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Fabrication and Characterization of Three-Dimensional Macroscopic All-Carbon Scaffolds

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Abstract

We report a simple method to fabricate macroscopic, 3-D, free standing, all-carbon scaffolds (porous structures) using multiwalled carbon nanotubes (MWCNTs) as the starting materials. The scaffolds prepared by radical initiated thermal crosslinking, and annealing of MWCNTs possess macroscale interconnected pores, robust structural integrity, stability, and conductivity. The porosity of the three-dimensional structure can be controlled by varying the amount of radical initiator, thereby allowing the design of porous scaffolds tailored towards specific potential applications. This method also allows the fabrication of 3-D scaffolds using other carbon nanomaterials such as single-walled carbon nanotubes, fullerenes, and graphene indicating that it could be used as a versatile method for 3-D assembly of carbon nanostructures with pi bond networks.

1. INTRODUCTION

The development of three-dimensional (3-D) all carbon scaffolds (porous structures) could lead to significant advancements in the field of energy storage, electronic devices, high performance catalysts, super capacitors, photovoltaic cells, field emission devices, smart sensors, and biomedical devices and implants [1–6]. 3-D microscopic scaffolds using carbon nanotubes have been successfully assembled by “bottom-up” (e.g. chemical vapor deposition) or “top-down” (e.g. capillary-induced self-assembly) approaches [7–12]. Using these strategies, microscopic 3-D random or patterned structures comprised of either aligned or entangled carbon nanotubes have been synthesized. Macroscopic scale (> 1mm in two or all three dimensions) structures of vertically aligned or entangled networks of pristine CNTs and graphene have also been fabricated [13–22]. However, the suitability of these approaches to control the porosity of the 3-D CNT structures or to form covalent bonds between CNTs, an important feature for many applications[23] still has to be demonstrated. Furthermore, the potential of these techniques to synthesize 3-D macroscale structures using other carbon nanomaterials such as fullerenes and graphene still needs to be investigated. Additionally, these approaches may present a practical challenge to develop macroscopic-

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Supplementary Information

Transmission electron microscopy, high resolution XPS elemental analysis, XPS survey spectrum, XPS high resolution scan of carbon 1s photoelectron peak using asymmetric peak fitting and Voigt function, XPS high resolution scan of oxygen 1s photoelectron peak, video of the crosslinked MWCNT scaffold and 360° view of the 3D reconstructed micro CT image of a MWCNT scaffold.

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scale (> 1mm in all 3 dimensions) carbon devices; either due to scalability issues, or high operational cost.

Towards the goal of fabricating 3-D all-carbon devices with macroscopic dimensions, we report the synthesis, and characterization of macroscopic, structurally-stable 3-D, all-carbon scaffold using MWCNTs. We also demonstrate that this facile method can in general be applied to fabricate 3-D, all-carbon scaffolds with different architectures (such as cylinders, disk etc.) using other carbon nanomaterials such as fullerenes, single-walled carbon nanotubes, and graphene.

2. MATERIALS AND METHODS

2.1 Fabrication of 3-D crosslinked carbon scaffolds

Multiwalled carbon nanotubes (Sigma Aldrich, Cat No. 659258), single walled carbon nanotubes (Sigma Aldrich, Cat No. 519308), Fullerenes (Sigma Aldrich, Cat No. 483036), benzoyl peroxide (BP, Luperox®, Sigma Aldrich, Cat No. 179981) and chloroform (CHCl_3 , Fisher Scientific, Cat No. BPC297) were used as purchased. Graphene nanoplatelets were synthesized and characterized by a literature method, and have been reported elsewhere [24]. The MWCNT scaffolds were fabricated by mixing MWCNT and BP at different mass ratios (BP: MWCNT = 1:0.5, 1:1, 1:2, 1:3 and 1:4). 1 ml CHCl_3 was added to the mixture to dissolve, and ensure uniform dispersion of BP (see supplementary information Figure S2 for the dispersion state of MWCNTs). The fullerenes, SWCNT and graphene nanoplatelet scaffolds were prepared by mixing BP with these carbon nanomaterials in the ratio 1:1. The BP-carbon nanomaterial mixture was subjected to bath sonication (30 minutes, Ultrasonicator FS30H, Fischer Scientific, Pittsburgh, PA), poured in custom machined Teflon molds (length = 1.2 mm, diameter = 0.5 mm), and incubated at 60°C for 24 hours. Post incubation, the molds were disassembled to obtain the cross-linked three-dimensional carbon scaffolds. 5 scaffolds were prepared for each experimental group. As a purification step after crosslinking, scaffolds were placed at 150°C for 20 minutes to remove the excess BP.

2.2 Raman Spectroscopy

Raman analysis was performed using a WITec alpha300R Micro-Imaging Raman Spectrometer using a 532 nm Nd-YAG excitation laser. Point spectra were recorded between 50–3750 cm^{-1} at room temperature.

2.3 Thermogravimetric Analysis (TGA)

TGA was performed using a Pyris Perkin Elmer diamond TGA instrument at the Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory, New York. Measurements were conducted on samples in alumina pan from 50 to 800 °C with a heating rate of 10 °C/min under an air flow of 100 ml/min.

2.4 Nanoindentation

Mechanical properties of purified MWCNT scaffolds were determined using nanoindentation (Triboindenter; Hysitron, Minneapolis, MN) with a Berkovich indenter tip. MWCNT scaffolds were attached to metal disks using cyanocrylate and mounted into the indenter. The points of indentation were selected at a distance no less than 100 μm away from each other. Samples were indented 7 times to determine elastic modulus (E_r) and material hardness (H). The tip area function was calibrated from indentation analysis on fused quartz, and drift rates in the system were measured prior to each indentation using standard indentation testing procedures [25]. First, a preload of 3 μN was applied to the system followed by a constant loading rate (10 $\mu\text{N}/\text{second}$). Then a hold segment at a fixed

system load was applied, followed by a constant unloading rate to retract the tip ($-10\mu\text{N}/\text{second}$), then another hold segment was imposed ($3\mu\text{N}$). The sample was indented with peak loads ranging from $\approx 15\mu\text{N}$ to $100\mu\text{N}$ [26]. The elastic response was calculated from the 20–90% portion of the unloading curve using methods previously described [27].

