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Integrating high electrical conductivity and photocatalytic activity in cotton fabric by cationizing for enriched coating of negatively charged graphene oxide

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ABSTRACT

Electroconductive textiles have attended tremendous focus recently and researchers are making efforts to increase conductivity of e-textiles, in order to increase the use of such flexible and low cost textile materials. In this study, surface conductivity and photo catalytic activity of standard cotton fabric (SCF) was enhanced by modifying its surface charge, from negative to positive, using Bovine Serum Albumin (BSA) as a cationic agent, to convert it into cationised cotton fabric (CCF). Then, both types of fabrics were dip coated with a simple dip and dry technique for the adsorption of negatively charged graphene oxide (GO) sheets onto its surface. This resulted in 67.74% higher loading amount of GO on the CCF making self-assembly. Finally, this coating was chemically converted by vapor reduction using hydrazine hydrate to reduced graphene oxide (rGO) for restoration of a high electrical conductivity at the fabric surface. Our results revealed that with such high loading of GO, the surface resistance of CCF was only 40 Ω/sq as compared to 510 Ω/sq of the SCF and a 66% higher photo catalytic activity was also achieved through cationization for improved GO coating. Graphene coated SCF and CCF were characterized using FE-SEM, FTIR, Raman, UV–vis, WAXD, EDX and XPS spectroscopy to ascertain successful reduction of GO to rGO. The effect of BSA treatment on adsorption of cotton fabric was studied using drop shape analyzer to measure contact angle and for thermal and mechanical resistance, the fabric was tested for TGA and tensile strength, respectively. rGO coated fabric also showed slightly improved thermal stability yet a minor loss of strength was observed. The high flexibility, photocatalytic activity and excellent conductivity of this fabric suggests that it can be used as an electrode material for various applications.

1. Introduction

Textiles have always been thought of as insulating materials; however, energy harvesting using electrically conductive textiles (e-textiles) have emerged as a promising field. Various techniques have been used to integrate electrical conductivity to the fabric. For instance, electrodepositing of gold and silver nanoparticles inside the microstructure of textile fibers (Pasta, Hu, La Mantia, & Cui, 2012), using of metallic fibers during fabric manufacturing and chemical metallization of the fibers (Akbarov et al., 2006). However, these techniques come at the cost of reducing the required flexibility of the fabric. On the other hand, other techniques such as extrusion of fibers with conducting particles, such as carbon derivatives, and synthesis of conducting polymer films on the fabric (Kaynak, Najar, & Foitzik, 2008) does not provide highly conductive textile materials. Therefore, impregnating textiles with materials like intrinsically conducting polymers, carbon nanotubes, graphene or metal based powders are being seen as alternatives (Hu et al., 2010; Molina, del Río, Bonastre, & Cases, 2008; Molina, Fernández, del Río, Bonastre, & Cases, 2013). Especially, graphene has attracted attention as a promising material in a wide range of applications due to its high surface area, chemical and thermal stability, conductivity, mechanical strength, and flexibility. However, during any impregnating technique, the surface of the cotton fabric carries a very important role in deciding the type and effect of interaction between the fabric and dissolution or suspension particles. Pretreatment of cotton fabric with cationic agents has been reported to enhance the uptake of anionic dyes in the textile dyeing industry by changing the surface characteristics of cotton fabric (Uğur & Sarıışık, 2011).

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Cationic agents react with cotton to impart cationic sites on cotton fabric by forming ether linkages with cellulosic fibers; the resultant is a cationized cotton fabric (CCF) carrying positive surface charge (El-Molla, Badawy, AbdEl-Aal, El-Bayaa, & El-Shaimaa, 2011). However, no efforts seem to have been made to study the effect of cationization on the adsorption interaction of Graphene oxide (GO) sheets on the surface of cotton fabric as both (cotton fabric and GO) show a negative surface charge in aqueous solution. However, in order to functionalize the low cost and flexible cotton fabric, it is important to develop methods for higher loading of GO to increase efficiency of the material in various applications. Therefore, it is necessary to study this interaction for enhanced loading of GO and increasing electrical conductivity and photocatalytic activity of the textile fabric.

2. Experimental

2.1. Materials

Graphite powder was purchased from Asbury Carbons (USA) (particles size < 100 μm). All the other chemicals including, sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), hydrogen peroxide (H_2O_2), hydrochloric acid (HCl), Bovine Serum Albumin (BSA) and hydrazine hydrate (N_2H_4) were purchased from Sigma-Aldrich (USA). De-ionized (DI) water, used throughout the experimental work, was purified by Puris® system. For reproducibility, standard cotton fabric (SFC) (ISO 105/F) was used and obtained from Korean Apparel Testing and Research Institute (KATRI). Briefly, it was 100% cotton woven fabric, weight of the fabric was 115 g/m^2 with warp 35 cm^{-1} and weft 31 cm^{-1}, desized, scoured and bleached with a wetting time of less than 3 s and a pH of 7.0. To remove any foreign material off the fabric, it was maintained in 0.5 M NaOH solution for 30 min, rinsed with plentiful DI water and then dried at 60 °C for 1 h. BSA is a protein and is pH sensitive because of its electrophoresis movement in aqueous media. The isoelectric point (p*I*) of BSA is 4.9, below which it shows positive surface charge and above its p*I*, it behaves negatively charged (Anirudhan, Tharun, & Rejeena, 2011). Hence, it can attach to both negatively and positively charged surfaces depending upon the working pH.

