

DOI: 10.1002/adma.200601748

Carbon Nanotube Aerogels**

By Mateusz B. Bryning, Daniel E. Milkie, Mohammad F. Islam, Lawrence A. Hough, James M. Kikkawa, and Arjun G. Yodh*

Aerogels are ultralight, highly porous materials typically fabricated by subjecting a wet-gel precursor to critical-point-drying (CPD) or lyophilization (freeze-drying) in order to remove background liquid without collapsing the network. Microscopically, aerogels are composed of tenuous networks of clustered nanoparticles, and the materials often have unique properties, including very high strength-to-weight and surface-area-to-volume ratios. To date most aerogels are fabricated from silica^[1] or pyrolyzed organic polymers.^[2,3] Practical interest in the former stems from their potential for ultralight structural media, radiation detectors, and thermal insulators,^[1] and in the latter from their potential for battery electrodes and supercapacitors.^[2] In this paper we investigate the properties of a new class of aerogels based on carbon nanotubes (CNTs).

Small-diameter CNTs, such as single- and few-wall CNTs, are exciting candidates for electrically conducting aerogels. Individually, these nanotubes are extraordinarily stiff^[4] and their electrical conductivity can be very large.^[4,5] Furthermore, ensembles of such nanotubes are useful aerogel precursors: they form electrically percolating networks at very low volume fractions^[6] and elastic gels in concentrated suspensions through van der Waals interaction mediated cross-linking.^[7,8]

Here we report the creation of CNT aerogels from aqueous-gel precursors by CPD and freeze-drying. CNT aerogels have been produced previously as intermediate phases during the process of drawing nanotube fibers^[9] from a furnace and during the process of making sheets from multiwall CNT for-

ests.^[10] By contrast, our aerogels were derived directly from CNT networks in suspension, and we could readily manipulate the network properties as a result. The flexibility afforded by this process enabled us to control CNT concentration, to utilize optimized CNT dispersion processes,^[11] to reinforce the networks with, for example, polyvinyl alcohol (PVA), and to infiltrate or backfill them with polymeric fluids. Here we describe these CNT aerogels and the processing methodologies used to synthesize them, and we characterize their electrical and mechanical properties. The CNT aerogels supported thousands of times their own weight after PVA-reinforcement, and, depending on processing conditions, their electrical conductivity ranged as high as ca. 1 Scm^{-1} . Although our starting chemical vapor deposition (CVD) nanotube material contained single- and few-wall CNTs (the latter being predominantly double-wall CNTs, DWNTs), the dispersion and preparation processes employed here are directly applicable to pure single-wall CNTs (SWNTs).^[11] CNT aerogel electrical and structural properties are also expected to be similar to pure SWNT samples because the electrical^[12] and tensile^[13] properties of bulk SWNTs and DWNTs are comparable.

Images of typical critical-point-dried aerogels are seen in Figure 1. Unreinforced aerogels were fragile, but strong enough to permit careful handling. Reinforcement of aerogels with PVA polymer^[14–16] improved the strength and stability of the aerogel. In this case, the aerogels could support at least 8000 times their own weight, as shown in Figure 1b. All of the aerogels (with or without PVA reinforcement) were highly porous, with pore sizes ranging from tens of nanometers up to one micrometer. Transmission electron microscopy (TEM) images like the one in Figure 1d, prepared by shredding (pulling apart) unreinforced CNT aerogels above a TEM sample grid, suggest nanotubes in the aerogels form a random filamentous network^[17] with little bundling. In the absence of bundling, the nanotube surface area is very large, a unique feature potentially useful for applications that require materials with large surface-area-to-volume ratios, including chemical sensors, reaction catalysts, and novel electrodes. The freeze-dried samples sometimes had a second porosity length scale of the order of tens to hundreds of micrometers as a result of ice crystals that formed during the freezing process and displaced nanotubes within the network.

