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A simple one-step approach to fabrication of highly hydrophobic silk fabrics

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ABSTRACT

Highly hydrophobic silk fabric surfaces were successfully fabricated using a simple one-step atomic layer deposition (ALD) process. The surface morphology, chemical composition, and structure of bare silk fabric and silk fabrics coated with titanium dioxide (TiO_2) subjected to 800 and 1600 ALD cycles were measured using scanning electron microscopy (SEM), field-emission scanning electron microscopy (FESEM), energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and scanning probe microscopy (SPM). The surface wettability of the silk fabrics was evaluated by determining their static water contact angles (WCAs) and roll-off angles. The results suggest that the good hydrophilicity of the surfaces of bare silk fabrics can be changed to high hydrophobicity by the application of TiO_2 nanoparticles to their surfaces using ALD. The high hydrophobicity achieved can be attributed to the increase in roughness of the silk fabric surface. The laundering durability of TiO_2-coated silk fabrics is greatly improved by increasing the thickness of the ALD TiO_2 films.

1. Introduction

Of the principal clothing fabrics, silk is the most favored high-quality textile materials because of its attractive characteristics, including its elegant appearance, softness, superior wear comfort, warmth, biodegradability, and low cost [1]. However, the large numbers of hydrophilic groups (carboxyl, hydroxyl and amine groups) on the backbone and side chains of the polypeptide molecules present in silk fibers contribute to making silk fabrics vulnerable to staining by dirt, rainwater, and debris. Therefore, development of functional silk fabrics with self-cleaning properties is an urgent concern for materials researchers in the textile industry [2].

A superhydrophobic surface is one on which the water contact angles is greater than 150° and the roll-off angles is less than 10° or one on which water either does not adhere or only weakly adheres [3–6]. The mechanism of lotus leaves suggests that a combination of low surface energy and high surface roughness is required to achieve a superhydrophobic surface. Micro- to nanoscale geometric structures have proven to be vital in producing superhydrophobic surfaces [7,8]. Therefore, modification of surface chemistry is crucial to achieving the high surface roughness that is characteristic of superhydrophobic surfaces [9,10].

Various microstructures have been developed using the available physical and chemical thin-film deposition methods, including pulsed laser deposition [11], plasma treatment [12], the sol–gel technique [13–15,8,16,17], chemical vapor deposition [18,19], and other techniques [20]. However, the reported methods are not appropriate for textiles, such as silk and cotton fabrics, because high treating temperatures are involved, and high temperatures can result in a considerable degree of thermal degradation. This can significantly affect the apparent quality and properties of the material [21]. There is a growing demand for a smart coating technique that can deposit uniform coatings onto flexible substrates at low temperatures and allow control of the thickness in the range of nanometers [22]. One technique for obtaining a conformal coating of well-controlled thickness that penetrates deep into crevices in the material surface is atomic layer deposition (ALD). ALD is a sequential cyclic low-temperature vapor deposition method for atomic layer control and conformal deposition using sequential, self-limiting surface reactions. This method can be used to deposit a variety of ultrathin films on virtually any substrate with very high aspect ratios [23–27].

In this study, a novel ALD method was employed to deposit titanium dioxide (TiO_2) film on silk fabrics to create nanoscale roughness. The hydrophobic properties of TiO_2-coated silk fabrics were measured to assess the feasibility of designing and creating silk fabric surfaces with the desired hydrophobic properties. Titanium dioxide was chosen as the deposition material rather than any of several other metal oxides because of its hydrophilicity and its resistance to acids and alkalis, in addition to the convenience of the ALD process as a means of applying titanium dioxide, which involves the use of inexpensive and relatively in sensitive precursors. In this study, this simple method exhibited very good experimental reproducibility and was used successfully to produce hydrophobic surfaces.

2. Materials and methods

2.1. Material

White bare silk fabrics (200 g/m^2) purchased from a local fabric store were degummed with a sodium carbonate solution. Titanium (IV) isopropoxide (TIP, 99.999% metals basis) was obtained from

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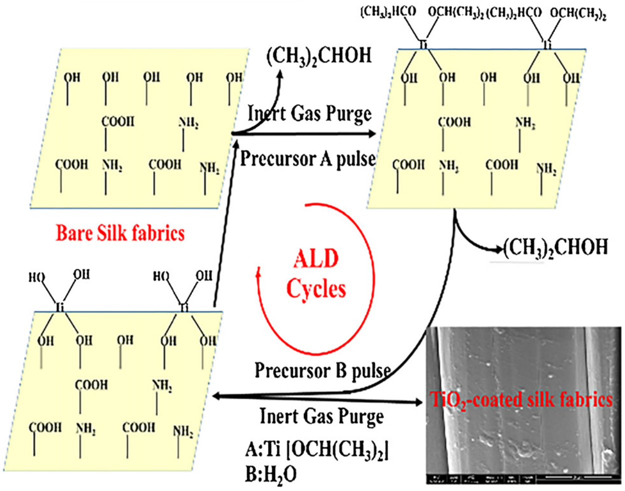

Fig. 1. Procedure for preparation of TiO_2-coated silk fabrics.

Aladdin Industrial Co., Ltd. Deionized water, purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA), was used in this study. The water had a resistivity of 10–16 MΩ cm. All chemicals were used without further purification.

