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Mesoporous Materials - June 2008

Interview Date: September 2008



Professor Mietek Jaroniec

From the Special Topic of [Mesoporous Materials](#)

According to our recent Special Topic on mesoporous materials over the past decade, the scientist ranking at #2 by total number of papers and #12 by total citations is Professor Mietek Jaroniec, with 80 papers cited a total of 2,260 times.

In [Essential Science IndicatorsSM](#) from [Thomson Reuters](#), Prof. Jaroniec's record includes 198 papers, mostly classified in the fields of Chemistry and Materials Science, cited a total of 5,861 times between January 1, 1998 and April 30, 2008. Prof. Jaroniec hails from Kent State University in Kent, Ohio, where he is a Professor in the Department of Chemistry.

In the interview below, he talks with ScienceWatch.com about his frequently cited work.

SW: Please tell us a little about your educational and research background.

I was born in Poland and underwent higher education in chemistry at the Marie Curie-Sklodowska University in Lublin, Poland, where I received an equivalent degree of M. Sc. in 1972, a Ph.D. in 1976, and a Doctor of Science degree in 1979. In 1985 I received a title of Professor and was a faculty member in the Department of Chemistry at the M. Curie-Sklodowska University until 1991.

In the meantime, I had a few visiting appointments, including Georgetown University (1984-85), McMaster University (1985-86) and Kent State University (1987, 1988-89). In 1991, I moved to Kent State University and have been a chemistry professor there since. In 2005 I received an Honorary Professor title from my *alma mater*.

SW: What first interested you in mesoporous materials?

The term "mesoporous materials" refers to solids with broad or narrow distribution of pores in the range between 2 and 50 nm, which form a disordered or ordered network. In my studies at M. Curie-Sklodowska University, I was primarily interested in interfacial chemistry, especially in physical adsorption from the gas and liquid phases on microporous (pore widths below 2 nm) and mesoporous solids. The solids studied, including carbons, silica gels, and other inorganic materials, featured broad pore size distributions and disordered porosity.

One of the intriguing questions, which initially attracted my attention, was the effect of pore size distribution (structural heterogeneity) on physical adsorption and related phenomena. It soon became evident that the computer simulations and experimental

studies of adsorption in uniform mesopores are essential for modeling physical adsorption in heterogeneous mesoporous solids. Therefore, two pioneering papers from Mobil Co. (Kresge CT, *et al.*, "Ordered mesoporous molecular sieves synthesized by a liquid crystal template mechanism," *Nature* 359[6397]: 710-2, 22 October 1992; Beck JS, *et al.*, "A new family of mesoporous molecular sieves prepared with liquid crystal templates," *JACS* 114[27]: 10834-43, 30 December 1992), reporting the self-assembly synthesis of ordered mesoporous silicas of hexagonal and cubic symmetry, immediately attracted my attention. These two papers initiated a separate research field spawning about ten thousand publications; because of this, the term "mesoporous materials" is often identified with "ordered mesoporous materials"(OMMs).

My adsorption experience primarily directed me towards usage of these well-defined mesostructures as model adsorbents for the refinement of the existing methods and the development of new ones for characterization of mesoporous materials. My prior experience in the organosilane modification of silica particles for chromatographic separations inspired me to study ordered mesoporous organosilicas. In the first case I was fortunate to collaborate with a highly motivated and talented graduate student and postdoctoral fellow, Michal Kruk (currently assistant professor at CUNY, Staten Island), and Professor Abdel Sayari (currently at Ottawa University). This collaboration led to the development of a simple and accurate method of pore size analysis of channel-like mesoporous materials ("Application of large-pore MCM-41 molecular sieves to improve pore size analysis using nitrogen adsorption measurements," *Langmuir* 13[23]: 6267-73, 12 November 1997), which is known as the KJS method.

The development of ordered mesoporous organosilicas has been an equally exciting topic because the self-assembly of appropriate organosilanes and surfactants or block copolymers creates almost unlimited possibilities in the synthesis of novel organosilica mesostructures of tailored porosity, surface and framework properties, and morphology.

SW: Your most-cited paper in our Special Topics analysis is the 2001 *Advanced Materials* paper, "Ordered mesoporous carbons." Would you talk a little bit about this paper—its findings and the significance for the field?

The popularity of this paper illustrates the importance of timely and concise review articles in rapidly growing areas of research. At the end of 1999 Professor Ryong Ryoo and co-workers from the Korean Advanced Institute of Science and Technology (KAIST) reported in *J. Phys. Chem. B* the synthesis of ordered mesoporous carbon (OMC) by using a cubic OMS, MCM-48, as a hard template. The hard-templating synthesis (nanocasting) involves the filling of pores of the template with carbon precursor, carbonization of the latter, and the dissolution of the siliceous template.

The 2001 *Advanced Materials* paper was the first review article devoted to the OMC materials; it was published just two years after discovery of OMC. Since the hard-templating synthesis of OMCs was one of the major advancements in the area of ordered mesoporous materials, this concise review attracted the attention of many scientists and stimulated the further development of OMCs.

SW: Your most-cited paper overall in *Essential Science Indicators* is the 2000 *Journal of the American Chemical Society* paper, "Synthesis of a new, nanoporous carbon with hexagonally ordered mesostructures." Why do you think this paper has garnered so much attention?

Porous carbons, especially active carbons, have been known for thousands of years because of their common usage in purification, pre-concentration, and separation processes. From a physicochemical viewpoint, active carbons are structurally heterogeneous due to the presence of fine pores (mainly micropores) of different sizes, shapes, and connectivity, which limit their accessibility to small molecules and hinder molecular transport through the pore network. Therefore, there was a great interest in the development of mesoporous carbons in order to extend their applicability for adsorption of larger molecules and to improve the kinetics of the aforementioned processes. Several recipes, which have been proposed for the development of mesoporous carbons, afforded materials with broad distribution of pores and disordered porosity.

Two landmark papers published in 1998 and 1999 showed a new way for the synthesis of carbons with ordered pores; the first one (Zakhidov AA, *et al.*, "Carbon structures with three-dimensional periodicity at optical wavelengths," *Science* 282[5390]: 897-901, 30 October 1998) is devoted to the fabrication of ordered macroporous (pore widths above 50 nm) carbons by using siliceous colloidal crystals as hard templates, whereas the second one (Ryoo R, Joo SH, Jun S, "Synthesis of highly ordered carbon

"The past fifteen years of remarkable progress in the synthesis of OMM have been accompanied by the development of a wide variety of potential applications of these materials..."

molecular sieves via template-mediated structural transformation," *J. Phys. Chem. B* 103[37]: 7743-6, 16 September 1999) reports the synthesis of ordered mesoporous carbons using the MCM-48 templates. Since the MCM-48 cubic structure consists of two interwoven three-dimensional pore systems, the resulting carbon is not a true inverse replica of the template because of a structural change during templating synthesis.

In contrast, the *JACS* paper (a collaborative effort of Professors Ryoo, Terasaki, myself, and our co-workers) reports the first synthesis of OMC, which is a true inverse replica of SBA-15 (hexagonally ordered mesoporous silica, OMS). This work shows the possibility of tailoring the OMC structure by selection of appropriate siliceous hard templates. Also, it provides additional evidence on the presence of interconnecting fine pores in SBA-15 (see response to the next question).

The SBA-15 template (which consists of hexagonally ordered cylindrical mesopores interconnected by irregular micropores), after filling its pores completely with carbon precursor followed by carbonization and silica dissolution, gives the inverse carbon replica, which is a collection of hexagonally ordered carbon rods interconnected by irregular carbon wires. If pores of the SBA-15 template are not filled completely, the resulting replica consists of hexagonally ordered interconnected carbon nanopipes. This example shows the attractiveness of hard-templating synthesis for fabrication of various carbon nanostructures. An additional advantage of this synthesis is the preservation of template morphology when the three-dimensional rigid OMSs are used as hard templates.

