Article

Fabrication of Superhydrophobic and UV-Resistant Silk Fabrics with Laundering Durability and Chemical Stabilities

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Abstract: To obtain a superhydrophobic surface, SiO₂ nanoparticles are deposited on the surface of silk fabric (SF) by Plasma Enhanced Chemical Vapor Deposition (PECVD) to form a hierarchical roughness structure. In addition, a durable superhydrophobic SiO₂@silk fabric was further prepared by hexamethyldisilazane (HMDS) modification. Compared with bare silk, the surfaces of the SiO₂@silk fabric exhibit higher surface roughness and excellent superhydrophobic activity, with a contact angle (CA) of ~152°. The excellent UV resistance of SiO₂@silk fabric was confirmed with high UV protection factor (UPF) values and a low UV transmittance. Moreover, both the laundering durability and chemical stability of the SiO₂@silk fabric were improved. Overall, this method is recognized as a promising approach to produce high-end fabric development. It can also guide the design of multifunctional fiber materials in the future.

Keywords: silk fabric; superhydrophobic coating; UV resistant; durability; HMDS

1. Introduction

Silk, a natural protein filament fiber, containing eighteen amino acids, has been widely used in textile manufacturing for a long time. Silk fiber has been regarded as “the queen of fibers” due to its many attractive characteristics, including its softness, comfort, high hygroscopicity, excellent mechanical strength, environmental stability, environmental friendliness, and renewability [1–5].

However, because of the abundant hydrophilic groups (hydroxyl, carboxyl, and amino) on the surface of silk fiber and fabric, it also brings some inherent defects, such as low thermal stability, high flammability, poor bacterial resistance, ease in being dirtied, and weak UV protection capability. This seriously hinders their extensive application for luxurious fashionable apparels [6,7]. Therefore, producing novel textiles, such as UV resistant and superhydrophobic silk fabrics, will help to meet the diversified needs of the consumer market.

Inspired by the lotus leaf, great efforts have been made to explore new superhydrophobic and UV resistant silk fibers/fabrics [8,9]. Ren et al. [10] reported a ZnO-PDMS coated fabric with good self-cleaning and UV resistance. Huang et al. [11] successfully constructed a robust superhydrophobic TiO₂@fabric with a hydrothermal reaction method on a cotton fabric surface, which demonstrated good mechanical stability and exhibited self-cleaning and UV resistant properties. The surface of the anatase TiO₂ sol was modified; then, the perfluorooctyl methacrylate (PFOMA) was used to prepare superhydrophobic fabric by thiolene click reaction, and this imparted the fabric with superhydrophobic and ultraviolet-blocking properties [12].

Although these studies have made some success in the field of preparing UV resistant silk fibers, the above methods, in many cases, are hardly able to form a stable coating structure, resulting in them being easily exfoliated from the surface of SF and, additionally, resulting in a deterioration of the superhydrophobic and anti-UV performances. Meanwhile, plenty of UV shielding agents can produce hydroxyl radicals and superoxide radicals under the UV light, owing to their high photocatalytic activities [13]. Given their strong oxidation properties, the radicals will damage the structure and composition of fibers/fabrics after they are further transmitted to the interface between UV shielding agents and fibers. PECVD is an effective conformal coating technology, which has the advantages of good uniformity, accurate thickness control, and strong adhesion. PECVD is a technology that uses glow discharge to ionize thin gas in a high frequency electric field to produce plasma. These ions are accelerated in the electric field to obtain energy, which can lead to the growth of thin film at low temperature [14]. SiO_2 is the most favored inorganic material and has been widely applied because of its excellent chemical stability, mechanical strength, and high transparency [15]. In this work, SiO_2 was coated onto silk fabric by PECVD, and a robust superhydrophobic SiO_2 @silk fabric was further constructed by HMDS modification. The modified silk fabrics exhibited excellent superhydrophobicity and anti-UV properties. Moreover, the chemical and laundering durability of the finished silk fabrics will be discussed in detail. In general, this method is considered to be a promising way to produce high-end fabric. It shows promise for the design of multifunctional fiber materials in the future.

