Porous cellulose paper as a light out coupling medium for organic light-emitting diodes

Jeong Hun Lee, Sohyeon Kang, Nae-Man Park, Jin-Wook Shin, Chul Woong Joo, Jonghee Lee, Seong-Deok Ahn, Seung-Youl Kang and Jaehyun Moon

Flexible Device Research Group, Electronics and Telecommunications Research Institute (ETRI), Daejeon, Republic of Korea; Department of Advanced Device Engineering, University of Science and Technology, Daejeon, Republic of Korea; Department of Creative Convergence Engineering, Hanbat National University, Daejeon, Republic of Korea

ABSTRACT
Porous nanocellulose paper was fabricated and applied as a light outcoupling medium. The nanocellulose papers were prepared using cellulose powder and a high-pressure homogenizing process. The translucent nanocellulose paper had high total transmittance and haze, and gave off diffuse light when the incident light passes through it. Through the application of the fabricated nanocellulose paper on the external surfaces of organic light-emitting diode (OLED) devices, it was possible not only to enhance the luminous efficiency but also to widen the angular light distribution. As this paper is intrinsically flexible, it can be applied to various forms of light sources bearing curvature.

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1. Introduction
There are various materials and structures in nature that may be used for engineering purposes. One typical example is cellulose, whose chemical formula is \((\text{C}_6\text{H}_{10}\text{O}_5)_n\). Cellulose exists abundantly in various structural forms of plants. In this work, the use of a porous cellulose film as a light outcoupling medium was explored.

Cellulose paper can be readily produced using cellulose/water slurry and the high-pressure extraction method [1]. In this work, cellulose paper consisting of nanometric fibrillated cellulose was investigated [2]. Nanocellulose does not require complicated patterning and can be mass-produced using relatively inexpensive materials. As it consists of nanometer-scale-diameter fibers, it is intrinsically porous. Thanks also to this structural feature, cellulose paper is naturally translucent and can scatter the incoming light. As the scattering occurs at the interfaces between the individual cellulose fibers and air, it can be used for external-light extraction. Such property can be useful for altering the optical traveling path of the air/substrate interface, and can help extract light, which is confined by the total internal reflection.

In this work, organic light-emitting diodes (OLEDs) were used as the light source for examining the light outcoupling capacity of cellulose paper. The planar geometry of OLEDs is an appropriate platform for films like cellulose paper [3]. Various light extraction methods have been suggested to enhance the coupling efficiency of OLEDs [4, 5]. The external quantum efficiency of OLED devices is a product of two terms: internal quantum efficiency and outcoupling efficiency. The first term can be determined by the ratio of the number of injected electron-hole pairs to the number of generated photons in the organic layer. Nearly 100% internal quantum efficiency has been achieved with phosphorescent materials [6], but the outcoupling efficiency is typically low (about 20%). The light loss is primarily due to the total internal reflection, wave-guided loss, and surface plasmon polaritons (SPPs) [7].

For extracting the light trapped by the waveguide or substrate mode, many approaches have been proposed: (1) modification of the substrate surface by applying various formed microlens arrays [8–11], sand-blasting [12], texturing the meshed surface [13], or using a diffractive film [14]; (2) using a periodic Bragg diffraction grating structure [15] or a quasi-periodic buckling structure around the anode for reducing the surface plasmon (SP) effect [16]; (3) introduction of a microcavity structure [17]; and (4) insertion of a low-index medium in the organic layer or between the anode and the substrate [18, 19]. Employing a scattering medium [20–22] in OLED devices is an effective light extraction method.
because it can minimize the changes in the light pattern and color over the viewing angle with the Lambertian distribution. In this work, translucent nanocellulose paper was applied as a scattering medium in an OLED device, and the luminous efficiency was enhanced.

