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Mechano-chemical stabilization of three-dimensional carbon nanotube aggregates

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ABSTRACT

Here we report a combined study of experiments and simulations to understand how chemical functional groups can mechanically stabilize aggregates of carbon nanotubes (CNTs). Ultralow density aggregates of chemically functionalized CNTs, in the form of macro-scale spheres made by freeze-drying method, show mechanical stabilization and near complete elastic recovery during deformation. Simulations of interacting functionalized carbon nanotube aggregates show better structural retention compared to non-functionalized CNTs under compression, suggesting that the atomic-level interactions between functional groups on adjoining CNTs help maintain structural rigidity and elastic response during loading. Aggregates of non-functionalized CNTs collapses under similar loading conditions. The dynamic mechanical responses of CNT macrostructures and mechano-chemical stabilization are directly observed using in-situ deformation inside a scanning electron microscope.

1. Introduction

Three-dimensional (3D) architecture materials via bottom-up approach assembly, is an interesting and growing area of research due to the ability to tailor the properties of the building blocks [1]. Using such techniques, many of the shortcomings, e.g., shaping, structural integrity, defects and material waste, can easily be overcome, as well as support the growing demand for multi-functional and intelligent materials [2]. The discovery of carbon nanotubes (CNTs) [3] and graphene [4,5], as one and two dimensional (1D and 2D) materials respectively, brought a new wave of research interest to design 3D structures from these building blocks and similar materials. In order to interconnect these nanomaterials to build a large-scale millimeter size 3D structure, several processing techniques based on bottom-up approaches using physical, chemical and electrical methods have been reported in the recent past [6–14]. Most of these syntheses gives rise to ultra-light-weight porous materials with high surface area and enhanced functional properties, which are useful in the applications of oil absorption, energy absorbing, and gas storage. The mechanical responses of most of the porous 3D architectures are valuable for high energy absorption applications.

Recently, the chemical functionalization of CNTs was reported to be useful in interconnecting and developing porous structures. But to date the mechanical advantage of such atomic scale functionalization of CNTs has not been clearly understood. In the current work, we report an easily scalable method of synthesizing 3D foam into spheres with millimeter to micrometer scales made up entirely of functionalized CNTs exhibiting completely elastic behavior until a high strain. An in-situ mechanical system attached to a high resolution SEM has been used to conduct quasi-static uniaxial compression on the individual building blocks and macroscopic sphere. The complete elastic behavior of these CNT spheres is further explained with help of detailed molecular dynamics (MD) simulations. The simulations addressed the role of functional groups in such kind of behavior.

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2. Experimental

Multiwall CNT (MWNT) powder was functionalized to attach carboxylic acid functional groups (−COOH) by nitric acid for 3–4 days in oil bath at 70–80 °C. Functionalized MWCNTs (50 mg) were sonicated in DI water (5 mL) for 1 h, then glutaraldehyde solution (35 μL), resorcinol (6 mg) and borax (0.5 mg) was added. The mixed solution was sonicated further for 4 h, then the solution was dropped directly into liquid nitrogen to form CNT spheres ($\varphi \approx 20$ μm to 3–4 mm). Fig. 1a inset shows the procedure used to prepare the CNT spheres (supplementary video SV1). The spheres were freeze-dried for 3–4 days (as shown in Fig. 1a), using a Millrock Technology freeze drier at approximately −50 °C and 40 mtorr. After freeze-drying, the density of the CNTs sphere is approximately 0.003 ± 0.001 gm/cc.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.08.085.

Scanning electron microscope (SEM) pictures were taken by FEI Quanta 400 ESEM, at scanning electricity of 15–20 kV; Transmission electron microscope (TEM) pictures were taken by JEOL 2100 Field Emission Gun TEM; X-ray photoelectron spectroscopy (XPS) data was examined by PHI Quantera XPS using Al Kα X-ray tube; and X-ray diffraction (XRD) data was measured by Rigaku D/Max Ultima II Powder XRD using Cu Kα X-ray tube.

