

SURFACE HYDROPHOBICITY MODIFICATION OF CELLULOSE FIBERS BY LAYER-BY-LAYER SELF-ASSEMBLY OF LIGNOSULFONATES

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Self-assembled multilayers of lignosulfonates (LS) were built up on both quartz slides and cellulose fibers using a Cu^{2+} -mediated layer-by-layer (LBL) technique. The growth of LS multilayers on quartz slides was monitored by UV-Vis spectroscopy, and the absorbance at 205 nm as well as at 280 nm was found to linearly increase with the number of layers. The formation of LS multilayers on fibers surfaces was characterized by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). The XPS results showed that the surface contents of the characteristic elements, S and Cu, of LS multilayers were increased with the number of layers, which suggests the deposition of LS- Cu^{2+} complexes on cellulose fibers. Furthermore, there was a good linear relationship between the calculated surface LS content and the increment of LS layers. The AFM morphology results confirmed that the cellulose microfibrils on fiber surface were gradually covered by LS particles, resulting in the increase of surface roughness as self-assembly proceeded. The hydrophobicity of cellulose fiber probed by dynamic contact angle was significantly increased due to LBL self-assembly of LS on its surface. The initial contact angle was increased from 0° to 115° as the cellulose fibers were modified with a 5-layer LS multilayer. The reduction rate of the contact angle was dependent on the number of layers. When the cellulose fiber was modified by a 5-layer LS multilayer, the contact angle shifted from 115° to 98° after 0.12 s, suggesting some degree of hydrophobic character. Therefore, this technique provides a simple but effective way for promoting hydrophobicity of cellulose fibers in a controllable manner.

Keywords: Lignosulfonates (LS); Layer-by-layer (LBL); Multilayer; Hydrophobicity; Cellulose fiber; Morphology

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INTRODUCTION

Layer-by-layer (LBL) self-assembly is a simple and effective method to fabricate ultrathin multilayer films on solid substrates (Decher et al. 1992, 1997; Sukhorukov et al. 1998). By using selected functional molecules or particles, the desired surface properties of a solid can be achieved in a controllable manner (Chen and McCarthy 1997). A great variety of building substances such as inorganic nanoparticles (Kim and Sohn 2002), polyelectrolytes (Guo et al. 2009), and biopolymers (Gao et al. 2010; Xu et al. 2005) have been used to produce multilayer structures.

The driving force for multilayer fabrication is diverse, including electrostatic interaction (Decher et al. 1992), hydrogen bonding (Kharlampieva et al. 2009), coordinate bonds (Doron-Mor et al. 2004), hydrophobic interaction (Lojou and Bianco 2004), biological recognition (Anzai et al. 1999), and the synergetic interaction of the above forces, etc. The potential applications of LBL self-assembled multilayers are broad, including biosensors (Wang et al. 2008; Decher et al. 1994), optoelectronic devices (Ziegler et al. 2002), separation membranes (Krasemann and Tieke 1998), and antireflection coatings (Zhang et al. 2008).

Recently, the LBL self-assembly technique has attracted considerable attention to the field of fiber modification. Cellulose fibers as the major component of paper materials have been extensively studied as the substrate materials (Lvov et al. 2006; Eriksson et al. 2005; Lu et al. 2007; Agarwal et al. 2009; Xing et al. 2007; Lingström et al. 2006, 2007; Zheng et al. 2006). By coating LBL multilayers of polyelectrolytes at the nanoscale level, some unique functions can be brought to cellulose fibers, such as high strength (Eriksson et al. 2005), high porosity (Lu et al. 2007), electroconductibility (Agarwal et al. 2009), biocatalysis (Xing et al. 2007), hydrophobicity (Lingström et al. 2007), or a combination of the above (Zheng et al. 2006). Since the implementation of the “plastic limit” policy in Europe Union and China, hydrophobic modification of cellulose fibers for substituted material has been a great concern to scientists all over the world (Werner et al. 2010). On the other hand, bleached kraft pulp with improved hydrophobicity (Sahin et al. 2002) is increasingly required for producing paper products with good oil-absorbability and printability but less loss of brightness and strength. Therefore, the controllable surface modification method based on LBL self-assembly is of worth to study because it provides the opportunity to manufacture high value and high performance paper products.

There have been several successful attempts showing surface hydrophobic modification of cellulose fibers based on LBL self-assembly of synthesized polyelectrolytes (Lingström et al. 2006, 2007), such as polyallylamine (PAH), polyacrylic acid (PAA), and polyethylene oxide (PEO), etc. Technical lignins, major by-products from the pulp and paper industry, can also serve as natural anionic polymers (Maximova et al. 2001; Myrvold 2008). Kraft lignin has been studied for promoting the surface hydrophobicity of cellulose fibers by alternatively depositing lignin in sequence with a cationic starch (Maximova et al. 2004). Lignosulfonates (LS), the most available lignin products, can also be utilized to fabricate self-assembled multilayers with cationic polyelectrolytes on solids surface (Paterno et al. 2001; Deng et al. 2010). Compared with other lignins, its excellent water-solubility and high amphiphilicity facilitate the LBL self-assembly operations. In a previous study we demonstrated a novel LBL assembly method for constructing LS multilayers on mica surface using Cu^{2+} as the binding agent. The highly hydrophilic mica surface came to have some degree of hydrophobic character after being modified with an 18-layer LS multilayer (Liu et al. 2009).