Densities of the CNT aerogels studied ranged from 10–30 mg mL^{-1} with no PVA reinforcement, to 40–60 mg mL^{-1} for aerogels reinforced in a 1 wt % PVA bath. The PVA con-

[*] Prof. A. G. Yodh, M. B. Bryning, D. E. Milkie, Prof. M. F. Islam,^[†] Dr. L. A. Hough,^[††] Prof. J. M. Kikkawa
Department of Physics and Astronomy, University of Pennsylvania
209 S. 33rd St. Philadelphia, PA 19104-6396 (USA)
E-mail: Yodh@physics.upenn.edu

[†] Current Address: Department of Chemical Engineering and Department of Materials Science & Engineering, 5000 Forbes Ave., Carnegie Mellon University, Pittsburgh, PA 15213-3890, USA.

[††] Current Address: Rhodia, Inc., 350 George Patterson Blvd., Bristol, PA 19007, USA.

[**] We gratefully acknowledge useful discussions about carbon nanotube networks with K. I. Winey, D. T. N. Chen, D. W. Kurz, and A. M. Alsayed. This work was supported by grants from the NSF (MRSEC DMR05-20020 (A.G.Y. and J.M.K.) and DMR-0505048 (A.G.Y.)), NASA NAG8-2172 (A.G.Y.) and DARPA/ONR (N00015-01-1-0831 (J.M.K.)). Supporting Information is available online from Wiley InterScience or from the author.

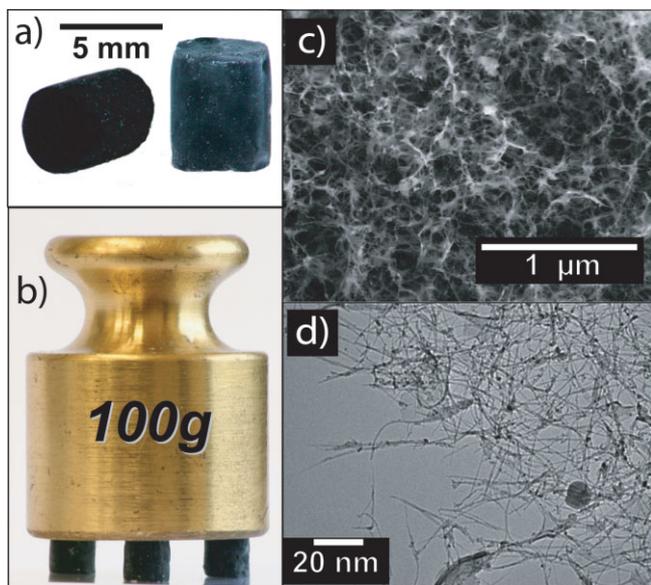


Figure 1. Images of aerogels. a) Macroscopic pieces of 7.5 mg mL^{-1} CNT aerogels. Pristine CNT aerogel (left) appears black, whereas the aerogel reinforced in a 1 wt % PVA bath (right) is slightly gray. b) Three PVA-reinforced aerogel pillars (total mass = 13.0 mg) supporting 100 g, or ca. 8000 times their weight. c) This scanning electron microscopy (SEM) image of a critical-point-dried aerogel reinforced in a 0.5 wt % PVA solution (CNT content = 10 mg mL^{-1}) reveals an open, porous structure. d) This high-magnification transmission electron microscopy (TEM) image of an unreinforced aerogel reveals small-diameter CNTs arranged in a classic filamentous network.

ment in the aerogels could be estimated by subtracting the known mass of the CNTs in each sample, as determined from the sample volume and initial CNT gel concentration. We found that the PVA content in the aerogel increased with increasing bath PVA concentration, and also depended on the CNT concentration. PVA to CNT weight ratios ranged between 1 and 6 for all reinforced samples, with most samples ranging between 2 and 3.^[18]

The electrical conductivity of the aerogels was found to depend on several factors, including nanotube and PVA content, and the drying process (i.e., freeze-drying or CPD). The freeze-dried samples were consistently less conductive than the critical-point-dried samples. We attribute this difference to disruptions of the nanotube network that occur during the freezing process, such as those described above. Samples created by CPD suffered significantly less mechanical distortion and had more reproducible conductivities.

