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Functionalization of cotton fabric with graphene oxide nanosheet and polyaniline for conductive and UV blocking properties

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ABSTRACT

Multifunctional cotton fabric with high electrical conductivity and ultrastrong UV radiation protection properties was successfully fabricated by coating graphene oxide (GO) nanosheet dispersion on fabric surface via vacuum filtration deposition (VFD) method, and then the treated fabric was assembled with polyaniline (PANI) by in-situ chemical polymerization process. The structure and morphological studies showed that the deposition of GO nanosheet is benefit to enhance the uniformity of aniline polymerization on the surface of PANI-GO-cotton fabric. Furthermore, the electrical resistivity of PANI-GO-cotton decrease approximately 10^6 times compared with control cotton, reached at 48.35 Ω cm. PANI-GO-cotton also performed ultrastrong UV radiation protection ability with a UPF value of 445.21, which is superhigher than that of control fabric (UPF rating at 6.86). Moreover, even repeated 10 times water laundering showed nearly no effect on electrical conductivity and UV radiation protection efficiency.

1. Introduction

Among the various intrinsically conductive polymers, polyaniline (PANI) is promising in both industrial and academic applications due to its good conductivity, easy synthesis, environmental stability, relative low cost and interesting redox properties [1–3]. Recently, inorganic nanoparticles incorporated polyaniline nanocomposite materials has attracted much interest worldwide because of the improved stability, conductivity and unique optical properties, etc. [4–8]. Especially, metal nanoparticles based polyaniline nanocomposites can be synthesized by simple and efficient methodologies to meet the expanding market of polymer nanocomposites. For instance, Savitha et al. [9,10] prepared PANI–TiO_2 (anatase) nanohybrid with low electrical resistance from $TiCl_4$ as precursor for Titania by a simple and facile one-pot method. Wanget al. [5] synthesized PANI–ZrO_2 nanocomposites by in-situ chemical deposition technique in the presence of hydrochloric acid (HCl) as dopant, simultaneously adding the nano-sized grade powder of ZrO_2 into the polymerization reaction mixture of aniline monomer. Furthermore, some improved PANI/inorganic nanocomposites with multifunctional properties such as PANI–ZnO, PANI–Fe_3O_4, PANI–NiO and PANI–MnO_2 also have been prepared and described in the published literature [11–16].

Different synthetic approaches are possible for the fabrication of nanoparticles incorporated polyaniline nanocomposites such as in-situ chemical polymerization, vapor phase deposition, electrochemical, oxygen plasma treatment, UV-induced polymerization, interfacial polymerization technique and graft copolymerization, etc. [17–20]. In-situ chemical polymerization performs several advantages over other method in the synthesis of nanoparticles incorporated polyaniline nanocomposites, such as eco-friendly, simplicity, lower cost, more homogenous mixing of the inorganic components and better control of the nanocomposites properties. Especially, aniline monomer is soluble in ethanol solution and can be deposited on fabric surface with in-situ chemical polymerization method, which is gentle to fabric substrate. Thus preparation

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of nanoparticles incorporated polyaniline nanocomposites via in-situ chemical polymerization method was widely used in the fabrication of polyaniline based functional textiles. For example, Zhao et al. [6] synthesized a conductive network consisting of PANI–ZnO nanocomposites immobilized on the surface of polyester fabric by in-situ chemical oxidative polymerization treatment. Saini et al. [7] prepared the coated fabric with improved electromagnetic interference shielding response ability by in-situ chemical polymerization and incorporation of magnetic nanoparticles, such as $BaTiO_3$ or Fe_3O_4 in polyaniline matrix.

Graphene is a two-dimensional form of graphite and has recently gained intense interest due to its outstanding mechanical, thermal, optical, electronic, and excitonic properties [21,22]. Graphene oxide (GO) nanosheet is the functionalized derivative of graphene, with a large number of hydrophilic functional groups on the surface, the electrical insulation of GO nanosheet resulting from the oxygen atoms conjugate structure limited its application in electronic area [23,24]. However, with better solubility and dispersion, it is accessible to combine GO nanosheet with polyaniline (PANI) or other organic polymer [25–27]. Also some researchers recently reported the excellent antibacterial activity and UV radiation protection property of GO nanosheet [28–30]. Therefore, PANI-GO becomes a suitable candidate for the fabrication of functional textiles by in-situ chemical polymerization method. The significant advantages of GO nanosheet incorporated PANI nanocomposites for the preparation of functional textiles are not only the excellent UV radiation protection ability, but also the presence of PANI can overcome the electrical insulation shortcoming of GO nanosheet [31]. It has also been reported that with various functional groups such as carboxyl, carbonyl and hydroxyl, epoxyl groups, which makes GO nanosheet to be readily soluble in water at molecular levels and resulting in adhering strongly onto the cotton fabric surface. Moreover, the partially hydrazine reduction procedure of PANI polymerization for GO nanosheet has also been investigated, which is benefit to increase the electrical conductivity of PANI-GO granular nanocomposites conductive network [32,33].

