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Atomic Layer Deposition of Titania on Cellulose Acetate for Enhanced Hemostasis

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Abstract

TiO₂ films may be used to alter the wettability and hemocompatibility of cellulose materials. In this study, pure and stoichiometric TiO₂ films were grown using atomic layer deposition on both silicon and cellulose substrates. The films were grown with uniform thicknesses and with a growth rate in agreement with literature results. The TiO₂ films were shown to profoundly alter the water contact angle values of cellulose depending upon processing characteristics. Higher rates of protein adsorption were noted on TiO₂-coated cellulose acetate than on uncoated cellulose acetate. These results suggest that atomic layer deposition is an appropriate method for improving the biological properties of hemostatic agents and other blood-contacting biomaterials.

Keywords

atomic layer deposition; cellulose; titanium oxide; hemostatic agent; hemocompatibility

Introduction

A variety of biologically-derived hemostatic agents, including cellulose, bone wax, chitosan, collagen, and gelatin, have been utilized over the years for reducing blood loss associated with trauma [1,2]. A hemostatic agent should exhibit several properties, including (a) the ability to stop hemorrhage from arterial and/or venous sources in a short time period, (b) use with minimal training, (c) low weight, (d) high stability, (e) low cost, (f) and biocompatibility (e.g., absence of cytotoxicity) [1–7].

There are several benefits to the use of plant-derived materials such as cellulose in hemostasis applications, including an absence of disease transmission from donor to recipient and an absence of antibody formation to coagulation factors [8]. Cellulose is a wood pulp-derived material that has been utilized in hemostasis for over sixty years; use of oxidized cellulose, oxidized regenerated cellulose, carboxymethylcellulose, and cellulose acetate has been described in the literature [1, 9–11, 12]. In addition, these porous, water-absorbable materials do not need to be removed after use because they are degraded within the body over several weeks, increasing patient satisfaction [1, 8, 11, 12]. Oxidized regenerated cellulose is commonly used for treatment of continuous venous bleeding. It should be noted that several studies indicate that unmodified cellulose provides no inherent hemostatic activity [13, 14]. For example, Wagner et al. utilized in vitro assays to assess platelet behavior, including aggregation and activation; they ranked the materials as follows: collagen>gelatin>oxidized regenerated cellulose [13]. Solheim et al. showed using platelet cascade studies that oxidized cellulose did not promote platelet aggregation [14]. In vivo studies have indicated a lack of bleeding prevention with cellulose-based hemostatic agents. For example, Karkos et al. found persistent postoperative oozing in patients treated with a carboxymethylcellulose mesh [15]. Kastl et al. found no differences in postoperative bleeding in sites treated with a carboxymethylcellulose dressing and untreated sites [16]. Some groups have investigated incorporating human-derived biologics within oxidized regenerated cellulose hemostatic agents. However, human-derived biologic-containing hemostatic agents elicited a cellular immune response in an immunocompetent murine model; decreases in material absorption, healing, and fibrin degradation were noted in athymic rats [17]. In addition, the human-derived components have problems related to disease transmission, anaphylactic reaction, and stability. For example, the HIV risk associated with blood-derived materials screened with the p24 HIV-1 antigen test is 1:700,000 [18]. Concerns also exist regarding the transmission of several viruses, including hepatitis A virus, hepatitis B virus, hepatitis C virus, human T-cell lymphotropic virus-1, Parvovirus B19, and spongiform encephalopathy agents.

Inorganic hemostatic agents may be applied to cellulose to improve its protein interaction properties. For example, atomic layer deposition (ALD) is a thin film growth technique that involves alternating self-terminating gas-solid chemical reactions between gaseous precursor molecules. Saturation with an inert gas is used to separate gas-solid chemical reactions. Since growth occurs in a layer-by-layer approach, film thickness can be readily controlled. Conformal growth of thin films may be achieved by saturating the substrate at each individual reaction. Due to these unique properties, ALD is uniquely suited for depositing conformal films onto porous substrates such as hemostasis devices.

