Localization of Conductivity towards Scalable and Sustainable Wearable Electronics

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Abstract:
Localized conductivity on fabrics is envisioned to make a shift in sustainable wearable electronics. Among the wearable electronics, localized conductivity has not been widely reported yet. Hence, we report a simple way to localize conductivity on polyester fabrics using reduced Graphene Oxide (rGO). Coupling agent, (3-aminopropyl) triethoxysilane (APTES) was used to change the chemically dormant nature of polyester fabrics, which made easy networking with GO. Then, the GO coating was substantially reduced to rGO, accomplishing conductive tracks on fabrics. rGO coated fabric showed a surface resistivity of 320 Ω. Even after 20 washing cycles, a significant change in surface resistivity was not observed which signifies a good wash fastness. APTES created a covalent bond network between rGO and polyester, which was proven by FTIR. This cost effective and sustainable method endows the electronic textile industry with a rapid improvement towards scalable production.

Keywords: Localized conductivity; Surface coating; Reduced graphene oxide; Silane; Polyester fabrics
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1. Introduction

Today, the progress of electronics and computer technologies are inexorable. Simultaneously, the society has become more dependent on technology. The advancement of technology has encompassed human life immensely, that we are now a slave to it and it necessitates us to keep these technologies as close to us as possible all day long. To suffice this, one can only think of clothing as the closest commodity to the human body. Now, clothing has come a long way from being a simple commodity of physical protection to wearable electronics and computers. The vision of wearable computers defines future electronic systems as an integral part of our everyday clothing serving as intelligent personal assistants. Wearable smart electronic devices have gained immense attention due to potential applications in smart multifunctional fabrics such as sensors, transistors, energy storage devices and photovoltaic devices [1,2]. Out of the existing conductive materials, graphene has drawn significant attention due to its ability to function alongside the human body or cloths to keep pace with body movement, while showing its desirable properties [3,4]. Graphene and rGO were coated on fabrics in various ways such as multiple dip and dry or vacuum filtration methods [5]. However, these fabrication methods are extremely slow and not sustainable in scalable production [6]. Further, using hazardous materials for electronic components is restricted in textile applications [7]. Moreover, highly demanded polyester fabrics are not easy to modify into wearable electronics due to less functional groups on its surface. Already reported modifications on polyester fabrics have been done through ionic or physical bonds which were unstable for multiple washes [8]. As a result, there is an immediate requirement to produce sustainable, non-toxic and customer benign conductive fabrics. If there is a flexibility to connect different electronic systems to a clothing, a wearable system becomes more versatile. Hence, custom made wearable electronics to assist individuals’ requirements will be more desirable in future. When producing custom made wearable electronics, localized conductivity plays a vital role in designing circuits only at desirable places on textiles which prevent coating entire garment to be conductive and assists coating even at the end of garment production. In this research, we pre-treat the polyester fabric with APTES to enhance surface functionality. This method facilitates depositing controlled quantities of conducting materials at specific locations on polyester fabric or at specific locations on finished garments requiring electronic devices in specific areas. Reduced graphene oxide is reported here as the conductive material.

2. Materials and Methods

2.1. Materials and reagents

White woven 100% polyester fabrics were obtained from the Weaving Laboratory, University of Moratuwa. Graphite flakes (∼150 µm) were purchased from Ashbury Graphite Mills, Inc (Ashbury, NJ). Phosphoric acid (H₃PO₄, 85%), Sulphuric acid (H₂SO₄, 99%), Potassium permanganate (KMnO₄, 99.9%), Hydrogen peroxide (H₂O₂, 30%), Hydrogen chloride (HCl, 37%), Ethanol (C₂H₅OH, 99%), (3-aminopropyl) triethoxysilane (APTES, 99%) and Sodium hydrosulfite (Na₂S₂O₄, 99.9%) were purchased from Sigma Aldrich. All chemicals were used without further purification.

