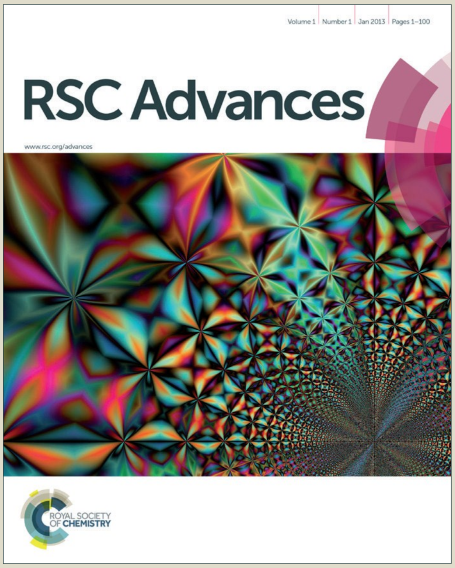
RSC Advances



Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

ARTICLE

TEMPO-mediated oxidized nanocellulose incorporating with its derivatives of carbon dots for luminescent hybrid films

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yaoquan Jiang,[a] Yafei Zhao,[a] Xin Feng,*[a] Jianhui Fang[b] and Liyi Shi[a]

The first use of nanocellulose extracted from bamboo fibers as fibrous network skeleton and carbon dots derived from nanocellulose as guest fluorescent nanomaterials to construct transparent, photoluminescent hybrid film is reported. The primary hydroxyls of nanocellulse are firstly converted to the carboxyl form by using TEMPO-mediated oxidation to enhance the interfacial interaction with carbon dots and then to assemble heterogeneous network architectures through covalent bonding. The carbon dots derived from TEMPO-mediated oxidized nanocellulose displays highly uniform spherical morphology with a narrow size distribution ranging from 6 nm to 11 nm. The resultant nanocellulose based hybrid film has high transparency in bright field and strong blue luminescence under UV excitation. Moreover, the biocompatible hybrid film extracted from biomass exhibits excellent thermal stability and outstanding mechanical durability, which will be utilized as an increasing potential to substitute petroleum-based film for diverse applications.

Introduction

With the over-consumption of non-renewable petroleum based polymers, transparent films derived from natural biopolymers with predominant characteristics of excellent biodegradability, biocompatibility and renewability have captured worldwide intensive attentions. Cellulose, one of the most abundant renewable biopolymers on earth, has been widely used for preparing highly transparent films with exceptional mechanical robustness and optical transparency.[1-3] Nanocellulose (NC) based films have been found to be ideal platforms to host a range of guest functional materials, which offer a prospective potential to supersede traditional plastic films for food packaging, separators, flexible displays, transistors, transparent conductive electrodes and so on.[2-9] The NC-based hybrid films with luminescent properties displayed exciting synergetic characteristics combined NC with luminescent materials, such as fluorescein, rare-earth up-converting luminescent nanoparticles (UCNPs), lanthanide complexes and semiconductor quantum dots.[10-12]

As one of the most promising fluorescent carbon nanomaterials, carbon dots (CDs) exhibit strong fluorescence, outstanding chemical stability, biocompatibility, aqueous dispersibility and non-toxicity with favorable size advantage (below 10 nm),[13,14] which can be acted as prominent candidates to replace the traditional rare-earth luminescent materials and semiconductor quantum dots in many applications such as sensors, security printing, bio-imaging, biomedicine and optoelectronic devices.[15-21] Traditionally, CDs were prepared by using graphites,[22,23] carbon nanotubes,[24-26] carbon fibers,[27] glycerol,[28,29] poly(ethylene glycol),[30] nanodiamonds,[21,31] candle soot[18,32] and petroleum coke[33] as carbon sources, Recently, a diverse set of cheap, natural and non-toxic available materials such as winter melon, food waste, plant leaf, potato, chitosan, cow milk and coffee grounds were also demonstrated for the synthesis of the photoluminescent CDs.[13,34-39] Generally, there is many hydroxyl, carboxyl or amino moieties on the CDs surface, which can be strategically manipulated for further functionalization and assembling with organic, polymeric, inorganic and biological materials.[40] NC is an excellent flexible matrix for the construction of diverse shapes of architectures, such as films, fibers and aerogels. In particular, the primary hydroxyls of NC were commonly converted to the carboxyl form by using TEMPO-mediated oxidation to enhance the interfacial interaction with other matrix components.[41,42]

In this study, the luminescent NC-based hybrid film was rapidly assembled by well-dispersed TEMPO-mediated oxidized NC (ONC) and its derived CDs under crosslinking procedures. As far as we know, no work has been reported for preparing CDs using ONC as starting materials. Herein, the photoluminescent CDs originated from ONC were directly introduced in the construction of CDs/ONC hybrid films based on the reaction of amino groups on CDs surface and the new TEMPO induced carboxyl groups on the surface of ONC. The flexible CDs/ONC hybrid film shows high transparency in bright field and strong luminescence under UV excitation. Meanwhile,

---

[a] *Research Center of Nano Science and Technology, Shanghai University, Shanghai 200444, P. R. China. Tel.: +86 21 66137257, Fax: +86 21 66136038, Corresponding Author:* E-mail: fengxin@shu.edu.cn.*

[b] *Department of Chemistry, Shanghai University, Shanghai 200093, P. R. China.*

Electronic Supplementary Information (ESI) available: [UV-vis spectra of ONC film and CDs/ONC hybrid film in Figure S1; AFM image of CDs/ONC hybrid film in Figure S2; ^{13}C-NMR spectrum of CDs/ONC in Figure S3; Photoluminescence emission spectra of CDs/ONC hybrid film after bending for (a) 500, (b) 1000 and (c) 2000 times in Figure S4.]. See DOI: 10.1039/x0xx00000x the hybrid film expresses outstanding thermal stability and mechanical durability after bending for 2000 cycles.

