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Incorporation of Polyaniline on Graphene - Related Materials/Cotton-Fabric by Interfacial Polymerization Pathway for Wearable Device

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ABSTRACT: Polyaniline (PANI)/ graphene composite on cotton fabric were prepared by a combination of in situ polymerization and solution process. In order to prepare PANI/graphene was initially grafted to graphene oxide via solution process where a concomitant reduction of GO occurred due to the hydrothermally and exposure of GO to KOH. The study was designed in order to have a clear understanding of the role of PANI as well as modified composite thereof under investigation. The structural, morphological, optical, and electrical properties of these fabrics have been studied. Nanostructured PANI/ graphene composite fabric was enhanced UV shielding the value of 447. It is found that the PANI/ graphene composite fabrics are increased electrical conductivity. The thermopower value of the PANI/ graphene composite fabric could reach 0.045 μVK^{-1}. Such materials are anticipated to be worthwhile for wearable electronic devices and as protective textiles.

Keywords: PANI; Cotton Fabric; Graphene, UV Shielding and Thermoelectric properties.

INTRODUCTION: The recovery of even a fraction of heat into electric power would have a striking impact on energy crisis. One way is thermoelectric generators (TEGs) which can directly convert heat to electric or vice versa. Among them, flexible thermoelectric generators have attracted tremendous attention because of a promising potential to convert body heat continuously into electric power that can be applied to wearable electronic devices. This improvement can arrest the use of greenhouse gas and enhance clean energy research. TEGs have many attractive features, such as long operating lifetime, no moving parts, no noise, easy maintenance, environmentally friendly and highly reliable. Integrating a power generator with cotton fabrics offers a promising solution to powering personal electronic devices. Ideally, wearable power generator should not only convert surrounding energy into electric energy but also its comfortable for implantable electronics for environmental monitoring or medical purpose, wireless monitoring systems for health care and ability to work in a remote area[1-3]. Thermoelectric (TE) power generation has attracted growing interest during the last years due to the increasing need for renewable energy sources and to achieving better energy conversion efficiency. It is very effective in harvesting electricity from waste heat with a temperature gradient relative to environmental temperature. For the practical uses of TE devices to spread, improvements in device performance and reductions in manufacturing costs are required[5, 6]. Therefore, nanocomposites material consisting of homogeneous and uniform dispersion of nanoparticles in the polymer matrix lead to higher TE properties. Moreover, the crystalline with amorphous polymer or polymer with nanoparticle interface create boundaries that scatter phonons, thus ensuring low thermal conductivity[7]. There are no reports are available by describing the incorporation of PANI/ graphene-composite based cotton fabric in the *in situ* polymerization assisted by hydrothermal performance for the application on WPG. The interaction of PANI/ graphene with textile material will make much difference in thermopower. In this study, we are able to modify cotton fabric with PANI/ graphene-composite by in situ polymerization assisted by hydrothermal technique at low temperature to develop a flexible TE material and its structural, morphological, electrical and thermoelectric properties were studied.

MATERIALS AND METHODS: All chemicals used in this study were analytical grade and was used without further purification. PANI/ Graphite was coated with cotton fabric by solution process and labeled as P1. Graphite oxide (GO) nanostructures are synthesized according to the modified Hummer's method as shown in figure 1. Briefly, the expandable graphite powders (2g) were stirred in 98% H_2SO_4 (35 ml) for 2 h. $KMnO_4$ (6g) was gradually added to the above solution while keeping the temperature less than 20°C. The mixture was then stirred at 35°C for 2 h. The resulting solution was diluted by adding 90 mL of

water under vigorous stirring and a dark brown suspension was obtained. The suspension was further treated by adding 30% H_2O_2 solution (10 mL) and 150 mL of distilled water. The resulting graphite oxide suspension was washed by repeated centrifugation, first with 5% HCl aqueous solution and then with distilled water until the pH of the solution becomes neutral. The GO nanostructures were obtained by adding 160 mL of water to the resulting precipitate and sonicated well to attain a uniform suspension of GO. After that, 0.5 g of PANI in 2 mL 1M HCL solution was added dropwise to be stirring for 20 min. The cotton fabric was immersed on PANI/GO solution assisted by ultrasonication method for 3 h, after that the fabric was removed and dried at 60°C for 2 h. Then PANI/ GO coated fabric was obtained and labeled as P2. Further, the PANI/ GO fabric and its solution taken for reduced GO (rGO) by simple hydrothermal process at 100°C for 10 h and collected sample labeled as P3. Consequently, the graphene reduction process achieved by one step hydrothermal approach after GO obtained. Briefly, the PANI/ exfoliate GO solution of pH was adjusted to reach 10 by the addition of KOH solution. Then, the cotton fabric (CF) is immersed in to the solution and it is transferred into a Teflon autoclave covered by a stainsteel reactor and kept at constant temperature at 100° C for 10 h. Finally, the obtained PANI/ graphene fabric was washed several times to remove the residuals followed by dried in a hot air oven at 150°C for 2 h in order to remove the water content and obtained sample were labeled as P4.

