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Novel method for preparing cellulose model surfaces by spin coating

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Abstract

A new, simplified method for preparing model surfaces of cellulose is introduced. Non-polar cellulose derivative trimethylsilyl cellulose (TMSC) was deposited onto untreated silicon substrate by spin coating, after which the coated TMSC was regenerated back to cellulose by vapour phase acid hydrolysis. By optimising the parameters of spin coating, a smooth cellulose film of ca 20 nm was obtained with roughness variation of max. 3 nm. With the well-defined morphology and chemical structure, combined with easy preparation, these model surfaces provide excellent means to explore the molecular level phenomena, taking place during various processes involving cellulose. Films were characterized using atomic force microscopy to illustrate the morphology and X-ray photoelectron spectroscopy to determine the chemical structure of the layers.

Keywords: Atomic force microscopy; Cellulose model surface; Spin coating

1. Introduction

Despite the abundance of cellulose and its importance for the human culture, ultrathin films of cellulose are a relatively new and surprisingly rare field of interest. To our knowledge, the only established way to manufacture ultrathin model surfaces from cellulose is the preparation of Langmuir–Blodgett films from trimethylsilyl cellulose (TMSC) which, once deposited on a smooth substrate, can be easily hydrolysed to cellulose by a simple acid hydrolysis. The method was introduced in the early 1990s by Wegner and co-workers [1,2] and developed further in studies with surfaces forces [3,4] and hydroxyl accessibility [5]. Smooth, ultrathin model surfaces provide excellent means to examine the chemical and morphological changes, taking place in various processes and phenomena involving cellulose, e.g. interactions with water (papermaking, paper recycling), photochemistry (yellowing of paper), thermal degradation (biomass gasification), etc. We feel that model surfaces have not been exploited to their full potential in cellulose research. The purpose of this paper is to describe a simplified procedure to prepare cellulose films with a thickness of the order of 10–50 nm.

The seminal difficulty of creating model surfaces from cellulose has been its reluctance of to dissolve into conventional organic and inorganic solvents. There is a number of solvents available, such as lithium chloride in dimethylacetamide [6], *N*-methylmorpholine-*N*-oxide (NMMO) monohydrate [7], or the cadmium complex with ethylenediamine (Cadoxen) [8] but while they are suitable for the analytical and synthetic purposes, they are very difficult to work with from the point of view of model surface preparation. This is also the reason why easily dissolving cellulose derivatives have been subjects for model surfaces with a wider interest than cellulose itself [9–12]. The elegance of the LB technique [1,2] lies in the easy transformation of the TMSC derivative to cellulose with vapour phase acid hydrolysis after the TMSC has already been deposited on the substrate (Scheme 1).

The LB technique, however, requires special equipment like the Langmuir-trough, and rather demanding conditions, e.g. a computer controlled thermostat. Therefore, we set out to establish spin coating as a new, simplified method to prepare smooth ultrathin films of cellulose. Spin coating is a process, in which a polymer or colloid containing liquid film is spread by centrifugal forces on a rotating substrate and the liquid is evaporated with the help of high speed spinning leaving a smooth, uniform film with thickness that can be modified by altering parameters such as original solution concentration, spinning speed, and choice of solvent

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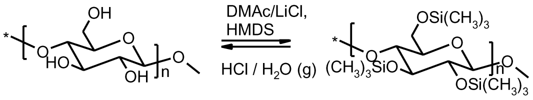

Scheme 1.

[13–15]. In addition, spin coaters are widely abundant in laboratories of polymer and surface science throughout the world.

Spin coating has generally been met with discontent in the literature on cellulose model surfaces. This is largely due to an early paper by Neuman et al. [16] which described preparation of cellulose films with spin coating by using trifluoroacetic acid as solvent for unmodified cellulose. This inevitably changes the chemical properties of cellulose [17]—a phenomenon highly undesirable since the chemical properties of model surfaces should be as close as possible to the original substance that is being modelled.

The new method for the preparation of cellulose model surfaces comprises of three stages, described as:

(i) Synthesis of TMSC from cellulose, performed in homogeneous environment.
(ii) Spin coating of the dissolved TMSC to a smooth substrate. Concentration of the TMSC solution, choice of solvent, and spin coating speed are parameters that determine the morphology and thickness of the layer.
(iii) Hydrolysis of the coated TMSC layer back to cellulose in a vapour phase acid hydrolysis. Hydrolysis determines the final chemical composition of the surface as well as the final morphology and thickness.

