POLYPUBLIE
Polytechnique Montréal

POLYTECHNIQUE MONTRÉAL
UNIVERSITÉ D'INGÉNIERIE

Titre: Title:	Physicochemical properties of cellulose nanocrystals treated by photo-initiated chemical vapour deposition (PICVD)
Auteurs: Authors:	Taraneh Javanbakht, Wendell Raphael, & Jason Robert Tavares
Date:	2016
Type:	Article de revue / Article
Référence: Citation:	Javanbakht, T., Raphael, W., & Tavares, J. R. (2016). Physicochemical properties of cellulose nanocrystals treated by photo-initiated chemical vapour deposition (PICVD). Canadian Journal of Chemical Engineering, 94(6), 1135-1139. https://doi.org/10.1002/cjce.22473

Document en libre accès dans PolyPublie
Open Access document in PolyPublie

URL de PolyPublie: PolyPublie URL:	https://publications.polymtl.ca/35050/
Version:	Version finale avant publication / Accepted version Révisé par les pairs / Refereed
Conditions d'utilisation: Terms of Use:	Tous droits réservés / All rights reserved

Document publié chez l'éditeur officiel
Document issued by the official publisher

Titre de la revue: Journal Title:	Canadian Journal of Chemical Engineering (vol. 94, no. 6)
Maison d'édition: Publisher:	Wiley
URL officiel: Official URL:	https://doi.org/10.1002/cjce.22473
Mention légale: Legal notice:	This is the peer reviewed version of the following article: Javanbakht, T., Raphael, W., & Tavares, J. R. (2016). Physicochemical properties of cellulose nanocrystals treated by photo-initiated chemical vapour deposition (PICVD). Canadian Journal of Chemical Engineering, 94(6), 1135-1139. https://doi.org/10.1002/cjce.22473, which has been published in final form at https://doi.org/10.1002/cjce.22473. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.

PHYSICOCHEMICAL PROPERTIES OF CELLULOSE NANOCRYSTALS TREATED BY PHOTO-INITIATED CHEMICAL VAPOR DEPOSITION (PICVD)

Taraneh Javanbakht, Wendell Raphael, Jason Robert Tavares*

Department of Chemical Engineering, École Polytechnique de Montréal, Montréal, Québec, Canada H3C 3A7

*Corresponding author: Jason Robert Tavares

E-mail: jason.tavares@polymtl.ca

Telephone: +1 (514) 340-4711 x2326

Cellulose nanocrystals (CNC) are novel nanomaterials produced by the pulp and paper industry. The surface properties of CNC are key factors for their dispersion in solvents. These polar materials disperse readily in water, but not in organic solvents. The ability to disperse into typically non-polar organic matrices is an indispensable requirement to exploit the growing market for nanocomposite materials. We present herein an innovative approach to modify the surface of CNC through scalable, gas-phase photo-initiated chemical vapor deposition (PICVD). Using syngas as a treatment precursor, we demonstrate the effectiveness of this technique to render the surface of the CNC compatible with mildly polar and non-polar solvents, evidenced by contact angle measurements. Further proof of this successful modification is given in the form of dispersion assays, showing for example the ability to disperse treated CNC in toluene (whereas untreated samples do not disperse). Suspensions in organic solvents remain stable in excess of two weeks. Chemical characterization through XPS and FT-IR confirms the presence of an oxygen-containing coating on the CNC surface.

Keywords: PICVD, photochemistry, cellulose nanocrystals, contact angle, FTIR, TEM, XPS

INTRODUCTION

Cellulose is a renewable, biodegradable, non-toxic nanomaterial and is the most abundant natural biopolymer on earth. It is a carbohydrate polymer with repeating -D-glucopyranose and hydroxyl groups per anhydroglucose unit, giving it a high degree of functionality. Its molecular structure explains its characteristic properties, such as hydrophilicity, chirality and biodegradability. The biological, chemical and mechanical properties of cellulose and its derivatives have been widely studied for a variety of applications, such as food, paper production, biomaterials and pharmaceuticals.[1,2]

Cellulose nanocrystals (CNC) are a new class of nanomaterials obtained from the acid hydrolysis of cellulose fibers. Nanoscale dimensions, high specific strength and modulus, high surface area and unique optical properties make CNC appropriate nanomaterials for many applications. These include nanocomposite films, drug delivery, protein immobilization and metallic reaction templates.[3]

Morphologically, CNC are typically observed as rigid spindle-like nanometric crystals. Some spherical shaped CNC in aggregation were also produced using acid treatment.[4,5] The relative degree of crystallinity and the geometrical aspect ratio of CNC are very important parameters controlling their properties. When these nanomaterials are prepared in sulphuric acid, they possess native negative charges on their surface, due to the formation of sulphate ester groups. This enhances their stability in aqueous solutions.[3] However, dispersion into non-polar media remains a principal challenge preventing the widespread use of CNC in nanocomposite materials. For this reason, surface compatibilization of the CNC is required.

