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Work function tunable metal-mesh based transparent electrodes for fabricating indium-free organic light-emitting diodes

Murali Gedda 1, Dipjoyti Das 2, Parameswar Krishnan Iyer 2,3 and Giridhar U Kulkarni 1,4,5

1 Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bengaluru-560064, India
2 Center for Nanotechnology, Indian Institute of Technology Guwahati, Guwahati-781039, India
3 Department of Chemistry, Indian Institute of Technology Guwahati, Guwahati-781039, India
4 Centre for Nano and Soft Matter Sciences, Bengaluru-560013, India
5 Author to whom any correspondence should be addressed.
E-mail: guk@cens.res.in

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Abstract
In order to realize low-cost and efficient organic light-emitting diodes (OLEDs), the transparent anode should have excellent optical and electrical properties, among other factors. Typically, transparent conductive oxides have been widely used for transparent top electrodes, but they suffer from several drawbacks. We herein report the fabrication of efficient indium-free transparent OLEDs using metal-mesh based top electrodes, made of any metal of choice, Au, Ag or Cu. The fabricated devices on inch square substrates exhibited superior emission characteristics without any color shift. In terms of workfunction matching, Cu did the best. With a Cu-TCE of low sheet resistance ($\sim 7 \, \Omega \, \text{sq}^{-1}$), uniform emission characteristics were achieved with relatively high current efficiency and luminance, comparable to those from the ITO based devices.

1. Introduction

There is a massive demand for organic optoelectronic devices to deliver low-cost and high-efficiency solutions for applications such as large-area displays and solid-state lighting [1, 2]. The significant advantages of OLEDs, in comparison to their inorganic equivalents, are their full-color capability, potentially low manufacturing costs, lightweight and wide viewing angle, making them quite attractive [3, 4]. However, there are pertinent issues that need to be addressed before the OLED technology more viable and many of the issues relate to the components. A typical OLED device consists of two electrodes, hole and electron transport layers and an emissive layer often based on small molecules or polymers. The backbone of both transport layers is the transparent conductive electrode (TCE), which permits visible light transmission and enables electrical biasing and current collection. Tin-doped indium oxide (ITO) coating on glass is commonly used for this purpose. However, the relatively high cost of sputtered ITO prohibits its use in large-area OLED applications. Degradation of the device induced by the migration of In atoms into the organic active layer further limits its usage [5, 6].

During the last decade, new nanomaterial-based transparent electrodes have been developed as alternatives to ITO. These include other metal oxides, graphene, ultrathin metal films, conducting polymers, patterned metal grids as well as conducting networks of carbon nanotubes and metal wires [7]. While each alternate offers certain advantages, it is not without shortcomings. For instance, graphene is highly transparent and moderately conducting, but its usage for large-area applications is not cost-effective. TCEs based on networks of Ag nanowires are already a commercial reality, although their application in OLED is still awaited for want of smoother electrodes [8–10].

Recently, a new recipe for TCE has been developed, in which a crack template is used for the deposition of the desired metal wire network to form a metal mesh-TCE (m-TCE) [11–14]. The method has many unique advantages. The wire width and thickness are tunable while ensuring a low network footprint (2D fill factor...
~10%) and a high degree of wire connectivity. Besides, the formation of overlapping wires at the junctions, which is a major drawback of the nanowire dispersion methods, is avoided as the junctions are seamless with the entire network lying in a plane. Moreover, with the right choice of the metal, the workfunction of the m-TCE can be tuned to suit the application. Thus, m-TCEs with different workfunctions have been successfully employed as transparent electrodes of organic solar cells and touchscreens \[12, 15–17\].

Herein, we report the fabrication of ITO free OLEDs using Au, Ag and Cu-TCEs prepared by the crack templating method. Synergistic effects of the workfunction on the performance of OLEDs have been explored. Cu-TCE based OLEDs exhibited a performance comparable to the ITO based control.

2. Experimental details

2.1. Transparent conducting electrode fabrication

Crackle lithography technique has been employed to produce m-TCEs. The detailed methodology of this technique has been reported elsewhere [12]. Briefly, a crackle template was prepared on glass by spin coating a crackle precursor (CP). Upon these templates, metal with optimum thickness is deposited by a physical vapor deposition (PVD) method followed by the lift-off process of CP to get m-TCE. In this work, we have chosen three different metal TCEs, Au, Cu and Ag, with optimized %T and Rs values. One square inch sized conventional glass pieces served as substrates for the fabrication of TCEs.

