

# Pores for Thought: Stand Up and Be Counted

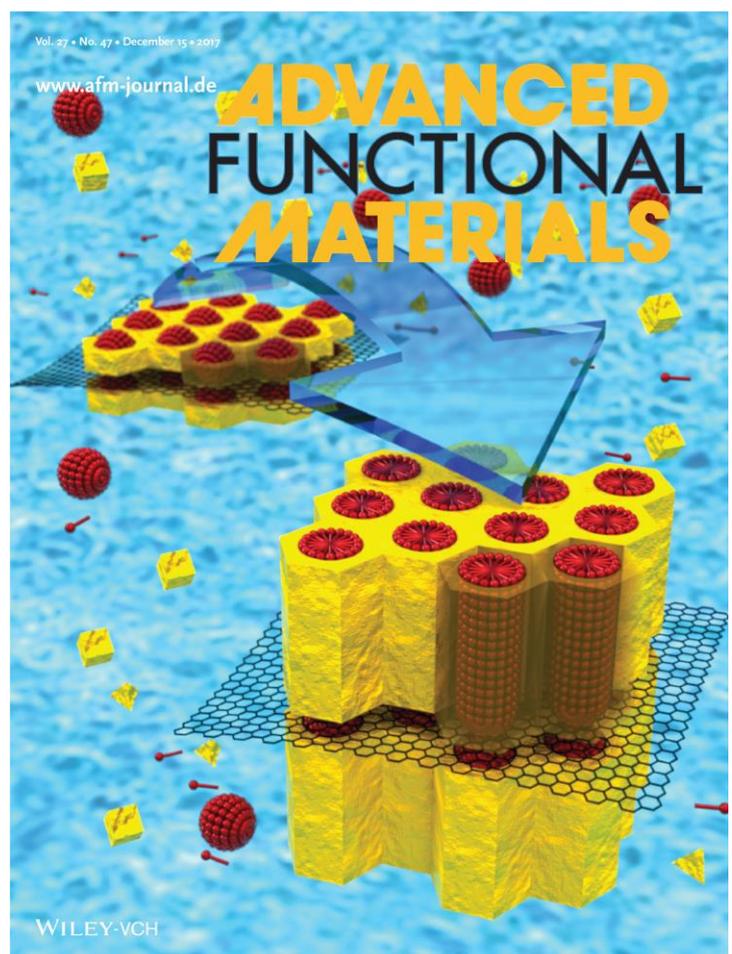
Zheng-Min Wang, Wendong Wang and Geoffrey Ozin have discovered a synthetic pathway to a sandwich-type nanocomposite of reduced graphene oxide and periodic mesoporous silica in which mesochannels of silica vertically align with respect to the graphene layers with tunable mesochannel depth and size. Deep insight into the formation mode of this novel class of materials obtains from a high photon flux small angle X-ray scattering technique and zeta potential-based solution chemistry, *Advanced Functional Materials* 2017, DOI: 10.1002/adfm.201704066.

Aristotle postulated Nature abhors a vacuum based on his observation that there are no examples of a vacuum in nature. His supposition, predicated on the grounds dense material in the surrounding continuum would collapse to fill the void, received support from Plato, who agreed a void is nothing and therefore cannot exist.

Today, with the ability to visualize atoms in solid-state materials with high-resolution electron microscopes, one finds that most solids viewed at the atomic scale are indeed dense. The constituent atoms making up the solid look like spheres packed as closely together as possible to minimize the formation of free space. This is the most stable state of solids and since the prehistoric Stone Age to today's Silicon age dense solids have dominated, enabled and shaped our existence.

As it turns out, Aristotle was not quite right with his postulate of "horror vacui", from the Latin "fear of empty space" as today there are as many documented solids filled with voids as there are dense solids. How could this be?

This is because while the thermodynamic most stable state of a solid cause voids within to



collapse, the kinetic stability of the solid, which controls the speed of the collapse, can be very slow allowing it to exist forever. This is the so-called metastable form of solids filled with voids and as many examples of this class of materials exist today as dense forms.

Perhaps the most familiar form of void-containing solids are the zeolites. They have inorganic compositions comprised of the elements aluminum, silicon and oxygen and have an open-structure based on a periodic array of nanometer scale voids, where a nanometer (nm) is a billionth of a meter. The International Union of Pure and Applied Science, IUPAC, designate this class of solids with void sizes below 2nm as microporous.

