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# Vapour-induced phase transformation in ultrathin cellulose films

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## Abstract

The structural transformation of thin amorphous cellulose films in water and organic solvent vapour has been studied using grazing-incidence X-ray diffraction and atomic force microscopy. Amorphous cellulose films transform to cellulose II upon exposure to water vapour, and cellulose IV<sub>II</sub> in the dimethyl sulfoxide (DMSO) vapour. The anisotropy in crystalline orientation has developed during the vapour exposure, due both to the surface and confinement effects in thin film geometry. The findings imply a novel route of the vapour treatment of cellulose films to obtain unique structures.

## 21 Introduction

22 Cellulose materials are processed in diverse ways to obtain unique structures and properties to meet  
23 the needs of different applications. Cellulose exhibits various polymorphs in response to changes in  
24 chemical environments. Cellulose I is the allomorph found in nature and can be converted to  
25 cellulose II through processes such as regeneration or mercerization (Langan et al. 2001; Sawada et  
26 al. 2022). Similarly, treatment with liquid ammonia or a series of diamines can convert cellulose I and  
27 II to cellulose III<sub>I</sub> and III<sub>II</sub>, respectively. Thermal treatment of cellulose III<sub>I</sub> and III<sub>II</sub> in glycerol leads to  
28 the formation of cellulose IV<sub>I</sub> and IV<sub>II</sub>, respectively. (Kroon-Batenburg et al. 1996; Gardiner and Sarko  
29 1985). However, the existence of cellulose IV<sub>I</sub> remains controversial, primarily due to the absence of  
30 cellulose IV<sub>I</sub> in isolated and highly crystalline states (Wada et al. 2004). On the contrary, Buleon and  
31 Chanzy prepared single crystals of cellulose IV<sub>II</sub> from dilute solution of cellulose triacetate with low  
32 molecular weight by deacetylation and subsequently precipitation (Buleon and Chanzy 1979).  
33 Alternatively, hydrothermal treatment is employed as a means to augment the durability of wood  
34 (Esteves 2009; Sandberg et al. 2013). This treatment involves subjecting wood to an excessive  
35 amount of water, which results in the co-crystallization of cellulose crystallites. Consequently, a new  
36 cellulose I' allomorph is formed, bearing resemblance to cellulose IV (Kuribayashi et al. 2016). This  
37 indicates that hydrothermal treatment has the potential to induce a transformative conversion to a  
38 cellulose IV-type structure. As phase transformations among allomorphs of cellulose have been  
39 mostly studied on bulk cellulose materials in forms of powder, fibre, chip and block, investigations  
40 on structures in cellulose thin films have been limited.

41 Cellulose thin films are used as model systems for studying surface of cellulosic materials to  
42 elucidate fundamentals in natural or industrial settings. Potential modern applications of cellulose  
43 have expanded to technological areas such as photoresists, photoelectronics, thermoelectrics,  
44 biosensors, and tissue engineering (Kontturi and Spirk 2019; Kontturi et al. 2006; Maver et al. 2015),  
45 which demands a deeper understanding and better control of cellulose materials. Crystallization in  
46 cellulose thin films often determines their properties in adhesion (Eriksson et al. 2007), water affinity  
47 (Tammelin et al. 2015), and enzymatic hydrolysis efficiency (Hall et al. 2010), hence the applicability  
48 in related cellulose-based devices. The in-depth knowledge of structure and properties of crystalline  
49 cellulose, particularly the alignment of polymer chains in thin films and near surfaces, is essential for  
50 the reliable design and fabrication of cellulose-based devices.

51 The molecular arrangement of cellulose in films is affected by the presence of interfaces and the  
52 geometric confinement in the normal direction (Balko et al. 2017; Resel 2008). Crystalline lattice  
53 order of cellulose in thin films is often elusive because of the confinement and substrate interactions  
54 in different film-forming processes (Jones et al. 2019). Similarly, crystallinities and mesostructures of  
55 cellulose in thin films depend heavily on the origin of the cellulose and film preparation methods  
56 (Aulin et al. 2009). The uncertainty in the formation of cellulose films, most commonly by spin-  
57 coating solutions of cellulose or derivatives followed by cellulose regeneration and solvent removal,  
58 could vary drastically due to the biodiversity of source materials and the high sensitivity to physical  
59 conditions in the process (Kontturi et al. 2011; Lu et al. 2020; Weißl et al. 2018). Process variations  
60 could often be contained through small molecule treatment.