For example, Kemell et al. created a titanium oxide (TiO₂)/cellulose composite by depositing a conformal TiO₂ coating on filter paper at 150–250 °C [19]. They subsequently created a replica structure by annealing the composite in air at 450 °C. The photocatalytic activity of the composite material was demonstrated by reduction of Ag(I). Hyde et al. demonstrated growth of aluminum oxide on nonwoven polypropylene and woven cotton substrates [20]. A fully wetting hydrophilic state or a metastable hydrophobic state was

observed based on the processing parameters, including the number of cycles and the processing temperature. Jur et al. described deposition of aluminum oxide thin films on polypropylene fiber substrates using ALD [21]. In their study, the film-substrate interface was shown to be correlated with the deposition temperature; lower deposition temperatures were associated with more abrupt transitions. Narayan et al. used ALD to coat all the surfaces of a nanoporous alumina membrane [22]. In in vitro studies, TiO₂-coated nanoporous alumina membranes showed similar viability rates to uncoated nanoporous alumina membrane control materials. Hyde et al. also described deposition of titanium oxynitride coatings on cellulose fiber substrates using ALD; fluorescent live/dead studies showed that the coated materials supported human adipose-derived adult stem cell growth [23].

In this study, we examined the structural and hemocompatibility properties of titanium oxide films prepared by means of ALD. Titanium dioxide thin films were deposited onto silicon, cellulose fibers, and cellulose acetate membranes from a tetrakis(dimethylamino)titanium (TDMAT) precursor. X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR) were used to determine chemical composition and crystal structure. Ellipsometry was used to evaluate thin film growth rates and film thickness uniformity. Cell viability was examined using the MTT (3-[4,5-dimethyl-2-thiazolyl]-2,5-diphenyl-2H-tetrazolium bromide) assay. Scanning electron microscopy of human platelet rich plasma-treated materials was performed; this in vitro technique has been used previously for examining interactions between blood components and the surface of a biomaterial [24].

Materials and Methods

Deposition was carried out in a custom built, hot-wall viscous flow tube reactor. TDMAT and water were used as the precursor and the reactant, respectively. Cellulose (C₆H₁₀O₅)_n, provides numerous –OH groups on the surfaces of the fibers. This chemical structure provides the TDMAT precursor with ample reaction groups for the initial ALD cycle. A proposed reaction scheme for TiO₂ ALD on cellulose fibers can be seen in Figure 1.

TDMAT was purchased from a commercial source (Strem Chemicals, Newburyport, MA) and was used as received. The precursor cell was maintained at 27°C and the precursor was dosed into the reactor using an argon carrier gas. Argon was received from a commercial source (National Welders, Charlotte, NC) and was passed through a Drierite® Air Purifier (W.A. Hammond Drierite Co. Ltd., Xenia, OH) to remove water. Deionized water (DI) was used as the reactant; it was obtained from a DI water system (Millipore, Billerica, MA), which was kept at 27°C during the runs in a stainless steel bubbler. Water was introduced into the reactor without an argon carrier gas.

Silicon wafers were prepared on heavily boron-doped p-type silicon, which was supplied by a commercial source (MEMC Electronic Materials Inc, St. Peters, MO). The silicon was initially cleaned using BakerClean™ (JT Baker, Phillipsburg, NJ) followed by submersion in 10% HF solution (buffered oxide etch) (JT Baker, Phillipsburg, NJ) until hydrophobicity was observed. The substrate then underwent an additional twenty-five seconds of HF washing in the same solution. This treatment was followed by ten minutes of treatment in a 100 mL DI water bath with 0.5 mL of ammonium hydroxide solution (Fisher) and 2 mL of 30% hydrogen peroxide solution (Fisher Scientific, Frnaklin Lakes, NJ) at 45°C to create a uniformly hydrogen-terminated chemical oxide. Finally, the wafers were blown dry using nitrogen. Bleached and mercerized woven cotton fabric (Textile Innovators, Windsor, NC) was used as received. Cotton fabric samples were cut into approximately 2 cm × 2 cm pieces before being used. The fabric samples were ~1 mm thick and were initially hydrophilic.

