Color in the Corners: ITO-Free White OLEDs with Angular Color Stability

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White organic light-emitting diodes (OLEDs) show great promise for energy-efficient, flat-panel, large-area, general illumination. Due to the potential for roll-to-roll processing and their thin, lightweight form-factor, they will be a visually attractive and low-cost alternative to shaded point light sources. Through incorporation of phosphorescent emitters into the emission layers, internal quantum efficiencies of these devices can reach almost 100%.1,2 Recently, white OLEDs with a power conversion efficiency/luminous efficacy (LE) of 30 lumens per watt (lm W−1) on a flat glass substrate, raised to a power conversion efficiency of 90 lm W−1 using outcoupling techniques, were reported.3,4 This efficiency is comparable to fluorescent light sources and shows great progress toward the promise of white OLEDs becoming a widespread source of general illumination. However, new challenges arise with area-emitting two-dimensional light sources. Not only do they have to offer high efficiency, low-cost, and even emission over the entire device area, they should also have Lambertian emission, and the white color must be stable over all angles, two properties which are particularly challenging to achieve in high-efficiency tandem white OLED structures.5–7 Without angular color stability, the appearance of items in a room illuminated via white OLEDs would be dependent on their location, whether they are in the center or the corners, which is unacceptable for general use.

The transparent electrode is a critical part of the white OLED structure, as a high-performance transparent conductor will be required to enlarge these devices from the lab scale to the commercial scale.8,9 These electrode materials are primarily evaluated on two metrics: sheet resistance in ohms per square (Ω sq−1) and optical transparency (%). A figure of merit for evaluating and comparing transparent conducting films has been defined, taking into account both properties, by dividing the material's DC conductivity σ by the absorption coefficient α. This ratio, σ/α, should be as high as possible, with values higher than 1 Ω−1 considered suitable for large-area applications.8,9 If the sheet resistance across the transparent electrode in a white OLED panel is too high, the result is increased operating voltage, resistive heating, non-uniform emission, and differential ageing across the device area.8,9 If the optical transmission is too low, light cannot escape the device, leading to a reduction in external quantum efficiency (EQE). In addition, for a transparent electrode to be device-compatible, the surface roughness needs to be low enough to prevent current leakage and shorting, as the organic layers in OLEDs have a total thickness of hundreds of nanometers. While indium tin oxide (ITO) has been the dominant transparent electrode for white OLEDs since their inception, many researchers are looking to replace ITO in large-area organic electronics.10,11 One consideration is the poor performance of ITO on flexible plastic substrates that would be required for roll-to-roll processing of low-cost white lighting.12 ITO on glass generally exhibits sheet resistances of 15 Ω sq−1 at 90% transmission, resulting in σ/α = 0.67 Ω−1, and the highest quality ITO on glass can reach figures of merit close to 1 Ω−1.12,13 However, the best ITO on polymer webs has a sheet resistance of 40 Ω sq−1 at the same transmission,12 due to the limited process temperature on polymer substrates, and thus σ/α = 0.25 Ω−1. Furthermore, ITO is brittle and tends to form cracks in flexible devices. Another consideration is increasing materials usage efficiency by moving from a sputtered transparent electrode material such as ITO12 to a solution-processed one. To this end, many solution-processed ITO alternatives have been studied, including conductive polymers,14–16 carbon nanotubes,17–19 reduced graphene oxide,20–23 and metal nanostructures.8,9,24–27 Many of these materials can also be vapor-deposited and show a superior performance. Han et al.28 reported highly efficient flexible green OLEDs on modified graphene electrodes, but these electrodes were deposited via chemical vapor deposition (CVD), CVD can also be used to fabricate carbon nanotube meshes.29,30 However, all reported carbon-based solution-processed electrodes have very high sheet resistances, resulting in figures of merit ranging from σ/α = 0.005 Ω−1 for graphene to σ/α = 0.02 Ω−1 for carbon nanotubes to σ/α = 0.08 Ω−1 for the polymer poly-(4,3-ethylene dioxythiophene) (PEDOT).16 None of these are close to either ITO on glass or to the requirement for large-area devices, and in practice would need to be used in conjunction with metal shunt lines, which decrease the device...
active area.\textsuperscript{[32–34]} Films based on metal nanostructures have been reported with higher figures of merit, from $\sigma/\alpha = 0.2 \ \Omega^{-1}$ \textsuperscript{[27]} to $\sigma/\alpha = 0.6 \ \Omega^{-1}$\textsuperscript{[9,25]} However, these values are still too low for large-area lighting purposes, and no high-efficiency white OLEDs have ever been fabricated using them.

