

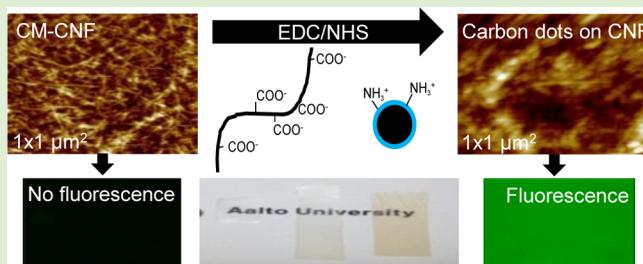
Modification of Cellulose Nanofibrils with Luminescent Carbon Dots

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ABSTRACT: Films and hydrogels consisting of cellulose nanofibrils (CNF) were modified by covalent EDC/NHS coupling of luminescent, water-dispersible carbon dots (CDs). Quartz crystal microgravimetry with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR) were used to investigate the attachment of CDs on carboxymethylated CNF (CM-CNF). As the first reported use of CD in nanocellulose products, we provide proof-of-concept for the synthesis of transparent and fluorescent nanopaper and for its tunable luminescence as confirmed by confocal microscopy imaging.



INTRODUCTION

Cellulose nanofibrils (CNF) are produced from cellulosic fibers via mechanical disintegration using high-pressure fluidizers,¹ high-pressure homogenizers,² cryo-crushing,³ or supergrinders.⁴ Several pretreatments have been proposed to facilitate the disintegration of the fiber cell wall.^{5,6} In addition to its biodegradability and abundance, CNF properties are of interest for numerous applications. This is in part because of its high aspect ratio and ability to form strong network structures.⁵ CNF is highly hydrophilic and forms hydrogels at very low solids content.⁷

In order for CNF to be used in high-end applications, including those in the biomedical fields, it has to be modified to adjust or develop the desired properties. A challenge is that chemical modification of CNF in a medium other than water causes unintended changes in surface properties, for example, surface passivation and aggregation.⁸ Recently, a method for heterogeneous modification of CNF in water was reported, which is based on polysaccharide adsorption.^{9,10} *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride/*N*-hydroxysuccinimide (EDC/NHS) coupling chemistry has also been successfully used in direct modification of carboxylated CNF in aqueous media.¹¹ Cellulose nanopaper, which is one simple product of CNF,^{12,13} has shown a great potential, especially in food packaging applications¹⁴ and in electronic devices.^{15–17} This stems from its smoothness, optical transparency, good oxygen barrier properties at low relative humidity, low thermal expansion, biodegradability, and light weight. The disadvantage of making CNF-based nanopaper is the slow dewatering of the film due to the high water binding capacity of CNF. However, recent attempts to increase the dewatering ability of CNF have made it appealing for large scale production and deployment in nanopaper.¹⁸

Carbon dots (CDs) were discovered in 2004¹⁹ during the purification process of single-walled carbon nanotubes. CDs

have low toxicity and they are nanosized, luminescent, and easy to functionalize.²⁰ The application potential of CDs is huge, for example, in biosensors,²¹ biomedical imaging,²² marker development, and anticounterfeiting,^{20,23} among others. Compared to highly toxic metal-based quantum dots (QDs), CDs are a promising alternative in biomedical and other applications. In addition, the possibility of making CDs dispersible in water facilitates its incorporation in highly hydrophilic CNF hydrogels which may open up new venues in cellulose-based diagnostics, sensors, and visual displays. However, despite their growing interest, to our knowledge there are no reports available on the use of CDs in combination with cellulosic materials. Therefore, the motivation of this work is to bring the photoluminescent properties of CD to CNF aqueous dispersions and to unveil the nature of their interactions at the molecular levels.

