

Fabrication of a Model Cellulose Surface From Straw with an Aqueous Sodium Hydroxide/Thiourea Solution

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ABSTRACT: Model cellulose surfaces were prepared with both microcrystalline cellulose and cellulose isolated from wheat straw with different molecular weights. A sodium hydroxide/thiourea aqueous solution, instead of any organic solvents, worked as the solvent for dissolving cellulose, and model cellulose films were prepared by a two-step method: first, the cellulose solution was deposited onto the surface of the substrate with the spin-coating method, and second, the as-prepared film was washed with deionized water to remove the impurities and was formed with a flattened surface. Atomic force microscopy

was used to measure the morphology, surface roughness, and thickness of the cellulose thin films. X-ray photoelectron spectroscopy and energy-dispersive X-ray spectrometry were used to characterize the surface chemical information of the films. The results revealed that model cellulose surfaces could form from both kinds of cellulose. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1330–1335, 2008

Key words: atomic force microscopy (AFM); films; surfaces

INTRODUCTION

Cellulose is a basic structural material in nature, and its superstructures with other molecules such as lignin, hemicellulose, and protein have key roles in the growth and survival of plants.^{1,2} There is still much unknown about the interactions between cellulose and other molecules, and this leads to problems in industrial applications, such as the pulping process in papermaking. Cellulose model surfaces have been regarded as ideal surfaces for investigating the interactions of cellulose with proteins and other chemicals.^{3–6}

By now, several methods have been reported for preparing cellulose model surfaces, and one of the basic processes is the deposition of a solution of cellulose or its derivatives. Among them, Langmuir–Blodgett deposition and spin coating are the two most attractive methods.^{7,8} Spin coating is a simple method used to apply uniform thin films to flat substrates. When a solution of cellulose or its derivatives is spin-coated onto the flat surface of a substrate, it produces a liquid film; synchronously,

the liquid is evaporated with the help of high-speed spinning.⁹ Then, regeneration is required to obtain a pure cellulose surface. Kontturi et al.¹⁰ recently reviewed the current state of the preparation of cellulose model films. Usually, an anchoring polymer is used to help cellulose to attach to the substrate.⁴

The dissolution of cellulose in a simple solvent is difficult. The early preparation of a cellulose model surface usually involved the use of cellulose derivatives to obtain a homogeneous solution, and a hydrolysis process was always required to obtain a cellulose model surface. Recently, the dissolution of cellulose in new solvent systems has been developed. Some green solvent systems have been reported, such as *N*-methylmorpholine-*N*-oxide,¹¹ ionic liquids,¹² and water-based solvent systems.¹³ Since the discovery that cellulose can be well dissolved in a precooling sodium hydroxide (NaOH) aqueous solution, much attention has been paid to using a new aqueous solvent system based on NaOH to increase the solubility of high-molecular-weight cellulose and improve its stability.^{14–17} Zhang et al.¹⁸ recently reported a series of water-based solvent systems for cellulose. They found that cellulose can be easily and quickly dissolved in precooled LiOH/urea, NaOH/urea, or NaOH/thiourea aqueous solutions, and this provides a chance to process cellulose, prepare novel fibers or resins, and synthesize derivatives of cellulose.

Zhang et al.¹⁹ recently also used water-based solvent systems to prepare regenerated cellulose films

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by using H_2SO_4 or its mixtures with inorganic salts as coagulation reagents. They found that the obtained thin films had a less dense structure with a stronger coagulant, whereas a relatively dense structure was formed with mild coagulants. In this study, we used a NaOH/thiourea aqueous solution as the solvent to dissolve cellulose, and we tried to prepare model cellulose surfaces by using the spin-coating method. The regeneration of cellulose was achieved only through the washing of films with deionized water.

Two kinds of cellulose were used as feedstock to prepare the cellulose model surface: microcrystalline cellulose and cellulose isolated from straw with a higher molecular weight. The celluloses were first dissolved in aqueous NaOH/thiourea solutions, and then the model cellulose thin films were prepared via the spin casting of the cellulose solution onto the polyacrylamide (PAM)-modified surface of mica. The morphologies of the films were measured and the roughness was analyzed with atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), and energy-dispersive X-ray (EDX) spectrometry.

