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Chemically interconnected light-weight 3D-carbon nanotube solid network

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ABSTRACT

Owing to the weak physical interactions such as van der Waals and π-π interactions, which hold nanotubes together in carbon nanotube (CNT) bulk structures, the tubes can easily slide on each other. Creating covalent interconnection between individual carbon nanotube (CNT) structures could remarkably improve the properties of their three-dimensional (3D) bulk structures. The creation of such nanoengineered 3D solid structures with improved properties and low-density remains one of the fundamental challenges in real-world applications. Here, we report the scalable synthesis of low-density 3D macroscopic structure made of covalently interconnected nanotubes using free-radical polymerization method after functionalized CNTs with allylamine monomers. The resulted interconnected highly porous solid structure exhibits higher mechanical properties, larger surface area and greater porosity than non-crosslinked nanotube structures. To gain further insights into the deformation mechanisms of nanotubes, fully atomistic reactive molecular dynamics simulations are used. Here we demonstrate one such utility in CO_2 uptake, whose interconnected solid structure performed better than non-interconnected structures.

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1. Introduction

The fabrication of macroscopic three-dimensional (3D) solid structures of nanotubes from chemically interconnecting of their individual nanotubes is a promising approach to harness the outstanding properties of nanotubes for development of new engineering materials [1–5]. Individual nanotubes in the as grown bundle stick together via weak physical van der Waals, π-π and hydrophobic interactions thereby making it easier to collapse in the presence of load thus limiting their physical properties as well as their performances in applications. Crosslinking individual nanotubes is one of the desirable methods to improve mechanical and physical properties of bulk structures [6,7]. Additionally, generating intermolecular junction between individual nanotubes exhibits interesting morphological and unique properties [4,8]. By controlling atomic-scale bridging between individual nanotubes, they can be ordered as covalently bonded 3D-solid networks with controllable physical properties such as density, porosity and mechanical properties [9,10].

Even though several chemical vapor deposition (CVD) methods [11,12], surface chemistry methods [13,14], and welding techniques [7,15] have been reported for building such 3D structures of nanotubes by creating atomic-scale bridges between individual tubular structures of CNTs, the fabrication of such nanoengineered 3D architectures remains one of the most significant challenges to integrate these materials in practical applications. Among all these approaches, the most promising and controllable approach is surface chemistry method because the properties of nanostructures can easily be manipulated by playing on surface functionalities. Additionally, this approach is crucial for the inexpensive mass production and selectivity of 3D-CNT solid network structures. CNT materials were produced using chemical functionalization,

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consisting of bonds with amines functional group. Recently, we reported Suzuki cross-coupling reaction for interconnection of individual CNTs using conjugate molecules to create light-weight and porous solid building blocks [13]. Such porous solid materials have a number of interesting properties such as lightweight, high-surface area etc. Their unique structure and exceptional properties demonstrated potential broad range of applications ranging from gas adsorption [14] [14], energy storage [16], environmental application [13] and mechanical damping [6]. For example, A. D. Leonard and co-workers used diazonium coupling chemistry for crosslinking carbon nanotubes [14]. As a result of diazonium coupling reaction, they obtained 3D-CNTs structures and used effectively for hydrogen storage [14]. In the other example, J. Zhu and co-worker used carboxylic acid functionalized single-walled CNTs and diamine terminal epoxy polymer for covalently interconnecting CNTs [17]. In this report, we functionalized surface of CNTs with allylamine monomer and used free-radical polymerization to create 3D-CNT solid structure (Fig. 1) and used the resulted light-weight porous architecture for CO_2 adsorption.

2. Experimental section

Multiwall carbon nanotubes (outer diameter:20–30 nm, inner diameter:5–10 nm, length:10–30 μm, Purity: >95 wt%) obtained from cheaptubes.com. The obtained CNTs were stirred in concentrated HNO_3 for 6 h at 70 °C to produce shortened CNTs and purify nanotubes from unwanted amorphous carbon and residual metal catalyst impurities. Additionally, the oxidation process produces oxygen containing functional groups, mainly carboxyl groups. The oxidized nanotubes filtered and washed with DI-water until pH:7 and dried overnight at 60 °C. After the oxidation process, the carboxyl groups were converted to acid chloride by reacting with thionyl chloride ($SOCl_2$) at 80 °C for 24 h and the resulted material filtered and washed with anhydrous ether. Then, CNTs were functionalized with allylamine monomer. In detailed, CNTs (0.5 g) dispersed in 50 ml DMF for 2 h sonication and allylamine monomer added into the dispersed CNTs solution with 5 mL trimethylamine. The mixture was stirred at 25 °C for 24 h under nitrogen, then washed with excess DI-water to remove unreacted allylamine. 3D-CNT solid structures was produced by free radical polymerization of nanotube monomers in DMF using azobisisobutyronitrile, AIBN (1 mol%) as initiator [18]. The polymerization reaction was performed at 80 °C for 24 h under nitrogen atmosphere. The final crosslinked nanotubes filtered and washed with DI-water. To create 3D solid structures, crosslinked nanotubes sonicated and freeze in liquid nitrogen and 3D porous CNTs solids obtained after freeze-drying process. The reaction was confirmed by Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM, FEI Quanta 400 ESEM FEG), and transmission electron microscope (JEOL 2100 Field Emission Gun TEM). Quantachrome BET surface analyzer was used to determine the surface area and pore size distribution. Here we also demonstrate the potential of the 3D solid macrostructure for CO_2 storage.

