Inorganic Nanotubes

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Holes do not only constitute the nature of Swiss cheese—on micro- or nanoscale they are also responsible for many interesting and useful characteristics of synthetic materials and compounds that occur in nature. Classical representatives of porous compounds are zeolites, whose well-defined pore sizes are on the scale of a few angstroms in the three-dimensional framework structures and their size can be adjusted with the help of suitable templates. Thanks to their porous structures these silicate or aluminosilicate solids have found important applications as ion exchange, drying, or sorbent materials and they are used as acid catalysts or catalyst supports. Firstly, their great temperature stability is particularly favorable. Beyond that, the steric restrictions imposed by the pore structure of the silicate framework play a dominating role in form-selective catalysis.

Despite their enormous possible applications, the chemical composition and structure limit the performance of microporous oxidic phases in a number of ways: as silicates they are insulators, the obtained pore sizes were limited for a long time up to sizes of approximately 13 Å, and the well-known representatives are, almost without exception, not redox active. Beyond that, the problem of shaping, that is the production of materials with defined structures on a nanoscopic scale, is completely unresolved. Thus two-dimensional structures on a (sub)microscopic scale can be produced with ease with lithographic techniques, but the step to three-dimensional and nanoscopic structures, however, is much more difficult. Specially nanostructured materials (that is, the inverse of the forms of pore structure that occurs in zeolites) are particularly interesting as a result of size quantization effects—extensive properties do not any longer follow simple proportionality laws. From a technical point of view, miniaturization of components also means that at the same time it is: faster, more efficient, and cheaper. Therefore, the development of procedures, which permit entry into the world of molecular machines,[2] is an essential scientific problem of the coming decade.

A first large step towards metallic nanoporous structures was made by Iijima in 1991, who discovered during the world-wide "buckyball-fever" graphitic, cylindrical nanostructures ("nanotubes"), which were formed spontaneously on top of the electrode surface of the light arc under catalytic participation of metals of the iron group.[2] In general, these nanotubes are nothing different from rolled-up layers of "graphite chicken wire" (which can be made up of several layers), where the ends of these tubes are closed by half spherical or polyhedral graphite domes. There are several possibilities in which the graphite layers can be rolled up into a cylinder arrangement, for example by joining opposite graphite hexagons at their lateral edges or linking them so they are displaced with respect to each other to form helical twisted tubes (Figure 1). Most nanotubes form fiber bundles with a cablelike filament structure, and monodisperse fractions can be isolated by ion-exclusion chromatography.[3] The tubelike structure is also reflected by the anisotropy of the electrical characteristics: depending upon their diameter and helicity the nanotubes can be insulators, semiconductors, or metals.[4] The idea of producing one-dimensional quantum wires from this creates a large fascination in the field of nanochemistry or physics.[5] It was even possible to fill the inside of the microtubuli with metals (for example, Pb, Ru)[6, 7] so that new types of metallic and magnetic materials becomes conceivable.

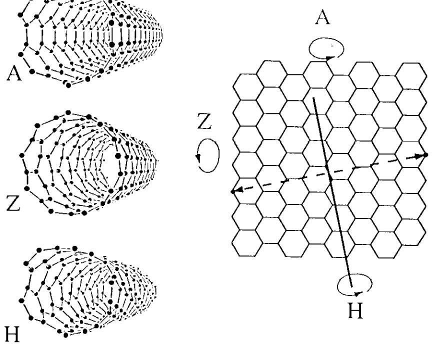

Figure 1. A graphite layer can be folded up in different ways to form nanotubes: the so-called armchair structure (A), a zigzag tube (Z), and a helical twisted tube (H).

In the general euphoria it was only noticed in passing that other compounds also possess characteristics that are close to those of the prominent carbon representatives. In general, all compounds possessing graphite-analogue layered structures