2.2. Synthesis of graphene oxide

GO was synthesized from graphite powder by the modified Hummer's (Hummers & Offeman, 1958) method in two distinct oxidation and filtering phases. During the oxidation phase, 5 g of graphite powder was added to 200 mL of concentrated H_2SO_4 in an ice bath with continuous stirring for 30 min. $KMnO_4$ (25 g) was added slowly at temperature no higher than 10 °C and was left stirring for next 30 min. Later, the mixture was allowed to react at 35 °C for about 6 h with vigorous stirring. To stop the reaction, the temperature was dropped to 10 °C with the use of ice, and 250 mL of D.I water was added very slowly. During the addition of water, the temperature was kept less than 55 °C. Afterwards, 5 mL of H_2O_2 (30%) was added and then, the mixture was stirred for 30 more min. Then, this mixture was kept for 2 h followed by rinsing the supernatant during the filtering phase, with 0.5 L of 10% HCl and then 0.5 L water. At that time, 250 mL of water was added to the resulting product to form dispersion. The GO was bath sonicated for 30 min. Removal of unexfoliated GO sheets was done by centrifugation of the solution for 5 min at 10,000 rpm. Finally, dialysis of the solution was realized to remove the inorganic ions in the suspension.

2.3. Modifying surface charge of cotton fabric

For the surface charge modification of cotton fabric, 0.15 g/L BSA powder was dissolved in DI water. BSA is a low molecular weight protein and is readily soluble in water. Cotton fabric was soaked in BSA solution for 5 min at room temperature and then dried at 60 °C for 30 min. Finally, the BSA functionalized fabric was washed three times to remove any residuals.

2.4. Coating graphene oxide on cotton fabric

For adsorption of GO sheets onto CCF, a 0.1% solution of GO was diluted from the stock solution and bath sonicated for 30 min. The pH of GO solution was 2.0 and the zeta potential at this stage was −22 mV. Fabric was soaked in that solution for 30 min at 80 °C, making it easier for GO sheets to bind on the surface of fabric by evaporating liquids of the dispersion slowly. It is of importance at this stage that temperature does not escalate beyond 80 °C, which would otherwise start thermal reduction of GO sheets and hinder its adsorption on cotton fabric. There was no significant change found to both pH and zeta potential of the solution after the dipping cycles. Then, GO coated CCF (CCF-GO) was kept for drying in oven at 80 °C for 30 min and this process was repeated to increase the loading of GO sheets on the fabric. Finally the samples were washed by DI water three times to remove any unattached GO sheets. Here, negatively charged GO sheets were chronically mustered on the surface of now positively charged cotton fabric until they covered the entire surface. For comparison SCF was also coated with GO sheets in the same manner to make SCF-GO.

2.5. Preparing graphene-coated cotton fabric

CCF-GO and SCF-GO were chemically reduced using hydrazine hydrate vapors to convert coated GO to rGO. Briefly, 0.1 M hydrazine hydrate solution was heated to boil and the fabric was treated with vapors only for 30 min inside a sealed flask. To eradicate the excessive amount of reducing agent from the surface of fabric, it was washed with plentiful amount of deionized water until the pH of washing water becomes neutral. Afterwards, the resulting graphene-coated CCF-rGO and SCF-rGO were dried at 100 °C in oven for 30 min. At this stage, it was important to dry the fabric at more than 90 °C so that all the liquid evaporates leaving behind converted conducting graphene.

2.6. Characterization

The surface charge (zeta potential) of the SCF, BSA molecule, CCF and GO was examined using HM-30G pH meter from DKK-TOA corporation, Japan. To measure the amount of GO loading on standard and BSA functionalized cotton fabric, OHAUS Explorer E00RR80 Precision Balance Scale was used. Visual examination for the amount of GO on the cotton fabric was carried by the help of digital photographs taken using software equipped Camscope ICS-305B, Sometech Co. Surface morphology and the elemental analysis, through energy dispersive X-ray photoelectron spectroscopy technique (EDX), of the fabrics was investigated by Field Emission-Scanning Electron Microscopy (FE-SEM) model, (JEOL JSM-6700F) after a very thin coating of Platinum on the samples by sputtering and at accelerating voltage of 15 kV. Fourier Transform Infrared (FTIR) spectra were recorded by using the Nicolet^{TM} iS^{TM} 10 FT-IR spectrometer from Thermo Fisher Scientific Inc, USA. All the samples were tested with ATR mode. The Raman spectra were measured using a Raman microscopy system (NRS-3100, JASCO, Japan). Intensities of carbon and oxygen functional group peaks, at the surface of fabric were measured through X-ray photoelectron spectroscopy (XPS) using Multilab ESCA 2000 system VG from