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Improved continuity of reduced graphene oxide on polyester fabric by use of polypyrrole to achieve a highly electro-conductive and flexible substrate

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ABSTRACT

A flexible and highly conductive fabric can be applied for wearable electronics and as a pliable counter electrode for photovoltaics. Methods such as surface coating of fabrics with conductive polymers and materials have been developed, but the roughness of fabric is a challenge because it creates discontinuity in the coated layer. The present study first coated polyethylene terephthalate (PET) fabric with reduced graphene oxide sheets; RGO and then filled the gaps with polypyrrole (PPy). The samples were first dipped in graphene oxide (GO) and then reduced to RGO. They were next coated with PPy by in situ polymerization. The results showed that the presence of oxidative agent during synthesis of PPy oxidized the RGO to some extent on the previously RGO-coated samples. PPy was more uniform on samples pre-coated with RGO in comparison those coated with raw PET. The RGO–PPy coated samples exhibited 53% and 263% lower surface resistivity values than samples coated only with PPy and RGO, respectively. There was no significant difference between the tenacity of samples but the bending rigidity of samples increased. The RGO–PPy coated fabric displayed properties, such as excellent UV blocking (UPF = 73), antibacterial activity, improved electrochemical behavior and thermal stability which make it a multifunctional fabric.

1. Introduction

A conductive fabric (CF) possesses the physical and mechanical properties of a textile, such as flexibility, elasticity and tactility [1]. CFs have potential applications in areas such as wearable electronics, supercapacitors, smart textiles, and E-textiles [2–5]. A number of methods have been developed for producing CFs. Among them, coating textile substrates with conducting materials is beneficial because it offers a high specific surface area and the porosity of the textiles increases their ability for chemical uptake over other substrates [3–5].

The latter property can be a disadvantage as well. Porosity and the inherent surface roughness of textiles create discontinuity on the surface after coating by a conductive material. This decreases electrical conductivity to less than that of a homogeneous smooth surface. Cui et al. coated cupro with silver nanowires to fabricate a highly electro-conductive textile. They postulated that stacking of the silver nanowires provides a conductive network [6]. Govaret and Vanneste used carbon nanotubes as the conductive agent coating cotton and polyester textiles [7]. Li et al. developed a textile-based flexible antenna using chemical synthesis of copper nanoparticles [8]. In studies such as these, coating textiles only with a conductive material does not provide high electrical conductivity.

Reduced graphene oxide (RGO) nano sheets have outstanding properties that include electrical and thermal conductivity [9–13]. Polypyrrole (PPy), a π-conjugated polymer, has been widely studied and offers advantages such as high thermal and chemical strength, good conductivity, and mechanical flexibility [14–17]. The combination of these materials creates π–π interactions between the RGO layers and the aromatic PPy rings (Fig. 1), enhancing the electrical conductivity and thermal stability of the resultant composite [18,19].

Yaghoubidoust et al. coated cotton fabric with graphene oxide (GO)/PPy bilayers. Improvements in electrical response and

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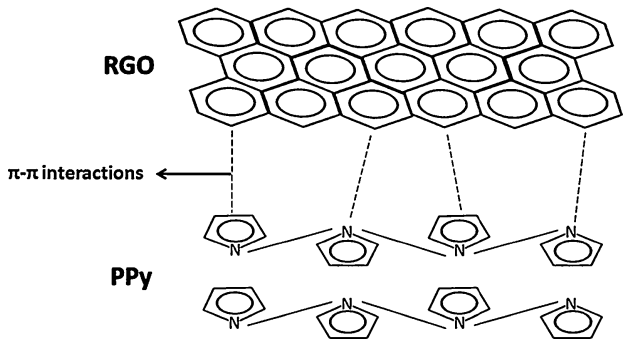

Fig. 1. Formation of π–π interaction (or π stacking layer) between RGO layers and aromatic PPy rings.

conductivity were recorded, suggesting the formation of a continuous conducting network and partial reduction of GO [18]. Molina et al. used GO as a counter ion for PPy-coated PET fabric. Although increasing the GO content decreased the electrical conductivity of the PET fabric, the main role of GO was reported to be the prevention of PPy from being solubilized at basic pH [19]. Wang et al. used RGO/PPy composite electrodes to electrochemically detect Hg^{2+} ions and reported high sensitivity (limit of detection as low as 30 ppt) and selectivity [20]. Zhang et al. reported high extraction selectivity and the capacity to detect traces of volatile terpenes using sulfonated reduced-graphene oxide/PPy(SRGO/PPy) [21]. Ye and Feng fabricated a hierarchically structured, low density, and highly compressible RGO/PPy aerogel as an efficient electrode for supercapacitors. They claimed that such electrodes exhibit highly specific capacitance of up to 253 $F g^{-1}$ [22]. Li et al. used a PPy fiber-RGO composite as cathode material for biocompatible zinc/polymer batteries. The battery delivered an energy density of 264 $mW h g^{-1}$ in 0.1 M phosphate buffer saline [23].