CDs were covalently and electrostatically attached to ultrathin films and hydrogels made from carboxymethylated CNF (CM-CNF). The attachment of CDs on the ultrathin films of CM-CNF was monitored *in situ* by using quartz crystal microbalance with dissipation monitoring (QCM-D) and surface plasmon resonance (SPR). The modified surfaces were characterized via atomic force microscopy (AFM). Also, CM-CNF hydrogels were modified by covalent binding of CD via EDC/NHS coupling chemistry. The effects of the modification on the surface charge, thermal stability and optical properties of the material were investigated using charge titrations, thermogravimetric analysis (TGA), transmission electron microscopy (TEM), and confocal microscopy. Nanopaper was produced from both carboxymethylated and CD-modified CM-CNF gels by filtration and hot pressing. The CM-

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CNF films were further coated with CDs by dipping. The morphology and photoluminescence of these films were evaluated using AFM imaging and confocal microscopy.

MATERIALS AND METHODS

Materials. *CM-Pulp.* A fully bleached birch kraft pulp from a Finnish pulp mill (kappa number 1; DP 4700; fines-free (SCAN-M 6:69)) was carboxymethylated to a degree of substitution of 0.052.²⁴ The carboxymethylated pulp (CM-pulp) was washed to its sodium-form.²⁵ The CM-pulps were fluidized with a microfluidizer (Microfluidics M110P, Microfluidics Corporation, MA) after five passes to produce CM-CNF.

Chemicals. All the chemicals used were of analytical grade. *N*-(3-Dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC) was purchased from Fluka and *N*-hydroxysuccinimide (NHS) from Thermo Scientific. Milli-Q water (Millipore Synergy UV unit; Millipore S.A.S. Molsheim, France) was used for the dilutions.

Carbon Dots. Water-dispersible CDs were synthesized and purified according to Liu et al.²⁶ except that the pyrolysis of glycerol was made in the presence of 2,2-(ethylenedioxy)-bis-(ethylamine) instead of 4,7,10-trioxa-1,13-tridecanediamine. The microwave-assisted pyrolysis was carried out for 10 min at 750 W. The resulting CDs are charge-stabilized by a cationic surface layer composed of amine groups which makes them water dispersible.

CNF-CD Hydrogels. CDs were attached to CM-CNF by EDC/NHS coupling. The synthesis was carried out in 1 mM sodium acetate/acetic acid (NaAc/HAc) buffer (pH 4.5) with a 2 g/L CM-CNF dispersion. The dispersion was mixed with magnetic stirring. A total of 119 mg/g of EDC and 460 mg/g of NHS was added to the CM-CNF dispersion, and finally, 3 or 30 mg/g of the CD dispersion was added (the CD dispersion was sonicated for 10 min prior to addition). The reaction was conducted overnight at room temperature and protected from light. The modified dispersion was dialyzed (12000–14000 Da) against distilled water for 8 days.

CM-CNF Nanopaper. Membrane filtration was used to produce CM-CNF or CNF-CD nanopaper. The CM-CNF gel was diluted to 1 g/L concentration with deionized water and mixed (magnetic stirring) for 1 h, followed by 5 min homogenization (Ultra-Turrax UTC, IKA-Werke GmbH & Co. KG, Staufen, Germany) and ultrasonication (2 min) to remove air bubbles from the gel. A total of 800 mL of CM-CNF was filtered on a glass filter funnel using two 0.65 μm DVPP filter membranes (EDM Millipore, Merck KGaA, Darmstadt, Germany) and until approximately 790 mL of water was drained from the film. The wet film was then pressed (standard paper press) for 15 min between filter membranes supported by blotting papers. Finally, the nanopaper was subject to heat treatment overnight, under press at 40 °C.

