Synthesis of Uniform Silica Rods, Curved Silica Wires and Silica Bundles Using Filamentous Fd Virus as a Template

Johan Buitenhuis and Zhenkun Zhang

Forschungszentrum Jülich GmbH, IFF - Weiche Materie, D-52428 Jülich, Germany

We explored fd as a template to direct the formation of silica nanomaterials with different morphologies through simple sol-gel chemistry[1]. Depending on the conditions silica nanowires can be formed, which seem to accurately transcript the bending conformation and the length of the fd viruses in solution. But also surprisingly straight silica rods may be formed, and under other conditions bow-tie-shaped bundles of rods are formed, which have a remarkably well defined shape and dimension.

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One dimensional anisotropic inorganic nanostructures such as tubes, rods, wires, fibers, etc. are in the focus of research interests due to their potential applications, for example in optical, electronic and mechanical devices, sensors and catalysis[2, 3]. The synthesis of these anisotropic nanostructures is a big challenge, because most inorganic materials do not form the desired structure by themselves. In contrast to inorganic systems, biological and organic materials, especially supramolecular systems, usually have a well defined structure down to the nano-scale. Using (bio)organic materials as a template to build up anisotropic inorganic nanostructures has therefore emerged as a highly attractive method in recent years[4]. The results described in the present paper may serve as a basis for the further development of the synthesis of inorganic materials using bio-polymers as a template. Similar routes of synthesis occur spontaneously in nature, for instance, in the formation of the silica cell wall of the Diatom, which is formed with an amazingly perfect pattern[5]. For the synthesis of nano-materials, rod-like viruses, carbon nanotubes, lipid nanotubes, rod-like structures formed from organogelators, single DNA etc. offer many templates to direct the formation of anisotropic inorganic materials with special structures and properties.

In this paper[1], the filamentous fd virus is used as a template to regulate the formation of silica nanomaterials with well-defined morphologies. Fd viruses have a length of 880 nm and a diameter of 6.6 nm. Each virus consists of a single-stranded circular DNA molecule packed in a sheath of 2,700 identical coating proteins. Besides of its role in biochemistry where it is used for molecular cloning, fd has also been used as a rod-like model system to understand some fundamental problems of complex fluids, because it is monodisperse in size and has a nearly hard rod conformation (persistence length 2.2µm)[6]. M13, a virus which is almost identical to fd, differing only in one amino acid per coating protein, has been intensively explored by Belcher, Hammond and co-worker as a template in the synthesis of metallic and other magnetic and semiconducting nanowires[7, 8].

Their strategy is to modify the coat protein of M13 via genetic engineering specifically for each metal or oxide, so that the coat protein can selectively induce precipitation or assembly of that specific metal or oxide on the surface of the virus. However, as far as we know, there is no report concerning the application of fd or M13 as a template for silica precipitation.

In contrast to the complicated genetic engineering route used with the M13 virus, we show here that wild-type fd virus can also be used as a template in the synthesis of inorganic materials using simple sol-gel chemistry. Under different conditions, using acid-catalyzed hydrolyzation and condensation of tetraethoxysilane as silica precursor, three kinds of morphologies are observed: 1) silica nanorods with a diameter of 20 nm and a homogeneous silica layer, 2) nanowires with a curved shape and 3) bow-tie-shaped bundles with well-defined shape and hierarchy. As far as we know, we are the first to use fd as a template for material synthesis and have observed several interesting structures.

All coating procedures were carried out at low pH where fd is positively charged and the amount of silica precursor (tetraethoxy silane) was estimated so that a silica layer of 1 nm could be formed on all fd viruses. At an fd concentration of 6 mg/mL and a pH of 2.3 straight silica rods are obtained. Along the axis of the rods, the diameter is constant and the silica layer is homogeneous (see Fig.1, top image). The surface of these rods is smooth under the maximum resolution of the TEM we used and the shape of the ends of the rods is semi-spherical. Although fd is semi-flexible and somewhat curved in dispersion, most of the rods are straight and only a few slightly curved rods are seen. Long rods with a length comparable to the length of intact fd are observed along with short rods, which might form from the silica coating of the fragments of decomposed fd. Some of the rods show a clear core-shell structure with a low contrast part along the center of the whole rod (Fig.1, top image). The low contrast part might be fd.

Bow-tie-shaped bundles of silica rods are formed (Fig.1, bottom left) if the straight rod dispersion de-
FIG. 1: Three different silica structures observed using the filamentous fd virus as a template.

scribed above is mixed with a methanol/ammonia mixture. This morphology is remarkable because as far as we know, no similar morphology has been reported for any other virus or organic template in the past. The formation of the bow-tie-shaped bundles itself seems to originate from an aggregation of (silica coated) fd viruses (and granular silica) after addition of the methanol/ammonia mixture, but the exact reason for the shape and size of the bundle remains unclear.

At lower fd concentration and a slightly lower pH, long, curved wires are observed entangled with each other (Fig.1, bottom right). The surface of these wires is less smooth than that of the straight rods described before, and the diameter of these wires shows a less sharp distribution. The contour length of these wires is in the range of that of intact fd, while long wires with a length twice that of fd are also observed. The longer wires seem to consist of two viruses sticking together by partial parallel overlap. These results imply that most fd remains intact during wire formation, in contrast to the case of the straight rods described above, where many rods much shorter than fd are observed. The curved shape of these wires probably originates from the bending configurations of the semi-flexible fd virus in aqueous media. Therefore, these hybrid silica wires show an example of a quite precise transcription of the template, here, semi-flexible fd. Whether or not the silica coating solidifies the fd virus completely so that the flexibility is lost is not clear.

For the templating mechanism to work, the affinity of the surface of the fd virus towards silica deposition has to be high enough, so that heterogeneous nucleation of silica onto the surface of the fd virus can compete with the homogeneous nucleation of silica in the solution (so-called secondary nucleation). In the present study the formation of silica is not limited exclusively to the surface of the fd virus, but also a lot of granular silica (Fig.1, top and bottom left) due to secondary nucleation is observed. Furthermore, the amount of silica precursor was taken such that it can form a 1 nm layer of silica around all fd viruses. Because the actual layer thickness observed is much larger than 1 nm and in addition part of the silica is lost in the secondary nucleation, this means that many fd viruses are not coated at all. It is not clear why some of the fd viruses are coated with a smooth silica layer with a narrow distribution of the diameter, while some other fd viruses are not coated at all.

We demonstrated the capability of fd viruses to be used as a template for the formation of 1D silica nanomaterials. Three nanostructures with distinct morphologies have been observed under different sol-gel conditions using TEOS as silica precursor: silica rods, wires and bow-tie-shaped bundles. Silica wires seem to transcript the bending conformation and length of intact semi-flexible fd, but under somewhat different reaction conditions also remarkably straight silica rods are formed. The bow-tie-shaped bundles may form from an aggregation of (silica coated) fd viruses under the conditions adopted here, leading to bundles with a defined dimension and shape. Compared with many other organic templates, fd is almost perfect because of its narrow size distribution and the homogeneous properties of its surface. Work devoted to further understanding the results obtained in this paper and exploring the above problems is ongoing.