Figure 2 summarizes our results for a variety of CNT and PVA bath concentrations. In Figure 2a, aerogel conductivity is plotted as function of CNT content, while the PVA-bath concentration is constant at 1 wt %. In Figure 2b, the conductivity is plotted against PVA-bath concentration, while the CNT content is fixed at 7.5 mg mL^{-1} . As can be seen, a 7.5 mg mL^{-1} CNT aerogel with no PVA had a conductivity of nearly 1 S cm^{-1} , significantly higher than typically obtained in solid CNT/polymer composites with comparable nanotube volume fractions of order 1%.^[6] Although the addition of

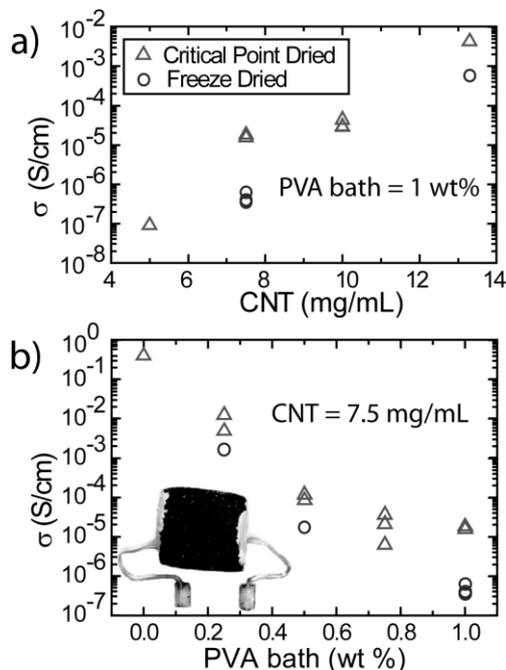


Figure 2. Conductivities of as-prepared CNT aerogel samples. a) Dependence of CNT content on the conductivity. The bath PVA content was fixed at 1 wt %. b) Dependence of aerogel conductivity on PVA content. CNT content was fixed at 7.5 mg mL^{-1} . The inset depicts the electrical connections to an aerogel sample.

PVA into the bath reinforced the physical structure of the aerogel, the electrical conductivity of the reinforced aerogels was initially significantly reduced. After reinforcement in a 1 wt % PVA solution, for example, the conductivity dropped by five orders of magnitude to ca. $10^{-5} \text{ S cm}^{-1}$. This level of conductivity is more typical of solid polymer composites with comparable nanotube volume fractions of order 1%.^[6] For comparison, aligned CNT/PVA fibers, which are significantly more dense (ca. 1.3 g cm^{-3}) have conductivities of ca. 10 S cm^{-1} .^[14]

Although the physical reinforcement provided by PVA is often desirable, the concurrent reduction in conductivity may present problems for certain applications. Interestingly, we discovered that short, high-current pulses applied to a PVA-reinforced aerogel sample produced stepwise, irreversible increases in network electrical conductivity. The net increase could be quite large, for example several orders of magnitude, as shown for a critical-point-dried sample in Figure 3. In a typical configuration, the sample was placed under high vacuum and 15 ms current pulses of increasing amplitude were applied across the sample as shown in Figure 3a. The current pulses were spaced at least 30 s apart and kept as short as possible to minimize bulk heating of the sample, which can cause significant distortion. The maximum current applied in our experiments was 100 mA, as limited by our instrumentation. A transient increase in conductivity was observed immediately after each pulse, followed by a partial rebound, as seen

