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Introduction: Functional Nanostructures

Professor Samuel Stupp earned his B.S. in chemistry from the University of California at Los Angeles and his Ph.D. in materials science and engineering from Northwestern University in 1977. He was a member of the faculty at Northwestern until 1980 and then spent 18 years at the University of Illinois at Urbana-Champaign, where he was appointed in 1996 Swanlund Professor of Materials Science and Engineering, Chemistry, and Bioengineering. In 1999, he returned to Northwestern as a Board of Trustees Professor of Materials Science, Chemistry, and Medicine, and later he was appointed Director of Northwestern's Institute for BioNanotechnology in Medicine. Professor Stupp is a member of the American Academy of Arts and Sciences, and he is a fellow of the American Physical Society, American Association for the Advancement of Science, World Technology Network, and World Biomaterials Congress. His awards include the Department of Energy Prize for Outstanding Achievement in Materials Chemistry, a Humboldt Senior Award, the Materials Research Society's Medal Award, and the American Chemical Society Award in Polymer Chemistry for his work on supramolecular self-assembly. He was recently Paris Sciences Medal lecturer at Ecole Supérieure de Physique et de Chimie Industrielles in Paris, Merck-Karl Visiting Professor of Organic Chemistry at MIT, and visiting professor at the Institut de Science et d'Ingenierie Supramoleculaires in Strasbourg. His areas of research include self-assembly, electronic and photonic properties of organic nanostructures, biomolecular mineralization, templating chemistry of inorganic nanostructures, and biomaterials for regenerative medicine.

The nanoscience revolution that sprouted throughout the 1990s is having great impact in defining the current and future interests of many chemists around the world. In the initial chapter of chemical nanoscience, the objective has been to study the synthesis and physical properties of objects in which at least one dimension lies in the range of 1 to 100 nanometers. Chemistry has traditionally operated outside the regime of nanostructures, dealing at one end with the construction of sub-nanometer molecules, but without strict control of shape in solution or the gas phase, and at the other end with crystals large enough to diffract X-rays coherently. Most physical chemistry has therefore focused in these two spaces outside the regime of nanostructures. Nanostructure chemistry was initially catalyzed by discoveries, for example, of fullerenes, carbon nanotubes, thiols on gold monolayers, and surfactant based syntheses of II–VI nanostructures. Over the past decade, these discoveries guided a great deal of

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synthetic work on nanostructures and on their physical characterization to discover the special properties of surface-rich objects. At the time, a thematic issue of *Chemical Reviews* on nanostructures was guest edited by Edwin A. Chandross and Robert D. Miller. Currently, we are seeing a number of important transformations in the field of chemical nanoscience. One is tackling rational synthesis to control not only size but also the shape of both organic as well as inorganic objects. Another important transformation is the increasing interest in connecting structure to function by design, and extending function to dynamics of nanostructures and not just to their static properties. Interest in function also motivates a growing interest in approaches to patterning of nanostructures in devices, using either top-down or bottom-up procedures. A very clear trend is also the search for function in nanostructures that makes them useful in biology and medical technologies. Various aspects of these important transformations and trends in the field of chemical nanoscience are reviewed in this issue by a collection of ten articles.

The two well-established areas of inorganic nanocrystal synthesis and properties as well as the area of self-assembled monolayers are reviewed in this issue, summarizing all major advances. A thorough review of metal and semiconductor nanocrystal synthesis and their properties is offered in the article written by Burda, Chen, Narayanan, and El-Sayed, connecting shape and composition to electronic and optical functions in these systems. This article also covers the field of catalytic functions in nanoscale transition metals, including fuel cell and hydrogenation reactions. The field of self-assembled thiolates on metal is reviewed by Love, Estroff, Kriebel, Nuzzo, and Whitesides. This review includes, among other topics, the use of monolayers for functions such as nucleation of crystals, alignment of liquid crystals, and modification of nanoparticles, and it also includes their use as model surfaces to study cells or as barriers to block etchants and electron transport. Nanofabrication will be of critical importance to translate the fruits of nanoscience into technology, and the state of the art in this area is reviewed in the article by Whitesides and his coauthors Gates, Xu, Stewart, Ryan, and Willson, with special emphasis on the use of new approaches such as molding and embossing using hard and soft transfer elements.

The transition to function of nanostructures through dynamics is of great scientific importance. The Michl laboratory introduces the topic in two articles, one on the synthesis of molecular rods (Schwab, Smith, and Michl) and then an article on artificial molecular rotors (Kottas, Clarke, Horinek, and Michl). As it becomes possible to enlarge the structures of rotors into the range of 1 to 100 nanometers and to organize them into lattices on surfaces, it will be possible to think about new functions for devices based on nanostructures. The topic of dynamics is further discussed in an article by Kinbara and Aida describing biological and bioinspired machines. These systems, which in biology operate using proteins and ATP as the fuel, could be replicated in completely synthetic systems and considered for biomedical applications to interfere with the nanomachineries of cells, either for basic science research or for novel therapies in medicine.

The least developed area in functional nanostructures is that of organic synthetic nanostructures. This is a structural space that has to develop chemically through the fields of supramolecular chemistry and self-assembly and also through the field of foldamers, organic molecules that can fold into nanoscale objects with defined shapes. This field is about emulating the structure and function of proteins and protein complexes using synthetic organic molecules. Three articles in this issue relate to this challenge, an article on supramolecular nanotube architectures by Shimizu, Masuda, and Minamikawa, an article by Nolte and coauthors Vriezema, Aragonès, Elemans, Cornelissen, and Rowan which offers a review on self-assembled nanoreactors based on organic molecules, and an article by Meijer with coauthors Hoeben, Jonkheijm, and Schenning which reviews supramolecular assemblies based on π-conjugated systems. The article by Meijer reviews the use of organic molecules to construct nanostructures with electronic functionality, and Nolte's article reviews the current state of research on micelles, vesicles, polymersomes, capsules, boxes, and protein cages. The article by Shimizu and his colleagues is representative of one-dimensional nanostructures based on amphiphiles, including those with tubular architectures. Finally, Rosi and Mirkin review the application of nanostructures of hybrid nature (organic−inorganic) as tools for diagnostics in medicine, sophisticated schemes to detect genes and proteins using organic functionalized forms of inorganic nanostructures. This article is very much representative of the growing interest in using nanostructures for advanced medicine. Our laboratory is also involved in this area, using biomolecular nanostructures for regenerative medicine, and I expect the application of chemical nanoscience in medicine is a field that will continue to grow. It has very rich possibilities as a tool to learn new science that has enormous human impact. Chemistry as an area of science has always aspired to be useful to humans, and conceivably a future issue of *Chemical Reviews* might treat this specific topic.

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