61 Manipulating interactions of cellulose with small molecules is central in the entire life cycle of  
62 processing and utilizing cellulose materials. We focus on the effect of water and dimethyl sulfoxide  
63 (DMSO). Water-induced recrystallization of amorphous cellulose to cellulose II in powders has been  
64 well characterized throughout the long history of cellulose research (Hermans and Weidinger 1946;  
65 Tyufekchiev et al. 2019), whereas those on thin film studies are recent. One example focuses on

66 ultrathin cellulose films, which are prepared using acid labile trimethylsilyl cellulose deposited  
67 through spin coating on silicon wafers and subsequently exposed to HCl vapour (Reishofer *et al.*  
68 2022).

69 On the other hand, the effect of DMSO treatment on the structural ordering of cellulose is less  
70 studied. Feizi (2021) reported that partial transformation from cellulose I to II occurred when  
71 cellulose nanocrystals (CNCs) were treated with DMSO, accompanied by a significantly enhanced  
72 wettability (Feizi and Fatehi 2021). In contrast, Yang (2017) reported unchanged cellulose I  
73 crystalline structure of nanofibrillated cellulose upon DMSO soaking (Yang *et al.* 2017). Further  
74 studies through quantifying phase transformation in amorphous cellulose thin films upon exposure  
75 to water or DMSO will add to the collection of literatures along this line of research. Our previous  
76 studies show the reversible transformation between cellulose II and IV<sub>II</sub> upon exposing the powder  
77 of near-monodisperse oligocellulose to liquid water and DMSO vapour, respectively (Zhang *et al.*  
78 2021). In this study, we prepare ultrathin amorphous cellulose films and measure the evolution of  
79 cellulose structures in films upon exposing to saturated water or DMSO vapour at elevated  
80 temperatures.

## 81 Experimental

82 Oligocellulose was prepared using a method modified from a previous report (Jiang *et al.* 2021).  
83 Specifically, 6.0 g of cellulose filter paper (Cytiva) was mixed with 200 mL of 85% H<sub>3</sub>PO<sub>4</sub> by mass  
84 (Shanghai Macklin Biochemical Technology Co., Ltd.). After storing in a freezer at -20 °C overnight  
85 and stirring at 60 °C for 10 hours, the mixture was slowly added to 400 mL deionized water (Merck  
86 Millipore). After filtration, the filtrate was mixed with 1200 mL methanol (Damao chemical reagent  
87 factory) and stored at room temperature overnight. The white precipitate was oligocellulose fraction  
88 DP7 with an average degree of polymerization (DP) of 7.68 and a polydispersity index (PDI) of 1.04.

89 DP7 was further fractionated using a previously reported method (Zhang *et al.* 2021). A solution of  
90 5.0% DP7 by mass in DMSO (Sigma-Aldrich) was homogenized at 90 °C and stored at 15 °C for 3  
91 hours. After filtering out precipitates, the solution underwent a freeze-thaw cycle between -20 °C  
92 and room temperature. The supernatant was precipitated in acetone (Xilong Scientific Co., Ltd.) 5 x  
93 by volume. The precipitates were collected through centrifugation, repeatedly washed using  
94 acetone, and dried in a vacuum oven at room temperature. The resulting oligocellulose has an  
95 average DP = 7.70 and PDI = 1.01 and is used in this study.