3. Results and discussion

The crosslinking mechanism between nanotubes rely on free-radical polymerization of allylamine monomer that covalently attached to nanotube surface. We assume that the crosslinking is taking place between individual nanotubes and each nanotube behaves as a crosslinker since more than one allylamine monomer linked on the surface of a nanotube structure and because of this reason the polymerization is not chain-polymerization. It creates a network between individual nanotubes because of multiple allylamine molecules on the surface of single nanotubes. The density of created porous 3D-CNTs solid structure is light-weight the density of 0.02 mg/mm^3 (Fig. 1c and d). The surface modification and crosslinking between individual nanotubes is confirmed by spectroscopic techniques (Fig. 2). Raman spectroscopy is one of the most effective way to confirm the chemical modifications on the surface CNTs. Raman spectra of nanotubes in general has two peaks, G-band and D-band [19]. The G-band is related to graphitic carbon and the D-band is related to sp^3 vibrations, which comes from the disorders on the surface of nanotubes [20]. The ratio between D and G-band (I_D:I_G), which is used to obtain information about structural changes as a result of functionalization, shows the defect density of the surface of CNTs. The Raman spectra of these CNTs show D-band

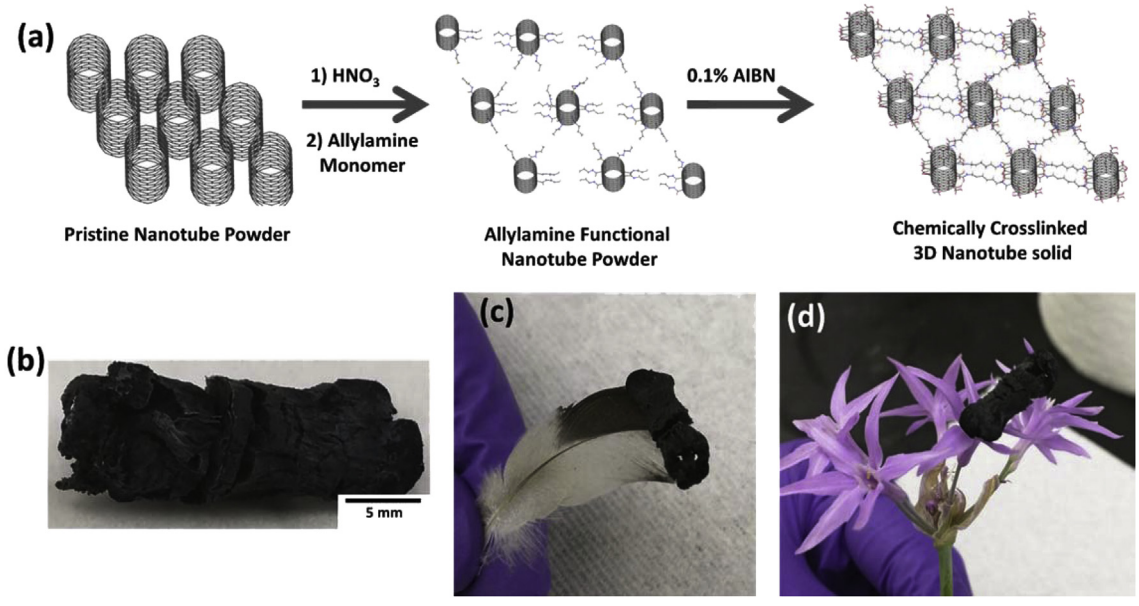

Fig. 1. (a) Schematic procedure of 3D-CNT porous solid synthesis: CNTs functionalized with allylamine monomer followed by free-radical polymerization using AIBN initiator, (b–d) the image of light-weight porous 3D-CNT foam (0.02 mg/mm^3) obtained after freeze-drying process. (A colour version of this figure can be viewed online.)