In this article, we report solution-processed composite transparent electrodes for high-efficiency white OLEDs that have figures of merit $\sigma/\alpha \geq 1 \ \Omega^{-1}$ while also imparting unique optical advantages to the devices fabricated using them. Based on silver nanowires (NW) embedded into poly (methyl methacrylate) (PMMA) films, the electrodes are fabricated entirely via scalable solution-processes. The ITO-free white OLED shows a luminous efficacy over 30 lm W$^{-1}$, which is on par both with the control devices fabricated on ITO and with the record devices reported in 2009.\textsuperscript{[2]} Due to the low sheet resistance and light scattering properties of the transparent electrode, the NW devices have increased current efficiency (CE), emission with a close to perfect Lambertian profile, and superior angular color stability to those devices fabricated on ITO. This is the first time a transparent electrode structure has been shown to stabilize angular color dependence for a white light emitter, which is a fundamental optical issue for two-dimensional tandem light sources.\textsuperscript{[4–7]}

The NW electrode fabrication process is shown in Figure 1a. First a 145 nm film of PMMA is spun onto either a glass or plastic substrate. Then the nanowires, suspended in isopropanol, are deposited via spray coating. An atomizing nozzle is used to control droplet size, and the system allows for control of flow rate, ventilation, and substrate temperature. The nanowire density is controlled by the amount of the suspension being sprayed, as the substrates pass back and forth under the nozzle until all wires have been deposited. The SEM image in Figure 1b shows the nanowires as deposited on top of a PMMA film. The spray-coating system successfully disperses the wires into a random, continuous mesh. Following wire deposition, the film is patterned using an infrared laser. SEM images of patterned films show that this laser patterning process ablates both the nanowires and the polymer from the substrate (see supplementary information). The wires then are embedded into the polymer to form the composite structure. Unlike previous studies of Ag nanowire meshes,\textsuperscript{[8,9,25,26]} no lengthy thermal annealing is necessary. The 30-second embedding step at 110 $^\circ$C is an effective replacement to annealing, as prior to embedding, the NW films have sheet resistances values in the k$\Omega$ sq$^{-1}$ to M$\Omega$ sq$^{-1}$ range. After embedding, these sheet resistances can be reduced to below 10 $\Omega$ sq$^{-1}$ on both glass and plastic substrates, even if the pressure is applied at room temperature (see supplementary information). This shows that the fusing of the junctions between nanowires can occur either thermally or mechanically. An SEM image of the fused junctions embedded into PMMA is shown in Figure 1c. Tapping-mode AFM studies of these films show that the RMS roughness over a 10-μm square area is between 6 and 8 nm. This is rougher than ITO, which has an RMS roughness between 1 and 3 nm, but is significantly less than the film thicknesses deposited in a white OLED, so that no increase of leakage current is expected. It is worth noting that,

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{Silver nanowire electrode processing and SEM images. a) Scalable step-by-step composite electrode fabrication process. b) SEM showing sprayed and embedded Ag nanowire mesh forming a continuous network. c) Close-up of fused nanowire junctions embedded into PMMA.}
\end{figure}
PMMA is an insulator with negligible absorption, the nanowire shows a greater spectral variance than our composite films. As was reported in previous studies of Ag nanowire mesh films, the nanostructures scatter light due to their small length scales and surface roughness. To determine the amount of scattering present in Ag nanowire/PMMA composites, specular and diffuse transmission measurements have been performed. Figure 2b shows the percentage of total light transmitted through the electrode that is scattered (haze = diffuse transmission/total transmission), the average value of which is 6.8% over the visible spectrum. Since the haze does not vary significantly with nanowire density, the representative data shown here is for a film with a sheet resistance of 12.5 $\Omega$ sq$^{-1}$ and an average transmission of 92% as shown in Figure 2a. While scattering is present and significantly contributes to the total transmission, its strength has been reduced in the case of the smooth composite when compared with studies of bare Ag nanowires, which show haze values up to 20%. Still, the diffuse transmission can greatly change the emission pattern of white OLEDs fabricated using these electrodes with respect to those fabricated on ITO, as ITO has negligible haze. To examine these scattering properties and to observe how they affect light-emitting devices, a highly-efficient, state-of-the-art white tandem OLED$^{[2,3]}$ was fabricated on our composite electrode exhibiting 12.5 $\Omega$ sq$^{-1}$ and 92% transmission, as well as on an ITO reference.

Tandem OLED structures are already widely used in industry by Kodak,$^{[35]}$ Novaled,$^{[36]}$ Panasonic,$^{[37]}$ LG Chem,$^{[37]}$ and others, because they exhibit advantages like high luminance and high efficiency. However, the comparatively thick optical cavity introduces a strong shift of the spectrum and color with the viewing angle,$^{[4–7]}$ which is not desired for general illumination. The layer structure used in this work and the performance characteristics of the devices are depicted in Figure 3. It is significant that, except for a thin PEDOT:PSS layer, the device structure fabricated on ITO is exactly replicated on the Ag nanowire/PMMA electrode. For earlier studies of Ag nanowire-based films this was not possible.$^{[38]}$ The current-voltage-luminance (IVL) curves (IVL) for both the ITO and NW samples are almost identical (Figure 3b). Due to the low roughness, the NW sample reaches a leakage current in the same order of magnitude as the reference. For high voltages (>6 V) the IVL-curve of the NW-OLED is flattened which is attributed to the injection barrier caused by the PEDOT:PSS. However, both devices start emitting light at 5 V (onset voltage), and require almost same driving voltage to reach a luminance (brightness) of 1000 cd m$^{-2}$ (5.9 V for ITO-OLED, 6 V for NW-OLED). We attribute the slight
luminance up to a level of 10 000 cd m\(^{-2}\), which is required for outdoor applications. The color change with increasing current density can be neglected (see supplementary information).

The spectral emission of both devices at 0° (perpendicular to the substrate) at the same current density (the same injection rate of charge carriers) is similar, with a slightly higher contribution of green and yellow light for the NW-OLED (Figure 3c). This spectral difference consequently leads to a higher current efficiency (CE = luminance/current density) for the NW device (Figure 3d).

increase in driving voltage to an increase in the hole injection barrier, as the work function of Ag (–4.3 V) has a greater disparity than that of ITO (at –5.0 eV) with respect to the HTL (–5.1 eV). For the NW-OLED, the injection occurs via the PEDOT:PSS overcoat (HOMO, approx. –5.0 eV) which can cause an increase in voltage. In the future, replacing the PEDOT:PSS layer with a thin, highly doped HTL may be able to achieve a reduced driving voltage, but this will require further optimization of the fabrication process and is therefore beyond the scope of this report. It is noteworthy that the NW-OLED achieves high luminance up to a level of 10 000 cd m\(^{-2}\), which is required for outdoor applications. The color change with increasing current density can be neglected (see supplementary information).

The spectral emission of both devices at 0° (perpendicular to the substrate) at the same current density (the same injection rate of charge carriers) is similar, with a slightly higher contribution of green and yellow light for the NW-OLED (Figure 3c). This spectral difference consequently leads to a higher current efficiency (CE = luminance/current density) for the NW device (Figure 3d).

Figure 3. Device structure and performance of the white tandem OLEDs with nanowire and ITO anode. a) Device layer architecture. b) Current density-voltage-luminance characteristics. c) Emission spectra at 1.5 mA cm\(^{-2}\). d) Current efficiency. e) External quantum efficiency. f) Luminous efficacy vs. luminance.
Light outcoupling (extracting light from the emission layer through the electrode and the substrate into air) is currently a challenge in developing highly efficient OLEDs.\(^\text{[39,40]}\) Due to total internal reflection, light modes are trapped in the organic layers (refractive index \(n \approx 1.7\pm2.0\)), the electrode (\(n \approx 1.7\pm2.1\) for ITO), and the substrate (\(n \approx 1.5\) for glass). The substrate modes can be extracted by attaching a glass half-sphere to the substrate. The external quantum efficiency and the luminous efficacy of the two devices are shown in Figure 3e and Figure 3f. At 1000 cd m\(^{-2}\) the EQE (LE) increases from 26.8\% (35.8 lm W\(^{-1}\)) to 42.8\% (63.0 lm W\(^{-1}\)) for the ITO-OLED and from 24.3\% (30.3 lm W\(^{-1}\)) to 37.9\% (53.9 lm W\(^{-1}\)) for the NW-OLED when attaching a half-sphere. Despite the slightly better EQE and LE of the ITO-OLED, the two devices are comparable, and the NW-OLED reaches remarkably high efficiencies compared to other studies (see supplementary information), with a similar strong enhancement using the outcoupling half-sphere. However, a cheap flat outcoupling structure like a microlens foil is more suitable for commercial applications than a big heavy glass half sphere. Using a microlens foil, the EQE (LE) is as high as 33.4\% (45.4 lm W\(^{-1}\)) for the ITO-OLED and 28.0\% (36.3 lm W\(^{-1}\)) for the NW-OLED. 

