Fabrication and Characterization of Carbon Nanotube/Graphene Hybrid Foam

M. Zhang[*], Y. Cui[*] and S. Li[* , **]

[*]High-Performance Materials Institute, Florida State University
2005 Lavy Rode, Tallahassee, FL, USA
mzhang@eng.fsu.edu
[**]School of Material Science and Engineering,
University of Shanghai for Science and Technology, Shanghai, China

ABSTRACT

We developed a simple and scalable method to fabricate carbon nanotube (CNT) and graphene hybrid foams. We use polymethylmethacrylate (PMMA) microspheres as template and polyacrylonitrile (PAN) as precursor to create crosslinks among CNTs and nanoscale graphene flakes around CNTs. The porosity and the pore size of the CNT foam can be turned by adjusting the concentration and particle size of PMMA spheres. The assembled CNT foams have a hierarchically porous structure and the pore size ranges from tens of nanometers to micrometers. The effect of PAN on crosslinking CNTs and creating graphene flakes was evaluated by using ultrathin freestanding CNT sheets. The observations of electron microscope and other measurements demonstrated that our approaches are effective.

Keywords: carbon nanotubes, graphene, foam, fabrication process

1 INTRODUCTION

Porous materials are a unique class of porous solids with a number of interesting structural features, such as lightweight, large pore volumes, and high surface areas [1]. Their unique structure and excellent properties demonstrated a wide potential applications ranging from energy absorption and damping in structural components to thermal management and scaffolds for biological applications [2]. Recently, a computer model is designed to place carbon nanotubes (CNTs) in the hole of a theoretical sponge network [3]. The CNTs are arranged in parallel, each nanotube is in contact with others but not all the way along the edge of the nanotubes. It is found that such special CNT three-dimensional (3D) networks adsorbed a significant amount of hydrogen, 5.5 wt% at room temperature, which is close to the target of hydrogen storage (6 wt% by 2015) of the Department of Energy, USA. CNT foam is a material with a porous structure constructed with nano-porous carbon. It is expected that CNT foam derives many of its functions from both its nanostructure and its microstructure and, as a result, has better performance than other types of carbon foams. CNT foams are also predicted to have tremendous potential application in energy storage.

There are various approaches for producing CNT foam. Yodh's group created CNT aerogels from aqueous-gel precursors by critical-point-drying and freeze-drying and used polyvinyl alcohol to reinforce the networks [4]. Zhai's group used poly(3-(trimethoxysilyl) propyl methacrylate) to disperse and functionalize multi-walled CNTs and freeze-dried wet gel to obtain "CNT aerogel", a honeycomb like structure [5]. Wu's group synthesized CNTs by floating catalyst chemical vapor deposition (CVD) and obtained a special CNT assembly with ultrahigh porosity-CNT sponges, in which nanotubes are self-assembled into a 3D interconnected framework [6]. Hata's group reduced the catalyst density to synthesize very long and randomly oriented clean CNTs by CVD, which form a CNT network where each CNT made contacts with numerous other CNTs [7]. It is still a great challenge to develop a technology that is simple, scalable, and a method without affecting CNTs' intrinsic properties. Besides, to control the size and distribution of the pores in CNT foam is required for fabricating the foam with expected properties.

Our approach differed from others. We made CNT foams by using polymer spheres as a template and the produced foam can have controllable pore size. The process involves coating CNTs on polymer spheres in a solution with polyacrylonitrile (PAN), obtaining a densely packed CNT/polymer composite, and then removing the polymer from the solid by heating the composite to a temperature higher than the polymer's boiling point. The previous positions of the polymer particles are the cells of the foam and the CNT networks form the struts of the foam. Further high-temperature treatment converts PAN precursor to graphene and graphene flakes, which crosslink CNTs to enhance the structural integrity and create high surface area of the foam.

2 EXPERIMENTAL

The CNTs used in this work were multi-walled CNTs with 4-6 walls, ~10 nm in diameter, and ~500 μm in length. The polymer template was polymethylmethacrylate (PMMA) microspheres with 27-32 μm in diameter. The PAN power had molecular weight of 15,000 g/mole.