2.2. Preparation of graphite oxide and aqueous graphene oxide (GO) dispersion
Flake graphite was oxidized by following the set procedure in improved Hummer’s method [9]. Oxidation time was for 4 h which is relatively a lower time period compared to the usual oxidation time of 12 h in improved Hummer’s method. A 9:1 mixture of concentrated H$_2$SO$_4$:H$_3$PO$_4$ (360:40 mL) was added to a mixture of graphite flakes (3.0 g, 1 wt equiv) and KMnO$_4$ (18.0 g, 6 wt equiv) using a magnetic stirrer. The mixture produces a slight exothermic temperature to 35–40°C. The reaction mixture was then heated to 50°C and stirred for 4 h. The colour of the mixture changed from dark purplish green to dark brown. It was then cooled to room temperature and poured onto ice (400 mL) with 30% H$_2$O$_2$ (5 mL) to stop the oxidation process. At this stage colour of the mixture changed to bright yellow, which indicated a high oxidation level of graphite. After settling the remaining solid material was then washed in succession with 200 mL of water, 200 mL of 30% HCl, and 200 mL of ethanol; and the mixture centrifuged (9000 rpm for 1 h), the resulting supernatant was decanted. The washing process was repeated until a pH of 4–5 was achieved [10]. Aqueous graphene oxide dispersions were prepared by suspending graphite oxide in water and sonicating for 30 min.

2.3. Silanization of polyester fabric with APTES

Using controlled drop wise addition of APTES to deionized water, 2 mmoldm$^{-3}$ solution was prepared. Then, purified polyester fabric was stirred in hydrolyzed APTES solution at 90°C for 1 hour. APTES modified fabric was padded and cured at 110 °C and washed thoroughly.

2.4. Synthesis of reduced graphene oxide on polyester fabrics

GO was coated on APTES functionalized polyester using two methods. In first method, polyester was fully coated by dipping in GO solution, whereas in second method, GO was localized on polyester by screen printing. Then solution was heated up to approximately 90°C to add reducing agent. At this stage, the reducing agent Na$_2$S$_2$O$_4$ was added to GO solution until it reduced to black colour rGO. This reduction was lasted 30 min. The fabric was washed several times with deionized water. rGO coated polyester fabrics were then removed and send through padding rollers which apply a uniform pressure along the surface of the fabric to remove excess water. The sample was then dried using an oven at 60°C for 6 h.

2.5. Characterization

rGO coated fabric samples were characterized by Fourier transform infrared spectrophotometry (FTIR-Bruker Vertex 80 4000-400 cm$^{-1}$ spectral range), Atomic force microscopy (AFM) using non-contact mode, scanned at 0.5 Hz scanning speed and Scanning electron microscopy (SEM)) (HITACHI SU6600 SEM coupled with EDX detector). An Autolab PGSTAT302 N potentiostat/galvanostat was used to perform EIS analyses. EIS measurements were performed in the $10^5$–$10^{-2}$ Hz frequency range. The amplitude of the sinusoidal voltage used was ±10 mV. Measurements were carried out in a two-electrode arrangement. To check the stability rGO coating on polyester, 20 washing cycles were performed at 50°C with non-ionic detergent Ultravon CN Ciba for 45 min (AATCC 61 (2A)).

3. Results and Discussion

GO wrapping via strong covalent bonds with APTES was used to obtain rGO/PET. APTES acting as a coupling agent creates hydroxyl groups on PET in order to react with hydroxyl groups in GO.
Silanol groups of hydrolyzed APTES react with GO, while its amine group reacts with ester bonds in PET forming strong amide bonds [11]. Silanol groups of hydrolysed APTES have a slightly acidic nature, which makes them react with OH groups of GO in a way similar to carboxylic acids [12,13] to form Si-O-C covalent linkages. FTIR proved this covalent linkage by the new peak located at 1100 cm$^{-1}$ in Figure 1 (ii) spectrum E.

**Figure 1** (i) FTIR spectra of (A) pristine polyester, (B) GO/PET, (C) rGO/PET, (ii) FTIR spectra of (D) APTES treated polyester, (E) APTES treated GO, (iii) Raman spectra of (A) rGO/PET, (B) GO/PET.
In Figure 1 (i) spectrum B, absorption bands in 3000-3600 cm\(^{-1}\) and 1055 cm\(^{-1}\) are attributed to hydroxyl groups of GO. When GO was reduced to rGO, all the peaks in Figure 1 spectrum C arising from oxidized groups were significantly reduced, indicating a reduction of the oxygen content in the sample. The mechanism of the reaction between APTES and polyester is a nucleophilic substitution. The initial reaction occurs via nucleophilic attack by the amino group of APTES on ester bond of polyester fibers in the same way to the aminolysis reaction. The second reaction is a substitution reaction between alkoxide group created by ester cleavage and one of hydroxyl groups of hydrolysed APTES. APTES holds both ends of ester together, resulting in no degradation in the polymer structure [14]. Covalent bonding between polyester and APTES is confirmed by new absorption peaks in spectrum D, located at 1645 cm\(^{-1}\). These are attributed to secondary amide groups, formed by direct aminolysis between aminated ends of APTES and surface ester groups of polyester fibers. After GO wrapping of fibers of pre-treated polyester, the raman spectrum B in Figure 1 (iii) exhibited typical GO spectral features, such as the D peak at 1340 cm\(^{-1}\) and the G peak at 1580 cm\(^{-1}\). Changes in the raman spectra confirm that the GO/PET was chemically converted into rGO/PET. The raman spectrum A in Figure 1 (iii) showed a d-shift in the G peak and an increase in the \(I_D/I_G\) ratio from 0.93 to 1.20.

