DOI: 10.1002/((please add manuscript number))

Article type: Communication

3D Macroporous Solids from Chemically Cross-linked Carbon Nanotubes

Sehmus Ozden¹, Tharangattu N. Narayanan², Chandra S. Tiwary¹, Pei Dong¹, Amelia H. C. Hart¹, Robert Vajtai¹, Pulickel M. Ajayan^{1*}

S. Ozden, Dr. C. S. Tiwary, Dr. P. Dong, A. H. C. Hart, Dr. R. Vajtai, Prof. P. M. Ajayan
Department of Material Science and NanoEngineering
Rice University
Houston, Texas 77005, USA
E-mail: ajayan@rice.edu
Dr. T. N. Narayanan
CSIR-Central Electrochemical Research Institute
Karaikudi, 630006, India

**Corresponding Author: ajayan@rice.edu*

KEYWORDS: Carbon nanotubes, chemical cross-linking, Suzuki reaction, three-dimensional, Palladium

If carbon nanotubes (CNTs) could be controllably interconnected, new types of 3D macroscopic carbon solids could be created with novel properties. The creation of such nanoengineered 3D architectures remains one of the most important challenges in nanotechnology. Production of nanoengineered 3D carbon structures, with controlled density and architecture, is one of the most desirable step for building next generation carbon based functional materials [1-3]. Current forms of CNT-based macrostructures include aligned CNTs [4], fibers [5], buckypapers [6,7], and aerogels [8, 9], each with different potential application areas such as supercapacitors [10,11], catalytic electrodes [12], dry adhesion [13], artificial muscles [14], gas adsorbers [15] and environmental applications [2, 16]. However, true 3D structures with covalent interconnections between building blocks such as CNT or graphene, are still challenging. For the inexpensive mass production and selectivity of 3D-CNT solid structures, chemical functionalization and cross-linking could be one of the most

controllable and scalable methods. Creating covalent junctions between CNTs is one of the most crucial steps to build CNT-based 3D macroscopic architectures [17]. Recently, there have been a few efforts to build such covalently interconnected 3D-CNT building blocks using chemical vapor deposition (CVD) technique [2, 3, 18] and solution chemistry [19, 20]. To create 3D-CNT based macro-architectures *via* solution chemistry, surface modification is one of the fundamental requirements. The essentials of chemical functionalization approach to create CNT frameworks rely on organic bridges which are bonded to CNTs and this approach has been used by several groups during the last decade [19, 21-23]. In these reports, CNT materials were produced using chemical functionalization, consisting of bonds with functional groups such as amines.

The Suzuki cross-coupling reaction, which is one of the most popular synthetic routes to create carbon-carbon (C-C) covalent junctions, has been used in a variety of real world synthetic applications. Some of which are the synthesis of natural products [24] and the formation of materials for energy and electronics [25]. It is a general method for creating carbon-carbon single covalent bonds between organic halides and boronic acid derivatives using Pd-based catalysts. Previously this crucial method has been used by Cheng and Adronov for the surface functionalization of CNTs [26]. Here, we report the scalable synthesis of 3D macroscopic solids made of covalently connected nanotubes *via* Suzuki cross-coupling (Figure 1). The resulting CNT solids are made of highly porous, interconnected structures made of chemically cross-linked carbon nanotubes. The CNT solids represent the next generation of carbon materials with several potential applications; we demonstrate here one such utility in the removal of oil from contaminated water [2, 3]. Raman spectroscopy (633nm laser), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM)(SEM, FEI Quanta 400 ESEM FEG), transmission electron microscope (TEM)(JEOL 2100 Field Emission Gun TEM), [and low temperature nitrogen absorbtion Quantachrome](#)

[Autosorb-3B BET surface analyzer](#) and thermogravimetric analysis (TGA) were used as characterization tools.

The Suzuki cross-coupling reaction occurs between aryl halide and boronic acid derivatives.

The reaction mechanism of the CNT interconnection using Suzuki cross-coupling reaction is shown in figure 2. Firstly, the CNTs ([Cheap tubes inc., 20-30 nm outer diameter, 10-30 \$\mu\$ m length](#)) were refluxed in concentrated HNO_3 for 18 hours to produce shortened and oxidized CNTs with oxygen-containing groups, the majority of which contain carboxyl groups (**1**) [27].