The fabrication process had a few stages. First, PAN powder was dissolved in dimethylformamide (DMF) to form a homogeneous PAN/DMF solution. Next, CNTs were dispersed well in PAN/DMF solution by using high power probe sonication. Then, the PMMA spheres were added to the CNT/PAN/DMF suspension. The mixture was subsequently stirred at 1000 rpm for 10 min to reach uniform dispersion of PMMA spheres in the CNT/PAN/DMF suspension. After this, the suspension was placed on a hot plate (50 °C) to evaporate DMF. Proper stirs were added to avoid sinking of PMMA spheres. Finally, a 2-cm-diameter sample with a thickness of 5 mm was obtained. The sample was dried in a vacuum oven at 70 °C for 12 hours to ensure complete removal of DMF. The CNT/graphene hybrid foam was obtained via a two-step heat treatment process, the same as the standard carbon fiber fabrication process. In the first step, the samples were heated in a tube furnace to 280 °C at 2 °C/min, followed by an isothermal hold for 3 hours in air. During this step, PMMA was removed and PAN polymer was pyrolyzed (stabilization of PAN) [8]. In the second step, the samples were treated at 1000 °C under 1 atm pressure in nitrogen gas with the flow rate of 80 ml/min for 1 hour. The graphene and graphene flakes were formed due to the carbonization of the stabilized PAN.

The variable CNT/graphene hybrid foams were prepared by adjusting the CNT/PMMA weight ratio and the amount of PAN. The concentration of the PAN/DMF solutions was 1 mg/ml and 2 mg/ml. The weight ratio of CNT to PMMA was 1/5, 1/7, and 1/10, respectively. Scanning electron microscopy (SEM, JEOL-JSM7401F, 10 KV) was used to characterize the morphology of the samples during the fabrication processes. For the observation of the inside structure, the samples were fractured in liquid nitrogen. The effect of the PAN was evaluated by using the CNT sheets. The CNT sheets were made by drawing CNTs directly from a sidewall of the CNT array and they are freestanding and ultrathin [9]. The CNTs in the sheet are aligned in the drawing direction. The CNT sheet was dip-coated in the PAN/DMF solution and dried, and then heat treated following the same process for foam fabrication to convert PAN into graphene and nano graphene flakes. High-resolution transmission electron microscopy (TEM, JEM-ARM200F, 200 KV) was used to observe the structures around CNTs and CNT joints.

3   RESULTS AND DISCUSSIONS

Figure 1 shows the morphology and structure of the sample with CNT/PMMA weight ratio of 1/10 before and after 280 °C as well as 1000 °C heat treatments. The CNTs form a random network around PMMA spheres (see Fig. 1a) and the pore size is in the tens of nanometers. After the composite was stabilization at 280°C for 3 hours, PAN converted into condensed heterocyclic ring structure [10]. At the same time, the PMMA spheres depolymerized into oligomers. Generally, the cross section of the oligomers is