EXPERIMENTAL

Chemicals

NaOH, thiourea, and microcrystalline cellulose (weight-average molecular weight = 6.87×10^4 g/mol) were acquired from Shanghai Chemical Reagents Co. (Shanghai, China) and used without further treatment. Wheat straw was collected from a farm in the east of China. Ultrapure water (18 M Ω cm) was prepared with a Millipore system (Milli-Q, San Diego, CA). Natural mica (muscovite) was purchased from Nilaco Corp. (Japan). Acrylamide (Shanghai Chemical Reagents) was purified from an aqueous ammonium sulfate solution at -5°C . PAM, with an average molecular weight of 7700 g/mol and a polydispersity index of 1.14, was synthesized in water by a raft-reagent controlled radical homopolymerization process and measured with a Waters 1515 gel permeation chromatograph and a Waters 2414 refractive-index detector. Narrow poly(ethylene oxide) standards were used in the calibration of the molecular weight and molecular weight distribution.

Anchoring of the polymer onto the surface of mica

PAM was used to attach the cellulose to the newly cleaved mica. The polymer was adsorbed onto the mica via the dipping of the plate in a 10^{-5} g/L aqueous solution of PAM, which was acidified to keep the pH at 3 by the addition of an aqueous HCl solution. At pH 3, PAM was positive and was adsorbed onto mica. The mica was removed from the solution

after 20 min and then was washed with ultrapure water to remove the unabsorbed PAM; at the end, the sample was immediately dried in an oven at 55°C for 15 min.

Isolation of cellulose from wheat straw

The process of cellulose isolation from straw can be found in ref.²⁰ in detail. In brief, first the straw was cleaned and cut into little pieces, and then it was treated with a mixture solution of toluene and ethanol (2 : 1 v/v) for 6 h to remove the wax; sequentially, the dewaxed straw was treated with 300 mL of H_2O at 55°C for 2 h, 3.0% H_2O_2 in 200 mL of 0.5M NaOH at 55°C for 2 h, and 200 mL of 2M NaOH at 55°C for 2 h. Furthermore, the concentration of NaOH in the mixture suspension was adjusted to 1M by the addition of water, and the suspension was heated at 170°C for 30 min to degrade the cellulose to some extent. Finally, the reactor was cooled to room temperature, and the insoluble residue was collected by filtration. After washing with water and drying at 60°C *in vacuo*, isolated cellulose was obtained. A Fourier transform infrared spectrum was used to identify the obtained cellulose.

Cellulose solutions

The microcrystalline cellulose was dispersed into an aqueous 6 wt % NaOH/5 wt % thiourea solution, and this was followed by freezing in a refrigerator under -5°C for 12 h. The freezing solution of cellulose was unfrozen in air for 10 h with stirring, and then we obtained a transparent solution of cellulose.

A similar process was used to prepare the solution of cellulose isolated from straw. The isolated cellulose could be well dissolved in the NaOH/thiourea aqueous solution. The molecular weight of the isolated cellulose was measured with a laser light scattering method (ALV/DLS/SLS-5022F, ALV-GmbH, Langen, Germany),²¹ and the weight-average molecular weight was 12.7×10^4 g/mol.

Model cellulose surface prepared by the spin-coating method

The mica covered with PAM was fastened onto the top of a spin-coating plate. The cellulose solution (40 μL) was deposited carefully with a pipette onto the modified mica surface. After spin coating at 1500 rpm for 15 s and at 2500 rpm for 15 s by a spin coater (S-1, Kemeit, Shanghai, China), cellulose thin films were obtained, and then they were placed in Milli-Q water for 1 h to remove the deposited inorganic salt three times with changed water. Finally,

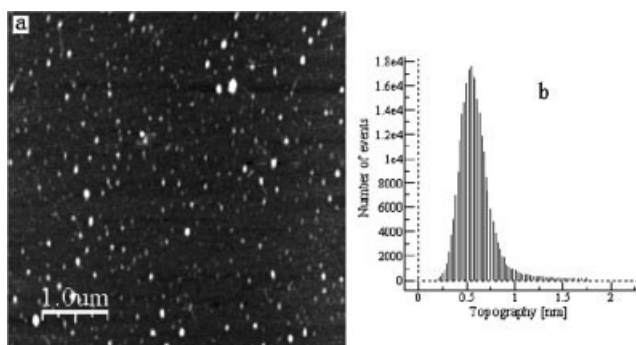


Figure 1 (a) Typical AFM height image of a PAM-modified surface of mica ($5 \mu\text{m}^2$) and (b) corresponding roughness analysis profile (topographical height distribution). The RMS of the surface in an area of $5 \mu\text{m}^2$ is 0.23 nm. The Z amplitude is 2.5 nm.

the samples were dried at room temperature *in vacuo*.

