Cellulose Nanocrystal: Polymer Hybrid Optical Diffusers for Index-matching-free Light Management in Optoelectronic Devices

Seyed Milad Mahpeykar, Yongbiao Zhao, Xiyen Li, Zhenyu Yang, Qiwei Xu, Zheng-Hong Lu, Edward H. Sargent, and Xihua Wang

Version Post-print/accepted manuscript


Publisher’s Statement This is the peer reviewed version of the following article: S. M. Mahpeykar, Y. Zhao, X. Li, Z. Yang, Q. Xu, Z.-H. Lu, E. H. Sargent, X. Wang, Advanced Optical Materials 2017, 5, 1700430, which has been published in final form at https://doi.org/10.1002/adom.201700430. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Self-Archiving.

How to cite TSpace items

Always cite the published version, so the author(s) will receive recognition through services that track citation counts, e.g. Scopus. If you need to cite the page number of the author manuscript from TSpace because you cannot access the published version, then cite the TSpace version in addition to the published version using the permanent URI (handle) found on the record page.

This article was made openly accessible by U of T Faculty. Please tell us how this access benefits you. Your story matters.
Cellulose Nanocrystal:Polymer Hybrid Optical Diffusers for Index-matching-free Light Management in Optoelectronic Devices

Seyed Milad Mahpeykar, Yongbiao Zhao, Xiyuan Li, Zhenyu Yang, Qiwei Xu, Zheng-Hong Lu, Edward H. Sargent,* and Xihua Wang*

S. M. Mahpeykar, Q. Xu, Prof. X. Wang
Department of Electrical and Computer Engineering, University of Alberta, Edmonton, Alberta T6G 2V4, Canada
E-mail: xihua@ualberta.ca
Dr. Y. Zhao, Prof. Z.-H. Lu
Department of Materials Science and Engineering, University of Toronto, 184 College Street, Toronto, Ontario M5S 3E4, Canada
Dr. X. Li, Dr. Z. Yang, Prof. E. H. Sargent
Department of Electrical and Computer Engineering, University of Toronto, 35 St. George Street, Toronto, Ontario M5S 1A4, Canada
E-mail: ted.sargent@utoronto.ca

Keywords: cellulose nanocrystals, polymers, optical diffusers, light scattering, optoelectronics

Cellulose nanofibers have recently been exploited for fabrication of optical diffusers due to their excellent light-diffusive behavior. However, for application of light management in optoelectronic devices, the need for an index-matching oil and lack of physical durability due to the usage of wood fibers as the matrix material is a major obstacle toward commercialization of cellulose-based optical diffusers. Here, a volumetric optical diffuser based on cellulose nanocrystals (CNCs) embedded in polydimethylsiloxane (PDMS) matrix, or CNP (cellulose nanocrystal:polymer) hybrid optical diffuser is reported. Replacing cellulose nanofibers to nanocrystals with decreased length enables easy processing of nanocrystals in various matrix materials. The proposed device is a better choice for light management in optoelectronics due to its high tolerance of physical stress and the lack of requirement for index-matching in light coupling. These benefits arise from the unique surface properties, mechanical flexibility and optical transparency offered by PDMS as the matrix material. In its optimized form, a CNP hybrid optical diffuser is shown to achieve higher haze values than other cellulose-based diffusers (up to 85%) while maintaining a high
degree of transparency (~85%). After integration with optoelectronic devices, CNP hybrid optical diffusers are proven to be more efficient in light management than previously reported cellulose nanofiber/wood pulp optical diffusers, without employment of any index-matching technique.

1. Introduction

Optical diffusers provide soft light with uniform spatial and directional intensity distribution. They have been extensively exploited for the purpose of uniform backlighting, brightness enhancement, efficiency improvement and increased sensitivity in liquid crystal displays (LCDs),[1-3] light-emitting diodes (LEDs),[4-6] solar cells,[7-9] and photodetectors,[10-12] all via excellent light scattering properties of optical diffusers.