2. Materials and Methods

2.1. Materials

The white bare silk fabrics (SFs, plain weave, 63.3 g/m^2) used in this study were obtained from Tongxiang Home Textile, Ltd. (Zhejiang, China). SiH_4 (Helium mixture, 10% of silane volume), N_2 (99.999% purity) and N_2O were purchased from Wuhan Minghui Co., Ltd. (Wuhan, China). HMDS was directly obtained from Aladdin Industrial Co., Ltd. (Shanghai, China). Ethanol ($\text{C}_2\text{H}_5\text{OH}$) was bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The high-purity water used in the experiments was purified using a Milli-Q Plus 185 water purification system (Millipore, Bedford, MA) and had a resistivity of $10\text{--}16 \text{ M}\Omega\cdot\text{cm}$ at 25°C . Prior to PECVD, the silk fabrics and silk fibers were cleaned by the high-purity water and ethanol.

2.2. Preparation of Superhydrophobic Silk Fabrics

SiO_2 nanofilms with plenty of active hydroxyl groups were prepared on the surface of silk fabrics by PECVD method. The reaction temperature was 150°C , the deposition pressure was 90 Pa, the RF power was 50 W, and the deposition time was 5 min. SiH_4 (Helium mixture, 10% of silane volume) and N_2O (99.999% purity) were used as reaction gas sources. The gas flow rate of SiH_4 was 65 sccm (sccm: standard milliliter/minute) and N_2O was 450 sccm, respectively. High purity nitrogen (99.999%) is scavenging gas, and its flow rate is controlled at no less than 13.4 sccm. Then, the SiO_2 @silk fabric was added to the Teflon reactor with a 30 mL methanol solution and 7.5 mL HMDS. This was put into the oven at 80°C for 6 h and cooled at room temperature to form the superhydrophobic silk fabrics. Finally, the corresponding sample, with SiO_2 coating of varied thickness, was modified by HMDS and marked as SF-n SiO_2 , where n indicated the time of SiO_2 deposition by PECVD, respectively.

It can be seen from Figure 1a that the PECVD process for SiO_2 deposition with SiH_4 and N_2O can be separated into a four-step reaction. When SiH_4 and N_2O are used to prepare SiO_2 thin films by plasma enhanced chemical deposition, the initial reactant is $(\text{SiH}_3)_2\text{O}$, which is adsorbed on the substrate surface and reacts with oxygen atoms to form silicon dioxide with a stoichiometric ratio. Firstly, N_2O is decomposed in the plasma to produce an oxygen atom or an oxygen radical, and the activated oxygen radical reacts with silane to form $(\text{SiH}_3)_2\text{O}$ or participates in the formation of oxide on the surface. Details are as follows:

Figure 1b shows the schematic illustration of the schematic process of the fabrication of superhydrophobic and UV resistant silk fabrics. The water droplet quickly spread and completely wetted the bare fabric with the CA of 0° , indicating that the silk fabric was superhydrophilic (left inset of Figure 1c). However, the CA increased to 152° on the surface of SF-5SiO₂ (right inset of Figure 1c), which showed excellent superhydrophobicity.

Figure 1. Schematic illustration (a) deposition SiO₂ coating on silk fabric by PECVD. (b) the preparation of superhydrophobic and anti-UV silk fabrics; (c) The morphology and contact angles of bare silk and modified silk fabric.

2.3. UV Radiation Treatment

The UV resistance of the coating is the focus of this study. Therefore, we put the prepared silk fabric under the UV aging lamp for 30 min. The power of the UV aging lamp is 40 mW/cm², the wavelength is 312 nm, and the distance between the UV aging lamp tube and the silk fabric is fixed at 20 cm.