2.2. Preparation of hydrophobic surfaces

The ALD TiO_2 coating process was carried out using a Savannah S100 ALD reactor (Savannah System, Cambridge NanoTech. Inc., USA) equipped with a gas-flow system. Titanium (IV) isopropoxide and H_2O were used as the titanium and oxygen precursors, respectively, to deposit TiO_2 at a temperature of 150 °C. High-purity nitrogen (N_2, 99.999%) was used as both the purge gas and carrier gas for both precursors. A steady flow of nitrogen at 50 sccm (standard cubic centimeters per minute) was used in the ALD process. Prior to the ALD processing, the degummed silk fabrics were placed in the ALD reactor and dried in a vacuum (~0.5 Torr) at 150 °C for 5 min. To produce adequate vapor pressures, the TIP was heated to 80 °C and the temperature of the water was maintained at the ambient temperature. In the first half cycle, water vapor was pulsed into the chamber for 0.05 s, the silk fabrics were exposed to water vapor for 8 s, and the reactor was then purged with nitrogen for 35 s. In the second half cycle, TIP was pulsed into the chamber for 0.2 s, the silk fabrics were exposed to TIP for 8 s, and the reactor was then purged with nitrogen for 35 s. Thus, the duration of one complete ALD cycle was 86.25 s. The schematic process of the fabrication of hydrophobic silk fabrics was exhibited in Fig. 1. The ALD cycling was repeated an appropriate number of times to obtain systematic variation in the coating thicknesses. To measure the thickness of the TiO_2 coating and determine whether the ALD reactions happen on the surface through color change, a monocrystalline wafer together with the silk fabrics were treated under the same deposition conditions.

2.3. Characterization

The surface morphologies of the bare silk fabric and silk fabrics coated with TiO_2 as described above were observed using a scanning electron microscope (SEM, JSM-5600 LV, operating at 20 kV) and a field-emission scanning electron microscope (FESEM, HitachiS-4800, operating at 5 kV). Prior to SEM observation, the samples were sputtered with a thin layer of platinum applied to the bare silk fabric and TiO_2-coated silk fabrics subjected to various numbers of ALD cycles. The elemental compositions of the bare silk fabric and TiO_2-coated silk fabrics were characterized using an energy-dispersive X-ray microanalysis system (EDS, Oxford INC A350) coupled to the FESEM and operated at 5 kV.

X-ray diffraction (XRD) was performed at room temperature using an X'Pert PRO XRD spectrometer (PANalytical, Holland) with a Cu-Kα radiation source at a generator voltage of 40 kV and a generator current of 50 mA.

The static water contact angles (WCAs) and roll-off angles of the bare silk fabric and TiO_2-coated silk fabrics were measured at room temperature using 5-μl deionized water droplets on a Dataphysics OCA 30 contact angle system (Dataphysics, Germany). Each droplet was dropped onto the sample surface from a distance of 5 cm by vibrating a syringe containing the deionized water. The static water contact angle and roll-off angle of each sample surface were determined by averaging values measured at five different sites on the surface.

The surface topologies of the bare silk fabric and TiO_2-coated silk fabrics subjected to different numbers of ALD cycles were also observed using a scanning probe microscope (SPM, XE-100, Park System Co). The surface roughness of each image was analyzed to quantify the arithmetic average roughness, expressed by the Ra parameters.

3. Results and discussion

3.1. Morphology observation and EDS analysis

The results of the scanning electron microscopy and EDS analysis conducted to observe the morphologies of the bare silk fabric and TiO_2-coated silk fabrics subjected to 800 and 1600 ALD cycles are shown in Fig. 2.

Fig. 2a, e, and i shows that the silk fabrics had tightly woven, fibrous structures and that the microstructures of the bare silk fabric and TiO_2-coated silk fabrics subjected to different numbers of ALD cycles appeared the same at low magnification, which is consistent with the conformal characteristics of the ALD process [24]. Fig. 2b shows that a single fiber of the bare silk fabric at a high magnification was smooth, in clear contrast to single fibers of the TiO_2-coated silk fabrics subjected to 800 and 1600 ALD cycles, as shown in Fig. 2f and j. The latter fiber surfaces (Fig. 2f and j) appeared to have a compact coating with a number of small particle clusters. Some larger particles were visible in the higher-magnification SEM images, as shown in Fig. 2g and k. The presence of these larger particles is attributable mainly to aggregation of adjacent TiO_2 nanoparticles, as a result of their inherently high specific surface area and high surface energy. The cracks and particle clusters significantly increase the surface roughness, by generating a more tortuous dual-size surface structure on the silk fabrics, and thereby enhancing the fabric's hydrophobicity or water repellency [28,29].

The results of the EDS analyses conducted to determine the chemical composition of the bare silk fabric and TiO_2-coated silk fabrics are illustrated in Fig. 2d, h, and l. Only carbon, nitrogen, oxygen, and platinum elements were detected from the spectra of the bare silk fabrics. The presence of platinum can be attributed to the coating layer used for the EDS measurement; the presence of carbon, nitrogen and oxygen can be attributed to the silk fabrics. After the ALD processing, elements such as carbon, nitrogen, oxygen, and platinum could be found in the EDS spectra. No other elements, except titanium were found in the EDS spectra, which confirms that Ti is present on the surfaces of TiO_2-coated silk fabrics.

To confirm that TiO_2 was deposited on the surfaces of the treated silk fabrics, the XRD spectra of the bare silk fabric and TiO_2-coated silk fabrics subjected to 800 and 1600 ALD cycles were recorded at room temperature. In addition, individual TiO_2