Experimental

Materials

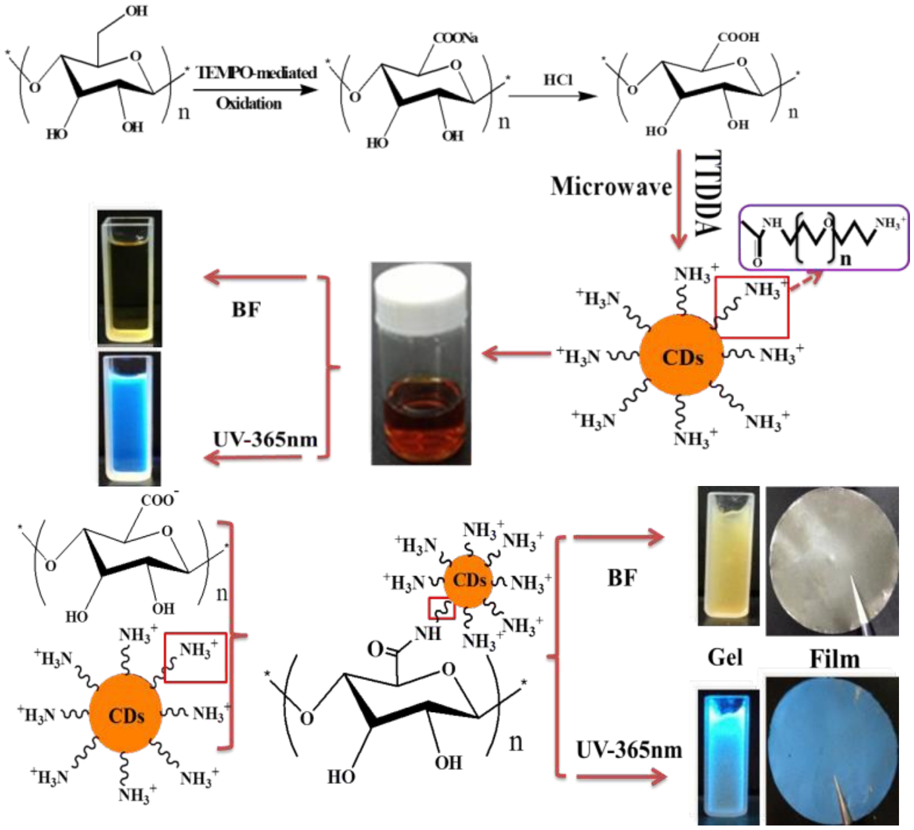
Sodium hydroxide, Trisodium phosphate, Sodium silicate, Acetic acid, Citric acid, Triton X-100, Nitric acid, Hydrogen peroxide, Sodium bromide, Hydrochloric acid, 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO), Sodium hypochlorite were all purchased from Sinopharm Chemical Reagent Co, Ltd. (Shanghai, China), Sodium Chlorite was purchased from Aladdin. 4,7,10-trioxa-1,13-tridecanediamine (TTDDA) was obtained from Sigma-Aldrich. All the reagents were of analytical grade and used as received without any further purification.

Preparation of NC

NC was obtained according to a modified protocol proposed in our previous work.[43] In brief, the bamboo fibers were mechanically smashed and extracted in 3 wt% aqueous NaOH solution at 100 °C for 5 h, followed by filtering and rinsing with deionized water for several times. Delignification was performed with 1 wt% NaOH, 0.4 wt% Na_3PO_4 and 0.4 wt% Na_2SiO_3 at 115 °C for 2.5 h under mechanical stirring, then filtered and washed with deionized water to neutral pH. The delignified fibers was firstly bleached with 3.5 wt% NaOH, 0.7 wt% $NaClO_2$, 150 mL CH_3COOH at 100 °C for 2 h, followed by filtering and washing with deionized water for four times. Subsequently, 0.05 wt% Triton X-100 and 5 wt% citric acid were added and heated at 70 °C for 4 h, then filtered and washed with deionized water to neutral pH. Finally, the resulting aggregates were immerged into the mixed 30 wt% H_2O_2 and 65 wt% HNO_3 solution (2:1 v:v) at 70 °C for 2 h to further bleach under vigorously mechanical stirring, followed by centrifuging and thoroughly washed with deionized water to neutral pH.