Cellulose acetate membranes were obtained from a commercial source (Millipore, Billerica, MA). These 25 mm membranes exhibited good sample-to-sample uniformity and demonstrated a nominal molecular weight limit of 500 Daltons.

A custom made, quartz sample holder was used to hold the samples during ALD experiments. Five 3 cm × 3 cm area spots were available for loading of samples on the quartz sample holder, whose positions were numbered one, pointing towards the flow, to five, pointing towards the pump; position one was the first to receive doses from the source lines. To minimize variations, cotton samples were placed in the second and third positions and were attached using a high-temperature polyamide tape. A silicon wafer was placed in the fourth position and was held in place using a metal clip. The first and fifth positions were left empty.

During ALD processing, pressure was maintained at 2 Torr. Cycles consisted of a ten second argon purge, five second TDMAT dose, ten second argon purge, and five second water dose. Prior to ALD processing, the substrates were introduced into the reactor, heated in vacuum (5×10^{-6} Torr) to 100°C, and dried for thirty minutes. Optimal processing times for purging and dosing were determined using quadrupole mass spectrometry (QMS) with a TC100 quadrupole mass spectrometer (Leybold-Inficon, East Syracuse, NY). Scans were conducted over a range of fifty Daltons. Every point was measured with a dwell time of sixteen milliseconds. Because of the range and the capability of the QMS, data points could only be obtained every two seconds.

Growth rate measurements of the TiO₂ films on silicon substrates were measured by ellipsometry. An Auto EL ellipsometer (Rudolph Technologies Inc., Flanders, NJ) was used to conduct measurements using an incidence angle of 75°. Three measurements were made at random spots on each sample in order to analyze the uniformity of the TiO₂ films. A S3200-N scanning electron microscope (Hitachi, Tokyo, Japan) equipped with an energy dispersive x-ray spectrometer was used to examine the TiO₂ films on cellulose acetate substrates.

X-ray photoelectron spectroscopy was used to determine film composition on the cotton fabric substrates. 5 mm × 5 mm samples of cotton fabric were cut and attached to the XPS sample holder using double sided copper tape. XPS measurements were performed using an Axis Ultra spectrometer (Kratos, Chestnut Ridge, NY) with an Al source and a spherical mirror analyzer; the instrument was operated in spectrum mode. The total pressure in the main vacuum chamber during analysis was $\sim 4 \times 10^{-7}$ Torr. Spectra were collected with the stage containing the samples at 0°. The take-off angle of the electrons was 90° and the angle of the incident X-ray beam interacting with the sample was 30°. The chemical elements present in the samples were identified from survey spectra. The survey scans started at 1200 eV and ended at -5 eV; 1 eV steps and a dwell time of 200 ms were used in this study. High resolution detail scans were performed around peaks of interest. Charge effect was corrected using C1s at 285.0 eV as a reference position. Data processing was performed using CasaXPS software (Casa Software, London, UK).

Fourier transform infrared spectroscopy was used to determine the crystalline structure of the films on silicon. The measurements were performed in controlled air and in transmission geometry using a Nicolet Magna 750 spectrometer (ThermoFisher, Waltham, MA). The non-polarized infrared beam-angle of incidence with the sample was changed from normal ($\theta = 0^\circ$) to grazing ($\theta = 75^\circ$) incidence.

The wetting properties of the TiO₂ films on silicon and cotton cellulose substrates were evaluated using static water contact angle measurements. These measurements were performed under ambient conditions (relative humidity of 60% and temperature of 25°C) by

measuring the angle of a 1 μL droplet of water dropped onto the surface of silicon or fabric from a 2 mm height. Angles were measured using ImageJ image processing software (National Institutes of Health, Bethesda, MD).