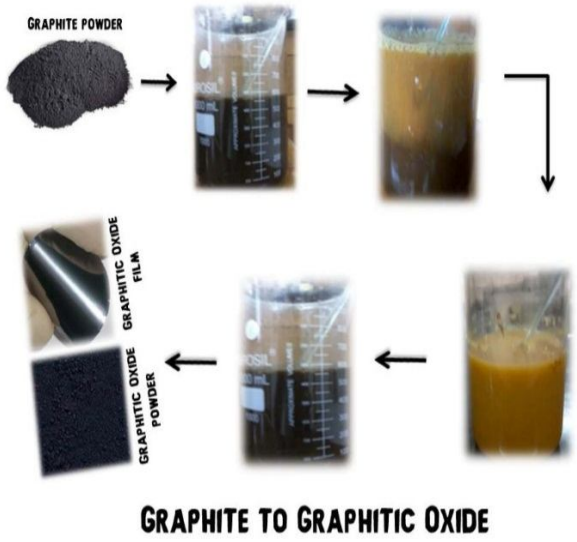

Figure 1: GO synthesis process by modified Hummers method.

The crystalline phase of products as investigated using x-ray diffraction (XRD) operated at 40 keV, 40 mA with CuKα radiation in the range of 10 - 80°C with a step of 0.02°. The morphology and microstructure were observed using a field emission scanning electron microscope (FESEM) with an accelerating voltage of 5 kV and an emission current of 15 µA. To study the elemental composition and distribution throughout the fabric, a detailed chemical analysis was carried out using energy dispersive spectrometry (EDS) mapping. The UV shielding effect of the coated fabric were analyzed by UV scattering and absorbing (Lapsphere UV1000F). The electrical property (I-V characteristics) of the sample was evaluated from JASCO solar simulator equipped with a Keithley pico-ammeter was carried out at room temperature.

RESULTS AND DISCUSSION: The photographic image of PANI/ Graphene related coated cotton fabric is shown in figure 2. The white color of the bare fabric changed into dark green tends to blackish green color after PANI/ GO/rGO/ graphene coating confirms that and it is uniformly coated on the CF.

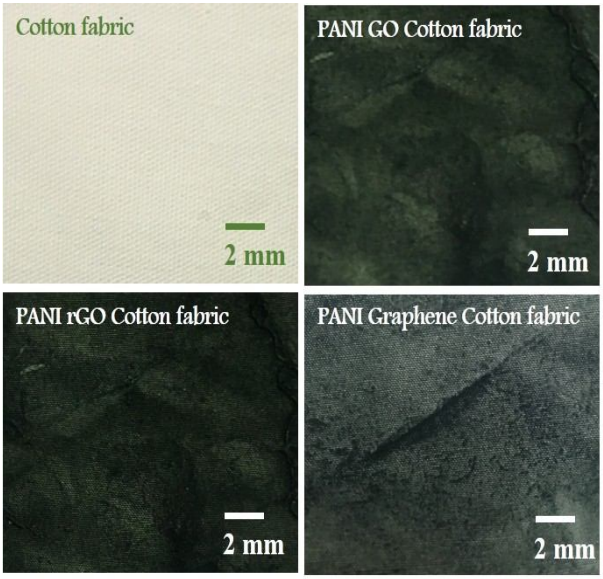

Figure 2: Photography of bare cotton fabric and PANI/ Graphene related coated cotton fabric.

From the FESEM images shown in figure 3, it is evident that the micromorphology of the cotton fabrics changed after each treatment step. The FESEM images revealed the PANI/ composite coated on the surface of single fibrous fiber and preferential as it is in the form of nanostructures as shown in figure 3. Figure 3 (pa, pb) shows for PANI coated cotton fabric of surface views and cross-sectional views. As per naked eye shows a uniform green color (Figure 2), which suggesting that PANI has penetrated into the CF.