In this work, the metal-mediated LBL self-assembly method was further applied in surface modification of cellulose fibers for the purpose of improving their hydrophobicity. The chemical compositions, morphological features and dynamic contact angles of the modified fiber surface were also measured.

EXPERIMENTAL

Materials

Sodium lignosulfonates (Na-LS) were kindly provided by Jangmen Sugarcane Chemical Factory Co. Ltd. (Guangdong, China). The LS were purified in a Milipore ultrafiltration unit (MA, USA) to remove the impurities (Ringena et al. 2005). Two membranes with molecular weight cut-off 10 k and 50 kDa were used. The reducing sugar in the purified LS fraction was determined using the DNS method after a two-stage dilute sulfuric acid reaction (Nguyen et al. 1999), and no carbohydrate was detected.

The quartz slides were purchased from AJ Nano-Science Development Co., Ltd. (Shanghai, China). The cellulose fibers were disintegrated from Xinhua No.1 filter papers (Hangzhou, China) and washed thoroughly with pure water. The water was Milli-Q Ultra pure water. All chemicals were all of analytical grade and were used without further purification.

Pretreatment of Quartz Slides

Before use, the slides were washed sequentially with ethanol and trichloromethane to remove the organic contaminants, then treated by piranha solution (30% H₂O₂, 70% H₂SO₄) at 80°C for 1h, and finally washed with pure water in an ultrasonic cleaner for 15 min. To generate more negative charges, further treatment was carried out by immersing the quartz slides in a H₂O/H₂O₂/NH₃ (5:1:1) solution at 70°C for 40 min with following water washing and air drying.

LBL Self-Assembly Process

A piece of functionalized quartz slide was first immersed into LS solution (200 mg/L, pH 12) at room temperature for 15 min. It was then rinsed thoroughly with pure water and dried in air. The slide was then immersed into CuSO₄ solution (50 mmol/L, pH 7) for 10 min, followed by rinsing and air-drying. The LBL self-assembly was achieved by repeating the above procedure.

LS multilayers were fabricated onto cellulose fibers surfaces in a similar manner as that of the quartz slide. The cellulose fibers were alternately immersed in LS solution with stirring (150 to 250 rpm) for 15 min and in CuSO₄ solution for 10 min. At the end of each step, the fibers were filtered in a Büchner funnel, rinsed with pure water and dried in air. All the treated-fiber samples were prepared with LS as the outermost layer. The number of layers in this work refers to the number of LS immersion step in the LBL process.

UV-Vis Spectroscopy

UV-Vis absorption spectra of LS multilayer were recorded from 200 to 800 nm on an Agilent 8453 UV-Vis spectrophotometer (Agilent, USA). The quartz slide coated with LS multilayer was placed perpendicular to the beam, and a clean slide was scanned as the blank. All absorption data presented in this work were the average of at least three scans.

X-ray Photoelectron Spectroscopy (XPS)

The cellulose fibers were made into sheets by vacuum filtration prior to XPS analysis. Test samples in circular form (about 0.5 cm²) were cut from the sheet and were mounted with screw-on clips to the sample holder. The samples were outgassed overnight under vacuum in a turbo-pumped chamber to stabilize the moisture content in the sample matrix. XPS spectra were recorded on a Kratos Axis Ultra spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromated Al K α X-ray source (150 W) and with an electron flood gun for charge compensation. The pass energy was 40 eV and 160 eV for high and low resolution spectra, respectively. Surface atomic ratios of oxygen to carbon (O/C) were calculated from low-resolution XPS spectra, and S 2p, Cu 2p, and C1s spectra were obtained from high-resolution XPS measurements.

Atomic Force Microscopy (AFM)

Samples for AFM were prepared following the protocol as described for XPS sample preparation. Three samples were made for each modified fiber. At least five different fibers from the same sample were scanned, and only images with reproducible features were reported. AFM measurements were performed on a Nanoscope IIIa Multimode scanning probe microscope (Veeco Co., USA) in tapping mode at room temperature. A J-type scanner and rectangular silicon cantilevers with resonance frequency about 290 to 320 kHz were used. All images were captured at a scan rate of 1 Hz and a resolution of 512 \times 512 pixels. Software Version 5.12r3 (Veeco Co., USA) was used for data recording and analysis. No image processing except flattening was made.

Dynamic Contact Angle (DCA) Measurement

The modified cellulose fibers were made into sheets as described above. After air-drying, the sheets were cut into 15 mm wide strips, and they were then kept in constant temperature and humidity room (23 $^{\circ}$ C, 50% RH) for 24 h. The dynamic contact angle of monolayer or multilayers coated sheet strips were measured at 23 $^{\circ}$ C and 50% relative humidity using a FIBRO 1100 DAT dynamic contact angle and permeability analyzer (FIBRO Systems, Sweden). The system consists of an automatic drop applicator and a video camera connected to a computer. A water drop with a volume of 4 μ L was placed onto the sample surface, and the contact angle was measured at a time interval of 20 ms.