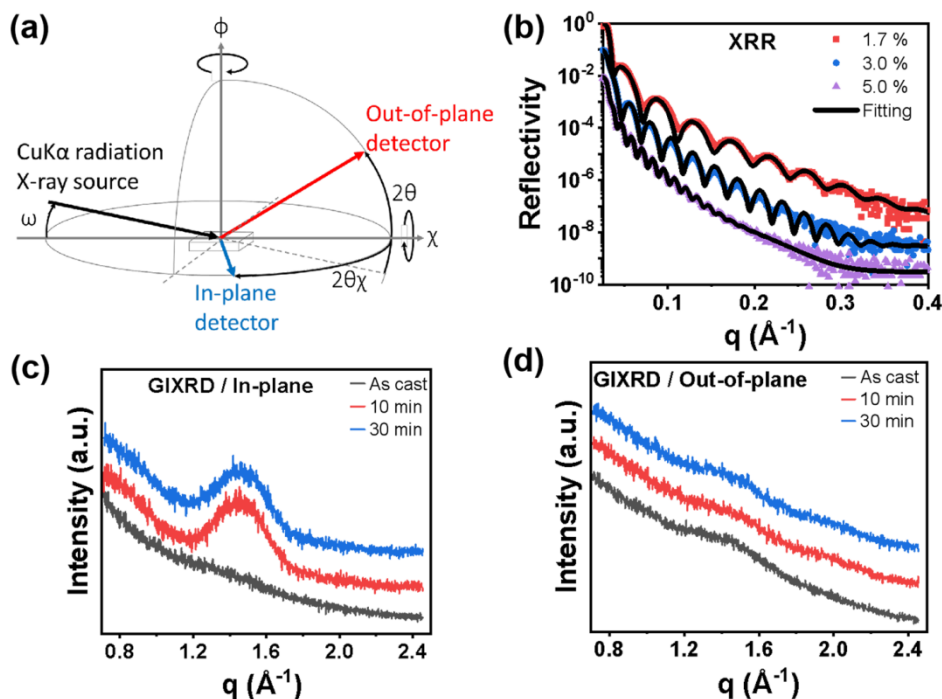
96 Molecular solutions of DP7 in anhydrous DMSO with DP7 concentrations varying from 1 to 5% by  
97 mass were homogenized at 70 °C for one hour and kept at room temperature. Thin films of DP7  
98 were fabricated by spin-coating on a 1.5 cm × 1.5 cm silicon wafer at 2500 rpm for 90 s in a dry  
99 environment with RH < 10% and used as-cast. Cellulose film specimens were sealed in saturated  
100 vapour of water or DMSO and stored at 90 °C for 10 min before quick termination for X-ray and AFM  
101 measurements. The identical specimens were exposed to saturated vapour for an additional 20 min  
102 and subsequently measured.

103 The thickness of DP7 films was measured using X-ray reflectivity (XRR) on a Rigaku SmartLab  
104 diffractometer equipped with CuK $\alpha$  radiation. Crystalline information of the films was obtained by  
105 grazing incident X-ray diffraction (GIXRD) on the same instrument. The surface topography of DP7  
106 films was examined using tapping mode atomic force microscopy (AFM) on a CSPM4000 instrument  
107 from Benyuan Co, Ltd. All measurements were conducted at the room temperature and in ambient  
108 atmosphere.

