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Highly conductive and flexible silk fabric via electrostatic self assemble between reduced graphene oxide and polyaniline

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ABSTRACT

In this paper, an electroconductive silk fabric is fabricated by electrostatic self assemble of reduced graphene oxide (RGO) and polyaniline (PANI) under acid aqueous solution lower the isoelectric point (pI) of silk. The RGO coated silk fabric (silk-RGO) is prepared by self assemble graphene oxide (GO) sheets on the surface of silk, then the GO reduced to RGO, and aniline (ANI) self-assembled on the surface of silk-RGO in situ polymerization of PANI. The results show that the electrical conductivity of silk is mainly influenced by the composition of outermost layer, the ANI and GO concentration, ANI dipping time also contribute to the electrical conductivity of silk. When PANI self-assembled on the outermost layer of silk-RGO, a blue-green, high conductive and flexible silk fabric with a lower electrical surface resistance of 0.330 K cm^{-1} was obtained. The SEM shows that RGO sheets formed a thin film on the surface of silk, and PANI deposited on the surface of silk with nanowires. The Raman and FTIR-ATR spectra of silk-PANI and silk-RGO-PANI are presented PANI characteristic peaks, and the thermostability of self-assembled samples enhanced.

1. Introduction

The various sources of textile can be summarized into two categories: manmade and natural. Polyester and polyamide are the major component of man-made fiber, cotton, wool and silk are the most important part of natural fiber [1]. As a part of flexible and electrical conductive material, the electrical conductive textile is widely used for medical care and electronic skin [2]. The electrical conductive textile not only has the general properties of electric conduction, but also has excellent wearable, flexible, lightweight and foldable performance [3]. Among all of the textile fiber, natural protein fiber silk has particular aesthetic qualities, biocompatibility and biodegradability properties, is a good electrical conductive substrate material used for medical care and electronic skin.

The preparation methods of electrical conductivity textile materials include spinning, blending and functional finishing [4]. Functional finishing method is suitable for all kinds of yarns or fabrics. The flexible and high electroconductive yarns or fabrics can be produced by choosing the proper conductive materials and technology [5–7]. Electrostatic self assembly is a functional finishing method to prepare electroconductive textiles, which utilize electrostatic interaction between two opposite charged materials to self assemble on the surface of a textile. Graphene oxide (GO) and polyaniline (PANI) can be used for electroconductive functional finishing of yarns or fabrics [6–9]. Due to various oxygen-rich functional groups (i.e., carboxy, carbonyl, hydroxyl and epoxy groups) on GO and modified GO, it was dissolved easily in aqueous solutions, and presented electronegativity. The negative charges of GO sheets tend to be adsorbed with the amino group of silk under acid aqueous solution, and reduced to reduced graphene oxide (RGO) [10,11]. As a most promising and versatile conducting polymer, PANI contains amounts of primary and secondary amino groups. In situ polymerization of aniline on the surface of fabrics in a mixed bath is the usual method to fabrication PANI electroconductive textile [12,13]. How to resolve the interaction on self assemble process is a key issue, the GO/PANI self assemble method to fabricate electroconductive textile is a new research topic [14,15].

Recently, most research work about GO, PANI or GO/PANI nanocomposites have been reported the mechanical, thermal, electrical and bioimaging properties [16–18]. GO and PANI can be used to fabricate electroconductive paper and fabric [19], electrochemical capacitor [20], Li-ion batteries [21,22], supercapacitors under an applied electric field [23,24]. There are more reports on graphene and polyaniline composite conductive textile materials, a graphene, PANI and silicon rubber (binder) ethanol solution was spincoated onto the Lycra substrate under a speed of 2000 rpm for 25s and repeated for three times to form conductive thin films [25], a conductive and anti-UV PANI-GO-

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cotton fabric was successfully fabricated by coating GO nanosheet (not reduction) dispersion on fabric surface via vacuum filtration deposition method, and then the treated fabric was assembled with PANI by in-situ chemical polymerization process [6], a conductive GO-PANI-etched carbon fiber cloth was fabricated novel hybrid architecture by easily coating reduced graphene oxide (RGO, reduced by hydrogen iodide) sheets on polyaniline nanowire arrays grown on flexible nitrogen-doped carbon fiber cloth [24], a graphene and polyaniline (PANI) woven-fabric composite films was by in-situ electropolymerization [26]. The binder impaired the electrical conductivity and complicated the process, the unreduced GO influenced the electrical conductivity of GO/PANI composition fabric, and the hydrogen iodide reduction method will destroy the silk substrate. Here, we report a simple two-step self-assemble process to obtain RGO/PANI conductive silk fabrics, the RGO firstly self-assembled on the surface of silk fabrics, and then in situ polymerization self assemble of PANI on the surface of silk-RGO. And GO and PANI composites showed significantly synergetic effect, it can be increased capacitances, thermostability, electrical conductivity, and electrochemical cyclability [27,28]. The complex of GO and PANI can remedy the limitation of single inorganic GO or organic PANI, and shorten the distance of circuit [14]. Electroconductive silk fabric has particular biocompatibility and biodegradability properties, which may be a potential application in medical care. A high graphene electroconductive textile are used to dipping GO solution and reduced the GO to RGO for many times of dipping and reducing process [6]. Graphene high conductive fabrics are usually obtained through repeated "dipping-reduction" GO solutions [14]. Self assemble GO and PANI on the surface of silk fabric is a simple and easy way to fabricate high electrical conductivity textile [5,6].