As a non-toxic and biodegradable material, cellulose nanocrystals (CNCs) are environmentally friendly. They are directly extracted from natural resources such as wood and other fiber supplies available in plants. They offer desirable bulk and nanoscale properties (e.g. high surface area for interaction with surrounding species)[13] that make them suited for use as substrates in devices such as sensors,[14] solar cells,[15] LEDs,[16] and transistors.[17] In addition, recently, cellulose nanofiber-based films and papers have attracted attention for their light scattering capabilities.[9,18,19]

Here, we propose, fabricate and characterize a new class of optical diffusers based on CNP hybrid films. Our hybrid diffuser achieves high haze values (up to 85%), which is significantly higher than cellulose nanofiber/wood pulp diffusers,[9,19] while maintaining a high degree of transparency (~85%). In addition, unlike previously reported cellulose nanofiber/wood pulp optical diffusers which require an additional index-matching layer between the diffuser and the device for efficient light coupling,[9,19] no index-matching is required for the diffuser here due to the hydrophobic surfaces offered by PDMS that allows direct attachment onto device substrates.
Through extensive characterization including spectrophotometry, laser beam delivery and angular power distribution, we prove that CNCs are an excellent filler material candidate in a volumetric optical diffuser thanks to their rod-like shape and wavelength-scale size in the order of a couple of hundreds of nanometers,\(^{(20)}\) which offer excellent broadband light softening in both the visible and near-infrared regime. Where most volumetric diffusers require a filler material with concentrations up to 15 wt% for efficient light scattering,\(^{(21,22)}\) CNP hybrid diffusers offer highly efficient light diffusion at CNC concentrations as low as 1 wt%. We further leverage the light management capabilities of CNP hybrid optical diffusers to demonstrate their potential in light absorption enhancement in semiconductor thin-films and light extraction improvement in organic LEDs.

2. Results and Discussion

2.1. Optical Diffusion, Transmission and Haze Analysis

**Figure 1a** shows a photograph of CNP hybrid optical diffusers with different CNC concentrations (from left to right: 0.5, 1, 2, and 4 wt.%). As is obvious from the appearance of the samples in the picture, a change in transparency and light diffusion behavior of the samples is observed with an increase in CNC concentration. The higher concentration of CNC provides lower transparency while offering better light diffusion performance. This is in agreement with other types of volumetric diffusers as it is known that the density of the filler material can directly affect the transparency and the haze (the percentage of total transmitted light that is diffusely scattered) of the diffuser.\(^{(21-23)}\) Additionally, it was observed that the flexibility and mechanical properties of PDMS enable the CNP diffusers to withstand harsh physical stresses such as stretch, twisting and bending (**figure 1b**) without any change in their properties, a feature that is not offered by cellulose nanofiber/wood pulp optical diffusers.\(^{[9,19]}\)

In order to optimize the amount of filler material for the hybrid diffuser, we measured the transmittance and haze of various CNP films with different CNC concentrations as a function of wavelength for the visible and near-infrared regions as is depicted in **figure 2**.
Transmittance and haze of a commercially available diffuser (labelled as market diffuser) from a solar simulator system were also measured for comparison. In the CNP device, both high transmittance and high haze values are achievable across a wide range of wavelengths (400-1100 nm) with the proposed diffuser structure, which can be attributed to the difference in refractive index of cellulose (~1.6)\textsuperscript{24} and PDMS (~1.4).\textsuperscript{25} This leads to Mie scattering\textsuperscript{26} which occurs when the size of the scattering particle is slightly smaller than or in the same range as the wavelength of light. No significant absorption was observed from the samples. Indeed, it is known that PDMS and CNCs have negligible absorption in the visible and near-infrared range of light. Compared to other cases, a 1 wt.% concentration for CNC in PDMS provides a high level of haze (more than 90%) while maintaining a high level of transparency at the same time. Furthermore, it provides performance comparable to that of a commercial diffuser. In all the other cases, either the transparency or the haze level are traded. For instance, in the case of a 4 wt.% CNC concentration, despite the fact that almost all light that is passing through the sample is being diffused (~100% haze), the transmittance is significantly lower than the acceptable level for an optical diffuser. In addition, from the results obtained, it can be concluded that the performance of CNP optical diffusers is almost independent of the wavelength of incident light which is a direct consequence of the randomness of their light scattering structure. The slightly better haze observed at longer wavelengths further affirms the notion that Mie scattering,\textsuperscript{26} which is more efficient for longer wavelengths of light, is the main contributor to light diffusion in CNP hybrid diffusers. Optical diffusion of a 635 nm laser beam by CNP hybrid optical diffusers with different concentrations of CNC and their comparison with a market diffuser are demonstrated in figure 3. The addition of CNC filler to PDMS as bulk material produces the observed light scattering, since no noticeable change on the laser beam was observed when passing through a PDMS film with no CNC addition (i.e. 0 wt.%). Better light softening performance and wider scattering angles were observed with the increase in CNP ratio, in agreement with the
observations from wavelength-dependent haze measurements in figure 2. The sample with 1 wt.% CNC offers almost the same performance as the market diffuser while providing wider scattering angles. This is attributed to the superior light scattering capabilities of CNCs as the filler material.