2.2. Optical characterization

The transmission of the TCEs was measured between the 300–1000 nm wavelength range using a UV–vis spectrometer (Perkin–Elmer, Lambda 900 UV/visible/near-IR spectrophotometer). A blank substrate in the reference beam in the UV–vis spectrometer is placed to ensure the substrate contribution is to be accounted.

2.3. OLED fabrication

OLEDs were fabricated by following basic device geometry with m-TCEs and demonstrated their potential. Two different ITO-free OLEDs with two different sets of interlayers are fabricated. In one of the sets, all the individual layers grew thermally (D1) and in the other set, solution processes were involved (D2). D1 consisted of three main layers, a hole injection layer (HIL), N,N′-Bis(3-methyl phenyl)-N,N′-diphenyl benzidine (TPD) (Sigma–Aldrich, purity 99%), the emitting layer (EL) of tris(8-hydroxyquinoline)aluminum (Alq3) (Sigma–Aldrich, purity 99.5%) layer and a hole blocking/electron transport layer (ETL) of 4,7-Diphenyl-1,10-phenanthroline (BPhen) (Sigma–Aldrich, purity 97%). These layers were sandwiched between a TCE anode and LiF/Al cathode, as shown in figure 1(a). The second device, D2, consisted of only two semiconducting layers, poly(3,4-ethylene dioxythiophene) polystyrene sulfonate (PEDOT: PSS) as HTL come HIL and Alq3 as ETL come EL with similar electrode geometry as shown in figure 1(b). In brief, D1 had the following structure: Glass/m-TCE/TPD/Alq3/BPhen/LiF/Al and D2 has Glass/m-TCE/PEDOT:PSS/Alq3/LiF/Al structure. The reference OLEDs were fabricated by keeping ITO in place of m-TCE. All other individual layers remained unchanged.

Figure 1. Schematic representation of ITO-free OLED device geometries and the corresponding flat band diagrams of devices D1 ((1a) and (1b)) and D2 ((1c) and (1d)). Three different ITO-free m-TCEs (Au, Ag and Cu) are considered to make OLED. A thin film of a green emitter, Alq3, served as an emissive layer in these OLEDs. Glass micro slides are used as the supporting substrates for the m-TCEs.
Subsequent deposition of TPD, Alq₃, and Bphen on both ITO and m-TCE were carried out in a vacuum chamber inside the glove box with Ar atmosphere (Jacomex) to get a thickness of 40 nm, 80 nm, and 30 nm respectively. To enhance the charge injection, a thin insulating buffer layer of 1 nm LiF was grown on the BPhen layer. Finally, we ended up with the OLEDs, D1, and reference to D1 fabrication by depositing 100 nm Al cathode film. For the fabrication of D2 OLED, the conducting polymer PEDOT: PSS was spin-coated on a TCE electrode with 3000 rpm rotation speed to get an optimum thickness of ∼40 nm. In our device, PEDOT: PSS was used for hole injection, besides, to minimize the surface roughness of wire mesh anode by filling the void spaces between adjacent wires. These polymer films were further annealed by placing them onto a hotplate with a fixed temperature of 120 °C. To increase the charge injection and to have high hydrophobicity, these PEDOT: PSS surfaces were UV-ozone treated for 30 min. On top of this polymer layer, the EL/ETL, Alq, of 80 nm thickness was vacuum deposited. Subsequent deposition of 1 nm LiF and 100 nm Al were done to create a cathode.

2.4. Electrical characterization

A source meter (Keithley 2400) was used for the measurement of the OLED current density v/s voltage characteristics. Konica Minolta CS 2000 spectroradiometer was used for measuring the brightness and electroluminescence (EL).

