Self-Assembly in Materials Synthesis

Matthew V. Tirrell and Alexander Katz, Guest Editors

Abstract

The synthesis of materials via self-assembly typically involves the spontaneous and reversible organization of small building blocks for the purpose of creating conglomerate structures over larger length scales. This introductory article describes self-assembly processes on several length scales, from subnanometer up to millimeter scales, and briefly summarizes some of the incredible diversity of materials that exhibit self-assembly. Articles in this issue cover self-assembly using zeolitic structures, organic molecular crystals, block copolymers, surfactants, mesoscale templates, and soluble crystallization additives.

Keywords: *block copolymers, materials synthesis, self-assembly, surfactants, templates, zeolites.*

Much of the scientific curiosity that is associated with self-assembly originates from the fact that we—as a human race—embody self-assembled structures over several decades of length scale, with many of these self-assemblies exhibiting intricate, dynamic structural behavior prevalent in biological systems, such as the protein hydrophobic interior. It is thus no surprise that a fundamental understanding of self-assembly promises in turn to explain many "self-assembled" mysteries, among them the origins of life. This is not to mention the technological and scientific applications of self-assembled materials, which provide control of structure and synthesis in a refined manner and at a high resolution that is inaccessible with most any other method.[1]

Given the breadth and depth of the elusive and penetrating concepts buried in a complete understanding of self-assembly, it has been impossible to cover everything—or, arguably, even most of the important areas—related to the synthesis of self-assembled materials in this single issue. Yet, as great editors, we have felt privileged to have the opportunity to do the best that we could in assembling this issue of *MRS Bulletin* dedicated to the theme of materials synthesized via self-assembly. Our particular choice of contributed topics and authors reflects a desire to highlight the synthesis of materials that can be designed by means of self-assembly in several different areas of application. Other methods of and issues in self-assembly have been reviewed in books and articles.[1–4]

We hope that this issue of *MRS Bulletin* provides a useful introduction to the field of design and synthesis of self-assembled materials, as well as a provoking interdisciplinary perspective that demonstrates similarities between what are conventionally considered to be disparate areas of research. This issue thus speaks to the interdisciplinary nature of materials synthesis via self-assembly, encompassing supramolecular chemistry, biochemistry, biology, mathematics, and physics, and has direct impact on applied sciences such as chemical, electrical, and mechanical engineering and materials science, among other disciplines.

The synthesis of materials via self-assembly involves the spontaneous and reversible organization of small building blocks for the purpose of synthesizing a larger conglomerate structure (Figure 1). The reversible aspect of the synthesis is critical because it allows the system to correct misassembled building blocks by essentially reverting that portion back to the disassembled state and reassembling. Typical forces that are used for the assembly include hydrogen bonding; van der Waals, electrostatic, capillary, and hydrophobic forces; metal–ligand interactions; and covalent chemical bonds (as during zeolite synthesis, where at high pH these covalent Si–O–Si interactions are reversible). Inherent to this description is a powerful "bottom-up" approach for assembling matter, which is driven at least in part by non-covalent interactions and enables the synthesis of complex architectures with little to no waste. This is in stark contrast to lithography-based methods of materials synthesis, which require removal of material via etching in order to synthesize a desired structure—a "top-down" approach. But another advantage of self-assembly is the minimum length scale that is accessible; this issue covers several self-assembled structures in materials that are less than 1 nm in length.

The article by Ward demonstrates how self-assembly in organic molecular crystals can be used for the separation of small molecules with only a fraction of an angstrom's difference in their kinetic diameters. Bein considers self-assembly in zeolites—crystalline aluminosilicates—and highlights how these can be used as versatile synthetic hosts for confining small molecules, with control of spatial

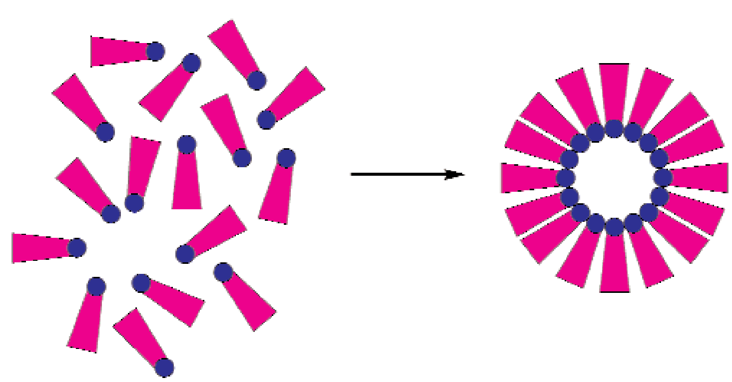


Figure 1. Illustration of basic self-assembly process. Individual wedges form a wheel shape as a result of chemical or physical interactions, with no outside intervention.

https://doi.org/10.1557/mrs2005.205 Published online by Cambridge University Press

positioning, orientation, and isolation as well as organization of donor–acceptor pairs. Although the inorganic frameworks (treated by Bein) and organic frameworks (Ward) for molecular encapsulation are different, they indeed share many similarities. One of these is the relevant length scale, as shown in Figure 2.