RESULTS AND DISCUSSION

Fabrication of LbL Multilayer of LS on Quartz Slides

It has been reported that the general trend of polyelectrolyte multilayers built up on a SiO₂ surface is consistent with that on cellulose fibers (Wågberg and Nygren 1999; Lingström et al. 2007). In order to demonstrate the feasibility of the metal-mediated LBL self assembly, a functionalized quartz slide was used as a model substrate for directly measuring the growth of LS multilayers. Since LS and copper ions are sensitive to UV light, UV-Vis absorption spectra of self-assembled multilayers of LS on the quartz slide were recorded, as shown in Fig. 1.

The absorption peak at 280 nm is typical for lignosulfonates containing phenolic-hydroxyls of the lignin phenyl propane monomers. The peak at 205 nm may be due to the absorption of both LS and Cu^{2+} , as in this work. The absorbance at 205 nm as well as at 280 nm was increased with the layer number of LS multilayer, exactly following a linear relationship (inner box in Fig. 1). This suggests that the same amount of LS was adsorbed on each layer and that the LBL self-assembly process is reproducible. Figure 1 also indicates that the baseline (absorbance at 500 nm) was shifted higher as self-assembly proceeded, which can be explained by the intensified light scattering caused by increased surface roughness of the substrate. In a previous study we also found an increase of surface roughness with the LS multilayer growing on mica substrates (Liu et al. 2009). However, the direct UV-Vis spectroscopic method was not suitable for the case of cellulose fibers. The indirect approach of determining the reduction of LS solution concentration is not practicable, because the adsorption of LS on cellulose is too low to be detected. Therefore, the growth of the LS multilayers on cellulose fibers was measured by determining the surface chemical compositions, for instance, the content of lignin as well as the characteristic elements Cu and S.

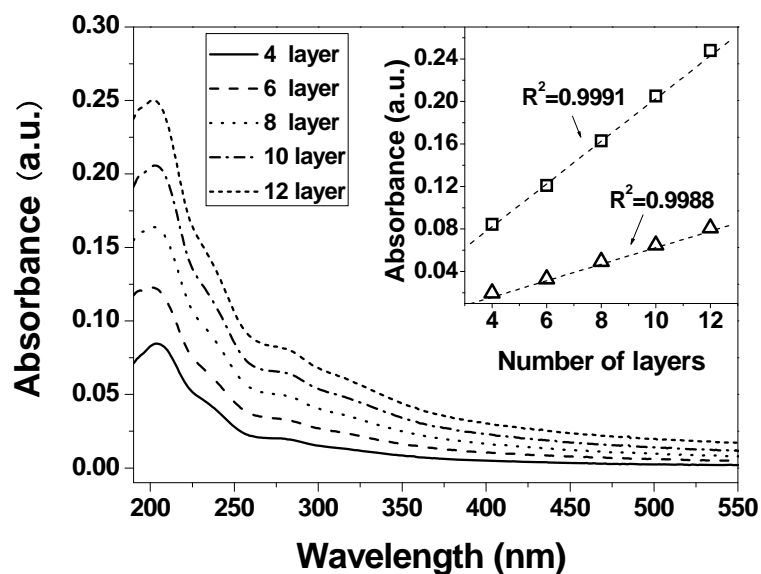


Fig. 1. UV-Vis absorption spectra of self-assembled LS multilayer on the quartz slide with different number of layers. Inset: absorbance at 205 nm (square symbol) and 280 nm (triangle symbol) vs. the number of layers

Layer-by-Layer Assembly of LS on Cellulose Fibers

Characteristic elements

In the LBL self-assembly system there are two characteristic elements, S and Cu. Since these elements were undetectable in raw cellulose fibers, we assumed that the Cu originated from the CuSO_4 and S was from sulfonic groups in the LS molecule. Although CuSO_4 also contains S, a subsequent washing was able to remove all the SO_4^{2-} attached on the fiber after self-assembly so that S was not detected in the rinse water. Furthermore, the elements Cu and S can exist in the form of LS-Cu^{2+} complexes in an LBL multilayer (Khvan and Abduazimov 1990). In addition, sulfonic groups exhibit higher coordinative

ability with Cu^{2+} ions than SO_4^{2-} in neutral solution. We assumed that LS is the main source of element S in LS multilayer assemblies. The growth of LS multilayer can thus be represented by the increased content of characteristic elements on the fiber surface.

The surface content of S and Cu were determined by XPS, and the results are shown in Fig. 2. The peak at 168.1 eV was assigned to S 2p, while that at 934.1 eV was Cu 2p. Figures 2a and 2b indicate that the intensities of S 2p and Cu 2p peaks were correspondingly increased with the increase of LS layers. The results confirm the feasibility of LBL self-assembly of LS on the cellulose fibers using Cu^{2+} as a mediator agent.