109

110 **Results and discussion**

111 XRR and GIXRD measurements of cellulose thin films are schematically illustrated in Figure 1a.



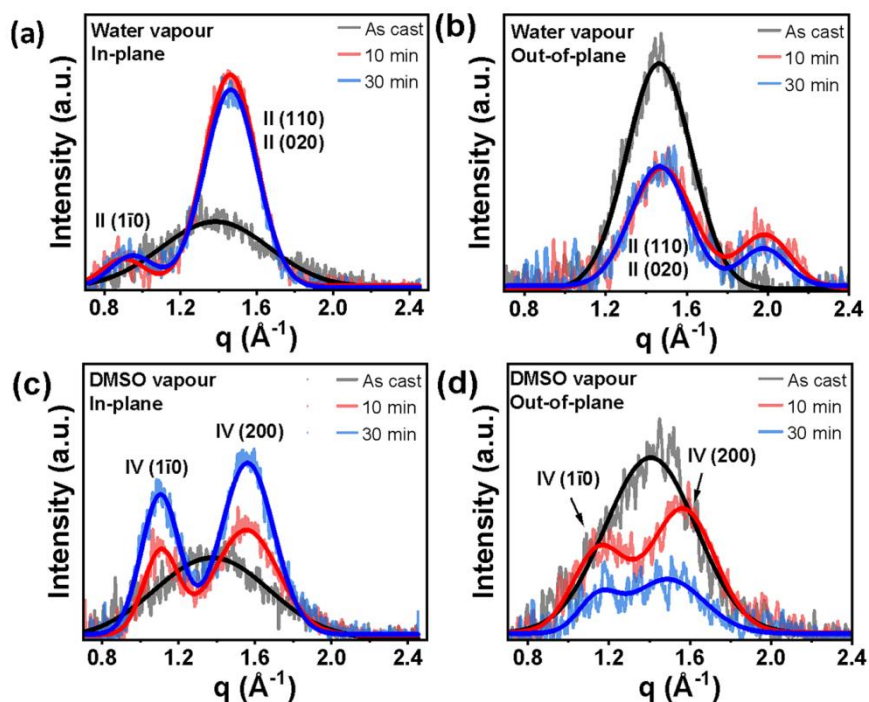
112

113 **Figure 1.** (a) Schematics of X-ray measurements in this study. The specimen plane is controlled by tilting angle  
 114  $\omega$ , rocking angle  $\chi$ , and rotating angle  $\phi$ , and the detector can scan either in the vertical out-of-plane circle ( $2\theta$   
 115 scan) or in the horizontal in-plane circle ( $2\theta\chi$  scan). For XRR,  $\omega$  and  $2\theta$  axes rotate simultaneously at a rate  
 116 ratio of 1:2. In GIXRD measurements, the incident angle of the X-ray beam  $\omega$  is  $0.2^\circ$ , slightly below the critical  
 117 angle of Si,  $\sim 0.22^\circ$ . The detector scans  $2\theta$  in the out-of-plane diffraction mode and scans  $2\theta\chi$  while rotating  
 118 sample at  $\phi = (2\theta\chi) / 2$  in the in-plane diffraction. (b) XRR of DP7 films from DP7 solutions of different  
 119 concentrations in DMSO by mass. The symbols are experimental data, and curves through symbols are the best  
 120 fitting using a single-layer model. XRR profiles are vertically shifted by a factor of 10 for clarity, and the  
 121 thickness from the best fit is labelled correspondingly. (c) In-plane and (d) out-of-plane GIXRD of the 47 nm  
 122 DP7 thin films before and after water vapour exposure for 10 and 30 min, respectively.

123 XRR of as cast films are shown in Figure 1b as symbols. The periodic oscillation in the specular  
 124 reflectivity corresponds to the interference primarily between the X-ray waves reflected from the  
 125 two interfaces of cellulose films, i.e., the air/cellulose and cellulose/substrate interfaces, respectively.  
 126 The solid curves through the symbols are the best model fitting assuming a single uniform layer with  
 127 a mass density of  $1.50 \text{ g/cm}^3$ . The thickness and roughness of films are  $15.0 \pm 0.5 \text{ nm}$  and  $0.5 \pm 0.1$   
 128  $\text{nm}$ ,  $24.0 \pm 0.2 \text{ nm}$  and  $0.7 \pm 0.1 \text{ nm}$ , and  $47.0 \pm 0.4 \text{ nm}$  and  $1.5 \pm 0.2 \text{ nm}$  for films cast from 1.7 %,   
 129 3.0 %, and 5.0 % solutions, respectively.

130 Figures 1c and 1d show as-recorded in-plane and out-of-plane GIXRD of the 47 nm DP7 films before  
 131 and after exposure to water vapour. GIXRD data of films upon DMSO vapour exposure are shown in  
 132 Figure S1 of the Supplementary Materials. The amorphous halo in both GIXRD profiles of the as-cast  
 133 sample indicates the lack of lattice order hence the amorphous state of the as-cast films. Upon  
 134 exposing to water vapour, diffraction features are prominent in in-plane geometry while rather  
 135 modest in the out-of-plane GIXRD.