approximately 1 nm, which is smaller than the nanopore formed by entangled CNTs [4-7, 11]. Therefore, the oligomers are readily expelled from the composite through the nanopores of CNT network. Eventually, the PMMA spheres were removed. As the original size of the PMMA spheres was preserved, cells were formed at the previous sites of the PMMA spheres in the composite as shown in Fig. 1b.
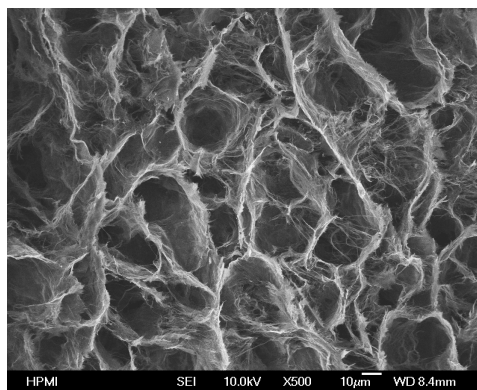
The cells in CNT foam are almost spherical and uniform. The wall of the cells in CNT foam (the struts of the foam) is made of a random network of long and
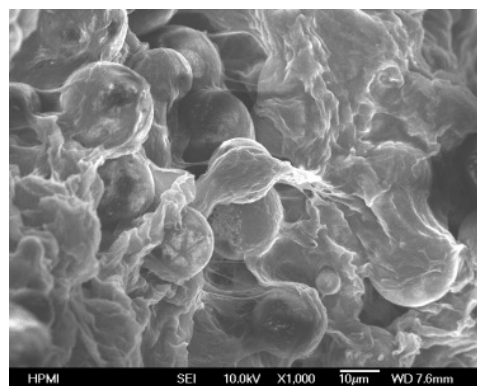
(a)
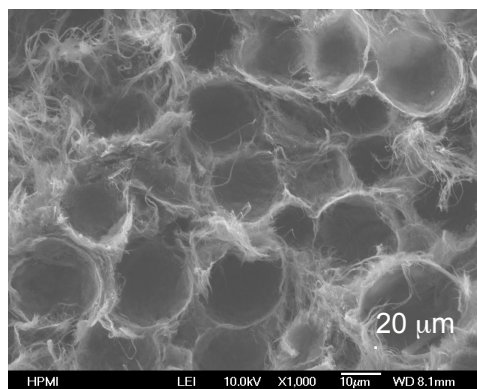
(b)

(c)

Figure 1: SEM images show (a) CNT/PAN/PMMA-spheres composite, (b) that after 280 °C heat treatment, and (c) that after 1000 °C heat treatment.

interconnected CNTs. The pore size there is in tens of nanometers. While the cells are formed after the removal of PMMA spheres, the diameter of the cell is equal to the diameter of PMMA spheres, namely in micrometer scale. Therefore, the prepared CNT foams have a hierarchically porous structure and the pore size ranges from tens of nanometers to micrometers. The thickness of the cell wall is around 1 μm when the weight ratio of CNT to PMMA sphere is 1/10. Because the length of multi-walled CNT (~500 μm) is more than 15 times longer than the size of a cell (~30 μm), the adjacent hollow capsules were connected by CNTs, which is good for the integrity of the structure. Further treated at 1000 °C, the structure of the foam did not collapse and maintained well (see Fig. 1c).

It is known that the PAN-derived condensed heterocyclic ring structure changes into graphitic structure after carbonization [12]. The yield of graphitic from stabilized PAN is typically about 60 wt% [8, 13, 14]. Meanwhile, the conversion of PAN to graphitic is accompanied by a volume decreasing of 50-70 % during the carbonization process [14]. Comparing Figs. 1b and 1c, the surface of the cells is smooth before carbonization, but rougher after carbonization. It is because that there is stabilized PAN coated on the wall surface of the cell and its volume decreases during carbonization. The cells retain during these processes.

When the CNT/PMMA weight ratio increases, the amount of cells (pores in microscale) decreases and the cells have thicker walls (CNT networks). The foam has fewer pores in microscale, but more pores in nanoscale.