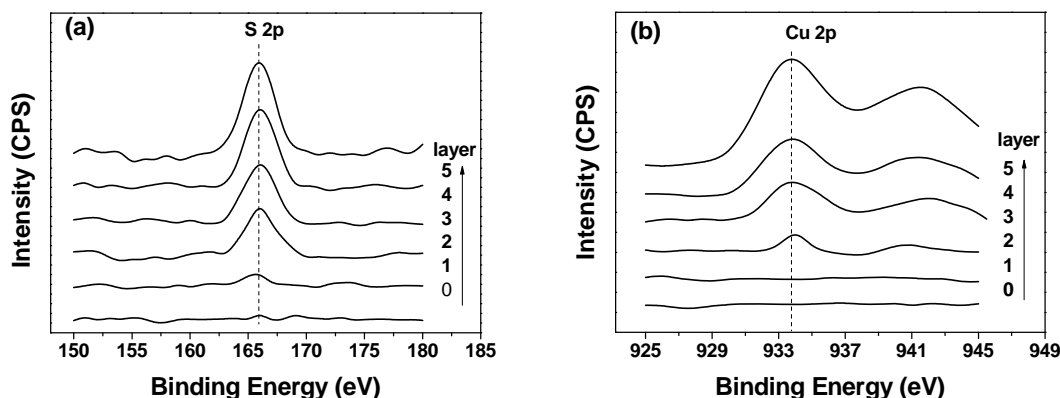


Fig. 2. XPS spectra in the S 2p and Cu 2p regions for the cellulose fibers surfaces modified with LS monolayer or multilayer: (a) S 2p (b) Cu 2p

Surface lignin content

The fiber surface lignin can be evaluated by two alternative XPS analysis approaches. The most commonly used one is based on determining the different atomic ratio of oxygen to carbon in cellulose and lignin. The theoretical O/C ratio for pure α -cellulose is 0.83, while that for our purified LS as calculated from Fig. 3a is 0.39. A decrease in O/C ratio of cellulose substrate indicates an increase in the LS content on the surface.

The other approach is to use a high-resolution C1s spectra in which different carbon components are discriminated and evaluated. Since the main detectable elements in purified LS are carbon, oxygen, and sulfur (as shown in Fig. 3a), the chemical bonds of carbon can be categorized into five main groups: C1 (C-C), C2 (C-O), C3 (O-C-O or C=O), C4 (O=C-O), and C5 (C-S), as shown in Fig. 3b. It has been reported that pure cellulose contains only C2 and C3 carbons (Maximova et al. 2001), thus C1, C4, and C5 carbons can be characterized for LS. However, the intensity of the C4 peak is very small due to the low content of carboxyl groups in LS. On the other hand, the peak of C5 carbon (286.2 eV) from the -C-SO₃H structure in LS is almost exactly overlapped with that of C2 carbon (286.3 eV). Therefore, these two peaks were fitted into one peak. The surface content of LS (ϕ_{LS}) can be quantified by determining the relative amount of C1 carbon as expressed by Eq. 1,

$$\phi_{LS} = \frac{C1 - \alpha}{\beta} \times 100\% \quad (1)$$

where $C1$ represents the area of the C1 peak divided by the total area of the C1s peak, α is a correction factor for the presence of contaminants, and β is the area of the C1 carbon of the purified LS (47% as calculated from Fig. 3c).

