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Preparation of conductive graphene/graphite infused fabrics using an interface trapping method

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ABSTRACT

Conductive fabrics are central to smart textiles, a concept that has been gaining attention for applications such as wearable electronics or biosensors. However, current approaches for creating electrically conductive fabrics struggle with issues ranging from low conductivity to skin irritation. The use of graphitic carbon has been investigated as a possible way to impart conductivity to fabrics, yet low loadings, required post-infusion reductions, or the need to remove additives, has limited the application of these materials. In this paper, we introduce an approach that infuses fabric with pristine few layer graphene (FLG)/graphite from natural bulk graphite using an interfacial trapping method. No additives or chemical modification of the graphite is required, and electrical conductivities an order of magnitude higher than previous approaches are achieved.

1. Introduction

Smart textiles, also known as E-textiles or electronic textiles, are gaining attention due to potential applications in biosensors, heat generation, and wearable electronics [1–5]. However, current methods of imparting conductivity, such as the incorporation of metals [6–8] or conductive polymers [9,10], often give less than optimal conductivity and can result in the loss of fabric flexibility, significant weight increases, undesirable changes in fabric texture, or skin irritation. In an effort to meet these challenges, a new approach, based on kinetically trapping pristine FLG from natural flake graphite, is presented. This approach enables electrically conductive fabrics incorporating FLG sheets on the surface of fibers. The fabrics show no degradation of properties, yet demonstrate remarkable electrical conductivity.

A popular approach to impart conductivity to fabrics is the incorporation of metal fibers and coatings, but their high density and undesirable interactions with the skin has led to the exploration of other materials, especially carbon-based materials. Carbon nanotubes [4] (CNT) and carbon black [11] have both been used to impart conductivity, yet low conductivity and concerns of possible CNT toxicity have limited their use. Graphene, with its outstanding mechanical and electrical properties [12], is an attractive candidate for producing conductive textiles. It is non-toxic, inexpensive, and has even shown signs of being a viable antibiotic [13].

Previous approaches to creating conductive fabrics based on graphene and graphite have included making graphene fibers from graphene oxide (GO) [14–16], infusing fabric with GO followed by its reduction to graphene [16–18], transferring a patterned film made through chemical vapor deposition

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(CVD) [5], and dispersing graphene with a surfactant, followed by the removal of the surfactant with nitric acid [17]. Although an improvement compared to metals, these methods all have their limitations: graphene produced through the reduction of GO has significantly reduced electrical and mechanical properties [18], CVD grown graphene is not cost effective for bulk material production, and harsh chemical treatments for the removal of surfactants adversely affects the mechanical and tactile properties of the fabrics.

2. Experimental

2.1. Sample preparation

A typical laboratory procedure starts with 100 mg natural flake graphite (Asbury Carbons Grade 3243) placed in a 20 mL glass scintillation vial. The vial is charged with 5 mL *n*-heptane (Fisher Scientific, 99% Optima), followed by 10 s of bath sonication (Branson Model 2510). This is then followed by tip sonication using a Cole-Parmer 750 Watt Ultrasonic Processor (20 kHz operating at 40% power) for 15 min. The initial bath and tip sonication breaks up large aggregates that are common in the graphite used. De-ionized water (5 mL) is then added and the mixture is once again bath sonicated and then tip sonicated at 40% power for 15 min. The second bath sonication facilitates the exfoliation and migration of FLG to the liquid-liquid interface. A 2.5 cm × 2.5 cm piece of fabric (for example, poly(ethyleneterephthalate) simulated leather, non-woven) is then placed into the scintillation vial. The vial is topped off with heptane, and placed into the bath sonicator for 1 h, followed by oven drying at 80 °C. The solvents and FLG/graphite left in the vial may be reused for future samples.

2.2. Conductivity measurements

The percolation threshold is determined using a four-line probe method with a Keithley 224 Programmable power supply ($I_{max} = 101.1 \times 10^{-3}$ A), while a 196 system DMA is used to measure the voltage. Resistance is first measured by creating an *I–V* plot with at least 10 data points. The sheet resistance is then determined using the relation $R_s = R(w/l)$, where w is the width of the sample and l is the distance between the leads.

3. Exfoliation of FLG

The major difficulty encountered in the use of natural flake graphite is suspending it in solution for infusion into a fabric. The past use of GO and surfactants were efforts to solve this difficulty. Here, using a recently developed interfacial trapping method [19], the challenge of suspending FLG in a solvent for fabric infusion is overcome without the need for surfactants or chemical modification of the graphite. Fig. 1 illustrates a demonstration of the kinetic trapping method and shows images of fabric before and after infusion with FLG. The method produces a fabric infused with a combination of graphite and pristine FLG, resulting in an electrically conductive fabric produced in a scalable and cost effective manner while retaining the fabric's mechanical strength and feel.

The kinetic trapping approach utilizes a mixed solvent system of water and heptane. As both water and heptane are poor solvents for graphene [20], neither one by itself will form stable FLG suspensions. The lack of good solvents for graphene has posed problems in the past, but the interfacial trapping relies on this insolubility. When the graphite is added to a water/heptane mixture it is initially found at the solvent interface where it serves to minimize the high interfacial energy of the two solvent phases. Once there, mild sonication speeds the exfoliation of the graphite into FLG sheets and these sheets spread to cover the interfaces, including climbing hydrophilic surfaces in contact with heptane vapor, as illustrated in Fig. 1A where FLG climbs the hydrophilic glass walls of the sample vial.

Rather than approach the challenge of graphite exfoliation and suspension by chemically modifying the graphite through defect forming oxidations, or by adding difficult to remove surfactants, we create a system in which the bulk stacked graphene sheet morphology of graphite is not the most thermodynamically stable arrangement. We start by creating a high-energy system composed of oil and water interfaces. Placing graphene sheets at these interfaces lowers the energy of the system and thus drives exfoliation and coating of hydrophilic surfaces possessing thin water layers, such as the glass vial walls shown in Fig. 1A or individual fibers of a fabric. The force holding the pristine FLG sheets at the liquid-liquid interface is substantial, as the sheets remain at the interface even under centrifugation forces exceeding 300,000 *g*. As graphene is not soluble in either the oil or the water phase, the kinetic barrier to forming graphene stacks more than 3–4 layers thick is very large, effectively trapping the sheets at the interface in their exfoliated state. The uptake of FLG and graphite by the fabric as described in this report is driven by this mechanism.

4. Infusion of fabric

The infusion of FLG into the fabric involves sonication of the fabric in a heptane/water mixture containing graphite, where a heptane/water interface is created at the surface of the slightly hydrophilic fibers of the fabric. Graphite is drawn into the fabric, and FLG is deposited on the fibers. As can be seen in the scanning electron microscopy images in Fig. 2, graphite particles are trapped between the strands of the fabric (Fig. 2A), while FLG flakes attach themselves to the fibers (Fig. 2B). Using this approach, the fabric can be loaded with as much as 15 wt.% graphitic material.

Control experiments using only water or only heptane show very different results. If only water is used as the solvent, almost no graphite is infused into the fabric and no conductivity is observed. With only heptane, it is only possible to load the fabric with approximately 10 wt.% graphite. As the fabric always contains some moisture, this is not unexpected; the real difference lies with the conductivity. Comparing fabrics infused with nearly identical loadings of graphite but with one infused in both solvents and one infused with only heptane, a fortyfold difference in conductivity is observed. Although containing roughly equal amounts of graphite, the lack of an extensive water/heptane interface in the latter

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