2.4. Characterization

The surface morphology of the samples was measured by field emission scanning electron microscope (FE-SEM, JEM-6510LV) at an operating voltage of 5 kV. The elemental composition of samples was analyzed by an X-ray energy dispersive spectroscopy (EDS) detector (QX200, Bruker, Germany) attached to the FE-SEM. The contact angle system (KRUS DSA100, Shanghai, China) was used to measure the static water contact angle of the super hydrophobic surface by using the seat drop method. Each layer was coated with 5 different points and about 5 μL of deionized water was dripped. In order to characterize the surface roughness of the samples, the atomic force microscope (AFM, Park Systems XE-100, Suwon, Korea) was used to test them, and the relevant parameters were calculated by the equipment software. According to the GB/T14337-2008, the mechanical properties of

the samples were tested along the radial direction on LLY-06E electronic single fiber strength tester (Laizhou Electronic Instrument Co., Ltd., Yantai, China). The test environment temperature is 20 °C, the relative humidity is 63%, and the tensile rate is 10 cm/min. Measurements of all samples were repeated 15 times and an average value was taken.

2.5. UV Resistance Evaluation

According to the European standard EN13758-2:2003, the anti-UV performance of the sample should be measured with an HB902 anti-UV penetration and sun protection tester. The samples prepared should be measured by monochromatic or polychromatic ultraviolet (UV) radiation. The total spectral transmission rays in the samples should be collected, and the total spectral transmittance should be measured. The total UV protection coefficient (UPF value) should be calculated by the following equation [16,17]:

$$UPF = \frac{\sum_{280nm}^{400nm} E_{\lambda} \times S_{\lambda} \times \Delta\lambda}{\sum_{280nm}^{400nm} E_{\lambda} \times S_{\lambda} \times T_{\lambda} \times \Delta\lambda} \quad (3)$$

where E_{λ} denotes the solar spectral irradiance ($Wm^{-2} \cdot nm^{-1}$), S_{λ} denotes the relative erythema spectral effectiveness, $\Delta\lambda$ denotes the wavelength interval, and T_{λ} represents the averaged spectral transmittance of the silk fabric.

We have measured the color-related parameters (K/S value, L^* , a^* , b^*) of silk fabrics before and after ultraviolet irradiation with an X-Rite color i7 computer color measurement and matching system. At the same time, in order to further assess the UV resistance of different silk fabrics, we calculated the whiteness index (WI) and yellowness index (YI) by using the following formula through the color-related parameters [18,19]:

$$WI = 100 - \sqrt{(100 - L^*)^2 + (a^*)^2 + (b^*)^2}; YI = \frac{142.86b^*}{L^*} \quad (4)$$

where L^* denotes the brightness ranging from 0 (black) to 100 (white); positive value a^* denotes red, negative value a^* denotes green, and a^* varies from -100 (green) to 100 (red); positive value b^* denotes yellowness, negative value b^* denotes blueness, and b^* varies from -100 (blue) to 100 (yellow), respectively.

2.6. Chemistry Stability Evaluation and Laundering Durability Evaluation

The silk fabrics were placed in 25 mL acid solution (hydrochloric acid)/alkaline (sodium hydroxide) solution with different pH values and placed in a glass beaker at 20 °C for 6 h. According to AATCC 61-2009 method, accelerated washing durability tests of silk fabrics were carried out under condition 2A. The size of the stainless steel lever locking tank is 75 × 125 mm (total volume 500 mL). The obtained silk fabrics were washed at 50 °C and 40 ± 2 rpm in 150 mL AATCC standard WOB detergent (0.15%, w/w) and 50 stainless steel balls. Under condition 2A, one laundering cycle is equivalent to 10 commercial or household laundering cycles.