TEMPO-mediated oxidation of NC (ONC)

TEMPO-mediated oxidation of NC was presented according to the procedure as described in the previous work.[44,45] Typically, 100 g NC suspension (8.2% wt%) was dispersed in 250 mL deionized water, 0.1090 g TEMPO, 1.0731 g NaBr and 40 mL NaClO (30 wt%) were added with continuous magnetic stirring at room temperature for 20 h. After oxidation, the suspension was centrifuged, washed and then re-dispersed into 100 mL water with addition of 1 mol/L HCl aqueous solution under continuous magnetic stirring at ambient temperature for 2 h, then centrifuged and washed until the pH was adjusted to 7. The as-prepared ONC was subjected to a high pressure homogenization process for several cycles at a pressure of 50 MPa.



Scheme 1. Schematic illustration of CDs derived from TEMPO-mediated oxidized NC and the resultant CDs/ONC hybrid films.

Preparation of CDs suspensions

Photoluminescent CDs was synthesized using ONC as starting materials according to a modified process as shown in previous reports.[29,46] In a typical procedure, 10 g ONC (2.15% wt%) mixed with 0.2 mL TTDDA were transferred to 50 mL Teflonautoclave and heated in a Microwave Reaction System (MDS-6, Sineo Microwave Chemical Technology Co. Ltd). The experimental conditions are shown in Table 1. Subsequently, the as-synthesized products were filtered with 0.22 μm membrane and further dialyzed by using dialysis bag to obtain CDs suspensions.

Table 1 Experimental parameters of the microwave reaction.

Step	Temperature (°C)	Time (min)	Power (W)
1	50	2	600
2	100	2	600
3	150	2	600
4	180	2	600
5	200	2	600

Preparation of CDs/ONC hybrid films

CDs/ONC (2.0 g) in a given ratio was added into 100 mL deionized water and ultrasonic dispersed to make a homogeneous solution at 700 W for 10 min by a high frequency ultrasonic treatment. Then the uniform suspension was transferred to an extruder at N_2 pressure of 2.0 MPa by using a pressured extrusion process,[10,11] and the transparent CDs/ONC hybrid films with 20 μm in thickness and 45 mm in diameter were finally fabricated and further dried in a vacuum oven for 10 min at 95 °C.

Characterization

Transmission electron microscopy (TEM) measurements were performed on JEM-200CX (JEOL, Japan) at an accelerating voltage of 120 kV. High resolution transmission electron microscopy (HRTEM) measurements were determined on JEM-2010F (JEOL, Japan) at operating voltage of 200 kV. Scanning electron microscopy (SEM) photographs were observed by using a field emission scanning electron microscope (FE-SEM, JSM-6700F, JEOL, Japan), the samples were metalized with Au under vacuum. CDs/ONC composite films were imaged via an atomic force microscope (AFM, Dimension 3100, Veeco Instruments, Inc., USA) in tapping mode. The size distribution of CDs was carried out with Dynamic light scattering (DLS) analysis on Zetasizer NANO-ZS90 (Malvern England). X-ray diffraction (XRD) patterns were taken with a D/MAX2200 X-ray diffractometer equipped with Cu Kα (λ = 1.5418 Å) radiation operating at 40 kV and 40 mA. The Fourier transform infrared spectroscopy (FT-IR) were recorded by a Thermo Nicolet 6700 spectrometer (Thermo Fisher Scientific, USA) in the spectral range from 4000 to 400 cm^{-1} using the pressed KBr discs prepared by making finely grinded samples mixed with dry KBr powder. UV-Vis spectra were recorded on a Shimadzu 2500-PC spectrophotometer at ambient temperature. Solid-state 13C nuclear magnetic resonance (NMR) spectrometer (Bruker Avance 500MHz, Bruker Daltonics, Germany) was used to verify the presence of functional groups in the obtained CDs/ONC. Thermogravimetric Analyzer (TGA, STA409PC, Netzsch, Germany) was used to study the thermal stability of the prepared samples at a heating rate of 10 ºC /min in the range of 30~1000 ℃ under an air atmosphere.

Results and discussion

The following formation mechanism of the CDs/ONC hybrid films was proposed in Scheme 1. The ONC was firstly TEMPO-mediated oxidized and then treated by microwave pyrolysis to form CDs with lots of amino groups on the surface. Thus, transparent CDs/ONC hybrid films with blue luminescence upon UV excitation at 365 nm were successfully achieved according to a covalent crosslinking between carboxyl groups of ONC and amino groups of the newly-formed CDs. Under bright field (BF), the CDs/ONC hybrid film display highly optical transparency. The morphology of the ONC, CDs and CDs/ONC composites were shown in Figure 1. It can be clearly seen from the TME image of ONC from Figure 1a that the ONC has a dimension of 1~2 μm in length and about 30 nm in width. The well-dispersed ONC nanofibrils with numerous hydroxyl groups were beneficial for film-making, especially transparent films.[7,10,11] CDs derived from ONC displays highly uniform spherical morphology with a narrow size distribution, the selected detection results are marked with circles and shown in Figure 1c. The DLS measurement of size distribution of the CDs indicates that the particle size mainly ranges from 6 to 11 nm (Figure 1d) corresponding to the HRTEM results. It is obvious that CDs conjoin with ONC nanofibrils as shown in Figure 1b, indicating CDs successfully attached on ONC surface. The quantum yield (QY) defined as the number of emitted photons relative to the number of absorbed photons, which depends on the synthetic procedure and surface chemistry. Herein, the quantum yield of CDs terminated with amino groups was determined to be 10.27% using quinine sulphate as a reference.

