Carbon 115 (2017) 409–421

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Carbon sponge-type nanostructures based on coaxial nitrogen-doped multiwalled carbon nanotubes grown by CVD using benzylamine as precursor

Emilio Muñoz-Sandoval, Alejandro J. Cortes-López, Beatriz Flores-Gómez,
Juan L. Fajardo-Díaz, Roque Sánchez-Salas, Florentino López-Urías*

Advanced Materials Department, IPICYT, Camino a presa San José 2055, Lomas 4a sección, San Luis Potosí, 78216, Mexico

ARTICLE INFO

Article history:
Received 15 September 2016
Received in revised form
12 December 2016
Accepted 5 January 2017
Available online 11 January 2017

Keywords:
Carbon
Sponges
Nanotubes
Nitrogen
Synthesis
Characterizations

ABSTRACT

Carbon sponges-type nanostructures (CSTN) based on coaxial nitrogen-doped multiwalled carbon nanotubes (CA-MWCNTs) were synthesized using the aerosol assisted chemical vapor deposition method involving the decomposition of a mixture of ferrocene, benzylamine, thiophene, and ethanol at 1020 °C under a flow of H_2/Ar. Sample morphology and composition profiles were analyzed by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, and thermogravimetric analysis (TGA). SEM and TEM characterizations demonstrated that the CA-MWCNTs consisted of a core MWCNT surrounded by graphite materials with low crystallinity which was confirmed by XRD and Raman spectroscopy. Depending where the CSTN were collected along the reactor, three types of core MWCNTs morphologies were found: (1) N-doped MWCNTs with a bamboo shape and zigzagged growth, (2) straight MWCNTs, and (3) wavy MWCNTs. The carbon CSTN showed to be highly hydrophobic with outstanding oil absorption properties. XPS characterizations suggest the presence of water-fearing chemical groups such as ester- and ethoxy-groups anchored on the surface of the CA-MWCNTs. The mechanism in which the three types of MWCNTs are formed, the nature of the shell disordered graphite materials, and the hydrophobicity of the carbon sponges-type are thoroughly discussed.

1. Introduction

Sponges based on carbon nanotube (CNT) networks have attracted attention due to their intrinsic physical-chemical properties [1]. Among the most important properties of the sponges are the hydrophobic and oleophilic properties which could be exploited on environmental remediation in oil spills [2]. Another property is the high surface areas of the carbon sponges that could serve to capture undesirable metals or chemical species in the environment [3]. Furthermore, carbon sponges could be used in the fabrication of supercapacitor, forever-rechargeable battery [4]. Mechanical properties of the carbon sponges are also outstanding; when they are deformed, these recuperate their original form, making them potentially important in the fabrication of artificial muscles [5]. The three dimensional networks in the carbon sponges can serve as scaffolding or a template to grow biological systems such as cell growth and artificial bone production [6]. The production of carbon sponges or carbon nanotube ramifications can be performed using different techniques such as the chemical vapor deposition (CVD) method using a one-step synthesis strategy [7–11], secondary growth CVD method on templates [12–14], and electron beam irradiation at high temperatures [15–17]. Using ferrocene and toluene as precursors in a typical CVD experiment will grow well aligned and straight multiwalled carbon nanotubes (MWCNT) [18].

The idea of introducing foreign atoms into the lattices of MWCNTs have been widely studied, atoms such as nitrogen [19], boron [20], phosphorous [21], oxygen [22], sulfur [23–30], among others, have been introduced to the graphitic layers of carbon nanotubes. Each atom has an effect on the morphology of the carbon nanotubes, but sulfur and chlorine have played a crucial role in the formation of carbon sponges because sulfur or chlorine produces changes in the grown direction of MWCNTs [7,29]. Carbon sponges made their debut in 2010. Gui et al. [7] reported the

---

* Corresponding author.
E-mail address: flo@ipicyt.edu.mx (F. López-Urías).

http://dx.doi.org/10.1016/j.carbon.2017.01.010

synthesis of highly hydrophobic and super-oleophilic carbon sponges using a single-step CVD method involving the decomposition of a mixture of ferrocene ($Fe(C_5H_5)_2$) and 1,2-dichlorobenzene ($C_6H_4Cl_2$) at 860 °C under a flow of H_2/Ar. They found this material can experience large strain deformations and recover to its approximate original shape and high absorption capability (80–180 times its own weight). Using the same experimental approach, Hashim et al. [11] synthesized boron-doped carbon sponges with properties similar to those found by Gui et al. [7]. Hashim et al. decomposed a solution consisting of toluene (C_7H_8), ferrocene, and triethylborane ($C_6H_{15}B$) at 860 °C with an argon flow of 2.5 L/min. Shan et al. [8] reported the use of sulfur in the production of nitrogen-doped multiwalled carbon nanotube (N-MWCNTs) sponges produced by CVD method using combinations of different precursors: **(1)** xylene and sulfur; **(2)** ferrocene and pyridine; **(3)** ferrocene, thiophene and xylene. They found that an increase in the diameter of the CNTs favors an increment in the elastic modulus and a drop in the electrical conductivity of the carbon sponges. Furthermore, Shan et al. claimed that the diameter of the carbon nanotubes can be controlled by changing the concentration of thiophene which was also reported by Wei et al. [31]. It is clear that carbon sponges have proven to be an excellent material for diverse applications; its super hydrophobicity coupled with its amazing oil-absorption capacity make the carbon sponges an excellent candidate for environmental remediation research. Although several efforts have been made to understand the chemical reactivity of the surface of carbon nanostructures through X-ray photoelectron spectroscopy (XPS) characterization and other techniques [32–37], physical and chemical facts of such super hydrophobicity are not entirely clear. Due to their exceptional chemical and physical properties new routes have been developed to fabricate carbon sponges [38–41]. For instance, these carbon nanomaterials were proposed as scaffolds in implants [42].