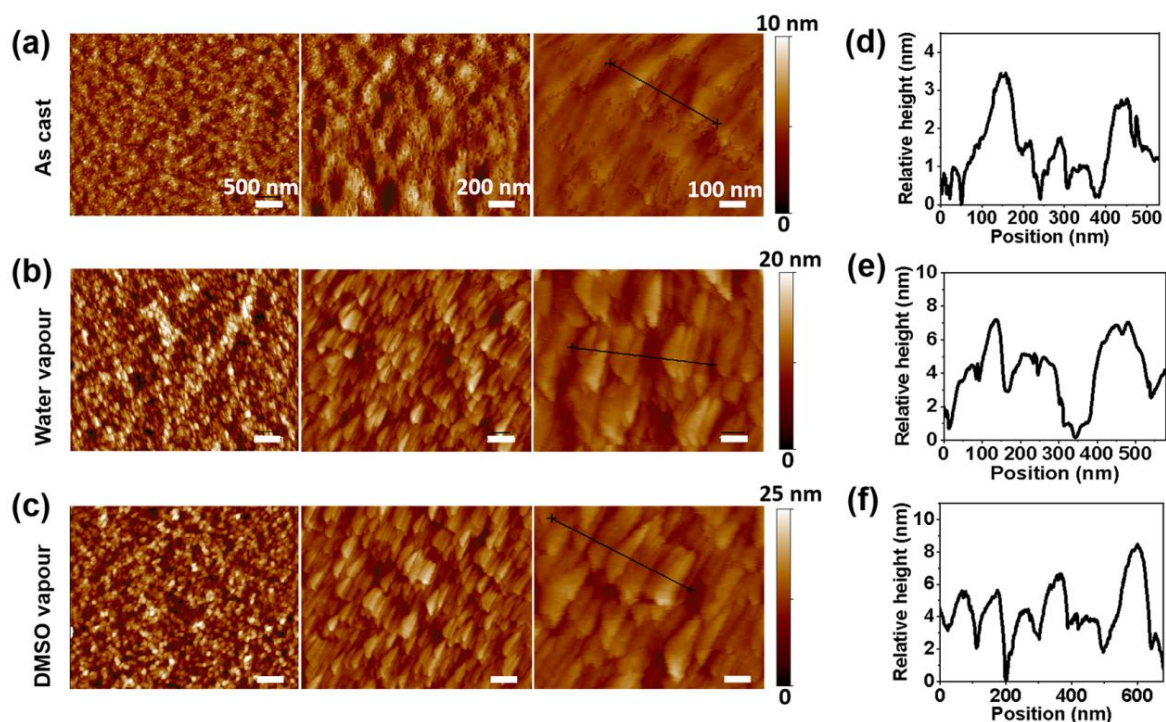
136



137 **Figure 2.** Background-subtracted in-plane (a, c) and out-of-plane (b, d) GIXRD of DP7 thin films before and after  
 138 exposing to water (a, b) and DMSO (c, d) vapour at 90 °C for 10 and 30 min, respectively. The curves through  
 139 the data are the best fit using Gaussian functions.

140 The diffraction features are better visualized after background subtraction and further characterized  
 141 through fitting with Gaussian functions, with the best fits shown as curves through the data in Figure  
 142 2. The fitting parameters are listed in the Supplementary Materials. Figure 2a shows diffraction  
 143 peaks at  $q = 0.9$  and  $1.5 \text{ \AA}^{-1}$ , which closely resembles  $(1\bar{1}0)$  and merged  $(110)$  and  $(020)$  of cellulose II  
 144 (Langan *et al.* 2001; Sawada *et al.* 2022), respectively. It implies that saturated water vapour  
 145 converts amorphous cellulose to cellulose II crystals with a unit cell containing two antiparallel  
 146 chains. Longer exposure time of up to 30 min in water vapour has caused little further change to the  
 147 GIXRD profiles, implying the kinetically slowing down of crystallization after 10 min. The different  
 148 scattering features in Fig. 2b suggest anisotropy in crystalline structures.