Nanopaper CD Coating via Solution Dipping. CM-CNF nanopaper was coated with CDs via solution dipping. The CM-CNF films were first immersed in Milli-Q water for 1 h. Then, the films were immersed in NaAc/HAc buffer solution for 20 min. Thereafter, the films were dipped in EDC/NHS solution (using 10 mM NaAc/HAc background buffer) for 20 min and thoroughly rinsed using the buffer solution. This led to the “activation” of the CM-CNF films, which were then dipped into a CD dispersion (0.1 g/L in 10 mM NaAc/HAc buffer) for 20 min. In order to remove any free, non-bound CDs from the films, they were dipped in the NaAc/HAc buffer solution for 10 min, followed by NaHCO₃ buffer (10 mM, pH = 8.5), rinsing for 10 min. Finally, the films were rinsed with water and dried overnight in a 40 °C oven under pressure between membrane filters supported by blotting papers.

CM-CNF Films for QCM and SPR Studies. CM-CNF was used to prepare films by the method reported by Eronen et al.²⁷ after slight modifications. The carboxymethylated CNF gel was diluted in water to a final concentration of 1.25 g/L and sonicated for 5 min in order to remove air bubbles. Gold-coated QCM-D and SPR sensors were treated for 10 min in a UV/ozone oven and immersed for 15 min in 1 g/L polyethylene imine (PEI) solution, followed by thorough rinsing with Milli-Q water and drying with N₂. The PEI-coated sensors were

spin-coated with CM-CNF dispersions (1.25 g/L, 60 s, 3000 rpm). Finally, the surfaces were dried in an oven (80 °C, 10 min) and placed in a desiccator until use (within 2 days after preparation). For the QCM-D and SPR measurements, the CM-CNF-coated sensors were placed in buffer solution (10 mM NaAc/HAc, pH 4.5) overnight for stabilization.

Methods. *QCM-D.* Quartz crystal microbalance with dissipation (QCM-D) measurements were performed with a Q-Sense E4 device (Västra Frölunda, Sweden) with controlled flow (100 μL/min). The measurement technique is based on a sensor (quartz crystals) that resonates at a certain frequency (and its overtones) unless mass (solvent or adsorbate) is added on the surface, which results in a reduction in the resonant frequency. Conversely, mass release produces an increase in frequency. In its simplest form, the shift in the frequency of vibration can be related to the change in mass according to the Sauerbrey equation.²⁸ In our experiments, the CM-CNF-coated QCM-D sensors were dried with N₂ gas, placed in the measurement chamber, and stabilized with the buffer solution until frequency stabilization. EDC/NHS solution was then injected to activate the carboxyl groups on the CM-CNF to amine reactive form (20 min, pH 4.5, 10 mM buffer concentration). The activated CM-CNF film was then exposed to CD dispersions (30 min, pH 4.5, 10 mM buffer concentration). CD coupling proceeded until reaching a plateau condition (no frequency shift was registered), which was followed by rinsing with buffer solution. In order to remove any loosely attached CD, the system was rinsed with a 10 mM NaHCO₃ buffer at relatively high pH (8.5) followed by rinsing with buffer at low pH (4.5). A reference test was also conducted following the same procedure explained before but without the EDC/NHS activation step. This facilitated the elucidation of the roles of electrostatic and noncovalent interactions between CM-CNF and CDs.

SPR. Surface plasmon resonance (SPR) measurements were carried out with a SPR Navi 200 (Oy Bionavis Ltd., Tampere, Finland). A constant flow rate of 100 μL/min was used during the measurements at a constant temperature of 25 °C. The change in SPR angle is caused by the shift in optical resonance at the interface between the solid surface and the sensor surrounding medium due to molecular adsorption.²⁹ This can be monitored as a function of time using controlled flow of the buffer or CD dispersion in the measurement chamber. The same experimental conditions and sequence followed in QCM-D experiments were applied in the SPR tests.

AFM and TEM. CM-CNF were imaged via atomic force microscopy in tapping mode (AFM, Dimension 3000, Bruker, Santa Barbara, CA, U.S.A.) prior to and after modification with CDs. No other image processing was used except flattening of the images to remove possible image tilting. The scan sizes were typically 1 × 1 μm² and 5 × 5 μm². A transmission electron microscope (TEM, 2010F, JEOL Ltd., Tokyo, Japan) operated at 120 V was used for CNF-CD and CD imaging. The carbon-coated TEM sample grid was purified with ethanol prior to addition of a drop of CNF-CD or CD dispersion. The solvent was evaporated in an oven (40 °C) for 4 h.