Several functionalization approaches are possible on CNC, given the presence of several reactive groups on their surface. Indeed, CNC possess several hydroxyl groups on their surface, where chemical reactions can be carried out. Roy et al. demonstrated that in the cellulose crystal lattice structure, among the three kinds of hydroxyl groups in each glucose residue (Fig. 1), the OH group on the sixth position of glucose molecules acts as a primary alcohol, and most modifications occur predominantly on this site.[6] Several chemical modifications of CNC, such as cationisation, carboxylation, silylation, esterification and polymer grafting have been reported.[7-12] The chemical modifications of CNC can improve its dispersion in medium polar solvents. A study showed that silylated whiskers of cellulose with degrees of substitution (DS) of

3

between 0.6 and 1 could be re-dispersed in medium polarity organic solvents.[13] The whiskers with moderate DS render the CNC surface hydrophobic.[3] Mixing CNC with polymers is another procedure to improve its dispersion in organic solvents. The mixture of modified CNC and low-density polyethylene was extruded and a better dispersion was reported in formulations with longer aliphatic chains.[14]

Oxidation, esterification, amidation, carbamation and etherification are the main categories of reactions carried out on CNC. Other surface modifications consist of using nucleophilic substitutions to introduce more complex functionality to CNC or applying multi-step modifications.[15] The majority of studies focusing on CNC modification make use of wet or solvent-based chemistry to generate new functional groups. The chemistry of these reactions tends to be complex, multi-step and done in a series of organic solvents (namely, dimethyl sulfoxide), the handling of which presents significant challenges in an industrial setting due safety hazards.[16,17] Furthermore, the yield of these solvent-based reaction schemes is limited and downstream separation of the CNC from the reaction media creates challenges regarding process scaling and economics. Gas-phase functionalization of CNC may circumvent the challenges associated with solvent-based processing.[18] Several researchers have studied the use of gas-phase techniques such as plasma processing,[19,20] but these remain challenging to implement at a large scale because of discharge volume constraints and specialized equipment requirements.

Our group's previous work focused on the design and development of a novel alternative gas-phase surface treatment approach, photo-initiated chemical vapor deposition (PICVD). It uses a simple gas precursor, exploits an affordable initiation source (UVC light) and operates under normal conditions.[18] In this paper, recent developments on the surface modification of CNC by PICVD are reported, along with extensive characterization of the resulting physicochemical properties, morphology and dispersion into a variety of polar and non-polar solvents.

EXPERIMENTAL

Chemicals

Celluforce provided CNC prepared from a wood-pulp source and subsequently spray-dried (spindle-like morphology, 250 ± 50 nm length). Hydrogen peroxide (chemical purity 50%) was purchased at Sigma-Aldrich. CO, H_2, and Ar (chemical purity 100%) were obtained from Air Liquide.

Photo-initiated chemical vapor deposition

The surface modification of the CNC was carried out using a PICVD micro-reactor illustrated in Figure 2 and detailed extensively in a previous publication.[18] CNC to be treated was first mechanically dispersed in toluene (unstable dispersion), as described by Salajková[21], then 2 drops (50 µL each) of this solution were immediately deposited onto polished copper sample holders and allowed to dry at room temperature for 24 hours. The deposition of sample drops was repeated five times. The copper sample holders were polished beforehand using deionized water and sandpaper (grit 1200 MX); Cu was retained as a sample holder as it was the material used in the initial PICVD investigation.[18] The CNC samples to be treated were placed inside the tubular quartz reactor at a distance of 30 cm from the inlet. Before each treatment sequence, argon was used to purge the reactor for 3 minutes. The precursor gas mixture (H_2 and CO) was injected with a molar ratio of 0.1/1 (H_2/CO) and was irradiated by two UVC lamps (main emission peak at 253.7 nm, irradiance of 5.5×10^{-4} W/cm^2 at 4.5 cm). The gas ratio was controlled by adjusting the individual mass flow of each gas (total gas flow rate was 376 ml/min). H_2O_2 was added to the reactor as a photoinitiator at a rate of 1 mL/h using a syringe pump. Treatment duration was set to 1h. A valve was placed at the reactor outlet to control the operating pressure in the reactor, maintained at 10 kPag for all experiments (based on conditions known to yield hydrophobic surface properties).[18] When the experiments were completed, the copper sample holders were carefully taken out of the reactor for analysis. All the surface treatments were carried out on three samples of CNC simultaneously and all experiments were repeated three times.