2. Experiments

To fabricate cellulose paper, commercially available cellulose powder, potassium hydroxide (KOH, Sigma Aldrich), and sodium chloride (NaCl, Sigma Aldrich) were used. All the purchased materials were used without further purification. Cellulose powder was dispersed in deionized (DI) water to form a 1 wt% solution. To remove the lignin and hemicelluloses, potassium hydroxide (2 wt%) and sodium chloride (2 wt%) were added to the cellulose solution, and the solution was chemically treated at 65°C for 2 hours. After treatment, the solution was rinsed with DI water to neutralize it. A centrifuge (2500 rpm for 3 minutes) was used to collect the residues on the bottom. The residues were passed through a high-pressure homogenizer (1,500 bar, Nano Disperser, Suflux) 10 times. This process yields nanofibrillated celluloses with 10–20 nm diameters and 1–2 μm lengths [23].

The transmittances and haze of the nanofibrillated cellulose were measured using a UV-visible spectrophotometer (100 Conc, Cary) and a haze meter (Haze-Gard Plus), respectively. For observing the surface morphology, a scanning electron microscope (SEM, FEI Sirion) was used.

Bottom-emission-type phosphorescent green OLEDs with a $10 \times 7 \text{mm}^2$ emission area were fabricated to evaluate nanocellulose paper with a light extraction function. The anode and cathode consisted of indium tin oxide (ITO, 70 nm) and LiF/Al (100 nm), respectively. On the ITO/glass substrate, the following were deposited sequentially via thermal evaporation. The charge generation and hole transport layers were 1,4,5,8, 9,11-hexaazatriphenylenehexacarbonitrile (Hat-CN) and 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane (TAPC), respectively. A Hat-CN (5 nm)/TAPC (30 nm)/ Hat-CN (10 nm)/TAPC (30 nm)/Hat-CN (10 nm)/TAPC (30 nm) alternating structure was used to stabilize the hole transport towards the emissive layer. The emitter host and dopant were 2,6-bis(3-(carbazol-9-yl)phenyl)pyridine (DCzPPy) and Tris(2-phenylpyridine)iridium (Ir(ppy) III), respectively. The emissive layer was 20 nm thick, and the dopant concentration was 7%. 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB) was used as the electron transport layer, with a 30 nm thickness. The entire deposition process was performed under below $6.66 \times 10^{-5}$ Pa base pressure. The OLEDs were glass-encapsulated in a N$_2$-filled glove box to prevent device degradation.

The fabricated nanocellulose paper was attached to the glass surface using an index-matching oil (Cargille, Series A-1806X). The refractive index of the oil was 1.49 at a 580 nm wavelength.

The electroluminescence (EL) spectra were measured with a goniometer-equipped spectroradiometer (CS-2000, Minolta). The current density-voltage ($J-V$) characteristics of the OLEDs were measured with a current/voltage source meter (Keithley 238).

3. Results and discussion

Figure 1 shows the actual images of the nanocellulose paper. Apparently, the paper bears high haze (Figure 1(a)). The apparent haze strongly indicates the paper's...
capacity to convert the straight concentrated incident light into a diffuse-type light. The diameter of the nanocellulose paper was 50 nm, but this is the facility limit. Theoretically, a very large nanocellulose paper can be produced. Figure 1(b) shows a schematic of the nanocellulose-paper-attached bottom-emission-type OLED. Light is emitted in the glass direction and passes through the nanocellulose paper.

Figure 2 shows the SEM images of the nanocellulose paper. The surface is fairly rough, with no apparent periodic structure. Close examination will reveal that the paper has randomly woven nanofibrous features. Papers with a high density are generally opaque, but as the paper-constituting fibers go down to the nanoscale, it is very difficult to obtain a fully compact structure [24]. Papers with a low density, on the other hand, have many air pores, making them translucent (Figure 1(a)). The refractive index mismatch between the components or structures in the scattering material affects the optical properties, such as the transmittance and reflectivity. Due to refractive index mismatch, many scattering phenomena occur and contribute to scattering. When paper fibers are made in nanoscale, the refractive index mismatch and back-scattering effect are largely reduced [25]. To be specific, the interfaces between the individual fibers and air act as light scattering sources. As there is no periodicity in the distribution of the aforementioned interfaces, the incident light is turned into diffuse light. The random distribution of nanofibers induces the roughness of the film surface, which contributes to forward scattering and diffuse transmission [26,27]. The microstructure of the nanocellulose fiber is filling without cavities, which prevents backward scattering and reflection [28]. These characteristics are potentially useful not only for enhancing the OLED emission but also for widening the angular light distribution.