3. Results

3.1. Surface Morphology and Composition Analysis

Figure 2a–d shows the FE-SEM images of SF and SF-5SiO₂. As shown in FE-SEM images, it can be seen that the surface of the bare silk fabric is very smooth (Figure 2a,b). In contrast, many dense cracks and a few particle clusters can be observed on the surface of SF-5SiO₂ (Figure 2c, d), which may be attributed to the aggregation of neighboring SiO₂ nanoparticles. The absence of cracks indicates that the SFs are completely covered by SiO₂ layers. The energy dispersive X-ray (EDX) analysis shows that there is a continuous, uniform and dense SiO₂ coating on the surface of SF-5SiO₂ (Figure 2e–h). Figure 2j–m shows that the arithmetic average roughness (R_a) measured was 118, 158, 125, and 121 nm

for the SF-nSiO₂ subjected to 2.5, 5, 7.5, and 10 min PECVD deposition, respectively. However, the Ra of bare silk fabric was only 74 nm (Figure 2i), which indicated that the SiO₂ coating prepared has a certain surface roughness. After the deposition of SiO₂ coating, the surface roughness of silk fabric increases. However, Ra is not a monotonic function of the PECVD exposure time. It reaches a maximum at around 5 min before it decreases, since silica further fills some of the grooves (weaving) on the surface of the silk fabric.

Figure 2. FE-SEM images of: (a,b) bare silk fabric, (c,d) SF-5SiO₂; (e–h) EDX mapping images of SF-5SiO₂; (i–m) AFM images of SF and SF-nSiO₂

3.2. Surface Wettability Analysis

The water contact angles of the SF-nSiO₂ were measured by using an OCA2.0 contact angle measurement system at 20 °C with a 5 μL water droplet. The contact angles were measured using the drop method at 5 different points on each sample. When water drops on the surface of silk fabric, it can be completely wetted; on the contrary, the surface of the modified silk fabric shows the superhydrophobicity with water contact angles (WCAs) of 152° (as shown in Figure 3). Superhydrophobic surfaces are improved by increased surface roughness. This is completely consistent with the theory that was originally reported [20,21]. To evaluate the stability of the wetting properties after UV exposure, the contact angles of SF-5SiO₂, before and after UV light treatment for 30 min, were measured and shown in Figure 4a,b. After UV irradiation, the wettability of the SF-5SiO₂ was almost unchanged (Figure 4b). And it exhibits excellent superhydrophobicity with WCAs of 150°, which indicates the wettability of the SF-5SiO₂ has a strong tolerance to UV light. It is very important to endow the surface of silk fabric with the superhydrophobic property for stain resistance.

3.3. UV Resistance Analysis

Figure 5a,b shows the UPF values and the UV transmittance curve for bare silk fabric and SF-nSiO₂. The UPFs for all samples were measured with 20 tests to find its average value. Compared with bare silk, the transmittance of the SF-nSiO₂ are lower, and the UPF values of the SF-nSiO₂ are higher, exhibiting excellent UV resistance properties. The results show that amorphous SiO₂ plays an important role in the diffusion barrier layer and the passivation layer [15]. In addition, we measured the K/S values of bare silk and SF-nSiO₂ before and after UV light irradiation, as shown in Figure 5c,d. Compared with bare silk, the K/S values of SF-nSiO₂ slowly increased and were lower than that of bare silk. This indicates that SF-nSiO₂ has UV resistance. SF-nSiO₂ does not easily fade after UV irradiation.

Figure 3. The contact angles of SF-nSiO₂ with different deposition times.

Figure 4. The contact angles of SF-5SiO₂: (a) before UV light treatment, and (b) after UV light treatment for 30 min.

Figure 5. (a) UPF values of SF and SF-nSiO₂; (b) Ultraviolet transmission spectra of SF and SF-nSiO₂; Color strength indicator, K/S value of SF and SF-5SiO₂: (c) without UV irradiation, (d) with UV irradiation for 30 min; (e) whiteness index, (f) yellowness index of SF and SF-5SiO₂ before and after UV irradiation for 30 min.