2.5 Micro-Computed Tomography

Micro-CT analysis was performed to quantify the 3D porosity of MWCNT scaffolds. A Scanco Medical microCT-40 (Scanco Medical AG, Bassersdorf, Switzerland) was used at 45 kV, 177 μA current and 900 ms integration time. A 3D Gaussian filter was applied to the images and a global threshold separated carbon nanotubes from noise [28]. The threshold value was determined by visual comparison between the thresholded and the raw gray-scale image and was optimized to accurately represent the raw images of scaffolds. For a $150 \times 150 \times 150$ voxel cube, total volume (TV), carbon nanotube volume (CNV) and scaffold volume fraction (CNV/TV) were determined. Three voxel cubes per scaffold were analyzed and the average of the three regions and its standard deviation is reported. The regions of analysis were selected in the center of the scaffold to eliminate the edge artifacts. The porosity of the scaffolds was calculated as:

$$\text{Porosity (\%)} = (1 - \text{scaffold volume fraction} [\frac{\text{CNV}}{\text{TV}}]) * 100$$

2.6 Electron Microscopy

Scanning electron microscopy (SEM) was performed using JOEL 7600F Analytical high resolution SEM at the Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory, New York. Crosslinked carbon nanotube specimens were placed on a conductive, double sided, carbon adhesive tab (PELCO, Ted Pella), and imaged at 1 and 5 kV accelerating voltages using a secondary electron imaging (SEI) detector. Transmission electron microscopy (TEM) was performed using FEI BioTwinG² TEM at Stony Brook University. The samples were imaged at 80kV using 300 mesh size, holey lacey carbon grids (Ted Pella, Inc.).

2.7 Image Processing

Image processing toolbox in MATLAB was used to quantify the porosity values of the crosslinked specimens. SEM images at various magnifications were cropped to remove the legends, and the scale bar, and were subjected to image processing steps such as edge detection, thresholding, median filtration, erosion and dilation followed by quantification of region properties. Porosity was calculated using $n=5$ images as the ratio of the total area of voids to the total area of the image.

$$\text{Porosity (\%)} = (\sum \text{Area of voids} / \text{area of the image}) * 100$$

2.8 Liquid Extrusion Porosimetry

Liquid extrusion porosimetry (LEP) was performed on purified MWCNT scaffolds using the PMI liquid extrusion porosimeter at Porous Materials Inc., Ithaca, NY. The CNT scaffolds were placed on a membrane and the sample chamber was filled with Galwick® (wetting liquid, surface tension ≈ 0 , propene, 1,1,2,3,3,3-hexafluoro, oxidized, polymerized) which penetrates into the pores of the sample. An inert gas under pressure was applied to extrude the liquid from the pores of the MWCNT scaffold. The volume and weight of the extruded

liquid was measured, and porosity and median pore diameter were calculated as described previously [29, 30].

2.9 Four Point Resistivity Measurements

Bulk resistivity was assessed by a four probe resistance measurement technique (Signatone S302-4, SP-4 probe) at Center for Functional Nanomaterials (CFN), Brookhaven National Laboratory, New York. Four point resistance measurements assess planar resistances for a theoretically infinitesimal thickness of sample. Thus, bulk material resistance can be derived from sheet resistance with a correction factor (F) to account for the thickness of the sample. The four, spring-loaded probes were equally spaced at 1.25 mm distances, with the two outer probes providing current and inner probes measuring voltage. Sheet resistance values for each MWCNT scaffold was measured at three different regions. Resistivity of the MWCNT scaffold was calculated by:

$$\rho = R_{\text{sheet}} * w * \frac{\pi}{\ln(2)} F$$

Where ρ is the bulk resistivity, R_{sheet} is the sheet resistance, w is the thickness of the sample (0.5 cm), and F is the correction factor. The conductivity was then obtained by calculating the $1/\rho$ value.

2.10 Statistical Analysis

Statistical analysis was performed using a student's "t" test and one-way anova followed by Tukey Kramer post hoc analysis. A 95% confidence interval ($p < 0.05$) was used for all statistical analysis.

3. RESULTS AND DISCUSSION

MWCNTs were thermally crosslinked via radical-initiated reaction using benzoyl peroxide. Briefly, a few drops of chloroform were added to the MWCNT-BP mixture (see method section for details), and the slurry was poured into prefabricated PTFE (Teflon®) molds (disk or cylinder molds), and incubated at 60°C for 24 hours. Benzoyl peroxide is a widely used initiator in free radical polymerization reactions [31]. It thermally decomposes to yield phenyl or benzoyloxyl free radicals, and CO₂ gas, and has been used for covalent functionalization of carbon nanotubes [32, 33]. Polymerization of formulations with reactive double bonds initiated by temperature-, or radiation-induced radicals is a widely-used method [34]. In the above reaction, the radicals react with the double bond network on the MWCNT structure; thereby forming active centers, which serve as inter-nanotube cross-linking sites. This results in the nanoscale crosslinking of carbon nanotubes, yielding macroscopic 3-D carbon scaffolds. The un-reacted BP and other volatiles (generated during the termination of radical crosslinking reaction) were removed by annealing the 3-D carbon scaffolds at 150 °C for 20 minutes. Figure 1 displays the digital images of representative unpurified and purified 3-D MWCNT scaffolds prepared by mixing MWCNTs and BP in the mass ratio 1:4. The unpurified scaffolds have a grayish-black tint, due to some residual BP (red circles), and purified scaffolds do not have this tint. The scaffolds are robust free-standing structures, and structurally stable; similar to polymeric scaffolds (see supplementary information S7 movie) [35].