In vitro cell viability was determined using the MTT assay. The uncoated membranes and TiO_2 -coated cellulose membranes were sterilized using ultraviolet B light for three hours on each side and rotated 90° every 45 minutes to ensure that all of the surfaces were sterilized. The membranes were placed in 24 well plates using Akwa Tears[®] (Akorn, Buffalo Grove, IL) in order to prevent the membranes from floating. Human epidermal keratinocytes (HEK) were seeded in KGM-2 media in twenty-four well plates. The media was changed after twenty-four hours. When the human epidermal keratinocytes reached 70% confluency, they were assayed for viability with MTT. Viability data was standardized using the uncoated cellulose as a control. Statistical comparisons were made using ANOVA (SAS 9.1 for Windows, Cary, NC).

The protocol for evaluating human platelet rich plasma-material interactions was described in a previous study [24]. Fresh whole blood was acquired from a healthy adult human volunteer. The presence of anticoagulants and other pharmacologic agents in the blood was evaluated with clinical laboratory studies, including platelet function, prothrombin time, and partial thromboplastin time. Sodium citrate was added to the whole blood in order to prevent coagulation. The blood was centrifuged by means of a commercial Plasma Saver system (Haemonetics, Braintree, MA), which was operated at 3500 rpm. This process was performed at 25°C for ten minutes, at 25°C for ten minutes, and at 4°C for one hour. In this multi-step process, the first centrifugation process served to separate low-platelet concentrated plasma from platelet rich plasma and red blood cells [25]. The platelet rich plasma-red blood cell mixture was separated. The platelet rich plasma was obtained from the lower portion of the test tube due to its high specific gravity. The platelet rich plasma was incubated for ten minutes at 37°C . It was subsequently frozen until testing. The test materials were immersed in the platelet rich plasma solution and incubated at 37°C for ten minutes. Weakly adherent platelets were removed by rinsing with 0.9% saline solution. The platelet rich plasma-exposed materials were fixed in 4% glutaraldehyde and critical point dried. Platelet rich plasma-exposed materials were then examined using a S3200-N scanning electron microscope (Hitachi, Tokyo, Japan).

Results and Discussion

Optimal ALD processing times for purging and dosing were determined using QMS. Signals were monitored for the TDMAT ligand, water, and argon. Each signal was normalized and was placed side-by-side for comparison in Figure 2. During the TDMAT dose, the $\text{H-N}(\text{CH}_3)_2$ signal increased and became saturated; a signal decrease during the argon purge was subsequently noted. This trend, schematically shown in Figure 1, is consistent with precursor adsorption and dissociation on the growth surface during the precursor dosing step, followed by surface species reaction and desorption during the water exposure step. The signal saturation is consistent with the self-limiting nature of the ALD process. As expected for the ALD process, this signal increases upon water exposure and decreases during the subsequent purge. The QMS analysis therefore indicates that the ALD recipe of ten seconds argon purge, five seconds TDMAT dose, ten seconds argon purge, and five seconds water dose is sufficient to achieve ALD growth of TiO_2 .

A characteristic of ALD behavior is that deposited film thickness is linearly proportional to the number of ALD cycles. Figure 3 shows the increase in TiO_2 film thickness as a function of the number of cycles for deposition on silicon at 100°C with an operating pressure of 2 Torr. The TiO_2 film thickness was measured using ellipsometry; six measurements were

obtained at random spots on the sample in order to verify the uniformity and conformality of the film. The growth rate shows a somewhat higher rate during the initial cycles, followed by linear growth. From the data presented in Figure 3, it was determined that growth of TiO_2 was $2.18 \pm 0.11 \text{ \AA}$ per cycle. This growth rate is comparable to reported growth rates using the same precursor and reactant [26, 27].

Using the same ALD procedure described above for silicon, TiO_2 was deposited on cellulose fibers that were woven together into a fabric. XPS was used to analyze the chemical composition of the TiO_2 films deposited on the fibers. It should be noted that XPS scans were performed on fabric samples, which enabled a multitude of individual fibers to be concurrently measured. The samples were stored in ambient conditions until analysis. The chemical composition of the films was measured in relation to the number of ALD cycles. A reference signal of 285.0 eV for C 1s was used to account for surface charging effects during XPS.

