole only devices (HODs) comprised (Fig. S3, Supplementary data) of ITO (with and without nanoparticles)/α-NPD/Al. The thickness of organic layers, α-NPD and Alq_3 was kept constant at 30 and 60 nm respectively for entire investigations. Thermal evaporation unit with glove box was equipped with digital quartz crystal thickness monitor (STM-100/MF, sycon instruments) to deposit organic and inorganic thin films. Atomic force microscopy (Agilent AFM non contact mode—5500 model) was used to analyze the coverage and morphological features of nanoparticles embedded anode. X-ray photoelectron spectroscopy (XPS) has been subjected to reveal the interface electronic properties of ITO. To unveil the plasmonic enhancement in OLED structure, time resolved photoluminescence (TRPL) measurement have been carried for hetero junction (α-NPD/Alq_3) deposited on ITO with and without metal nanoparticles by time correlated single photon counting technique. The electroluminescence setup equipped with Keithley 2400 SMU, ocean optics USB 2000 + RAD spectroradiometer with electrical probe station have been employed to explore the I–V–L characteristics of OLEDs.

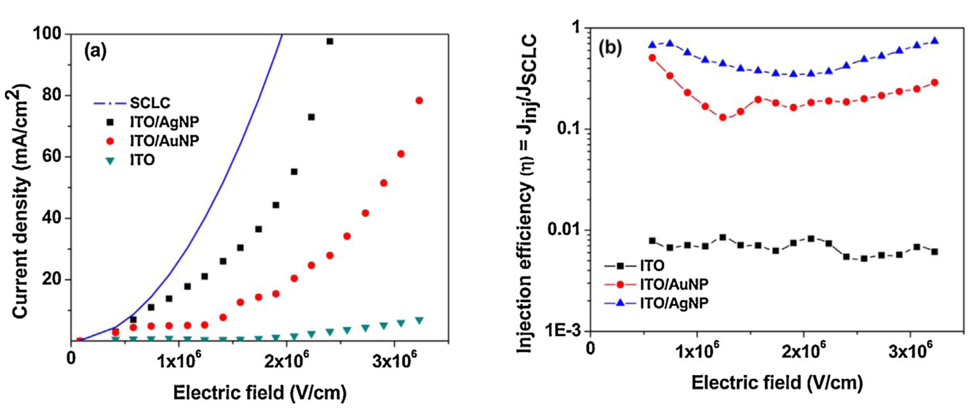

Fig.2. (a) Simulated SCLC plot with the measured electric filed–current density (*E–J*) plot of hole only devices with and without metal nanoparticles. (b) Comparison of injection efficiencies in HODs with and without metal nanoparticles.