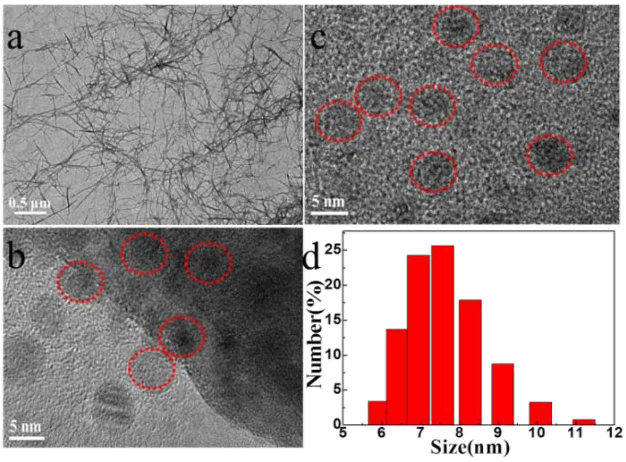


Figure 1. TEM image of (a) ONC fibrils; HRTEM images of (b)CDs/ONC composites and (c) CDs. (the detected objects are selected and marked with circles); (d) Size distribution histogram of CDs.

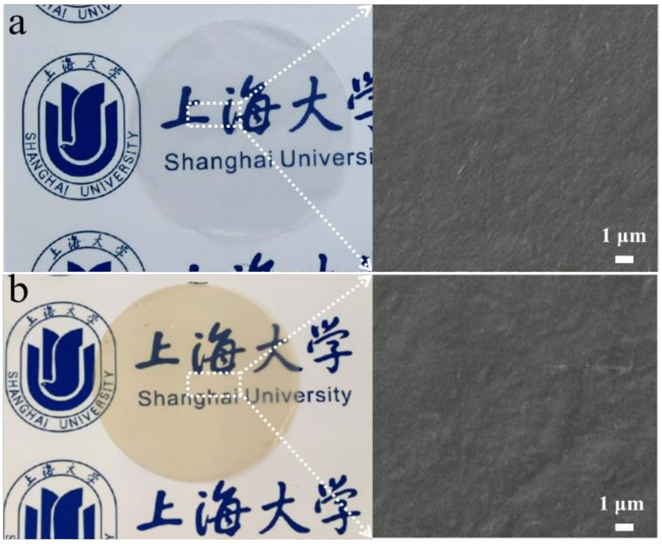


Figure 2. Digital images (left) and SEM images (right) of ONC film (a) and CDs/ONC composite film (b).

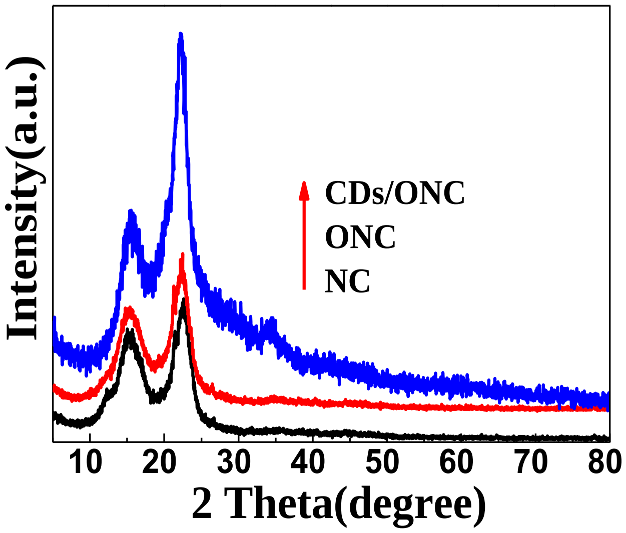


Figure 3. XRD patterns of NC, ONC film and CDs/ONC hybrid film.

After the pressured extrusion of ONC suspensions and CDs/ONC composite suspensions to squeeze out the excess water, highly transparent ONC film and CDs/ONC hybrid film were ultimately fabricated, respectively (Figure 2). As the diameter of ONC is in nanometric scale, the ONC film and CDs/ONC hybrid film display highly optical transparency. The school emblem of Shanghai University behind the transparent films is very clearly detected. However, the transmittance of CDs/ONC hybrid film slightly decreases with the addition of CDs as shown in UV-vis spectra (Figure S1, Supporting Information). SEM images of the surface morphologies of the transparent ONC film and CDs/ONC hybrid film are presented in the right-hand columns of Figure 2. It can be seen that the surface of the ONC film is considerably smooth, but the flatness of CDs/ONC hybrid film decreases with the combination of CDs into the network of ONC fibrils, the large surface roughness is also clearly confirmed by the height AFM image (Figure S2, Supporting Information).