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should be able to form nanotubes or fullerene-type structures. In fact, amorphous boron nitride tubes can be formed by conversion of cesium and *B*,*B*,*B*-trichloroborazine at 1100 °C.[8] MoS_2 and its analogues of transition metal chalcogenides are the counterparts to graphite and C_{60} in carbon chemistry. This similarity can easily be understood based on their crystal structures. The Group 6 chalcogenides are layered materials with hexagonal symmetry similar to graphite, and they possess the typical honeycomb structure of graphite. It was shown recently that MQ_2 compounds ($M = Mo, W$; $Q = S, Se$) are also capable of forming closed fullerene-type structures,[9] nano- and microtubes,[10] as well as onion-shell-type structures. [11] They possess the structure of concentrically nested fullerene cylinders, where the WS_2 tubes have a less regular structure than the corresponding carbon compounds, as is shown by the different wall thickness and the presence of some amorphous material that is separated at the exterior of the tubes. The nearly defect-free WS_2 nanotubes are rigid as a consequence of their structure and do not permit a plastic deformation. Therefore, if a tube meets a second tube or a WS_2 crystal during growth the entire cavity structure collapses and forms a WS_2 band, which can be twisted along its longitudinal axis and also exhibits stacking faults (Figure 2). Finally, several WS_2 nanotubes can be twisted through van der Waals interactions into a rope-type structure. The chemical and physical characteristics of the new modification of these long-known dichalcogenides should be of special interest. The fullerene-type WS_2 possesses special tribological characteristics,[9] whereas MoS_2, with an onion-shell structure, shows a particularly high chemical reactivity, for example, in intercalation reactions.[11]

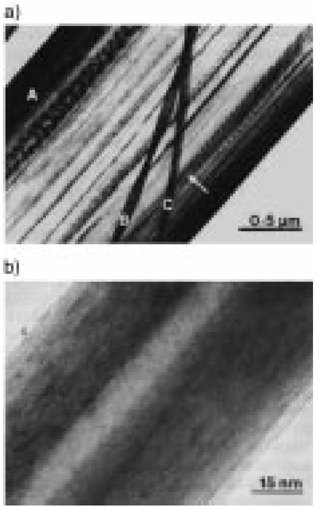

Figure 2. a) WS_2 microtube (A) with a diameter of 2 µm, twisted tape (B) with a width of 0.1 µm, and rope structure (C), which consists of at least two nanotubes. The arrow marks a WS_2 nanotube with a diameter of less than 20 nm that is situated on another WS_2 nanotube; b) high resolution transmission electron microscopy (HRTEM) picture of a WS_2 nanotube with a diameter of 73 nm and a number of stacking faults.

Curved structures are not only limited to examples of carbon and molybdenum or tungsten sulfide, and perhaps the most popular examples of tubelike structures with diameters in the nanometer range are formed by asbestos minerals (for example, chrysotil), whose fibrous characteristics are determined directly by the tube structure of fused tetrahedron and octahedron layers.

Layered compounds are necessary for the formation of nanotube structures, and even cyclic compounds can be stacked to a rich variety of tubelike structures by skillful synthetic utilization of donor–acceptor interactions. Cyclic octapeptides, for example, which contain glutamate building blocks at two opposite positions, form molecular stacks, which are stabilized by hydrogen bonds (Figure 3).[12] This stacking of molecules causes the formation of needle-shaped crystals on a macroscopic scale, which consist of parallel aligned nanotubes with an inside diameter of approximately 0.8 nm and a length of some hundred nanometers. This "functionality" of the nanotubes is confirmed by the fact that tubes embedded in membranes form a tunnel, whose ion flux is approximately three times as high as that of a natural ion channel.

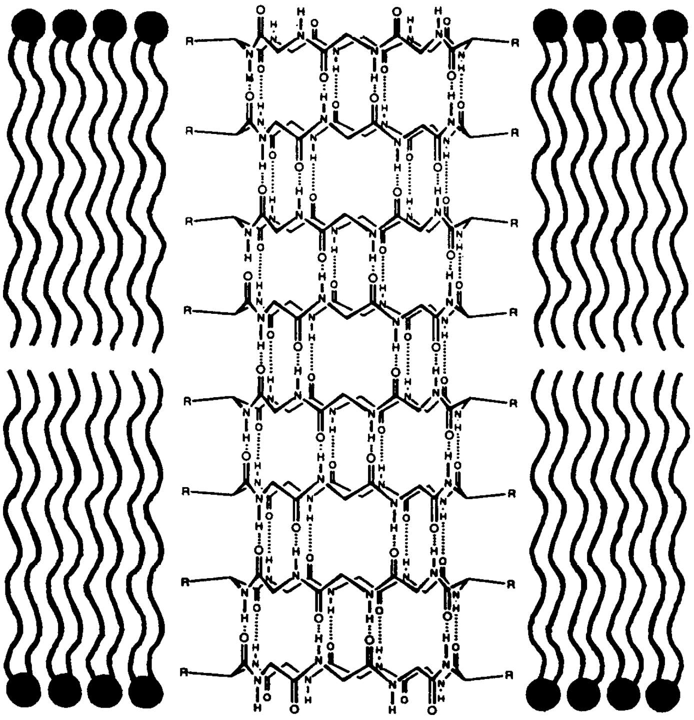

Figure 3. A batch of eight cyclic octapeptides forms a synthetic ion channel. The hydrogen bonds between the NH and CO groups that correspond to the bonding pattern in a β-sheet structure are marked with dots. Therefore the tube could not only be viewed as a a stacking of eight rings but also as a rolled-up β-sheet.

