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Multifunctional surface modification of silk fabric via graphene oxide repeatedly coating and chemical reduction method

Jiliang Cao [a,b], Chaoxia Wang [a,*]

[a] Key Laboratory of Science & Technology of Eco-Textile, Ministry of Education, School of Textile & Clothing, Jiangnan University, Wuxi, Jiangsu, 214122, China

[b] Department of Materials and Chemical Engineering, Henan University of Engineering, Zhengzhou, Henan, 450007, China

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ABSTRACT

Multifunctional silk fabrics with electrical conductive, anti-ultraviolet and water repellent were successfully prepared by surface modification with graphene oxide (GO). The yellow-brown GO deposited on the surface of silk fabric was converted into graphitic black reduced graphene (RGO) by sodium hydrosulfite. The surface properties of silk fabrics were changed by repeatedly RGO coating process, which have been proved by SEM and XPS. The SEM results showed that the RGO sheets were successive form a continuously thin film on the surface of silk fabrics, and the deposition of GO or RGO also can be proved by XPS. The electrical conductivity was tested by electrical surface resistance value of the silk fabric, the surface resistance decreased with increasing of RGO surface modification times, and a low surface resistance value reached to 3.24 KΩ cm^{-1} after 9 times of modification, indicating the silk obtained excellent conductivity. The UPF value of one time GO modification silk fabric (silk-1RGO) was enhanced significantly to 24.45 in comparison to 10.40 of original silk. The contact angle of RGO coating silk samples was all above of 120°. The durability of RGO coated silk fabrics was tested by laundering. The electrical surface resistance of silk-4RGO (65.74 KΩ cm^{-1}), silk-6RGO (15.54 KΩ cm^{-1}) and silk-8RGO (3.86 KΩ cm^{-1}) fabrics was up to 86.82, 22.30 and 6.57 KΩ cm^{-1} after 10 times of standard washing, respectively. The UPF value, contact angle and color differences of RGO modified silk fabric slightly changed before and after 10 times of standard washing. Therefore, the washing fastness of electric conduction, anti-ultraviolet and water repellent multifunctional silk fabrics was excellent.

1. Introduction

Silk has been used as textile for more than 4000 years, and it is called the 'queen of textiles' for its unique advantages [1]. Serine, glycine, and alanine are the three major amino acids in mulberry silks, and the above amino acids generally make up about 82% of total mass [2]. Silk not only has the general properties (flexibility, glossiness, excellent moisture absorbency, anti-static, fairly resistant to acids and mechanical strength) of conventional textile, but also has excellent aesthetic qualities, biocompatibility and biodegradability [3,4].

The functional finishing of silk fabrics has attracted great attention recently [5–7]. Electrical conductive finishing often coating the silk fabrics with metal ion solution (i.e. copper, silver) [5]. The electrical conductive can be also obtained by coating polypyrrole via in situ oxidative polymerisation in an aqueous solution of pyrrole at room temperature using $FeCl_3$ as catalyst [8–10]. Polyaniline and Poly(3,4-ethylenedioxythiophene) electrical conductive silk fiber were prepared by in situ polymerization aniline and 3,4-ethylene-dioxythiophene monomer respectively [11]. The Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) coated silk fibers to act successfully as interconnects in a device were demonstrated in a fully functional 555 timer circuit [12]. Photodegradation lead to apparent of silk fabrics as visible yellowing, loss of mechanical strength and a reduction in the amounts of tyrosine, tryptophan and histidine residues. Photoyellowing is mainly due to free radical photooxidation of the tryptophan and tyrosine residues absorb UV wavelengths from sunlight, leading to the formation of yellow products. The anti-ultraviolet finishing of silk fabrics was also very important [6]. Anti-ultraviolet silk fabrics

Abbreviations: GO, graphene oxide; RGO, reduced graphene oxide; silk-nRGO, n time GO modification silk fabric ($1 \leq n \leq 9$); SEM, scanning electron microscopy; XPS, X-ray photoelectron spectroscopy; UPF, Ultraviolet Protection Factor; T[UVA], transmission of UVA; T[UVB], transmission of UVB; △E, color differences.

* Corresponding author.
E-mail address: wangchaoxia@sohu.com (C. Wang).

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were obtained by coating nanoscale TiO_2 on the surface of the fabrics, or using covalently-bound UV absorber reacted with the amino groups of silk [13]. The superhydrophobic silk fabric was achieved by sprayed a water soluble silica nanoparticles on the surface of silk fabrics [14]. Flame retardant finishing of silk fabric are mostly by graft copolymerization of flame retardant monomers, such as phosmer M, phosmer CL or vinyl phosphate dimethyl 2(methacryloyloxyethyl) phosphate [15–17].

Graphene is a two dimensional (2-D) single or few layers of *sp*-bonded carbon sheets, has excellent electronic, mechanical and thermal properties, can be used in electrode, capacitor [18], intracellular imaging and drug delivery materials [19], smart textile [20,21] or functional finishing agent for textile. A flame retardant cotton fabric was prepared by self assembly of polyacrylamide and GO [22]. Ultraviolet protection cotton fabrics were achieved by self assembly of graphene oxide and chitosan, or functionalize the surface of cotton fabric by graphene nanoplate via pad-dry-cure method [23]. The antimicrobial activity of GO silanized with *N*-(trimethoxysilylpropyl) ethylenediamine triacetic acid against Gram-negative and Gram-positive bacteria was higher than GO [24]. A graphene electrical conductivity film was achieved by coating GO on electrospun silk fibroin scaffolds or dropping silk fibroin on RGO film [25]. Bovine serum albumin modified silk fabrics coated GO via repeatedly dipping and hydrazine vapor reduction method, and its electrical surface resistance value can meet the electron conductive requirement of wearable electronics [26].