Contact angle measurement

The contact angle measurements were achieved by placing 2 µL of solvents (deionized water, toluene, n-dodecane) on the CNC supported by the copper sample holder. The sessile drop contact angle being stable on the minute time frame, one measurement per location was taken immediately using a FDS tensiometer (OCA DataPhysics TBU 90E). The measurements were carried out on several spots on the un-treated and treated CNC. The images were taken 5 seconds after deposition of the solvent drops on the CNC surface. Rough surface energy calculations were accomplished using the Owens-Wendt model (using the tensiometer software package), by analyzing contact angles for water and another solvent.

Dispersion in solvents

CNC dispersion in solvents was assessed before and after surface treatment by PICVD. Solvents retained for the dispersion assays were deionized water (18.2 MΩ cm^{-1}), toluene, ethanol and n-dodecane. Treated CNC were dispersed by placing the copper sample holder in 10 mL of solvent and sonicating for 5 min (5 cycles, each cycle lasting 1 minute). A Cole Parmer 500 watt ultrasonic homogenizer CP505 was used for the sonication of samples.

Fourier Transform Infrared (FTIR) Spectroscopy

Chemical characterization of CNC was achieved using a Perkin Elmer Spectrum 65 FTIR spectrometer equipped with a ZnSe crystal attenuated total reflectance (ATR) probe, in the range of 600-4000 cm^{-1}. For each sample, 32 scans were recorded at a resolution of 4 cm^{-1}.

X-Ray Photoelectron Spectroscopy

Further chemical analysis was conducted by collecting survey, C1s, O1s, and N1s high-resolution spectra of both treated and untreated CNC on a VG ESCALab 3 Mk II, using nonmonochromated Mg Kα radiation (1253.6 eV), at a power setting of 300 W. The instrument resolution was 0.7 eV. Samples were deposited onto silica substrates, using two-sided adhesive Cu tape. The base pressure during scanning was less than 1x10^{-9} torr. Electrons were detected at a perpendicular takeoff angle, using 0.05 eV steps, and spectra were analyzed using the VG Avantage software package.

RESULTS AND DISCUSSION

Dispersion in solvents

1 mg/mL of untreated CNC were dispersed in deionized water. The complete and stable dispersion of the sample was observed after sonication (Figure 3a). As expected, untreated CNC could not be dispersed in toluene – immediate settling was observed following sonication. On the other hand, PICVD-treated CNC could be completely dispersed in toluene at a concentration of 1 mg/mL. Visual inspection indicated that the treated CNC toluene dispersion remained stable for at least two weeks (Figure 3b). Dispersion quality assessment through dynamic light scattering (DLS) was attempted, but proved inconclusive due to the high aspect ratio of the dispersed CNC.

Contact angle measurement

While the surface of the samples was not completely smooth and homogeneous, significant and repeatable trends can be observed, clearly showing that PICVD treatment has an impact on wettability. Indeed, the sessile drop water contact angles climbed from 54° ± 14° for untreated CNC (Figure 4a) to 110° ± 12° following treatment (Figure 4b). The contact angle values of untreated and treated CNCs with various solvents are reported in Table 1. PICVD treatment increased the affinity of the CNC surface towards non-polar (n-dodecane, toluene) and mildly polar (ethanol) solvents, observed through a significant decrease in the sessile drop contact angle. All contact angle measurements were stable on the minute timeframe. Further, the surface energy measured before and after treatment indicates that PICVD leads to a decrease in surface energy (from roughly 43 to 25 mN/m in the case where water and n-dodecane are used as solvents for calculation). This behavior compares well with the solvent-based silylation work conducted by Goussé et al.[13] and de Menezes et al.[14]

FTIR analysis

Figure 5 shows the FTIR spectra of untreated (a) and treated (b) CNC. The broad band in the region 3500-3200 cm^{-1} is attributed to the free O-H stretching vibration of the OH groups in cellulose molecules. Its relative decrease after PICVD treatment offers preliminary evidence that the surface OH groups have been partially reacted and replaced. In addition, the peaks observed in the spectra of CNC in the region 1649-1641 cm^{-1} correspond to the carbonyl group. The peak observed at 1050 cm^{-1} is due to the C-O-C pyranose ring stretching vibration, which is abundant

in the structure of the CNC molecules. The C-C ring breathing band at 1150 cm^{-1} and the C-O-C glycosidic ether band at 1100 cm^{-1}, both of which arise from the polysaccharide component, are gradually lost or merge with the 1050 cm^{-1} peak in CNC, which is due to the hydrolysis and reduction in molecular weight during preparation.[22] In the FTIR spectrum of the treated CNC, the peak at 2925 cm^{-1} is attributed to the C-H alkane stretching, which may correspond to the polymerization products on the surface of the samples. The characteristic C-H stretching vibration is also observed at 2894 cm^{-1}; it is more intense in the FTIR spectrum of the untreated sample in comparison to the treated one. This may be due to a decrease in the C/O ratio because of surface treatment.