A detail scan of the Ti 2p signal is presented in Figure 4. The intensity of the Ti peak was noted to increase with the number of ALD cycles. Distinct peaks can be seen at 458.8 eV and 464.7 eV, which represent Ti 2p_{3/2} and Ti 2p_{1/2}, respectively. An accepted value for the Ti 2p_{3/2} signal in TiO_2 is 458.8 eV [28]. After one ALD cycle, a small peak for Ti 2p_{3/2} starts to become visible. This peak becomes much more pronounced between 10 and 20 ALD cycles. At this point, the TiO_2 film prevents interaction between the XPS beam and the cellulose fiber substrate. The subsequent XPS readings come solely from the TiO_2 film.

Figure 5 presents a detail scan of the O 1s spectrum. A peak can be seen at 533.0 eV for untreated cotton. This peak is attributed to C-O bonds, which are found in the cellulose structure. The C-O peak decreases as the number of ALD cycles increases. A peak becomes visible at 530.3 eV, which is attributed to Ti-O bonds in TiO_2 [29, 30].

The XPS detail scan of C 1s is presented in Figure 6. The C 1s spectrum for the cellulose fibers is separated into three different signals. A peak is observed at 286.6 eV, which is indicative of C-O bonds that are found in the cellulose structure. Shoulder peaks are also noted at 285.0 eV (C-C bonding) and 288.0 eV (O-C-O bonding) [31]. The peaks associated with cellulose become less prominent in films that were prepared with a higher number of ALD cycles; the peaks associated with the TiO_2 film become more prominent in films that were prepared with a higher number of ALD cycles. The presence of C-C bonds near the surfaces of the films was attributed to atmospheric contamination. A more accurate understanding of film purity may be obtained by limiting atmospheric exposure prior to analysis.

Detailed scans were also performed around the N 1s peak in order to evaluate the N contribution by the TDMAT precursor. As mentioned previously, nitrogen doped TiO_2 is considered to be a more efficient photocatalyst. Figure 7 shows the detail spectra for N 1s; no obvious nitrogen peaks were observed. Based on the XPS data, it can be seen that the films are mainly TiO_2 ; no trace amounts of titanium nitrides or oxynitrides were noted.

TiO_2 is a polymorphic material; several phases, including anatase, rutile, and brookite, may be obtained [32]. The anatase and rutile phases of TiO_2 are most commonly encountered. FTIR was used to investigate the crystalline structure of TiO_2 films on silicon. Figure 8 shows the spectra of a 10 nm-thick film. No features were observed in the region between 1450 and 1750 cm^{-1} , which is associated with carbon-based contamination. The absence of obvious features indicates that the as grown layer is amorphous. After thermal treatments at 450°C and 600°C, the FTIR spectra measured in normal transmission show features at 437 cm^{-1} (peak 1), which are associated with the transverse optical (TO) mode of anatase TiO_2 [33, 34]. At grazing incidence ($\theta = 75^\circ$), a significant shoulder appears around 850 cm^{-1}

(peak 2); the longitudinal optical (LO) mode of anatase TiO_2 is expected at this location (Berreman effect) [33, 34, 35]. The presence of SiO_2 at the interface between the TiO_2 film and the silicon substrate was noted in all of the samples (peaks 3 and 4). TO and LO peaks are also visible in TiO_2 films on cellulose after heat treatment at 400°C (Figure 9).

One important use of TiO_2 is to create photo-induced hydrophilic surfaces [36, 37, 38]. The hydrophilicity of TiO_2 films can be increased by light irradiation in the long wave UV region (320–400 nm); this reaction mechanism has been described elsewhere in detail [39, 40]. Static water contact angle measurements were conducted to examine the hydrophilic properties of TiO_2 on silicon and fiber substrates. Contact angle measurements were performed after deposition of TiO_2 and after illumination with long wave UV light.