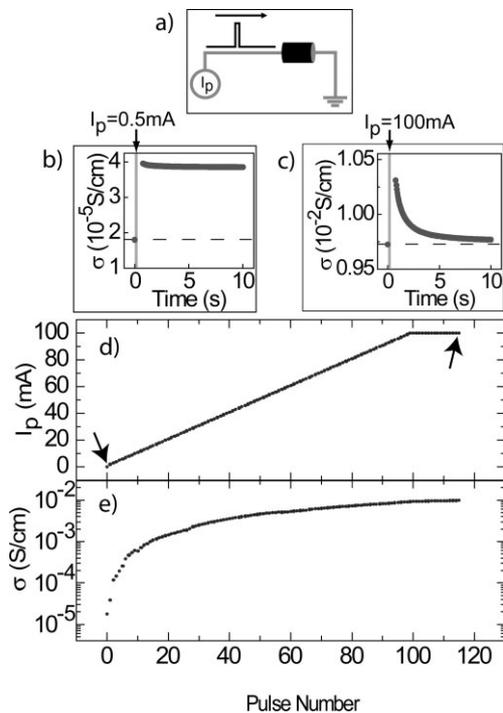


Figure 3. a) Discrete current pulses, I_p , applied across a sample, as shown in this schematic, improved the electrical conductivity of PVA-reinforced CNT aerogels. b) A 15 ms, 0.5 mA current pulse (depicted by the vertical gray line) was applied to a 13.3 mg mL^{-1} CNT critical-point-dried sample reinforced in a 0.5 wt% PVA bath. The conductivity improved by ca. $2\times$ after the pulse, and remained at the new level indefinitely. c) A 15 ms, 100 mA current pulse was applied across the same sample, after the sample had undergone repeated current pulses and the starting resistance was much lower. Although the current here was much higher, conductivity improved only transiently, presumably because of heating, and returned to the original value in a matter of seconds. d,e) The full breakdown history of this sample. d) Pulsing current was linearly increased up to 100 mA (pulse duration was always 15 ms; pulses were spaced more than 30 s apart). Each point represents a discrete current pulse. Arrows point to the pulses depicted in (b) and (c). e) The corresponding steady-state conductivity, measured 30 s after each pulse. Notice that the conductivity improved by several orders of magnitude after repeated pulsing.

in Figure 3b and c. Following a stepwise increase of the current with each pulse up to the 100 mA instrumentation limit, the conductivity of all the samples was ca. $10^{-2} \text{ S cm}^{-1}$, regardless of the initial conductivity. This appears to be the limit for our samples at this current/pulse-duration combination. Repeated pulsing at a constant current level did not significantly change the resistance of the sample. However, currents beyond the 100 mA used here might result in even higher final conductivities, perhaps up to those of pristine aerogel or higher.

Measurements of sample mass and volume before and after applying current pulses, as well as scanning electron microscopy (SEM) imaging suggest that the aerogel structure did not noticeably change either macroscopically or microscopically during this pulsing process as long as the duration of the cur-

rent pulses was minimized to reduce bulk heating of the sample. Although the mechanism for this breakdown is not fully understood, one interpretation is that the current pulses effectively remove or decompose PVA at the junctions between the nanotubes. Preliminary results suggest the breakdown can be effected either in a vacuum or in a gaseous atmosphere, with subtle differences depending on environment.

Finally, these CNT aerogels present a distinctive opportunity for creating composite materials with exceptional electrical conductivities and unique compositions. Although heavily researched, CNT composites have not as yet provided the levels of electrical conductivity that might be anticipated based on the conductivity of isolated nanotubes. This can be partly attributed to the often contradictory goals of dispersing CNTs in a host material while simultaneously attempting to form a strongly connected nanotube network.^[6,19] As a result, and because of the difficulty of dispersing single-wall and small-diameter CNTs in most materials, methods for creating composites are usually highly specific to a particular host material and are sensitive to many variables.^[6]

In the process described herein, the aerogel CNT network was created under controlled conditions, and the conductivity could therefore be significantly higher than is possible with other methods. This optimized nanotube network could then be backfilled with a host material. For example, we found that immersing the aerogel in a liquid led to complete impregnation of the aerogel through a “wicking”^[20] or infiltration^[21] process. The liquid could be a polymer or other material that could be subsequently cured to form a solid composite. For highly viscous liquids, the process was aided by placing the sample under vacuum. We successfully impregnated PVA-reinforced aerogels with Epon 828 epoxy resin with Epikure 3234 crosslinker, and with Silbond H-5, a partially polymerized silica that was cured to produce silica/CNT composites. Our initial results with epoxy indicated that, upon backfilling and curing, the conductivity remained constant to within a factor of two. As the nanotube network was formed independently of the host material, the process should be useful for making composites that might not be otherwise feasible, for example based on ceramic slurries or even metals.^[22]