However, it is clear that the PANI particles are very evenly deposited on the fabric, and are seen as small globules. The diameter of the globules varies from 0.12 to 1.2 µm. Figure 3 (p1a, p1b) shown under the polymerization condition, the PANI/ graphite composite obtained evenly distributed over the surface of the fabric. Moreover, it is reported that the morphology of PANI consists of a large number of honeycombed clews. Figure 3 (p2a, p2b) it can be seen the PANI/GO well dispersed onto the CF surface by ultrasonication and drop casting process. Furthermore, it was indicated that the PANI/GO granular membrane can be uniformly deposited on the CF under the proper preparation conditions through in-situ polymerization. Figure 3 (p3a, p3b) images of PANI/ rGO composite show that PANI is present in different types of structures, PANI nanofibers are intercalated into GO layers and also cover the GO. It is expected that polar epoxy and carboxyl groups of GO function primarily as the charge compensating sites which interact with the radical cations of the NH groups of PANI, thus the composite resultant PANI/ rGO. Figure 3 (p4a, p4b) the natural wrinkles and creases on the pristine CF surfaces were found to be covered and smoothed with a layer of PANI/ graphene. In addition, the fibers of the fabric were found to be finely covered by the grafted PANI layer, which would impart electrical conductivity to the CF.

Figure 4 shows the XRD pattern of PANI/graphite, PANI/GO, PANI/rGO, and PANI/ graphene, where CF and PANI show the intense peak at 2θ = 14.5°, 16.2° and 23°. GO at 2θ = 9° (due to 0 0 2 plane) which clearly indicates the oxidation of graphite affecting its crystal structure and the interlayer spacing which has increased 3.2 to 6.5 Å. Further the reduction of GO revels a broad peak at 2θ = 25.8° which gives rGO by hydrothermal approach. The reduction of GO to graphene using KOH was further supported and these results we can conclude that the reduction of GO to graphene was successfully occurred in the presence of KOH.

To investigate the UV shielding effect of the PANI/ graphene-composite coated on cotton fabric, were measured in the wavelength region 200 nm to 800 nm. The calculated ultraviolet protection factor (UPF) values were shown in figure 5 respectively. When compare with graph coated fabric are found to be much higher than those of the reference ones (CF; 6.66), which indicate that the CF show improved blocking of UV radiation. The UPF value of PANI/ graphene- composite coated fabric showed as 447, which was excellent, very good UV shielding respectively, because as seen in FESEM image finely covered by the grafted PANI later.

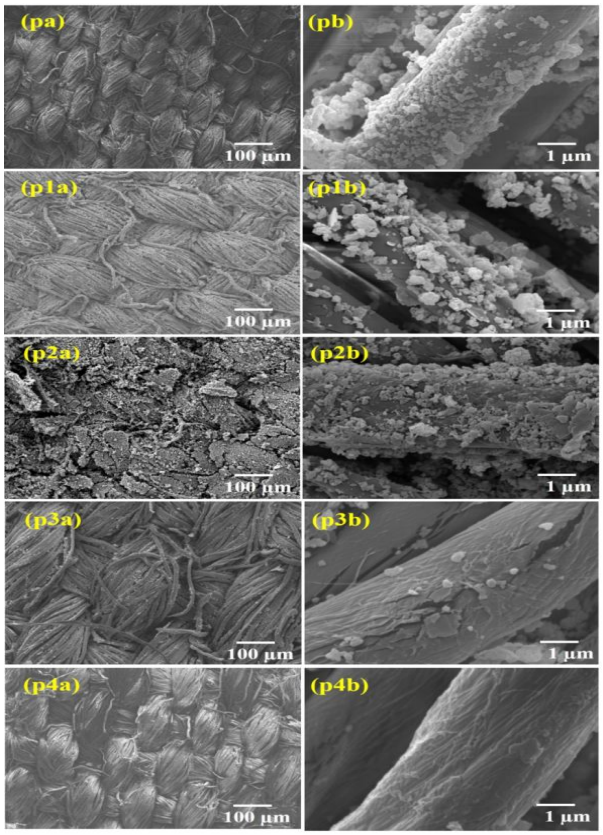

Figure 3: FESEM observation of (pa,b) PANI-coated CF, (p1a,b) PANI/ Graphite coated CF, (p2a,b) PANI/ GO coated CF, , (p3a,b) PANI/ rGO coated CF, and (p4a,b) PANI/ Graphene coated CF.

