



## Antifouling coating of cellulose acetate thin films with polysaccharide multilayers

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### ABSTRACT

In this investigation, partially deacetylated cellulose acetate (DCA) thin films were prepared and modified with hydrophilic polysaccharides with the layer-by-layer (LbL) technique. As polysaccharides, chitosan (CHI) and carboxymethyl cellulose (CMC) were used. DCA thin films were manufactured by exposing spin coated cellulose acetate to potassium hydroxide solutions for various times. The deacetylation process was monitored by attenuated total reflectance-infrared spectroscopy, film thickness and static water contact angle measurements. A maximum of three bilayers was created from the alternating deposition of CHI and CMC on the DCA films under two different conditions namely constant ionic strengths and varying pH values of the CMC solutions. Precoatings of CMC at pH 2 were used as a base layer. The sequential deposition of CMC and CHI was investigated with a quartz crystal microbalance with dissipation, film thickness, static water contact angle and atomic force microscopy (AFM) measurements. The versatility and applicability of the developed functional coatings was shown by removing the multilayers by rinsing with mixtures containing HCl/NaCl. The developed LbL coatings are used for studying the fouling behavior of bovine serum albumin (BSA).

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### 1. Introduction

Besides other materials, cellulose acetate (CA) was one of the first polymers used for filtration membranes in water purification (Kutowy & Sourirajan, 1975). CA is a renewable and bio-based material which exhibits several reliable properties such as moderate hydrophilicity, high biocompatibility, good desalting properties, and a high potential flux (Han, Zhang, Shao, Kong, & Lv, 2013; Hayama, Yamamoto, Kohori, & Sakai, 2004). Despite its advantages, CA has poor fouling resistance, which is caused by the accumulation of biological foulants (bacteria, cells, proteins, etc.) on the membrane surface (Jones & O'Melia, 2001; Koseoglu-Imer, Dizge, & Koyuncu, 2012). Fouling can lead to a drastic decline in permeate flux, filtration efficiency and lifetime of a membrane. To overcome this, surface functionalization of the CA substrate is an

option. Among other techniques, available the layer-by-layer (LbL) technique is a simple and straightforward approach. This method is based on the alternate exposure of a substrate to positively and negatively charged components. It provides the possibility to introduce a large variety of functional materials into a coating (Findenig et al., 2012; Hadj Lajimi, Ferjani, Roudesli, & Deratani, 2011). This makes the technique a powerful tool to create customized anti-fouling surfaces. Polysaccharides (PS) are promising materials for creating such surfaces due to their diverse chemical composition (Bauer et al., 2013). Even though multilayer coatings from water soluble PS are known, (Hadj Lajimi et al., 2011; Radeva, Kamburova, & Petkanchin, 2006) their influence on the protein rejection behavior has not been studied extensively. Hadj Lajimi et al. (2011) investigated the LbL assembly of chitosan and alginate on CA membranes. The BSA coated surfaces were subsequently tested for their salt rejection properties (Hadj Lajimi et al., 2011). Keeping this fact in mind, we became interested if chitosan (CHI) and carboxymethyl cellulose (CMC) on CA can be used for reducing the fouling of BSA (Jeyachandran, Mielczarski, Rai, & Mielczarski, 2009).

Both, chitosan and CMC are renewable, biocompatible, non-toxic and biodegradable (Bulwan et al., 2012). CMC is negatively charged in aqueous solution and can adsorb irreversibly on cellulose-based substrates (e.g. deacetylated cellulose acetate) via

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relatively selective cellulose-cellulose interactions (Kargl et al., 2012; Laine, Lindstrom, Nordmark, & Risinger, 2002). CHI, a positively charged PS, has found application in the medical field (e.g. drug delivery), and is also able to bind CMC irreversibly via complex formation (Zhang, Chen, Li, & Liu, 2007; Zhang et al., 2013).