Encapsulation on a slightly larger length scale dictated by the self-assembly of block copolymers (typically 5 μm–1 μm) is demonstrated for the confinement of nanoparticles by Yoon et al. in this issue, where coassembling high-dielectric-constant materials within block copolymer micro-domains is required for photonic applications.

Cölfen and Yu demonstrate nucleation and growth of inorganic nanoparticles using block copolymers as templates (double hydrophilic block copolymers), as well as other approaches for controlling mineralization that are inspired by biological processes. The Cölfen and Yu article highlights the inspiration for much of self-assembly: biological systems, which are known to exhibit self-organization on several length scales. The parallels between nanoparticle nucleation for photonics (Yoon et al.) and biomineralization (Cölfen and Yu) go beyond length scale, as seen in Figure 2; they include the use of biopolymers and surfactants as insoluble matrices for biomineralization (Cölfen and Yu) akin to synthetic opals for photonics applications (Yoon et al.).

New vistas for self-assembly are proposed and demonstrated in the contribution by Boncheva and Whitesides, which addresses length scales of self-assembly too large for molecule synthesis and too small for conventional mechanical manipulation. The physical principles behind the templating strategies described are similar in concept to those discussed by other authors, albeit on larger length scales. Also addressed are methods of positioning and organizing molecules into functional devices for electronics.

In collecting the manuscripts for this issue, we wished to address the following question: is there an added benefit, perhaps even larger than the sum of the parts, for having scientists communicate and cross-fertilize ideas in areas dealing with materials synthesis via self-assembly? The five seemingly unrelated areas highlighted in this issue—self-assembly with zeolitic structures, organic molecular crystals, block copolymers, surfactants, mesoscale templates, and soluble crystallization additives—point to one unified direction. All are limited by what one can synthesize via self-assembly rather than the designs and goals of the scientists who try to create new forms of matter and interfaces. All share similarities of how to confine molecules in materials, as well as how to organize these molecules in a preferred orientation and interfacial structure that can be amplified into larger-scale hierarchical order. They also share future directions: incorporation of chiral information, dynamic self-assembled materials (as opposed to equilibrated static structures), and fabrication of multidimensional and multifunctional materials via self-assembly. Some of these are being demonstrated in model self-assembling systems that have not been reviewed here; notable among these is progress toward functional chiral self-assembling materials and related stereochemically pure structures.[5–8] Such structures consist of either all right-handed or all left-handed assemblies of molecular components, not a mixture of both. A further open-ended question arising from comparing the five articles is, are self-assembled materials chemical or mechanical in nature? Similar questions have been pondered with enzymes,[9] yet the distinction is not clear, especially considering self-assembly in a dynamical context.

It is our hope that the contributions in this issue of *MRS Bulletin* will serve as a beacon of invitation for scientists to use self-assembly and will inspire those who are unafraid to cross conventional boundaries between disciplines to apply creative solutions and parallels between various knowledge bases in the design and synthesis of new materials.

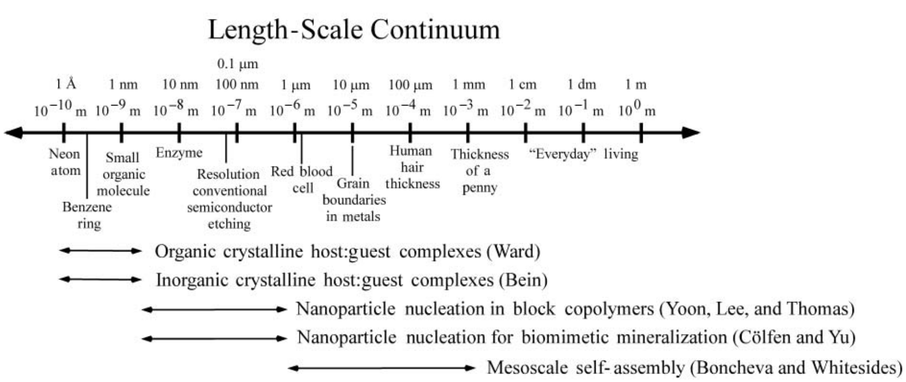


Figure 2. Schematic representation of relevant length scales for various processes and forms of matter. The double arrows on the bottom of the figure represent the distribution of length scales for self-assembly of materials for each of the articles in this issue.