The phase compositions of the hybrid films were further investigated by XRD analysis. Figure 3 shows the XRD patterns of NC, ONC and CDs/ONC hybrid film. The peaks at 14.7º, 16.5º, 22.7° and 35.0° were attributed to the typical (101), (101), (200), and (040) reflections of cellulose I.[47] No significant distinction was observed between NC and ONC, implying that the ONC maintains the typical cellulose I after TEMPO mediated oxidization process. When CDs attached to the surface of ONC fibrils, an obvious increase could be found in the peaks intensity of XRD patterns of CDs/ONC hybrid film because the CDs give a broad reflection peak centered at 4.3 Å.[48]

FT-IR analysis was further used to confirm the combination between CDs and ONC. The FT-IR spectra of NC, ONC and CDs/ONC were shown in Figure 4. The peaks at 3097 and 1559 cm^{-1} from the FT-IR spectrum of CDs/ONC hybrid film are attributed to the N-H vibration, whereas the same signals cannot be observed from FT-IR spectra of ONC and NC.[49] The peak at 1736 cm^{-1} is ascribed to C=O vibration of carboxyl groups, so as to the C=ONR vibration at 1644 cm^{-1} in the acylation reaction,[46,48,50] the formation of C=ONR bonds was also demonstrated at a chemical shift of 170.9 ppm from 13C NMR spectrum of CDs/ONC hybrid film[48] (Figure S3, Supporting Information). The peaks at 72.0 ppm (C-2 and C-3), 68.7 ppm and 69.5 ppm (C-5 and C-6), 62.5 ppm (C-6), 30.2 ppm and 37.6 ppm (C-1 of methylene group) were attributed to the six carbon atoms of the ONC unit, respectively.[48,51] It is convincingly implied that the acylation reaction between CDs and ONC was clearly verified. The results clearly indicated that CDs were covalently attached on the ONC surface and successfully assembled with ONC to form homogeneous transparent films. The UV-Vis absorption and photoluminescence emission spectra were investigated accordingly. As shown in Figure 5, the as-obtained CDs and CDs/ONC hybrid film possess an obvious shoulder peak at about 300 nm in the UV-vis absorption spectra, attributing to the n–π* transition of C=O bonds or other connected groups[51]. When excited in the range of 340-400 nm, the CDs exhibit strong blue photoluminescence centered at 456 nm, however,

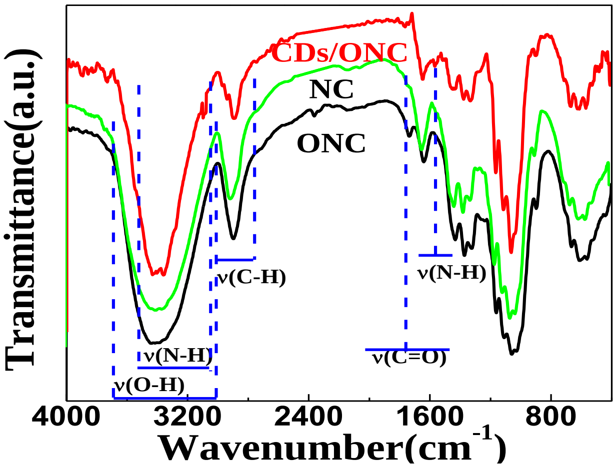


Figure 4. FT-IR spectra of NC, ONC film and CDs/ONC hybrid film.

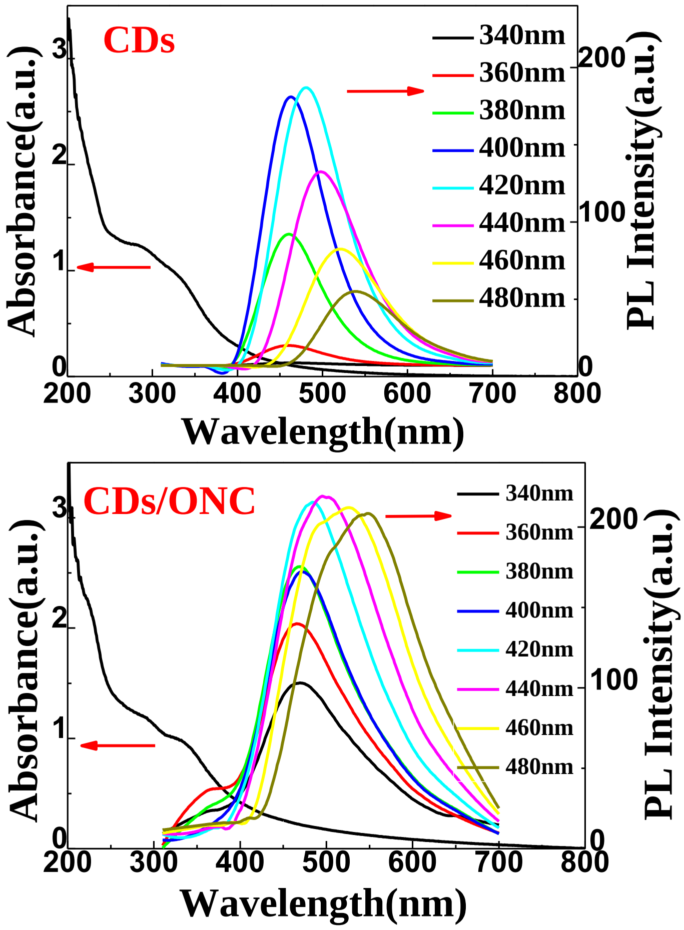


Figure 5. UV-vis absorption and photoluminescence emission spectra of CDs and CDs/ONC hybrid film.