149 In comparison, exposing thin films to DMSO vapour yields diffraction peaks at  $q = 1.1$  and  $1.6 \text{ \AA}^{-1}$ ,  
 150 resembling  $(1\bar{1}0)$  and  $(200)$  of cellulose IV<sub>II</sub> (Gardiner and Sarko 1985), respectively, for both in-plane  
 151 (Fig. 2c) and out-of-plane diffraction (Fig. 2d), suggesting the transformation to a mostly cellulose IV  
 152 phase. After additional 20 min in DMSO vapour, the in-plane diffraction intensity increases while the  
 153 out-of-plane diffraction intensity decreases, indicating the continuous evolution of crystalline  
 154 structures. The variations in peak location and relative intensities are likely due to the anisotropy  
 155 and imperfections of crystallites formed under confinement, as illustrated below.



156

157 **Figure 3.** AFM micrographs of DP7 thin films for (a) as-cast, (b) exposed to water vapour, and (c) exposed to  
 158 DMSO vapour in different magnifications, with scale bars at 500 nm (left column), 200 nm (middle column),  
 159 and 100 nm (right column), respectively, with lateral dimensions from tens to hundreds of nanometres. (d)  
 160 Height profiles along the black line in (a) showing features of ca.3 nm. (e, f) Height profiles along the black line  
 161 in (b, c) show lamellae thickness of ca. 3 - 6 nm.

162 Figure 3 shows AFM micrographs of as-cast (Fig. 3a), water-treated (Fig. 3b), and DMSO-treated (Fig.  
 163 3c) DP7 films in three magnification scales. The as-cast film has a rather smooth surface of RMS  
 164 roughness of 1.1 nm, due partly to somewhat regular fine features. Those after vapour treatments  
 165 show significantly roughened granular surfaces with a roughness of ca. 4.0 nm. High magnification  
 166 scans reveal stacks of thin platelets with lateral dimensions up to a few hundred nanometres,  
 167 apparently lamellae crystallites of DP7, consistent with the diffraction data. The heights of lamellae  
 168 are found from the line scans, as shown in Figs. 3e and 3f, to be in the range of 3 – 6 nm, in line with  
 169 the extended-chain crystals of DP7. Given the crystal habits, it is only natural for crystallites to grow  
 170 preferentially in the flat-on geometry under the confinement of the film thickness of 47 nm, i.e., the  
 171 c axis along the film normal and ab plane parallel to the film surface plane.

172 Solvent vapour induces the phase transformation in ultrathin cellulose films to the same crystalline  
 173 structure as that in the bulk oligocellulose, namely type II in water or IV<sub>II</sub> in DMSO (Zhang *et al.* 2021).  
 174 The essential differences due to the thin film geometry are in two aspects, namely the surface and  
 175 confinement effects. When DP7 molecules are exposed to the vapour of polar solvents, chain ends  
 176 of oligocellulose preferentially segregate to the surface, lowering the energy barrier for transforming  
 177 to crystallites. On the other hand, as crystals grow larger and more perfect with the exposure time,  
 178 more diffraction planes (dominantly indexed by the a, b axes) align perpendicular to the film surface  
 179 due to the confinement of film thickness, consistent with the experimental data that the increase of  
 180 in-plane diffraction is coupled with the decrease in out-of-plane diffraction intensity. Furthermore,  
 181 the difference in diffraction features of in-plane and out-of-plane diffraction is due to the anisotropy  
 182 and/or heterogeneity in the lateral dimensions. As much remain unknown in the intriguing  
 183 crystallization behaviour of cellulose in thin films, detailed understanding of transformation kinetics  
 184 and crystallography structures is among the topics of future studies.



185 **Summary**

186 Amorphous cellulose thin films have been prepared by spin-coating solutions of oligocellulose in  
187 DMSO, and subsequently exposed to water or DMSO vapour. Structures of cellulose films as-  
188 prepared and after vapour exposure have been measured using grazing-incidence X-ray diffraction  
189 and atomic force microscopy. The amorphous cellulose films transform to cellulose II upon the  
190 exposure to water vapour, and cellulose IV<sub>II</sub> in DMSO. As lamellae of extended-chain crystallites  
191 develop in films during the exposure time, they orient preferably in parallel to the film plane,  
192 presumably due both to the surface and the confinement effects in the thin film geometry. The  
193 findings imply a novel route of the vapour treatment of cellulose films to obtain desirable crystalline  
194 structures and physical properties. As this preliminary work adds to the literature in better  
195 understanding cellulose films, more comprehensive studies are required to reveal details of the  
196 structural evolution and understand mechanisms of vapour-induced phase transformation in  
197 amorphous cellulose near surfaces and in confinement.