Few studies have investigated the effect of the combination of RGO and PPy for textiles [18,19,24,25]. GO has been used as a doping agent [19] and RGO–PPy has been used on cotton or nylon lycra [18,24,25]. But, there is no publication for connecting RGO by PPy on a pliable surface like PET. The state of art is that RGO shows more electrical conductivity in compare with GO and PET as a synthetic and hydrophobe fabric shows more potent to maintain hydrophobe RGO on its surface and it is more resistance to acidic condition. The fabricated flexible substrate can be used for wearable electronics and photovoltaic applications as a pliable counter electrode. Besides improving electrical conductivity, PET fabric offers antibacterial activity and UV blocking ability with improved electrochemical behavior and thermal stability. These properties have been investigated using quantitative antibacterial activity, UV protection factor, cyclic voltammetry, and thermogravimetric analysis.

2. Experimental

2.1. Materials

Twill weave polyethylene terephthalate (PET) fabric (143 $g m^{-2}$ area density, 150 dtex yarn linear density) was used as the substrate. Pyrrole monomer, 30% hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$), ferric chloride ($FeCl_3$), sodium hydrosulfite ($Na_2S_2O_4$), sulfuric acid, and hydrochloric acid (37%) were purchased from Merck Co. (Germany). The pyrrole was purified by vacuum distillation and kept in the dark at 5 °C until use [26]. Natural flake graphite powder (particle size of <20 μm) was purchased from Sigma–Aldrich (Germany). Double distilled water was used for all experiments.

2.2. Methods

2.2.1. Graphene oxide synthesis

Synthesis of GO was performed according to the modified Hummer's method [27]. Briefly, a solution containing 50 ml sulfuric acid and 2 g graphite powder was magnetically stirred at 25 °C for 24 h. Next, 7 g of $KMnO_4$ was gradually introduced into the solution at a temperature below 15 °C and the solution was stirred at 50 °C for 2 h. Then, 140 ml of distilled water was added to the solution with 10 ml of hydrogen peroxide before being further stirred for 30 min. The solution was centrifuged and washed with 5% HCl and distilled water three times. The resulting brown pasty product (1% w/v) was exfoliated in an ultrasonic bath (Wise Clean; 100 W; 40 kHz; Korea) for 60 min.

2.2.2. PET fabric impregnation with GO and GO reduction on its surface

PET samples were immersed in GO dispersion at 70 °C for 1 h. They were then cured in an oven at 80 °C for 60 min. RGO nanosheets were formed by immersing GO-coated samples in $Na_2S_2O_4$ solution (2% w/w) under constant stirring at 90 °C for 60 min. They were then washed twice with water and dried at 80 °C for 30 min.

2.2.3. Chemical oxidative polymerization of pyrrole on fabric samples

In a typical experiment, pyrrole (0.1 M) was dissolved in distilled water and the solution was cooled to between 0 and 5 °C. Next, the fabric samples were soaked in the solution (L:R = 1:30) and kept at 0–5 °C for 30 min. The initiator was then added (oxidant to monomer ratio = 1:1.25) and the solution was stirred constantly at 0–5 °C for 2.5 h, completing the polymerization. The samples were removed from the solution and washed with distilled water. Prior to testing, they were dried in a desiccator for 24 h.

3. Characterization

An attenuated total reflection Fourier transform infrared spectrometer (Thermo-Nicolet Nexus 870; USA) was used to collect ATR-FTIR spectra at400–4000 cm^{-1} at a resolution of 4 cm^{-1}. The Raman spectra were recorded in a Thermo-Nicolet FT Raman 960 (USA) equipped with a He–Ne laser beam (wavelength of 633 nm). Contact angle measurements were conducted on a contact angle goniometer (Krüss contact angle measuring system; model G10; Germany) using sessile drop (5 μl deionized water droplet). Morphological observation of the samples was performed by field emission scanning electron microscopy (FE-SEM; Mira3; Tescan; Czech Republic). Surface topography of the raw and treated PET fabrics was observed by atomic force microscopy (AFM; Ara-Pazhoohesh; Iran) in tapping mode.

The electrical conductivity was measured according to the AATCC 76-2000 standard method. Surface resistivity was calculated using equation (1) as:

$$R_s = R \times \frac{w}{l} \quad (1)$$

where R_s is sheet resistance in Ω/sq, R is the measured resistance in ohms, and w/l is the ratio of the distance between two electrodes to their lengths.

Surface resistivity of all treated samples were assessed after immersing in an ultrasonic bath for 30 min to determine the adhesiveness of GO, RGO, PPy, and RGO–PPy to the PET fabric. A potentiostat/galvanostat (EG&G 273A;USA) was employed for cyclic voltammetry (CV) measurements in a three-electrode arrangement to evaluate electrochemical performance. The counter electrode employed was made of platinum and a strip