an interesting finding is that the CDs/ONC hybrid film presents a slightly stronger blue photoluminescence centered at 460 nm. With the increase of the excitation wavelength to 480 nm, the intensity of the emission of CDs decreases and the spectra shift from 456 nm to 540 nm.[53] On the other hand, the luminescent emission intensity for CDs/ONC hybrid film is stronger than that of CDs with the increased excitation wavelength (longer than 420 nm). By contrast, no detectable photoluminescence was observed when the pure ONC film was irradiated under the same conditions. It can be clearly seen that the CDs and CDs/ONC hybrid film exhibit similar luminescent behaviors, both of them reveal excitation-dependent emissions. The wavelength-dependent behavior may result from the size distribution and surface chemistry of CDs. Since CDs and CDs/ONC have similar particles sizes, the quantum effects can be excluded from comparison. In fact, the exact PL mechanism of CDs is currently unresolved and requires further investigation to look into in depth, there has been an envisagement that it is associated with passivated surface defects of the core carbon particles. Therefore, the PL phenomenon can be deduced that the numerous functional groups such as amide groups in the CDs/ONC surface introduce plenty of defects as excitation energy traps and lead to the stronger blue photoluminescence of CDs/ONC hybrid film.[54]

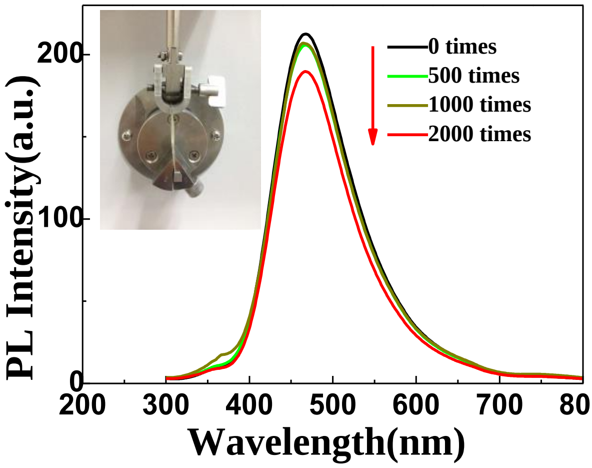


Figure 6. Photoluminescence emission spectra of CDs/ONC hybrid film after bending test (λex = 380 nm).

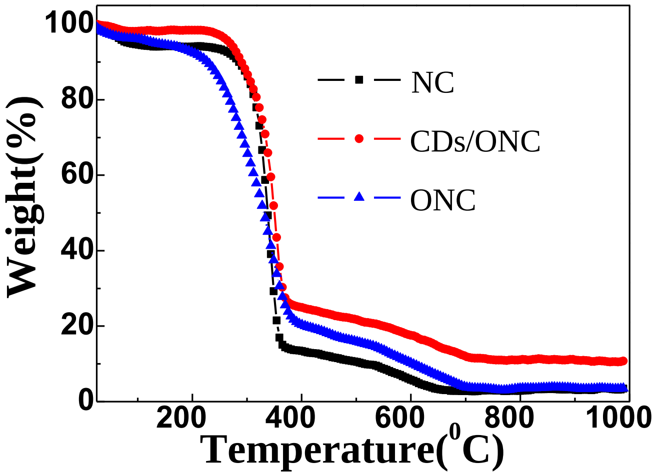


Figure 7. TG curves of the NC, ONC film and CDs/ONC hybrid film under an air atmosphere.

Owing to the excellent printability, outstanding thermal stability and mechanical flexibility, transparent hybrid films have been demonstrated as kinds of prospective candidates to supersede plastic films for various flexible applications. Figure 6 shows the PL emission spectra of CDs/ONC hybrid film excited at 360 nm before and after bending at 135° for 500, 1000 and 2000 times. An exhilaratingly finding is that the PL intensity of the hybrid film exhibits no meaningful decrease (less than 5%) after bending for 2000 times (Figure S4, Supporting Information). Thermogravimetry (TG) analysis was performed to investigate the thermal stability of CDs/ONC hybrid film. Figure 7 demonstrates the thermal decomposition of NC, ONC film and CDs/ONC hybrid film under an air atmosphere. In all the TG curves, the small weight losses below 120 °C apparently results from evaporation of adsorbed water or low molecular weight compounds. The CDs/ONC hybrid film exhibits a large weight loss due to the thermal decomposition of NC at between 240 °C and 370 °C with 10 wt% residual weights at 1000 °C. Whereas ONC film displays a significant weight loss owing to the decomposition of oxygen containing groups in ONC at between 120 °C and 390 °C with 3 wt% residual weights at 1000 ℃. The result indicates that the incorporation of CDs has a slight effect on the thermal degradation behavior of ONC film, which can be further concluded that CDs were successfully attached on the ONC surface.[44,55]

Conclusions

In summary, we report the first use TEMPO-mediated oxidized nanocellulose as the bioresources to direct synthesize photoluminescent CDs via a typical microwave pyrolysis approach. The ONC fibrils and the derivatives of CDs were covalently cross-linked to construct transparent CDs/ONC hybrid film with blue luminescence by using a pressured extrusion method. The CDs/ONC hybrid film presented high transparency, excellent excitation-dependent PL behavior, outstanding thermal stability and mechanical flexibility. The PL intensity of the hybrid film exhibits negligent decrease less than 5% even after bending for 2000 cycles. In addition, the biocompatible and nontoxic CDs/ONC hybrid film should encourage their research and exploration in a multitude of environmentally friendly application areas in future.