198

199 **Availability of data and materials**

200 The data that support the findings of this study are available from the corresponding author upon  
201 request.

202

203 **Associated content**

204 *Supporting materials*

205 GIXRD patterns of 5 % DP7 thin films, peak fitting parameters for GIXRD patterns of DP7 thin films.

206

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210

211 **Competing interests**

212 The authors declare no competing financial interest.

213

214 **Authors' contributions**

215 Z.M. produced the oligocellulose samples. P.L. prepared thin films and made the measurements. P.L.  
216 and W.L. wrote the manuscript draft. H.W. conceived the idea and edited the manuscript. H.W.  
217 and T.Z. supervised the project. All authors reviewed and revised the manuscript.

218

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223

## 224 References

- 225 Aulin C, Ahola S, Josefsson P, Nishino T, Hirose Y, Osterberg M, Wagberg L (2009) Nanoscale  
226 Cellulose Films with Different Crystallinities and Mesostructures-Their Surface Properties  
227 and Interaction with Water. *Langmuir*, 25(13): 7675-7685.
- 228 Balko J, Portale G, Lohwasser RH, Thelakkat M, Thurn-Albrecht T (2017) Surface induced orientation  
229 and vertically layered morphology in thin films of poly (3-hexylthiophene) crystallized from  
230 the melt. *J. Mater. Res.*, 32(10): 1957-1968.
- 231 Buleon A, Chanzy H (1980) Single crystals of cellulose IV<sub>II</sub>: preparation and properties. *J. Polym. Sci.,*  
232 *Polym. Phys. Ed.*, 18(6): 1209-1217.
- 233 Eriksson M, Notley SM, Wågberg L (2007) Cellulose thin films: degree of cellulose ordering and its  
234 influence on adhesion. *Biomacromolecules*, 8(3): 912-919.
- 235 Esteves B (2009) Wood modification by heat treatment: A review. *BioResources*: 370-404.
- 236 Feizi ZH, Fatehi P (2021) Changes in the molecular structure of cellulose nanocrystals upon  
237 treatment with solvents. *Cellulose*, 28(11): 7007-7020.
- 238 Gardiner ES, Sarko A (1985) Packing analysis of carbohydrates and polysaccharides. 16. The crystal  
239 structures of celluloses IVI and IVII. *Canadian journal of chemistry*, 63(1): 173-180.
- 240 Hall M, Bansal P, Lee JH, Realff MJ, Bommarius AS (2010) Cellulose crystallinity—a key predictor of  
241 the enzymatic hydrolysis rate. *FEBS J.*, 277(6): 1571-1582.
- 242 Hermans P, Weidinger uA (1946) On the recrystallization of amorphous cellulose. *J. Am. Chem. Soc.*,  
243 68(12): 2547-2552.
- 244 Jiang F, Zhang X, Hwang W, Nishiyama Y, Briber RM, Wang H (2021) Oligocellulose from acid  
245 hydrolysis: A revisit. *Appl. Surf. Sci.*, 537: 147783.
- 246 Jones AO, Resel R, Schrode B, Machado-Charry E, Röthel C, Kunert B, Salzmann I, Kontturi E,  
247 Reishofer D, Spirk S (2019) Structural Order in Cellulose Thin Films Prepared from a  
248 Trimethylsilyl Precursor. *Biomacromolecules*, 21(2): 653-659.
- 249 Kontturi E, Spirk S (2019) Ultrathin films of cellulose: a materials perspective. *Front. Chem.*, 7: 488.
- 250 Kontturi E, Suchy M, Penttila P, Jean B, Pirkkalainen K, Torkkeli M, Serimaa R (2011) Amorphous  
251 characteristics of an ultrathin cellulose film. *Biomacromolecules*, 12(3): 770-777.
- 252 Kontturi E, Tammelin T, Österberg M (2006) Cellulose—model films and the fundamental approach.  
253 *Chem. Soc. Rev.*, 35(12): 1287-1304.
- 254 Kroon-Batenburg L, Bouma B, Kroon J (1996) Stability of cellulose structures studied by MD  
255 simulations. Could mercerized cellulose II be parallel? *Macromolecules*, 29(17): 5695-5699.
- 256 Kuribayashi T, Ogawa Y, Rochas C, Matsumoto Y, Heux L, Nishiyama Y (2016) Hydrothermal  
257 transformation of wood cellulose crystals into pseudo-orthorhombic structure by  
258 cocrystallization. *ACS Macro Lett.*, 5(6): 730-734.
- 259 Langan P, Nishiyama Y, Chanzy H (2001) X-ray structure of mercerized cellulose II at 1 Å resolution.  
260 *Biomacromolecules*, 2(2): 410-416.
- 261 Lu R, Zhang X, Fu L, Wang H, Briber RM, Wang H (2020) Amorphous cellulose thin films. *Cellulose*, 27:  
262 2959-2965.
- 263 Maver T, Maver U, Mostegel F, Griesser T, Spirk S, Smrke DM, Stana-Kleinschek K (2015) Cellulose  
264 based thin films as a platform for drug release studies to mimick wound dressing materials.  
265 *Cellulose*, 22: 749-761.
- 266 Reishofer D, Resel R, Sattelkow Jr, Fischer WJ, Niegelhell K, Mohan T, Kleinschek KS, Amenitsch H,  
267 Plank H, Tammelin T (2022) Humidity Response of Cellulose Thin Films. *Biomacromolecules*,  
268 23(3): 1148-1157.