In summary, we have created carbon nanotube aerogels from wet-gel precursors that differ significantly from gelatin-nanotube foams^[23] and high-temperature aerogels^[9] reported previously. The nanotube aerogels were strong and electrically conducting, offering potential improvement over current carbon aerogel technologies for applications such as sensors, actuators, electrodes, thermoelectric devices, et cetera, as well as silica-based aerogel applications. We demonstrated that the aerogels could be significantly reinforced by small amounts of PVA, albeit at the cost of reduced conductivity; the network conductivity, however, could be at least partially restored by applying current pulses through the sample. Lastly, the aerogel structures could be backfilled with polymeric fluids, which, in turn, could be cured to create novel electrically conducting solid composites.

Experimental

CNTs were obtained from Thomas Swan, Inc. (Elicarb SW, batch K1713). The CVD process used to produce this material aims to maximize SWNTs, but some amounts of double- and triple-wall CNTs were also present [18,24]. We suspended the as-received CNTs in water with sodium dodecylbenzene sulfonate (NaDDBS) surfactant (Acros Organics) under 55 KHz bath sonication [11]. In this solution, CNT weight fractions ranged from 0.005 to 0.013 (5 to 13 mg mL⁻¹) and the surfactant/CNT weight ratio was 5:1. Higher CNT concentrations were impractical with this method because of aggregation. The CNT solution was poured into a cylindrical mold (4.7 mm diameter) and left overnight to set into an elastic gel [7,25]. The gel was transferred to and then soaked in a large heated (90 °C) water bath containing 0.00 wt % (for unreinforced aerogels), 0.25 wt %, 0.50 wt %, 0.75 wt %, or 1.00 wt % added PVA (Sigma P1763). The bath solution was changed at least three times over the course of 3–5 days. This procedure effectively removed the surfactant, as evidenced by using SEM and TEM imaging and by using energy dispersive X-ray spectroscopy (EDX) [18]; the PVA reinforces the gel structure [14].

The samples were then cut into ca. 5 mm long pieces. For freeze-drying, the gel was removed from the bath, flash-frozen by immersion in liquid nitrogen, and placed in a freeze-dryer (Labconco FreeZone 4.5 L Benchtop Freeze-Dry System) overnight. For CPD, the gel was removed from the bath and placed into anhydrous ethanol overnight for solvent exchange. The gels were then subjected to CPD in a Tousimis SAMDRI-PVT-3B critical-point-dryer using the manufacturer-recommended drying procedure. Briefly, the sample was placed in the drying chamber and cooled below 0 °C. The ethanol solvent was replaced by liquid CO₂ by flushing the chamber for several minutes. The chamber was then sealed and heated above the critical point of CO₂ (31.1 °C, 72.8 atm; 1 atm = 101 325 Pa). After stabilizing for several minutes, the pressure in the chamber was slowly released over ca. 20 min at a constant temperature. The samples were not distorted significantly from their original shapes by processing; swelling, or shrinkage was usually less than 5 % of the mold dimensions.

The electrical conductivity of the aerogels was measured by a two-probe method in high vacuum (< 10⁻⁵ torr; 1 torr = 133.322 Pa), after painting the flat surfaces of the cylindrical samples with conductive paint (DuPont 4929N), see the inset of Figure 2b. Separate four-point conductivity measurements were conducted by painting additional parallel ring electrodes around the circumference of the sample, in a geometry described in Bryning et al. [6]. By isolating the bulk sample conductivity from any electrode-contact resistance, these measurements confirmed that the breakdown occurred in the bulk of the sample, and not just at the electrodes.

