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High brightness phosphorescent organic light emitting diodes on transparent and flexible cellulose films

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Abstract

Organic light-emitting diodes (OLED) were fabricated on flexible and transparent reconstituted cellulose obtained from wood pulp. Cellulose is naturally available, abundant, and biodegradable and offers a unique substrate alternative for the fabrication of flexible OLEDs. Transparent cellulose material was formed by dissolution of cellulose in an organic solvent (dimethyl acetamide) at elevated temperature (165 °C) in the presence of a salt (LiCl). The optical transmission of 40- μ m thick transparent cellulose sheet averaged 85% over the visible spectrum. High brightness and high efficiency thin film OLEDs were fabricated on transparent cellulose films using phosphorescent Ir(ppy)₃ as the emitter material. The OLEDs achieved current and luminous emission efficiencies as high as 47 cd A⁻¹ and 20 lm W⁻¹, respectively, and a maximum brightness of 10 000 cd m⁻².

Keywords: OLED, cellulose, flexible, phophorescence, brightness, efficiency

(Some figures may appear in colour only in the online journal)

1. Introduction

Organic light emitting diodes (OLEDs) are a rapidly growing technology with applications in major markets, such as lighting and displays. In the field of electronic displays where the dominant technology is liquid crystal displays (LCD), OLEDs are distinguished by the fact that they are an emissive light source that does not require an additional backlight source, thus reducing both the form factor and the power requirements. In addition, OLEDs provide a high contrast ratio (with completely black state [1]), wide viewing angles, fast response times that makes it a superior choice for high-speed videos.

Applying printed electronics technology to the OLED fabrication onto paper substrates would result in lightweight low-cost flexible displays. Furthermore, the incorporation of natural biomaterials, such as cellulose, is an important step forward towards the goal of fully biodegradable electronics. Given the global distribution of electronic products and their ever-decreasing life cycle, biodegradable electronics is a potential solution for the ecological problems caused by electronic wastes [2]. This confluence of desirable properties between printing technology and paper substrates has spurred investigations of various types on devices on (and in) paper [3, 4]. A few examples include organic field effect transistor (OFET) arrays [5], roll-to-roll printed solar cells [6], chemical vapor deposited solar cells [7], electro-chromic displays [8], and paper based sensors for microfluidic applications [9]. It must be pointed out, however, that the use of paper as substrate material is only a beginning. To achieve true sustainable electronics will require the use of renewable materials for all of the device components. Furthermore, the production of the starting materials and the actual device fabrication will need to minimize environmentally damaging practices.

Previous reports on OLED fabrication on various forms of cellulose have demonstrated feasibility of the concept but exhibited limited performance [10, 11]. In this paper we report on flexible phosphorescent OLEDs fabricated on transparent paper substrates that demonstrate low turn on voltage, high brightness, high current and luminous efficiencies. Transparent paper as a substrate for OLEDs has several advantages: optical transparency allows the fabrication of conventional OLED bottom emitting structures, light weight and flexible, biodegradable [12]. In addition, as shown below the transparent reconstituted paper films exhibit a surprisingly smooth surface. In general, paper stock is significantly lower in cost compared to conventional OLED substrates: glass or plastic. Currently, specialty biopolymers are still more expensive than many of their conventional plastic counterparts [13]. However, it is expected that with increasing use, growing markets and with environmental regulations the availability of these materials will expand while their pricing will be more competitive.

2. Experimental details

2.1. Materials

Reconstituted cellulose can be synthesized from naturally occurring cellulose, such as wood pulp. The process involves [14] dissolution of fine wood pulp (crystalline cellulose [Type 20] from Sigma Aldrich) into an organic polar solvent (99.99% pure dimethylacetamide-DMA-from Sigma Aldrich). followed by heat treatment, constant stirring and addition of a salt (LiCl). A 7% solution of cellulose in DMA was 'activated' at \sim 165 °C for 30 min. Cellulose activation is a thermal process wherein (C–H) bonds between cellulose polymer strands are broken and replaced with methyl bonds [15]. When the slurry cooled to 100 °C, LiCl was added (10 g/100 g of solution) and the temperature was held for 12 h under constant stirring. The addition of LiCl to the cellulose solution prevents the reformation of the C-H bonds upon cooling. When the solution reaches room temperature it is suction filtered. The resulting solution is diluted in DMA to reduce its viscosity (five parts DMA to one part cellulose solution). A thin cellulose film is created by drop casting from a 1 cm thick solution, which results in a dry film with 10 μ m thickness as shown in figure 1. It is important to note that increasing the concentration of cellulose solution results in thicker films. The LiCl is then removed by rinsing in water. The cellulose obtained by this method is considered to be reconstituted rather than regenerated and is as biodegradable as conventional cellulose. This methodology to form cellulose films was patented by Turbak et al [14].

2.2. Material characterization

2.2.1. Optical transmission. The optical transmission was measured on the various cellulose samples using a Perkin Elmer UV/vis/NIR Lambda 900 model. The optical transmittance of several transparent substrates are compared in figure 2: a 100 μ m thin Corning[®] WillowTM Glass (Corning Inc., Corning, NY) substrate, 10 and 40 μ m reconstituted cellulose films, and a 40 μ m reconstituted cellulose film with a 1 μ m parylene C coating. The transmittance of the Willow Glass is greater than 90% over the entire range. The transmittance of the 10 μ m cellulose film is nearly the same as that of the Willow Glass, ranging from 88% at 400 nm to 90% at 850 nm. The thicker 40 μ m cellulose film has a



Figure 1. Reconstituted cellulose for OLED fabrication-transparent cellulose film (10 μ m).



Figure 2. Optical transmission versus wavelength for Corning willow glass (100 μ m), transparent cellulose films (10 and 40 μ m), and transparent cellulose (40 μ m) with 1 μ m parylene C coating.

transmission of 83% at 400 nm increasing to 86% at 850 nm. The addition of a 1 μ m parylene layer to the 40 μ m cellulose film introduces optical interference fringes, but does not affect the average transmission of ~85%.

2.2.2. Fourier transform infra-red (FTIR) spectroscopy. FTIR spectroscopy was performed using a Thermo Scientific Nicolet 6700 FTIR system with a Smart Orbit module to compare chemical bonding of the reconstituted transparent cellulose films and conventional cellulose (photocopy) paper. As seen in figure 3, the peaks between 1000 and 1200 cm⁻¹ correspond to cellulose [16, 17]. The band near 1160 cm⁻¹ corresponds to the anti-symmetric bridge stretching of C–O–C groups in cellulose, while the band between 1300 and 1500 cm⁻¹ is representative of the CH₂ wagging vibrations or the C–H bond bending in cellulose. The peak at ~1700 cm⁻¹ corresponds to the C=O group, while the band near 3400 cm⁻¹ due to O–H vibrations is representative of the water content in the material. The overall similarity of FTIR spectra confirm that the reconstituted cellulose films are quite comparable to



Figure 3. FTIR analysis of transparent cellulose and comparison to conventional photocopy paper.

conventional photocopy paper. The minor differences that are observed between the two spectra are probably due to the additives introduced in copy paper.

2.2.3. Surface properties. Surface properties of the cellulose were investigated using scanning electron microscopy (SEM) and atomic force microscopy (AFM) to determine surface morphology and roughness. Water contact angle (WCA) measurements were obtained as an indicator of the hydrophobicity/philicity and hygroscopicity of the cellulose films. SEM photographs of the 40- μ m cellulose film are shown in figure 4(a). In general, the surface is remarkably featureless, with occasional micron-size defects being observed, as seen in the insert to figure 4.

AFM was performed using the Nanosurf Easyscan 2 AFM instrument. Figure 4(b) shows a typical AFM scan of a 10 μ m × 10 μ m region of the 40 μ m cellulose film surface, yielding an average roughness of ~4.4 nm. The roughness of the surface remains approximately the same after the deposition of a 1 μ m parylene C film on top of the cellulose substrate. By comparison, the surface roughness of a microscope glass slide is ~2 nm.

Cellulose materials are quite hygroscopic due to the ability of the hydrogen-terminated glucose units in the cellulose chains to absorb large quantities of water. While absorbtion of water does not dissolve the cellulose, it leads to swelling and it affects the properties of the materials used to fabricate devices. A WCA of 84° was measured for the 40 μ m cellulose film using an FTA 1000 drop shape analyzer instrument, as seen in figure 4(c). To reduce the hygroscopicity of the transparent cellulose a 1 μ m parylene C film is deposited to seal the cellulose substrate and prevent the introduction of liquids and gases during device fabrication (especially during PEDOT deposition and post-processing, as described in section 2.3.1) and subsequent operation. This increases the WCA to 90°.

2.2.4. Thermogravimetric analysis. Thermogravimetric analysis (TGA) was performed using NETZSCH STA 409 PC Luxx TGA/DSC instrument over the temperature range of



Figure 4. Surface properties of transparent (40 μ m) cellulose films: (a) scanning electron microscopy (SEM) image, 50× magnification; inset photo at 5.0*k*× magnification; (b) atomic force microscopy, indicating the average surface roughness of the film; (c) water contact angle (WCA) on cellulose and on 1 μ m parylene C coated cellulose film.