X-Ray Photoelectron Spectroscopy

The presence of carbon and oxygen peaks on the untreated and treated CNCs was observed in the survey spectra (data not shown). A small peak of silicon, which corresponds to the analysis substrate, was also observed. In the treated CNC survey spectrum, we observed small iron peaks, which may be due to the presence of iron pentacarbonyl, a known contaminant from the CO tank. The high-resolution O1s spectra of the untreated and treated samples are represented in Figures 6a and 6b, respectively. In Figure 6a, the peak at 533 eV is attributed to an oxygen atom linked in an O-C bond.[23] The peaks at 532.2 eV and 530.7 eV are attributed to C=O and COOH bonds, respectively. In Figure 6b, the peaks at 533 eV, 531.5 eV, 530 eV and 528.7 eV are attributed to C-O, C=O, COOH and O-Fe bonds, respectively. The O/C percentage ratios of the untreated and treated CNC were 0.79 and 1.01. This result indicates an increase in the amount of the oxygen on the surface of the treated CNC in comparison to the untreated sample, which may be due to the surface treatment of the samples with PICVD. The increase of the peak intensities in Figure 6b in comparison to those of the peaks in Figure 6a revealed that the surface of the treated sample by PICVD was oxidized. This could be due to the presence of the oxygen from the reagents used in this technique.

ADDITIONAL OBSERVATIONS

A study on the dispersion of CNC in water revealed that increasing its concentration from 1 % to 7 % changes its physical state from a colloidal suspension to a gel.[24] The thermal gelling of CNC occurs when the gel strength is improved at room temperature.[25] While the cellulose-solvent interactions occur in the system, changes in the solvent due to the cellulose, and changes

in the cellulose due to the presence of the solvent can also occur.[26] In our study on the physicochemical properties of the CNC before and after surface treatment, the untreated CNC was used in an aqueous suspension at a concentration of 1 mg/mL. However, untreated samples prepared at a higher concentration (4 mg/mL) exhibited gelling after one month. The gel formation in concentrated CNC suspensions was not observed in organic solvents. The gel formation of microcrystalline cellulose has been previously reported.[27] The author indicated that this phenomenon is due to the rupture of the inter-chain hydrogen bonds. However, further investigation is needed to explore the nanostructural modifications of CNC due to its gelation. Because we did not observe the gel formation in the case of treated CNC, this may serve as an indication that the treatment affects hydrogen bonding between the CNC.

CONCLUSIONS

Surface functionalization of CNC by PICVD has been studied in this proof-of-concept work - results show this is an appropriate technique for the surface treatment of CNC, addressing the need to improve their compatibility with non-polar matrices. While the treated samples displayed the ability to disperse in model solvents, further investigation will focus on the direct dispersion into commodity polymers of interest (e.g. polyethylene, polylactic acid). The chemical characterization of the surface provides insightful information into the reactions taking place in the PICVD system, namely that the –OH groups on the CNC surface are the key reaction sites, and that a high oxygen-content coating is present after treatment. Subsequent investigation will pursue avenues of research opened by this study, namely looking more closely at the deposition kinetics of the surface treatment, and adjusting the reactor configuration to allow for treatment of larger sample sizes (e.g. fluidized bed configuration). These studies are likely to allow implementation of PICVD in an industrial context for the large-scale treatment of this renewable, environmentally friendly biomaterial.

REFERENCES

[1] D. G. Coffey, D. A. Bell, A. A. M. Henderson, Stephen, Ed., *Food Polysaccharides and Their Applications*. **1995**, 124.

[2] M. M. de Souza Lima, R. Borsali, *Macromol Rapid Commun*. **2004**, 25, 771.

[3] B. L. Peng, N. Dhar, H. L. Liu, K. C. Tam, *Canad J Chem Engin*. **2011**, 9999, 1.

[4] J. Zhang, T. J. Elder, Y. Pu, A. J. Ragauskas, *Polym*. **2007**, 69, 607.

[5] N. Wang, E. Ding, R. Cheng, *Langmuir*. **2008**, 24, 5.

[6] D. Roy, M. Semsarilar, J. T. Guthrie, S. Perrier, *Chem Soc Rev*. **2009**, 38, 2046.

[7] Y. Habibi, H. Chanzy, M. Vignon, *Cellulose*. **2006**, 13, 679.

[8] M. Hasani, E. D. Cranston, G. Westman, D. G. Gray, *Soft Matter*. **2008**, 4, 2238.

[9] B. Braun, J. R. Dorgan, *Biomacromol*. **2009**, 10, 334,.

[10] V. K. Thakur, Scrivener Publishing LCC. **2015**.

[11] Y. Habibi, *Chemical Society Review*. **2014**, 43, 1519.

[12] Y. Habibi, L. A. Lucia, O. J. Rojas, *Chemical Review*. **2010**, 110, 3479.

[13] C. Goussé, H. Chanzy, G. Excoffier, L. Soubeyrand, E. Fleury, *Polymer*. **2002**, 43, 2645.