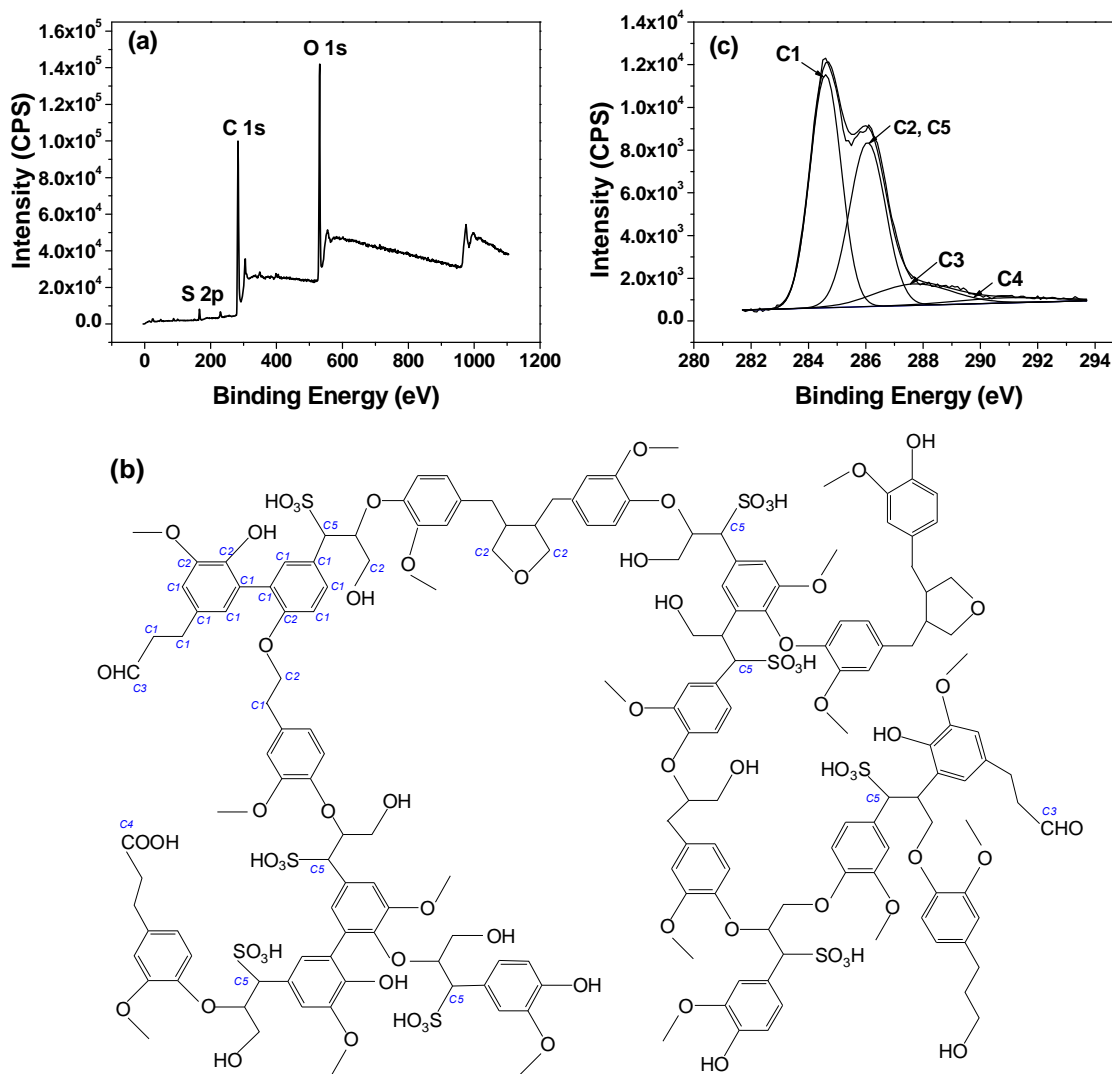


Fig. 3. XPS spectra of the purified LS powder and a proposed structure of LS: (a) low-resolution survey scan, (b) a proposed structure of LS, (c) high-resolution C 1s spectrum

The XPS results for the raw and modified cellulose substrates are illustrated in Fig. 4 and listed in Table 1. The O/C ratio decreased progressively with the increment of LS layers. As a 5-layer multilayer was formed on the substrate, the O/C ratio reached 0.4, which is very close to the O/C ratio for purified LS. This suggests that the cellulose substrate was almost completely covered by LS. With respect to the fact that XPS has a detection depth of 10 nm (Zhang and Komvopoulos 2009), it can be assumed that the average thickness of LS multilayer was at least 2 nm. In our previous study (Liu et al. 2009), an AFM measured thickness of LS monolayer on mica was 2.14 nm.

It can also be found from Table 1 that the calculated LS content was increased with the number of layers as LBL assembly proceeded. For raw cellulose fibers, a small C1 peak on the sample surface was detected, which is possibly due to contamination during sample preparation. Hence, α in Eq. 1 is 5.1%, which is used for correlation. The intensity of the C2/C5 peak was apparently decreased, although more $-C-SO_3H$ structures were assembled on the surface during the LBL process. This means that the contribution of C5 carbon is relatively low compared to the C2 carbon. In addition, the intensity of the C3 peak was also decreased with the number of layers, and the variation of peak intensities of C4 carbons was not significant, which is probably because of the fitting accuracy.

The plots of calculated LS content vs. layer number can be fitted into a linear expression with R^2 higher than 0.9 (Fig. 5). This result is in good agreement with that obtained from LS multilayer formation on the quartz slide as described above. For fibers modified with a 5-layer LS multilayer, the calculated LS content on surface was over 87%, significantly higher than that for pulp fibers, such as kraft pulp (Gustafsson et al. 2003), TMP, CTPM (Koljonen et al. 2003), etc.