"The popularity of this paper illustrates the importance of timely and concise review articles in rapidly growing areas of research."

SW: Another key paper is the 2000 *Chemistry of Materials* paper, "Characterization of the porous structure of SBA-15." Would you sum up this paper and its findings for our readers?

SBA-15, one of the most-popular OMMs reported in 1998 in *Science* (Zhao DY et al., "Triblock copolymer synthesis of mesoporous silica with periodic 50 to 300 angstrom pores," 279[5350]: 548-52), is a hexagonally ordered mesoporous silica obtained by using poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymers as soft templates. Initially, it was suggested that SBA-15 is a large-pore counterpart of MCM-41, which is a solely mesoporous material synthesized by using cationic surfactants as soft template. According to this suggestion, the only difference between SBA-15 and MCM-41 was the size of mesopores, which in the former case were much larger. Thus, both MCM-41 and SBA-15 were supposed to be two-dimensional (2D) hexagonally ordered mesoporous silicas.

The 2000 *Chemistry of Materials* paper and subsequent one (*J. Phys. Chem. B*) shows that this is not true for the SBA-15 samples reported so far. In fact, SBA-15 exhibits a 3D microporous-mesoporous network, which consists of 2D hexagonally ordered cylindrical mesopores interconnected by irregular complementary pores such as micropores and fine mesopores. An accurate analysis of adsorption data, post-synthesis modification, and inverse replication studies proved the presence of complementary fine pores in the mesopore walls of SBA-15. Solid evidence has been provided by the above *JACS* paper, which reports a successful synthesis of a true inverse carbon replica of SBA-15; this would be impossible if SBA-15 had no interconnecting microporosity.

SW: What are the practical applications (or potential applications) of these materials?

In the preface of a recent special issue "Templated materials" of *Chemistry of Materials* (20[3]: 599-600, 12 February 2008) edited by Professor Ferdi Schüth and myself, we wrote: "The past fifteen years of remarkable progress in the synthesis of OMM have been accompanied by the development of a wide variety of potential applications of these materials, ranging from adsorption, catalysis, separations, gas storage and environmental cleanup to drug delivery, sensing devices, optoelectronics, nanotechnology, energy storage and conversion." This special issue contains many invited reviews and original papers, which report on the potential applications of OMMs.

SW: What should the "take-away lesson" be about your work?

Soft-templating and hard-templating strategies provide tremendous possibilities for the synthesis of novel ordered mesostructures of tailored porosity, surface and framework properties, and morphology. Examples of the aforementioned OMMs as well as extensively studied metal-organic frameworks (MOFs) show that we are still in the beginning of an exciting journey and a lot will be done in the development of novel ordered nanostructures and especially in the area of their applications.

The three papers presented in this interview were performed in collaboration with Professor Ryoo's group (KAIST), which is one of the most active and productive groups in the area of OMMs. The

aforementioned papers show how much can be done through international collaboration. Therefore, I would like to thank Prof. Ryoo and his group as well as other past and current graduate students and collaborators for their fruitful interactions. ■

Mietek Jaroniec, Ph.D.
Department of Chemistry
Kent State University
Kent, OH, USA

Professor Mietek Jaroniec's most-cited paper with 473 cites to date:

Jun S, *et al.*, "Synthesis of new, nanoporous carbon with hexagonally ordered mesostructure," *J. Am. Chem. Soc.* 122(43): 10712-3, 1 November 2000. Source: *Essential Science Indicators* from Thomson Reuters.

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View a Fast Moving Front comment by [Mietek Jaroniec](#) from 2004.

Keywords: mesoporous materials, interfacial chemistry, pore size distribution, structural heterogeneity, physical adsorption, mesoporous organosilicas, ordered mesoporous carbons, SBA-15, soft templating, hard templating, ordered nanostructures.



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