To obtain a better understanding and control on the growth of the multilayers under different pH (Schoeler, Poptoshev, & Caruso, 2003; Shiratori & Rubner, 2000) and charge densities, (Glinel, Moussa, Jonas, & Laschewsky, 2002; Schoeler, Kumaraswamy, & Caruso, 2001) it is advantageous to use thin CA model films (ca. 30 nm thickness) instead of membranes. Membranes exhibit great complexities in terms of composition, roughness, morphology, which often leads to results that are not directly comparable. However, model films consist of thin coatings on flat substrates and can be manufactured by a simple spin coating technique. In this case, a comprehensive characterization of the substrates can be carried out and modern surface analytical techniques can be utilized. One such technique for monitoring *in situ* self-assembly of charged PS on thin films is the quartz crystal microbalance with dissipation (QCM-D) (Dixon, 2008; Findenig, Kargl, Stana-Kleinschek, & Ribitsch, 2013). QCM-D allows studies on the interaction of dissolved polymers or proteins with thin solid films by measuring the frequency changes of an oscillating quartz crystal. Furthermore, QCM-D allows to probe polymer–polymer interaction, complex formation, surface hydration and viscoelastic properties of the adsorbates. The purpose of this study was therefore to prepare deacetylated cellulose acetate (DCA) model films, to explore their properties and to use them for the deposition of multilayers from CMC and CHI. To elaborate and develop the built up of thin LbL films from these polyelectrolytes two different methods were employed. In the first method, the same ionic strength and pH value was used for both polyelectrolyte solutions. In the second method, the pH value was varied for electrolyte free CMC solutions and kept constant for the CHI solutions. The potential application of the developed coatings is shown in the fouling behavior of BSA.

## 2. Experimental

### 2.1. Material and methods

Cellulose acetate (CA, acetyl content: 39.8 wt.%, degree of substitution, DS: 2.5, molecular weight,  $M_w$ : 30 kDa), sodium salt of carboxymethyl cellulose, (CMC, DS: 0.7,  $M_w$ : 90 kDa), chitosan, CHI (deacetylation: 75–85%, low molecular weight, viscosity at 25° (1 wt.%, in 1 wt.% acetic acid) 20–300 mPa·s, product Number: 448869), bovine serum albumin (fraction V,  $\geq 96\%$ ), disodium phosphate heptahydrate ( $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium dihydrogen phosphate monohydrate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ) and glacial acetic acid ( $\geq 99.7\%$ ) were purchased from Sigma-Aldrich, Austria. 1,4-dioxane was purchased from Carl Roth GmbH, Austria. Silicon wafers with a thickness of 100 nm and a surface orientation of 100 was purchased from Silchem, Freiburg, Germany. Surfs ( $\text{SiO}_2$ ) substrates were purchased from Nanolane, France. QCM-D sensors coated with a gold layer (QX301) were purchased from LOT-Oriel, Germany. Double distilled water was used for all sample preparations.

### 2.2. Substrate cleaning and thin film preparation

For spin coating of cellulose acetate, three different substrates were used. Silicon wafers were cut into pieces of  $2 \times 2 \text{ cm}^2$ , rinsed with ethanol (Sigma-Aldrich, Austria), rinsed with pure water and immersed into a “piranha” solution ( $\text{H}_2\text{SO}_4$  (98 wt.%) /  $\text{H}_2\text{O}_2$  (30 wt.%), 70:30, v/v) for 15 min. Afterwards the wafers were rinsed with water, stored in water for at least 15 min and blow-dried with nitrogen gas. QCM-D-sensors were soaked into a mixture of

$\text{H}_2\text{O}/\text{H}_2\text{O}_2$  (30 wt.%) /  $\text{NH}_4\text{OH}$  (5:1:1; v/v/v) for 10 min at 70 °C, then immersed in a “piranha” solution for 40 s, and then rinsed with pure water and blow dried with nitrogen gas. Surfs ( $\text{SiO}_2$ ) were used as received. Cellulose acetate was dissolved in 1,4-dioxane ( $10 \text{ g l}^{-1}$ ), stirred for 2 h at room temperature, filtered using a  $0.2 \mu\text{m}$  PTFE filter. 100  $\mu\text{l}$  of the cellulose acetate solution were deposited onto a cleaned substrate and then rotated for 60 s at a spinning speed of 4000 rpm and an acceleration of  $2500 \text{ rpm s}^{-1}$ . All spin coated substrates were dried at 50 °C in an oven for 12 h, cooled to room temperature and eventually stored for further use.