In this letter, the synthesis of CSTN using the Aerosol-Assisted Chemical Vapor Deposition (AACVD) method is reported. Ferrocene and thiophene are dissolved in a solution containing benzylamine and ethanol. The samples are characterized by means of SEM, TEM, XRD, XPS, FTIR, TGA and Raman spectroscopy. In order to quantify the degree of graphitization of the carbon sponges, a deconvolution by the XRD (002) peak was performed. XPS spectrum also was deconvoluted to identify the different types of chemical species, functional groups, carbon materials (sp^2 or sp^3 bonding), nitrogen doping (N-quaternary, N-pyrrolic, N-pyridine), the C1s, N1s, and O1s. Furthermore, density functional calculations in N-doped and pristine bilayer graphene with intercalated H, Fe, and O are performed to elucidate the effect in the interlayer distance. To the best of our knowledge, investigations of carbon sponges using unconventional benzylamine and ethanol solutions in a CVD arrangement at high temperature have not been reported.

2. Methodology

2.1. Experimental details

CSTN were produced by the AACVD technique involving the decomposition of a mixture of ferrocene (1.6%), benzylamine (48.7%), thiophene (0.3%), and ethanol (49.4%) at 1020 °C under a H_2/Ar carrier flow of 0.8 l/min for 2 h growth. The grown material was collected from the reaction quartz tube by scraping its inner walls. The samples were classified according to the zone where they were grown. In Fig. 1a, a schematic representation of the AACVD setup is displayed, the different regions alongside the reactors are labeled by "S". Fig. 1b shows the range of temperature where the different precursor are decomposed. According to the temperature profile along the reactor (see Fig. SI-1); S3 and S4 have the highest temperatures. Electron microscopy: SEM (Helios Nanolab 600 Dual Beam) and HRTEM (FEI Tecnai F30) were used for morphological characterization of the samples. For SEM, small amounts of as-synthesized material were deposited on carbon tape over aluminum pins. For HRTEM, small amounts of the samples were ultrasonicated in ethanol and deposited over copper holey carbon TEM grids. Synthesized samples were analyzed with a Renishaw microRaman spectrometer with a 633 nm excitation laser wavelength. The nitrogen content in the CSTN were measured by X-ray photoelectron spectroscopy (XPS) using a PHI 5000 VersaProbe II equipment with a monochromatic Al-êá source (1486.7 eV). Thermo-gravimetric analysis were performed using a STA 6000 Perkin-Elmer under the following conditions: Samples were heated in simultaneous thermal analyzer in a temperature range of 50–950 °C with heating speed of 10 °C/min under dynamic flow of oxygen (20 mL/min). X-ray powder diffraction patterns were obtained using a Bruker XD8 ADVANCE. The deconvolution analysis was performed using the software Spectral Data Processor SDP 4.1. For the quantification of superhydrophobicity the angle of contact was measure four times to each sample using a ramé-hart instrument. For absorption measurements, the sample were submerged in the substance and weighted in a balance Mettler Toledo Modelo: XS205 several times. For the oil absorption test a mixed substance of Canoil cooking oil and Pinto color oil was used. Methanol, chloroform, pump oil, diesel, gasoline, vegetable oil, N,N-dimethylformamide, ethylene glycol also were used to test the absorption capacity of CSTN. Samples < 5 mg of CSTN material was previously weighed then dropped over the substance and left there over 5 min. The relation between the volume absorbed and the initial volume of the CSTN was calculated. We also obtained BET isotherms were obtained in Quantachrome NOVA 1200e equipment following the next conditions. Samples were degassed by 13 h keeping a heating temperature of 200 °C then N_2 gas was used as analysis gas to be physisorbed on the carbon nanotubes surface.

2.2. Theoretical details

Structural and electronic properties of single layer and double layer graphene were simulated using Density Functional Theory [43]. Spin polarized calculations were performed using the generalized gradient approximation (GGA) [44] with PBE parametrization was selected for the exchange-correlation functional [45] implemented in the SIESTA code [46,47]. The wave functions for the valence electrons were represented by a linear combination of pseudo-atomic numerical orbitals using a Double-ζ basis (DZP), while core electrons were represented by norm-conserving Troullier-Martins pseudopotentials in the Kleyn-man-Bylander nonlocal form [48,49]. The real-space grid used for charge and potential integration is equivalent to a plane-wave cut-off energy of 150 Ry. The pseudo-potentials (pp's) were constructed from 1, 4, 5, 6, and 8 valence electrons from the H, C, N, O, Fe ions (H:$1s^1$, C:$2s^2 2p^2$, N:$2s^2 2p^3$, O:$2s^2 2p^4$, and Fe:$3d^6 4s^2$). The single and two layer graphene were simulated with a 5 × 5 superlattice with 72 and 144 atoms respectively. We have considered 10 × 10 × 1 k-points, periodic boundary conditions for two dimensional systems, and an inter-structures distance was kept to a minimum of 30 Å in z-direction to avoid lateral interactions. In the calculations, all atoms contained in the system were relaxed using a conjugated gradient and variable cell methods, the total energy was calculated when the forces were converged to less than 0.04 eV/Å. The binding energy is determined by means of $E_{bind} = E_{syst} - n_N E_N - E_{Fe} - nc E_C$, where E_{syst} is the total energy of the complex system. E_N, E_{Fe}, and E_C are the energies of isolated N, Fe and C atoms respectively. Values of n_N, n_{Fe}, and n_C correspond to the number of N, Fe and C atoms respectively. The formation energy was determined by $E_{form} = E_{syt}$