Acknowledgements

This work was financially sponsored by Natural Science Foundation of Shanghai (13ZR1415100, 15ZR1415100).We are also grateful to Instrumental Analysis & Research Center of Shanghai University.

Notes and references

1 M. Nogi, s.Iwamoto, A. Nakagaito and H. Yano, *Adv. Mater.*, 2009, **21**, 1595.
2 Z. Fang, H. Zhu, C. Preston, X. Han, Y. Li, S. Lee, X. Chai, G. Chen and L. Hu, *J. Mater. Chem. C*, 2013, **1**, 6191.
3 M. Österberg, J. Vartiainen, J. Lucenius, U. Hippi, J. Seppälä, R. Serimaa and J. Laine, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4640.
4 Y. Jiang, Y. Song, M. Miao, S. Cao, X. Feng, J. Fang and L. Shi, *J. Mater. Chem. C*, 2015, **3**, 6717.
5 F. Jiang, L. Yin, Q. Yu, C. Zhong and J. Zhang, *J. Power Sources*, 2015, **279**, 21.
6 J. Huang, H. Zhu, Y. Chen, C. Preston, K. Rohrbach, J. Cumings and L. Hu, *ACS Nano*, 2013, **7**, 2106.
7 H. Koga, T. Saito, T. Kitaoka, M. Nogi, K. Suganuma and A. Isogai, *Biomacromolecules*, 2013, **14**, 1160.
8 H. Koga, M. Nogi, N. Komoda, T. Nge, T. Sugahara and K. Suganuma, *NPG Asia Mater.*, 2014, **6**, e93.
9 Y. Song, Y. Jiang, L. Shi, S. Cao, X. Feng, M. Miao and J. Fang, *Nanoscale*, 2015, **7**, 13694.
10 J. Zhao, Z. Wei, X. Feng, M. Miao, L. Sun, S. Cao, L. Shi and J. Fang, *ACS Appl. Mater. Interfaces*, 2014, **6**, 14945.
11 M. Miao, J. Zhao, X. Feng, Y. Cao, S Cao, Y. Zhao, X. Ge, L. Sun, L. Shi and J. Fang, *J. Mater. Chem. C*, 2015, **3**, 2511.
12 J. Xue, F. Song, X. Yin, X. Wang and Y. Wang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 10076.
13 X. Feng, Y. Jiang, J. Zhao, M. Miao, S. Cao, J. Fang and L. Shi, *RSC Adv.*, 2015, **5**, 31250.
14 A. Sachdev, I. Matai, and P. Gopinath, *J. Mater. Chem. B*, 2015, **3**, 1217.
15 E. Goh, K. Kim, Y. Kim, H. Jung, S. Beack, W. Kong, G. Scarcelli, S. Yun and S. Hahn, *Biomacromolecules*, 2012, **13**, 2554.
16 Q. Zhao, Z. Zhang,B. Huang, J. Peng, M. Zhang and D. Pang, *Chem. Commun.,* 2008, **41**, 5116.
17 P. Luo, S. Sahu, S. Yang, S. Sonkar, J. Wang, H. Wang, G. LeCroya, L. Cao and Y. Sun, *J. Mater. Chem. B*, 2013, **1**, 2116.
18 S. Ray, A. Saha, N. Jana and R. arkar, *J. Phys. Chem. C*, 2009, **113**, 18546.
19 L. Cao, X. Wang, M. Meziani, F. Lu, H. Wang, P. Luo, Y. Lin, B. Harruff, L. Veca, D. Murray, S. Xie and Y. Sun, *J. Am. Chem. Soc.*, 2007, **129**, 11318.
20 Y. Dong, N. Zhou, X. Lin, J. Lin, Y. Chi, and G. Chen, *Chem. Mater.*, 2010, **22**, 5895.
21 C. Fu, H. Lee, K. Chen, T. Lim, H. Wu, P. Lin, P. Wei, P. Tsao, H. Chang and W. Fann, *Proc. Natl. Acad. Sci. U.S.A.*, 2007, **104**, 727.
22 Y. Sun, B. Zhou, Y. Lin, W. Wang, K. Fernando, P. Pathak, M. Meziani, B. Harruff, X. Wang, H. Wang, P. Luo, H. Yang, M. Kose, B. Chen, L. Veca and S. Xie, *J. Am. Chem. Soc.*, 2006, **128**, 7756.
23 H. Li, X. He, Z. Kang, H. Huang, Y. Liu, J. Liu, S. Lian, C. Tsang, X. Yang and S. Lee, *Angew. Chem. Int. Ed.*, 2010, **49**, 4430.
24 M. Bottini, C. Balasubramanian, M. Dawson, A. Bergamaschi, S. Bellucci and T. Mustelin, *J. Phys. Chem. B*, 2006, **110**, 831.
25 X. Xu, R. Ray, Y. Gu, H. Ploehn, L. Gearheart, K. Raker and W. Scrivens, *J. Am. Chem. Soc.*, 2004, **126**, 12736.
26 J. Zhou, C. Booker, R. Li, X. Zhou, T. Sham, X. Sun and Z. Ding, *J. Am. Chem. Soc.*, 2007, **129**, 744.
27 L. Bao, C. Liu, Z. Zhang and D. Pang, *Adv. Mater.*, 2015, **27**, 1663
28 X. Wang, K. Qu, B. Xu, J. Ren and X. Qu, *J. Mater. Chem.*, 2011, **21**, 2445
29 C. Liu, P. Zhang, F. Tian, W. Li, F. Li and W. Liu, *J. Mater. Chem.*, 2011, **21**, 13163.
30 A. Jaiswal, S. Ghosh and A. Chattopadhyay, *Chem. Commun.*, 2012, **48**, 407.
31 S. Yu, M. Kang, H. Chang, K. Chen and Y. Yu, *J. Am. Chem. Soc.*, 2005, **127**, 17604.
32 H. Liu, T. Ye and C. Mao, *Angew. Chem. Int. Ed.*, 2007, **46**, 6473.
33 M. Wu, Y. Wang, Y. Wu, C. Hu, X. Wang, J. Zheng, Z. Li, B. Jiang and J. Qiu, *Carbon*, 2014, **78**, 480.
34 S. Park, H. Lee, E. Park, S. Lee, J. Lee, S. Jeong, C. Kim, Y. Lee, Y. Huh and J. Lee, *ACS Appl. Mater. Interfaces*, 2014, **6**, 3365
35 L. Zhu, Y. Yin, C. Wang and S. Chen, *J. Mater. Chem. C*, 2013, **1**, 4925.
36 V. Mehta, S. Jha, R. Singhal and S. Kailasa, *New J. Chem.*, 2014, **38**, 6152.
37 X. Gong, W. Lu, M. Paau, Q. Hu, X. Wu, S. Shuang, C. Dong and M. Choi, *Anal. Chim. Acta.*, 2015, **861**, 74.
38 L. Wang and H. Zhou, *Anal. Chem.*, 2014, **86**, 8902.
39 P. Hsu, Z. Shih, C. Lee and H. Chang, *Green Chem.*, 2012, **14**, 917.
40 S. Lim, W. Shen and Z. Gao, *Chem. Soc. Rev.*, 2015, **44**, 362.
41 Y. Wang, L. Heim, Y. Xu, G. Buntkowsky and K. Zhang, *Adv. Funct. Mater.*, 2015, **25**, 1434.
42 H. Orelma, I. Filpponen, L. Johansson, M. Österberg, O. Rojas and J. Laine, *Biointerphases*, 2012, **7**, 61.
43 Y. Cao, Y. Jiang, Y. Song, S. Cao, M. Miao, X. Feng, J. Fang and Shi, *Carbohydr. Polym.*, 2015, **131**, 152.
44 N. Lin, C. Bruzzese and A. Dufresne, *ACS Appl. Mater. Interfaces*, 2012, **4**, 4948.
45 T. Saito, Y. Nishiyama, J. Putaux, M. Vignon and A. Isogai, *Biomacromolecules*, 2006, **7**, 1687.
46 R. Liu, J. Zhang, M. Gao, Z. Li, J. Chen, D. Wu and P. Liu, *RSC Adv.*, 2015, **5**, 4428.
47 Q. Lu, W. Lin, L. Tang, S. Wang, X. Chen and B. Huang, *J. Mater. Sci.*, 2015, **50**, 611.

