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Full Length Article

Functionalization of cotton fabrics through thermal reduction of graphene oxide

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ABSTRACT

Graphene oxide (GO) was in-situ reduced on cotton fabrics by a simple heat treatment, which endowed cotton fabrics with multi-functions. GO was coated on the surface of cotton fabric through a conventional "dip and dry" approach. Reduced graphene oxide (RGO) was obtained from GO in the presence of cotton by heating under the protection of nitrogen. Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy, Raman spectroscopy and scanning electron microscopy were employed to characterize the complexes of RGO and cotton (RGO/cotton). The RGO/cotton fabrics showed good electrical conductivity, surface hydrophobicity and ultraviolet (UV) protection properties. These properties did not deteriorate significantly after repeated fabric bending and washing.

1. Introduction

Functional textiles with electrical conductivity, hydrophobicity, antibacterial and ultraviolet (UV) protection properties have attracted great attention in recent years [1–8]. Several strategies have been developed to fabricate conductive textiles. For example, carbon nanotubes (CNTs) have been used as a promising candidate for fabricating conductive textile composites [9,10]. Besides, electrical textiles were prepared through in-situ chemical polymerization of polypyrrole and polyaniline on cotton fabrics [11–13].

Cotton is the predominant natural fiber in the textile industry because of its natural softness, high hygroscopicity, superior wear comfort and skin-friendliness. Nevertheless, cotton fabrics exhibit weak UV protection and low electrical conductivity [14–16], which limits the application of cotton in different fields. Moreover, functional modification of cotton fabric is one way to add value and satisfy the increasing needs from consumers [17–22]. The abundant hydroxyl groups on the surface of cotton provide active sites for functionalization of fibers with particular additives. Graphene, as a two-dimensional carbon nanomaterial, has received tremendous attention owing to its outstanding mechanical, thermal, optical, electronic properties [23,24]. Graphene as one of carbon materials possesses high electrical conductivity. Modification of cotton substrate based on graphene can impart conductivity to the substrate materials [25,26].

However, graphene synthesized using chemical method contains few polar groups, which limits the application of graphene in textiles due to weak bonding force with fibers. Graphene oxide (GO) is a functionalized derivative of graphene, with a large number of polar groups that can easily bind with fiber surfaces [27–29]. GO is hydrophilic and can readily disperse in water. Various reduction methods such as thermal and chemical reduction were developed to restore its electrical conductivity [30–33]. RGO has been used in textile field to develop the functionalization of cotton fabrics. Surface coating of graphene or graphene composites rendered textiles with different functions, including electrical conductivity, thermal conductivity, UV blocking and hydrophobicity [34–39]. It was reported that reducing agents including hydrazine hydrate, sodium borohydride and ascorbic acid could reduce GO to graphene. Although effective in reducing graphene oxide, most of these methods are complex and may result in pollution of environment because of the toxicity of some reducing agents. Thus, it is important to explore environment friendly reduction methods of GO.

In this study, the functionalization of cotton fabric was realized by in-situ thermal reduction of GO adsorbed on cotton. Combination of cotton and GO was achieved by a conventional "dip and dry" approach. The GO on cotton fabrics was reduced. Reduced graphene oxide (RGO) was obtained from reduction of GO on cotton by heat in nitrogen atmosphere. The coating of RGO on cotton imparted dif-

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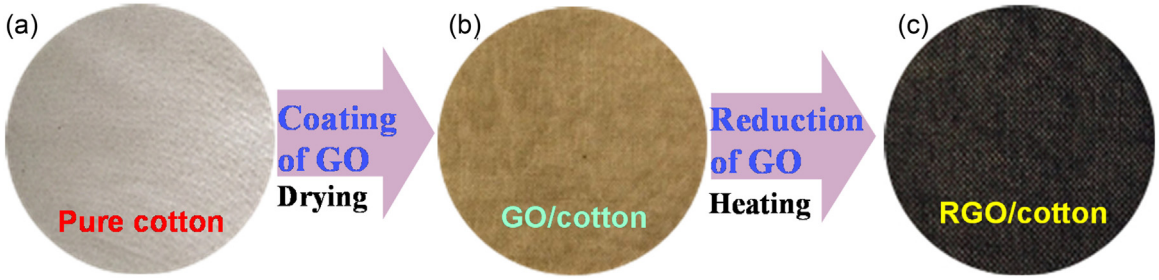

Fig. 1. Preparation process of RGO/cotton and photos corresponding to (a) pure cotton, (b) GO/cotton and (c) RGO/cotton.

ferent functions to cotton fabrics, such as electrical conductivity, ultraviolet blocking and hydrophobicity.