3.1 Raman Spectroscopy

The Raman spectra of the pristine MWCNT, the unpurified, and purified MWCNT scaffolds (MWCNT: BP mass ratio = 1:4) are presented in Figure 2A. The pristine MWCNT used as

the starting material shows the characteristic D, G, and G' bands at 1355 cm^{-1} , 1580 cm^{-1} , and 2694 cm^{-1} respectively (Figure 2A, blue line). The I_D/I_G ratio for pristine MWCNTs is 0.07, The G band in the Raman spectra has been attributed to the intrinsic vibration of sp^2 bonded graphitic carbon atoms, whereas the D band corresponds to the defects induced in the nanotube structure due to disruption of the $\text{sp}^2\text{ C}=\text{C}$ bonds [36]. The Raman spectrum of the unpurified (Red line), and purified (green line) MWCNT scaffolds (MWCNT: BP mass ratio = 1:4) shows a substantial increase in the intensity of the D band. The I_D/I_G ratio for the unpurified and purified MWCNT scaffolds is 0.85, and 0.14, respectively. The Raman spectrum of the unpurified MWCNT scaffolds also shows additional minor peaks at 1000 cm^{-1} , 1230 cm^{-1} and 1775 cm^{-1} , which can be attributed to the breathing mode (C-C stretching) of benzene ring, C-O bond stretching (vibration of the peroxide chain) and C=O bond stretching (aryl carbonate functional group), respectively [37, 38]. These peaks are routinely observed in the Raman spectra of most radical functionalization reactions with BP [39]. The intensities of these peaks were relatively minor compared to the D and G bands, and were repeatedly observed only in the Raman spectra of unpurified MWCNT scaffolds. The decrease in the I_D/I_G ratio, and the absence of the minor peaks in the Raman spectrum of the purified MWCNTs scaffolds compared to the unpurified MWCNTs scaffolds suggests that the disruption of the $\text{sp}^2\text{ (C}=\text{C)}$ bonds for the purified MWCNTs scaffolds is due to crosslinked C-C bonds, covalent carbonyl, benzoyloxyl and phenyl functional groups formed during crosslinking reaction [33], and non-covalent π - π interactions between the MWCNTs and the aromatic groups of unreacted BP [40], and benzoyloxyl/phenyl radical by-products. The annealing of the unpurified MWCNT scaffolds removes the unreacted BP, and the reaction by-products which decompose between 100 – 150°C . The heating procedure de-adsorbs the unreacted BP and by-products, and partially restores $\text{sp}^2\text{ (C}=\text{C)}$ bonds decreasing the I_D/I_G ratio. However, the I_D/I_G ratio of the purified MWCNT scaffolds is still more than two orders greater than pristine MWCNTs indicating the presence of C-C, C-O and C=O bonds. The above assessment is further corroborated by TGA analysis.

3.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) has been widely used for the characterization of carbon based nanomaterials [41–44]. The TGA spectra of the pristine MWCNT, the unpurified and the purified MWCNT scaffolds (MWCNT: BP mass ratio = 1:4) is presented in Figure 2B. The TGA spectra of pristine MWCNTs is similar to previous reports [43], and exhibit negligible weight loss (0.05%) up to 700°C confirming its high thermal stability, and purity. Thermal decomposition of unpurified and purified MWCNT scaffolds can be divided into three temperature zones, 0 – 150°C , 150 – 500°C and $> 500^\circ\text{C}$. In first temperature zone between 0 – 150°C , the % weight loss of unpurified and purified MWCNT scaffolds was 43.06%, and 0.03% respectively. The high % weight loss observed for the unpurified MWCNT scaffolds can be attributed to the removal of residual water vapor, unreacted BP, and other volatiles (possible benzoyloxyl, and phenyl adducts formed during termination of the crosslinking reaction). The purified MWCNT scaffolds show negligible % weight loss indicating the high temperature annealing completely removes the unreacted BP, and other volatile by-products adsorbed on the unpurified MWCNT scaffold. In the second temperature zone between 150 – 500°C , the % weight loss is similar for the unpurified (16.51%), and the purified MWCNT (15.06%) scaffolds, and corresponds to the removal of functional groups attached to MWCNTs [43]. Finally, above 500°C , the observed % weight loss for the unpurified and purified MWCNT scaffolds corresponds to the thermal degradation of the MWCNT with sp^2 and sp^3 carbon atoms [41–43].

3.3 Nanoindentation

Nanoindentation was performed on purified MWCNT scaffolds (MWCNT:BP mass ratio = 1:1 and 1:2). Table 1 summarizes values of elastic modulus (Er) and hardness (H) measured

by 7 indents (at least 100 μ m distance between each indent). Representative force-displacement curve is presented in Figure 3 (MWCNT:BP mass ratio = 1:2). Er and H values of MWCNT scaffold (1:1) were 38.45 ± 14.42 MPa and 1.82 ± 0.54 MPa, respectively. MWCNT scaffold (1:2) exhibited Er of 45.72 ± 18.78 MPa and H of 3.47 ± 1.73 MPa, higher than 1:1 MWCNT:BP scaffold. These elastic modulus values for MWCNT scaffolds are much higher than the values measured for various polymeric, graphene and CNT based foams [15, 21, 45]. For example, the CNT assembly reported by Xu et al. possessed storage modulus of 1 MPa and loss modulus of 0.3 MPa [15]. Young's modulus of 3D graphene assemblies as reported by Zhang et al. was 1.2–6.6 MPa[21], Shi et al. was ≈ 290 kPa[46] and Wang et al. was ≈ 260 kPa [47]. The relatively high values of elastic modulus and hardness of MWCNT scaffolds further corroborates the formation of nanoscale, covalent crosslinks between MWCNTs necessary to achieve the measured mechanical strengths at a macroscopic scale.

3.4 X-ray Photoelectron Spectroscopy and Electrical Conductivity

Quantitative XPS chemical composition analysis, and high resolution carbon 1s and oxygen 1s analysis of the purified MWCNT scaffolds (MWCNT: BP mass ratio = 1:4) was also performed (see supplementary information). The quantitative XPS chemical composition analysis showed that carbon (94.1%) and oxygen (5.54%) were the primary elements in the scaffolds. The high resolution carbon 1s and oxygen 1s analysis indicate that oxygen is mainly present as an element of carboxyl functional group. The carboxyl groups could be due to the presence of trace amounts of benzyloxyl moieties that get covalently attached to the MWCNTs during the radical initiation reaction, and/or carboxylic acid groups formed due to reaction of active radical sites on the MWCNTs with oxygen impurities during the radical termination reaction. Furthermore, the bulk electrical conductivity of purified MWCNT scaffolds (cylinders, 6 mm length, 5 mm diameter, MWCNT: BP mass ratio = 1:4) was calculated to be 2×10^{-1} S cm $^{-1}$ from four point resistivity measurements [48], and satisfy the conductivity requirements for a large number of electrical applications [49]. This electrical conductivity value is similar or higher than a large number of thin films prepared using carbon nanotubes or graphene with large networks of sp 2 carbon atoms, and scattered regions of sp 3 carbon atoms, but lower than thin films of carbon nanotubes or graphene with only sp 2 carbon networks [50–52]. Thus, the Raman, TGA, XPS, and conductivity results taken together implies that the chemical composition of the purified MWCNT scaffolds mainly comprises of sp 2 carbon networks with sp 3 carbon junctions at the crosslinking sites.

3.5 Electron Microscopy

SEM was performed on the MWCNT scaffolds to characterize their structure, and confirm the cross-linking of the nanotubes (Figure 4). Figure 4A and B show low resolution SEM images of a representative unpurified MWCNT scaffold prepared by mixing MWCNT and BP in a ratio of 1:4. The cross-sections clearly show interconnected MWCNT networks that form the macroscopic 3-D architecture. The high resolution SEM in Figure 4C and D also display the crosslinking between individual MWCNTs, and the formation of junctions (red arrows, Figure 4D). Unlike polymer chains that coil together tightly with no inter-chain space or air pockets, the cross-linked MWCNT network is highly porous. The pores are irregular shaped, and interconnected. (Representative TEM images (supplementary information, Figure S1) display the formation of crosslinks between individual MWCNTs, further corroborating SEM results).

3.6 Micro Computed Tomography (micro-CT) and SEM Image Processing

The porosity and pore size of the unpurified and purified MWCNT scaffolds was further evaluated by microCT and SEM image analysis. No statistically significant difference was observed in the porosity and pore size values for unpurified, and purified. Thus, only the

analysis of purified MWCNTs is presented. MicroCT is a well-established method used to characterize the macroporosity of 3-D crosslinked scaffolds [53]. Figure 5A displays a 3-D reconstructed microCT image of a 1.23 mm × 1.23 mm × 1.23 mm section of a representative unpurified MWCNT (MWCNT: BP = 1:0.5) scaffold. Figure 5B, C, and D show the top, middle, and bottom section of the 3-D image displayed in Figure 5A, and clearly confirm the presence of pores (blue color represents the voids). These observations were consistent throughout all individual cross-sections of the microCT reconstructed images. The analysis of the microCT slices determined the pore sizes to be between 100–300 μm. The pores were interconnected, and distributed throughout the structure (see supplementary information S8 movie for a representative 360° view of 3-D microCT reconstructed MWCNT scaffold. The scaffolds can be examined from any angle of view at up to 6 μm resolution by shifting, rotating, and magnifying them in virtual space, and provide further visual support of the interconnected pores).

The macroporosity of the scaffolds fabricated by mixing MWCNTs with BP at different mass ratios (between 1:0.5 to 1:4) was determined from the microCT data, and is presented in Figure 6A and Table 2. The results show that porosity of MWCNT scaffolds decreased from 85% to 21% with increase in the amount of BP added for crosslinking the MWCNTs. It should be noted that the white and grey solid interconnected structures (Figure 5B, C and D) in the microCT images have nanometer sized pores, which cannot be visualized due to the microCT's resolution limit of 6 μm. The macroporosity within these structures can be clearly visualized in the images by SEM (see Figure 4). To further quantify the macroporosity, a widely-used and accepted literature technique[54–57] was used to perform image processing on a series of SEM images, and calculate the porosity within the white solid structure structures seen in the microCT images (see methods section for details). The porosity calculated by this method corresponds to the surface porosity, and has been used to estimate the porosity values for sandstones, and tissue engineering polymeric scaffolds [54–57]. The pore sizes from this analysis were determined to be between 125–750 nm. The macroporosity of the various MWCNT scaffolds (MWCNT:BP mass ratios between 1:0.5, to 1:4) is presented in Figure 6B and Table 3. The results show a trend similar to the microCT porosity data with a decrease in porosity from 43.42% to 23.62% with increase in MWCNT:BP mass ratio.

3.7 Liquid Extrusion Porosimetry (LEP)

In addition to microCT and SEM image processing, LEP was performed to assess the porosity of MWCNT scaffolds. LEP is a widely used, IUPAC recommended, non-hazardous (no mercury) method to assess the porosity of ceramics, food products and nonwoven fibrous filter media beds [58–61]. The porosity (%) and median pore diameter for all MWCNT scaffolds (MWCNT:BP mass ratios between 1:0.5, to 1:4) is presented in Figure 5C and Table 4. The results show a trend similar to microCT and SEM image analysis. The macro-porosity and median pore diameter decreased from 94.48% to 20.19% and 324.48 μm to 115.87 μm, respectively, with increase in MWCNT:BP ratio. The microCT, SEM porosity and LEP results taken together indicate that the porosity of MWCNT scaffolds can be tuned by varying the amount of crosslinking agent – BP. The higher amount of BP leads to the increase in the amount of active sites on the MWCNTs thereby inducing a higher crosslinking, and thereby, alters the porosity [62].

The thermal cross-linking method discussed above to fabricate 3-D MWCNT scaffolds can be easily adapted to fabricate 3-D scaffolds of various geometries (e.g. disks or cylinders) with other carbon nanomaterials such 0-D fullerenes, 1-D single-walled carbon nanotubes or 2-D graphene as starting materials (see Figure 7A). Figure 7B–D show the SEM images of scaffolds fabricated using these nanomaterials. The SEM cross-sections clearly show the macroscopic 3-D architectures due the crosslinking of these carbon nanomaterials. The

SWCNT scaffolds show topography similar to the MWCNT scaffolds. The fullerene and graphene scaffolds show topography that is distinctly different from the MWCNT and SWCNT scaffolds. Additional studies are required, and are currently underway to understand how the dimensionality these nanoscale building blocks affects the structure, and porosity of the 3-D scaffolds. Nevertheless, the fabrication of these 3-D all carbon macro-sized scaffolds opens avenues for further experimental and theoretical studies to elucidate the structure- (geometry, porosity) function (thermal, mechanical, electrical, and electromagnetic properties) relationships.

The introduction of carbon nanotechnology into large number of macro-scale applications for energy storage [21, 63, 64], thermal management [65], catalysis [4], electronic devices [2], and biomedical implants [66] would require the assembly of nanoscale building-blocks such as carbon nanotubes, fullerenes, and graphene to be assembled in structurally robust 3D architectures. An important issue affecting this development is the formation of covalent junctions between the building blocks [20, 23]. The results of this work introduce a novel, facile, cheap, and scalable method to fabricate 3D carbon nanotubes with chemically cross-linked junctions between sp^2 carbon atoms, which can be easily adapted to other carbon nanostructures such as fullerenes and graphene. Additionally, while the scaffolds architectures presented in this work are disk-shaped or cylindrical, one can also envision adapting this fabrication method using molds with complex geometries to tailor the shapes of the scaffolds. The insights from further structure-function relationship studies should provide the guiding principles for the large-scale production of macroscopic all-carbon devices with specific requirements for applications in clean energy technology, information technology, and healthcare.

4. SUMMARY

In summary, we report a simple method to fabricate macroscopic, 3-D, free standing, all-carbon scaffolds using multiwalled MWCNTs as the starting materials. The scaffolds prepared via radical initiated thermal crosslinking, and annealing of MWCNTs possess macroscale interconnected pores, robust structural integrity, stability, and conductivity. The porosity of the three-dimensional structure can be controlled by varying the amount of radical initiator. This method also allows fabrication of 3-D scaffolds using other carbon nanomaterials such as single-walled carbon nanotubes, fullerenes, and graphene indicating that it could be used as a versatile method for 3-D assembly of carbon nanostructures with pi bond networks. Additionally, the fabrication process of the scaffolds is rapid, cheap, and scalable, and can be adapted to fabricate scaffolds with various geometries (e.g. cylinders, disks) thereby opening avenues for structure-function studies towards the development of macroscopic all-carbon devices.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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References

1. Dai H. Carbon nanotubes: synthesis, integration, and properties. *Acc Chem Res.* 2002; 35(12): 1035–44. [PubMed: 12484791]

2. Sun DM, Timmermans MY, Tian Y, Nasibulin AG, Kauppinen EI, Kishimoto S, et al. Flexible high-performance carbon nanotube integrated circuits. *Nat Nanotechnol.* 2011; 6(3):156–61. [PubMed: 21297625]
3. Fan Z, Yan J, Zhi L, Zhang Q, Wei T, Feng J, et al. A three-dimensional carbon nanotube/graphene sandwich and its application as electrode in supercapacitors. *Adv Mater.* 2010; 22(33):3723–8. [PubMed: 20652901]
4. Xiong W, Du F, Liu Y, Perez A Jr, Supp M, Ramakrishnan TS, et al. 3-D carbon nanotube structures used as high performance catalyst for oxygen reduction reaction. *J Am Chem Soc.* 2010; 132(45):15839–41. [PubMed: 20949940]
5. Ma L, Sines G. Fatigue of isotropic pyrolytic carbon used in mechanical heart valves. *J Heart Valve Dis.* 1996; 5 (Suppl 1):S59–64. [PubMed: 8794033]
6. Sitharaman B, Shi X, Walboomers XF, Liao H, Cuijpers V, Wilson LJ, et al. In vivo biocompatibility of ultra-short single-walled carbon nanotube/biodegradable polymer nanocomposites for bone tissue engineering. *Bone.* 2008; 43(2):362–70. [PubMed: 18541467]
7. Huang JQ, Zhang Q, Zhao MQ, Xu GH, Wei F. Patterning of hydrophobic three-dimensional carbon nanotube architectures by a pattern transfer approach. *Nanoscale.* 2010; 2(8):1401–4. [PubMed: 20820723]
8. Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, Siegal MP, et al. Synthesis of large arrays of well-aligned carbon nanotubes on glass. *Science.* 1998; 282(5391):1105–7. [PubMed: 9804545]
9. Bennett RD, Hart AJ, Miller AC, Hammond PT, Irvine DJ, Cohen RE. Creating patterned carbon nanotube catalysts through the microcontact printing of block copolymer micellar thin films. *Langmuir.* 2006; 22(20):8273–6. [PubMed: 16981735]
10. De Volder M, Tawfik SH, Park SJ, Copic D, Zhao Z, Lu W, et al. Diverse 3D microarchitectures made by capillary forming of carbon nanotubes. *Adv Mater.* 2010; 22(39):4384–9. [PubMed: 20814919]
11. Qu J, Zhao Z, Wang X, Qiu J. Tailoring of three-dimensional carbon nanotube architectures by coupling capillarity-induced assembly with multiple CVD growth. *Journal of Materials Chemistry.* 2011; 21(16)
12. Chakrapani N, Wei B, Carrillo A, Ajayan PM, Kane RS. Capillarity-driven assembly of two-dimensional cellular carbon nanotube foams. *Proc Natl Acad Sci U S A.* 2004; 101(12):4009–12. [PubMed: 15016913]
13. Endo M, Muramatsu H, Hayashi T, Kim YA, Terrones M, Dresselhaus MS. Nanotechnology: ‘buckypaper’ from coaxial nanotubes. *Nature.* 2005; 433(7025):476. [PubMed: 15690030]
14. Cao A, Dickrell PL, Sawyer WG, Ghasemi-Nejhad MN, Ajayan PM. Super-compressible foamlike carbon nanotube films. *Science.* 2005; 310(5752):1307–10. [PubMed: 16311330]
15. Xu M, Futaba DN, Yamada T, Yumura M, Hata K. Carbon nanotubes with temperature-invariant viscoelasticity from –196 degrees to 1000 degrees C. *Science.* 2010; 330(6009):1364–8. [PubMed: 21127248]
16. Gui X, Wei J, Wang K, Cao A, Zhu H, Jia Y, et al. Carbon Nanotube Sponges. *Advanced Materials.* 2010; 22(5):617–21. [PubMed: 20217760]
17. Worsley MA, Kucheyev SO, Satcher JHH, Hamza AV, Baumann TF. Mechanically robust and electrically conductive carbon nanotube foams. *Applied Physics Letters.* 2009; 94(7):073115–3.
18. Kim KH, Oh Y, Islam MF. Graphene coating makes carbon nanotube aerogels superelastic and resistant to fatigue. *Nature nanotechnology.* 2012; 7(9):562–6.
19. Schiffres SN, Kim KH, Hu L, McGaughey AJH, Islam MF, Malen JA. Gas Diffusion, Energy Transport, and Thermal Accommodation in Single-Walled Carbon Nanotube Aerogels. *Advanced Functional Materials.* 2012:n/a–n/a.
20. Worsley MA, Pauzauskie PJ, Olson TY, Biener J, Satcher JH, Baumann TF. Synthesis of Graphene Aerogel with High Electrical Conductivity. *Journal of the American Chemical Society.* 2010; 132(40):14067–9. [PubMed: 20860374]
21. Zhang X, Sui Z, Xu B, Yue S, Luo Y, Zhan W, et al. Mechanically strong and highly conductive graphene aerogel and its use as electrodes for electrochemical power sources. *Journal of Materials Chemistry.* 2011; 21(18):6494–7.

22. Biener J, Stadermann M, Suss M, Worsley MA, Biener MM, Rose KA, et al. Advanced carbon aerogels for energy applications. *Energy & Environmental Science*. 2011; 4(3):656–67.
23. Hashim DP, Narayanan NT, Romo-Herrera JM, Cullen DA, Hahm MG, Lezzi P, et al. Covalently bonded three-dimensional carbon nanotube solids via boron induced nanojunctions. *Sci Rep*. 2012;2.
24. Paratala BS, Jacobson BD, Kanakia S, Francis LD, Sitharaman B. Physicochemical Characterization, and Relaxometry Studies of Micro-Graphite Oxide, Graphene Nanoplatelets, and Nanoribbons. *PLoS ONE*. 2012; 7(6):e38185. [PubMed: 22685555]
25. Oliver WC, Pharr GM. Improved techniques for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *Journal of Materials Research*. 1992; 7(6): 1564–80.
26. Mesarovic SD, McCarter CM, Bahr DF, Radhakrishnan H, Richards RF, Richards CD, et al. Mechanical behavior of a carbon nanotube turf. *Scripta Materialia*. 2007; 56(2):157–60.
27. Ozcivici E, Ferreri S, Qin YX, Judex S. Determination of bone's mechanical matrix properties by nanoindentation. *Methods Mol Biol*. 2008; 455:323–34. [PubMed: 18463828]
28. Judex S, Garman R, Squire M, Donahue L-R, Rubin C. Genetically Based Influences on the Site-Specific Regulation of Trabecular and Cortical Bone Morphology. *Journal of Bone and Mineral Research*. 2004; 19(4):600–6. [PubMed: 15005847]
29. Jena A, Gupta K. Liquid extrusion techniques for pore structure evaluation of nonwovens. *International Nonwovens Journal*. 2003; 12(3):45–53.
30. Jena, A.; Gupta, K. Determination of Pore Volume and Pore Distribution by Liquid Extrusion Porosimetry Without Using Mercury. 26th Annual Conference on Composites, Advanced Ceramics, Materials, and Structures: B: Ceramic Engineering and Science Proceedings; John Wiley & Sons, Inc. 2008. p. 277-84.
31. Braun, D. *International Journal of Polymer Science*. 2009. Origins and Development of Initiation of Free Radical Polymerization Processes.
32. Ying Y, Saini RK, Liang F, Sadana AK, Billups WE. Functionalization of carbon nanotubes by free radicals. *Org Lett*. 2003; 5(9):1471–3. [PubMed: 12713301]
33. Peng H, Reverdy P, Khabashesku VN, Margrave JL. Sidewall functionalization of single-walled carbon nanotubes with organic peroxides. *Chem Commun (Camb)*. 2003; (3):362–3. [PubMed: 12613613]
34. Graeme Moad, DHS. *The Chemistry of Radical Polymerization*. 2. Amsterdam; Boston: Elsevier; 2006. fully rev
35. Ishigami N, Ago H, Motoyama Y, Takasaki M, Shinagawa M, Takahashi K, et al. Microreactor utilizing a vertically-aligned carbon nanotube array grown inside the channels. *Chem Commun (Camb)*. 2007; (16):1626–8. [PubMed: 17530081]
36. Dresselhaus MS, Dresselhaus G, Saito R, Jorio A. Raman spectroscopy of carbon nanotubes. *Physics Reports*. 2005; 409(2):47–99.
37. Zyat'kov IP, Rakhimov AI, Pitsevich GA, Gogolinskii VI, Androsyuk ER, Sagaidak DI. Effect of fluorine-containing substituents on spectral structural characteristics of aroyl peroxides. *Journal of Applied Spectroscopy*. 1983; 39(1):798–802.
38. Vacque V, Sombret B, Huvenne JP, Legrand P, Suc S. Characterisation of the O-O peroxide bond by vibrational spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*. 1997; 53(1):55–66.
39. Baibarac M, Baltog I, Lefrant S, Mevellec JY, Bucur C. Vibrational and photoluminescence properties of the polystyrene functionalized single-walled carbon nanotubes. *Diamond and Related Materials*. 2008; 17(7–10):1380–8.
40. Baskaran D, Mays JW, Bratcher MS. Noncovalent and Nonspecific Molecular Interactions of Polymers with Multiwalled Carbon Nanotubes. *Chemistry of Materials*. 2005; 17(13):3389–97.
41. Rinzler AG, Liu J, Dai H, Nikolaev P, Huffman CB, Rodríguez-Macías FJ, et al. Large-scale purification of single-wall carbon nanotubes: process, product, and characterization. *Applied Physics A: Materials Science & Processing*. 1998; 67(1):29–37.

