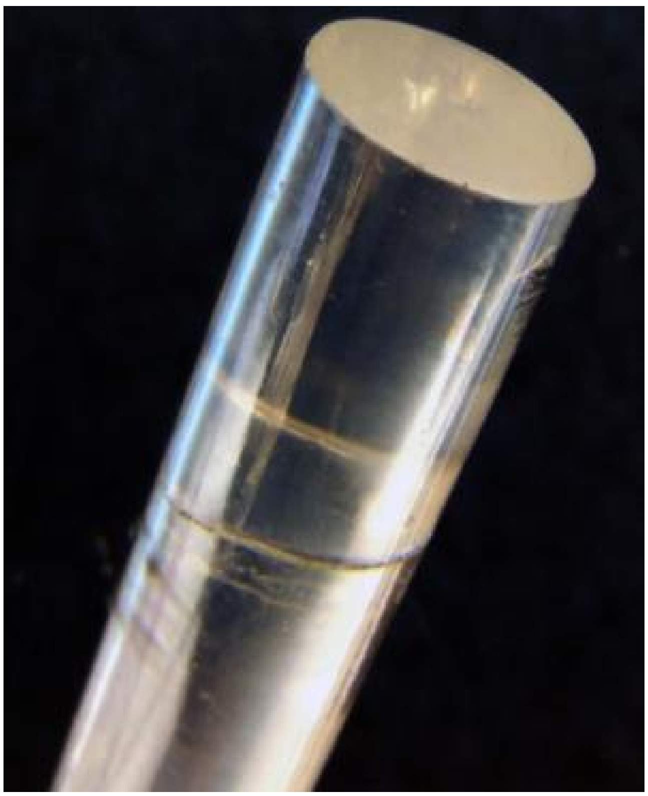
Marine sponge forms a glass filament with a perfect periodic arrangement of nanopores

February 24 2014, by Katja Schulze



A segment of approximately one-centimetre-thick glass rod that is used by Monorhaphis chuni to attach itself to the ocean's floor. The inner structure of the filament, passing through the centre of this giant glass rod, resembles the structure of synthetic mesoporous materials. However, the microstructure of this naturally occurring material is more regular than the synthetic counterparts. Credit: Igor Zlotnikov / MPI of Colloids and Interfaces

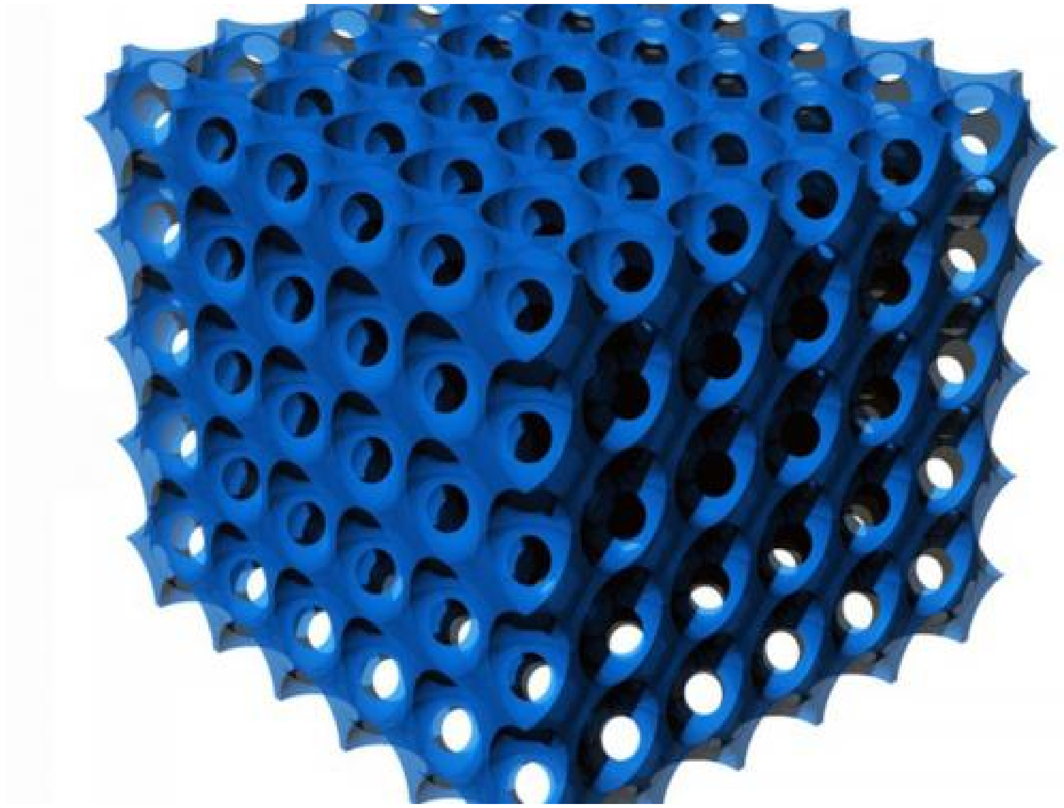
Materials made by man and those made by biological organisms often deal with similar synthesis challenges – occasionally converging on an analogous solution independently. One example is the giant glass rod that is used by the sea sponge M. chuni to anchor itself in marine environments. A collaborative effort by researchers from the Max Planck Institutes of Colloids and Interfaces and of Microstructure Physics has now uncovered and analysed the nanostructure of the filament passing through the centre of this giant glass rod.