25–550 °C. Figure 5 shows the TGA characteristics of several types of cellulosic materials: a transparent cellulose film and a group of opaque materials consisting of conventional photocopy and filter papers, and a specialty ultra-smooth paper (SAPPI Corp). The opaque paper samples have a similar TGA characteristic, with an onset of mass loss (10%) at 310–320 °C followed by a rapid decrease in remaining mass. The transparent cellulose sample exhibits a more gradual pattern of mass loss, with a 10% stability temperature of 250 °C, followed by a



Figure 5. Thermogravimetric analysis of transparent cellulose and cellulose containing films.

more complete mass loss transition region starting at \sim 300 °C. The gradual mass loss in the region from \sim 150 to 300 °C could be due to a combination of loss of solvent still present in the sample and the decomposition of a range of cellulose chains of different lengths [18]. The TGA result indicates that the OLED fabrication process on transparent cellulose should have a temperature limit of \sim 150–200 °C.

2.3. Methods

2.3.1. Substrate preparation. The cellulose film used as substrate is fairly water resistant. A parylene layer is deposited primarily to prevent gases generated during PEDOT post-bake from reaching the cellulose and degrading it. OLEDs have also been fabricated directly on cellulose, without parylene and PEDOT layers and they have fairly good characteristics. However, the addition of the PEDOT layer has resulted in approximately doubling of the luminous efficiency. A $1-\mu m$ layer of parylene C polymer was deposited by chemical vapor deposition (CVD) using a Specialty Coating PDS 2010 Parylene Coater system. The deposition takes place in a vacuum chamber at a pressure of \sim 15–30 mTorr. The substrate is maintained at room temperature during the deposition. The monomer *p*-xylylene is heated to $690 \,^{\circ}$ C in the furnace of the CVD system and forms poly(p-xylylene) when it is exposed to the room temperature substrate where it forms a thin transparent polymer coating layer on the substrate.

2.3.2. Deposition of anode. A thin layer of ITO (80 nm) was deposited using DC magnetron sputtering (DV-602 Denton Vacuum system) as the anode. The deposition was carried out using a In_2O_3/SnO_2 (90/10 wt%) target in an Ar ambient at room temperature. The base pressure of the system was maintained at 10^{-6} Torr. The deposition pressure of 3 mTorr



Figure 6. OLED device structure: (a) HOMO/LUMO energy levels of phosphorescent OLED, indicating charge flow and light emission; (b) device and thin film dimensions.

resulted in a deposition rate of ~4 nm min⁻¹. The sputtering was carried out for 20 min for an ITO film of ~80 nm. The ITO film had an average transmission of ~81% in the visible range (450–750 nm) and an as-deposited sheet resistance of 34 Ω/\Box . A thin layer (~65 nm) of the conducting polymer PEDOT:PSS was then spin coated on the ITO to enhance the hole injection capability of the anode. The PEDOT:PSS film was allowed to dry at room temperature for ~15 min and then cured at 90 °C for 90 min. It was found that rapid heating and cooling of PEDOT:PSS on ITO leads to cracking of the polymer layer due to thermal stress. This was prevented by a slow ramp-up and ramp-down rate of 1 °C min⁻¹. The curing of PEDOT:PSS improves the morphology and increases the electrical conductivity of the film [19].

2.3.3. Fabrication of OLED. After PEDOT:PSS (Clevios P VP Al 4083 from Heraeus) was spun onto the ITO electrode the devices were transferred to an ultra-high vacuum molecular beam deposition system (SVT Associates) where all the small molecule organic layers and metal layers of the OLED stack were deposited in situ. All OLED materials were purchased from Lumtec Corp. (>99% purity). The emission is produced primarily by the green (~515 nm) phosphorescent dye molecule Tris[2-phenylpyridinato-C2,N]iridium(III) or Ir(ppy)3, which is known to have a nearly 100% maximum quantum emission efficiency [20]. The substrate was at near room temperature (i.e. unheated) during the deposition process. The OLED stack was similar to that used in the fabrication of high efficiency phosphorescent green OLEDs [20] on glass substrates. In this device stack NPB (N, N'-Di-[(1-naphthyl)-N, N'-diphenyl]-1,1'-biphenyl)-4,4'-diamine) is deposited as the hole transport/electron blocking layer, CBP (4,4'-Bis(9carbazolyl)-1,1'-biphenyl) doped with Ir(ppy)₃ at 10 wt% acts is the emissive layer, BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) as the hole blocking layer and Alq3 (tris(8-hydroxyquinolinato)aluminum) as the electron transport layer. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) energy levels of the OLED layers are indicated in figure 6(a) along with the direction of charge transport through the device. A composite Al/LiF (aluminum/lithium fluoride) layer served as the cathode, injecting electrons into the device. The thicknesses of the various layers were optimized to achieve the highest emission efficiency from the completed device. Layer thicknesses and device dimensions are shown in figure 6(b). Voltage was supplied to the respective electrodes using a voltage source and contacts were made using flat alligator clips. The observed emission with a peak at 515 nm is quite similar to that reported [20] from CBP/Ir OLEDs on glass. Since the OLED device itself was not sealed against oxygen and water vapor penetration, measurements were performed in a controlled nitrogen environment. The photoemission spectral measurements were made using an Ocean Optics Spectrometer SD 2000.