To further compare the UV resistance of the different silk fabrics, the WI and YI were calculated. As Figure 5e,f shows, it is obvious that the WI and YI of the PECVD-coated silk fabrics have only slightly changed, compared with that of bare silk before the UV irradiation. This indicates that the deposition of SiO₂ on the surface of silk fabric, through PECVD technology, will not affect the bulk silk

fabric. After continuous exposure to UV light for 30 min, the WI of bare silk significantly reduced from 93 to 56, while the YI increased from 8 to 68, exhibiting yellowing. In this case, the main reason for the yellowing of silk fibers is that the amino acids with aromatic rings (such as tryptophan, tyrosine, and phenylalanine) in silk produce chromogenic conjugated systems under the action of UV light [22,23]. However, the WI and YI of the SF-5SiO₂ did not change as much as that of bare silk under the same conditions, which demonstrates that SiO₂ coating can decrease the yellowing of silk fabrics after UV treatment. This corresponds with the K/S analysis above. In conclusion, the SF-nSiO₂ prepared has excellent UV resistance.

3.4. The Mechanical Properties Analysis

In addition, the mechanical properties of materials are important for evaluating their practical applications. It is necessary to improve the mechanical properties of silk fabrics as they are very easily damaged. Thus, we applied tensile tests to all samples before and after UV irradiation for 30 min, and the average values for tensile stress and work fracture of all samples are given in detail in Figure 6a,b. To obtain accurate results, the values of tensile stress and work fracture of all samples were measured 10 times to obtain an average value. It is clearly seen that the values of tensile stress and work fracture of SF-nSiO₂ are higher than that of bare silk. Moreover, the large increase in tensile stress and work fracture indicates that SiO₂ can enhance the mechanical properties of silk fibers.

Figure 6. (a) Tensile tests; (b) Work fracture of SF and SF-5SiO₂ before and after UV irradiation for 30 min.

3.5. Chemistry Stability and Laundering Durability Analysis

For functional textiles, the contradiction between excellent functional characteristics and long-term durability and stability has always been a problem difficult to solve by scholars. Up to now, research progress has been unsatisfactory, especially for protective textiles with special functional coating. When these textiles, with special functional surfaces, contact with each other or with other substances outdoors, the functional coatings on their surfaces will wear to varying degrees due to sunlight, friction, or other external forces. They might also completely lose their functions, resulting in the failure of functional fabrics, which greatly limits the practical application and development of functional fabrics. The chemical stability and laundering durability are also key factors in determining the application of functionalized fabrics. Therefore, we have evaluated the chemical durability of SF-5SiO₂ by soaking it in different pH solutions for 6 h, and it maintained excellent superhydrophobic properties, which indicated that the finished silk fabric has excellent chemical stability (Figure 7a). In addition, the SF-5SiO₂ was washed for different cycles according to the method of American Association of Textile Chemists and Colorists 61-2006 methods. The WCAs and WSAs of all samples were measured. After 30 cycles of repeated washing, the SF-5SiO₂ remained superhydrophobic (Figure 7b), which might be due to the formation of a stable chemical bond between the SiO₂ coating and the silk fabrics.

Figure 7. (a) Chemical stability of SF-5SiO₂; (b) Laundering durability of SF-5SiO₂.

4. Conclusions

In this study, a robust superhydrophobic and UV resistant silk fabric was successfully prepared. Compared with bare silk, the surface of the SF-5SiO₂ exhibits higher surface roughness and excellent superhydrophobic activity with a contact angle of ~152°. The excellent UV resistance of SF-nSiO₂ was confirmed with a high UPF value and a low transmittance, in the wavelength range of 280–400 nm. Moreover, both the laundering durability and chemical stability of the SiO₂@silk fabric was improved. Based on these results, it can be concluded that PECVD is a promising modification method to endow silk fabrics with high UV protection and superhydrophobic properties. Overall, this method is recognized as a promising approach to producing high-end fabric. It can also guide the design of multifunctional fiber materials in the future.

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