AFM measurements

A commercial atomic force microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA), equipped with a J scanner, was used to measure the morphologies of the cellulose films. A silicon probe (model TESP, Nanoprobes, Digital Instruments) with a cantilever length of $125 \mu\text{m}$ and a resonant frequency of about 300 kHz was used. The radius of curvature was about 30 nm, and the tip height was 20–25 μm . The scan rates were between 0.5 and 1.0 Hz. The obtained images were treated and analyzed with WSxM software (4.0 Develop 7.71, Nanotec Electronica, Madrid, Spain) and Photoshop 6.0 (Adobe).

Film thickness measurements

To measure the thickness of a cellulose film, a small area of the film surface was scratched by the AFM tip via scanning in the contact mode so that the surface of the substrate was exposed. Then, the topography in a large area was measured in the tapping mode. The thickness was obtained by a section line analysis of the AFM height image.

XPS spectra

XPS spectra were recorded on an Escalab MK II photoelectron spectrometer (VG Scientific Ltd., United Kingdom).

EDX measurements

A Shimadzu (Osaka, Japan) Superscan SSX-550 scanning electron microscope was used for the space-resolved analysis. The apparatus was equipped with an EDX spectrometer to measure the major elements

and their distribution in the sample. The measurements were carried out under a low vacuum, and the backscattered electron images were recorded

RESULTS AND DISCUSSION

PAM has been reported to be a good anchoring polymer for preparing cellulose model surfaces.⁴ Figure 1 shows a typical AFM height image of the surface of mica anchored by PAM. There appear to be many small spots on the surface of mica about 50 nm in diameter. There is still much unknown about the anchoring mechanism of PAM. However, it is believed that the electrostatic force between PAM and mica should have a key role. The mica surface is negatively charged, and acidic PAM has a positive charge because of the protonation of the amine groups, so PAM can be fixed on the surface of mica by electrostatic interactions. PAM molecules have a strong affinity to cellulose through the hydrogen bonds between the hydroxyl groups of cellulose and the amide groups of PAM. Figure 1(a) shows that the coverage degree of the mica surface is not so high, but the distribution of the absorbed PAM is homogeneous, and this is helpful for further fixation of cellulose on the surface. Figure 1(b) shows the roughness analysis of the surface shown in Figure 1(a). The average height of the surface is about 0.63 nm, and the root mean square roughness (RMS) is 0.23 nm.

Then, the PAM-anchored mica surface was used as the substrate to prepare cellulose thin films via the spin coating of aqueous NaOH/thiourea solutions of cellulose with various concentrations. Figure 2(a) shows a typical AFM height image of the as-prepared microcrystalline cellulose thin film with a cellulose solution at a concentration of 1.0% (w/w). In comparison with Figure 1(a), the surface of the

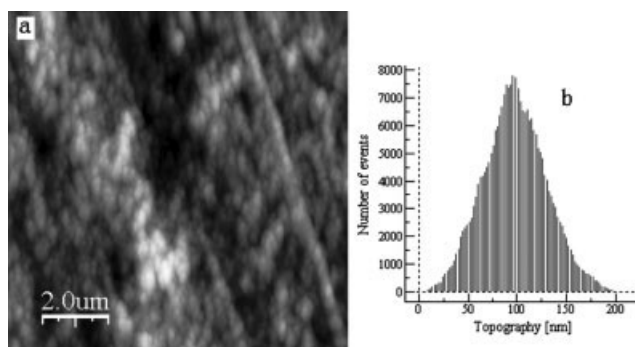


Figure 2 (a) Typical AFM height image of a cellulose film surface ($10 \mu\text{m}^2$, Z amplitude = 220 nm) and (b) corresponding roughness analysis profile. The cellulose film was prepared via the spin coating of an aqueous NaOH/thiourea solution of microcrystalline cellulose with a concentration of 1.0% (w/w). The RMS of the film in an area of $10 \mu\text{m}^2$ is 32.1 nm.