The researchers discovered that it is structured almost exactly like the nanoporous man-made nanomaterials, which are relevant for many applications in fields such as biomedicine, sensor technology and chemical catalysis. M. Chuni forms the glass around regularly arranged proteins, called silicateins, measuring approximately five nanometres in size. This creates a structure resembling stacks of eggs in cartons, where the eggs correspond to the protein molecules, while the cartons represent the glass. Artificial glass nanoporous structures are produced around droplets of fats or complex polymers. However, the size and the spatial arrangement of the pores in materials produced in this way are not as uniform as of the protein-filled cavities in the glass filament of M. chuni.

The amount of surface area often plays an important role in materials used in medicine and technology and normally, it should be as large as possible. It can accommodate, for instance, large quantities of pharmaceutical agents and release them gradually in the body. In chemistry, the efficiency of numerous processes is dependent on catalysts exhibiting a large surface on which reactions can occur. In sensors, for example, the sensitivity is strongly dependent on the amount of surface to which the detected molecules can attach. Porous structures are a good example for such materials.

Materials having pores measuring between 2 to 50 nanometres are particularly well suited for such purposes. Scientists refer to these as mesoporous structures, to distinguish them from structures that are microporous, having smaller pores, or macroporous, with larger pores. Recently, Igor Zlotnikov and Peter Fratzl, who study biomaterials at the Max Planck Institute of Colloids and Interfaces in collaboration with the team of Peter Werner from the Max Planck Institute of Microstructure Physics, Emil Zolotoyabko from the Israeli Institute of Technology and Yannicke Dauphin from the Université P. & M. Curie, have discovered a mesoporous material in nature, namely in the glass sponge Monorhaphis chuni. The sponge lives on the bottom of the Indian and Pacific Oceans, and forms an approximately one-centimetre-thick glass rod to attach itself to the ocean's floor. Over the course of its life, the rod can grow up to three meters in length. The glass filament, passing through the centre of this rod, is perforated with pores having a diameter of about five nanometres. Each pore is occupied by an egg-shaped protein molecule, called silicatein, connected to the protein molecules in adjacent pores through holes in the glass.

The glass sponge sets standards for the regularity in size and arrangement of pores



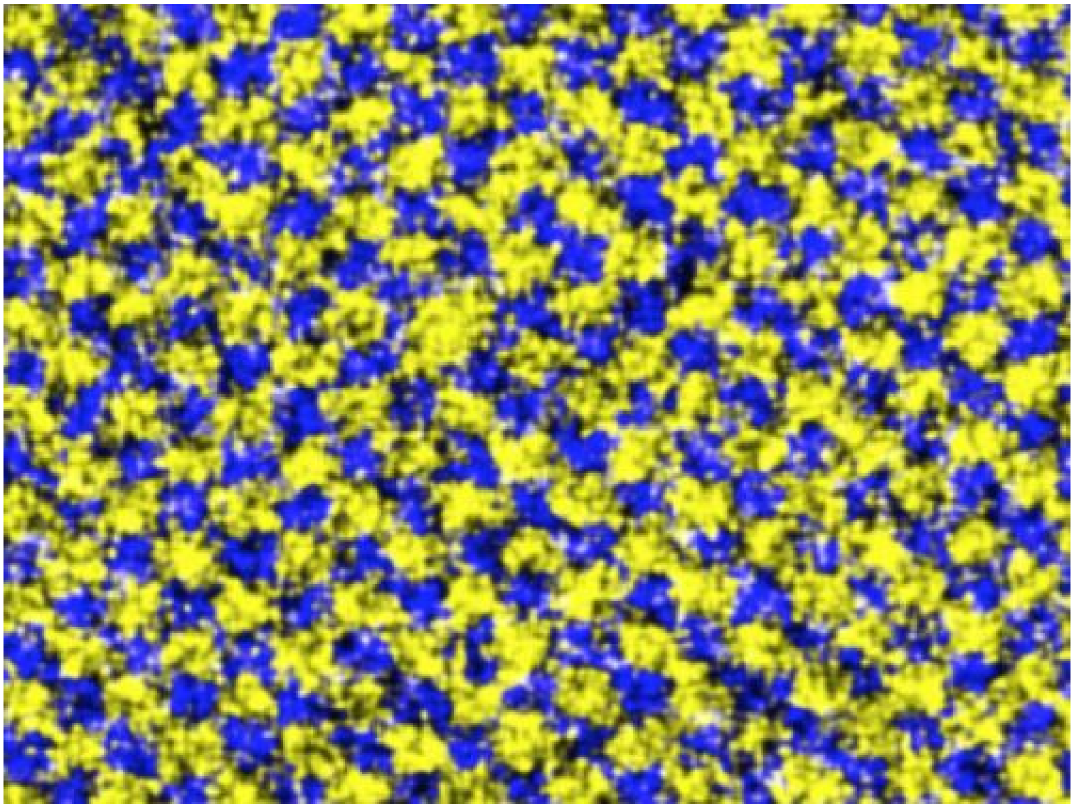
Pore distribution in the glass filament resembles stacked, pallet-like egg cartons. Each cavity is occupied by one protein molecule, called silicatein, measuring approximately five nanometres in size. Credit: Igor Zlotnikov / MPI of Colloids and Interfaces