- 269 Resel R (2008) Surface induced crystallographic order in sexiphenyl thin films. *J. Phys.: Condens.*  
270 *Matter*, 20(18): 184009.
- 271 Sandberg D, Haller P, Navi P (2013) Thermo-hydro and thermo-hydro-mechanical wood processing:  
272 An opportunity for future environmentally friendly wood products. *Wood Mater. Sci. Eng.*,  
273 8(1): 64-88.
- 274 Sawada D, Nishiyama Y, Shah R, Forsyth VT, Mossou E, O'Neill HM, Wada M, Langan P (2022)  
275 Untangling the threads of cellulose mercerization. *Nature Communications*, 13(1): 6189.
- 276 Tammelin T, Abburi R, Gestranus M, Laine C, Setälä H, Österberg M (2015) Correlation between  
277 cellulose thin film supramolecular structures and interactions with water. *Soft Matter*,  
278 11(21): 4273-4282.
- 279 Tyufekchiev M, Kolodziejczak A, Duan P, Foston M, Schmidt-Rohr K, Timko MT (2019) Reaction  
280 engineering implications of cellulose crystallinity and water-promoted recrystallization.  
281 *Green Chem.*, 21(20): 5541-5555.
- 282 Weißl M, Niegelhell K, Reishofer D, Zankel A, Innerlohinger J, Spirk S (2018) Homogeneous cellulose  
283 thin films by regeneration of cellulose xanthate: properties and characterization. *Cellulose*,  
284 25: 711-721.
- 285 Wada M, Heux L, Sugiyama J (2004) Polymorphism of cellulose I family: reinvestigation of cellulose  
286 IVI. *Biomacromolecules*, 5 (4): 1385-1391.
- 287 Yang X, Wang X, Liu H, Zhao Y, Jiang S, Liu L (2017) Impact of dimethyl sulfoxide treatment on  
288 morphology and characteristics of nanofibrillated cellulose isolated from corn husks.  
289 *BioResources*, 12(1): 95-106.
- 290 Zhang X, Jiang F, Torres-Luna C, Nishiyama Y, Briber RM, Wang H (2021) Solvent-Assisted  
291 Fractionation of Oligomeric Cellulose and Reversible Transformation of Cellulose II and IV.  
292 *ACS Biomater. Sci. Eng.*, 7(10): 4792-4797.

293