### 2.2.1. Deacetylation of cellulose acetate (CA) films

Spin coated CA films were placed into polystyrene petri-dishes (4 cm in diameter). 15 ml of 0.1 M potassium hydroxide solution was deposited in the petri-dish. The films were immersed in the KOH solution for different times (0, 10, 20, 25, 30, 40, 60 min). The films were soaked into pure water (15 ml) for 10 min twice and finally blow dried with nitrogen gas.

### 2.3. Sample preparation for multilayer coatings and protein adsorption

The concentration of chitosan was 0.1% (w/v). The pH of the solution was adjusted to pH 3 with glacial acetic acid until complete dissolution and then to 5.5 with 0.1 M NaOH (Sigma-Aldrich, Austria). The carboxymethyl cellulose concentration (for LbL method I) was 0.1% (w/v) at pH 5.5. The pH of the solution was adjusted using 0.1 M HCl. In both cases, the ionic strength of the solutions was adjusted to 150 mM with potassium chloride (KCl). Carboxymethyl cellulose, 0.2% (w/v) (for pre-coating of DCA) at pH 2 and 0.1% (w/v) (for LbL method II) at pH 2, 3, 4 and 5.5 were prepared by adjusting the pH with 0.1 M HCl with no additional electrolyte. BSA ( $10 \text{ mg ml}^{-1}$ ) was dissolved in 10 mM phosphate buffer (PBS) at pH 7. The ionic strength of the buffer solution was adjusted to 100 mM with NaCl.

### 2.4. Attenuated total reflectance-infrared (ATR-IR) measurements

ATR-IR spectra were recorded for spin coated CA and DCA films using a PerkinElmer Spectrum GX Series-73565 FTIR-spectrometer at a scan range of  $4000$  to  $650 \text{ cm}^{-1}$ . A total of 32 scans were performed for all measurements with a resolution of  $4 \text{ cm}^{-1}$ . QCM-D Au-sensors were used as substrates.

### 2.5. Quartz crystal microbalance with dissipation (QCM-D)

A QCM-D device (model E4 from Q-Sense, Gothenburg, Sweden) was used to investigate the multilayer coatings from CMC and CHI on the DCA films. The QCM-D instrument determines changes in frequency ( $f$ ) and dissipation ( $D$ ) of an oscillating quartz crystal. Deposition of mass or changes in the rigidity of material on the crystal surface can be detected. Negative frequency shifts ( $\Delta f$ ) indicate a deposition of mass whereas positive dissipation shifts ( $\Delta D$ ) are caused by a reduced rigidity of the coating. The QCM-D measurements were conducted at the fundamental frequency of 5 MHz and its overtones. A detailed description of the QCM-D technique can be found elsewhere (Höök, Rodahl, Brzezinski, & Kasemo, 1998; Rodahl, Höök, Krozer, Brzezinski, & Kasemo, 1995). For the data analysis in this study, the changes in the third overtone's frequency and dissipation ( $\Delta f_3$ ,  $\Delta D_3$ ) were used. For all QCM-D experiments, sensors coated with DCA films were mounted into the QCM-D flow cell and the initial resonance frequency of the sensor was measured. Afterwards, the films were equilibrated with pure water followed by rinsing with the background solution (pH 2 water or 150 mM KCl at pH 5.5) until a constant frequency was established. Two types

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