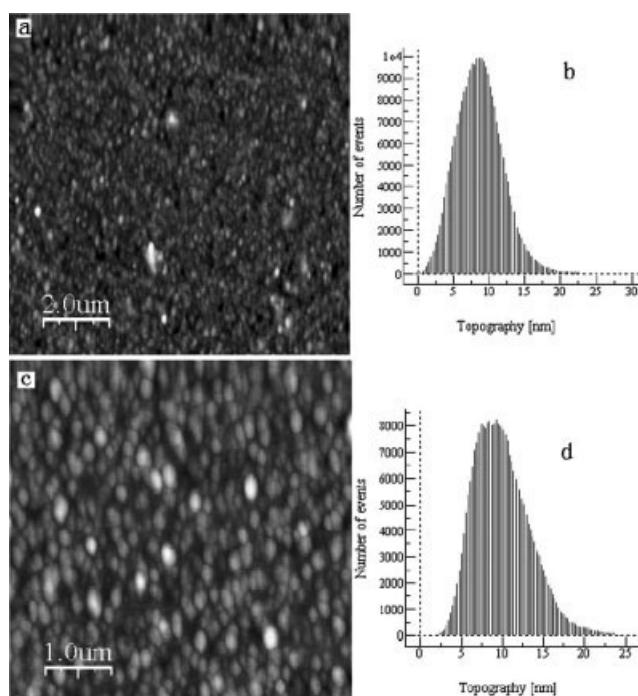


Figure 3 (a,c) Typical AFM height images of a cellulose film surface with scanning areas of 10 and $5 \mu\text{m}^2$ [(a) Z amplitude = 43 nm and RMS = 3.39 nm and (c) Z amplitude = 26.4 nm and RMS = 3.38 nm] and (b,d) corresponding roughness analysis profiles. The cellulose film was prepared through the spin coating of a NaOH/thiourea solution of microcrystalline cellulose with a concentration of 0.2% (w/w).

mica is completely covered by cellulose particles about 200 nm in diameter. The average height of the surface is about 100 nm [Fig. 2(b)], and the RMS of the surface in an area of $10 \mu\text{m}^2$ is 32.1 nm. The surface is rather coarse, and this indicates multilayer adsorption of cellulose on the substrate. Therefore, a diluted solution of cellulose is needed to prepare a lower roughness surface. When a cellulose film is prepared with a 0.5% cellulose solution, the surface is still coarse with an RMS of 13.6 nm, and the average height of the surface is about 35 nm, but it is much lower than that in Figure 2; this indicates that a decrease in the concentration of the cellulose solution favors a relatively flat surface. With the concentration of the cellulose solution is sequentially reduced to 0.2%, a much flatter surface is expected. As shown in Figure 3(a), the newly prepared cellulose film has a very flat surface. The average height of the film now is about 8.9 nm, and the RMS is 3.39 nm in an area of $10 \mu\text{m}^2$ [Fig. 3(b)]. Figure 3(c) is a zoom-in AFM height image of a small area in Figure 3(a); there clearly appear many small particles about 200 nm in diameter. The surface is full of nanoparticles; the RMS of the area is 3.38 nm and is nearly the same as that in the big area, indicating that the film is rather homogeneous. The average height of

the surface is 10.2 nm [Fig. 3(d)], which is also close to that in the big area. The formation of the cellulose nanoparticles is a result of the regeneration of cellulose by the water washing process.

The thickness of the cellulose film was also measured by the AFM method. It has been reported that it is safe to scratch the soft polymer layers adsorbed onto the surface of mica or silicon substrates through the scanning of a small area of the surface in the contact mode at a higher tip force and then through the scanning of a larger area in the tapping mode to measure the height of the thin film.²² Figure 4 shows an AFM height image of a cellulose thin film measured in an area of $10 \mu\text{m}^2$ after the scratching of a small area by an AFM tip working in the contact mode. There appears a square with exposure of the mica surface. The section line analysis [Fig. 4(b)] clearly shows that the thickness of the cellulose thin film is about 25 nm. The reasons that the particles are about 200 nm in diameter but the film thickness is only 25 nm are the broad effects of the tip and the collapse of particles in the Z direction due to the association of particles with one another in the direction parallel to the substrate.

All these results reveal that by the use of the new cellulose solution system, an aqueous NaOH/thiourea solution, a cellulose model surface can be successfully obtained through the control of the concentration of the cellulose solution. The model surface is more predominant than a film prepared by means of organic solvents because there are no residues of any organic solvents; this is important in studying the interactions of biomolecules such as proteins with the model cellulose surface.²³

Sequentially, we tried to use the cellulose isolated from wheat straw as feedstock to prepare the model surface. In the experiment, the isolated cellulose with a molecular weight of 12.7×10^4 g/mol was dissolved in an aqueous 6% NaOH/5% thiourea

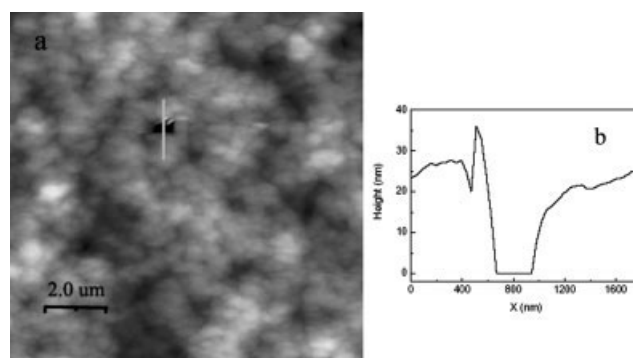


Figure 4 (a) AFM height image of the cellulose thin film in Figure 3 with a scratched region formed by scanning in the contact mode with a higher tip force to remove the surface cellulose and (b) section line analysis of the thickness of the thin film. The Z amplitude is 50 nm.

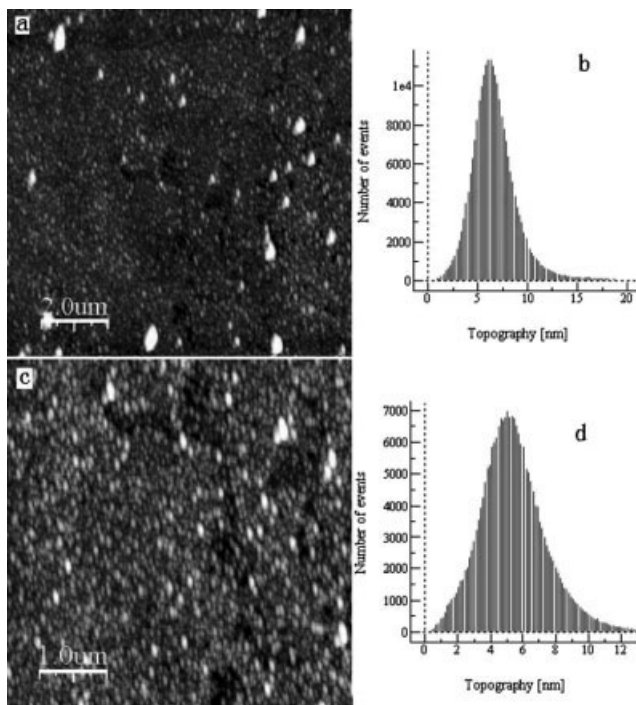


Figure 5 (a,c) Typical AFM height images of a cellulose film surface in areas of 10 and 5 μm^2 [(a) Z amplitude = 41.6 nm and RMS = 2.7 nm and (c) Z amplitude = 13.5 nm and RMS = 2.04 nm] and (b,d) corresponding roughness analysis profiles. The cellulose film was prepared via the spin coating of an aqueous NaOH/thiourea solution of isolated cellulose from wheat straw with a concentration of 0.3% (w/w).

solution at a low temperature. After spin coating, a cellulose thin film was formed. Figure 5 shows typical AFM height images of the film with both 10- and 5- μm^2 areas [Fig. 5(a,c)]. The surface is also flat and homogeneous, except that several big aggregates coexist on the surface. The average heights of the 10- and 5 μm^2 -area surfaces are about 6.5 and 5 nm, and the RMS values are 2.7 and 2.04 nm, respectively.

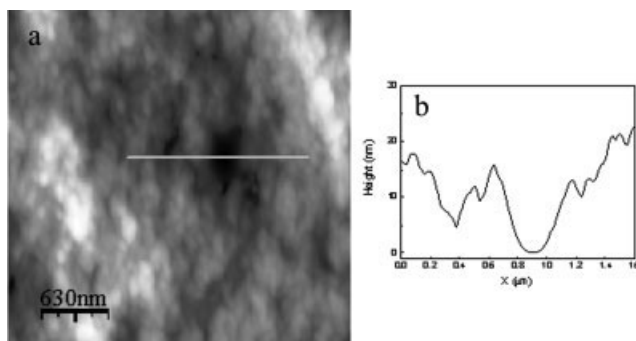


Figure 6 (a) AFM height image of the cellulose thin film in Figure 5 with a scratched region formed by scanning in the contact mode with a higher tip force to remove the surface cellulose (Z amplitude = 47 nm) and (b) section line analysis of the thickness of the thin film.