"Mesoporous glass structures are among the most studied materials. This makes it even more exiting to find them in nature," says Igor Zlotnikov. "Presumably, this structure is not limited to M. chuni, but can also occur in other glass sponges." However, not only does M. chuni produces a mesoporous material that is technologically relevant; the sponge sets standards in terms of size distribution and arrangement of the pores. In the sample that Igor Zlotnikov and his colleagues studied, all pores have the size of the inhabiting protein molecule and they are completely regularly arranged. Metaphorically speaking, the structure resembles egg cartons that are stacked one on top of another like pallets.

The researchers used two characterization techniques to gain an accurate picture of the internal architecture of the filament. First, they employed X-ray analysis at the BESSY II synchrotron facility in Berlin. Experiments with X-ray diffraction usually serve to identify the atomic periodic structure of crystals. However, Igor Zlotnikov's team used a variant of this technology to reveal structural periodicity on a larger scale, namely, on the scale of the pores size and their spatial arrangement. The results were confirmed in cooperation with the team working with Peter Werner from the Max Planck Institute of Microstructure Physics using high resolution transmission electron microscopy. In addition to structural details, this technique allows researchers to make assertions about local chemical composition.

But what surprised the researchers even more than the periodicity of the structure that was revealed is the way in which M. chuni produces it: "It's absolutely astonishing that nature and mankind converged on a similar manufacturing method independently", says Peter Fratzl, Director at the Max Planck Institute of Colloids and Interfaces. To continue with the image of the egg cartons, the glass sponge first stacks one or maybe even several layers of eggs – that is, protein molecules – and then fills the gaps with cardboard, or in this case glass.

Pore size varies in synthetic mesoporous materials



An image from a transmission electron microscope (TEM/EDX), which allows mapping of the chemical composition of the structure, shows periodic structure of silicatein molecules (yellow) and glass (blue) inside the filament. Credit: Peter Werner/MPI of Microstructure Physics; Andreas Graff/Fraunhofer Institute for Mechanics of Materials IWM

Since the protein molecules, which serve as a kind of a model for the surrounding glass structure, are all in the same size, the pores in the obtained material also have the same diameter and form a completely uniform structure. Achieving this precision via synthetic methods is difficult, even though the mesoporous glass is created in a very similar manner. Here, organic droplets around which the glass is produced determine the pore shape. Subsequently, the droplets are dissolved out of the nanostructure using a detergent – in principle, nothing other than a dishwashing liquid. However, scientists can't adjust the size of the droplets as precisely as the biochemical apparatus of a living organism that controls the size of the proteins. Thus, the pore size in synthetic mesoporous materials varies, and the cavities don't arrange themselves into a perfectly regular pattern.

"With silicatein or other proteins, it would be possible to produce mesoporous materials having a completely uniform pore size and a perfectly periodic arrangement", says Igor Zlotnikov. "That would be very expensive." Mimicking regularly structured materials similar to those found in M. chuni, for the time being, is not the goal of Max Planck researchers. They are currently investigating whether the mesoporous structure is as uniform over large regions of the glass filament as it is in the 100 micrometer section they analysed for the current publication. "Besides that, we focus on the relationship between the structure and the mechanical properties of the entire glass rod", says Peter Fratzl. Also there, M. chuni sets standards in terms of structural optimization to enhance its mechanical behaviour.

More information: Zlotnikov, I., Werner, P., Blumtritt, H., Graff, A., Dauphin, Y., Zolotoyabko, E. and Fratzl, P. (2013)," A Perfectly Periodic Three-Dimensional Protein/Silica Mesoporous Structure Produced by an Organism." *Adv. Mater*. DOI: 10.1002/adma.201304696

Provided by Max Planck Society