3. OLED emission properties

The current (I) and luminance (L) of the phosphorescent green OLEDs as a function of voltage (V) are shown in figure 7. The



Figure 7. Electrical characteristics of OLED on transparent cellulose 40 μ m film: (a) linear scale current versus voltage; (b) log scale current and luminance versus voltage, indicating an emission turn-on-voltage of ~4 V.

luminance measurements were performed using a standard voltage source and a Konica Minolta CS-200 luminance meter under the control of a LabViewTM program.

In figure 7(a) the current is plotted on a linear scale versus voltage, indicating a series resistance (R_S) calculated to be ~14.5 k Ω . The significant R_S value could be due to a combination of factors: increased resistance of ITO deposited on paper as compared to glass, change in contact resistance due to an increased barrier to hole injection, etc. In figure 7(b) the I-V and L-V characteristics are shown as semi-logarithmic functions. The luminance turn-on voltage occurred at ~4 V, reaching the nominal electronic display value of 100 cd m⁻² at 5.5 V. In general, the fabricated OLEDs exhibited similar characteristics, with an emission turn-on at a bias of ~3.75–4 V. At a bias of 5 V, all devices exhibited stable emission with a luminance in the range of 40–75 cd m⁻².

The luminance is plotted versus current and current density (*J*) in figure 8(a). The *L*–*I* characteristics exhibits a linear relationship up to a current density of \sim 5 mA cm⁻² which yields a luminance of \sim 2500 cd m⁻². At higher values of current a sub-linear *L*–*I* relationship is observed, due to the increasing effect of voltage drop across *R*_S. The OLED reached a luminance of 10 000 cd m⁻² at \sim 1.1 mA.



Figure 8. Emission characteristics of phosphorescent OLED on transparent cellulose: (a) luminance versus voltage, highest luminance $\sim 10\,000$ cd m⁻²; (b) current efficiency and luminous efficiency versus luminance in the range of several hundred cd m⁻², covering most types of electronic displays.

The emission efficiency of the OLED is shown in figure 8(b). The current efficiency (cd A⁻¹) and luminous (or power) efficiency (lm W⁻¹) are plotted as a function of luminance in the range of several hundred cd m⁻², which covers most types of electronic displays. The OLED registered a highest current efficiency of 47 cd A⁻¹ and highest power efficiency of 20 lm W⁻¹. The current and power efficiency are fairly constant for the brightness range of 100–1000 cd m⁻², corresponding to a current range of approximately 10–100 μ A and a voltage range of 4–8 V.

By comparison, the highest previously reported [10] luminance and efficiencies of OLEDs fabricated on paper (using fluorescent Alq3 emission) were 620 cd m⁻², ~1 cd A⁻¹ and 0.5 lm W⁻¹. There are several factors which may have combined to produce this significant improvement over previous OLEDs fabricated on transparent cellulose: (1) use of a phosphorescent [Ir(PPY)3] versus a fluorescent [Alq3] emitter previously used [10], which typically results in a ~4-fold increase; improved design (optimization of layer thicknesses); (2) a smoother cellulose surface $-\sim4$ nm in this work as S Purandare et al



Figure 9. Photographs of OLEDs operating on cellulose substrates rolled into a complete cylindrical structure indicating flexibility and transparency.

compared to >30 nm [10] and >200 nm [21]; (3) use of PEDOT to enhance hole injection into the device.

Photos of OLEDs in operation while the substrate was flexed into a 360° roll with a 1.5 mm radius of curvature are shown in figure 9, illustrating the OLED flexibility and transparency of the substrate. No change in brightness was noticeable during the flexing and the device performed quite well after the flexing. Since the cellulose substrate is transparent, an OLED-based array can also be used as a decorative art capable of showing the background information.

4. Summary and conclusions

A new generation of flexible OLEDs with phosphorescent emitters fabricated on transparent paper has been reported. The results presented here represent a leap in luminance (10000 cd m⁻²) and emission efficiency (\sim 50 cd A⁻¹ and 20 lm W⁻¹) of 1–2 orders of magnitude over previously reported OLEDs on paper. The level of performance achieved indicates the potential for this low-cost and environmentally friendly approach to OLED fabrication to become commercially relevant in the near future.

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