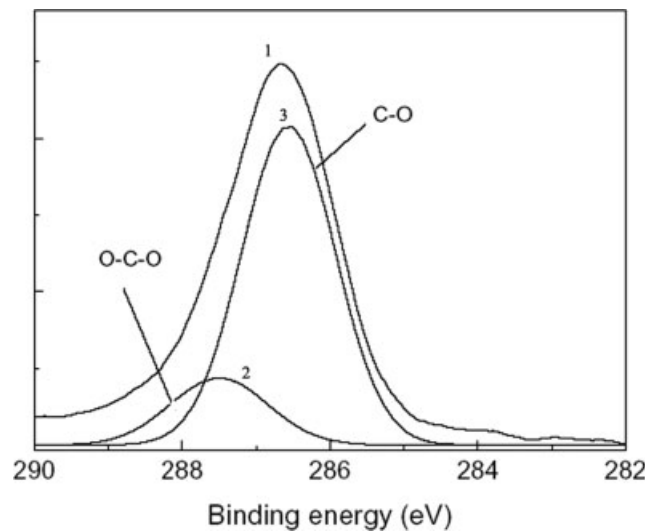


Figure 7 XPS measurements of the cellulose surface on PAM-modified mica.

The surface is much flatter than that prepared from microcrystalline cellulose. The reason may be that the cellulose isolated from wheat straw with a higher molecular weight more easily forms interpenetration structures than microcrystalline cellulose.

The thickness of the cellulose thin film was measured by the AFM scratching method. As shown in Figure 6, the section line analysis of the exposed surface reveals that the height of the cellulose thin film is about 22 nm.

The chemical properties of the thin film were measured by both XPS and EDX. Figure 7 shows the C1s spectrum from the XPS measurements. Curve 1 shows a total broad peak for the C1s spectrum, and curve 2 and curve 3 show the individual peaks of

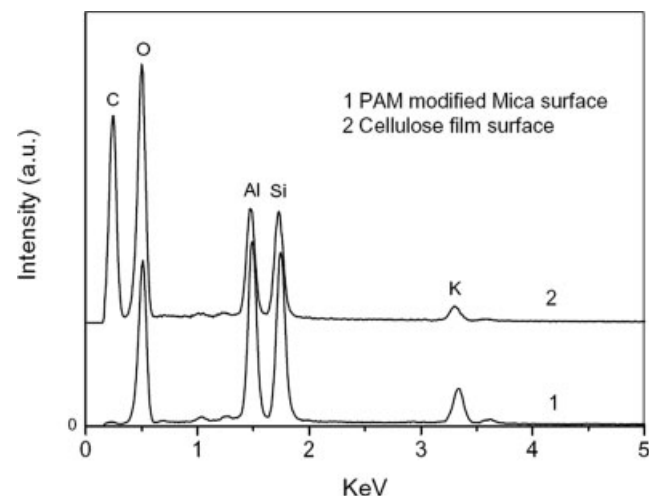


Figure 8 EDX of the surface of PAM-modified mica and a cellulose thin film prepared with cellulose from straw.

the C1s spectrum for O—C—O and C—O, respectively, obtained by Gaussian multipeak fitting. There are two kinds of carbon (O—C—O and C—O), and the ratio of carbons with two bonds to oxygen to carbons with one bond to oxygen (O—C—O/C—O) is 0.22, which is very close to the theoretical value of 0.2 in pure cellulose²⁴ and indicates that the surface is covered by cellulose. Figure 8 shows the EDX spectrum of the surface of the mica and the thin film of cellulose from straw. The main elements of the surface are C and O, and Al, Si, Fe, and K come from the substrate of mica. Clearly, in comparison with EDX of PAM-modified mica, there are no new signals of Na and S appearing in the spectra of the cellulose film, and this indicates the removal of NaOH and thiourea from the surface.

CONCLUSIONS

An aqueous NaOH/thiourea solution was used as a solvent to dissolve cellulose. Both microcrystalline cellulose and cellulose isolated from wheat straw were used as feedstock. The isolated cellulose was prepared by an alkali treatment and a sequential alkali degradation process. After the spin coating of the cellulose solutions onto the PAM-modified mica surfaces, model cellulose surfaces were obtained for both kinds of cellulose. AFM measurements revealed that RMS of the cellulose thin film was about 3.38 nm for microcrystalline cellulose and 2.04 nm for the cellulose isolated from straw in an area of 5 μm^2 . It provides a new route for preparing model cellulose surfaces directly from straw with an environmental solvent system.

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