Charge Measurements. The surface charge of CM-CNF before and after modification with CDs was measured at two different pH values (pH 4.5 and 8.5) by using polyelectrolyte titration.³⁰ The ionic strength was set to 0.1 mM in all experiments. A Mütek particle charge detector (PCD 03, Mütek Analytic GmbH, Herrsching, Germany) was used to detect the neutralization point after addition of poly-(diallyldimethylammonium chloride) (PDADMAC, high molecular weight, 6.19 meq/g) titrant. Potassium polyvinylsulphate (KPV, CD 2.85 × 10⁻⁷ eq/mL) was used as polyelectrolyte titrant in the case of CDs.

TGA. Thermogravimetric analysis (TGA, Q500, TA Instruments, New Castle, DE) was carried out using freeze-dried samples. Approximately 10 mg of the given sample was placed on a platinum pan and heated from 30 to 800 °C (10 °C/min) under a nitrogen atmosphere. The thermal stability of the CNF-CD and reference CM-CNF was compared.

Confocal Microscopy. Confocal microscopy was used to study the fluorescence of CD-modified nanopaper. The microscope used was a Leica TCS SP2 CLSM (Leica Microsystems CMS GmbH, Manheim,

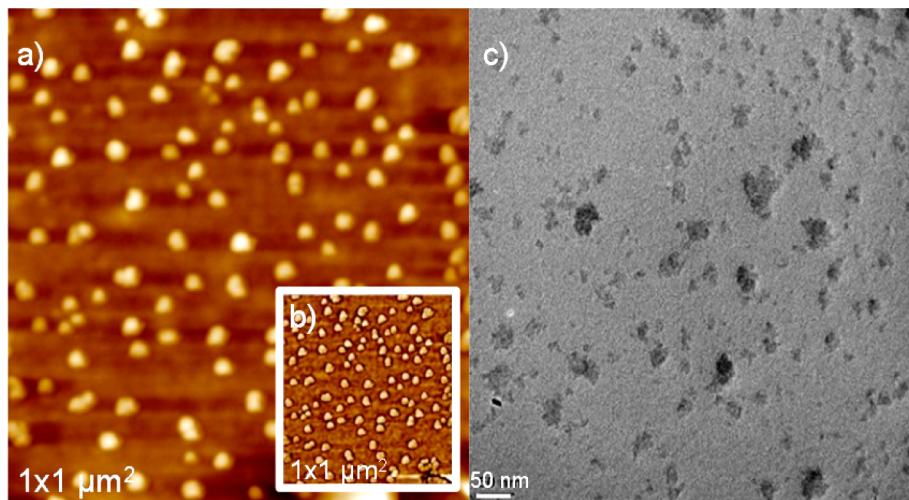


Figure 1. AFM (a, on mica) and TEM (c, on carbon-coated grids) images of CDs dried from water dispersions on the respective solid support. An AFM phase image ($1 \times 1 \mu\text{m}^2$) is also included (b). The z-scale in the AFM images is 16 nm. The scale bar in the TEM image is 50 nm in length.