**Figure 4a-d** illustrate the angular intensity distribution of a 635 nm laser beam after passing through a CNP hybrid optical diffuser with different concentrations of CNC. As the concentration of filler material increases, the light scattering angles are wider and the intensity distribution becomes more uniform, consistent with the visual observations of light diffusion from figure 3. In the case of the sample with 4 wt.% CNC concentration, the intensity distribution is very close to an ideal diffuse surface with Lambertian distribution (dashed line). This emphasizes the light diffusion ability of the hybrid diffuser being able to offer a Lambertian-like distribution with only 4 wt.% concentration of the filler material.

Since it is expected from an optical diffuser to maintain its performance at different incident light angles, the dependence of the performance of CNP hybrid optical diffusers on the incident light angle for different concentrations of CNC was investigated as shown in **figure 4e**. It is clear that at oblique angles, CNP hybrid optical diffusers offer even higher performance than a normal light incidence. The incident light has to travel a longer path inside the light scattering medium at oblique angles and, in this case, the chance of light being scattered increases due to the high density of scattering sites created by CNCs embedded into PDMS matrix. The maintenance of light diffusion efficiency at different incident angles suggests that the CNP hybrid diffusers can be useful in ambient light harvesting applications since in the case of ambient light, the incident direction can be randomly oriented most of the times.

In a volumetric diffuser, because the light scattering material is distributed inside the bulk material, the thickness of the diffuser can play an important role in light management performance. Therefore, the thickness optimization of CNP hybrid films for the desired
transparency and haze is an important step in the design of an optimally performing optical diffuser. Based on the results in figure 2, it was concluded that a 1 wt.% concentration of CNC offers an optimal combination of transparency and haze. Therefore, this configuration was used for the thickness optimization. As shown in figure S1 (see Supporting Information), although thicker diffuser film provides a higher degree of haze due to the longer light traveling path created inside the scattering medium, the transmittance of the diffuser is reduced. It is therefore reasonable to infer that a 1 mm thick diffuser has optimum transmittance and haze values (~85%) for optoelectronic applications, which is a better offering than that of cellulose nanofiber/wood pulp optical diffusers. [9,19]

2.2. Index-matching-free Light Management in Optoelectronic Devices

Due to the excellent light scattering capabilities offered by CNP hybrid optical diffusers, one potential application of the proposed optical diffuser is the enhancement of light extraction properties of LEDs. LEDs are known to suffer from light trapping inside the substrate due to total internal reflection contributed by the substrate/air refractive index contrast.[27] The proposed optical diffuser can be exploited to enhance light extraction efficiency in an organic LED by being directly attached to the glass substrate of the device. This can provide local scattering sites and refractive index change to suppress part of the total internal reflection at the substrate/air interface as shown in figure 5a. Unlike reported cellulose-based optical diffusers,[9,19] no index-matching layer between the diffuser and the device is required in this study due to the strong adhesion of PDMS film onto device substrates that leaves no air gap in between.

