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Electrophoretic stabilization of freestanding pristine graphene foams with carbon nanotubes for enhanced optical and electrical response

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ABSTRACT

Graphene materials, including three-dimensional foams, are commonly transferred from growth substrates using polymer stabilization processes. Even after harsh chemical and annealing treatments to remove the polymer, residues remain which compromise the electronic, thermal, gravimetric, and chemical properties of the graphene. To overcome this, we present a scalable, clean approach to stabilize graphene foams by conformal electrophoretic deposition of web-like networks of surfactant-free single-walled carbon nanotubes directly from polar solvents. We demonstrate these coatings to yield a pristine stabilized graphene material exhibiting 50x lower electrical resistance and a 10 cm^{-1} optical red-shift in the Raman G′ double resonance mode in comparison to polymer-stabilized graphene. This approach enables the formation of three-dimensional architectures of nanomaterials without the adverse effects associated with residual impurities from polymer and chemical processing.

1. Introduction

The two-dimensional, atomically-thin configuration of graphene has enabled the understanding of new physics and chemistry in two-dimensional materials which has been the foundation for the emergence of a broad range of graphene-based applications in areas such as catalysis, sensing, energy systems, and electronics [1]. Ideal material performance intrinsic to suspended graphene, such as high mobility and excellent electrical and thermal properties, are compromised when the graphene is interfaced with a substrate or polymer surface [2]. Two-dimensional architectures of rebar graphene, which provides physical stabilization of graphene with carbon nanotubes, have been recently demonstrated [3]. However, recent efforts to construct three-dimensional (3-D) structures of graphene, where graphene is grown from a sacrificial metal foam [4], have emphasized the presence of significant material processing challenges in developing pristine, functional materials for diverse applications. The use of polymethylmethacralate (PMMA) based transfer processes universally employed for graphene stabilization have been demonstrated to generate irreversible residue formation that withstands chemical or annealing treatments and adversely modifies the electronic and optical properties of the graphene materials. This has been observed to result in the optical blue-shifting of the G′ double resonance mode in Raman spectroscopy studies [5]. Such issues are more prevalent with 3-D graphene structures due to the increased surface area of the substrate on which the graphene is grown and the challenge of complete PMMA removal from a 3-D matrix rather than a planar 2-D film.

Here, we emphasize the advantages of using electrophoretically deposited SWCNTs to stabilize 3-D graphene foam materials (Fig. 1a,b) without the use of PMMA or other conventional polymer stabilization routes. Utilizing SWCNTs suspended in surfactant-free polar solvents [6–8], electrophoretic processing is scalable, inexpensive [9], capable of integration with manufacturing platforms, such as roll-to-roll or industrial systems [12–14], and overcomes the limitations of other SWCNT electrophoretic approaches which utilize surfactant [10,11]. We specifically observe stabilization of 3-D graphene foams that are found to maintain pristine optical response and significantly improved electrical response in comparison to PMMA-stabilized materials.

2. Experimental

2.1. Materials

All materials and chemicals were commercially available and used without further purification. Raman analysis was carried out using a Renishaw inVia Raman microscope with a 532 nm laser

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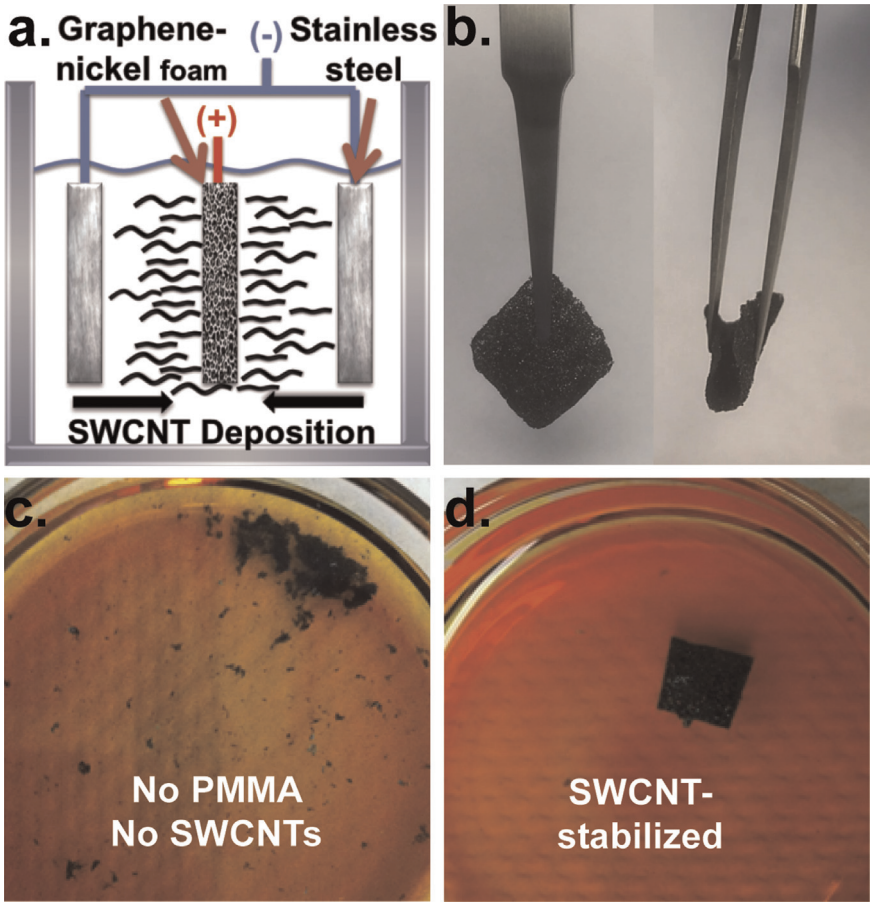