Figure 3 shows the measured transmittance and haze of the fabricated nanocellulose paper as a function of the wavelength in the whole visible range. The total
transmittance is approximately 90% in the whole visible range (Figure 3(a)). This indicates that much of the incident light passes through the paper, with marginal internal light trapping. Due to the physical presence of numerous cellulose fiber-pore interfaces, the diffuse transmittance was as high as 83% in the whole visible range. The reported refractive index \((n)\) of cellulose \(((C_6H_{10}O_5)_n)\) is 1.47 in the visible range [29]. As the refractive index of air is 1, the high diffuse transmittance is thought to have originated from the optical contrast between the cellulose fiber and the air pore. The direct transmittance was as low as 4%.

Figure 3(b) shows the haze of the paper. Haze is calculated as the ratio of the diffuse transmittance to the total transmittance. It is approximately 93% in the whole visible range. The inset of Figure 3(b) shows the apparent light scattering effect of nanocellulose paper. A conventional white-light source of light-emitting diodes was used. When light passes through the paper, instead of displaying a sharp light dot, a broad circular shape appears. In summary, nanocellulose paper has high total transmittance and haze. The wavelength-independent transmittance and haze indicate the paper's negligible optical dispersion property.

Figure 4(a) shows the current density-voltage-luminance \((J\text{-}V\text{-}L)\) characteristics of the OLED with and without nanocellulose paper applied to the external surface of the glass. The emission area was \(7 \times 10^{-2} \text{mm}^2\). As expected, the presence of nanocellulose paper did not alter the \(J\text{-}V\) characteristics of the OLEDs. The \(L\) of the OLEDs with nanocellulose paper measured in the normal incidence direction \(\theta = 0^\circ\) was higher than that in the planar case, indicating light extraction due to the nanocellulose paper. To quantify the nanocellulose paper capacity in terms of the external quantum efficiency (EQE, \%) and power efficacy (PE, \text{lm/W}), an integrating sphere was used (Figure 4(b,c)). The EQE and PE values of the nanocellulose-paper-attached OLED were higher in the whole \(J\) range that was considered. High light extraction was observed in the lower \(J\) range. At the \(J\) of \(10^{-3} \text{A/cm}^2\), the EQE values of the planar and nanocellulose-paper-attached OLEDs were 20.5 and 17.3\%, respectively. The PE values were 43.1 and 37.7 \text{lm/W}. Thus, the attachment of nanocellulose paper made it possible to increase the EQE and PE values by 21 and 14.3\%, respectively. This result is equivalent to the decrease of the optical loss or wave guiding at the glass-air interface.
Figure 4(d) shows the angular luminance distributions of the planar and nanocellulose-paper-attached OLEDs. In the normal incidence direction ($\theta = 0^\circ$), the difference in $L$ is not significant. As the viewing angle increases, however, the $L$ difference becomes noticeable. The $L$ values of the nanocellulose-paper-attached OLEDs were higher in all directions, but the highest enhancement was achieved at $\theta = 50^\circ$. Due to the nanocellulose paper capacity of outcoupling the confined light at the glass-air interface, the angular luminance distribution was widened and expanded.

Figure 5 shows the normalized angular EL spectra of the OLEDs. Due to the fine thickness of a few hundred nanometers and the stack structure, the microcavity effect is intrinsically present in OLEDs [30,31]. The presence of a microcavity in the EL spectra induces angular dependency, which demerits the emission quality. In the planar case, the angular dependency can be noticed. As the viewing angle changes, the width of the EL spectra becomes bigger, and an additional shoulder develops at a higher angle of around 550 nm (Figure 5(a)). The aforementioned effects of the attachment of nanocellulose paper are significantly reduced. Compared to the planar OLED, the OLED equipped with nanocellulose paper showed much lower angular dependency and marginal change in the EL spectra line shape (Figure 5(b)). Thus, the perceived emission of the OLED equipped with nanocellulose paper is expected to offer uniform emission over a wide range of viewing angles.

