Fabrication and characterization of three-dimensional macroscopic all-carbon scaffolds

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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 [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 (>1 mm 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 macroscopic scale 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-scale (>1 mm 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.

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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), fullerences (Sigma–Aldrich, Cat No. 483036), benzoyl peroxide (BP, Luperox®, Sigma–Aldrich, Cat No. 179981) and chloroform (CHCl₃, 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 (MWCNT:BP = 1:0.5, 1:1, 1:2, 1:3 and 1:4). 1 ml CHCl₃ was added to the mixture to dissolve, and ensure uniform dispersion of BP (see Supplementary information Fig. S2 for the dispersion state of MWCNTs). The fullerences, 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 min, Ultrasonicator FS30H, Fischer Scientific, Pittsburgh, PA), followed by a constant loading rate (10 lN/s). Then a hold segment was imposed (3 lN). The sample was indented with peak loads ranging from ≈15 lN to 100 lN [26]. The elastic response was calculated from the 20% to 50% portion of the unloading curve using methods previously described [27].

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 and 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 cyanoacrylate 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 (Eᵣ) and material hardness (Hᵣ). 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 µN/s). Then a hold segment at a fixed system load was applied, followed by a constant unloading rate to retract the tip (–10 µN/s), then another hold segment was imposed (3 µN). The sample was indented with peak loads ranging from ≈15 µN to 100 µN [26]. The elastic response was calculated from the 20% to 50% portion of the unloading curve using methods previously described [27].

2.5. Micro-computed tomography

Micro-CT analysis was performed to quantify the 3-D 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 3-D 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 × 150 × 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:

\[ \text{Porosity} = \left( 1 - \frac{\text{CNV}}{\text{TV}} \right) \times 100 \]

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 80 kV 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.

\[ \text{Porosity} = \left( \sum \text{Area of voids/area of the image} \right) \times 100 \]
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\textsuperscript{10} (wetting liquid, surface tension \( \approx 0 \), propane, 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 \cite{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 resistivity 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:

\[
\rho = \frac{R_{\text{sheet}} \times w \times \pi}{\ln(2) \times F}
\]

where \( \rho \) is the bulk resistivity, \( R_{\text{sheet}} \) 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\textsuperscript{10}) molds (disk or cylinder molds), and incubated at 60 °C for 24 h. Benzoyl peroxide is a widely used initiator in free radical polymerization reactions \cite{31}. It thermally decomposes to yield phenyl or benzoyloxyl free radicals, and CO\textsubscript{2} gas, and has been used for covalent functionalization of carbon nanotubes \cite{32,33}. Polymerization of formulations with reactive double bonds initiated by temperature-, or radiation-induced radicals is a widely-used method \cite{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 min. Fig. 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), while 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) \cite{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 Fig. 2A. The pristine MWCNT used as the starting material shows the characteristic D, G, and G’ bands at 1355 cm\textsuperscript{-1}, 1580 cm\textsuperscript{-1}, and 2694 cm\textsuperscript{-1}, respectively (Fig. 2A, blue line). The \( I_D/I_G \) ratio for pristine MWCNTs is 0.07. The G band in the Raman spectra has been attribute to the intrinsic vibration of sp\textsuperscript{2} bonded graphitic carbon atoms, whereas the D band corresponds to the defects induced in the nanotube structure due to disruption of the sp\textsuperscript{2} C=\textequiv C bonds \cite{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, 1230 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 MWCNT scaffolds compared to the purified MWCNT scaffolds suggests that the disruption of the sp$^2$ (C=O) bonds for the purified MWCNT scaffolds is due to crosslinked C–C bonds, covalent carbonyl, benzoyloxy and phenyl functional groups formed during crosslinking reaction [33], non-covalent π–π interactions between the MWCNTs and the aromatic groups of unreacted BP [40], and benzoyloxy /phenyl radical by-products. The annealing of the unpurified MWCNT scaffolds removes the unreacted BP, and the reaction by-products which

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**Fig. 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. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
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 μm distance between each indent). Representative force–displacement curve is presented in Fig. 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 andCNT 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 3-D 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.