2. Experimental

Preparation of TMSC: 2 g of microgranular cellulose (Aldrich) was dissolved to lithium chloride in dimethylacetamide as described elsewhere [18]. After the cellulose had completely dissolved the solution was heated to 80 °C in a water bath and 20 ml of hexamethyldisilazane (HMDS) (Aldrich) was added in a steady flow within an hour in a nitrogen atmosphere. The mixture was then cooled down and some methanol was added to enhance the crystallization of TMSC. The crystallization was left to proceed overnight. The crystallized TMSC was filtered and dissolved into 80 ml of tetrahydrofuran and re-crystallized in 1000 ml of methanol. After filtration the re-crystallized TMSC was washed several times with methanol and dried in a vacuum desiccator.

The TMCS was dissolved into toluene or chloroform and spin coated with a spinning rate of 1000 to 6000 rpm with acceleration of 2800 rpm/s. The substrates used were untreated silicon wafers (Topsel), cut to ca 3×3 cm^2 pieces.

The regeneration of TMSC to cellulose was done by a simple acid hydrolysis. A small amount of 2.0 M hydrochloric acid was placed on the bottom of a specifically designed glass container with a holder for the spin coated wafers. The vapour pressure was allowed to stabilize for an hour, after which the wafer was placed in the container and the vapour phase acid hydrolysis was performed for 1 min.

X-ray photoelectron spectroscopy (XPS) was performed using VG Escalab 200 system with an aluminium anode (Al Kα = 1486.3 eV) operating at 510 W with a background pressure of 2×10^{-9} mbar. The spectra were recorded with 20 eV pass energy, 0.1 eV step, and 0.1 s dwelling time. The angle between the X-ray beam and the surface normal of the sample was kept at 0° unless otherwise mentioned. Using synthetic Gaussian–Lorenzian peaks the carbon 1 s spectra were resolved into different contributions of bonded carbon that are known to exist in the cellulose and TMSC molecules. The chemical shifts for the peaks were gained from literature [19,20]. The spectra were charge corrected by setting the $C-H_X$ (hydrocarbon) contribution in C1s emission to 285.0 eV.

Atomic force microscopy (AFM) was performed with Solver P47 base with a SMENA head. The cantilever of choice was non-contact gold-coated NSG01 manufactured by NT-MDT. The typical force constant of the tip was 5.5 N/m and the typical resonance frequency 150 kHz. All measurements were performed in the non-contact mode in laboratory air and room temperature.

A Tencor P-10 step profiler was used to determine the thickness of the samples. The tip diameter was 12.5 μm, scanning speed 0.02 mm/s, sampling rate 100 Hz, and stylus force 8 mg. The TMSC surfaces were scratched before the hydrolysis since the soft TMSC was easier to scratch than the cohesive cellulose layer. The thickness was determined as the height difference from the lowest point in the scratch to a smooth point on the surface. Three measurements were performed with each sample, each on a different scratch, all under laboratory air and room temperature.

3. Results and discussion

XPS was performed on the surfaces to determine how close the chemical composition of the model surfaces are to pure cellulose. Fig. 1a shows the widescan spectrum of XPS from a coated TMSC and cellulose after a subsequent hydrolysis with hydrochloric acid. Spin coating has been performed on a silicon wafer substrate. The lack of elements other than carbon and oxygen in the cellulose surface is evident (XPS is insensitive to hydrogen). The TMSC contains expectedly silicon peaks which disappear completely during the hydrolysis to cellulose, proving the silicon contribution to originate solely from the TMSC. In addition, the lack of peaks due to silicon in cellulose is verification for the relative uniformity of the film; XPS would reveal the holes in the coating as silicon contributions from the silicon wafer substrate in the wide scan.

The resolved carbon spectrum from the XPS (Fig. 1b)

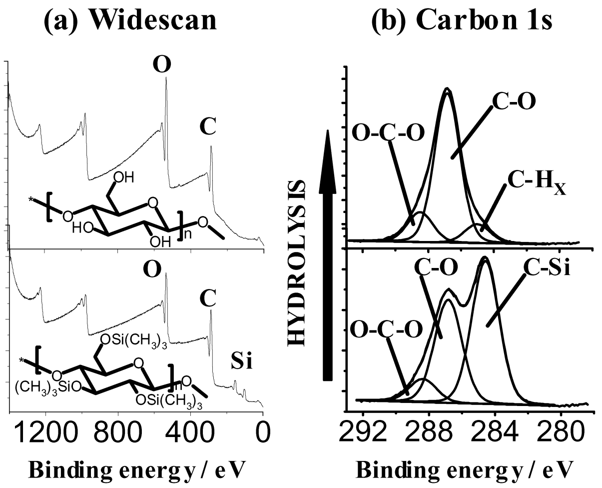

Fig. 1. The hydrolysis of spin coated TMSC on silicon to cellulose illustrated with X-ray photoelectron spectroscopy (XPS). Widescan (a) shows all the elements on the surface of the coatings, and the resolved carbon 1 s peak (b) shows the carbons of different bonding status on the surfaces. TMSC has been spin coated from 10 g/l solution with 4000 rpm spinning speed on silicon. Cellulose has been acquired in 1 min vapour phase hydrolysis with 2.0 M hydrochloric acid.