2. Experimental

2.1. Materials

White plain weave cotton fabrics (120 g·m^{-2}), with 125 picks (thread/cm) in weft direction and 115 ends (thread/cm) in warp direction, were used in this study. Graphene oxide (GO) nanosheets with a thickness of 0.8-1.2 nm and two-dimensional length of 0.5–5 μm were provided by Nanjing Xianfeng Nano Science and Technology Ltd, China. Sodium hydroxide (NaOH) was purchased from Chengjie Chemical Reagent Co., Ltd. All chemicals were of analytical grade and used without further purification.

2.2. Instruments

Scanning electron microscopy (SEM) measurements were performed with a Supra 55 VP field emission SEM. Fourier transform infrared (FTIR) spectra were collected on a FTIR spectrometer (Tensor 27, Bruker, Germany) at attenuated total reflectance (ATR) mode. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM800 XPS system with Kα source and a charge neutralizer. Raman analysis was performed on a Renishaw inVia Raman microscope system (Renishaw plc, Wotton-under-Edge, UK). A 50×/N.A. 0.75 objective and a 785-nm near-IR diode laser excitation source (500 mW, 100%) were used in all measurements. Raman spectra were recorded using a mounted CCD camera with integration time of 20 s by single scan. The surface-wetting properties of untreated and RGO/cotton fabric surfaces were evaluated by measuring static water contact angles using a JY-PHb contact angle system at room temperature (25 °C). UV protection factor (UPF) of fabrics was obtained by UV spectrophotometer (HD902C). The surface electrical resistivity of different fabric samples was measured by OHM-STAT RT-1000 digital surface electrical resistivity tester.

2.3. Preparation of RGO/cotton fabric

The preparation process of the RGO/cotton fabric is illustrated in Fig. 1. GO nanosheets in water were sonicated for 30 min at room temperature and a stable GO suspension was obtained. Cotton fabric was soaked in 1 mol L^{-1} hot NaOH solution (80 °C) for 1 h and then rinsed with abundant water. Subsequently, the fabric was dried for 24 h in vacuum. Cotton fabric samples (4 × 4 cm) were dipped into graphene oxide suspensions with different concentrations (0.4, 0.7 and 1.0 mg L^{-1}) and kept in solution for 2 h at 60 °C under sonication. Brownish yellow cotton fabric samples with GO were obtained after drying at room temperature. Three cycles of "dip and dry" were performed to prepare GO coated cotton fabric (GO/cotton). RGO/cotton fabric was obtained by heating RGO/cotton fabric at different temperatures (160, 200 and 250 °C) for 2 h in nitrogen atmosphere. The detailed conditions for preparation of samples are listed in Table 1.

Table 1
Treatment conditions for different fabrics.

Sample ID	GO concentration (mg ml^{-1})	Heating temperature (°C)
GO—C-07	0.7	/
RGO—C-04-200	0.4	200
RGO—C-07-160	0.7	160
RGO—C-07-200	0.7	200
RGO—C-07-250	0.7	250
RGO—C-10-200	1	200

2.4. Durability test to washing

In the present work, water washing durability test of the obtained RGO/cotton fabric was carried out according to AATCC Test Method 61–2006. A standard color-fastness to washing laundering machine (Model SW-12AII, Wenzhou Darong Textile Instrument Co., Ltd., China) was used in a washing procedure. The RGO/cotton fabric (5 × 10 cm) was washed in a rotating closed canister containing 200 mL of detergent aqueous solution (0.37 wt%) and 10 stainless steel balls. The properties of RGO/cotton fabric including electrical conductivity, UV protection ability and hydrophobicity were evaluated after water washing, respectively.

3. Results and discussion

3.1. Preparation and characterization of RGO/cotton fabrics

The pure cotton fabric samples changed to brownish yellow from white after the samples were dipped into graphene oxide suspension and dried in a vacuum oven (Fig. 1a and b). The color change implies that GO nanosheets were adsorbed to the fabrics. The GO coated cotton fabric samples were heated under the protection of nitrogen and the color of fabrics converted into black from brownish yellow (Fig. 1c), which may be due to production of RGO from GO on cotton during heat treatment.

SEM was employed to observe the morphologies of different samples. Fig. 2a displays SEM image of GO used for treatment of cotton. The laminar structure of the GO was easily visible in the SEM image (Fig. 2a). No observable impurities were found on the surface of untreated cotton fibers (Fig. 2b). After cotton fabrics were treated with GO, laminar layers were observed clearly to affix on the surface of cotton fibers from the SEM images (Fig. 2c and d), which indicates that GO nanosheets have been successfully assembled around cotton fibers. The laminar structures were still seen on the surface of cotton fibers after the GO sheets were reduced by heat treatment (Fig. 2e and f). The RGO nanosheets remained attached on cotton fiber though thermal reduction was performed,