Experiment title:
In-situ SAXS investigations of (bio)polymer-mediated silicas: diatoms as an inspirational source for the development of porous silicas

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Report:

a. The formation mechanism of silica hollow spheres

In nature silica polymerization in diatoms involves biopolymers e.g. polyamine-modified proteins and proceeds under ambient conditions. It will be of great economic interest to be able to mimick the natural processes of biomineralization and to create new silica structures based on the way nature proceeds. In diatoms multi-component systems made of species-specific proteins and other organics e.g. polyamines may be used as templates. Polyethylene oxide (PEO)-based polymers, with their commercial availability and multiple structural derivatives, has been selected as a model template instead of the complicated diatomic proteins.

At Eindhoven University we have studied the synthesis of silica hollow spheres templated by PEO-PPO-PEO block copolymer emulsions. The synthesis method has the advantages of well-defined multilamellar shell structure, high-uniformity in particle size, by a low-cost and efficient synthesis (cheap silica source, a few hours at room temperature or 80 ˚C). Preliminary study indicated that these monodisperse silica hollow spheres may well be a good carrier system for potential drug-delivery purposes. However, the formation mechanism is still unclear.

In order to get insights on the formation mechanism of silica hollow spheres, the emulsion solution was extensively studied by SAXS. The scattering data revealed that acidified aqueous PEO-PPO-PEO block copolymer solution contained micellar fibers, with a diameter of a couple of nanometers. After the addition of TMB-EtOH mixture, the size of particles quickly grew bigger, which is in line with the cryo-TEM observation. The diameter of the emulsion droplets depended on the pH value of the solution - approximately 100 nm at lower pH of 1.0, whereas quickly grew bigger with the increase of the pH. Upon the addition of the sodium silicate solution the size of these droplets increased continuously. These data indicated that the sodium silicate must play a role in the increase in particle size. Indeed it is known that silicic acid coordinates to a cationic surfactant. Also hydrogen bonds are known to be formed between silica and PEO-PPO-PEO, which may lead to a decreased emulsifying action of the block copolymer, leading to larger, but stable emulsion droplets.

b. Rod-structured silicas templates Guanosine columnar aggregates

Diatomaceous silica is characteristic of diversified ordered pore structures with amorphous silica cell walls, which resembles man-made mesoporous silica e.g. MCM-41. The preparations of inorganic frameworks with organized porosity, and the fabrication of materials on the nanometer length scale, are two prominent objectives of modern materials chemistry. Ordered arrangements of mesoporous channels have been produced in a range of silica-based materials by surfactant liquid crystal templating. In this approach different lyotropic phases of a large variety of surfactants and amphiphilic polymers have been used to structure the developing silica phase that grows around these self-assembled organic templates, resulting in numerous new mesophases.

Guanosines have shown a peculiar ability to self-assemble to give stable structures e.g. fibres, highly-ordered gels, chiral aggregates, and interestingly, chiral columnar aggregates in isotropic solutions. The latter one has a layered structure: the inner part is composed of a stacked array of planar units, the G-quartets, formed by four guanines hydrogen-bonded. Because of the dissymmetric nature of the molecules, the G-quartets do not stack in register, but are rotated one with respect to the other. In the centre of the G-quartets there is a potassium ion that interacts via coordination with the eight oxygen atoms of the eight surrounding guanines. Such a chiral aggregate was exteriorly surrounded by phosphate groups, which made it a good model compound for the highly phosphorylated diatomaceous proteins.

At Eindhoven University rod-structured silicas has been successfully synthesized using guanosine columnar aggregates as templates. TEM study showed that, in addition to quite some spherical particles, considerable amount of plate-like silicas with well aligned rod-like structures could be observed. The formation of such ordered mesostructured silicas was monitored in-situ by SAXS during this experimental session. However, less useful information could be obtained because of the extremely fast silica precipitation. The SAXS study on the as-made solid samples revealed the presence of spherical particles in a bigger length scale and rods in a smaller length scale, which is in good agreement with TEM observation. Detailed sample characterization is still ongoing at Eindhoven.

c. UV-ozone treatment – a mild method to remove organics from silicas.

At Eindhoven University we have made good progress with the use of UV/ozone to remove the organic templates from the silica samples. Both nitrogen physisorption and TGA analyses indicated few organics remained in the silica structure after UV/ozone treatment. But it is unknown if the silica properties e.g. fractal dimensions, surface roughness, as well as structural factors will change during this process. A series of SAXS measurements were carried out in order to compare the scattering profile of wet silica gels, as-made silica solids, as-calcined samples and samples treated by UV/ozone method. The data indicated that this room temperature process is indeed a mild method to keep the fragile structure.

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