3. Simulation methodology

Classical molecular dynamics simulations (MD) were performed using the CHARMM [15,16] force field, as available in the LAMMPS code [17]. We used (10, 10) CNTs tubes of 180 Å length. The functionalized structures (CNTs with carboxyl acid group (−COOH)) were generated randomly, inserting these groups along the tube external layers. For the present study, we considered tubes with a level of functionalization of about 20%. All the parameters to describe the bonded (bond, angle and dihedral) and non-bonded (van der Waals and Coulomb) interactions were obtained using CGenFF [18]. The porous 3D structures were generated by trying to mimic the experimental conditions where the tubes interact with

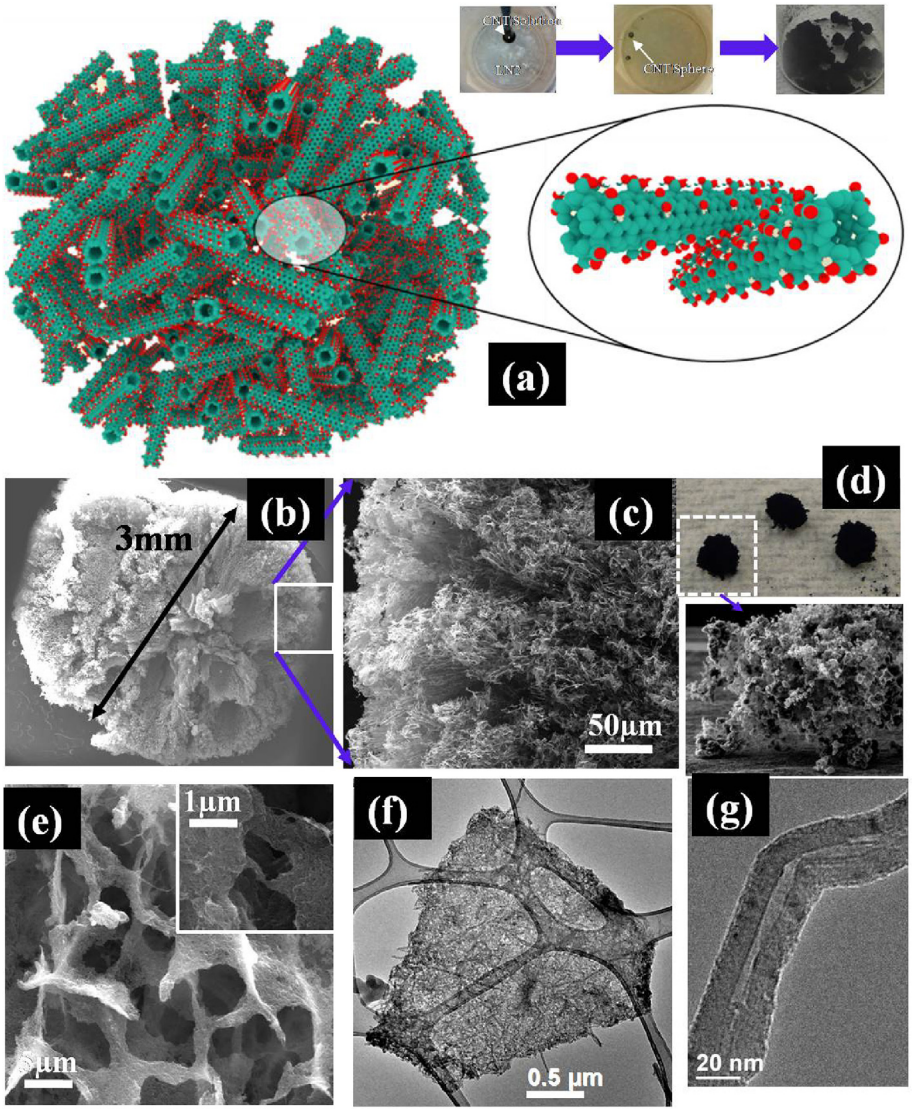

Fig. 1. Morphological properties of CNTs spheres. (a) Schematic of the 3D CNTs spheres, inset shows fabrication method. (b) Nominal diameter of the CNTs spheres (~3 mm). (c) High magnification SEM image of sphere showing porous morphology. (d) SEM image (using 65 tilted) of side view of 3D architecture, Inset shows uniform size of the sphere (e) Highly porous interconnected network structure. Inset shows high magnification image of interconnect (f) Bright field TEM showing the CNTs sheets which form the interconnected 3D network. (g) HRTEM images showing the structure integrity of multiwall CNTs spheres after functionalization. (A colour version of this figure can be viewed online.)