3. Results and discussions

OLEDs with two different sets of interlayers were fabricated (figure 1) with m-TCEs as anodes. A standard ITO electrode was used to make a reference device in each configuration. In the first configuration (D1), the individual layers were grown by thermal evaporation and in the second (D2), both solution and thermal processes were employed. While fabricating with D1 configuration, the layers were deposited as a stack, TPD/Alq/BPhen (see figure 1(a)), while in D2 (figure 1(c)), a solution-processed PEDOT:PSS layer was on top of Alq. Thus, the two sets of layers were sandwiched between the m-TCE (or ITO) anode and LiF/Al cathode. The flat band diagrams are shown in figures 1(b) and (d) for D1 and D2 respectively with three possible anodes (ITO not shown). The workfunction of the anode plays a crucial role in improving the OLED characteristics specifically the operating voltage and the brightness. It has been reported that a larger anode workfunction would reduce the potential barrier for holes reaching the emissive layer thereby enhancing the device performance [18]. Upon biasing the device, the charge carriers drift towards the electrodes to generate strong interfacial fields that promote the charge injection into the semiconductor [19].

The photograph of a pixelated OLED device is shown in figure 2(a). For clarity, the bottom contact pads are labeled with numbers and the illumination from pixel-2 is illustrated along with the applied bias between the bottom (m-TCE) and the Al cathode electrodes. Figure 2(b) is the photograph of the patterned m-TCE anode of the device. The FESEM image of a patterned pixel reveals the percolated metal wire network of m-TCE, as shown in figure 2(c). There is a slight variation in the contrast along the metal mesh in figure 2(c) attributable to local charging, which gets minimized once the charge injection layers are deposited. The m-TCEs of Au, Cu, and Ag were optimized to show excellent transmittance and low sheet resistance ($R_s$), as shown in figures 2(d) and (e). The Cu-TCE showed relatively low sheet resistance compared to the other two. A major concern for the m-TCE is its surface roughness, particularly if the thickness of the deposited metal is high. This way, the sheet resistance could be brought down, but the increased surface roughness leads to short-circuiting in the device. Similarly, any attempt to enhance the transmission by increasing the line spacing of the metal wires can cause dark areas in the fabricated OLED if the spacing is beyond the diffusion length of the charge carriers. Further, the recombination process involving the charge carriers injected from the counter electrode occurs only in the vicinity of the grid lines. By considering all such issues, we fabricated ~50 nm thick metal mesh with the optimum values of transmittance and $R_s$ in the range of 84%–87% and 7–20 $\Omega$ sq $^{-1}$, respectively (see figures 2(d) and (e)). It should be noted that the m-TCEs while replacing ITO also provide the solution to the issues such as defect absorption in the visible spectrum akin to ITO [19, 20].

The D1 and D2 type devices were characterized while placed inside the Ar-glovebox without any encapsulation. The electro-luminance from the individual pixels was monitored while applying the bias and the data obtained is presented in figures 3 and 4 for D1 and D2 configurations, respectively. A photograph of the Cu-TCE based OLED is shown in figure 3(a) as an example where bright green emission can be seen from one of the pixels. From the EL characteristics in figure 3(b), we see that the relative spectral intensity from the Cu-TCE device is much higher compared to those from Ag-TCE and Au-TCE based devices, although smaller when compared to the reference ITO device (see inset of figure 3(b)). The current density versus voltage characteristics (J-V) shown in figure 3(c) also represent a similar scenario. Voltage-dependent brightness (L-V) curves of all three m-TCEs along with ITO ones can be seen in figure 3(d). The superior performance of the Cu-TCE based OLED can be ascribed to its low sheet resistance as well as the high workfunction of Cu, which may reduce the
potential barrier significantly to help efficient hole injection into the emissive layer. The extracted parameters are summarized in table 1. However, the interfaces within the device required a revisit to make the performance comparable to that of ITO device.

Although the turn-on voltages are close to that of the ITO based device, the luminescence and current efficiencies are relatively lower. These results bring out the role of the interface between the anode and the TPD layer. In order to have an efficient hole-injection without sacrificing transmittance of the bottom anode, the thickness of TPD was reduced to 40 nm but at the cost of increased interface roughness. Evidently, devices with a
smoother interface than m-TCE should show a better performance. This issue was addressed by coating the hole-injection layer (PEDOT:PSS), via solution processing so as to just submerge the metal wire network.

