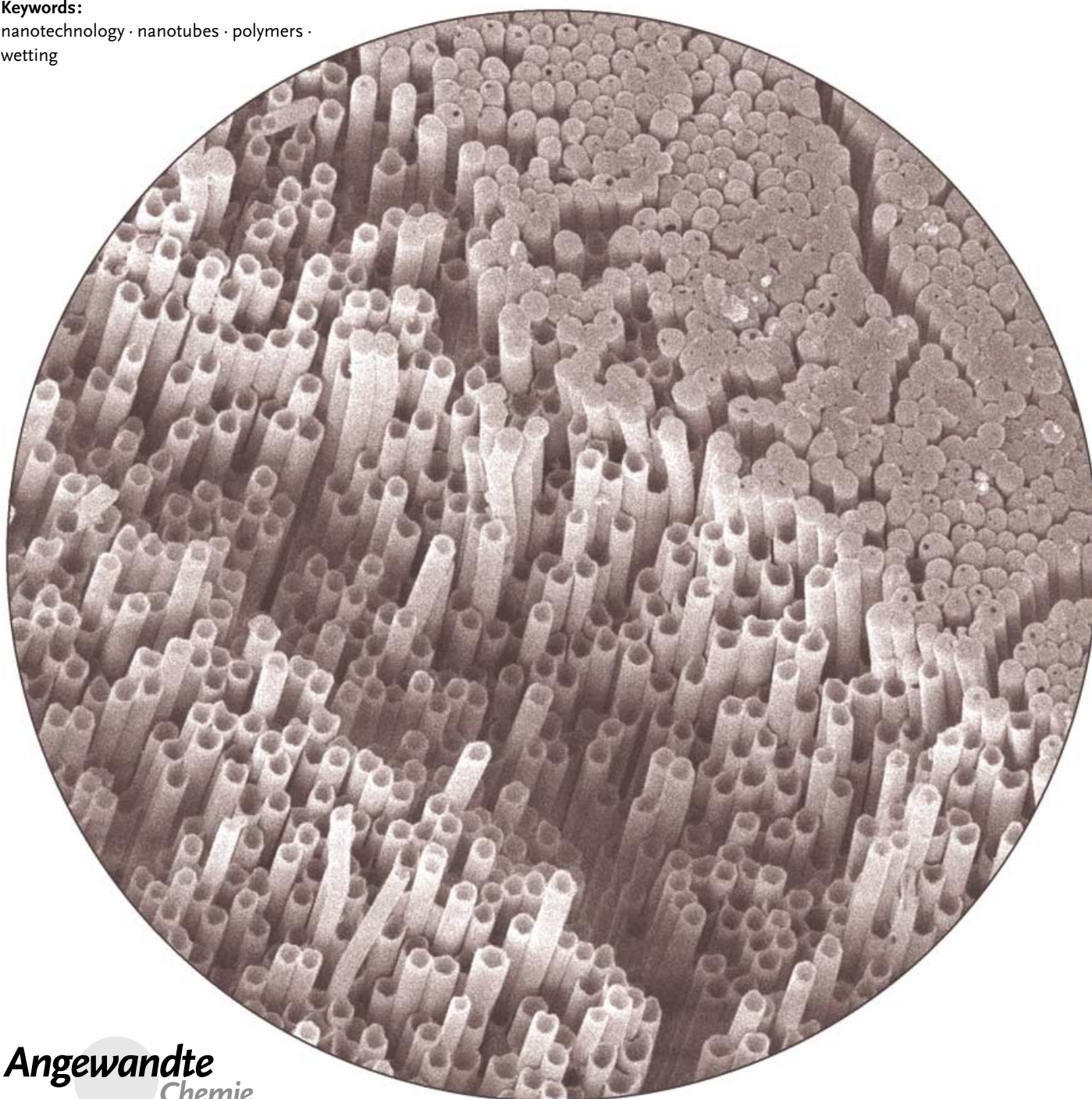# Nanotubes by Template Wetting: A Modular Assembly System

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Angewandte
Chemie

*T*he wetting of porous templates with polymer melts and solutions or polymer-containing mixtures is a simple and versatile method for the preparation of tubular structures with diameters ranging from a few tens of nanometers to micrometers. The tube walls can be made of a multitude of materials, some of which have thus far been altogether impossible to use or very limited in their ability to be incorporated into nanostuctures. Template wetting also makes it possible to modify the nanotubes in a variety of ways, for example through the controlled generation of pores or the embedding of nanoparticles into the walls. This method offers a promising approach to functionalized nanotube–template hybrid systems and free-standing nanotubes.

From the Contents

1. Nanotubes—Beyond Carbon

Since their discovery by Iijima over a decade ago,[1] nanotubes have often been equated with carbon nanotubes. Depending on their composition, they can have a variety of mechanical, electrical, and thermal properties;[2,3] can be conductors or semiconductors; and can have extremely high heat-conduction capabilities, or outstanding mechanical strength. Their application as components in composites, color flat-panel displays, and gas sensors, as well as in hydrogen and ion-storage units is under consideration or is about to be realized.[4] Carbon nanotubes with multiple graphite-like wall layers are produced by arcing between graphite electrodes,[1,5] or by the catalytic vapor deposition of carbohydrates in the presence of metal nanoparticles.[6] Single-walled carbon nanotubes (SWNTs) can be obtained by the combined use of catalysts and concentrated carbon-containing vapors, which are obtained by either arcing[7,8] or laser ablation. One modification of the production process is based on the implementation of conventional thin-layer techniques to prepare substrates for the growth of parallel carbon nanotubes through chemical vapor deposition. In this way we can obtain extensive nanotube arrays.[10,11]

In view of the understandable fascination with carbon nanotubes, their properties, and possible applications, the potential of nanotubes whose walls consist of other materials, such as polymers, metals, semiconductors, or ceramics, are often underrated. However, this is quite unjust, because carbon is in no way ideal as an all-purpose material for popular applications. In general, the tubular form offers considerable advantages, because nanotubes can be used as pipes, microcavities, or microcapsules, and can be arranged in parallel to functionalized membranes. When fixed in a porous membrane, nanotubes form easily handled nanostructured hybrid systems with extremely large surfaces, which have considerable advantages over systems involving nanoparticles formed by other means in such fields as catalysis and sensor technology. However, nanotubes can only be used in such applications if the chemical and physical properties of their walls can be tuned over a wide range. One prerequisite for this is naturally the ability to incorporate a broad spectrum of materials. The first applications for nanotubes not made of carbon were demonstrated by Martin and co-workers in such areas as the separation of racemic mixtures,[12] sensors,[13] substance separation,[14] or in membranes for selective ion transport.[15]

2. Nanotubes by Self-Assembly and Template Processes

The preparation of nanoscopic tubular objects is still an undertaking of material science, and can be extremely technically demanding. Frequently, special processes must be implemented or even developed to obtain materials with the required specifications. Correspondingly, methods have been described, which at least partially meet these demands. In general, two fundamental strategies have been pursued: 1) self-assembly and 2) the use of templates made of materials that can be easily nanostructured in a defined manner.

A process introduced by Schmidt and Eberl is based on rolling up a thin film, which is held under mechanical tension and attached to a sacrificial layer bound to a rigid substrate. When the sacrificial layer is removed, the film rolls itself into a nanotube.[16] