Controlling Wettability, Wet Strength, and Fluid Transport Selectivity of Nanopaper with Atomic Layer Deposited (ALD) Sub-nanometer Metal Oxide Coatings

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Modification	Chemicals	Reactions	Reaction time	Attractions	Drawbacks
Esterification ¹⁻²	Acetic anhydride in pyridine/acid halide reagents/fatty acid chloride in toluene	To introduce acetyl functionalities	>10 h	Substitute the polymer hydroxyl groups of cell wall with acetyl groups	The degree of acetyl substitution had a crucial influence on material properties
Silylation ³	Silane	Silane undergo hydrolysis, condensation and bond forming stage to get silanol, which react with hydroxyl group, forming stable covalent bonds	> 5 h	Silane -coupling agents improve the degree of crosslinking in the interface region	At high silvation, the chains in core of crystal become silvlated, resulting in disintegration of crystals and loss of original morphology
Grafting ⁴⁻⁶	Polymers	Attachment of presynthesized polymer onto cellulose by coupling agents/ in-situ initiated polymerization on cellulose surface	>10 h	The reaction can be conducted in aqueous media instead of organic solvents, no need of solvent exchange	Cellulose only partially disperse in polymers, causing low mechanical properties
Surfactant ⁷	Surfactants	Adsorption of surfactant on cellulose	>5 h	Disperse well in nonpolar solvents	Lower the mechanical property of cellulose
ALD (this work)	AlO _x /TiO _x	AlO _x /TiO _x bond with hydroxyl group	10-30 min	Solvent free, Fast and Clean	Not efficient

Table S1: Reported Surface Modification Methods for Cellulose

Table S1. summarized the reported work on cellulose surface modification, usually the traditional solvent treatment needs a long reaction time and a harsh chemical reaction environment. Our work is based on vapor phase modification, which is fast and clean, however, the lower cycle deposition only get Armstrong thickness or atomic scale loading of metal oxide, which could be strong under mild water molecule attack, long time water contact and high energy attacking would

still cause the break of our films, this need to be further studied to get the most efficient and economic recipe.



Figure S1: (*a-h*) Deconvolution spectrums of *n*th scan on same spot for same cellulose specimen.



Figure S2: (*a*) Binding energy change of different functional groups as a function of scan number (nth scan); (b) Atomic percentage change of different functional groups as a function of scan time (minute).

For lower cycle deposition of ALD process, only several Armstrong thickness could be got from the deposition, which brings extreme difficulties for material characterization, XPS is a surface sensitive technique with high element resolution and is widely applied for thin film material characterization. Therefore, XPS is the major technique used in this paper for low cycle ALD coated CNF films. However, it is known that nature polymers are fragile under X-ray beam exposure, they suffer from degradation in any high energy beams. To find the time limit for cellulose that could survive in X-ray environment and at the same time, obtaining spectrums with good resolution, we did a series of X-ray degradation study on pure cellulose film.

During the operation of XPS, focused beam X-ray (monochromatic Al K α , beam diameter = 400 µm, E _{photon} = 1486.6 eV) is generated to iridate the cellulose specimen in ultrahigh vacuum (10⁻⁸ Torr), electrons with certain kinetic energy would be ejected from specimen and been transferred into the detector, this process may cause cellulose backbone and sidechain scissions happen, which degrades the cellulose chain degradation. To study the critical time for cellulose to begin degradation, we did continuous scan on one specimen, each scan takes one minute to finish and will generate a spectrum. A default XPS point probe has five scans to generate an average spectrum with less noise. Here, we did twenty scans for one spot on one specimen and did the deconvolution for each scan to study about the chemical structure change of cellulose. Figure S1 shows the deconvoluted spectrums for nth scan (n = 1, 2, 3, 4, 5, 10, 15, 20). Obviously, all

spectrums could be fitted into four functional groups, which are C-C at 284.8 eV, C-O at 286.62 \pm 0.23 eV, O-C-O at 287.76 \pm 0.34 eV and C=O at 289.27 \pm 0.14 eV. Theoretically, pure cellulose shouldn't have any C-C and C=O group in its structure, however, most of the literatures reported that chemical pulping, bleaching, fining process would inevitably oxidize cellulose and bring C=O into the structure, meantime, organic hydrocarbon in the air could deposit on any surface, which show C-C signal in XPS. It is clear to see from the deconvoluted spectrums that the first three scans show similarly ratio of four different functional groups, while the C-O/O-C-O increase after the fourth scan and it keeps increasing, this phenomenon means that back chain of cellulose is being depolymerized by x-ray attack. Figure S2. (a) shows the binding energy change of different functional groups as a function of scan number, the fourth scan also show a giant change of atomic percentages of these groups, O-C-O cleave into C-O groups, causing a big increase of C-O percentage and accompany with a decrease of O-C-O percentage. Therefore, we think it is reasonable to use XPS for cellulose characterization for the first three minute, after that, cellulose begin to degrade.

200 mg anthrone was fully dissolved in 100 mL 98% H_2SO_4 by magnetic stirring for 20 minutes, and the solution was carefully stored in a refrigerator at ~15 °C. The standard is prepared as follows: 1mL deionized water were fully mixed with 4 mL anthrone acid solution, while for cellulose samples, 0.5 mL deionized water and 0.5 mL after sonication solution were mixed with 4 mL anthrone acid solution. All vials are heated in boiling water for 10 mins to make sure cellulose are fully oxidized by H_2SO_4 . To measure the uv-vis transmittance of prepared solution, all solutions are diluted to 1/40 by mixing 0.1 mL solution with 3.9 mL H_2SO_4 . Table 1 shows the recipes of anthrone method for standard and specimens.