References

1. G.M. Whitesides and R. Grzybowski, *Science* **295** (2002) p. 2418.
2. W. Jones and C.N.R. Rao, eds., *Supramolecular Organization and Materials Design* (Cambridge University Press, Cambridge, UK, 2002).
3. D.N. Reinhoudt, ed., *Perspectives in Supramolecular Chemistry, Vol. 4* (John Wiley & Sons, West Sussex, England, 1999).
4. M. Tirrell, *AIChE J.* **51** (2005) p. 2386.
5. P. Hayoz, A. von Zelewsky, and H. Stoeckli-Evans, *J. Am. Chem. Soc.* **115** (1993) p. 5111.
6. J.H. Jung, Y. Ono, K. Hanabusa, and S. Shinkai, *J. Am. Chem. Soc.* **122** (2000) p. 5008.
7. A. Jouaiti, M.W. Hosseini, and N. Kyritsakas, *Chem. Commun.* **17** (2002) p. 1898.
8. D. Fiedler, D.H. Leung, R.G. Bergman, and K.N. Raymond, *Acc. Chem. Res.* **38** (2005) p. 349.
9. R.J.P. Williams, *Trends Biochem. Sci.* **18** (1993) p. 115.

https://doi.org/10.1557/mrs2005.205 Published online by Cambridge University Press

Matthew V. Tirrell

Alexander Katz

Thomas Bein

Mila Boncheva

Matthew V. Tirrell, Guest Editor for this issue of *MRS Bulletin*, is dean of the College of Engineering at the University of California, Santa Barbara. He received his undergraduate education in chemical engineering at Northwestern University and his PhD degree in polymer science from the University of Massachusetts in 1977. From 1977 to 1999, he was on the faculty of Chemical Engineering and Materials Science at the University of Minnesota, where he served as head of the department from 1995 to 1999. His research has been in polymer surface properties, including adsorption, adhesion, surface treatment, friction, lubrication, and biocompatibility. He has coauthored 250 papers and one book, and has supervised 60 PhD students.

Tirrell was a Sloan fellow and a Guggenheim fellow. He has received a Camille and Henry Dreyfus Teacher–Scholar Award and several awards from AIChE: the Allan P. Colburn Award for Excellence in Publications by a Young Member of the Institute, the Charles M.A. Stine Award, and the Professional Progress Award for Outstanding Progress in Chemical Engineering. He also delivered the AIChE Institute Lecture in 2001.

Tirrell is a member of the National Academy of Engineering and a fellow of the American Institute of Medical and Biological Engineers, the American Association for the Advancement of Science, and the American Physical Society. In 2003, he concluded more than two years of service as co-chair of the steering committee for the National Research Council report, "Beyond the Molecular Frontier: Challenges for Chemistry and Chemical Engineering," published by the National Academy Press.

Tirrell can be reached by e-mail at tirrell@engineering.ucsb.edu.

Alexander Katz, Guest Editor for this issue of *MRS Bulletin,* is an assistant professor of chemical engineering at the University of California, Berkeley. He received his BS and MS degrees in chemical engineering at the University of Minnesota and was awarded a Fannie and John Hertz Foundation fellowship for doctoral work at the California Institute of Technology. He conducted postdoctoral studies in supramolecular chemistry in Strasbourg, France, as an NSF international research fellow and was subsequently appointed to his current position in 2000.

Since that time, Katz has begun an interdisciplinary research program focused on the design and synthesis of functional nanoscale interfaces in hybrid organic–inorganic materials, relying on molecular templating strategies. He has been awarded three patents, with two others currently pending, covering his different research areas. He has also been awarded a Young Scientist Prize from the International Association of Catalysis Societies for his research group's discovery of Cal-silica grafted calixarene materials.

Katz can be reached by e-mail at katz@cchem.berkeley.edu.

