# *DE NOVO* CARBON NANOMATERIALS: OPPORTUNITIES AND CHALLENGES IN A FLAT WORLD

*This special issue of the Journal of Materials Research contains articles that were accepted in response to an invitation for manuscripts.*

## Introduction

Guest Editors:

Cengiz S. Ozkan
*University of California–Riverside, Riverside, California 92521-0001*

Markus J. Buehler[a)]
*Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4301*

Nicola M. Pugno
*Università di Trento, I-38123 Trento, Italy*

Kang Wang
*University of California–Los Angeles, Los Angeles, California 90095-0001*

This Focus Issue of the *Journal of Materials Research* contains articles in the broad area of *de novo* carbon nanomaterials. As an emerging area of research, the exploitation of this class of materials has set off enormous opportunities for innovation.[1] More than 20 years ago, in the 1990s, carbon nanotubes were studied for their remarkable material properties (optical and mechanical, and others).[2–5] More recently, the field has exploded to incorporate numerous applications for graphene,[6–11] which can now be fabricated in large scales.[12] Similarly, additional two-dimensional carbon allotropes, such as graphdiyne, and three dimensional nanocarbon architectures, such as graphene-nanotube architectures and graphene foam, have emerged and invoke remarkable properties of their own,[13–15,21] several of which have been manufactured.[16,22–24] In the past, controlling the architecture of a material was limited to the macroscale, but we are beginning to see the merger of the concepts of material and structure.

Carbon nanomaterials are exciting because of their remarkable diversity of mechanical, physical and chemical properties, which derive from the different allotropes including nanotubes, fullerenes, diamond, as well as graphene and its allotropes, with consequent applications in different fields such as nanoelectronics, optoelectronics, biosensors, drug delivery, energy conversion and storage. The paradigm of building complexity from a single type of atom (carbon with a variety of chemical bonds/structures it can form) by creating structural diversity at different scales is reminiscent of the means by which biological systems create functional materials, where the paradigm is to rely on simple amino acids to create a stunning diversity of proteins and related materials[17] (Fig. 1). The systematic exploitation of this concept of "hierarchical structuring" in the world of carbon materials is only at its beginning, but holds great promise.

A specific challenge is the linking of scales from the nano to the macro via the creation of hierarchical architectures using carbon nanomaterials as building blocks. Here, novel material properties emerge because of the synergistic interaction across the scales, where the properties of the union is more than the sum of its parts.[17–20] This strategy provides access to a very broad set of functional properties that include switchability, tunability and mutability in the design of *de novo* carbon nanomaterials. Applications of such multi-scale engineered materials range from nanoelectronics to medicine to novel construction materials and could have wide implications to facilitate new technological innovations at the interface of materials science, engineering and biology.[25–30] This Focus Issue offers a snapshot of the state of the art in the manufacturing, synthesis, and modeling of carbon nanomaterials and related hierarchical architectures with understanding of energy, mechanical and physical properties.

Overall, twelve articles are featured in this Focus Issue, representing both experimentation and modeling. Topics include the growth of novel carbon nanostructures comprising hierarchical architectures of graphene flower-like morphologies of graphene sheets, and the presentation of new carbon nanotube materials. Such *de novo* carbon materials facilitate new technological innovations at the interface of materials science, engineering, and biology. Innovative approaches are described for fabricating energy storage devices such as supercapacitors, which are designed for very high power density applications. Supercapacitors offer a broad spectrum of applications for various power and energy requirements, and they are designed for large numbers of rapid charge and discharge cycles.

The combination of mechanical, thermal and physical properties for three-dimensional nanocarbon architectures is presented and discussed in several articles. Hierarchical

[a)]Address all correspondence to this author.
e-mail: mbuehler@mit.edu
DOI: 10.1557/jmr.2013.14

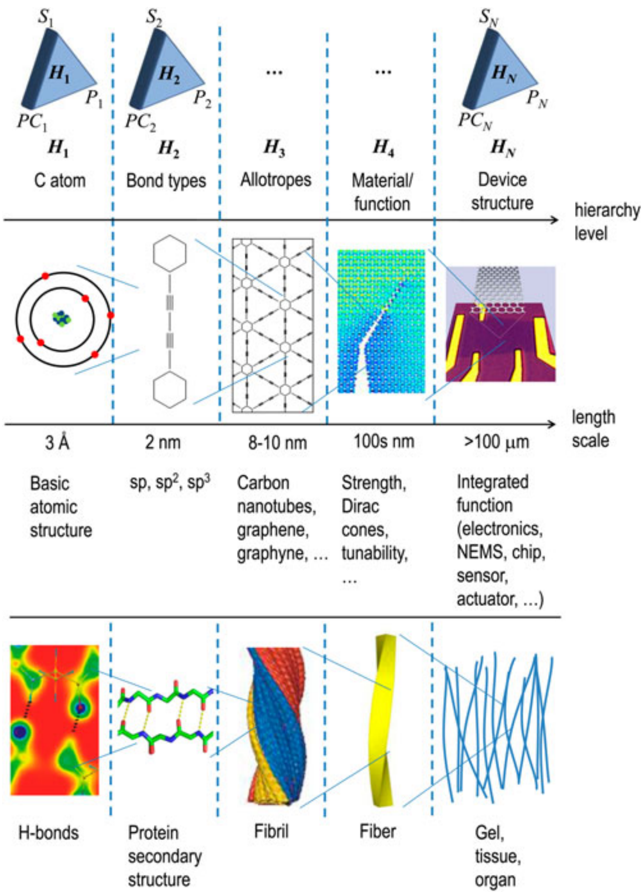


FIG. 1. **Illustration of hierarchical design space of carbon materials from the atomic structure of carbon atoms to the integrated assembly in a device**. The realization of multiple structural levels in *de novo* carbon materials is emerging as an exciting opportunity to create enhanced function at the macroscopic or device scale. Function emerges as a complex interplay of structure (S)-property (P)-process (PC) relationships that act at individual hierarchical levels ($H_1 \ldots H_N$). Together, the material behavior is more than the sum of its parts and can be exploited for innovative applications. The lower part shows an analogy to protein materials, depicting a similar paradigm in multi-level structuring to create a certain material function (here, an example of an amyloid protein material is shown). Figure adapted from Ref. 20 with images from Ref. 15. The graphene device is based on Ref. 7 and the image is taken from: http://www.newsdesk.umd.edu/images/scitech/graphene.gif.

architectures based on carbon nanomaterials are used in an application of pillared graphene nanostructures that provide exceptional thermal transport characteristics, showcasing a possible realization of this concept. These and other examples demonstrate that the manufacturing of such materials is not merely a theoretical concept, but holds real promise to change the way we think about materials design and incorporates a true bottom-up approach.

This collection of papers can only provide a brief overview of current materials innovations and issues being addressed, but will hopefully stimulate much further research activity. We are thankful to all authors and reviewers who contributed in the development of this Focus Issue, and hope that readers will enjoy the research and discussion presented. We also acknowledge the staff at the Materials Research Society and Cambridge University Press for their dedication and support.

## REFERENCES


1. A.K. Geim and K.S. Novoselov: The rise of graphene. *Nat. Mater.* **6**(3), 183–191 (2007).
2. R. Saito, M. Fujita, G. Dresselhaus, and M.S. Dresselhaus: Electronic-structure of graphene tubules based on C-60. *Phys. Rev. B* **46**(3), 1804–1811 (1992).
3. R. Saito, M. Fujita, G. Dresselhaus, and M.S. Dresselhaus: Electronic-structure of chiral graphene tubules. *Appl. Phys. Lett.* **60**(18), 2204–2206 (1992).
4. N.M. Pugno: Graded cross-links for stronger nanomaterials. *Mater. Today* **13**(3), 40–43 (2010).
5. N.M. Pugno: The design of self-collapsed super-strong nanotube bundles. *J. Mech. Phys. Solids* **58**(9), 1397–1410 (2010).
6. K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos, and A.A. Firsov: Two-dimensional gas of massless Dirac fermions in graphene. *Nature* **438**(7065), 197–200 (2005).
7. J.H. Chen, C. Jang, S. Xiao, M. Ishigami, and M.S. Fuhrer: Intrinsic and extrinsic performance limits of graphene devices on $SiO_2$. *Nat. Nanotechnol.* **3**(4), 206–209 (2008).
8. R.K. Paul, M. Ghazinejad, M. Penchev, J. Lin, M. Ozkan, and C.S. Ozkan: Synthesis of a pillared graphene nanostructure: A counterpart of three-dimensional carbon architectures. *Small* **6**(20), 2309–2313 (2010).
9. S. Guo, M. Ghazinejad, X. Qin, H. Sun, W. Wang, F. Zaera, M. Ozkan, and C.S. Ozkan: Tuning electron transport in graphene-based field-effect devices using block co-polymers. *Small* **8**(7), 1073–1080 (2012).
10. S. Gilje, S. Han, M. Wang, K.L. Wang, and R.B. Kaner: A chemical route to graphene for device applications. *Nano Lett.* **7**(11), 3394–3398 (2007).
11. L. Liao, Y.C. Lin, M. Bao, R. Cheng, J. Bai, Y. Liu, Y. Qu, K.L. Wang, Y. Huang, and X. Duan: High-speed graphene transistors with a self-aligned nanowire gate. *Nature* **467**(7313), 305–308 (2010).
12. K.S. Kim, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.H. Ahn, P. Kim, J.Y. Choi, and B.H. Hong: Large-scale pattern growth of graphene films for stretchable transparent electrodes. *Nature* **457**(7230), 706–710 (2009).
13. A. Hirsch: The era of carbon allotropes. *Nat. Mater.* **9**(11), 868–871 (2010).
14. S.W. Cranford and M.J. Buehler: Mechanical properties of graphyne. *Carbon* **49**(13), 4111–4121 (2011).
15. S.W. Cranford, D.B. Brommer, and M.J. Buehler: Extended graphynes: Simple scaling laws for stiffness, strength and fracture. *Nanoscale* **4**(24), 7797–7809 (2012).
16. A.L. Ivanovskii: Graphynes and graphdyines. *Prog. Solid State Chem.* (2012) In Press.
17. M.J. Buehler: Materials by design–A perspective from atoms to structures. *MRS Bull.* **38**(2), 169–176 (2013), doi: 10.1557/mrs.2013.26.
18. J. Zang, S. Ryu, N. Pugno, Q. Wang, Q. Tu, M.J. Buehler, and X. Zhao: Multifunctionality and control of the crumpling and unfolding of large-area graphene. *Nat. Mater.* (2013), doi: 10.1038/NMAT3542.
19. N.M. Pugno: The role of defects in the design of space elevator cable: From nanotube to megatube. *Acta Mater.* **55**(15), 5269–5279 (2007).
20. M.J. Buehler: Strength in numbers. *Nat. Nanotechnol.* **5**(3), 172–174 (2010).

21. E. Pop, V. Varshney, and A.K. Roy: Thermal properties of graphene: Fundamentals and applications. *MRS Bull.* **37**, 1273–1281 (2012).
22. J. Lin, M. Penchev, G. Wang, R.K. Paul, J. Zhong, X. Jing, M. Ozkan, and C.S. Ozkan: Heterogeneous graphene nanostructures: ZnO nanostructures grown on large-area graphene layers. *Small* **6**(21), 2448–2452, November 5, 2010.
23. S. Ravindran, G.T. Andavan, and C.S. Ozkan: Selective and controlled self-assembly of zinc oxide hollow spheres on bundles of single-walled carbon nanotube templates. *Nanotechnology* **17**, 723–727 (2006).
24. W. Wang, S. Guo, M. Penchev, I. Ruiz, K. Bozhilov, D. Yan, M. Ozkan, and C.S. Ozkan: Three dimensional few layer graphene and carbon nanotube foam architectures for high fidelity supercapacitors. *Nano Energy*, http://dx.doi.org/10.1016/j.nanoen.2012.10.001, 2012.
25. H. Gao, Y. Kong, D. Cui, and C.S. Ozkan: Spontaneous insertion of DNA oligonucleotides into carbon nanotubes. *Nano Lett.* **3**(4), 471–473 (2003).
26. X. Wang, F. Liu, G.T. Andavan, X. Jing, K. Singh, V.R. Yazdanpanah, N. Bruque, R.R. Pandey, R. Lake, M. Ozkan, K.L. Wang, and C.S. Ozkan: Carbon nanotube–DNA nanoarchitectures and electronic functionality. *Small* **2**(11), 1356–1365 (2006).
27. S. Ravindran, S. Chaudhary, B. Colburn, M. Ozkan, and C.S. Ozkan: Covalent coupling of quantum dots to multiwalled carbon nanotubes for electronic device applications. *Nano Lett.* **3**(4), 447–453 (2003).
28. D. Cui, F. Tian, C.S. Ozkan, M. Wang, and H. Gao: Effect of single wall carbon nanotubes on human HEK293 cells. *Toxicol. Lett.* **155**(1), 73–85 (2005).
29. K. Galatsis, K.L. Wang, M. Ozkan, C.S. Ozkan, Y. Huang, J.P. Chang, H.G. Monbouquette, Y. Chen, P. Nealey, and Y. Botros: Patterning and templating for nanoelectronics. *Adv. Mater.* **22**(6), 769–778 (2010).
30. J. Lin, D. Teweldebrhan, K. Ashraf, G. Liu, X. Jing, Z. Yan, R. Li, M. Ozkan, R.K. Lake, A.A. Balandin, and C.S. Ozkan: Gating of single-layer graphene with single-stranded deoxyribonucleic acids. *Small* **6**(10), 1150–1155 (2010).