Figure 5b and 5c show the performance of the LEDs as a function of applied bias voltage without and with diffusers. The luminance is substantially improved when the optical diffuser is attached, although devices show the same current density-voltage (J-V) behavior. This confirms that the integration of optical diffuser into the LED can improve the light extraction capability. A deeper look into the brightness of the devices with optical diffusers having
various concentrations of CNC reveals that a 1 wt.% CNP hybrid optical diffuser provides the highest light extraction performance. This can be attributed to its optimized transparency and haze. It was found that a 0.5 wt.% concentration makes almost no difference in light extraction from a LED possibly because of its low level of haze and a 4 wt.% concentration can result in lower luminance than the control device without a diffuser probably due to its lackluster degree of transparency.

The external quantum efficiency (EQE) and power efficiency of the device as a function of luminance without diffuser and with diffusers having different concentrations of CNC is illustrated in figure 5d and S2, respectively. The results are consistent with the observations in figure 5c: 1 and 2 wt.% CNP hybrid diffusers offer almost the same light extraction enhancement while a 0.5 wt.% device results in fairly the same performance as the control device with no diffuser and the 4 wt.% device provides a lower performance than the control device. Thanks to its superior light extraction capabilities, the proposed CNP hybrid optical diffuser is able to enhance the EQE of the device by about 15% on average which showcases its great potential for light extraction enhancement and superiority to cellulose nanofiber/wood pulp optical diffusers. These hybrid films are applicable to any previously fabricated LED device since the light extraction structure is not part of the device structure and can easily be laminated on any device and could be replaced in case of degradation.

The application of CNP hybrid optical diffusers can be extended to the enhancement of light absorption inside the active layer of thin-film solar cells and photodetectors. To demonstrate the capability of light absorption enhancement, CNP hybrid optical diffusers were integrated with a 200 μm thick silicon slab as illustrated in figure S3a (see Supporting Information).

Figure S3b depicts the amount of absorption in the silicon slab versus incident light wavelength without diffuser and with diffusers having different concentrations of CNC. The absorption in the silicon slab can be significantly enhanced with the addition of a CNP hybrid optical diffuser. The optical diffuser extends the light path length inside the slab, and this
increases the chance for light absorption. In addition, a portion of the observed absorption enhancement could be the result of lower light reflection from the surface of silicon since the optical diffuser can reduce the refractive index contrast between air (1) and the silicon slab (~3) by its intermediate refractive index (~1.5). However, the high concentrations of CNC are not as effective in enhancing the absorption due to the reduction in transmittance of the diffuser at high concentrations as shown in figure 2. For example, a lower transmittance is observed from the 2 wt.% CNC sample although it offers higher haze compared to its 1 wt.% counterpart which can be considered the reason behind observing similar light absorption enhancement in silicon slab for both concentrations (figure S3). From these results, we conclude that 1 wt.% for CNC is an optimized concentration for light management applications.

3. Conclusion

In summary, we reported on a volumetric optical diffuser based on CNP hybrid materials. By offering a simple and low-cost fabrication process as well as compatibility with large-scale production using CNC as filler, the proposed optical diffuser is well chosen to integrate into optoelectronic devices for light management especially due to its insensitivity to physical damage at its surface and the lack of requirement for an index-matching layer between the diffuser and the optoelectronic device thanks to the unique surface properties, mechanical flexibility and optical transparency offered by PDMS as the bulk material. This CNP diffuser provides excellent capabilities for broadband light softening in both visible and near-infrared regime and highly efficient light diffusion at concentrations as low as 1 wt%. It was shown that, in its optimized form, a CNP hybrid optical diffuser is capable of achieving super-high haze values (up to 85%) while maintaining a high degree of transparency (~85%). We leveraged the light management capabilities of CNP hybrid optical diffusers to demonstrate their potential for light absorption enhancement in thin-film silicon solar cells and light extraction improvement in OLEDs.
4. Experimental Section

*Synthesis of cellulose nanocrystals:* Acid hydrolysis technique was used to synthesize CNCs.\[^{28}\] In brief, the process was performed in two Pfaudler 50 gallon acid-resistant glass-lined reactors with a steam-heated jacket. Sulfuric acid with the concentration of 64% was used with an initial reaction temperature of 45 °C. This was followed by a centrifuge step using a GEA Westfalia SC-35 separator. The next step in the process was a microfiltration step performed by a GEA filtration-ultrafiltration plant. The wet CNC powders obtained from this step were then dried in an SPX-Anhydro Model 400 spray dryer plant under an inlet temperature of 220 °C and an outlet temperature of 85 °C.