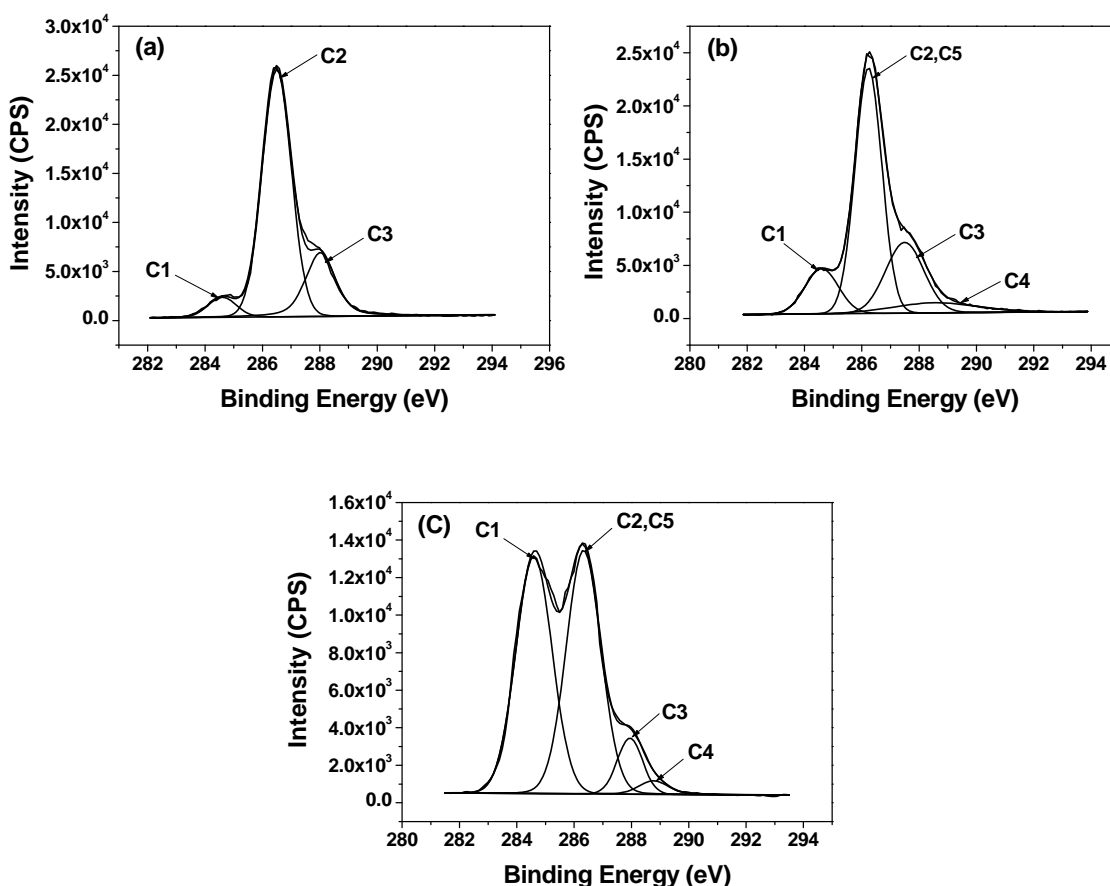
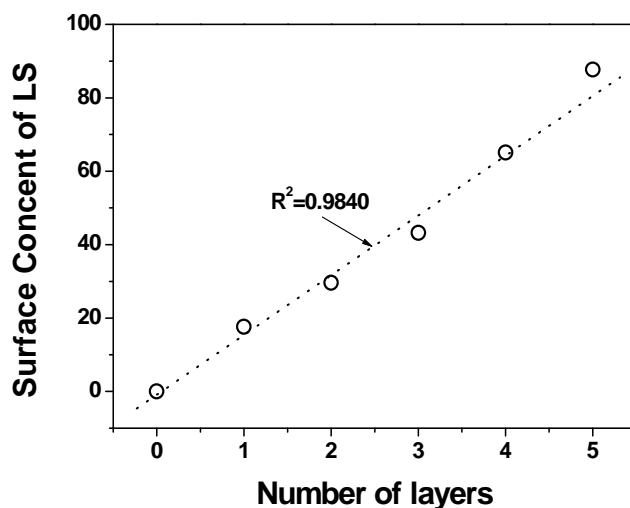


Fig. 4. High-resolution spectrum of C1s for raw and modified cellulose fibers: (a) raw cellulose fibers, (b)-(c) cellulose fibers modified with LS monolayer and a 5-layer LS multilayer, respectively

Table 1. XPS Results of Cellulose Fibers Modified by LbL Assembly of LS

Number of layers	Atomic ratio (O/C)	C 1s total=100%				Φ_{LS} (%)
		C1 (%)	C2, C5 (%)	C3 (%)	C4 (%)	
0	0.80	5.1	72.7	22.2	-	0
1	0.60	13.4	57.5	25.3	3.8	17.6
2	0.56	19.0	58.0	19.1	3.9	29.6
3	0.51	25.4	53.4	17.6	3.7	43.2
4	0.45	35.7	49.6	10.8	3.9	65.1
5	0.40	46.3	44.8	5.1	3.8	87.7

**Fig. 5.** The surface content of LS on fiber surface as a function of the number of layers

Proposed mechanism

In order to understand the process of LBL self-assembly of LS on a cellulose fiber surface, it is necessary to give a hypothesis about the mechanism behind this assembly process. For the first layer, since the substrates, i.e. quartz slide and cellulose fiber, are highly hydrophilic and negatively charged, the electrostatic repulsion between substrate and LS makes it impossible to form a LS monolayer on the substrate surface, so we hypothesized that the driving force for the formation of a LS monolayer on substrate surface is a hydrophilic effect.

The Cu^{2+} ion can coordinate with functional groups (sulfonic, carboxyl, and phenolic hydroxyl groups) of lignin derivatives (Khvan and Abduazimov 1990; Guo et al. 2008). It was suggested that LS bound to Cu^{2+} to form LS- Cu^{2+} complexes. We proposed that the action of Cu^{2+} changed the supermolecular structure of LS, and thus resulted in the formation of LS- Cu^{2+} complexes at the interface between the LS monolayer and Cu^{2+} solution. Because the amount of Cu^{2+} was in excess, there are probably large amounts of coordination-unsaturated LS- Cu^{2+} complexes formed, on which water molecules could coordinate to the unsaturated coordination sites of Cu^{2+} (Liu et al. 2009). During the next step of LS self-assembly, the ionized sulfonic, carboxyl and phenolic hydroxyl groups in new LS solution, which have higher affinity to Cu^{2+} than water molecule, have substituted the water molecule to coordinate with Cu^{2+} to form a new layer of LS. The driving force for the formation of subsequent LS multilayer is a coordination effect.