Received: August 1, 2006

Revised: October 3, 2006

Published online: February 1, 2007

- [1] L. W. Hrubesh, *J. Non-Cryst. Solids* **1998**, *225*, 335.
- [2] R. W. Pekala, J. C. Farmer, C. T. Alviso, T. D. Tran, S. T. Mayer, J. M. Miller, B. Dunn, *J. Non-Cryst. Solids* **1998**, *225*, 74.
- [3] R. W. Pekala, *J. Mater. Sci.* **1989**, *24*, 3221.
- [4] M. S. Dresselhaus, G. Dresselhaus, P. Avouris, *Carbon Nanotubes: Synthesis, Structure, Properties, and Applications*, Springer, Berlin **2001**.
- [5] J. Kong, E. Yenilmez, T. W. Tomblor, W. Kim, H. J. Dai, R. B. Laughlin, L. Liu, C. S. Jayanthi, S. Y. Wu, *Phys. Rev. Lett.* **2001**, *87*, 106 801.
- [6] M. B. Bryning, M. F. Islam, J. M. Kikkawa, A. G. Yodh, *Adv. Mater.* **2005**, *17*, 1186.
- [7] L. A. Hough, M. F. Islam, P. A. Janmey, A. G. Yodh, *Phys. Rev. Lett.* **2004**, *93*, 168 102.
- [8] B. Vigolo, C. Coulon, M. Maugey, C. Zakri, P. Poulin, *Science* **2005**, *309*, 920.
- [9] Y.-L. Li, I. A. Kinloch, A. H. Windle, *Science* **2004**, *304*, 276.
- [10] M. Zhang, S. L. Fang, A. A. Zakhidov, S. B. Lee, A. E. Aliev, C. D. Williams, K. R. Atkinson, R. H. Baughman, *Science* **2005**, *309*, 1215.
- [11] M. F. Islam, E. Rojas, D. M. Bergey, A. T. Johnson, A. G. Yodh, *Nano Lett.* **2003**, *3*, 269.
- [12] J. Q. Wei, H. W. Zhu, B. Jiang, L. J. Ci, D. H. Wu, *Carbon* **2003**, *41*, 2495.
- [13] Y. J. Li, K. L. Wang, J. Q. Wei, Z. Y. Gu, Z. C. Wang, J. B. Luo, D. H. Wu, *Carbon* **2005**, *43*, 31.
- [14] B. Vigolo, A. Pénicaud, C. Coulon, C. Sauder, R. Paillet, C. Journet, P. Bernier, P. Poulin, *Science* **2000**, *290*, 1331.
- [15] B. Vigolo, P. Poulin, M. Lucas, P. Launois, P. Bernier, *Appl. Phys. Lett.* **2002**, *81*, 1210.
- [16] P. Poulin, B. Vigolo, P. Launois, *Carbon* **2002**, *40*, 1741.
- [17] W. Zhou, M. F. Islam, H. Wang, D. L. Ho, A. G. Yodh, K. I. Winey, J. E. Fischer, *Chem. Phys. Lett.* **2004**, *384*, 185.
- [18] Details are included in the Supporting Information.
- [19] M. B. Bryning, D. M. Milkie, M. F. Islam, J. M. Kikkawa, A. G. Yodh, *Appl. Phys. Lett.* **2005**, *87*, 161 909.
- [20] J. Wang, L. Angnes, H. Tobias, R. A. Roesner, K. C. Hong, R. S. Glass, F. M. Kong, R. W. Pekala, *Anal. Chem.* **1993**, *65*, 2300.
- [21] F. M. Du, C. Guthy, T. Kashiwagi, J. E. Fischer, K. I. Winey, *J. Polym. Sci. Part B* **2006**, *44*, 1513.
- [22] O. Hjortstam, P. Isberg, S. Soderholm, H. Dai, *Appl. Phys. A: Mater. Sci. Process.* **2004**, *78*, 1175.
- [23] M. Nabet, M. Sano, *Langmuir* **2005**, *21*, 1706.
- [24] Based on in-house characterization and personal correspondence with A. Pénicaud, P. Poulin, T. Swan, Inc.
- [25] L. A. Hough, M. F. Islam, B. Hammouda, A. G. Yodh, P. A. Heiney, *Nano Lett.* **2006**, *6*, 313.