This oxidative procedure is also necessary to remove unwanted amorphous carbon and other residual metal impurities [28, 29]. Then, the carboxyl groups (CNT-COOH) (**1**) were converted to the corresponding acid chloride (CNT-COCl) by reacting with SOCl_2 at 80°C for 24 h (**2**). Tetrakis(triphenylphosphine) palladium(0) ($\text{Pd}(\text{PPh}_3)_4$) was added under argon to a mixture of 1,4-phenyldiboronic acid and anhydrous Cs_2CO_3 in anhydrous toluene followed by CNT-COCl (**2**). The reaction mixture was then heated at 100°C for 5 days. The resulting material was filtered and washed with water to remove excess Cs_2CO_3 and unreacted 1,4-phenyldiboronic acid. The reaction mechanism starts with the oxidative addition of CNT-COCl (**2**) to the Pd(0) to form a Pd(II), CNT-CO-Pd-Cl (**3**), complex structure; after which the base, Cs_2CO_3 , replaces the chloride on the palladium complex. Transmetalation starts with adding 1,4-benzenediboronic acid. Then the reductive elimination gives the boronic acid functional CNTs (CNT-CO-Ph-B(OH) $_2$) (**5**). After repeating the same mechanism between boronic acid functionalized CNTs and chlorinated CNTs (CNT-COCl) (**2**) the final CNT-CO-Ph-CO-CNT (**6**) coupling product was formed.

To create junctions between CNTs using solution chemistry, surface modification of CNT is necessary. The modifications of the surface of the CNTs are confirmed using Raman spectroscopy [30] (figure 3a). Raman spectra of CNTs typically has two peaks, the G-band which is closely related to vibrations of sp^2 carbon materials, and the D-band which comes from the disorder of CNT sidewalls [31]. A quantitative measure of defect density in the CNT

sidewalls can be determined from the ratio between these two bands, $I_D:I_G$. This ratio is used for obtaining information about the structural changes as a result of functionalization [32, 33].

The Raman spectra of these CNTs show a disorder mode (D-band) and graphitic mode (G-band) at 1349 cm^{-1} and 1571 cm^{-1} respectively. As a result of functionalization, the intensity of the D-band increases due to sp^3 carbons in the CNTs after acid treatment [34, 35]. The intensity ratio between the D-band and G-band (I_D/I_G) increased from 0.59 to 1.06 because the disorder on the surface of CNTs increased [34, 36].

XPS analysis was used for quantitative chemical analysis of the pure, chlorinated, and cross-linked CNTs (figure 3). The C1s core level peak positions of the carbon atoms are approximately at 285 eV and the peak position of oxygen is around 532 eV. After oxidation of CNTs the ratio of oxygen increased from 1.2% to 11%. In high resolution XPS characterization of pure CNTs, the C-C and O-C=O bond peak is at 284.6 and 284.8 eV respectively (figure 3b). In the XPS spectrum of the chlorinated CNTs, the peak around 200 eV represents chlor (Cl) atom (figure 3c). The peaks at 284.4 eV, 285 eV and 285.9 eV correspond C-C, O-C=O and C-Cl bonds respectively in figure 2c. According to the survey scan of XPS characterization the amount of chlorine constitutes 1.4% by weight of the sample. Figure 3d shows the XPS spectrum of the CNTs after the Suzuki cross-coupling reaction where C-C, C=O and C-O bonds are at 284.5 eV, 284.9 eV and 285.8 eV respectively. Chlorine atoms disappear after the Suzuki cross-coupling reaction as shown in figure 3d. These peaks are indicate that the coupling reaction took place successfully. Apart from the spectroscopy characterizations the junctions were imaged using scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM).

