Improving the Light Quality of White Light-Emitting Diodes Using Cellulose Nanocrystal-Filled Phosphors

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Light-emitting diode (LED) lighting delivers better performance and reliability, and substantially lowers the total cost of ownership compared with conventional lighting. The most common white LED is generally produced using a blue LED chip and phosphor combination to generate white light. This type of phosphor-converted white LED can be a great alternative to the more expensive 3 chip RGB (red, green, blue) LED. Herein, cellulose nanocrystals, a wood-derived biopolymer, are used with phosphor to improve the uniformity of correlated color temperature (CCT) and luminous flux from the white LED. These nanocrystals can scatter light strongly and for an optimized concentration of nanocrystals, it is found to increase the luminous flux of the white LED by over 30% compared with the reference sample without any nanocrystal. The CCT uniformity is also improved from 173.45 K for the reference sample to 59 K for the optimized sample. The chromaticity coordinates are also studied and found to be shifting toward lower correlated color temperatures with increasing cellulose concentrations. Combining these results with low cost, wide availability, and environmental impact, cellulose nanocrystals can play an important role in the future generation of white LEDs.

1. Introduction

White light-emitting diodes (LEDs) are long-lasting and energy-efficient. As the future of solid-state lighting, LEDs are replacing incandescent light bulbs and compact fluorescent lamps (CFLs) in outdoor and indoor applications.[1] The most common approach to produce white LEDs is to use a blue LED chip and yellow phosphor.[2] In these phosphor-converted white LEDs, the short-wavelength (blue light) LED is used to excite the phosphor and down-convert higher energy short-wavelength photons to low energy long-wavelength photons and combine both types of photons to create a perceived white spectrum.[3]

This technique has several advantages such as simple fabrication, low cost, and high conversion efficiency compared with other techniques such as using individual red, green, and blue LEDs that are used to generate white spectrum or using UV-LEDs to excite red, green, and blue phosphors.[4]

The performance of LEDs depends on different factors, including luminous efficiency, color rendering index (CRI), and correlated color temperature (CCT).[5] Luminous efficiency can be improved by various techniques such as nanostructured blue-chip, sapphire substrate with cone-shaped nanopattern,[6] GaN nanoparticles as phosphors and QDs as charge-transfer medium,[7] and air voids between GaN nanoparticles and the GaN layer.[8,9] Dual structure phosphor layer and textured phosphor structures were also found to improve luminous efficiency.[10,11] In a recent work, a series of Bi3+, Zn2+, La3+, and Eu3+-doped CaGaxOy (CGO) phosphors were prepared for white LED application and found to have high luminous efficiency.[12] On the contrary, red phosphor technologies[13,14] and multiple lateral quantum wells (QWs)[15,16] have been reported to enhance the CRI value of white LEDs. Carbon quantum dot (QD)-based white LEDs were also reported recently that showed a CRI value of 91, the highest among rare-earth and inorganic semiconductor QD-based white LEDs.[17]

Another important parameter that determines the performance of LEDs is the uniformity of CCT which is the difference between high color temperature (a bluish type of white or cool white) and low color temperature (a yellowish type of white or warm white) at the various angles.[18] Nonuniform emission of white light can cause by the uneven angular distribution of CCT and can lead toward an unwanted phenomenon known as “yellow ring.”[19] Conformal phosphor structure can produce better uniformity of angular CCT by reducing the CCT deviation, but such structure has poor light extraction due to large light reflection.[20] Different types of remote phosphor packaging were proposed and factors such as surface curvature of the phosphors and location of the phosphors were studied to improve the color homogeneity of the white LEDs.[21–23] Other methods such as improved silicon lens design[24] and patterned sapphire substrate[25] were studied to improve the homogeneity of the white LEDs. TiO2 nanoparticles were incorporated into the packaging materials to resemble a graded-refractive-index multilayer structure.[26] By modifying the surface of TiO2 nanoparticles and
dispersibility, CCT uniformity was improved in another work.\textsuperscript{[27]} In another work, blue laser irradiation was used to control the spatial phosphor particle spatial distribution to improve CCT uniformity.\textsuperscript{[28]} Red phosphor thin films (PTFs) with different \textit{MgO} nanoparticle concentrations were also used that improved the CCT by 8.81\%\textsuperscript{[29]} In such a device, light can be scattered by nanoparticles which, in turn, could strongly influence the optical path and change the CCT deviation in white LEDs.\textsuperscript{[30]} More recently, boron nitride nanoparticles were studied for reflection enhancement of an inverted packaging structure.\textsuperscript{[31]} However, some of these methods enhance the uniformity of CCT at the cost of luminous efficiency,\textsuperscript{[32,33]} and thus it is important to find a balance between luminous efficiency and CCT uniformity that could help white LEDs to become the primary solid-state light source.

In this study, cellulose nanocrystals (CNCs), a biopolymer derived from wood, were used to improve the performance of white LEDs. CNCs have superior light scattering capability and are promising candidates for optical diffusers.\textsuperscript{[34,35]} Filling CNCs into the phosphor layer enabled better utilization of blue light which increased the luminous flux. Furthermore, such scattering capability of CNCs also helped to reduce angle-dependent CCT deviation.