Table 1 summarizes the figures of merit for the devices under study and can be regarded as benchmark for further work on ITO-free white OLEDs.

<table>
<thead>
<tr>
<th>at 1000 cd m(^{-2})</th>
<th>voltage [V]</th>
<th>current density [mA cm(^{-2})]</th>
<th>CIE 0° (CIE 75°)</th>
<th>CRI 0° (CRI 75°)</th>
<th>CCT 0° (CCT 75°)</th>
<th>CE [cd A(^{-1})]</th>
<th>EQE [%]</th>
<th>LE [lm W(^{-1})]</th>
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</thead>
<tbody>
<tr>
<td>ITO-OLED</td>
<td>5.9</td>
<td>2.6</td>
<td>0.507/0.449</td>
<td>73</td>
<td>2420</td>
<td>43</td>
<td>26.8</td>
<td>35.8</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>{0.477/0.496}</td>
<td>{56}</td>
<td>{3060}</td>
<td>{33.4}</td>
<td>{4.3x}</td>
<td>{4.5x}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>{0.030/0.047}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NW-OLED</td>
<td>6.0</td>
<td>2.3</td>
<td>0.493/0.468</td>
<td>69</td>
<td>2680</td>
<td>49</td>
<td>24.3</td>
<td>30.3</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>{0.507/0.465}</td>
<td>{65}</td>
<td>{2510}</td>
<td>{28.0}</td>
<td>{1.2x}</td>
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</tr>
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<td></td>
<td></td>
<td></td>
<td>{0.014/0.003}</td>
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\(^a\)with outcoupling foil; \(^b\)with outcoupling half-sphere.

In conclusion, we have demonstrated solution-processed Ag nanowire/PMMA composite electrodes that are suitable for large-area applications. Superior performance to conventional ITO electrodes is achieved and light scattering from the nanowire surface is observed. The efficiency of white OLEDs fabricated on these electrodes is enhanced in the case of current efficiency and similar in the case of luminous efficacy/external quantum efficiency when compared to the same highly efficient OLEDs on ITO. High luminous efficacy of over 30 lm W\(^{-1}\) is achieved with the NW-OLED at an application relevant brightness of 1000 cd m\(^{-2}\). This can be increased to 54 lm W\(^{-1}\) using outcoupling techniques, which, at this time, is the highest luminous efficacy reported for an ITO-free white OLED. In addition, Rosenow et al.\(^\text{[3]}\) have demonstrated the potential to reach luminous efficiencies of 90 lm W\(^{-1}\) for this OLED structure on ITO using advanced light outcoupling methods. Thus we believe that further improvement in light efficacy can be achieved with our composite electrodes as well. Finally, the scattering properties of the nanowire surface lead to stabilized viewing angle characteristics, with a greatly reduced color shift and almost perfect Lambertian emission, ameliorating the angular dependency that has been a fundamental optical issue in tandem white OLEDs. This angular color stabilization has never before been demonstrated using a transparent electrode, and with the complement of high performance and scalable fabrication methods, we believe these silver nanowire electrodes could help usher in the age of large-area white OLED lighting.
at 6 × 10^4 psi. The mild heat softens the polymer to aid the nanowire junctions in sinking below the polymer surface, which is critical to avoid local thinning and shorting in thin-film devices built on top. To further reduce roughness for OLED fabrication, 50 nm of PEDOT:PSS (Clevios AI 4083) was spun onto the electrodes following 20 min of UV-ozone treatment. The substrates were then heated at 150 °C for 20 min to remove the water from the PEDOT:PSS films.