BET surface analyzis was used to determine the surface area and porosity of the pristine CNTs and the 3D-CNT solids. Freeze dried pristine CNT and 3D-CNT solids were degassed 17 hours at $200\text{ }^{\circ}\text{C}$, then BET surface analyzis carried out. The N_2 absorption shows a -type-II isotherm that exhibits a negligible concave section, that is -known to be pointed to

microporous volume uptake and a quick ascent in total volume close $P/P_0 = 1$ indicating a macroporous material (Figure S6a). The BET surface area (S_{BET}) area of 3D-CNT solids (177 m^2/g) is larger than the one for the pristine CNTs (166 m^2/g) (Figure S6b). CNT and 3D-CNT solid have similar average pore size distribution and the cumulative pore volume of 3D-CNT solid is higher than CNTs. (Figure S6c).

The structure of the 3D-CNT macrostructure is shown in figure 4. A few conditions such as oxidation rate, reaction time, and different ratios of the initial materials were varied during the experiment. The best results were obtained from 18 hours of oxidation in HNO_3 and at least 5 days reaction time of the Suzuki coupling reaction due to increased functionalization ratio. These longer oxidation and Suzuki coupling times enable the CNTs to form 3D solid macrostructures after lyophilization (freeze-drying) due to higher CNT cross-coupling ratios. CNTs were found to form a solid macrostructure when they have enough functional groups to cross-link with covalent interconnection. The image of a 3D-CNT solid network is shown in figure 4g which contains various network morphologies in different regions. The 3D-CNT solid structure is highly porous as can be seen in figure 4c. In the morphology of the solid structure observed in figure 4c, CNT bundles are interconnected as a network, creating the microporous structures. The other morphology is observed in figure 4a and 4d where the CNTs form a layer by layer assembly, into thin films. Additionally, CNTs can also be formed into macrotubular architectures (Figure 4e). Cross-coupling of the CNTs can be observed in the SEM images included in figure S3 of the supporting information. The low magnification image in figure S3 reveals interconnections between CNTs. These Y-junctions of CNTs can be either end-to-side or end-to-end junctions which as a result of the oxidation step, where the ends of CNTs and the surfaces of CNTs were oxidized. TEM was used to obtain more detailed morphological information of the CNT junctions, shown in figure 5. In order to confirm the presence of the CNT junctions, bright field images were obtained. It was further found that linkers with different shapes yield CNTs with more complex architectures

1 compared to simple junction geometries (figure 5a). Figure 5b shows multi-terminal CNT
2 junctions and their representative schematic figure is shown on the bottom of TEM images. In
3
4 general it has been observed that the end-to-end junctions are more prevalent than other types
5
6 of junctions, due to the ends of nanotubes being preferentially modified. The ends of the
7
8 CNTs are chemically more reactive than their sides because of the presence of defects at these
9
10 sites (figure S4). The TEM images of X-junction CNTs that have been formed as a result of
11
12 side-to-side functionalization are shown in figure 5c. All these types of junctions are essential
13
14
15 for the CNTs to form solid structures.
16
17

18
19 Recent reports have proven that one of the potential applications of such porous CNT solids is
20
21 in oil absorption from water since these are typically oleophilic. Following some of the
22
23 previous reports on the oil absorption capacity of vapor grown 3D-CNT solids, the 3D-CNT
24
25 solids made here by chemical cross-linking were demonstrated for the same application. The
26
27 absorbed oil (used engine oil) has been shown to be removed easily by burning the material in
28
29 air without destroying the structure. The 3D-CNT solid material obtained in this study
30
31 absorbed ~120 times its own weight of oil within four minutes (Figure S6).
32
33
34
35
36
37

38 In conclusion, we have reported the well-known Suzuki cross-coupling reaction as an
39
40 approach to create covalently bonded CNT networks. As a consequence of the cross-linking
41
42 of the CNTs, the formation of highly porous 3D solids occurred. Additionally, multi-terminal
43
44 junctions of CNTs in end-to-end, end-to-side and side-to-side configurations were observed in
45
46 the microstructure, also as a result of the cross linking. The approach demonstrates the ability
47
48 to interconnect nanostructures such as carbon nanotubes using interface controllable
49
50 chemistry that can lead to scalable synthesis of 3D solids with controlled morphologies and
51
52 multifunctional properties.
53
54
55
56
57
58