The synthesis of zeolite-type compounds with a well-defined pore structure in the mesoscopic range was introduced by the work of Beck and Kresge.[13] The structure-directing template is now not a single solvated organic molecule anymore, but a regular liquid-crystalline arrangement of tenside molecules formed by self-assembly. The size of the template molecules determines the pore size of the oxidic phases formed and, within certain limits, permits a tailoring of mesoporous solid-state materials.[14] The pore sizes, which can be adjusted by using tenside molecules, are now in the range of up to 10 nm. A modified strategy using amphiphilic triblock copolymers even permits the synthesis of silica phases with pore sizes up to 30 nm.[15] In addition to SiO_2, other oxidic compounds such as silicoaluminophosphates,[16] aluminoborates,[17] titanium silicalites,[18] or zirconium oxides[19] were synthesized. The properties of these materials can be adjusted so precisely, depending upon the intended purpose, that the spectrum of applications ranges from optical fibers[20] to carriers for polymerization catalysis.[21]

In contrast to the synthesis of porous compounds, the synthesis of free nanotubes is much more difficult. Silica nanotubes were first produced as a "spin-off" product during the synthesis of spherical silica particles by hydrolysis of tetraethylorthosilicate (TEOS) in a mixture of water, ammonia, ethanol, and D,L-tartaric acid. [22] A crucial step in regard to the direct template synthesis of ceramic nanotubes was reported only recently by the group of C. N. R. Rao in Bangalore:[23] as "self-assembly" reactions (a type of modern alchemy) are not very straightforward with respect to the desired product and particularly its shape,[24] they used carbon nanotubes as templates, on which technically relevant oxides such as ZrO_2 were deposited by hydrolysis of $ZrOCl_2$. The carbon template can be completely removed in a subsequent calcination step. The ZrO_2 nanotubes consist of a 1:1 mixture of monoclinic and tetragonal ZrO_2. The synthesis of single-phase tetragonal ZrO_2 nanotubes fails because of the phase transition from the monoclinic to the tetragonal form of ZrO_2. However, one can obtain high-temperature stable nanotubes based on the corresponding Y_2O_3-stabilized tetragonal phase.

Even this phase—although stable at high temperature and accessible in a direct manner—does not eliminate the central chemical deficit of most porous oxide materials: it is neither redox active nor semiconducting or metallic. Attempts to solve this problem can only involve compounds of redox-active metals of Groups 5–8. Several years ago Suib and co-workers described for the first time the synthesis of molecular sieves with octahedrally coordinated metal centers. These redox-active microporous manganese oxides with todorokite-[25] and cryptomelane-type structures[26] can be produced by sol–gel procedures as well as hydrothermally. Similar to the case of the mesoporous silicates, the synthesis of redox-active mesoporous manganese oxides by using amphipilic templates is possible as a result of complementary electrostatic interactions at the boundary surface between the organic template and the oxidic inorganic components.[27] In a similar fashion, Nesper and co-workers[28] recently achieved the synthesis of vanadium oxide nanotubes of the composition $V_2O_{4.8}$-$(C_{16}H_{33}NH_2)_{0.68}$, which can possess open or closed tube ends depending of the synthesis procedure (Figure 4). These findings are of practical importance, since the controlled synthesis of open carbon nanotubes[29] originally caused difficulties. In contrast to the zirconia tubes, the vanadium oxide tubes are not stable at high temperatures and therefore cannot be calcinated. The template, however, can be removed by ion exchange. It is also remarkable that the diameter of the tubes at approximately 50 nm is unusually large, so that the formation mechanism may be different from that discussed with mesoporous silicate phases. The characteristic property of vanadium oxide tubes is their mixed-valent and therefore redox-active behavior, as is apparent from their black color and paramagnetic behavior.