42. Hou P, Liu C, Tong Y, Xu S, Liu M, Cheng H. Purification of single-walled carbon nanotubes synthesized by the hydrogen arc-discharge method. *Journal of Materials Research*. 2001; 16(09): 2526–9.
43. Chen IWP, Richard L, Haibo Z, Ben W, Chuck Z. Highly conductive carbon nanotube buckypapers with improved doping stability via conjugational cross-linking. *Nanotechnology*. 2011; 22(48):485708. [PubMed: 22072011]
44. Kosynkin DV, Higginbotham AL, Sinitskii A, Lomeda JR, Dimiev A, Price BK, et al. Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature*. 2009; 458(7240):872–6. [PubMed: 19370030]
45. Gibson, LJ.; Ashby, MF. *Cellular Solids: Structure and Properties*. Cambridge University Press; 1997.
46. Xu Y, Sheng K, Li C, Shi G. Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process. *ACS Nano*. 2010; 4(7):4324–30. [PubMed: 20590149]
47. Tang Z, Shen S, Zhuang J, Wang X. Noble-Metal-Promoted Three-Dimensional Macroassembly of Single-Layered Graphene Oxide. *Angewandte Chemie International Edition*. 2010; 49(27):4603–7.
48. Smits F. Measurement of sheet resistivities with the four-point probe. *Bell Syst Tech J*. 1958; 37(3):711–18.
49. Chung DDL. Electrical applications of carbon materials. *Journal of Materials Science*. 2004; 39(8): 2645–61.
50. Lau C, Cervini R, Clarke S, Markovic M, Matison J, Hawkins S, et al. The effect of functionalization on structure and electrical conductivity of multi-walled carbon nanotubes. *Journal of Nanoparticle Research*. 2008; 10(0):77–88.
51. Sahoo NG, Rana S, Cho JW, Li L, Chan SH. Polymer nanocomposites based on functionalized carbon nanotubes. *Progress in Polymer Science*. 2010; 35(7):837–67.
52. Stankovich S, Dikin DA, Dommett GHB, Kohlhaas KM, Zimney EJ, Stach EA, et al. Graphene-based composite materials. *Nature*. 2006; 442(7100):282–6. [PubMed: 16855586]
53. Shi X, Sitharaman B, Pham QP, Liang F, Wu K, Edward Billups W, et al. Fabrication of porous ultra-short single-walled carbon nanotube nanocomposite scaffolds for bone tissue engineering. *Biomaterials*. 2007; 28(28):4078–90. [PubMed: 17576009]
54. Guarino V, Guaccio A, Netti P, Ambrosio L. Image processing and fractal box counting: user-assisted method for multi-scale porous scaffold characterization. *Journal of Materials Science: Materials in Medicine*. 2010; 21(12):3109–18. [PubMed: 20922560]
55. McCullen SD, Stevens DR, Roberts WA, Clarke LI, Bernacki SH, Gorga RE, et al. Characterization of electrospun nanocomposite scaffolds and biocompatibility with adipose-derived human mesenchymal stem cells. *Int J Nanomedicine*. 2007; 2(2):253–63. [PubMed: 17722553]
56. Grove C, Jerram DA. jPOR: An ImageJ macro to quantify total optical porosity from blue-stained thin sections. *Computers & Geosciences*. 2011; 37(11):1850–9.
57. Hunt RKRKP. Mineralogy of fine-grained sediment by energy-dispersive spectrometry (EDS) image analysis – a methodology. *Environmental Geology*. 2002; 42(1):32–40.
58. Rouquerol, Jean; Baron, Gino; Denoyel, Renaud; Giesche, Herbert; Groen, Johan; Klobes, Peter, et al. Liquid intrusion and alternative methods for the characterization of macroporous materials (IUPAC Technical Report). *Pure and Applied Chemistry*. 2012; 84(1):107–36.
59. Miller B, Tyomkin I. Liquid Porosimetry: New Methodology and Applications. *Journal of Colloid and Interface Science*. 1994; 162(1):163–70.
60. Datta AK, Sahin S, Sumnu G, Ozge Keskin S. Porous media characterization of breads baked using novel heating modes. *Journal of Food Engineering*. 2007; 79(1):106–16.
61. Hutten, IMM. *Handbook of Nonwoven Filter Media*. Elsevier; 2007.
62. Manley TR, Qayyum MM. Crosslinked polyethylene at elevated temperatures. *Polymer*. 1972; 13(12):587–92.
63. Kolpak AM, Grossman JC. Azobenzene-Functionalized Carbon Nanotubes As High-Energy Density Solar Thermal Fuels. *Nano Letters*. 2011; 11(8):3156–62. [PubMed: 21688811]