2. Experimental Section

Figure 1a,b shows the device structures of conventional phosphor-converted white LEDs and our LEDs with CNC-filled phosphors, and Figure 1c shows the top view (photo) of our LED device. A blue LED chip (Shenzhen Getian Opto-Electronics Co., Ltd., 3030 blue SMD LED) with an emission peak between 460 and 470 nm was outsourced with operating voltage 2.4–3 V. Then CNCs were uniformly mixed with yttrium aluminum garnet (YAG) phosphors and the polydimethylsiloxane (PDMS) (Dow Corning, Sylgard 184 kit) and dispensed in the package. The reference sample only had a uniform mixture of phosphor and PDMS. To investigate the effect of CNCs on the improvement of the luminous flux and CCT of our LEDs, different concentrations of the CNCs were added to the phosphor and PDMS mixture. The size of the phosphors was around 4 μm, and individual CNC and CNC clusters were sized between 100–200 nm and 1–3 μm, respectively. Figure 2 shows the experimental setup that was used to characterize the LED. All light from the LED was captured using an integrating sphere which was connected to a spectrometer (Ocean Optics, FLAME-S-VIS-NIR-ES) by an optical fiber. The detector (spectrometer) was connected to a workstation where the data were recorded and analyzed.

3. Results and Discussion

The influence of phosphor concentration on the performance of white LEDs was first investigated to find an appropriate phosphor concentration for studying white LEDs using CNC-filled phosphors. Figure 3a shows the emission spectra of white LED structures with different concentrations of phosphor.

![Figure 1](image1.png)

**Figure 1.** a) Schematic cross-sectional view of conventional structure; b) CNC-embedded structure; and (c) top view of the LED chip.

![Figure 2](image2.png)

**Figure 2.** Experimental setup to characterize the performance of LEDs.
Phosphor concentration can change blue and yellow light intensities in the emission spectra and based on the result, 14 wt% phosphors were chosen as the luminous flux was the highest at this concentration. More information about this can be found in Figure S1 and S2, Supporting Information. Figure 3b shows the effect of applied voltage on a white LED with 14 wt% phosphors ranging from 2.4 to 2.6 V. It shows that with increased voltage luminous flux also increased. For the remainder of this work, all the samples were prepared with 14 wt% phosphors concentration and characterized at 2.6 V.

After that, different concentrations of CNCs were mixed with phosphor and more information about mixing phosphor and CNCs can be found in Figure S3, Supporting Information. Figure 4a shows the luminous flux of white LEDs with different concentrations of CNCs. The luminous flux of the reference sample (phosphor only) was around 247 lumens and it started increasing with increasing concentration of CNCs and an increase of around 33% was recorded with 6 wt% CNCs compared with the reference sample. CNC-embedded white LED structures had higher yellow light intensities compared with the reference sample due to improved conversion of blue photons which resulted in a higher luminous flux and efficiency. These CNCs can scatter light which has been thoroughly analyzed and discussed in our previous work [3, 14, 36, 37]. This scattering effect of CNCs increased the luminous flux by increasing the optical path length of blue light which led to the higher possibility of exciting yellow phosphor and generating yellow photons. Though with the increasing concentration of CNCs, transmission through the CNCs will start to decrease. Luminous flux of the white LED structure was found to be around 235 lumens at 12 wt% CNCs concentration which is due to the light trapping and absorption phenomenon between CNCs and phosphor materials and because of that for subsequent studies this sample was not considered. Figure 4b shows the CCTs with different concentrations of CNCs. The CCT of the reference sample was around 4470 K and it decreased with increasing CNCs concentration due to the higher yellow conversion ratio. Figure 5 shows the emission spectra of the reference.
and CNC-embedded white LED structures. Due to increased scattering, blue light had a higher likelihood to excite yellow phosphors and this increased utilization rate of blue light increased the output of yellow light, resulting in the enhancement of luminous flux.

To further understand the scattering effect of the CNCs on the CCT and luminous flux, angle-dependent CCTs of the white LED structures containing different concentrations of CNCs were measured, as shown in Figure 6a. Angle-dependent CCTs showed better uniformity with the addition of CNCs which indicates increasing CNCs yielded a stronger scattering effect. The uniformity of the CCTs was determined by subtracting maximum CCT and minimum CCT. For the reference sample, it was found to be around 173.45 K which decreased with increasing concentration of CNCs and reached a value of around 59 K for 6 wt% CNCs, as shown in Figure 6b. The reference sample and 6 wt% CNCs sample showed CCTs of approximately 4220 and 3985 K, respectively, at 0° viewing angle which implies a reduction of blue light due to the addition of CNCs with the phosphor. Figure 6b also shows that increasing concentration of CNCs will increase the figure of merit (FOM) which is defined as

\[
FOM = \frac{\text{Lumen}_{\text{CNCs}} - \text{Lumen}_{\text{No CNCs}}}{\Delta \text{CCT}}
\]

In the end, the color qualities of the CNC-embedded white LED structures were evaluated by measuring the chromaticity coordinates, which is a widely adopted standard. The chromaticity coordinates of the CNC-embedded white LED structures are shown in Figure 7a. As the CNCs concentration was increased, there was a gradual shift of the chromaticity coordinates to the yellow region which means that the intensity of the yellow light was increasing and thus reducing the CCTs. The angular-dependent emission intensity was also studied, as shown in Figure 7b. It shows that CNC-embedded white LED structures can exhibit superior performance and produce high-quality white light at different viewing angles.