Thomas Bein is a professor of physical chemistry in the Department of Chemistry and Biochemistry at Ludwig Maximilians University of Munich. He received his undergraduate and PhD degrees from the University of Hamburg and Catholic University Leuven, respectively. He has been a visiting scientist at DuPont Central Research and Development, an assistant professor at the University of New Mexico, and an associate professor and then full professor at Purdue University. He was chair of the Department of Chemistry at Ludwig Maximilians University until 2004. His fields of research include functional nanostructures, zeolites, solid-state chemistry, host–guest chemistry, self-assembly, physical chemistry of surfaces, heterogeneous catalysis, and molecular electronics.

Bein was the recipient of the DAAD and the Alfried Krupp von Bohlen und Halbach-Stiftung scholarships. He has participated on numerous conference advisory boards, particularly those associated with the International Zeolite Conference. He has written, edited, or contributed to more than 150 publications, in addition to sitting on the editorial boards of such journals as *Chemistry of Materials, Microporous Materials,* the *Journal of Porous Materials,* and *Chemical Communications.*

Bein can be reached by e-mail at bein@lmu.de.

Mila Boncheva is a research chemist for Firmenich SA. She received her MSc degree from Sofia University in Bulgaria in 1986 and her PhD degree from EPFL in Switzerland in 1997 (with H. Vogel). She joined Firmenich's Corporate Research and Development Division in Geneva, Switzerland, in 2004. Her present research interests include surface science, self-assembly, skin biology, molecular encapsulation, and materials science.

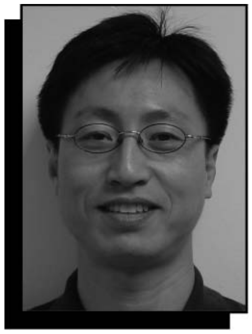
Boncheva can be reached by e-mail at mila.boncheva@firmenich.com.

Helmut Cölfen is a private docent at the University of Potsdam, Germany, and is a senior scientist and head of the analytical service in the Colloid Chemistry Department of the Max Planck Institute of Colloids and Interfaces. He studied chemistry at the University of Duisburg and completed his PhD degree in 1993, supervised by Werner Borchard. After postdoctoral work at the Nottingham Centre for Macromolecular Hydrodynamics (NCMH) with Stephen Harding, he joined the Max Planck Institute of Colloids and Interfaces in 1995 and finished his habilitation on "Biomimetic Mineralization" in 2001 with Markus Antonietti. His current research is focused on the synthesis and analysis of double hydrophilic block copolymers, biomimetic mineralization and nonclassical crystallization, and analytical ultracentrifugation. He has received a number of awards, including the Hermann Schnell Award from the German Chemical Society (GDCh).

Cölfen can be reached at the Max Planck Institute of Colloids and Interfaces, Colloid

https://doi.org/10.1557/mrs2005.205 Published online by Cambridge University Press

Helmut Cölfen



Wonmok Lee

Edwin L. Thomas

Michael D. Ward

Chemistry, Research Campus Golm, D-14424 Potsdam, Germany, and by e-mail at coelfen@mpikg.mpg.de.

Wonmok Lee is a research staff member at Samsung Advanced Institute of Technology in Korea. He received his MS and PhD degrees in polymer chemistry at the Pohang University of Science and Technology in Korea under Taihyun Chang in 2001. He then joined Paul V. Braun's group at the University of Illinois at Urbana-Champaign, where he studied photonic-bandgap materials based on colloidal crystals and multiphoton polymerization until 2003. He subsequently joined Edwin L. Thomas's research group at the Massachusetts Institute of Technology, studying polymer-based photonic-bandgap materials until 2004.

Lee's research interests include photonic crystals based on various self-assembly techniques, multiphoton polymerization and anionic polymerization, polymer characterization methods, and proton exchange membranes for fuel cells.

Lee can be reached by e-mail at wonmok.lee@samsung.com.

Edwin L. Thomas is director of the Institute for Soldier Nanotechnologies at the Massachusetts Institute of Technology. He has also served as associate head of the Department of Materials Science and Engineering and as director of MIT's polymer science and technology program. Additionally, he and others from MIT co-founded OmniGuide Communications Inc. in Cambridge. Before joining MIT, Thomas founded and served as the co-director of the Institute for Interface Science and was head of the Department of Polymer Science and Engineering at the University of Massachusetts. His research interests include polymer physics and engineering of the mechanical and optical properties of block copolymers, liquid-crystalline polymers, and hybrid organic–inorganic nanocomposites. He holds a BS degree from the University of Massachusetts and a PhD from Cornell University.