### 3.2. 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 Fig. 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°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 and 500°C, the %weight loss is similar for the unpurified and purified MWCNT scaffolds (cylinders, 6 mm length, 5 mm diameter, 150.06%) 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 sp² and sp³ 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 μm distance between each indent). Representative force–displacement curve is presented in Fig. 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 3-D 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 benzoyloxyl 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 × 10⁻¹⁰ 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 sp² carbon atoms, and scattered regions of sp³ carbon atoms, but lower than thin films of carbon nanotubes or graphene
Fig. 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. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 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).
with only sp² 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 sp² carbon networks with sp³ 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 (Fig. 4). Fig. 4A and B shows 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 Fig. 4C and D also displays the crosslinking between individual MWCNTs, and the formation of junctions (red arrows, Fig. 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, Fig. 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]. Fig. 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. Fig. 5B–D shows the top, middle, and bottom sections of the 3-D image displayed in Fig. 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 and 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.

Fig. 5 – (A) Representative 3-D reconstructed microCT image of unpurified MWCNT scaffold, and the (B) top, (C) middle and (D) bottom microCT slice of the reconstructed 3-D MWCNT scaffold image. The blue color in the images represents void spaces. Scale bar: (A) 100 µm, (B–D) 300 µm (MWCNT:BP mass ratio = 1:4). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
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 and 1:4) was determined from the microCT data, and is presented in Fig. 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 (Fig. 5B–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 Fig. 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 Section 2 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 and 750 nm. The macroporosity of the various MWCNT scaffolds (MWCNT:BP mass ratios between 1:0.5 and 1:4) is presented in Fig. 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 and 1:4) is presented in Fig. 5C and Table 4. The results show a decreasing trend in porosity and average pore diameter as a function of MWCNT:BP ratio, similar to microCT and SEM image analysis. The macro-porosity and median pore diameter

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**Table 2 – Porosity of MWCNT scaffolds calculated from microCT analysis.**

<table>
<thead>
<tr>
<th>MWCNT:BP ratio</th>
<th>Porosity (%) by microCT</th>
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<tbody>
<tr>
<td>1:0.5</td>
<td>84.67 ± 1.70</td>
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<tr>
<td>1:1</td>
<td>79.26 ± 1.77</td>
</tr>
<tr>
<td>1:2</td>
<td>70.29 ± 2.34</td>
</tr>
<tr>
<td>1:3</td>
<td>68.80 ± 5.72</td>
</tr>
<tr>
<td>1:4</td>
<td>21.31 ± 1.52</td>
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</tbody>
</table>

**Table 3 – Porosity of MWCNT scaffolds calculated from SEM analysis.**

<table>
<thead>
<tr>
<th>MWCNT:BP ratio</th>
<th>Porosity (%) by SEM image processing</th>
</tr>
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<tr>
<td>1:0.5</td>
<td>43.42 ± 2.88</td>
</tr>
<tr>
<td>1:1</td>
<td>44.121 ± 3.66</td>
</tr>
<tr>
<td>1:2</td>
<td>39.895 ± 2.72</td>
</tr>
<tr>
<td>1:3</td>
<td>32.389 ± 4.93</td>
</tr>
<tr>
<td>1:4</td>
<td>23.623 ± 2.02</td>
</tr>
</tbody>
</table>

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**Table 4 – Porosity and median pore diameter of MWCNT scaffolds determined from liquid extrusion porosimetry.**

<table>
<thead>
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<th>MWCNT:BP ratio</th>
<th>Porosity (%) by liquid extrusion porosimetry</th>
<th>Median pore diameter (μm)</th>
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<tr>
<td>1:0.5</td>
<td>94.485</td>
<td>324.48</td>
</tr>
<tr>
<td>1:1</td>
<td>85.694</td>
<td>312.96</td>
</tr>
<tr>
<td>1:2</td>
<td>68.275</td>
<td>288.76</td>
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<td>1:3</td>
<td>48.305</td>
<td>141.00</td>
</tr>
<tr>
<td>1:4</td>
<td>20.194</td>
<td>115.87</td>
</tr>
</tbody>
</table>

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Fig. 6 – (A) and (B) are porosity of purified MWCNT scaffolds fabricated with different mass ratios of BP (between 1:0.5 and 1:4) as determined by microCT and SEM image processing analysis, respectively. (C) Porosity of purified MWCNT scaffolds analyzed by liquid extrusion porosimetry.
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 Fig. 7A). Fig. 7B–D shows 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 of carbon nanostructures.

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 3-D 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 3-D carbon nanotubes with chemically cross-linked junctions between sp² 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

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.

Fig. 7 – (A) Optical images of thermally-crosslinked 3-D, 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.
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 pibond 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.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2012.10.035.

References