Herein, in the present work, we report the facile fabrication of PANI-GO-cotton fabric using vacuum filtration deposition (VFD) process and in-situ chemical polymerization, then the structures of control cotton, GO-cotton, PANI-cotton and PANI-GO-cotton were characterized by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM), etc. Moreover, the electrical conductivity and UV radiation protection properties of nanocomposites coated cotton fabric was measured, and the mechanism was further investigated.

2. Experimental

2.1. Materials

Graphite powder was purchased from Huadong Graphite Factory, China. All other materials including sulfuric acid (H_2SO_4, 98%), hydrochloric acid (HCl, 37%), potassium permanganate ($KMnO_4$, 99.99%), sodium nitrate ($NaNO_3$, 99.99%), hydrogen peroxide (H_2O_2, 30%), sodium hydroxide (NaOH, 99.99%), ethanol (CH_3CH_2OH, 96%), aniline (An, C_6H_7N, 98%) and ammonium persulfate (APS, $(NH_4)_2S_2O_8$, 99.99%) were supplied by National Medicine Group, Shanghai, China. Desized, scoured and bleached 100% woven cotton fabric was used as the substrate and distilled water was used in the preparation of all solutions.

2.2. Synthesis of GO nanosheet

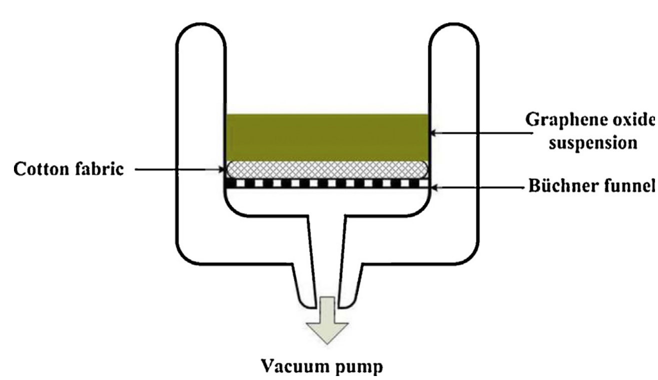
In this scenario, graphene oxide (GO) nanosheet was synthesized from graphite powder by the modified Hummer's method. Briefly, concentrated H_2SO_4 was added into a 250 mL flask filled with graphite in an ice bath, followed by the addition of $NaNO_3$, and then solid $KMnO_4$ was gradually added with stirring. 10 min later the ice-bath was removed and the system was heated at 35 °C for 30 min. Subsequently, excess distilled water was slowly added into the system and was stirred for another 30 min. Then 80 mL of hot water with 70 °C and 3% H_2O_2 aqueous solution were added to reduce the residual $KMnO_4$ until there was no gas being produced. The mixture was filtered and washed 3 times with 5% aqueous HCl to remove metal ions and then washed with distilled water to remove the remained acid. A homogeneous suspension is collected after filtering the trace black residues and GO nanosheet powder was obtained after freezing and drying of the suspension.

2.3. Preparation of GO-cotton fabric

To begin with, sodium hydroxide (NaOH) was taken as the preferred alkali for alkaline treatment, which was considered as an efficient method to increase GO nanosheet deposition and polyaniline polymerization on cotton fabric surface. In details, the specimens of woven cotton fabric were treated with sodium hydroxide solution of 2% (w/v) at the temperature of 85 °C for 30 min in liquor ration of 1:40. The vacuum filtration deposition (VFD) fabrication method was performed according to the literature reported by Zhang et al. [34], which was inspired by the VARTM (vacuum assistant resin transfer molding) used in composites manufacturing industry. In this study, vacuum filtration deposition was used to disperse the GO nanosheet aqueous solution (concentration of 5 mg/mL) into the cotton fabric surface to fabricate GO-cotton fabric, and the deposition process as illustrated in Scheme 1. The treated cotton fabric was subsequently dried at 60 °C for 30 min, and the obtained fabric was coded as GO-cotton.

2.4. Preparation of PANI-GO-cotton fabric

The GO-cotton fabric specimen without crease were immersed in a bottle containing 20 mL aniline monomer and 80 mL anhydrous ethanol for 90 min. Afterwards, a homogeneous padder was used to control the weight of fabric with the wet pick up of 120%. Then required amounts of ammonium persulfate (APS) at 1:1 molar ratio with aniline, and chlorhydric acid (HCl) at 1:0.5 molar ratio with aniline were added into aqueous solutions. The polymerization procedure was performed in the aqueous solutions at the temperature of 20 °C for another 120 min, thus nanocomposites coated cotton fabric was obtained and coded as PANI-GO-cotton. Also the cotton fabric specimen without vacuum filtration deposition of GO nanosheet aqueous dispersion was treated via the above mentioned in-situ chemical polymerization



Scheme 1. Schematic of graphene oxide (GO) coated cotton fabric fabricated by vacuum filtration deposition process (VFD).