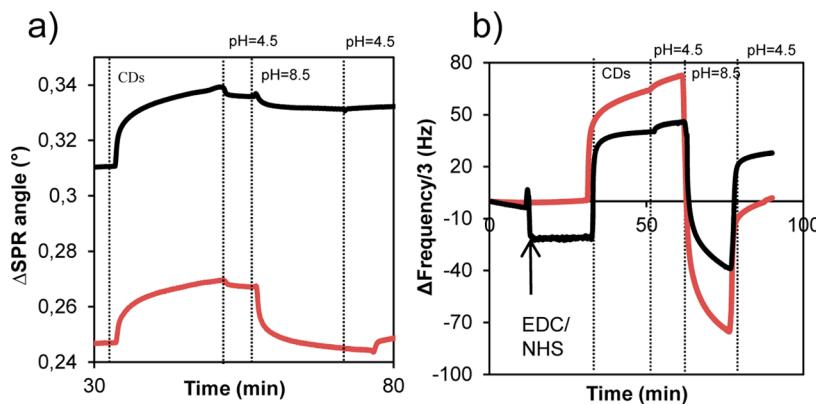


Figure 2. Effect of CDs attachment (pH 4.5; 10 mM ionic strength) on EDC/NHS-activated (black line) and nonactivated (red line) CM-CNF films as a function of elapsed time, as measured by (a) SPR and (b) QCM-D. The ionic strength was kept constant (10 mM) throughout the measurements.

Germany). The images ($750 \times 750 \mu\text{m}^2$) were obtained by using excitation and detection wavelengths of 488 and 500–530 nm, respectively. The intensity images (cross section and surface) were scanned using an averaging mode and constant imaging conditions (laser powers of 700 and 650 V during surface and cross-section imaging, respectively).

RESULTS AND DISCUSSION

Characterization of CDs. The charge density of the CDs, as measured by polyelectrolyte titration, was $+500 \mu\text{mol/g}$ at pH 4.5. No cationic charge was detected at pH = 8.5 due to the deprotonation of the surface ammonium ion groups in CD. AFM and TEM imaging was used to determine the size of the CDs (Figure 1). Both imaging techniques indicated that the dried CDs formed aggregates with sizes in the 10–30 nm range.

Attachment of CDs on CNF Films. The attachment of CD on CM-CNF films was monitored in SPR and QCM-D experiments (see the respective sensograms in Figure 2).

The SPR angle increased when CDs were introduced onto the CM-CNF surface immersed in pH 4.5 buffer, which is indicative of the affinity between CD and CM-CNF (Figure 2a). This is expected to be the result of electrostatic interactions between the oppositely charged cellulose nanofibrils and CD nanoparticles. When the pH was increased to pH = 8.5, the CDs became uncharged, resulting in a reduced

electrostatic interaction, as can be clearly observed in the case of CNF surfaces (red profile in Figure 2). However, for the CM-NFC surfaces activated with EDC/NHS prior to CD injection (black sensograms in Figure 2a), the CDs remained on the surface even after rinsing at pH 8.5. This is taken as an indication of the EDC/NHS-mediated coupling between the carboxyl groups of the CM-CNF and the amine surface groups of the CDs. The experiments were also performed with a QCM-D in order to further investigate the effect of CD attachment on CM-CNF (Figure 2b). The EDC/NHS activation of CM-CNF resulted in a slight decrease in the resonance frequency of the system. This indicates that there is an increase in the effective mass of the substrate as a result of the activation of the carboxyl groups in CM-CNF. Introduction of CDs clearly increased the resonance frequency of the system. The CDs interact with the highly water-swollen CM-CNF film, as expected for cationic, highly charged polyelectrolytes.³¹ Thus, the CDs displace bound water from the CM-CNF film upon adsorption, which is observed as an increase in resonance frequency and a decrease in the energy dissipation (-11×10^{-6}). In addition, the irreversibility of the attachment of CDs on CM-CNF was tested by rinsing the films with a pH 8.5 buffer. In the case of CM-CNF, substantial water swelling was observed (decrease in frequency) due to the dissociation of the

carboxyl groups. When the pH 4.5 buffer was shifted back, no change in total mass of the film (compared to the starting condition) was observed. This is an evidence that the CDs were removed from the CM-CNF surface during the high pH rinsing, in a similar manner as was observed in SPR experiments. However, when the CDs were adsorbed on the activated CM-CNF surface, the film did not swell substantially at high pH, which is most probably due to the activation of the carboxyl groups. Moreover, when the pH was changed back to pH = 4.5, the resonance frequency of the system shifted, if compared to the initial conditions (30 Hz for the third overtone). This suggests that the CDs were covalently attached onto the activated CM-CNFs and that they irreversibly reduced the amount of water bound to the surface. Furthermore, the dissipation of the system was markedly decreased upon CD attachment (-10×10^{-6}), which indicates reduced viscoelasticity and also points toward successful binding of CDs onto the CM-CNF substrate. The films were imaged with AFM before and after the QCM-D measurements in order to observe changes in morphology upon CD attachment (Figure 3).