A comparison of the contact angles for TiO_2 films on the two substrates can be seen in Figure 10. From examination of the cellulose samples, it can be seen that the untreated fabric has a contact angle of 0° . After only 1 ALD cycle, the fabric substrates exhibit a contact angle of approximately 113° . This contact angle does not change until more than 25 cycles of TiO_2 have been deposited using ALD. This increased hydrophobicity may be attributed to the presence of un-reacted methyl groups on the surfaces of the cellulose fibers or to the fact that the TiO_2 film makes the nanoscale fibers more rigid, which decreases the contact between the water droplet and the fibers. For samples treated with more than 20 cycles of TiO_2 , the cellulose fibers become very hydrophilic; contact angles of 0° are noted. The contact angle measurements on the silicon samples are significantly different than the measurements on the cellulose-based fabrics. After deposition of initial ALD cycles, the TiO_2 films on silicon exhibit a contact angle of approximately 80° . The contact angle decreases to 70° after 10 cycles and does not significantly change for up to 100 cycles. Ho et al. noted the use of hydrophilic materials as hemostatic agents [41].

Scanning electron micrographs of unmodified cellulose acetate and TiO_2 -coated cellulose acetate are shown in Figure 11. The fibrous structure in each sample was observed. No significant differences in fiber structure between unmodified and TiO_2 -coated cellulose acetate were noted.

MTT cell viability data for the unmodified cellulose material and the TiO_2 -coated materials are shown in Figure 12. No statistical difference in viability was observed between the unmodified cellulose material and the TiO_2 -coated materials. Therefore, no toxicity was associated with the TiO_2 film. Shih et al. utilized in vitro testing for demonstrating interactions between platelet rich plasma and semiconducting materials, which were considered for use in medical devices [42]. In their work, copper oxide (CuO) and n-type silicon were shown to not react with platelets and blood; in contrast, Cu_2O and p-type silicon were shown to activate aggregation of platelets. Adhesion and aggregation of platelet rich plasma components were observed using scanning electron microscopy. Figure 13 contains scanning electron micrographs of uncoated cellulose acetate after interaction with platelet rich plasma and Figure 14 contains scanning electron micrographs of TiO_2 -coated cellulose acetate after interaction with platelet rich plasma; Figure 14(b) contains more hazy features, which are indicative of protein adsorption, than Figure 13(b).

TiO_2 has been used as a hemostatic agent for several decades; for example, it is a component of styptic pencils, which are used in the treatment of minor skin wounds (e.g., shaving cuts) [43]. Tsyganov et al. suggest that hydrophilic TiO_2 surfaces exhibit enhanced calcium phosphate adsorption, which influences protein adsorption [44–48]. Uchida et al. indicated that smooth titanium metal exhibits thrombogenic behavior [49]. Yang et al. demonstrated that a nano/submicron-scale TiO_2 network provides enhanced blood coagulation [50]. More recent work by Maitz et al. suggests that nanocrystalline and amorphous titanium oxide

provide higher platelet adhesion but lower clotting cascade activation than crystalline titanium oxide [51].

Conclusions

Cellulose-based substrates represent a readily available, sustainable raw material for the production of blood-contacting biomaterials. Previous research has evaluated the use of cellulose-based structures, both modified and unmodified, as implantable materials with positive results [16–17, 23]. In addition, cellulose structures possess surfaces with ample reaction groups for ALD chemistries; facile coating of these substrates using a variety of ALD processes may be achieved.

ALD provides surface modification of the cellulose acetate substrate with nanoscale precision. It should be noted that ALD provides an environmentally friendly method for manufacturing of biomaterials through a combination of natural raw materials and an efficient modification technique. Based on prior research, it is reasonable to expect that the hemostatic behavior of ALD-modified cellulose acetate will translate to other ALD-modified polymeric substrates; creation of a variety of hemostatic polymeric materials may be achieved by means of ALD [19–23].