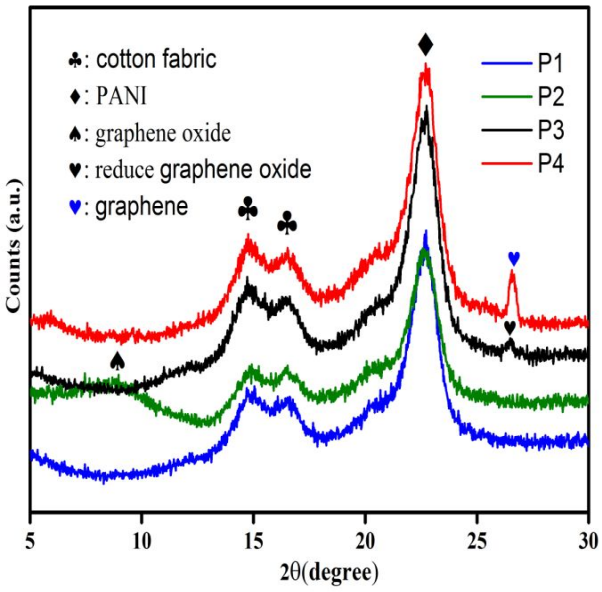

Figure 4: XRD pattern of PANI/ graphite/ GO/ rGO/ graphene-coated cotton fabri.

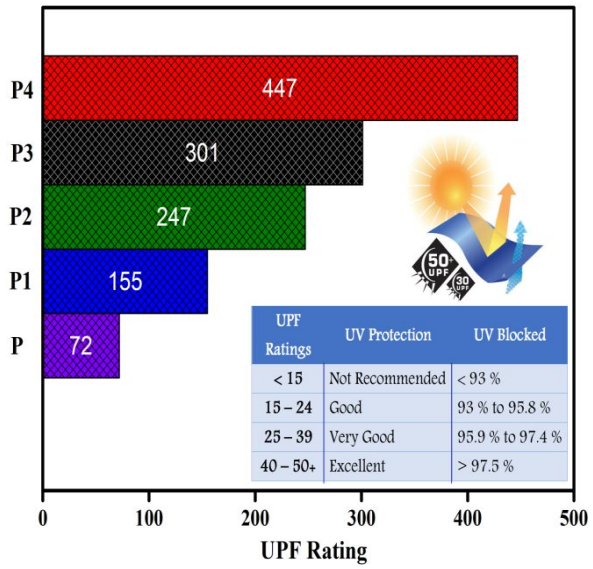

Figure 5: UV shielding properties of PANI/ graphite/ GO/ rGO/ graphene-coated cotton fabric.

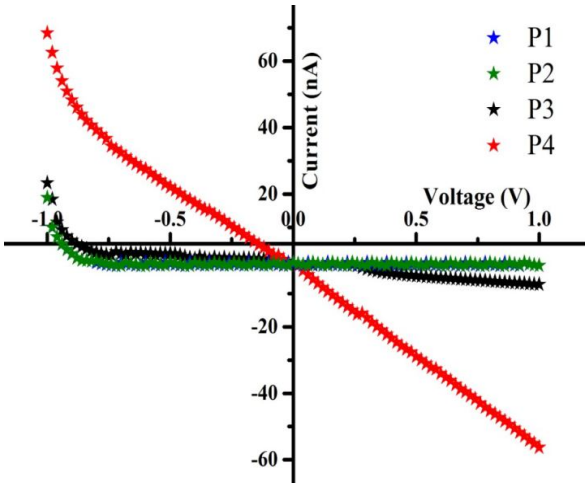

Figure 6: I-V characteristics of the PANI composites coated fabric.

The electrical property of the prepared CF was also further investigated. Figure 6 shows the I-V curves of the fabric in the applied voltage of -1 to +1 V at 0.2 V interval, and the resultant PANI/ graphene composite coated CF increase rapidly due to the electrical conductive network consist of PANI/ graphene grafted on CF. Typically, the other PANI composite shows the aggregated construction of PANI granular member could severely weaken the electrical ability of conductive network.

Table 1: Thermoelectric properties.

Sample code	Carrier Concentration (cm^{-3})	Resistivity (ohm-cm)	Mobility (cm^2/V-s)	Seebeck coefficient (μVK^{-1})
P4	3.95×10^{19}	2.71×10^{-3}	58.3	45

As a contrast, the TE properties of PANI/graphene composite might have the dominant influence on the electrical conductivity, while the ordering degree of PANI molecular chain arrangement and the interface effects are the major factors on influencing the Seebeck coefficient.

CONCLUSION: We proposed a materials design for the development of PANI composite graphene cotton fabric and also composite method to control the conduction type and carrier concentration. The XRD patterns of the nanostructures revealed that, apart from carbon fabric, PANI and graphene, no other reaction phases are present. The FESEM image of the nanostructure. The presented work demonstrates that simply prepared fabrications of PANI/graphene composite are efficient Seebeck enhancement up to 45 µV/K.

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