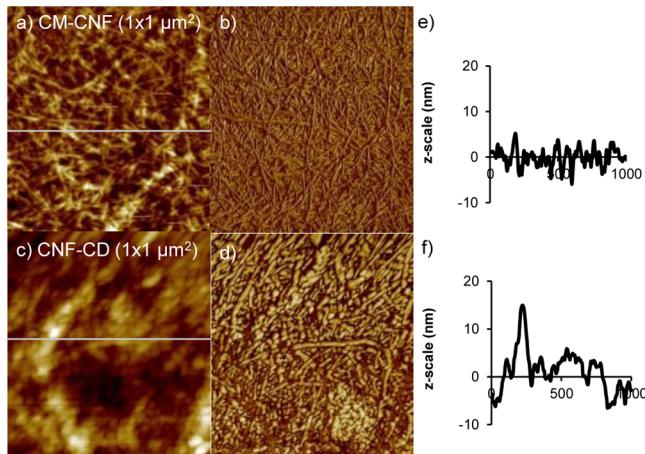


Figure 3. Carboxymethylated CNF (CM-CNF) imaged with an AFM ($1 \times 1 \mu\text{m}^2$) before [(a) height and (b) phase images] and after the CD attachment [(c) height and (d) phase images]. Profiles in (e) and (f) correspond to the z-scale (nm) of the surface prior and after CD attachment, respectively.

The topography of the CM-CNF film clearly changed upon covalent attachment of CD (Figure 3). In addition, the height profile of the film was increased substantially due to the added CDs. There is also an indication that the CDs attached on the CM-CNF film as individual particles (there is no evidence of CD aggregates on the surface).

Synthesis of CNF-CD. Carboxymethylated CNF was modified in aqueous media in a hydrogel form. After the synthesis and purification of the samples, they were titrated with polyelectrolytes at two different pH conditions so that the effect of the incorporated CDs could be revealed as dependent on the presence of protonated amine and deprotonated carboxyl groups (carboxyl groups are fully dissociated at pH 8.5) in the system. Based on the titration results, the surface charge of the CM-CNF was clearly decreased as a result of the covalent attachment of CDs (Figure 4d). In addition, TEM images revealed the presence of CDs on the CM-CNF substrate (Figure 4c).

As expected, the surface charge of CM-CNF decreased as a result of CD attachment (Figure 4d). Based on the titration