Thomas was the recipient of the 1991 High Polymer Physics Prize of the American Physical Society, the 1985 American Chemical Society Creative Polymer Chemist Award, and an Alexander von Humboldt fellowship at the University of Freiburg. He was elected a fellow of the American Physical Society in 1986. He has been a visiting professor, senior scientist, fellow, and/or assistant professor at various universities, including the Centre National de Recherche Scientifique for Macromolecules in Strasbourg, France, Bristol University, Cambridge University, and the University of Minnesota. He has written or co-authored approximately 300 publications, including one undergraduate textbook, and he holds 11 patents.

Thomas can be reached by e-mail at elt@mit.edu.

Michael D. Ward is a faculty member of the Department of Chemical Engineering and Materials Science at the University of Minnesota. He is also a Distinguished McKnight University Professor, an associate editor for *Chemistry of Materials,* and director of the University of Minnesota Materials Research Science and Engineering Center.

Ward received his BS degree in chemistry from William Paterson College of New Jersey in 1977 and his PhD degree from Princeton University in 1981. He was a Welch postdoctoral fellow at the University of Texas, Austin, between 1981 and 1982, at which point he joined the research staff at Standard Oil of Ohio in Cleveland. In 1984, he became a member of the research staff at DuPont Central Research and Development, and in 1990, he joined the faculty at the University of Minnesota.

Ward can be reached by e-mail at wardx004@umn.edu.

George M. Whitesides is the Flowers University Professor at Harvard University. His present research interests include physical organic chemistry, materials science, biophysics, complexity, surface science, microfluidics, self-assembly, micro- and nanoscience, cell biology, and optics. He obtained an AB degree from Harvard in 1960 and a PhD degree from the California Institute of Technology in 1964. He was on the faculty at MIT from 1963 to 1982, at which time he returned to Harvard.

Whitesides can be reached by e-mail at gwhitesides@gmwgroup.harvard.edu.

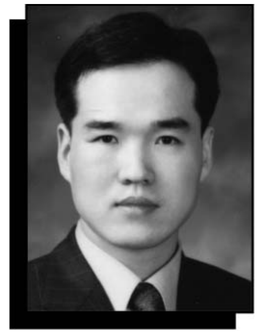
Jongseung Yoon is a doctoral candidate in materials science and engineering at the Massachusetts Institute of Technology. He received his BS degree in fiber and polymer science from Seoul National University in Korea in 1996. After fulfilling his military service duty, he began pursuing his PhD degree at MIT in the group of Edwin L. Thomas, which he joined in 2001. His current research is focused on block copolymer nanocomposite photonic-bandgap materials, including control of microdomain orientation of block copolymer photonic crystals, stimulus-responsive self-assembled bolck copolymer photonic structures, and fabrication of photonic-bandgap lasing devises based on self-assembled block copolymer nanocomposites doped with optically active gain materials.

Yoon can be reached by e-mail at jsyoon@mit.edu.

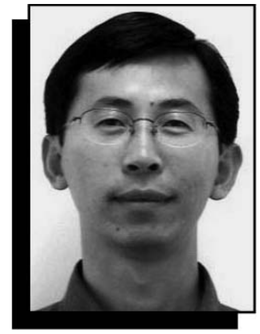
Shu-Hong Yu is a professor and the acting head of the Division of Nanomaterials and Chemistry at Hefei National Laboratory for Physical Sciences at the Microscale and the Department of Materials Science and Engineering at the University of Science and Technology of China. He received his BSc degree in 1988 from Hefei University of Technology and his PhD degree in 1998 from the University of Science and Technology of China. He worked as a JSPS research fellow from 1999 to 2001 in Masahiro Yoshimura's Materials and Structures Laboratory at the Tokyo Institute of Technology. He was subsequently an Alexander von Humboldt research fellow at the Max Planck Institute of

https://doi.org/10.1557/mrs2005.205 Published online by Cambridge University Press

George M. Whitesides



Jongseung Yoon



Shu-Hong Yu

Colloids and Interfaces in Potsdam, Germany, working with Helmut Cölfen and Markus Antonietti.

Yu has authored or co-authored more than 80 refereed journal publications and one patent. His research focuses on bio-inspired self-assembly strategies, biomimetics, and novel mild chemical routes for the rational design of new nanostructured modular materials, as well as their related properties and applications. He also serves on the editorial board for *Current Nanoscience.*

Yu can be reached at the Hefei National Laboratory for Physical Sciences at the Microscale, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China, and by e-mail at shyu@ustc.edu.cn. □

MRS 2005 Fall Preview! See page 745!

https://doi.org/10.1557/mrs2005.205 Published online by Cambridge University Press