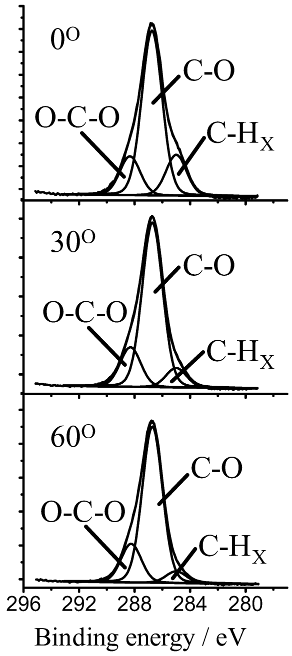

Fig. 2. The angle dependent X-ray photoelectron spectroscopy (XPS) measurements of cellulose surface on silicon. Angle between the surface normal and the X-ray beam is indicated with each resolved carbon peak of the XPS spectrum. Cellulose is obtained with 1 min vapour phase hydrolysis with 2.0 M hydrochloric acid from TMSC which was spin coated from 10 g/l toluene solution with 4000 rpm spinning speed.

illuminates further the chemical structure of the TMSC and cellulose surfaces. The C–Si contribution of the TMSC carbon spectrum is 53%. This corresponds to a degree of substitution of 2.3, the theoretical maximum being 3 with all three hydroxyl groups in each cellulose monomers substituted by a trimethylsilyl group. In cellulose, hydrolysed from TMSC, the ratio of carbons with two bonds to oxygen to carbons with one bond to oxygen (O–C–O/C–O) ranged between 0.20 and 0.24 within 20 samples, which is very close to the theoretical value of 0.2 in pure cellulose. Similar values have been acquired with the XPS analysis of LB films of cellulose [3]. The oxygen-less carbon contribution (C–H_X) in the cellulose XPS carbon spectrum (Fig. 1b) is caused by the ubiquitous hydrocarbon impurities and its appearance is somewhat arbitrary in quantity, ranging between 5 and 10% in different samples. The differences in the C–H_X peak depend on the conditions in the laboratory during the sample preparation and the conditions in the spectrometer itself. Transferring the sample in air and oil from the vacuum pump of the spectrometer result in hydrocarbon impurities on the surface and, indeed, more or less every sample analysed by the XPS contains the C–H_X peak [21]. Another possible source for the C–H_X contribution is the TMSC solvent toluene, but it is doubtful that any of it is left at this stage, especially in the ultra high vacuum conditions in the XPS chamber. By varying the angle between the X-ray beam and the surface normal of the sample, it is possible to make the XPS more surface sensitive: the lower the angle, the more the sensitivity is towards the surface [22]. Angle dependent measurements with the XPS revealed that the C–H_X contribution grows considerably as the angle is decreased (Fig. 2), which means that the hydrocarbons are on the extreme outer layers of the surface. This encouraged us to dismiss the C–H_X contribution in the resolved carbon peak of cellulose as merely a surface impurity, not an integral part of the cellulose network.

As for the morphology of the cellulose model surfaces, spin coating of the TMSC remains the pivotal step in our process, determining the roughness and thickness of the films. Viscosity, density, and vapour pressure of the spin coating solution are known to affect the eventual thickness and uniformity of the films, as is the spinning speed of spin coating [23,24]. In other words, one can influence the end result with the choice of solvent, concentration of the solution, and spinning speed.

TMSC dissolves into the ordinary non-polar organic solvents. The optimal solvent proved to be toluene, mainly due to its relatively low vapour pressure, i.e. low volatility. Furthermore, toluene is a common, relatively harmless laboratory solvent with no complex safety precautions required. The TMSC films spun from 10 g/l toluene solution to silicon wafers varied in thickness between 35 and 80 nm, depending roughly on the spinning speed that was varied between 1000 and 6000 rpm. After the hydrolysis of TMSC to cellulose, the thickness of the films decreased considerably and the fluctuation between the different measurements diminished: with a spinning speed of 4000 rpm, 10 g/l toluene solution of TMSC, and hydrolysis of TMSC with 2.0 M hydrochloric acid in vapour phase, the thickness of the cellulose surfaces was 18 ± 1.5 nm with the roughness of ca 10% (Fig. 3b). The smoothness of the cellulose film is