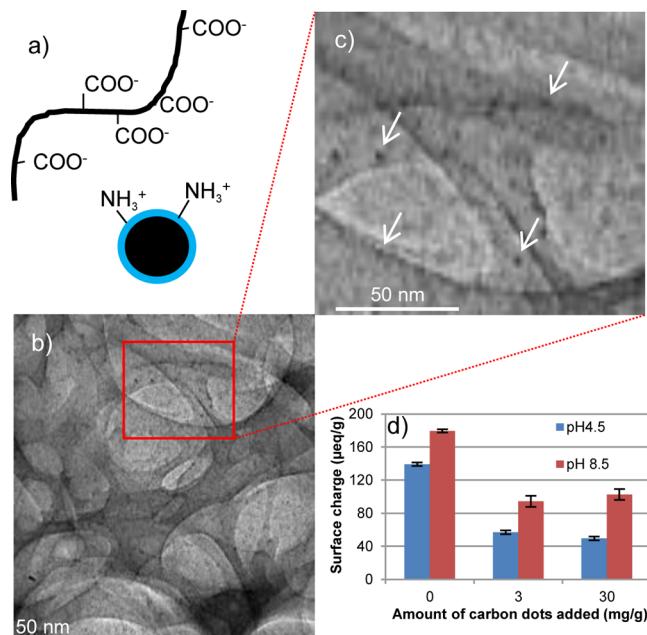


Figure 4. (a) Modification of CM-CNF gel with CDs. (b) TEM image correspond to a CNF-CD (30 mg/g CD dosage) dried on a carbon-coated TEM sample grid (50 nm scale bar). (c) Enlarged view from one section of (b) illustrating the presence of CDs (inserted arrows indicate a few of them). (d) The development of surface charge of CNF-CD as a function of CD addition. CM-NFC and CNF-CD were titrated with polyelectrolytes of opposite charge (PDADMAC) at two different pH conditions (pH = 4.5 and 8.5, 0.1 mM ionic strength).

results, 45% of the surface carboxyl groups took part in CD binding, as calculated by the decrease in surface charge of CM-CNF prior to and after CD attachment (titration at pH 8.5). It should be noted that some side reactions as well as minor aggregation of CM-CNF may take place during the synthesis which in turn can decrease both the surface charge of CNF-CD and the binding efficiency of CDs. The CD loading of the CNF-CD was calculated based on the increased difference in the surface charge of CM-CNF at pH 4.5 and 8.5 conditions. The relative change (decrease) in the surface charge was found to be 5 and 13 $\mu\text{mol/g}$ for the 3 and 30 mg/g CD addition. The actual CD loading on CM-CNF was calculated by dividing the relative change in surface charge by the charge density of CDs, resulting in 10 ± 6 and 26 ± 6 mg/g, respectively. This indicates that nearly all the added CDs were attached to the CM-CNF. It should be noted here that the titration results from the 3 mg/g CD addition are only to be taken on a relative basis, as the calculated CD loading is higher than the initial addition of CDs. However, larger CD addition (30 mg/g) seems to be more suitable for the polyelectrolyte titration method, and therefore, more reliable results were obtained with the increased CD loading. The CNF-CD was also imaged via TEM after synthesis (Figure 4b,c), giving a further indication that the CDs were incorporated on the CNFs. Finally, the CNF-CD was freeze-dried and analyzed by TGA (Figure 5).

TGA results (Figure 5) indicate an increase (by approximately 35 °C) of the degradation temperature of CM-CNF when CDs were covalently attached.

CM-CNF Nanopaper. Nanopaper was produced from CD-modified CNF (CNF-CD) as well as from carboxymethylated CNF (CM-CNF). It was interesting to note that, compared to carboxymethylated CNF, the filtration time during nanopaper

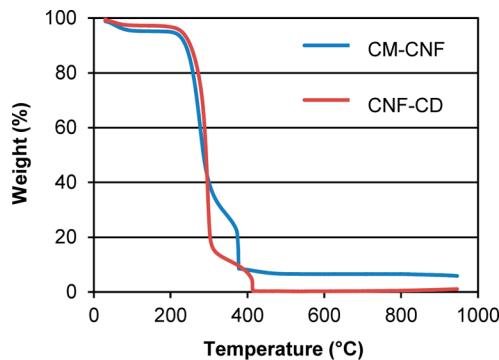


Figure 5. TGA thermogram of the dried CNF-CD (red line) and CM-CNF (blue line).

manufacture was 20% faster in the case of CNF-CD. Based on the QCM-D results the bound water in the CM-CNF film was irreversibly decreased as a result of the CD binding, which supports the observation of a facilitated removal of water also in the case of CNF-CD nanopaper. The carboxymethylated CNF film was modified by dipping, as a post-treatment. The film was first activated with EDC/NHS and then dipped in CD dispersions and thoroughly rinsed with both water and NaHCO₃ buffer to remove any unbound CDs from the film surface. Digital camera and confocal microscope images of the films (CM-CNF, CD-coated CM-CNF, and CNF-CD films) are included in Figure 6.