59 Experimental Section

60
61
62
63
64
65

Synthesis of covalently interconnected 3D-CNT solids: CNTs (12 mg) were refluxed in concentrated HNO_3 for 18 hours to produce shortened and oxidized CNTs, which have terminal, mainly carboxyl, oxygen-containing groups,. The oxidized CNTs were then washed with DI-water until pH=7. Then CNTs were refluxed in 50 ml SOCl_2 and 2 ml 1,2-dichlorobenzene for 24 hours. The CNTs were sonicated for 10 min and added to a flask. Next, 60 mg $\text{Pd}(\text{PPh}_3)_4$ and 160 mg Cs_2CO_3 in toluene (30 ml) were added to said flask. The reaction was run at 100 °C, for 5 days under Ar atmosphere. Then the final product freeze dried.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgments

This work has been supported by U.S. Department of Defense: U.S. Air Force Office of Scientific Research (AFOSR) for the project “MURI: Synthesis and Characterization of 3-D Carbon Nanotube Solid Networks” through the award # FA9550-12-1-0035.

REFERENCES

- [1] P. M. Ajayan, O. Z. Zhou, *Top. Appl. Phys.* **2001**, 80, 391.
- [2] D. P. Hashim, N. T. Narayanan, J. M. Romo-Herrera, D. A. Cullen, M. G. Hahm, P. Lezzi, J. R. Suttle, D. Kelkhoff, E. Munoz-Sandoval, S. Ganguli, A. K. Roy, D. J. Smith, R. Vajtai, B. G. Sumpter, V. Meunier, H. Terrones, M. Terrones, P. M. Ajayan, *Sci. Rep.* **2012**, 2, 363.
- [3] X. C. Gui, J. Q. Wei, K. L. Wang, A. Y. Cao, H. W. Zhu, Y. Jia, Q. K. Shu, D. H. Wu, *Adv. Mater.* **2010**, 22, 617.
- [4] A. Y. Cao, P. L. Dickrell, W. G. Sawyer, M. N. Ghasemi-Nejhad, P. M. Ajayan, *Science* **2005**, 310, 1307.
- [5] Y. L. Li, I. A. Kinloch, A. H. Windle, *Science* **2004**, 304, 276.

- [6] M. Endo, H. Muramatsu, T. Hayashi, Y. A. Kim, M. Terrones, N. S. Dresselhaus, *Nature* **2005**, 433, 476.
- [7] S. M. Cooper, H. F. Chuang, M. Cinke, B. A. Cruden, M. Meyyappan, *Nano Lett.* **2003**, 3, 189.
- [8] J. H. Zou, J. H. Liu, A. S. Karakoti, A. Kumar, D. Joung, Q. A. Li, S. I. Khondaker, S. Seal, L. Zhai, *Acs Nano* **2010**, 4, 7293.
- [9] M. B. Bryning, D. E. Milkie, M. F. Islam, L. A. Hough, J. M. Kikkawa, A. G. Yodh, *Adv. Mater.* **2007**, 19, 661.
- [10] D. N. Futaba, K. Hata, T. Yamada, T. Hiraoka, Y. Hayamizu, Y. Kakudate, O. Tanaike, H. Hatori, M. Yumura, S. Iijima, *Nat Mater* **2006**, 5, 987.
- [11] Y. W. Cheng, S. T. Lu, H. B. Zhang, C. V. Varanasi, J. Liu, *Nano Lett.* **2012**, 12, 4206.
- [12] J. E. Trancik, S. C. Barton, J. Hone, *Nano Lett.* **2008**, 8, 982.
- [13] L. T. Qu, L. M. Dai, M. Stone, Z. H. Xia, Z. L. Wang, *Science* **2008**, 322, 238.
- [14] J. Foroughi, G. Spinks, G. G. Wallace, J. Oh, M. E. Kozlov, S. L. Fang, T. Mirfakhrai, J. D. W. Madden, M. K. Shin, S. J. Kim, R. H. Baughman, *Science* **2011**, 334, 494.
- [15] P. M. Sudeep, T. N. Narayanan, A. Ganesan, M. M. Shaijumon, H. Yang, S. Ozden, P. K. Patra, M. Pasquali, R. Vajtai, S. Ganguli, A. K. Roy, M. R. Anantharaman, P. M. Ajayan, *Acs Nano* **2013**, 7, 7034.
- [16] A. Srivastava, O. N. Srivastava, S. Talapatra, R. Vajtai, P. M. Ajayan, *Nat. Mater.* **2004**, 3, 610.
- [17] J. M. Romo-Herrera, M. Terrones, H. Terrones, S. Dag, V. Meunier, *Nano Lett.* **2007**, 7, 570.
- [18] C. S. Shan, W. J. Zhao, X. L. Lu, D. J. O'Brien, Y. P. Li, Z. Y. Cao, A. L. Elias, R. Cruz-Silva, M. Terrones, B. Q. Wei, J. Suhr, *Nano Lett.* **2013**, 13, 5514.
- [19] A. D. Leonard, J. L. Hudson, H. Fan, R. Booker, L. J. Simpson, K. J. O'Neill, P. A. Parilla, M. J. Heben, M. Pasquali, C. Kittrell, J. M. Tour, *J. Am. Chem. Soc.* **2009**, 131, 723.
- [20] Y. C. Zhang, A. A. Broekhuis, M. C. A. Stuart, T. F. Landaluce, D. Fausti, P. Rudolf, F. Picchioni, *Macromolecules* **2008**, 41, 6141.
- [21] J. W. Zhang, D. Z. Jiang, *Compos. Sci. Technol.* **2011**, 71, 466.
- [22] P. W. Chiu, G. S. Duesberg, U. Dettlaff-Weglikowska, S. Roth, *Appl. Phys. Lett.* **2002**, 80, 3811.
- [23] M. Palma, W. Wang, E. Penzo, J. Brathwaite, M. Zheng, J. Hone, C. Nuckolls, S. J. Wind, *J. Am. Chem. Soc.* **2013**, 135, 8440.

