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Self assembled graphene layers on polyurethane foam as a highly pressure sensitive conducting composite

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ABSTRACT

Nano-flakes of graphene can be suitably anchored on a polymer surface to create functionally more active material. Here, a simple method is reported for uniform coating of graphite-oxide onto flexible polyurethane foam and its further conversion to graphene–polyurethane composite. As prepared foam is quite flexible, highly compressible, homogeneous and electrically conducting that exhibits high pressure sensitivity. The material is characterized by scanning electron microscopy, Fourier transform infrared spectroscopy, thermogravimetric analysis to study the morphology, chemical interaction between constituent phases and thermal stability respectively. These studies confirm that graphene is strongly immobilized on polyurethane surface by chemical linkage. The influence of applied pressure on electrical conductivity shows that current increases by more than five orders of magnitude for a small change in pressure (just 0.5 atmospheres) yielding pressure sensitivity of 4×10^5/atmosphere.

1. Introduction

Graphene, a two dimensional lattice of sp^2-bonded carbon atoms, undoubtedly has become an extremely important material for the current scientific research [1,2]. It is a basic building block of other allotropes of carbon, such as bulk graphite, carbon nanotubes and carbon quantum dots [3–5]. The long range π-conjugation, periodic nature and layer thickness of its honeycomb lattice imparts extraordinary electrical, thermal, mechanical and optical properties that are desirable for novel device applications. Some special properties, like electrons/holes as a mass-less Dirac fermions [6] with very large mobility [7], despite a zero carrier density near the Dirac points the existence of minimum electrical conductivity ($\sim 4e^2/h$) [8], ambipolar field effect properties [9], room temperature existence of quantum hall effect [10] has made the graphene a unique and challenging material that needs a rigorous theoretical and experimental understanding.

The above properties appeal that graphene can be suitably blended with other materials, so that a better functional composites can be created to use as chemical/biological sensors [11], rechargeable batteries [12], supercapacitors [13,14], pressure/temperature/humidity sensors [15], transparent electrodes [16] and so on. In this respect, putting graphene with certain polymers to make conducting composites would be an interesting aspect from scientific and technological point of view. Conductive polymer composites based on conductive fillers has been the subject of intense research in last few decades [17]. It is well known that electrical conductivity of these composites can change drastically, by more than few orders, near the critical composition of conducting phase, known as percolation threshold (x_c). It is important to note that the critical composition is highly function of morphology, level of mixing and chemical interaction of the constituent phases [17–19]. The x_c ranges from just $\sim 10^{-3}$ v% to as high as 50–60 v% in case of low dimensional to bulk materials, respectively [20]. In general, all these composites are relatively incompressible mediums whose conductivity is only tuned by composition. However, it is desirable to produce these as a highly compressible material so that its conductivity can be tuned not only with composition but also with applied pressure. Hence, in a composite, with a fixed composition, the conducting particles can be evenly distributed and situated quite close to each other without any physical contact. Under small compression they can come close to each other to establish conducting contact and would go back to original state once the pressure is released. This mechanism permits a systematic tuning of electrical conductivity with pressure. For last couple of years, our group has been working in the development of such composites as pressure sensors, it has been demonstrated that depending on the percentage of conducting phase the charge transport can be either controlled by classical mechanism or by quantum mechanical tunneling [21,22]. In present work, we aim to develop highly compressible polyurethane (PU) foam grafted with graphene-layers, without loss of original compressibility of polymer, whose conductivity can be controlled with applied pressure.

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2. Experimental details

Materials used: Flexible PU foams were obtained from local source; these were from Kurlon Limited, Bangalore, India. Natural graphite powder, potassium permanganate ($KMnO_4$), sulphuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), hydrazine hydrate ($N_2H_4{\cdot}H_2O$) were of analytical grade and were obtained from sd-Fine chemicals, India. These were used without further purification. Double distilled water was used to process and wash all the samples.

2.1. Preparation of polyurethane–graphene foam

PU foam used in our experiment is a nonconductive, soft, household sponge like material that could be reversibly compressed under small pressure without loss of original compressibility. Firstly, the flexible PU foam was soaked for a minute in hydrazine hydrate and washed thoroughly with distilled water. The color of the foam changed from yellow to white. Decolorizing was done in order to remove the dye so that there is proper binding of graphite oxide (GO) with the foam. GO, an oxidation product of graphite, is used as a source of graphene sheets. GO was synthesized from natural graphite powder by graphite oxidation with $KMnO_4$ in concentrated H_2SO_4 according to Hummer's method, the details of this procedure is described elsewhere [23]. As-synthesized GO sample was redispersed in distilled water to get colloidal solution (0.5 mg in 1 ml of water).