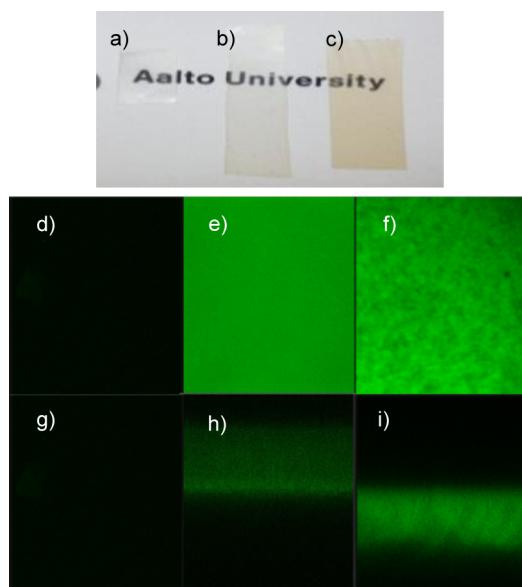


Figure 6. Digital camera images of films of (a) CM-CNF, (b) CD-coated CM-CNF, and (c) CNF-CD. The confocal microscopy images were taken from the surface (d–f) and the cross-section (g–i). Images (d) and (g) correspond to CM-CNF film, (e) and (h) are the CD-coated CM-CNF films, and (f) and (i) are the CNF-CD films.

Carboxymethylated CNF nanopaper appeared rather transparent and did not show fluorescence (Figure 6a,d). Upon modifying the activated CM-CNF film by dipping (covalent attachment of CDs), the film became fluorescent (Figure 6b,e). It should be noted that only the surface of CD-coated film was fluorescent, as observed from the cross-section image (Figure 6h). The film remained transparent, but a slight change in color occurred due to surface modification (see Figure 6b).

Nanopaper produced from the modified CNF-CD gel was fluorescent throughout the film (Figure 6f,i), as revealed by confocal microscopy imaging from the surface and the cross-section of the film. Also in this case the film was transparent and had a slight brownish color (Figure 6c). The film roughness was measured via AFM line profiles. The film roughness was decreased from 45 to 30 nm as a result of the surface modification upon CD-dipping ($5 \times 5 \mu\text{m}^2$ AFM height image). The CNF-CD film had a surface roughness of 31.1 nm. All in all, it is demonstrated that nanopaper can be manufactured from both CM-CNF and CNF-CD. Dipping of the carboxymethylated and EDC/NHS activated CM-CNF film in CD dispersions presents a simple and effective procedure for nanopaper coating. CD coating produced a smoother nanopaper surface when compared to that of the CM-CNF film. CD-modified CNF may find use in various biosensing applications by virtue of its fluorescence and the surface functional groups. CNF-CD may also be utilized in anticounterfeit applications, for example by printing the fluorescent CNF-CD gel on a paper substrate.

CONCLUSIONS

It is demonstrated for the first time that luminescent CDs can be covalently attached in aqueous media to cellulose nanofibrils (CNF) via EDC/NHS coupling. CDs did not aggregate during drying when they were embedded in the CM-CNF matrix. The thermal stability of the CM-CNF was increased by attachment of CDs. In addition, they were able to irreversibly remove bound water from the CM-CNF when attached on its surface. Transparent, smooth, and fluorescent nanopaper was produced from CNF-CD. A decreased filtration time of the CM-CNF gel was achieved by CD-modification during nanopaper manufacture. The CM-CNF film was also surface modified with CDs by simple dipping. This resulted in a decrease in the roughness of the film, and a strong fluorescence. Further work is needed to demonstrate the potential of CD-modified CM-CNF in anticounterfeit and biosensing applications.

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Notes

The authors declare no competing financial interest.

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