- [24] S. R. Chemler, D. Trauner, S. J. Danishefsky, *Angew. Chem. Int. Ed.* **2001**, 40, 4544.
- [25] F. Naso, F. Babudri, G. M. Farinola, *Pure Appl. Chem.* **1999**, 71, 1485.
- [26] F. Y. Cheng, A. Adronov, *Chem. Mater.* **2006**, 18, 5389.
- [27] I. D. Rosca, F. Watari, M. Uo, T. Akaska, *Carbon* **2005**, 43, 3124.
- [28] Z. W. Wang, M. D. Shirley, S. T. Meikle, R. L. D. Whitby, S. V. Mikhlovsky, *Carbon* **2009**, 47, 73.
- [29] H. Hu, B. Zhao, M. E. Itkis, R. C. Haddon, *J. Phys. Chem. B* **2003**, 107, 13838.
- [30] R. Graupner, *J. Raman Spectrosc.* **2007**, 38, 673.
- [31] M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. Jorio, *Phys. Rep.* **2005**, 409, 47.
- [32] C. D. Doyle, J. D. R. Rocha, R. B. Weisman, J. M. Tour, *J. Am. Chem. Soc.* **2008**, 130, 6795.
- [33] M. S. Strano, C. A. Dyke, M. L. Usrey, P. W. Barone, M. J. Allen, H. W. Shan, C. Kittrell, R. H. Hauge, J. M. Tour, R. E. Smalley, *Science* **2003**, 301, 1519.
- [34] Z. H. Qu, G. J. Wang, *J. Nanosci. Nanotechnol.* **2012**, 12, 105.
- [35] H. Z. Geng, K. K. Kim, K. P. So, Y. S. Lee, Y. Chang, Y. H. Lee, *J. Am. Chem. Soc.* **2007**, 129, 7758.
- [36] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, *Carbon* **2008**, 46, 833.

Figure 1. Schematic of the 3D-CNT solid macrostructure synthesis from CNT powder. Initial CNT powder were oxidized in HNO_3 then converted to acid chloride. CNTs were covalently interconnected via Suzuki coupling reaction which is palladium catalyst based coupling reaction. After lyophilization (Freeze Drying) 3D-CNT solid structure formed.