[14] A. de Menezes, G. Siqueira, A. A. S. Curvelo, A. Dufresne, *Polymer*. **2009**, 50, 4552.

[15] S. Eyley, W. Thielemans, *Nanoscale*. **2014**, 6, 7764.

[16] O. van den Berg, J. R. Capadona, *Biomacromol*. **2007**, 8, 1353,.

[17] C. Weder, S. J. Rowan, et al, US Patent. **2013**, 8, 344,060 B2.

[18] C. A. D. Dion, W. Raphael, E. Tong, J. R. Tavares, *Surface Coating Technol*. **2014**, 244, 98.

[19] B. Balu, J. S. Kim, V. Breedveld, D. W. Hess, *Contact Angle Wettab Adh*. **2009**, 6, 235.

[20] P. Samyn, A. Airoudj, M. -P. Laborie, A. P. Mathew, V. Roucoules, *Eur Phys J Appl Phys*. **2011**, 56, 24015.

[21] M. Salajková, Licentiate Thesis, University of Stockholm, **2012**.

[22] S. Maiti, J. Jayaramudu, K. Das, S. M. Reddy, R. Sadiku, S. S. Ray, D. Liu, *Carbohydrate Polymers*. **2013**, 98, 562.

[23] L. -S. Johansson, J. M. Campbell, *Surface Interf Analysis*. **2004**, 36, 1018.

[24] J. McCrank, *Natural Ressources Canada*. **2009**.

[25] K. Bakeev, B. J. Huebner, H. Yang, US patent. **2013**, WO2013103771 A1.

[26] R. J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, *Chemical Society Reviews*. **2011**, 40, 3941.

[27] C. M. Tipton, *Hydrocolloids*, Part 1, edited by K. Nishinari, Elsevier **2000**, 251.

Graphical abstract. Photo-initiated chemical vapour deposition (PICVD) using syngas and UVC light allows for the hydrophobic modification of cellulose nanocrystals (CNC)

Figure 1. Anhydroglucose unit of cellulose with a numbering system for carbon atoms.

Figure 2. The photo-initiated chemical vapour deposition reactor.

Figure 3. a) Untreated CNC in deionized water and b) PICVD treated CNC in toluene.

Figure 4. Contact angles of a) the untreated and b) the treated CNC with water.

Figure 5. FTIR spectra of a) untreated CNC and b) treated CNC.

Figure 6. XPS O1s high-resolution spectra of a) untreated CNC and b) treated CNC.

Solvent	Polarity index	Contact angle before treatment [°]	Contact angle after treatment [°]	Surface energy before treatment [mN/m]	Surface energy after treatment [mN/m]
Water	9.0	54 ± 14	110 ± 12	----	----
Denatured ethanol	5.2	8 ± 5	0 + 2	42 ± 7	34 ± 5
Toluene	2.4	8 ± 3	0 + 2	42 ± 5	32 ± 2
N-dodecane	0.3	29 ± 11	0 + 2	43 ± 4	25.3 ± 0.3