XPS and FTIR data indicate that our ALD process produces pure and stoichiometric TiO₂ films on silicon and on cellulose; neither carbon nor nitrogen contamination from precursor residues was noted. The films grow with thickness uniformity and with a growth rate in agreement with literature results. The TiO₂ film can profoundly change the water contact angle of the cellulose depending upon process characteristics. TiO₂-coated cellulose acetate exhibited greater protein adsorption than unmodified cellulose acetate. These results suggest that ALD is an appropriate method for improving the hemostatic properties of blood-contacting biomaterials.

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Figure 1. Schematic showing preparation of TiO_2 -coated cellulose fibers using ALD. The TDMAT reacts with the $-\text{OH}$ terminated surface of the cellulose fibers, leaving a methyl terminated surface. Water subsequently reacts with the methyl groups, creating a surface with $-\text{OH}$ groups. This process is repeated over a number of cycles to obtain a film with the desired thickness.

Figure 2. Quadripole mass spectrometry of ALD-deposited TiO₂. Intensities of the TDMAT ligand, argon, and water are presented as functions of processing time. Green arrows indicate TDMAT dosing and black arrows indicate water dosing. Times between arrows represent argon purges.

Figure 3.

Growth rate of TiO₂ films on silicon. Thickness of TiO₂ films as a function of the number of ALD cycles was determined using ellipsometry. Titanium dioxide was deposited using a temperature of 100°C and a pressure of 2 Torr. The linear growth rate is characteristic of the ALD process.

Figure 4. XPS detail spectra of Ti 2p for TiO₂ films deposited on cellulose fibers. The Ti 2p signal, which consists of two distinct peaks, was noted to increase with the number of ALD cycles.

Figure 5.

XPS detail spectra of O 1s for TiO₂ films deposited on cellulose fibers. The peak, which was attributed to Ti-O bonding, was noted to shift to lower binding energies in thicker films.

Figure 6. XPS detail spectra of C 1s for TiO₂ films deposited on cellulose fibers. The C-O and O-C-O peaks were shown to decrease as the number of ALD cycles was increased. The C-C peak increased as a result of film contamination.

Figure 7. XPS detail spectra of N 1s for TiO₂ films deposited on cellulose fibers. No distinct peak can be seen for N 1s, demonstrating the purity of the TiO₂ films.

Figure 8.

FTIR spectra of as grown and thermally treated TiO_2 films on silicon. Absorbance versus wavenumber (cm^{-1}) data is reported. Peaks 1 and 2 are the TO and LO modes of TiO_2 , respectively. Peaks 3 and 4 are the TO and LO modes of SiO_2 , respectively.

Figure 9. FTIR spectra of TiO₂ films on cellulose after heat treatment at 400°C. The TO and LO modes of anatase TiO₂ are noted for TiO₂-coated cellulose.

Figure 10.

Static water contact angle for TiO₂-coated fabrics and silicon. The ALD cycle number versus static water contact angle is shown. This graph shows that very thin layers of TiO₂ (<50 Å) produce a hydrophobic effect on the normally hydrophilic cellulose fibers. The fabric samples are significantly more hydrophobic than the corresponding silicon samples. The metal oxide may act to reinforce nanoscale fibrils and thus increase the hydrophobicity of the material.

Figure 11. Scanning electron micrograph of unmodified cellulose acetate (top) and TiO_2 -coated cellulose acetate (bottom). No significant differences in fiber structure between the unmodified cellulose acetate and the TiO_2 -coated cellulose acetate were noted.

Figure 12. MTT viability of uncoated cellulose acetate and TiO₂-coated cellulose acetate. No statistical difference in viability was noted; no toxicity was observed.

Figure 13. Scanning electron micrograph of unmodified cellulose acetate after exposure to human platelet rich plasma.

Figure 14. Scanning electron micrograph of TiO₂-coated cellulose acetate after exposure to human platelet rich plasma. Blurry areas indicate protein adsorption.