AFM Morphology of LS Multilayers on Cellulose Fiber

The surface morphology of cellulose fibers modified with LS multilayer was visualized by tapping-mode AFM. Representative AFM phase images are shown in Fig. 6. The morphological features (Fig. 6a) show that the raw cellulose fibers have regularly ordered microfibrils with diameter of about 40 to 60 nm. When coated with LS layers, the fibril surface of substrate was gradually covered with particles and granules (see Fig. 6b-6d).

Meanwhile, the boundary of cellulose microfibrils became vague, and almost complete coverage of granular particles on surface was achieved (5-layer multilayer). These particles can be assumed to be individual LS granules because: (1) the increment of granular particles with the number of layer was in accordance with that of LS content as measured by XPS, (2) all LS assemblies were performed in an alkaline solution (pH 12) in which all LS functional groups were dissociated, and (3) the mean diameter of the granules was measured to be about 40 to 100 nm, which was in accordance with the size of LS granule assembled on mica as we reported previously (Liu et al. 2009).

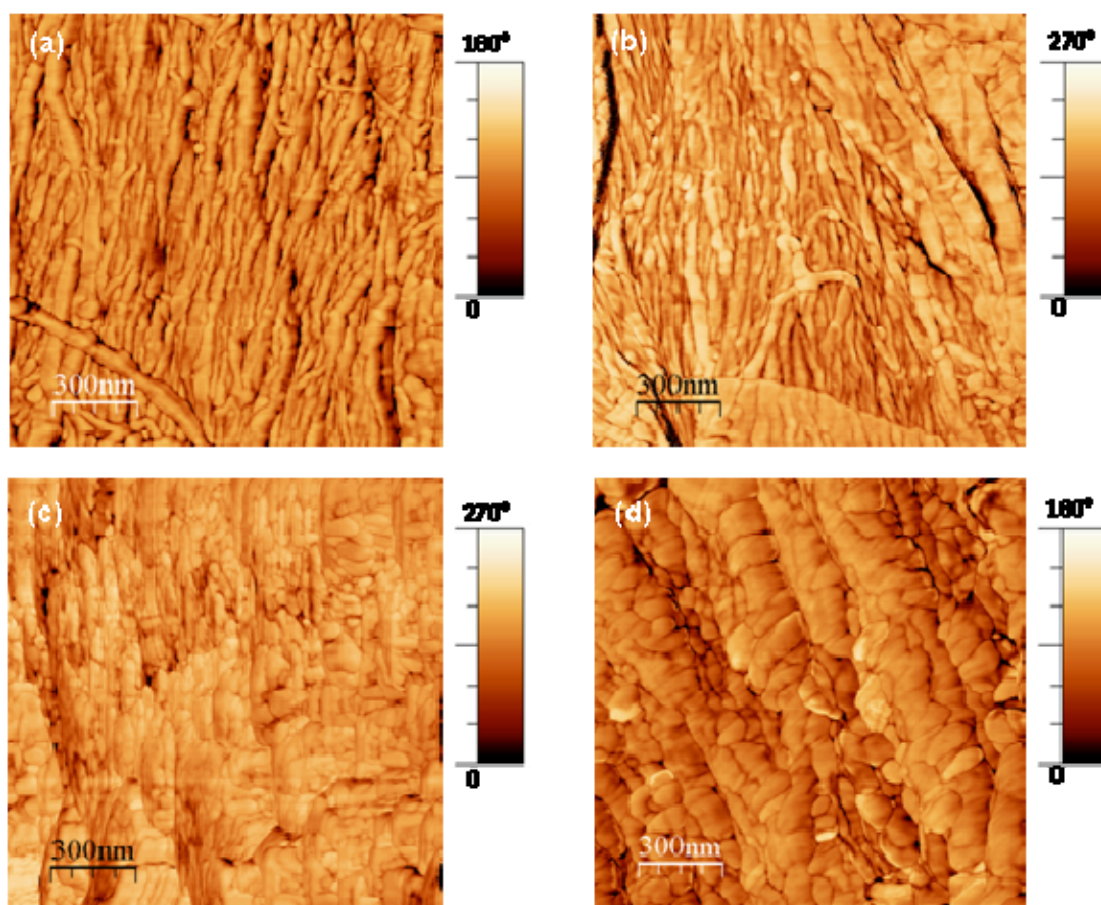


Fig. 6. AFM phase images of raw and modified cellulose fiber: (a) raw cellulose fiber, (b)-(d) cellulose fiber modified with 1-layer, 2-layer and 5-layer of LS, respectively

Wetting Properties of Modified Cellulose Fibers

The wetting properties of solid materials can be characterized by the contact angle that a drop of fluid makes with the surface. Unlike on those substrates, such as mica, quartz, glass, etc., with extremely homogeneous and flat surfaces, the formation of water contact angle on a cellulose fiber is not a static but a dynamic process. As soon as the dropped water contacts the fiber surface, it instantly experiences an implantation process that can be divided into three stages: adhesion, penetration, and then spreading. Therefore, the angle formed between the moving liquid interface and the solid surface, the so-called dynamic contact angle, is usually used to quantify the wetting properties of cellulose fibers and the paper products.