Table 1: Contact angles and surface energy values for treated and untreated CNC with various solvents, arranged by descending polarity index.
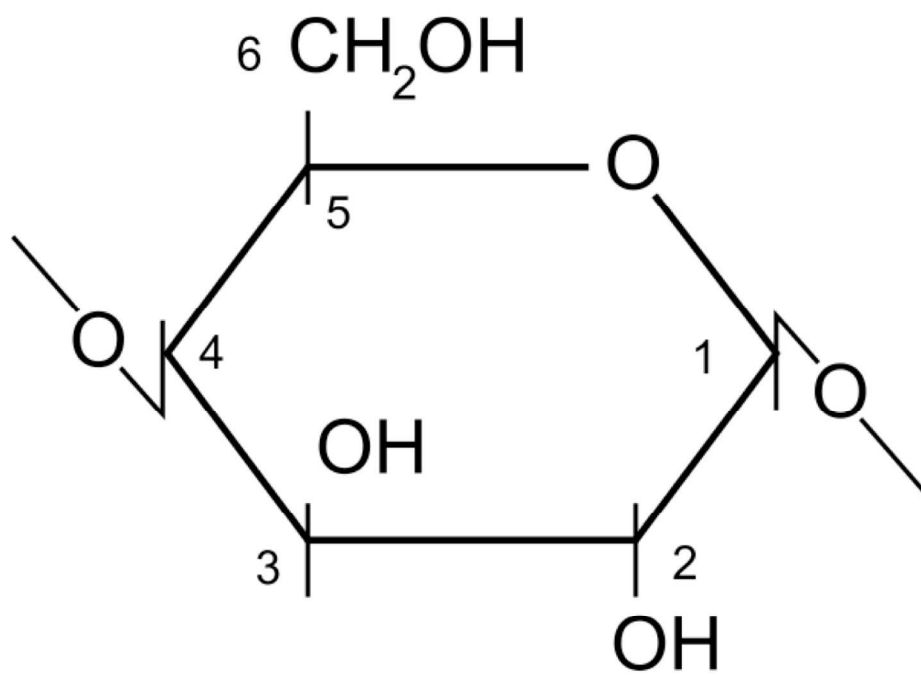
Figure1
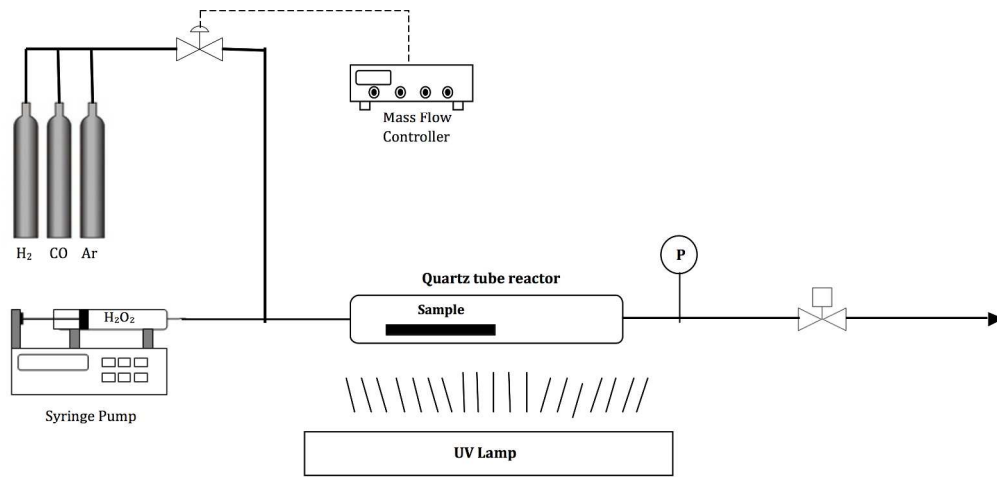