**Figure 2** SEM images of (A) pristine polyester, (B) (C) rGO/PET and (D) washed rGO/PET.
Figure 3 Atomic force microscopic topographical 3D images of (E) pristine polyester fiber surface and (F) rGO/PET fiber surface.

Scanning electron microscopic (SEM) images and atomic force microscopic (AFM) images were employed to observe the fiber surface morphology of pristine and rGO/PET fabrics. SEM image of pristine polyester fabric (Figure 2 A) indicates a smooth fiber surface after the purification. Figure 2 B and C show the thin layers of rGO wrapped around the polyester fibers. The typical morphology of rGO sheets with the wrinkles can be observed in the 3D image (Figure 3 F). This uniform wrapping of rGO thin sheets on polyester fibers induced a good conductivity.

White colour pre-treated polyester fabric changed to yellowish-brown after the GO coating. Then the colour changed to black after chemical reduction of GO to rGO (Figure 4 A and C). The electrical conductive property of rGO/PET was demonstrated with an LED in Figure 4 G. Figure 4 H shows the lighting of the LED even when the rGO/PET was severely twisted. The electrical conductive property of rGO localized garments was demonstrated with an LED in Figure 4 I and J.

Infra-red (IR) image in Figure 4 B shows absence of heat due to non-conductivity of pre-treated polyester. Figure 4 D and F clearly demonstrate the heat arisen due to the conductivity of rGO fully coated and rGO localized polyester, respectively. rGO printed area appeared in yellow colour due to the heat, while unprinted area in purple colour showing absence of heat.
Figure 4 Images of (A) pre-treated polyester, (B) IR of non-conductive pristine polyester, (C) rGO/PET, (D) IR of conductive rGO/PET, (E) screen printed rGO, (F) IR of screen printed conductive rGO, (G) an LED integrated with rGO/PET, (H) an LED integrated with rGO/PET twisted 360°, (I) and (J) localized rGO on a garment.

An Autolab PGSTAT302N potentiostat/galvanostat was used to perform Electrochemical impedance spectroscopy (EIS) analysis of rGO/PET. EIS facilitates measuring surface resistivity in addition to phase angle. Measurements were carried out using two rectangular copper electrodes (0.5 cm × 1.5 cm) separated by 1.5 cm and pressed to the dry textile sample. The measured area of the textile was a square of 1.5 cm, so the measured impedance modulus (\( |Z| \)) was equal to the surface resistivity (\( \rho / |Z| \)) [15]. Figure 5 shows the bode plots for GO/PET and rGO/PET. In Figure 5 A, the impedance modulus (\( |Z| \)) of GO/PET is greater than \( 10^9 \) \( \Omega \) for low frequencies due to the disrupted sp\(^2\) bonding of GO. However, the |Z| of rGO/PET significantly decreases to 320 \( \Omega \) for 0.01 Hz. Figure 5 B indicates the phase angle at different frequencies. GO/PET presents a phase angle of approximately 90°, a typical value of an insulating material which acts as a capacitor. However, in rGO/PET, 0° phase angles were obtained in majority of the frequency ranges, except for the frequency beyond \( 10^4 \) Hz, indicating that the fabrics behaved like conductive materials and showing a resistive behaviour, respectively.
After the twentieth washing cycle, characterization results of rGO coated polyester fabrics were compared with those of unwashed fabrics. No significant difference was observed in surface morphology of twenty times washed (Figure 2 D) and unwashed rGO coated polyester samples, confirming the strong covalent bond network between rGO and polyester. Moreover, retention of conductivity is confirmed in Figure 5 A which shows that $|Z|$ of the washed rGO/PET is 550 $\Omega$ for low frequencies.

### 4. Conclusions

We report the use of rGO on polyester to produce conductive textiles. Ease in the localization of conductivity using this reported method on lightweight and inexpensive polyester fabrics can positively alter consumers’ perspective on fashionable wearable electronics. Improved wash fastness properties of the reported method also support the above factor. These flexible textile conductors with excellent properties will open up avenues to improve production scalability of wearable electronics for mass scale markets.
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Conflicts of Interest

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

References