*Fabrication of CNP hybrid optical diffusers:* CNP hybrid optical diffusers with different concentrations of CNC were fabricated as follows. First, PDMS precursor was made by mixing a silicone elastomer with curing agent from a Sylgard 184 kit (Dow Corning) in 10:1 ratio. Different amounts of CNC powder (0.5-4 wt%) were then added to the PDMS precursor and vigorously mixed together using a combination of manual stirring and a vortex mixer to ensure uniform distribution of CNCs inside the mixture. The CNP mixture was then degassed in a vacuum desiccator for 60 min before being poured into a polystyrene petri dish. The resulting film was then left on a pre-leveled platform at room temperature overnight to form a uniformly thick film and then was cured on a hot plate at 80 °C for 2h. The thickness of the film was controlled by carefully adjusting the amount of volume for the mixture that was being poured into the petri dish. After the curing step, the film could easily be peeled off due to the hydrophobicity of polystyrene.

*Characterizations:* Transmittance and haze results were obtained using the 150 mm integrating sphere module of a Perkin-Elmer Lambda 1050 UV–Vis–NIR Spectrophotometer. A custom-made fixture was used to hold the sample at the sample beam entrance port of the sphere. Angle-dependent specular transmissions were measured using the same setup with the sample being located on a rotating stage. For transmittance measurement, all the ports of the
integrating sphere except the reference and sample beam entrance ports were kept closed. In the case of haze, the back port of the integrating sphere was opened to prevent the specular transmission from the sample to be captured by the detector.

Visual demonstrations of optical diffusion by samples were performed using a 635 nm laser diode (Newport) as the light source with the sample covering the output window of the laser diode. The light passing through the diffuser samples was projected on a white screen located in front of the laser diode. The angular intensity distribution of the laser beam was acquired by a Thorlabs power meter situated in the same horizontal plane as the center of the laser beam. The angular position of the power meter was then changed using a custom-built fixture to measure the light intensity at different angular positions with respect to the center of the laser beam.

The effect of CNP hybrid optical diffusers on light absorption enhancement in silicon was investigated using a 200 μm thick silicon slab with optical diffuser samples being directly attached to the silicon surface. The absorption measurement was accomplished by putting the sample at the center of the integrating sphere of a Perkin-Elmer Lambda 1050 UV–Vis–NIR Spectrophotometer using a center mount sample holder.

In order to test the application of CNP hybrid optical diffusers on light extraction improvement in organic LEDs, diffuser samples were directly attached to the back side of the glass substrate of the device fabricated according to a published procedure. The OLED structure was formed of ITO (Indium-doped Tin Oxide) / NPB (N,N′-di(naphth-2-yl)-N,N′-diphenyl-benzidine) (70 nm) / Alq3 (tris-(8-hydroxyquinoline)) (60 nm) / LiF (Lithium fluoride) (1 nm) / Al (Aluminum) (100 nm). Quantum efficiency, luminance, the power efficiency and current-voltage characteristics of the OLED device were measured using a HP 4110B source-meter, a calibrated luminance meter (Konica Minolta LS-110) and an
Ocean Optics USB2000 spectrophotometer with an integrating sphere in the air and at room temperature.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

This work was supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) Discovery Grant and the Alberta Innovates-Bio Solutions (AI-Bio). The authors would like to thank Mike Xia of the National Institute for Nanotechnology for providing access and technical support for spectrophotometry. We also would like to acknowledge CMC Microsystems for the provision of CAD products and services through Canada’s National Design Network. S.M.M. acknowledges the Alberta Innovates - Technology Futures Graduate Student Scholarship.