The mechanical properties of these CNT foams and aerogels originate from the bending modulus of CNTs or entanglements between them. Most of the CNT foams and aerogels rely on van der Walls forces at CNT-CNT junctions. The CNT-based structures undergo structural collapse or plastic deformation with a reduction in compressive strength when they are subjected to cyclic strain [15]. Large deformations are observed at the struts and nodes of the inter-tube structure of the CNT foams and aerogels. To fabricate cellular solids, which are strong, robust, and have large surface area, the CNT joints need to be reinforced. Generally, polymers are utilized to reinforce the structural integrity of the CNT-based porous network. Here, we used PAN to reinforce the CNT network by locking the contacted CNTs and generate connections between CNTs because PAN can be carbonized to form strong C-C bonding when it is treated in an inert gas over 1000 °C. The effect of PAN was evaluated by using CNT sheets. Figures 2a and 2b show the TEM images of the CNTs connected by graphene flakes when the concentration of the PAN/DMF solution is 1 mg/ml and 2 mg/ml, respectively. The TEM images reveal that PAN polymer changed into graphitic after the carbonization. The graphitic was accumulated at the joints between CNTs because the PAN precursors were mainly concentrated on the CNT joints by strong capillary force during evaporation of DMF [16]. Meanwhile, some of the CNTs surfaces are also coated with graphitic. When the concentration of PAN/DMF solution increases to 2 mg/mL, a layer of PAN is uniformly coated on the CNTs surface. Consequently, all the surface of the CNTs was coated by graphene and graphene flakes after carbonization (Fig. 2b). The graphitic, like a jacket, can "lock" the CNTs. The sliding of CNTs can be confined by the jacket under high loading to dissipate energy. Since the nanotubes in CNT foam are long and one nanotubes belong to many joints, the "locking" and sliding will definitely increase the robustness of the CNT foam. The PAN enhancement does not affect the structural integrity of the CNT foam or the porosity of the nanotube network.
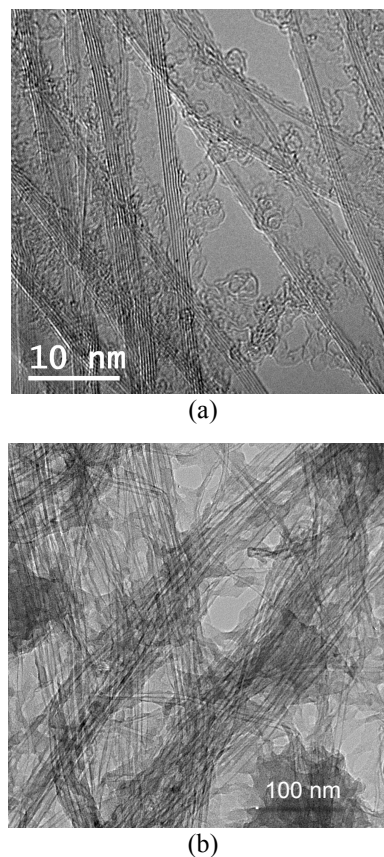

(a)

(b)

Figure 2: TEM images of the CNTs connected by graphene and graphene flakes when the concentration of the PAN in DMF solution is (a) 1 mg/ml and (b) 2 mg/ml.

We measured the mechanical properties of CNT sheet and PAN-treated CNT sheet to evaluate the locking effect of PAN to CNT joints. We found that the tensile strength of the PAN treated sheet experienced a five-fold increase.

4   CONCLUSION

We developed a simple and scale method for fabricating CNT/graphene hybrid foams. Using PMMA microspheres as template and PAN as reinforcement agent, the CNT/graphene hybrid foams were prepared from a

suspension of CNTs, PAN, and PMMA spheres in DMF. The PMMA spheres are removed by a heating process and the micro-pores formed at the previous sites of the PMMA spheres. The effects of PAN are confirmed by using ultrathin CNT sheets. The prepared CNT/graphene foams have a hierarchically porous structure and the pore size ranges from several nanometers to tens of micrometers. The technology developed in this research can be used to fabricate the foams with controlled porosity and structural integrity by adjusting the concentration of polymer particles and their size as well as the amount of PAN precursors. Due to the integration of micropores and nanopores, the prepared CNT/graphene hybrid foams are expected to have potential applications in a variety of areas, such as catalyst support, energy absorption, separation, chemical reactor, sensor, medicine and solar cell. Moreover, such highly porous and conductive structures can be filled with other functional materials to form novel structures for emerging applications.

REFERENCES

[1] Jikun Chen, Xuchun Gui, Zewei Wang, Zhen Li, Rong Xiang, Kunlin Wang, Dehai Wu, Xugui Xia, Yanfei Zhou, Qun Wang, Zikang Tang, Lidong Chen, "Superlow Thermal Conductivity 3D Carbon Nanotube Network for Thermoelectric Applications," ACS Applied Matericals & Interfaces, 4, 81-86, 2012.