Due to various oxygen-rich functional groups (i.e., carboxy, carbonyl, hydroxyl and epoxy groups) on GO, it was dissolved easily in water, and presented negative charges in aqueous solution [27,28]. The amino group of silk fabric can be presented positive charges in acid aqueous solution. Therefore, the GO sheets are tend to absorb on the surface of silk fabric via an electrostatic interaction between the carboxy of GO and amino of silk. On the other hand, the graphene presented excellent electrical conductivity, it can absorb the UV rays at the range of 100–281 nm, reflected the UV rays of wavelength more than 281 nm, and exfoliated graphite oxide sheets possess amphiphilic properties with an edge-to-center distribution of hydrophilic and hydrophobic domains [29–31]. In this paper, the electrical conductivity, water repellent and anti-ultraviolet finishing of silk fabrics via GO repeatedly coating and chemical reduction method.

2. Experimental

2.1. Materials

The pure silk crepe de chine fabric was supplied from Shandong Huaxing Textile Co., Ltd, China. The fabric was cleaned by marinating in 2 g L^{-1} sodium carbonate and 2 g L^{-1} peregal O aqueous solution at 60 °C for 1 h, washed thoroughly with deionized water, and then dried at 60 °C in vacuum overnight. Single layer graphene oxide (GO, diameter 0.5–2 μm, thickness 0.8–1.2 nm, single layer ratio about 80%, and purity >99.8%) was bought from Nanjing XFNANO Materials Tech Co., Ltd, China. Sodium hydrosulfite, acetic acid and sodium acetate were purchased from sinopharm chemical reagent Co., Ltd, China, all of chemically pure grade.

2.2. Preparation of silk-RGO fabrics

GO surface modified silk fabric was performed by "dip-dry-reduced" method. GO solutions (2 g L^{-1}) were prepared by mixing single layer GO thin film with water in an ultrasound bath for 1 h below 30 °C. The silk fabrics were soaked in the GO solution (pH 4.10) at 20 °C for 60 min, and the liquor ratio for the weight of silk to volume of GO dispersion liquid was 50: 1. After drying at 80 °C for 2 h, the GO coated silk fabrics were immersed in an aqueous solution containing 5 g L^{-1} sodium hydrosulfite at 90 °C for 1 h to reduce the GO to RGO. Finally, the RGO coated silk fabrics were thoroughly rinsed in warm deionized water, and then drying at 60 °C for 12 h (as shown in Fig. 1). The sample surface modification with different times (1–9) of RGO was obtained (silk-1RGO to silk-9RGO) by repeating the same procedure mentioned in Fig. 1. One sample surface modification with GO (silk-GO, no treatment with sodium hydrosulfite) was also obtained for comparison with the silk-nRGO samples.

2.3. Testing and characterization

2.3.1. Scanning electron microscopy (SEM)

The surfaces of the original, GO-coated and RGO-coated silk fabrics were observed using a SU1510 scanning electron microscope (SEM, JEOL Ltd., Tokyo, Japan, operating at 10 kV) under 5000 magnifications.

2.3.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) spectra was carried out by a Kratos Axis Ultra HAS X-ray photoelectron spectroscopy (Kratos Analytical/Shimadzu Group Co., Japan) using an Al Ka as excitation source.

2.3.3. FTIR

Slik fabrics and GO thin film were characterized by FTIR with a Nicolet is 10 FTIR spectrophotometer (Thermo Electron Corporation, MA, USA).

2.3.4. Raman

Raman spectra of GO thin film were acquired with a Jobin Yvon Raman spectrometer (LabRAM HR Evolution UV/Vis/NIR) using 532 nm laser excitation.

2.3.5. Optical absorption spectroscopy

The optical absorption spectroscopy of GO solution was tested by a UV-1800 UV–vis spectrophotometer (Shimadzu Co. Ltd.).

2.3.6. Electrical surface resistance measurements

The electrical surface resistance of the samples was measured by a SZT-2A four-probe tester made by Suzhou Tongchuang Electronics Co. Ltd. The electrical surface resistance test range was 10^{-4} to 10^{5} Ω cm^{-1}.

2.3.7. Anti-ultraviolet properties measurements

The anti-ultraviolet properties which include Ultraviolet Protection Factor (UPF), transmission of UVA and UVB (T[UVA] and T[UVB] respectively) of original, GO-coated and RGO-coated silk fabrics were tested by a UV-2000F ultraviolet transmittance fabric analyzer from US Labsphere according to the Australian/New Zealand Standard AS/NZS 4399:1996.

2.3.8. Fabric porosity measurements

The silk fabrics photographed 40 magnifications by a DZ3 video zoom microscope (Union Co., LTD) and the fabric porosity was calculated by photoshop and Matlab soft-wares according to the references [32]. The mean fabric porosity was obtained by measuring 4 times for every sample.

2.3.9. Contact angle measurements

The contact angle of water was measured using the KRÜSS DSA100 Drop Shape Analysis System (KRÜSS GmbH, Germany), and the contact angle values were recorded after 3 s when the water drop began to still on the silk matrixes.