Received: ((will be filled in by the editorial staff))
Revised: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))

**References**


Figure 1. (a) Photograph of CNP hybrid optical diffusers with different CNC concentrations (from left to right: 0.5, 1, 2, and 4 wt.%). The change in transparency and light diffusion behavior of the samples with an increase in CNC concentration is obvious from the picture. (The scale bar is 1 cm) (b) Physical durability of the diffusers allows application of stretch, twisting and bending without any effect on their optical properties.
Figure 2. Transmittance and haze of CNP hybrid optical diffusers with different concentrations (wt.%) of CNC as a function of wavelength. High transmittance and haze values are achievable across a wide range of wavelengths with the proposed diffuser structure. Transmittance and haze of a commercially available diffuser are also included for comparison.

Figure 3. Optical diffusion of a 635 nm laser beam by CNP hybrid optical diffusers with different concentrations (wt.%) of CNC and comparison with a market diffuser.

Figure 4. (a-d) Angular intensity distribution of a 635 nm laser beam after passing through a CNP hybrid optical diffuser with different concentrations of CNC: (a) 0.5, (b) 1, (c) 2, and (d)
4 wt.%. As the concentration of CNC increases, the distribution becomes more uniform. The sample with 4 wt.% concentration is very close to an ideal diffuse surface with Lambertian distribution (dashed line). (e) Dependence of specular transmission of CNP hybrid optical diffusers on the incident light angle for different concentrations of CNC. At oblique angles, more light diffusion can be observed from the diffusers.

Figure 5. Light extraction enhancement in LEDs using CNP hybrid optical diffusers. (a) Schematic of the device structure with the integration of hybrid optical diffuser. (b) J-V curves of the device without and with diffusers. (c) Device brightness as a function of applied bias voltage without and with diffusers. (d) External quantum efficiency of the device without and with diffusers having different concentrations of CNC. The diffuser with 1% wt. CNC has the highest enhancement in the efficiency of the device.
Light management is an essential necessity for emerging optoelectronic devices with low efficiency. A new class of optical diffuser is reported by leveraging cellulose nanocrystals embedded in a polymer matrix. Taking advantage of widely used and cheap materials together with facile fabrication, the proposed optical diffuser provides efficient light management for common optoelectronic devices without any third-party index-matching requirement.

Seyed Milad Mahpeykar, Yongbiao Zhao, Xiyán Li, Zhenyu Yang, Qiwei Xu, Zheng-Hong Lu, Edward H. Sargent,* and Xihua Wang*

Cellulose Nanocrystal:Polymer Hybrid Optical Diffusers for Index-matching-free Light Management in Optoelectronic Devices
Supporting Information

Cellulose Nanocrystal:Polymer Hybrid Optical Diffusers for Index-matching-free Light Management in Optoelectronic Devices

Seyed Milad Mahpeykar, Yongbiao Zhao, Xiyan Li, Zhenyu Yang, Qiwei Xu, Zheng-Hong Lu, Edward H. Sargent,* and Xihua Wang*

Figure S1. Transmittance and haze of 1 wt.% CNC/PDMS hybrid optical diffusers with different thicknesses as a function of wavelength. Although higher thicknesses can provide higher haze, the transmittance of the diffuser can be severely affected by the thickness. A 1 mm thick diffuser seems to have optimum transmittance and haze values for optoelectronic applications.
Figure S2. Power efficiency of the OLED device without diffuser and with diffusers having different concentrations of CNC. The diffuser with 1% wt. CNC concentration has the highest enhancement in the efficiency of the device.

Figure S3. Demonstration of the potential application of CNC/PDMS hybrid optical diffusers for light management in silicon solar cells. (a) The schematic of the light scattering effect of the diffuser on a silicon slab. (b) Absorption in a 200 µm thick silicon slab versus incident light wavelength without diffuser and with diffusers having different concentrations of CNC. The absorption in silicon slab is significantly enhanced with the addition of a CNC/PDMS diffuser. However, high concentrations of CNC can reduce the absorption due to the reduction in transmittance of the diffuser. A concentration of 1 wt.% for CNC seems to be the optimized concentration for this application.