Figure2

Figure3a
118x95mm (300 x 300 DPI)

Figure3b
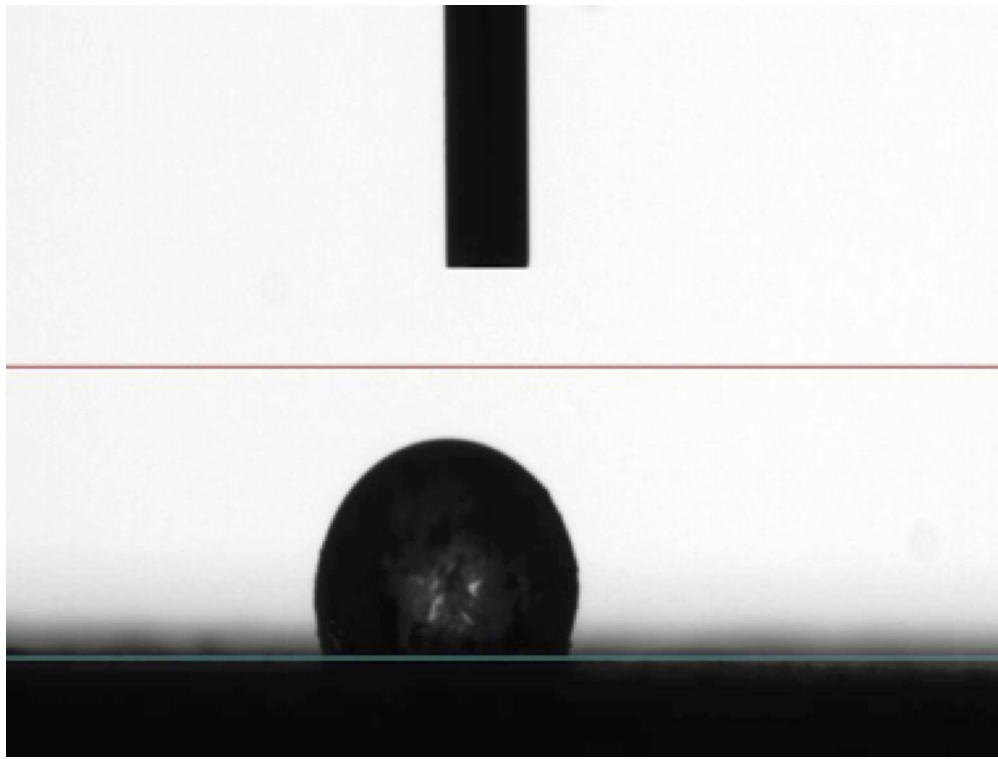113x95mm (300 x 300 DPI)
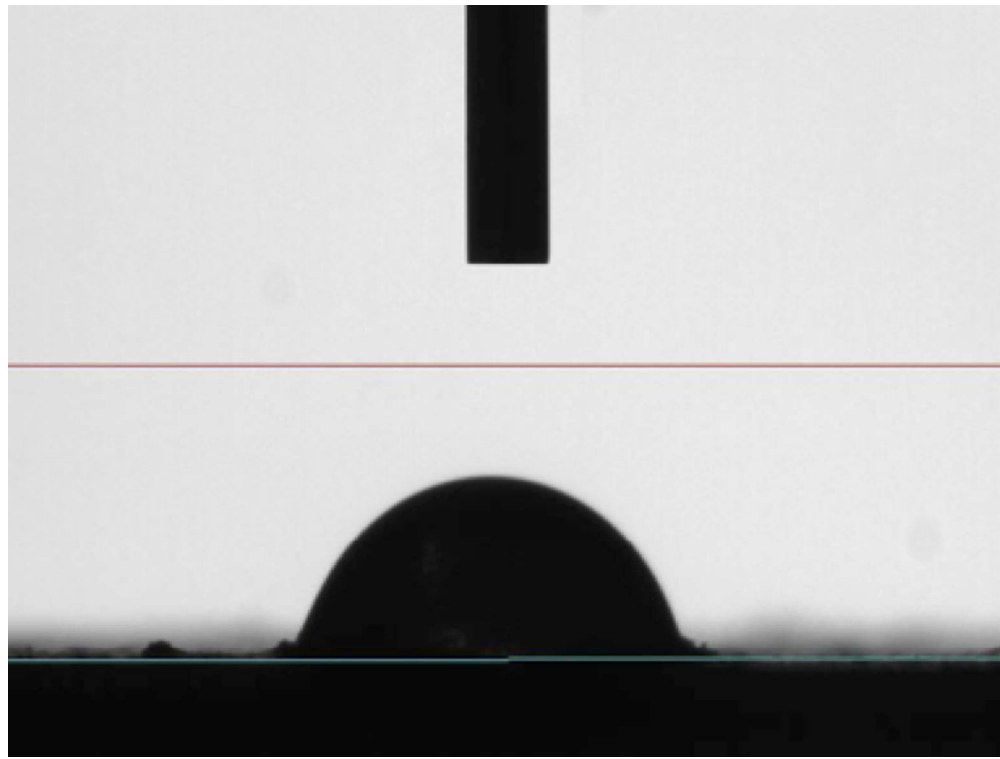
Figure4a
135x101mm (300 x 300 DPI)