Today the composition of microporous materials includes most elements of the periodic table. They are synthesized using organic molecules as a 'template' to direct the assembly of the inorganic species. The organic molecule fills space in the organic-inorganic composite and its subsequent removal by chemical means creates nanometer size voids, comparable to the size of the organic molecule in the inorganic solid.

Microporous materials have found wide-ranging applications that include, separating mixtures of molecules based on size such as oxygen and nitrogen in air, capture, storage and release of large amounts of gaseous molecules such as greenhouse gas carbon dioxide, spatially selective catalytic transformations such as crude oil refining to high-octane gasoline.

The quest to make larger void sizes using the template-based synthesis method requires more than a single organic molecule. This is achievable with a 'supramolecular template' composed of an assemblage of organic molecules. With this synthetic strategy it has proven possible to boost the achievable range of void sizes to the mesoscale range, defined by IUPAC as 2-50nm, thereby expanding the application opportunities for this new class of mesoporous materials that were impossible with the smaller voids in microporous materials.

This is the background relevant to a recent breakthrough in the field of periodic mesoporous materials, the subject of this news article.

It originates with the work of Charles Kresge and coworkers at Mobil Research, New Jersey who discovered that aqueous solutions of self-assembling organic molecules called surfactants, the constituent molecules of soap, could direct the assembly of siliceous building blocks to form mesoporous silica materials with periodically organized voids tailorable with nanometer precision in the size range 2-10 nm.

This breakthrough, reported in the journal Nature 1992, today with more than 17,000 citations, enabled materials researchers for the first time to escape from the 1 nm prison imposed by the void sizes of microporous zeolites. This advance spawned exciting new scientific and technological explorations of solids permeated with regular arrays of mesoscale voids.

Inspired by this spectacular development, Geoffrey Ozin and coworkers at the University of

Toronto working with Charles Kresge at Mobil Research discovered that surfactants could direct the self-assembly of oriented periodic mesoporous silica films on substrates, such as mica and graphite, published in the journal Nature 1996. These films contained mesoscale channels oriented parallel to and registered with the surface of the substrate. The direction of the channels in these films seemed controlled by the pre-organization of the surfactant template on the substrate, which co-assembled with and directed the condensation polymerization of the siliceous precursor to form the periodic mesoporous silica film, the mechanism of which depended on the structure and wettability of the substrate surface.

While useful in optics, fluidics, microelectronics, and chemical sensing, and drug delivery to name a few applications, the discovery of these periodic mesoporous silica films inspired a worldwide effort to find ways and means to coerce the channels to stand up vertically on the substrate. The motivation was that experimental realization of mesoscale vertical channels on a range of substrates would expand the range of opportunities available to periodic mesoporous silica films, examples being in drug storage and delivery, large molecule separations, and charge-storage super-capacitors, to name but a few possibilities.

In response to this need, an international collaborative effort between a team from the National Institute of Advanced Industrial Science and Technology (AIST), Japan and the University of Toronto, Canada, discovered that single sheet graphene was able to compel the channels of periodic mesoporous silica film to grow vertically and in a honeycomb pattern with respect to its surface. This discovery, published in the ACS Nano, 2010, revealed that these oriented films grew on both sides of the graphene sheet with vertical channels on each side and remarkably registered with respect to one another. A graphene surface directed cooperative co-assembly mechanism explained this surprising observation.

With this knowhow, the next challenge for the Japanese-Canadian team was to develop a synthetic strategy to control the diameter and length of the channels. This research, published in the journal Advanced Functional Materials 2017, necessitated a detailed understanding of the self-assembly of the structure directing surfactants and silica precursors on the graphene substrate, which was achieved by high photon flux synchrotron based operando small angle X-ray scattering. The results showed that vertical alignment of the mesoscale channels was triggered by a surfactant pre-assembly on the graphene surface. Reaction time controlled the depth of the channels in the range of 12.5 to 38.4 nm. The length of the surfactant hydrocarbon chain, its concentration and the solution temperature enabled channel diameter tuning from 2-5 nm.

With this newfound understanding, it is now possible to explore a myriad of application opportunities for periodic mesoporous silica composites with graphene, comprised of controlled diameter and length vertical silica channels standing up on either side of nanometer thick sheets of electrically conducting graphene that can exploit the unique

chemical and physical properties of the two nanocomponents.

Imagine electrically and optically stimulated and programmed release of pharmaceuticals, pesticides and herbicides contained in these vertical channel films; imagine the storage and retrieval of digital information in each channel, enabling next generation  $10^{15}$  petabyte memory; imagine different color light absorption and emission from semiconductors contained in each channel, for ultrahigh resolution cameras and displays.