48 F. Wang, Z. Xie, H. Zhang, C. Liu and Y. Zhang, *Adv. Funct. Mater.*, 2011, **21**, 1027.
49 S. Ruan, J. Qian, S. Shen, J. Zhu, X. Jiang, Q. He and H. Gao, *Nanoscale*, 2014, **6**, 10040.
50 M. Bulota, S. Tanpichai, M. Hughes, S. Eichhorn, *ACS Appl. Mater. Interfaces*, 2012, **4**, 331.
51 K. Hattori, E. Abe, T. Yoshida and J. Cuculo, *Polym. J.*, 2004, **36**. 123.
52 S. Zhu, Y. Song, X. Zhao, J. Shao, J. Zhang and B. Yang, *Nano Res.,* 2015, **8**, 355.
53 S. Baker and G. Baker, *Angew. Chem. Int. Ed.*, 2010, **49**, 6726.
54 Y. Yang, J. Cui, M. Zheng, C. Hu, S. Tan, Y. Xiao, Y. Qu and Y. Liu, Y. *Chem. Commun.*, 2012, **48**, 380.
55 J. Cai, S. Kimura, M. Wada and S. Kuga, *Biomacromolecules*, 2009, **10**, 87.

Graphical Abstract

Transparent, photoluminescent hybrid film was constructed using nanocellulose as fibrous network skeleton and CDs derived from nanocellulose as fluorescent nanomaterials.