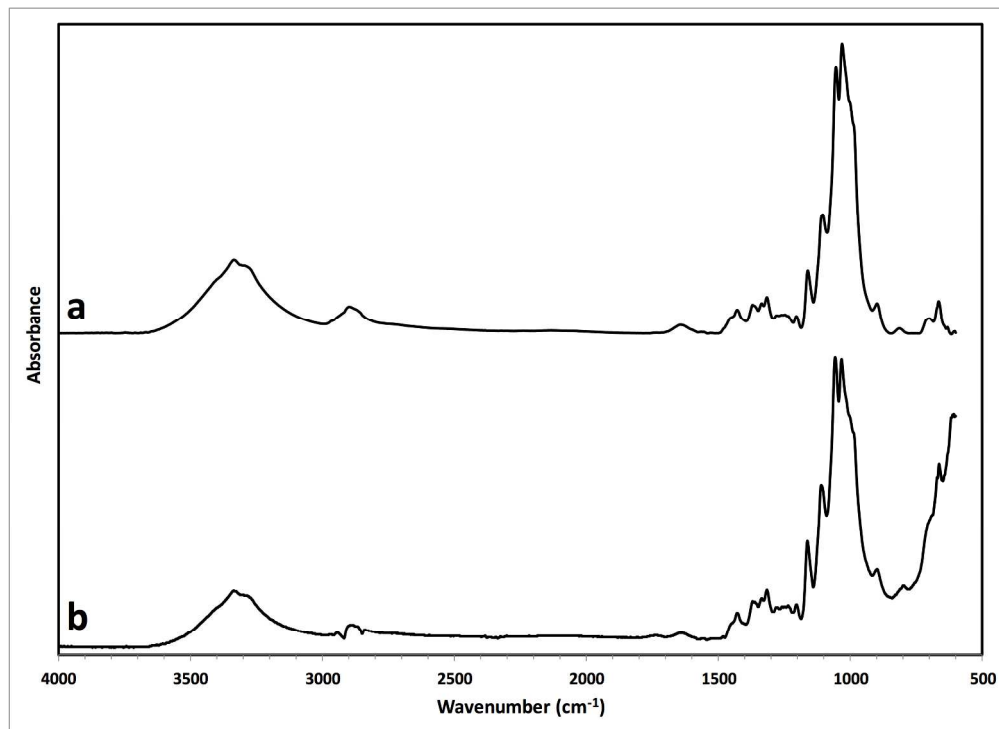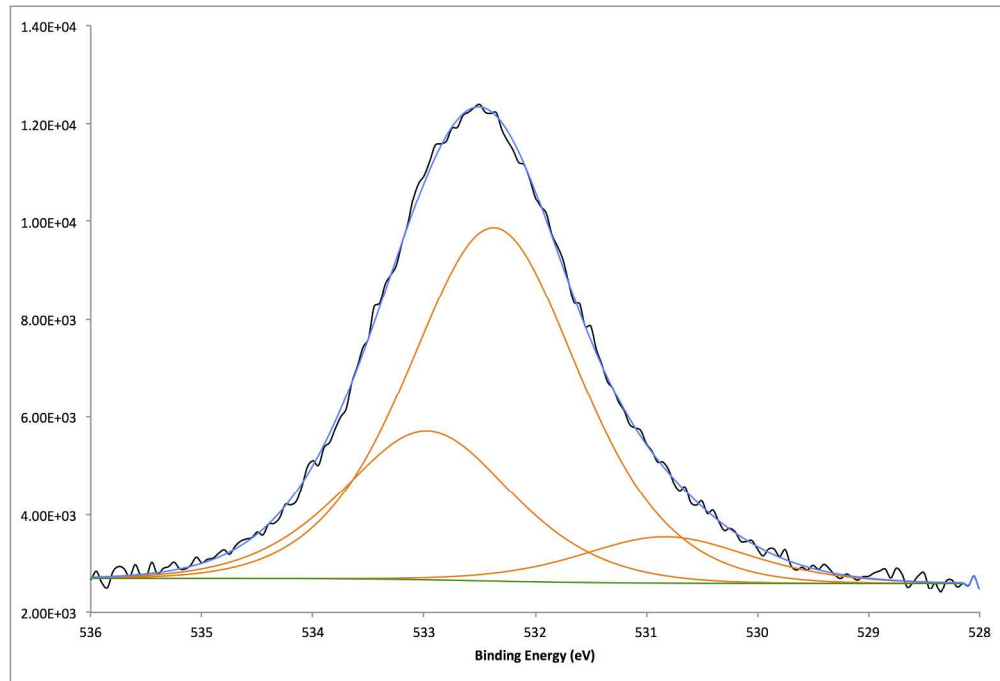Figure4b
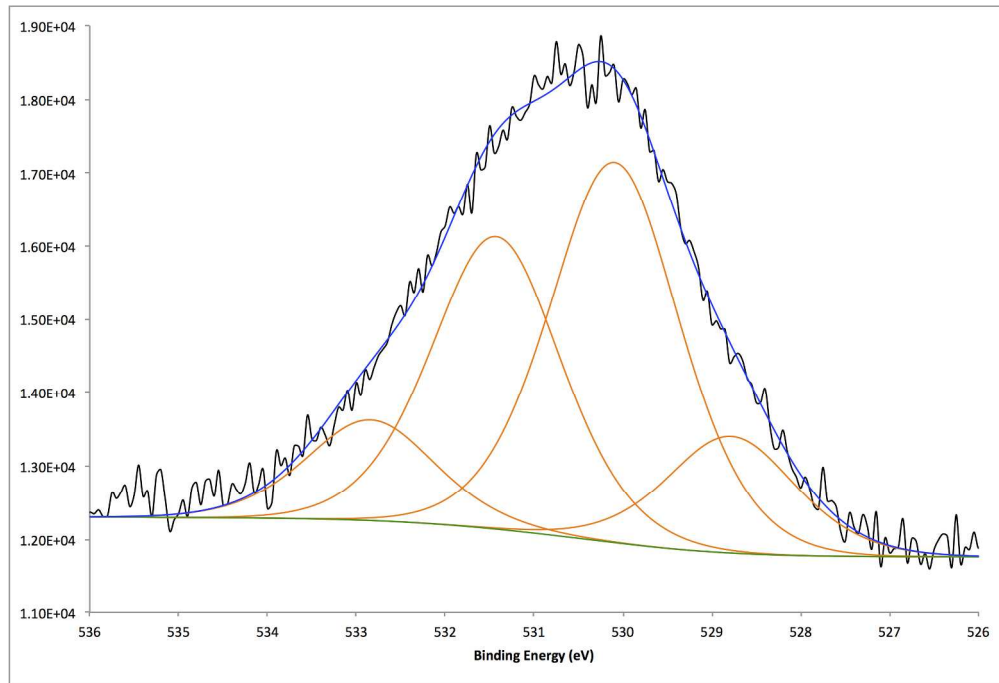135x101mm (300 x 300 DPI)

Figure5

Figure6a

Figure6b

Most Relevant Contributions

- Facile, gas-phase approach to functionalize cellulose nanocrystals (CNC)
- Ability to make CNC hydrophobic and dispersible in non-polar solvents