[2] Sumanjeet Kaur, Pulickel M. Ajayan, Ravi S. Kane, "Design and Characterization of Three-Dimensional Carbon Nanotube Foams," Journal of Physical Chemistry B, 110, 21377-21380, 2006.

[3] Bassem Assfour, Stefano Leoni, Gotthard Seifert, Igor A. Baburin, "Packings of Carbon Nanotubes – New Materials for Hydrogen Storage," Advanced Materials, 23, 1237-1241, 2011.

[4] Mateusz B. Bryning, Daniel E. Milkie, Mohammad F. Islam, Lawrence A. Hough, James M. Kikkawa, Arjun G. Yodh, "Carbon Nanotube Aerogels," Advanced Materials, 19, 661-664, 2007.

[5] Jianhua Zou, Jianhua Liu, Ajay Singh Karakoti, Amit Kumar, Daeha Joung, Qiang Li, Saiful I. Khondaker, Sudipta Seal, Lei Zhai, "Ultralight Multiwalled Carbon Nanotube Aerogel," ACS Nano, 4, 7293–7302, 2010.

[6] Xuchun Gui, Jinquan Wei, Kunlin Wang, Anyuan Cao, Hongwei Zhu, Yi Jia, Qinke Shu, Dehai Wu, "Carbon Nanotube Sponges," Advanced Materials, 22, 617-621, 2010.

[7] Ming Xu, Don N. Futaba, Takeo Yamada, Motoo Yumura, Kenji Hata, "Carbon Nanotubes with Temperature-Invariant Viscoelasticity from -196° to 1000°C," Science, 330, 1364-1368, 2010.

[8] Xiaofan Luo, Patrick T. Mather, "Conductive shape memory nanocomposites for high speed electrical actuation," Soft Matter, 6, 2146-2149, 2010.

[9] Mei Zhang, Shaoli Fang, Anvar A. Zakhidov, Sergey B. Lee, Ali E. Aliev, Christopher D. Williams, Ken R. Atkinson, Ray H. Baughman, "Strong, transparent, multifunctional, carbon nanotube sheets," Science, 309, 1215-1219, 2005.

[10] E. Fitzer, W. Frohs, M. Heine, "Optimization of Stabilization and Carbonization treatment of PAN fibres and structural characterization of the resulting carbon fibres," Carbon, 24, 387-395, 1986.

[11] Miguel A. Correa-Duarte, Adam Kosiorek, Witold Kandulski, Michael Giersig, Luis M. Liz-Marzan, "Layer-by-Layer Assembly of Multiwall Carbon Nanotubes on Spherical Colloids," Chemistry of Materials, 17, 3268-3272, 2005.

[12] Han Gi Chae, Marilyn L. Minus, Asif Rasheed, Satish Kumar, "Stabilization and Carbonization of gel spun polyacrylonitrile/single wall carbon nanotube composite fibers," Polymer, 48, 3781-3789, 2007.

[13] Han Gi Chae, Young Ho Choi, Marilyn L. Minus, Satish Kumar, "Carbon nanotube reinforced small diameter polyacrylonitrile based carbon fiber," Composties Science and Technology, 69, 406-416, 2009.

[14] Michal Kruk, Bruno Dufour, Ewa B. Celer, Tomasz Kowalewski, Mietek Jaroniec, Krzysztof Matyjaszewski, "Synthesis of Mesoporous Carbons Using Ordered and Disordered Mesoporous Silica Templates and Polyacrylonitrile as Carbon Precursor," J. Phys. Chem. B, 109, 9216-9225, 2005.

[15] Kyu Hun Kim, Youngseok Oh, M. F. Islam, "Graphene coating makes carbon nanotube aerogels superelastic and resistant to fatigue," Nature Nanotechnology, 7, 562-566, 2012.

[16] Nirupama Chakrapani, Bingqing Wei, Alvaro Carrillo, Pulickel M. Ajayan, Ravi S. Kane, "Capillarity-driven assembly of two-dimensional cellular carbon nanotube foams," Proceedings of the National Academy of Sciences of the United States of America, 101, 4009-4012, 2004.