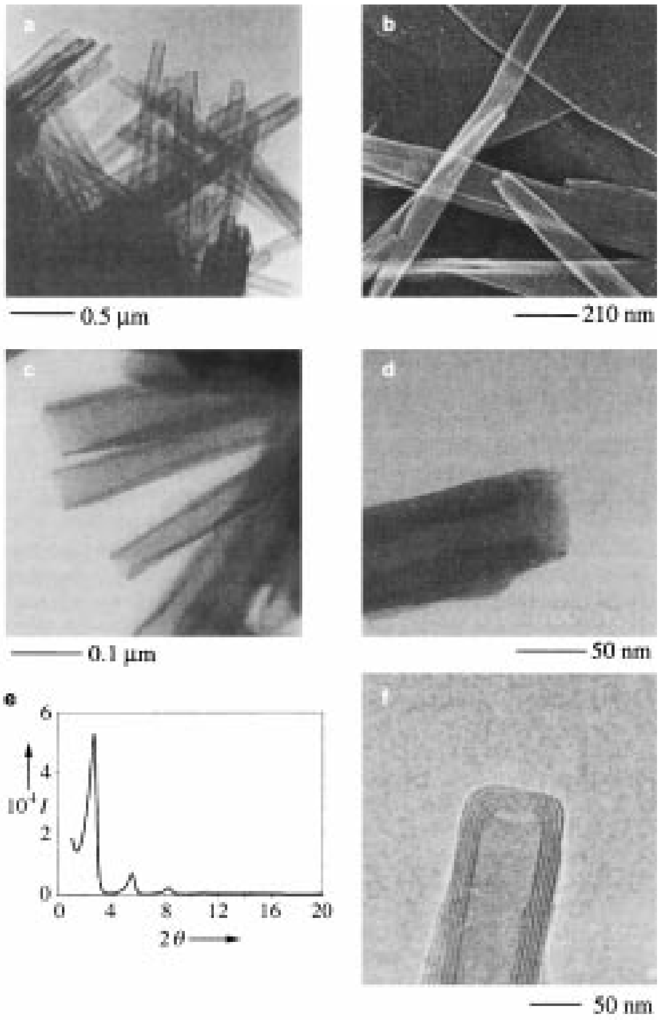

Figure 4. a) Scanning electron microscopy picture of open vanadium oxide nanotubes with a length up to 2000 nm. b) Low resolution TEM image showing that isolated or deformed tubes are produced as the main product after precipitation. c), d) In the high resolution TEM image the multilayered character of the walls is shown clearly. The free diameters of the tubes range between 25 and 35 nm and the outside diameters between 50 and 70 nm. e) X-ray diffraction diagram of a powder sample. The reflection of highest intensity has a *d*-value of approximately 3.3 nm, which corresponds to the distance of the vanadium oxide layers. f) Nanotubes with closed ends.

The work of the groups of Remškar, Rao, and Nesper demonstrates the successful application of different methods to the synthesis of nanostructured binary inorganic compounds. However, different intriguing questions still remain unanswered and leave space for speculations and future research. Since the discovery of carbon nanotubes, the scientific community has been dreaming of molecular wires, nanoreactors, nanoscopic biosensors, or possibilities to separate biological compounds by size exclusion. Some of these dreams are already realized in their initial stages: for example, metallic oxides[30] such as MoO_2 as well as different metalloproteines such as metallothioneines, cytochrome, or lactamase[31] can be inserted into carbon nanotubes. Interesting questions in the case of WS_2 concern the size of the band gap, which is dependent on the tube diameter, and the reactivity in intercalation reactions since layered chalcogenides are suitable cathode materials in Li-secondary batteries. For example, semiporous MoS_2 is more reactive by a factor of two than crystalline 2H-MoS_2,[11] and microtubular TiS_2 building elements, which have been attached to nanoscopic Au templates by CVD procedures, possess significantly higher unloading capacities than conventional TiS_2 electrodes.[32] Apart from their temperature stability and the ionic conductivity the mechanical stability is particularly relevant in the case of (Y_2O_3-stabilized) ZrO_2, as it is known that the Young modulus of carbon nanotubes is a factor of two larger than that of silicon carbide fibers.[33] The outstanding property of the vanadium-oxide tubes is definitely their redox activity; of special interest here are the size dependency of the electronic characteristics (for example, electrical conductivity) and the catalytic behavior.