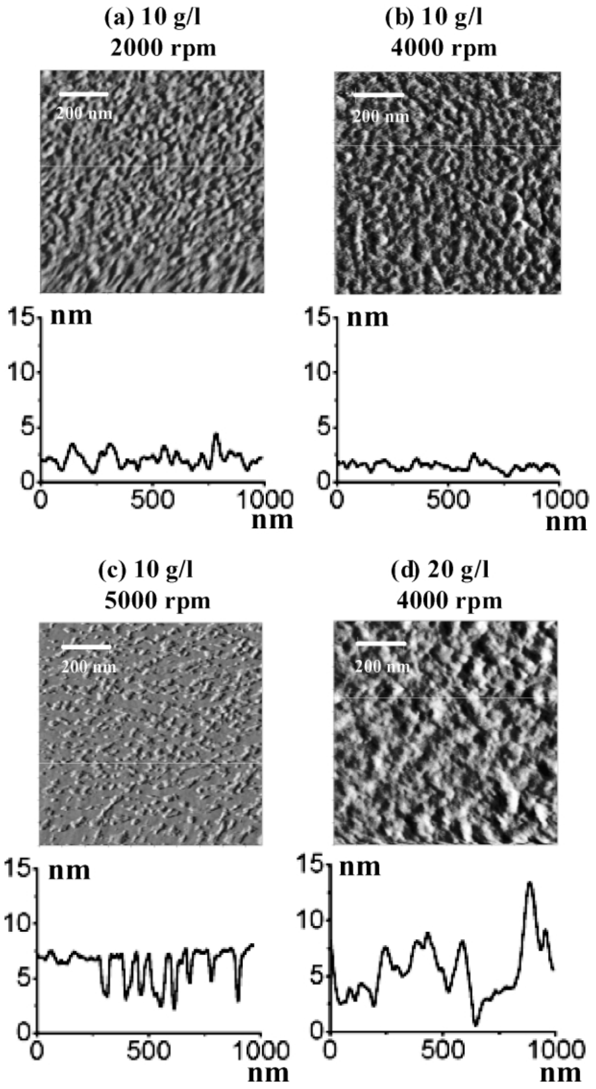

Fig. 3. Atomic force microscopy images of cellulose surfaces and corresponding roughness profiles from a scan indicated with a line on each image. Cellulose is hydrolysed from TMSC with 2.0 M hydrochloric acid. TMSC has originally been spin coated onto silicon from 10 g/l toluene solution with a spinning speed of 2000 rpm (a), 4000 rpm (b), and 5000 rpm (c), or from 20 g/l toluene solution with a spinning speed of 4000 rpm (d).

apparent; the thickness for the corresponding TMSC layer (4000 rpm, 10 g/l TMSC) was 43 ± 4 nm, with the roughness of ca 20%. The thinning and smoothening of the films while hydrolysing the TMSC to cellulose is expected because TMSC belongs to a group of so-called hairy rod polymers with its rigid backbone of anhydroglucose units and bulky trimethylsilyl side chains [1,2]. Cellulose, in turn, has a very orderly structure with its hydroxyl groups contributing to inter- and intramolecular hydrogen bonding [25].

Several parameters were tried out in search of the aforementioned optimal values. In Fig. 3 shows AFM images of three other cellulose films: Fig. 3a and c illustrate the effect of spinning speed while all the other parameters have been retained similar to the film in Fig. 3b. The evidence reveals that with 4000 rpm, the smoothest layer was achieved. 20 samples were prepared with similar parameters in order to verify the uniformity and smoothness of the films. Increasing the concentration of the TMSC solution resulted in a thicker film (48 ± 5 nm); however, also the roughness increased to ca 20% (Fig. 3d). The reasons behind the increased roughness are unclear. Sukanek [24] suggests that with increased viscosities the film is sometimes left non-uniform on a larger scale during spin coating. However, the chemical composition of the film is also important and XPS as a very surface sensitive method is not fully adequate of characterising thicker films like these. Further possibilities and characterisation methods with the films are being investigated at the moment and the results will be published elsewhere.

In the case of volatile solvents, such as chloroform, the roughness of the films was unsatisfactory: AFM showed the variation in the height profile to be around 20 nm in a cellulose film of ca 30 nm thickness. This can be expected from the theory of spin coating [26,27]: the uniformity of spin coated film occurs at the late stages of spin coating, and chloroform is simply too volatile and evaporates completely from the thinner regions while the film is still in the non-uniform state, leaving the surface rough.

4. Conclusions

1. With chemical modification of cellulose to TMSC, spin coating, and subsequent hydrolysis of coated TMSC back to cellulose, we have established a new method to prepare ultrathin cellulose model surfaces.
2. The smoothest cellulose films were obtained using toluene as a solvent for TMSC, silicon wafer without pre-treatment as a substrate, and 4000 rpm as the spinning speed in spin coating. These parameters resulted in a cellulose layer of around 20 nm with a roughness profile of max. 3 nm.
3. The chemical composition of these films is very close to pure cellulose. The XPS revealed O–C–O/C–O ratios ranging from 0.20 to 0.24 with the samples, 0.20 being the theoretical value for pure cellulose.

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