**White OLED Fabrication:** Organic materials were commercially purchased and purified by vacuum gradient sublimation. Pre-structured ITO coated glass substrates (Thin film devices Inc.) were cleaned using ultrasonic treatment in N-Methyl-2-pyrrolidone (NMP), distilled water, and ethanol. The substrates were heated out at 110 °C for 30 min in

**Experimental Section**

**Composite Electrode Fabrication:** Borofloat 33 glass substrates (Schott) were cleaned using detergent, de-ionized water, acetone, and boiling isopropanol. PMMA 2% solid solution in anisole (MicroChem Corp.) was spun onto these substrates at 1250 rpm to create a 165 nm thick film. These substrates were then loaded into a spray-coating system that delivered 1 mg/mL of silver nanowires suspended in isopropanol (Seashell Technology, Inc.) onto the substrates held at 80 °C. Following this, the blanket films were patterned using a computer-controlled, rastered infrared CO 2 laser (Epilog). A flat-plate press heated to 110 °C was used to embed the nanowires into the polymer for 30 s

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**Figure 4.** Angular dependent performance of the white tandem OLEDs at 1000 cd m^−2_. Spectral emission intensity for various viewing angles for ITO-(a) and NW-OLED (b). c) Normalized radiant intensity. d) CIE color coordinates vs. viewing angle. e) Photographic image of four operating NW-OLEDs.
nitrogen atmosphere and immediately transferred to ultra high vacuum (UHV). Organic and metal layers are deposited by thermal evaporation in a UHV chamber (Kurt J. Lesker Co.), at a base pressure of 10⁻⁷ mbar without breaking the vacuum. Evaporation rates and thicknesses of all layers were measured in sput via quartz crystals. Doping is achieved by co-evaporation. After processing, OLEDs were immediately encapsulated in nitrogen atmosphere with a getter including glass lid using a UV-curing epoxy resin.ITO- and NW-OLEDs were fabricated simultaneously in one run, eliminating run-to-run variability.

The used materials in chronological order of deposition were N,N,N',N'-Tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) doped with 2 wt.% of 2,2'-[(perfluoronaphthalene-2,6-diylidene)dimalononitrile (F6-TCNQ) (30 nm), 2,2',7,7'-Tetakis(N,N-diphenylamino)-9,9'-spirobifluorenon (Spiro-TAD) (10 nm), the blue fluorescent emitter N,N',N''-tris(1-phenyl-1H-benzimidazol-2-ylidene)dimalononitrile (TCTA) doped with the green phosphorescent emitter Iridium(III)bis(2-methylphenylbenzo-[f]thieno[3,2-b]thiophen)(acetylacetonate) (Ir(MDQ)2(acac)) (5 nm), 4P-NPD (3 nm), Bathophenanthroline; 4,7-diphenyl-1,10-phenanthroline (BPhen) (10 nm), BPhen doped with cesium (Cs) (90 nm), silver (Ag) (0.5 nm), MeO-TPD doped with 2 wt.% F6-TCNQ (75 nm), Spiro-TAD (10 nm), 2,2'-[(perfluoronaphthalene-2,6-diylidene)dimalononitrile (TCTA) doped with the green phosphorescent emitter 8 wt.% Tris(2-phenylpyridine) iridium(III) (Ir(ppy)3) and 1 wt.% of the yellow phosphorescent emitter Bis(2-(9,9-dihexylfluorenyl)-1-ptyridine) acetylacetonate iridium(III) (Ir(dfppy)2(acac)) (5 nm), 2,2'-(1,3,5-Phenylen)tris(1-phenyl-1H-benzimidazol) (TBPi) doped with 8 wt.% Ir(ppy)3 and 1 wt.% Ir(dfppy)2(acac) (5 nm), TBPi (10 nm), BPhen doped with Cs (60 nm), and aluminium (Al) (100 nm).

Characterization: Electrode sheet resistance was measured using a four-point probe connected to a source meter (Keithley). Transparency measurements were taken using a white light source coupled with a monochromator and detected using integrating sphere (Newport) and silicon photodiode (Newport). The transmission of a bare glass substrate was taken and used as a baseline measurement. Then the transmission of a substrate with the electrode fabricated on it was measured and compared to the bare substrate baseline to yield the percentage of light transmitted through the electrode without the inclusion of substrate reflection. To calculate haze, the same measurement was taken without the integrating sphere and the two transmission values were compared. The figures of merit reported in this study were calculated from transmission (over 400–800 nm) and conductivity values, both ours and from literature, assuming negligible reflection and wavelength dependence.

All OLED characterizations were done in air and under ambient temperature. Current-voltage-luminance curves were measured using a source measure unit (Keithley SMU 2400) and a calibrated Si-photodiode. Spectral radiation was recorded with a calibrated spectrometer (Instrument Systems GmbH CAS140). The relative efficiencies as a function of luminance measured with the fast integrating sphere and the two transmission values were compared. The figures of merit reported in this study were calculated from transmission (over 400–800 nm) and conductivity values, both ours and from literature, assuming negligible reflection and wavelength dependence.

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