4. Simulation

In this section, a simulation study is presented to study the effect of two different types of CNC–phosphor structures for white LED applications. Zemax ray tracing software was used for this work. Figure 8a,b shows the two different LED structures without any lens that were studied to understand the effect of CNCs. The size of the LED chip was 1 × 1 mm² and had five layers: p-GaN, a multiquantum well (MQW), n-GaN, sapphire substrate, and metal alloy film. The thicknesses of the layers were set at 150 nm, 100 nm, 4 μm, 140 μm, and 0.1 μm, respectively. Refractive indices and absorption coefficient values were taken from elsewhere.[38,39] The dispensing-coated phosphor–silicone layer was constructed as a spherical cap. The size of phosphor was 4 μm and its optical properties were taken from elsewhere.[39] To represent blue and yellow light, two specific
wavelengths, 454 and 569 nm, were chosen where the blue light was assumed to be radiated from the top surface of the chip with Lambertian distribution.[40] This blue light was absorbed and reemitted into yellow light from the phosphor–PDMS layer. A hemisphere detector was placed on top of this structure to cover –70° to 70° viewing angles. After that, CNCs were also constructed using a precise optical model described in our previous work.[3,36] The size of these CNCs was set at 4 μm and concentration was tuned at 6 wt%. The scattering coefficient was obtained by Mie theory which depends on the distribution of CNCs. A similar model with the lens was simulated in our previous work[3] and compared with published data[38] that verified the accuracy of this particular model. Two different kinds of structures were investigated: 1) two layers of CNCs and phosphors as shown in Figure 8a, and 2) a single layer made of CNC-filled phosphors as shown in Figure 8b.

Figure 8c shows the angular-dependent CCT variation for different white LED structures. For phosphor only sample, variation in CCT was 270 K. It was reduced to 224 K for the sample that had one layer of CNCs and one layer of phosphors. This further reduced to 200 K for the sample that had a single layer with CNC-filled phosphors. This figure also shows that samples with CNCs had lower CCT at 0° viewing angle than the phosphor only sample, which verified the scattering ability of CNCs that enabled better utilization of blue light. As discussed earlier, this simulation study showed our approach of filling CNCs into the phosphor layer enabled better utilization of blue light, which increased the average CCT while maintaining low CCT deviation for white LEDs. In addition to the improvement in CCT, CNCs also helped the enhance luminous intensity and flux for white LEDs. Figure 9 shows the polar plot of angular luminous intensity distribution for different types of CNCs and phosphor structures. The sample with a single CNC-filled phosphor layer showed 39.6% enhancement of luminous flux (126.16 lumens), which is the integral of angular luminous intensity over the hemisphere detection in simulation, and the sample with separate CNC and phosphor layers showed 27.3% enhancement of luminous flux (115 lumens) compared with the sample with phosphor only (90.34 lumens). This study showed that mixing the CNCs and phosphors would yield better results because scattered blue light will have higher chances of getting reabsorbed by phosphors which would emit yellow light and reduce CCT deviation.
5. Conclusion

In conclusion, the effect of CNCs to improve the light quality of white LEDs was investigated. It was found that adding 3 wt% CNCs with phosphor increased the luminous flux by around 11% and it increased to around 33% for 6 wt% of CNCs. This enhancement in light output was due to the scattering ability of CNCs that enabled better utilization of the blue light. This also helped to increase the uniformity of angle-dependent correlated color temperature and for 6 wt% CNCs concentration, uniformity improved to 59 K compared with 173.45 K of the reference sample. The chromaticity coordinates showed a shift of CCT toward the yellow region that also verified the scattering ability of CNCs. Lumen output was also increased between -75° and 75° viewing angles. A simulation model was also developed to compare the performance of two different kinds of CNC-phosphor structures, and it was found that mixing CNCs and phosphors would yield better CCT and increase light output. In this work, YAG phosphor was chosen due to its superior thermal stability and brightness and though other phosphors can be chosen based on requirements it is important to make sure about its thermal stability as, otherwise, the luminescence of phosphor and quality of light from white LED will decrease. PDMS type and mixing technique can also change the optical properties and even though the mechanical properties of CNCs and PDMS mixture have already been studied which did not show significant degradation, further investigation is needed, first, to understand the effect of PDMS on the light quality of white LED and, second, to find out the change in optical properties of such film over time. Going forward, this study provides an excellent platform for future efforts to investigate the potential of CNCs for application in solid-state lighting.

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) and Alberta Innovates-Alberta Bio Future. F.I.C. acknowledges the Alberta Innovates – Technology Futures Graduate Student Scholarship.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords

cellulose, correlated color temperature, light-emitting diodes, scattering

Received: January 8, 2021
Revised: February 6, 2021
Published online: March 12, 2021

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