Next, the PU foam is soaked in GO colloidal and left to dry in open conditions for an hour. Foam color changes from white to dark brown. After complete drying in open condition, the foam is soaked in hydrazine hydrate to convert graphite oxide to graphene without damaging the foam. Then it is washed thoroughly in distilled water many times till the water pH becomes normal. At the end it was sonicated for few times in water to remove unadherent excess graphene and then it was left for drying under room light conditions. A large number of trials (about twenty) are carried out for self assembly of graphene on PU foam for different concentration of GO in water and for different time scales of soaking. It is found that the end product has a fixed amount of graphene loaded in PU. In case of thicker solution of GO, slightly more amount of unadherent material was noticed after the sonication. Hence, in the present synthesis the composition of graphene is fixed to 3 wt%. The original, GO coated and reduced GO (graphene) coated PU foams are shown in Fig. 1(a). The deposition of GO and graphene is clearly visible from this figure, and even conversion from GO (dark brown) to graphene (dark) is also seen clearly.

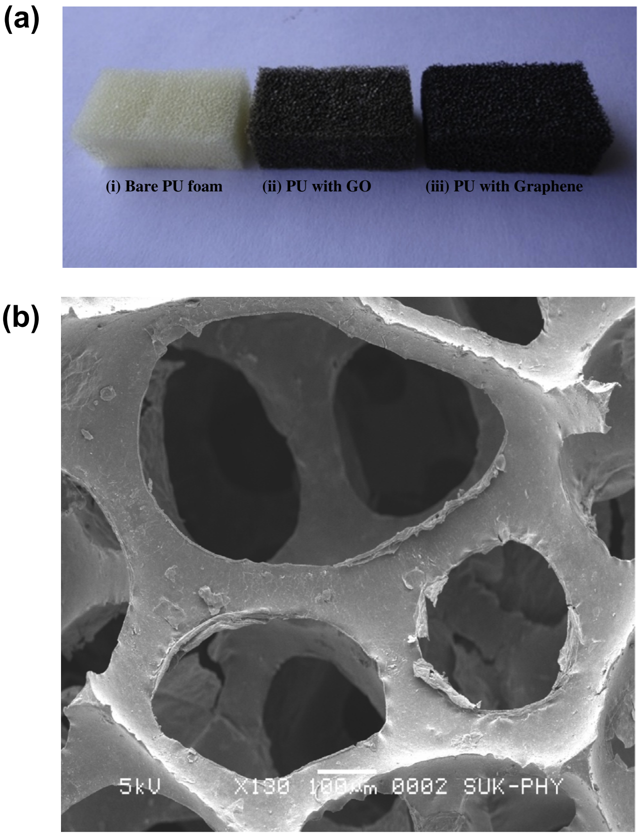

Fig. 1. (a) Photographs of (i) bare PU foam, (ii) PU with GO and (iii) PU with graphene. (b) Scanning electron micrograph of PU–graphene foam.

2.2. Characterization of polyurethane–graphene foam

The binding affinity of graphene on PU foam is studied by Fourier transform infrared (FTIR) measurements. The FTIR measurements of the samples were recorded in the range 400–4000 cm^{-1} in ATR mode with ZnSe crystal using Bruker alpha-T series unit. To study the surface morphology, JEOL JSM-6360 scanning electron microscope (SEM) was employed. Thermal stability of these foams was determined by thermogravimetric analysis (TGA) (TA instruments-Water LLC, New castle, USA). TGA was carried out on the samples weighing 10 mg each in platinum crucibles with a heating rate of 10 °C/min under dry nitrogen atmosphere. The pressure-dependent electrical conductivity measurements across the film thickness were carried out using our simple home-built setup using Keithley electrometers.

3. Results and discussion

3.1. Surface morphology

First, the porosity of PU foams were estimated using a simple equation $P = 1 - \frac{\rho_{app}}{\rho_{solid}}$, where P is porosity, ρ_{app} is the apparent density determined from the measured mass and volume of PU foam of known size, ρ_{solid} is the density of solid polyurethane foam and is equal to 1.2 g/cm^3 [24]. To estimate the proper value of average porosity, the apparent density of many PU foams (more than 30 pieces) of typical size $15 \times 15 \times 13\ mm^3$ was measured and finally the estimated average porosity of our PU foam found to be 96%, that is quite high and hence these films posses good compressibility and large internal surface area. The amount of graphene loaded in PU foams was estimated by taking the weight difference between pristine PU and fully converted PU–graphene foams and it is close to 3 wt%.

The surface morphology of pristine, GO and graphene loaded PU foams were observed with SEM and the typical results for only PU–graphene foam is shown in Fig. 1(b) (patterns for bare PU and PU–GO foam are shown in supplementary information as Fig. S2). The PU foam exhibits 3D-hierarchical mesoporous structure with the pore size ranging from 100 to 600 μm. These PU foams have many advantages as supporting material to graft graphene, (i) there is large porosity having smooth internal surface that makes easy flow of GO solution so that at the end a uniform deposition of graphene-flakes can be achieved, (ii) the smooth inner and outer layers of these skeletons are free from the inter-junctions that enhances superior electrical conducting path and (iii) it also has very high density of hydrophilic moieties inside and outside the skeleton that is responsible for super water absorption capacity, the present foam absorbs water more than 30 times its weight. Hence, these foams are ideal materials to develop pressure sensitive conducting