Applied Surface Science 440 (2018) 177–185

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Natural printed silk substrate circuit fabricated via surface modification using one step thermal transfer and reduction graphene oxide

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ARTICLE INFO

Article history:
Received 28 October 2017
Revised 20 December 2017
Accepted 9 January 2018

Keywords:
Hot press transfer
Graphene
Silk
Electric conductive
Printed circuit

ABSTRACT

Graphene conductive silk substrate is a preferred material because of its biocompatibility, flexibility and comfort. A flexible natural printed silk substrate circuit was fabricated by one step transfer of graphene oxide (GO) paste from transfer paper to the surface of silk fabric and reduction of the GO to reduced graphene oxide (RGO) using a simple hot press treatment. The GO paste was obtained through ultrasonic stirring exfoliation under low temperature, and presented excellent printing rheological properties at high concentration. The silk fabric was obtained a surface electric resistance as low as 12.15 KΩ cm^{-1}, in the concentration of GO 50 g L^{-1} and hot press at 220 °C for 120 s. Though the whiteness and strength decreased with the increasing of hot press temperature and time slowly, the electric conductivity of RGO surface modification silk substrate improved obviously. The surface electric resistance of RGO/silk fabrics increased from 12.15 KΩ cm^{-1} to 18.05 KΩ cm^{-1}, 28.54 KΩ cm^{-1} and 32.53 KΩ cm^{-1} after 10, 20 and 30 washing cycles, respectively. The results showed that the printed silk substrate circuit has excellent washability. This process requires no chemical reductant, and the reduction efficiency and reduction degree of GO is high. This time-effective and environmentally-friendly one step thermal transfer and reduction graphene oxide onto natural silk substrate method can be easily used to production of reduced graphene oxide (RGO) based flexible printed circuit.

1. Introduction

Graphene has displayed as an important material in different fields due to its unique properties such as: high electric and thermal conductivity, multi-functionality, excellent mechanical properties and easy functionalization [1,2]. The field of textiles has obtained great development, modern textiles no longer considered as mere garments they required incorporate new functionalities. Graphene-based fabrics have been reported to have electric conductive, anti-UV performance, antimicrobial, flame resistance, water-repellency, etc. Among all the functionalities, electric conductive is the most concern topic [3,4]. Graphene-based conductive materials include graphene/polymer blended membrane, graphene coated polymer membrane, graphene/polymer electrostatic spinning film, graphene-based regenerated fiber and graphene-based fabric [5–8]. Graphene-based conductive fabric has become an issue in research due to the flexibility, high conductivity and durability, etc. [2,3,9].

Graphene-based conductive textiles are employed in antistatic materials, real-life applications, sensors for electrodes or strain, solar cells, flexible supercapacitive materials, electromagnetic shielding, etc. [3,10–14]. Mainly, three methods have been developed in bibliography for the production of graphene-based fabrics/yarns. The first one is coating of graphene oxide (GO) on the surface of fabrics or yarns by dipping, padding, brushing, filtration deposition, etc. [10,11,15]. The second one is using CVD method deposition of graphene on a Cu mesh, and then removed by an acid treatment, after this process only the graphene fabric structure remained [16–18]. And the third one is printing GO or graphene paste on the surface of fabrics to obtained subtle pattern designs [19–21]. Coating GO on the surface of fabrics is the most widely adopted method due to its easy application. As well, the GO is cheaper than graphene and can be synthesized in larger scale due to the chemical oxidation process methods. In addition, the

Abbreviations: GO, graphene oxide; RGO, reduced graphene oxide; RGO/silk, GO hot press transfer printed silk fabric; SEM, scanning electron microscopy; FTIR-ATR, Fourier transform infrared attenuated total reflectance spectroscopy.

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https://doi.org/10.1016/j.apsusc.2018.01.094
0169-4332/

negative charges of GO tend to interact with the hydrophilic groups of the fiber, thus increasing the absorption and fixation of GO on the surface of fabric [10,15,22,23]. What's more, its conductivity can be partially restored after reduction of GO to reduced graphene oxide (RGO) [23,24].

Coating GO on the surface of fabrics is the most widely adopted method to obtain graphene-based conductive textiles, however a conductive circuit requires a printing method [20]. Inkjet printing, screen-printing and transfer printing method is suitable to obtain graphene-based conductive circuit textiles [19–21]. Inkjet printing is proved to be an effective method to prepare graphene-based conductive circuit textiles by functionalized graphene nanoplatelets ink [19,25]. Screen-printing method has recently been reported to pattern graphene onto woven cotton textiles [20]. Transfer printing has been widely reported to prepare electric conductive Si/SiO_2 patterned substrate materials by transfer printing of graphene films which deposition on Cu foils to the Si/SiO_2 substrate [17,26,27]. It is well known that the hot press transfer printing process offers very high transfer efficiency and fine pattern, has been used to print polyester, modify cotton or silk fabrics. There is a strong affinity between disperse dyestuffs and polyester or hydrophobic modified natural fibers in hot pressing process [28,29]. Silk fabrics are lightweight and have a smooth surface, hard to printing fine pattern, so hot press transfer printing is an appropriate choice for printing silk fabrics.

In a previous study, we were successfully obtained RGO conductive silk fabrics via the dipping and sodium hydrosulfite reduction method [10]. This method was required reduction of GO on the surface of silk fabrics by chemical reductant and repeatedly dipping-reduction treatment. In the present work, a flexible printed circuit was fabricated by a hot press transfer method to pattern RGO onto the surface of silk fabrics. First, a high concentration GO paste was screen-printed on the surface of transfer paper, and then the GO transferred from transfer paper to the surface of silk fabrics by hot press process with migration mechanism and the printed GO reduced to RGO at the same time (Scheme 1). As a consequence of the strong interaction between the carboxy, hydroxyl or epoxide groups of GO and the amino groups of silk fibers, excellent washability was achieved. Furthermore, the hot press process not only transferred the GO from transfer paper to the surface of silk fabrics, but also thermal reduced vast majority of GO to RGO with no chemical reductant.

2. Experimental

2.1. Materials

The pure silk 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. Sodium hydrosulfite ($Na_2S_2O_4$), acetic acid (CH_3COOH), sodium acetate (CH_3COONa), sulfuric acid (H_2SO_4), sodium nitrate ($NaNO_3$), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2) and hydrochloric acid (HCl) were purchased from sinopharm chemical reagent Co., Ltd, China, all of chemically pure grade.

2.2. GO preparation

GO was prepared from graphite flakes according to the improved ultrasonic Hummers GO synthesis method. Concentrated H_2SO_4 (23 mL) was drop-casted into a flask with 1 g graphite flakes, 0.5 g $NaNO_3$ and 3 g $KMnO_4$. The mixture was ultrasonic stirred for 1 h at 5 °C. Then the reaction system was ultrasonic stirred at 35 °C for 0.5 h in an oil bath. 46 mL deionized water was dropwise added into the mixture with constantly ultrasonic stirring, and the temperature was hold on 35 °C for 0.5 h after the deionized water dripped off. Then the system was cooled down to 25 °C and poured into 20 mL 3% H_2O_2 solution. The color of the mixture turned golden indicated the removal of residual $KMnO_4$. The mixture was purified by washing in succession with deionized water and centrifugation. The GO dispersion was centrifuged at 4000 rpm for 10 min to remove unexfoliated GO. And then the exfoliated GO supernatant was centrifuged at 8000 rpm for 30 min to separate the GO from the solution. The final centrifugal sediment was freeze dried to obtain the GO powder.

2.3. Preparation of GO paste

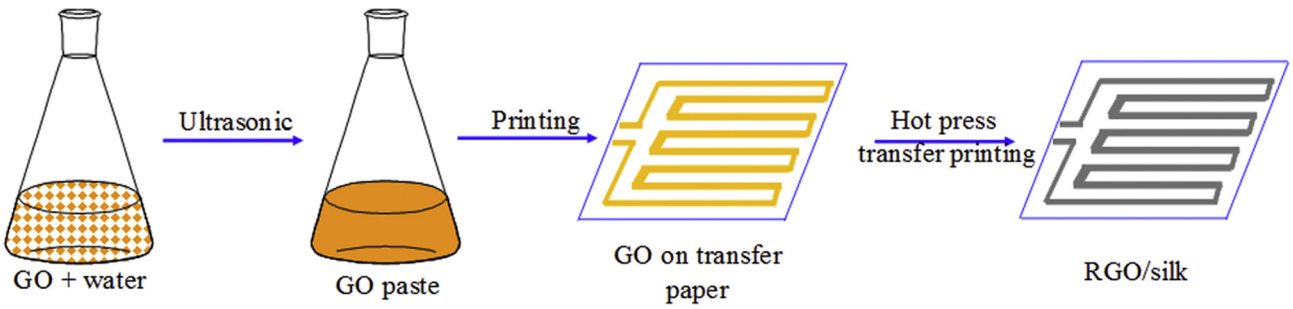
In order to prepare the GO paste, GO powder (1.00 g, 1.75 g, 2.50 g) and deionized water (50 mL) were added into three glass bottles. The pH value of GO solution was adjusted by CH_3COOH and CH_3COONa to 4.10. The mixture was then ultrasonic 5 h at 10 °C, and stirring the GO solution constantly to obtain a thick GO paste.

2.4. GO paste printing of transfer paper

Superfine uncoated smooth transfer paper of 100 g m^{-2} was printed using the prepared GO printing paste by the silk screen technique.

2.5. GO hot press transferred from transfer paper to silk fabrics

Manual heat transfer press manufactured by Shanghai Yatai Instrumentation Co., Ltd was used. Samples of silk fabrics was covered with transfer paper, hot press transfer printing of the silk fabric was carried out at 190–230 °C for 0–240 s. The GO paste was not only transferred from transfer paper to the surface of silk fabrics, but also reduced to RGO through this hot press process.



Scheme 1. Illustration of the hot press transfer printing of GO on the surface of silk fabrics.