Fig. 1. (a) Schematic illustration of the EPD process and resulting structure (b) of SWCNT stabilized graphene foams. Graphene foam material with no stabilizing agent (c) and with a coating of SWCNTs (d) after dissolution of the metal template.

excitation. Electrical characterizations and depositions were performed using a Keithley 2400 Sourcemeter.

Nickel foam (~110 ppi, porosity 70–80%) was purchased from MTI, 1-methyl-2-pyrollidone (NMP) (99.5%) and iron (III) chloride (45%) were purchased from Sigma-Aldrich and single-walled carbon nanotubes (HiPCO, purified) were purchased from Unidym (purified, 99%).

2.2. Methods

Graphene foams were grown on nickel foam templates at 850 °C at low pressure (~0.1 Torr) with an initial 10 min anneal under 2 sccm H_2 and 200 sccm Ar followed by a 5 min exposure to C_2H_2 under respective flow rates of C_2H_2:H_2:Ar of 0.3:3:500 before cooling down to room temperature under Ar/H_2. PMMA assisted graphene foams were fabricated as previously described [4] using iron (III) chloride as the etchant and including an additional annealing step of 2 h under ambient conditions at 300 °C. The EPD solution is prepared by mixing 10 mg of SWCNTs in 20 ml of NMP via sonication. EPD is performed at a 0.5 cm separation of the nickel foam to two stainless steel counter electrodes and an applied potential of 120 V for 20 min.

3. Results and discussion

Without stabilization, graphene foam breaks apart during etching of the sacrificial metal template (Fig. 1c). In order to stabilize a freestanding foam, the graphene foam was either placed into a PMMA matrix or coated by a thin layer of SWCNTs (Fig. 1d) to yield a freestanding, structurally stable material after full dissolution of the metal template in a process illustrated in Fig. 2a–d. Although EPD with SWCNTs has been readily carried out with anionic surfactants, surfactant residues can strongly inhibit the physical properties of the material important for applications [15,16], thereby posing no benefit over conventional PMMA processing. We therefore performed EPD of surfactant-free SWCNTs dissolved directly in N-methyl-2-pyrrolidone (NMP) polar solvents. As NMP is a solvent with a high electron donor number, dispersed nanomaterials suspended with NMP acquire a net negative charge through electron transfer reactions with the solvent molecules [17]. This approach led to controllable, surfactant-free depositions of SWCNTs on graphene foam materials consisting of single and few-layer graphene. Representative SEM and TEM images of these depositions emphasize the role the SWCNTs play in the mechanical integrity of the 3-D freestanding structure (Fig. 2e) and the few-layer nature of the graphene material (Fig. 2f, g).

In order to characterize the benefit of the SWCNT coating we studied the electrical and optical properties of the foam materials. To characterize the electrical properties, two-electrode current–voltage scans were performed on both SWCNT and PMMA stabilized graphene. As the thickness of the foam materials in both cases are identical and both samples exhibited a linear, Ohmic response, we calculated the resistivity of PMMA stabilized foam to be $1.8 \times 10^{-4}\ \Omega\,m$, and the resistivity of the SWCNT stabilized sample to be $3.5 \times 10^{-6}\ \Omega\,m$ (Fig. 3a) based on the linear slope of *I–V* curves obtained. This indicates a nearly 50x improvement in sample resistivity and a value approaching bulk metals when using SWCNT stabilization. Furthermore, we performed optical