Another question concerns the directed synthesis of non-carbon based nanostructured materials. There are only a few conclusive ideas for generally applicable manufacturing processes or even for only the imagination of materials, which are accessible to nanostructuring with simple methods.[34] The successful synthesis of "nanodevices" is often still based on serendipity; a systematic material development is performed only to a limited extent. Promising starting materials for the development of tubelike elements seem to be layered compounds; furthermore, materials that can be deposited by means of sol–gel procedures in the form of thin films are obvious suitable candidates.

A real synthetic challenge is the shaping of ceramic building elements. Besides carbon and tungsten diselenide tubes, which are made by traditional high-temperature techniques of solid-state chemistry, the method of choice for the synthesis of nanostructured oxides, which can be partially found in mineralized biostructures, seem to be template-supported hydrothermal or sol–gel procedures. In order to find practical solutions for the shaping problem chemical research has to work out suitable shape-directing models at a molecular level in the coming years. The formation of a solid phase is initiated by the nucleation process. The activation energy for the nucleation can be very high; everybody has probably observed that the precipitation of salts from thermodynamically unstable, supersaturated solutions can fail to appear for months. The crucial factor for this barrier is the energy for the formation of a new phase boundary. Only if the lattice energy for the formation of a crystal over-compensates its surface energy can a new phase be formed. Therefore the simulation of the processes at the organic–inorganic boundary surface is of special importance since it can be safely assumed that the formation of a thermodynamically stable crystal nucleus is induced homogeneously, that is, by a local supersaturation, or heterogeneously, that is, epitactically, by the formation of a template surface with well-defined structural patterns. Here the ions bind preferentially to certain positions at the organic boundary surface; this leads to a decrease of the nucleation energy as a result of attractive electrostatic interactions. The resulting growth pattern follows that of the template: the solid shows a form that is dictated by the organic matrix. Another goal of these biomimetic syntheses is the construction of hierarchical structures that allow the heterogeneous nucleation process to be influenced and finally to control the growth of nanoscale structures.

While nature produces filigrane structures with unbelievable ease, such as those of the coccolith sphere of *E. huxlei* (Figure 5), synthetic chemistry still has extraordinary trouble in producing only the simplest structures. Only two-dimensional samples can be produced directly with the help of lithographic techniques. Therefore, from a materials science perspective the morphogeneses of such structural elements represents a phenomenon, for which there is no equivalent from synthetic chemistry so far. Whereas the living cell produces structures that execute complicated functions in adjustable ways as a consequence of their modular design principles, scientists still have to learn this lesson of nature. This problem may be associated with the fact that cell machinery sits between all chairs in the "drawer system" of science disciplines. Biologists are usually too busy trying to understand the cell functions to think about possible alternatives. For the "bottom-up" approach of the chemists the systems are too big and difficult to handle, since they are stabilized not only by covalent but also by numerous hydrogen bonds. Finally, physicists use a "top-down" approach by etching structures in materials with the help of lithographic procedures; their methodology is limited therefore by the technical possibilities of miniaturization.

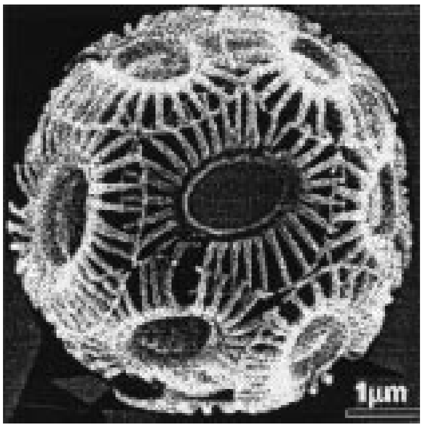

Figure 5. Intact coccosphere of *E. huxlei*, which shows the structure of the individual coccoliths in front of the cell wall (scanning electron microscopy image).

One possibility for the solution of the shaping problem for example would be the use of cellular structures as matrices for the biomimetic structuring of materials. The slow down of molecular transport processes by biological cell membranes as well as their stereochemical influence on the structure of the developing phase, however, limits the attainable growth rates so much that a synthesis of materials on a laboratory scale is hard to realize. However, one could achieve a sufficiently high material throughput, if open, porous cellular structures (for example, of hemp) are used as "moulding forms", that is, the technical realization of the materials as biogenous building processes are important now, not as phytological ingredients. The versatility and significance of nanochemistry in modern materials research becomes apparent by imagining the possibilities of arranging nanoparticles by self-organisation processes in complex superstructures.

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