In the present paper, our research group studied the dipping/sodium hydrosulfite reduction, brush coating/ultraviolet curing reduction and vacuum filtration deposition/hot press reduction method on RGO conductive cotton, wool and silk fabrics [29–31]. In consideration of the high electrical conductivity of graphene, the excellent deposition and homogeneous distribution performance of PANI, and the biocompatibility, flexible and portable of natural silk protein fiber, this paper was adopted GO and PANI as a complex conductive material for electroconduction fishing of silk fabrics with self assembly method. The GO was firstly coating on the surface of silk fabrics, and reduced the GO to RGO, then silk-RGO in situ polymerization of ANI by a process of self assemble in ANI, hydrochloric acid and ammonium persulfate mixed bath (the process are shown in Fig. 1). The highly conductive and flexible silk fabric is obtained by a simple two-step self-assemble between reduced graphene oxide and polyaniline. The combination of RGO with PANI self-assembled on the silk flexible substrate brings some intriguing properties in view of their synergistic effects. Furthermore, the biocompatibility, flexible and portable of silk are ensure the silk-RGO-PANI fabrics have a potential application in wearable, electronic skin, etc.

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 purchased from Nanjing XFNANO Materials Tech Co., Ltd, China. Aniline (ANI), ammonium peroxydisulfate, sodium hydrosulfite, hydrochloric acid (37%), acetic acid and sodium acetate were purchased from sinopharm chemical reagent Co., Ltd, China. All reagents were of chemical pure grade.

2.2. Preparation of silk-RGO

Silk-RGO was obtained by "dip-dry-reduced" method. 2 g L^{-1} of GO solution was prepared by dispersing single layer GO thin film in water ultrasound for 1 h. The silk fabrics were soaked in the GO solution (pH 4.10) at 20 °C for 1 h. The liquor ratio was 50 to 1. After drying at 80 °C for 2 h, the GO coated silk fabrics were allowed to immersed in an aqueous solution containing 5 g L^{-1} sodium hydrosulfite at 90 °C for 1 h. Finally, silk-RGO were thoroughly rinsed in warm deionized water, and then dried at 60 °C for 12 h.

2.3. Preparation of silk-RGO-PANI

Silk-RGO-PANI was obtained by in situ polymerization of aniline. Aniline (0.0025 mol) was added to 45 mL of 1 mol L^{-1} hydrochloric acid aqueous solution. Silk-RGO fabrics (3 × 3 cm^2) were soaked in the above solution and then stirred at 20 °C for 24 h. The polymerization was carried out at a temperature of 10 °C, 5 ml 0.5 mol L^{-1} ammonium peroxydisulfate solution dropwise added into the above aniline solution within 30 min. After 4 h, the silk-RGO-PANI was thoroughly rinsed in warm deionized water, and vacuum dried at 60 °C for 12 h. The PANI coated silk (silk-PANI) fabrics were obtained by the same method.

2.4. Testing and characterization techniques

Scanning electron microscopy (SEM) observation of the surfaces of the original, RGO-coated, PANI coated silk fabrics and PANI coated silk-RGO fabrics were carried out using a SU1510 scanning electron microscope (JEOL Ltd., Tokyo, Japan) under 2000 and 5000 magnifications. Silk fabrics uncoated and coated with GO, RGO, PANI and RGO/PANI were characterized by FTIR-ATR with a Nicolet iS10 FTIR spectrophotometer (Thermo Electron Corporation, MA, USA). Raman spectra were acquired with a Jobin Yvon Raman spectrometer (LabRAM HR Evolution UV/Vis/NIR) using 532 nm laser excitation. TGA/SDTA 851e (Mettler Toledo) was used for thermal analysis of silk, silk-GO,

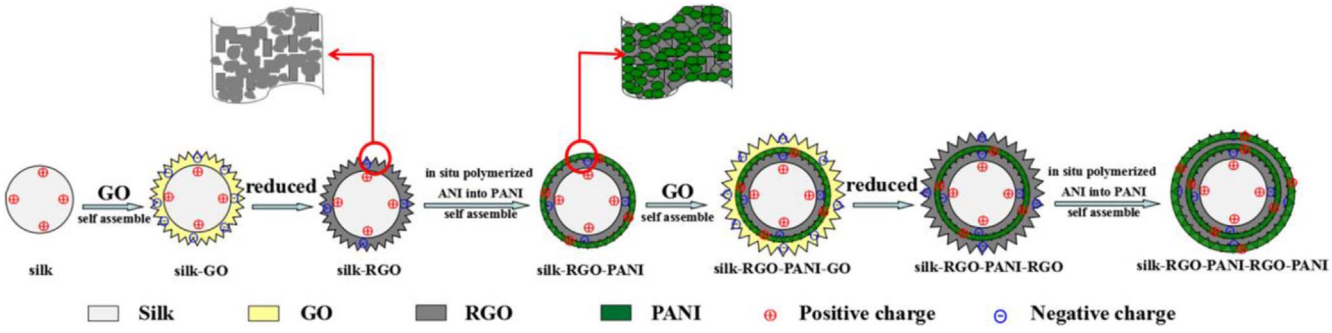

Fig. 1. Electrostatic self assemble of RGO and PANI on the surface of silk fabric.