	Standard	Samples
Deionized Water	1 mL	0.5 mL
Cellulose Dispersed Solution	0 mL	0.5 mL
Anthrone Acid solution	4 mL	4 mL

Table S2: Recipes of Anthrone Method for Standard and Specimens

To make calibration standard, different concentration (0.1, 0.25, 0.5, 0.75,1.0, 1.25, 1.5 and 2.0 g/L) of CNF dispersion was made as standard solutions. UV-VIS absorption spectra was plotted in Figure S3 (a), and the function of absorption *vs*. concentration was plotted in Figure S3(b). By calculating the slope of the plot, we can get the constant ε ·l.



Figure S3: (a) UV-VIS absorption spectra of calibration standards; (b) the function of absorption vs. concentration.

To further understand adventitious carbon adsorption to ALD metal oxide surfaces and its effects on wettability we also studied AIO_x and TiO_x films deposited on Si substrates. Figure S4 shows XPS survey scans and water contact angle wettability studies for 10cy-ALD AIO_x and TiO_x films prepared on silicon wafers. In general, we find that adventitious carbon adsorption to these surfaces appears to occur more slowly than to the ALD coated nanopapers. To account for this, we looked at both "freshly prepared" surfaces and surfaces that had been heated to 150 °C for 4h to accelerate carbon adsorption kinetics. Freshly prepared surfaces were quickly transported from the reactor to the XPS system within < 30 min using a plasma cleaned aluminum foil case (to minimize adventitious carbon exposure). It is clear that there is a small peak of carbon even on freshly made surfaces, however, after the annealing process, this peak increase significantly. WCA measurements are shown in Figure S4 (c-d). Evident in these images is that the freshly made surfaces are hydrophilic. However, after "aging" (heating to 150 °C for 4h), the contact angle increases and the C 1s content appears consistent with the amounts we observe on the nanopaper. These results suggest that these ALD made metal oxide surfaces do adsorb adventitious carbon

that can lead to hydrophobicity, but it is not yet clear why this adsorption may occur faster on ALD coated nanopapers. Thus, these results cannot fully identify whether adsorption of adventitious carbon from the atmosphere or degradation of the cellulose due to exposure to the ALD precursors is the main source for the adsorbed hydrocarbons observed on the ALD coated nanopapers.



Figure S4: (*a*)*XPS survey scans of freshly prepared and* 150 °C / 4*h* heated 10cy-ALD AlO_x films on silicon (Inset is comparison of C 1s); (*a*)*XPS survey scans of freshly prepared and* 150 °C / 4*h* heated 10cy-ALD TiO_x films on silicon (Inset is comparison of C 1s); (*c*)Photographs of water drops on freshly prepared and 150 °C / 4*h* heated 10cy-ALD AlO_x films on silicon (Inset is corresponding WCA photos); (*d*) Photographs of water drops on freshly prepared and 150 °C / 4*h* heated 10cy-ALD AlO_x films on silicon (Inset is corresponding WCA photos); (*d*) Photographs of water drops on freshly prepared and 150 °C / 4*h* heated 10cy-ALD AlO_x films on silicon (Inset is corresponding WCA photos).



Figure S5: (a) Concentration of dispersed cellulose as a function of sonication time for nanopaper with (a) ncy-ALD $AlO_x + 150$ °C oven heating and (b) ncy-ALD $TiO_x + 150$ °C oven heating.



Figure S6: (a-l) Deconvoluted core-level spectrums of Al 2p, C 1s and O1s for control, n cy AlOx.



Figure S7: (a-l) Deconvoluted core-level spectrums of Ti 2p, C 1s and O1s for control, n cy TiOx.

The after deconvoluted core-level spectrums of Al 2p / Ti 2p, C 1s and O 1s for n cy TiO_x and n cy AlO_x are shown figure 1 and 2, respectively. It is clear that the unmodified cellulose nanopaper doesn't show any Ti or Al signal, however, C 1s and O1s peaks are analyzed here for controls. Cellulose has a chemical structure of polysaccharide, which is composed of thousands of $\beta(1 \rightarrow 4)$ linked D-glucose units, carbon and oxygen are the only two elements in cellulose, and XPS can tell the element oxidation state by studying about the binding energy and peak deconvolution. In our cellulose specimen, C 1s core-level spectrum could be deconvolute into four peaks, which are C-C/C-H (284.8 eV), C-O-C (286.4 -286.8 eV), O-C-O (287.8 - 288.3 eV) and C=O (288.8 - 289.2 eV). Adventitious carbon is used for charging reference; therefore, the spectrums of all elements are shifted according to the reference. O 1s of control has only one peak, which corresponds to C-O-H/O-C-O (532.8 - 532.9 eV), while the O 1s of ALD modified cellulose show a growing trend of peak width, which corresponds to the newly formed inorganic-oxygen bond (Ti-O and Al-O). It is important to notice that Al 2p peak only show one deconvoluted peak, which correspond to Al₂O₃ in NIST database, and this confirms that ALD of TMA precursor will produce a one oxidation state of aluminum. Unlike TMA precursor, TiCl₄ react with water and form a more complex compound TiO_x , which is composed of Ti^{2+} , Ti^{3+} and Ti^{4+} oxides.



Figure S8: Concentration of dispersed cellulose for control and just dose 10 cycles water.

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