Figure 4 illustrates the EL spectra, J-V and L-V characteristics of the fabricated green-OLEDs on Au, Ag and Cu-TCEs as well as ITO, all with the device geometry, D2. At an injection current of 20 mA cm$^{-2}$, the measured forward voltages are 6.5, 5.8 and 5.5 and 7.2 V for the OLEDs with Au, Ag, Cu and ITO TCEs, respectively. The relative changes in forwarding voltages can be attributed to the sheet resistance variations. Remarkably, the forward voltage of the ITO-based device was relatively higher compared to the values from the m-TCE devices. The J–V curves are considerably linear with the reduction in the forward voltage. In particular, the Cu-TCE based OLED with a low forward voltage could provide efficient lateral diffusion pathways that then inject current into active junctions of the OLED via the hole injection layer. Accordingly, the EL intensity was enhanced in comparison, as shown in figure 4(b). The stable EL peak position for all OLEDs indicates that the emission is independent of the TCE material. The smooth variations of the current with the applied bias seen in the plot goes well with the observed uniform emission of the pixel without developing defective black spots (figure 4(c)).

Importantly, the brightness of the Cu-TCE based OLED got enhanced in the D2 configuration to become comparable with that of the ITO OLED. The two device parameters are compared in table 2. The maximum luminance of the Cu-TCE based OLED was 4300 cd m$^{-2}$ and it is almost equal to that of the device employing commercially available ITO electrodes (see table 2). A reduced hole injection barrier from the Cu-TCE anode in OLEDs and lower sheet resistance accomplished remarkable device performance comparable to that of the other two (Au and Ag) m-TCEs. The current efficiency and maximum current were measured to be 5.38 cd A$^{-1}$ and 800 A m$^{-2}$, respectively. In spite of lower transmittance of the m-TCE the performance of this OLED was almost identical to that of the ITO-based device as the power loss induced by the waveguide modes typically associated with the ITO anode [21], is likely to be suppressed in the former. Therefore, it can be concluded that the performance of the Cu-TCE based OLEDs is much comparable to the ITO OLEDs and considering scalability and cost, these ITO-free electrodes may be quite attractive.

Figure 4. OLED characteristics with D2 device geometry. (a) Photograph of glowing OLED fabricated with Cu-TCE anode. (b) EL spectra of all three m-TCE based OLEDs recorded for 20 mA current bias and corresponding J-V characteristics (c). (d) Voltage-dependent brightness characteristics of all m-TCE OLEDs. Characteristic plots of the ITO reference device are also included.

### Table 1. Comparison of performances of D1 OLEDs with the ITO based device.

| Anode  | Turn-ON voltage (V) | Maximum brightness (cd m$^{-2}$) | Luminous efficiency |
|--------|---------------------|----------------------------------|---------------------|
| ITO    | 4.64                | 4298                             | 5.70                |
| Ag-TCE | 4.16                | 521                              | 0.20                |
| Au-TCE | 6.16                | 103                              | 0.71                |
| Cu-TCE | 5.61                | 796                              | 0.99                |
4. Summary

In summary, we have demonstrated a highly robust and easily processable metal wire network TCE as an excellent alternative to the traditional transparent ITO electrode in the fabrication of OLEDs. We chose Au, Ag and Cu for the fabrication to bring out the additional functionality of workfunction tunability of anodes. In order to obtain desired transmittance and sheet resistance values, the wire width and the density were optimized. All m-TCEs showed excellent characteristics, and in particular, Cu-TCE exhibited transmittance of 85% at 550 nm and sheet resistance of ~7 Ω sq⁻¹. The roughness of the network arising from the wire thickness was mitigated by coating a smooth layer of the hole-injection layer (PEDOT:PSS). The luminance obtained (4300 cd m⁻²) with Cu-TCE was comparable to that of ITO based OLEDs at a relatively lower turn-on voltage. The reduced potential barrier for hole injection and lower sheet resistance of the Cu-TCE played a key role in this outstanding device performance. We envisage that m-TCEs with their simple and low-cost fabrication may fulfill the role of transparent electrodes in optoelectronic devices particularly involving large areas. The workfunction tunability allows subtle matching of the energy levels within the device.

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ORCID iDs

Murali Gedda © https://orcid.org/0000-0003-1247-6623
Giridhar U Kulkarni © https://orcid.org/0000-0002-4317-1307

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