The contact angle of unmodified wet fibers is 0° due to the superhydrophilic nature of the cellulose. During an air-drying process, the hornification of fibers may have a slight influence on their wetting properties. Hence, the control fiber sample was prepared by cycling the immersion and air-drying processes 10 times, which corresponds to a preparation of a 5-layer multilayer of LS. The initial contact angle at 0.02 s was about 18° , and after 0.08 s the contact angle decreased to 0° . This suggests that hornification has less effect on hydrophobicity of filter paper fibers than in the case of chemical pulp fibers (Köhnke et al. 2010). This can be explained by the fact that the filter paper fibers were all produced from cotton fibers, which have a higher crystallinity than other fibers.

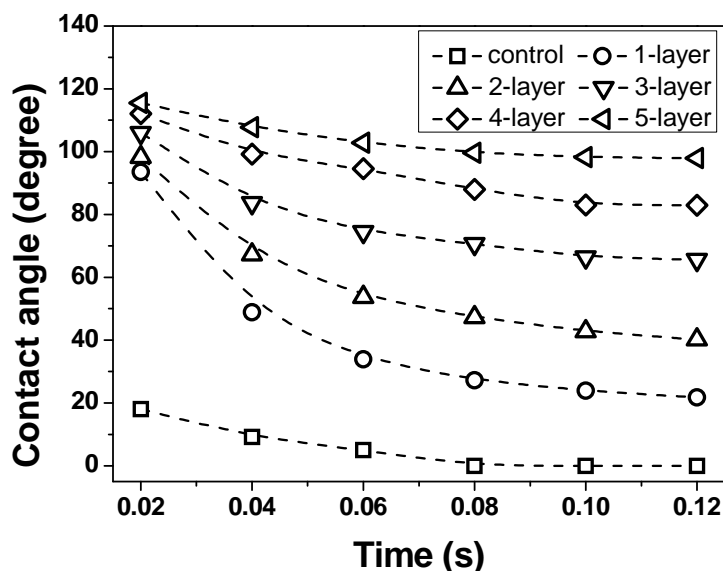


Fig.7. Effect of a LS monolayer and LS multilayer on wetting properties of cellulose fibers

The hydrophobicity of cellulose fibers was significantly promoted by its modification with a layer of LS (see Fig. 7). An initial contact angle of 93.5° was achieved, which suggests a certain degree of hydrophobic character. But the contact angle decreased to 21.8° after 0.12 s. The possible reason is that the amount of LS in one layer is too low to fill up the valleys between cellulose microfibrils. As a result, the capillary force was still able to drive the penetration of water drops, and the contact angle downshifted instantly. As the LBL assembly proceeded, the substrate surface was

covered by more LS particles, and the contact angle at 0.12s was correspondingly promoted. However, the increment of initial contact angle was very slight. Here, we propose that the coverage of LS on the substrate surface modified by a monolayer was very high so that no significant improvement of initial contact angle was obtained. The initial contact angle of 5-layer LS modified fiber reached 115.5° and slightly decreased to 97.9° after 0.12 s. These results suggest that the hydrophobicity modification of cellulose fibers by LBL assembly of LS was feasible and controllable, simply by choosing the layer number of LS, depending on the need.

It may be worth noting that Cu^{2+} ions can catalyze oxidation of LS to corresponding aldehydes in air (Taraban'ko et al. 1995), so air oxidation of self-assembled LS multilayers would be expected to occur slowly. However, we did not find considerable difference for the XPS, AFM, and DCA measurement of LS multilayer after the samples were stored 3 days. In fact, the stability of LS multilayer is very important for their practical application, and the effects of storage time, pH, and ambient temperature on the stability of LS multilayers will be considered in our future study.

CONCLUSION

A layer-by-layer (LBL) self-assembled multilayer of lignosulfonate (LS) mediated by Cu^{2+} ions was successfully built up on quartz slides and cellulose fibers. The LS content on the substrate's surface was linearly increased with the number of LS layers. The increment of characteristic elements (S and Cu) with the growth of LS multilayers was also observed. The morphology of modified surfaces was visualized by AFM, and the results showed that a granular phase of LS gradually covered the surface of cellulose fiber as the LBL assembly proceeded. The hydrophobicity of cellulose fibers was significantly increased with LS self-assembly. The initial contact angle of 5-layer LS modified fiber reached 115.5° and slightly decreased to 97.9° after 0.12 s of exposure to water. These results suggest that the hydrophobic modification of cellulose fibers by LBL assembly of LS was feasible and can be achieved in a controllable manner.

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