64. Lee SW, Yabuuchi N, Gallant BM, Chen S, Kim B-S, Hammond PT, et al. High-power lithium batteries from functionalized carbon-nanotube electrodes. *Nat Nano*. 2010; 5(7):531–7.
65. Romo-Herrera JM, Terrones M, Terrones H, Dag S, Meunier V. Covalent 2D and 3D Networks from 1D Nanostructures: Designing New Materials. *Nano Letters*. 2006; 7(3):570–6. [PubMed: 17355117]
66. Shi X, Sitharaman B, Pham QP, Spicer PP, Hudson JL, Wilson LJ, et al. In vitro cytotoxicity of single-walled carbon nanotube/biodegradable polymer nanocomposites. *J Biomed Mater Res A*. 2008; 86(3):813–23. [PubMed: 18041725]

Figure 1. Optical images of representative thermally-crosslinked 3-D, macroscopic (A) unpurified and (B) purified MWCNT scaffolds; prepared as cylinders (5 mm diameter, 10 mm length), and disks (5 mm diameter, 4 mm thickness).

Figure 2.

(A) Representative Raman spectra of pristine multiwalled carbon nanotubes (blue trace) and the 3-D crosslinked MWCNT scaffolds (MWCNT: BP mass ratio = 1: 4) before (red trace) and after (green trace) purification. (B) TGA curves of pristine MWCNTs, MWCNT scaffolds before- and after- purification.

Figure 3. Representative loading-unloading curve during nanoindentation of MWCNT scaffold (MWCNT: BP mass ratio = 1:2). The red dots are raw data, green dots are analyzed data. The slope of the best fit line (blue) was used to calculate elastic modulus.

Figure 4. Representative low (A–B), and high (C–D) resolution scanning electron microscopy images of unpurified MWCNT scaffold cross-sections (MWCNT: BP mass ratio = 1: 4).

Figure 5. (A) Representative 3D reconstructed microCT image of unpurified MWCNT scaffold, and the (B) top, (C) middle and (D) bottom microCT slice of the reconstructed 3D MWCNT scaffold image. The blue color in the images represents void spaces. Scale bar: (A) 100 μm , (B, C and D) 300 μm (MWCNT: BP mass ratio = 1: 4).

Figure 6.

(A) & (B) are porosity of purified MWCNT scaffolds fabricated with different mass ratios of BP (between 1:0.5 to 1:4) as determined by microCT and SEM image processing analysis, respectively. (C) Porosity of purified MWCNT scaffolds analyzed by liquid extrusion porosimetry.

Figure 7.

(A) Optical images of thermally-crosslinked 3D, macroscopic unpurified cylinder (5 mm diameter, 8 mm thickness), and discs (5 mm diameter, 3 mm thickness) fabricated using SWCNTs, fullerenes and graphene oxide nanoplatelets as starting material. (B), (C) and (D) are scanning electron microscopy images of unpurified scaffolds fabricated using SWCNTs, fullerenes and graphene oxide nanoplatelets, respectively.

Table 1

Mechanical properties of MWCNT scaffolds determined by nanoindentation

<i>Indent #</i>	<i>MWCNT:BP 1:1</i>		<i>MWCNT:BP 1:2</i>	
	Er (MPa)	H (MPa)	Er (MPa)	H (MPa)
1	39.44	1.89	55.62	2.07
2	35.01	1.74	39.87	4.77
3	33.84	1.96	28.72	0.73
4	31.77	1.97	38.94	4.83
5	16.12	1.01	84.08	4.72
6	53.4	2.77	34.59	2.26
7	59.59	1.4	38.25	4.91
Mean $\pm$ SD	38.45 $\pm$ 14.42	1.82 $\pm$ 0.54	45.72 $\pm$ 18.78	3.47 $\pm$ 1.73

Table 2

Porosity of MWCNT scaffolds calculated from microCT analysis

MWCNT: BP Ratio	Porosity (%) by microCT
1:0.5	84.67 ± 1.70
1:1	79.26 ± 1.77
1:2	70.29 ± 2.34
1:3	68.80 ± 5.72
1:4	21.31 ± 1.52

Table 3

Porosity of MWCNT scaffolds calculated from SEM analysis

MWCNT: BP Ratio	Porosity (%) by SEM image processing
1:0.5	43.424 $\pm$ 2.88
1:1	44.121 $\pm$ 3.66
1:2	39.895 $\pm$ 2.72
1:3	32.389 $\pm$ 4.93
1:4	23.623 $\pm$ 2.02

Table 4

Porosity and median pore diameter of MWCNT scaffolds determined from liquid extrusion porosimetry

MWCNT: BP Ratio	Porosity (%) by liquid extrusion porosimetry	Median pore diameter (μm)
1:0.5	94.485	324.48
1:1	85.684	312.96
1:2	68.275	288.76
1:3	48.305	141.00
1:4	20.194	115.87