4. Conclusion

Nanocellulose paper was fabricated using cellulose powder and a high-pressure homogenizing process. The paper was translucent and turned the straight incident light into diffuse light. This paper was applied to organic light-emitting diodes (OLEDs) to extract the light confined at the glass-air interface. Through the use of this paper alone, it became possible to enhance the external quantum efficiency (EQE) by 20.5%, and to suppress the detrimental angular dependency of the electroluminescence (EL) spectra. Due to the simple and inexpensive fabrication of the paper, the proposed approach offers a highly competitive method for fabricating light extraction structures. In addition, due to the paper’s lightness and flexibility, it can be applied to light sources with arbitrary shapes without the concern of adding to the weight.

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Notes on contributors

Jeong Hun Lee received his B.S. and M.S. Polymer Science and Engineering degrees from Chungnam National University in 2015 and 2017, respectively. He joined Electronics Telecommunications Research Institute (ETRI) in Daejeon, South Korea in 2018. His current research interests include light extraction
technologies for organic light-emitting diode (OLED) devices and biometric sensors.

**Sohyeon Kang** received her B.S. and M.S. Material Science and Engineering degrees from Chungnam National University in 2015 and 2017, respectively. She joined ETRI in 2017 and worked on light extraction technologies for OLED devices.

**Nae-Man Park** received his B.S. and M.S. Physics degrees from Hanyang University, Seoul, South Korea in 1995 and 1997, respectively. He then shifted his major to engineering and received a Ph.D. Materials Science and Engineering degree from Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea in 2002. Since then, he has been a principal researcher at ETRI. His current research interests include the nanocellulose material and its applications.

**Chul Woong Joo** received his B.S. and M.S. degrees in polymer science and engineering of organic electronics devices from Dankook University in 2008 and 2010, respectively. He joined ETRI in 2011. His current research interests include device architectures in OLED devices, printed electronics, and flexible and near-infrared optoelectronics.

**Jin-Wook Shin** received his B.S. and M.S. from Myongji University and Kwangwoon University, respectively. In 2018, he received his Ph.D from Tohoku University in Japan. He joined ETRI, Daejeon, Rep. of Korea, in 2009. His current research interests include light extraction technologies and graphene applications for organic light-emitting devices.

**Jonghee Lee** received his B.S., M.S., and Ph.D. Chemistry degrees from Korea Advanced Institute of Science and Technology (KAIST), Daejeon, South Korea in 2002, 2004, and 2007, respectively. He joined ETRI in 2007 and worked on white organic light-emitting diodes (WOLEDs) for display and lighting applications. Then he moved to Institut für Angewandte Photophysik (IAPP, Prof. Karl Leo’s group) at Technische Universität Dresden in Germany in 2010, as a post-doc. After 2 years (2012), he joined ETRI again and has since worked on the new-concept display mode as well as light extraction techniques for OLEDs.

**Seong-Deok Ahn** received his B.S. Chemistry degree from Hanyang University in 1991, and his M.S. and Ph.D. Chemistry degrees from KAIST in 1994 and 2000, respectively. In 2000, he joined ETRI. His research has focused on skin electronics, biometric recognition devices, and flexible displays.

**Seung-Youl Kang** received his B.S. Physics degree from Seoul National University, Seoul, South Korea in 1995, and his Ph.D. Materials Science and Engineering degree from Carnegie Mellon University, Pittsburgh, Pennsylvania, USA in 2003. From 2003 to 2004, he was a postdoctoral associate at Max-Planck Institute, Stuttgart, Germany. He joined ETRI in 2004. His current research interests include flexible electronics, functional nanomaterials, and OLEDs.

**Jaehyun Moon** received his B.S. degree from Korea University, Seoul, South Korea in 1995, and his Ph.D. Materials Science and Engineering degree from Carnegie Mellon University, Pittsburgh, Pennsylvania, USA in 2003. From 2003 to 2004, he was a postdoctoral associate at Max-Planck Institute, Stuttgart, Germany. He joined ETRI in 2004. His current research interests include flexible electronics, functional nanomaterials, and OLEDs.

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