Figure 2. The Suzuki coupling reaction mechanism. (1) oxidized CNTs, (2) chlorinated CNTs, (3) CNT-CO-Pd(II)-Cl complex structure, (4) CNT-Pd(II)-Ph-B(OH)₂, (5) boronic acid functionalized CNTs, (6) interconnected CNTs.

Figure 3. (a) Raman spectra of pristine CNTs powder, chlorinated CNTs and 3D-CNT solid macrostructure, (b) XPS spectra of pristine CNTs powder, (c) chlorinated CNTs powder, (d) 3D-CNT solid macrostructure.

Figure 4. Scanning electron microscopy (SEM) images of different region of the porous 3D-CNT solid structure. (a, d) layer by layer CNT thin films, (b, c, f) CNT bundles as a network, (e) 3D-CNT after lyophilization of the covalently connected CNTs via Suzuki coupling reaction formed as tubular structure, (g) 3D-CNT solid macrostructure.

Figure 5. High resolution transmission electron microscopy (HR-TEM) of the 3D-CNT structures, (a) high and low (inserted) magnification image of Y-junction of CNTs with representative schematic image, (b) high and low (inserted) magnification image of end-to-end junction of CNTs with representative schematic image (c) high and low (inserted) magnification image of X-junction CNTs with representative schematic image.

Figure 6. (a) Photograph of oil-water batch at $t=0$ min and inset shows 3D-CNT solid structure before use, (b) 3D-CNT solid absorbing oil at $t=1$ min, (c) 3D-CNT solid absorbing oil at $t=4$ min, (d) weight-to-weight oil absorption capacity of the 3D-CNT solid structure.

KEYWORDS: Carbon nanotubes, chemical cross-linking, Suzuki reaction, three-dimensional, Palladium catalyst

*Sehmus Ozden, Tharangattu N. Narayanan, Chandra S. Tiwary, Pei Dong, Amelia H. C. Hart, Robert Vajtai, Pulickel M. Ajayan**

Title: 3D Macroporous Solids from Chemically Cross-linked Carbon Nanotubes

Supporting Information

3D Macroporous Solids from Chemically Cross-linked Carbon Nanotubes

Sehmus Ozden¹, Tharangattu N. Narayanan², Chandra S. Tiwary¹, Pei Dong¹, Amelia H. C.

Hart¹, Robert Vajtai¹, Pulickel M. Ajayan^{1}*

Synthesis of 3D-CNT Solid Macrostructure

CNTs (12 mg) were refluxed in concentrated HNO₃ for 12 hours to produce shortened and oxidized CNTs, which are terminated with oxygen-containing groups, mainly carboxyl groups. Oxidized CNTs washed with DI-water until pH=7. Then CNTs were refluxed in 30 ml SOCl₂ and 2 ml 1,2-dichlorobenzene for 24 hours. CNT and CNT was sonicated 10 min and added to flask. 60 mg Pd(PPh₃)₄ and 160 mg Cs₂CO₃ was added in toluene (30 ml). The reaction was run at 100 °C, for 144 hours under Ar atmosphere. The final product dispersed in DI-water and freeze dried.

Figure S1. Photograph of (A) pristine CNT powder, (B) 3D-CNT solid structure after Suzuki coupling reaction and lyophilization.

Figure S2. Scanning electron microscope (SEM) images of porous 3D-CNT solid macrostructure. CNTs formed like layered sheets.

Figure S3. Scanning electron microscope (SEM) images of CNT network/junctions after Suzuki coupling reaction.

Figure S4. Transmission electron microscope (TEM) of 3D-CNT network.

Figure S5. Thermogravimetric analysis graph (TGA) of pristine, oxidized, chlorinated CNTs and 3D-CNTs.

Figure S6. (a) The N_2 adsorption isotherm of pristine CNTs and 3D-CNT solid (b) BET Surface area of Pristine CNTs and 3D-CNT solid (c) DFT method pore size distribution and

cumulative pore volume of pristine CNTs and 3D-CNT solids. (BET surface analysis has
been done after freeze drying of pristine CNTs and 3D-CNT solids)

Production Data

[Click here to download Production Data: Figures with Captions.docx](#)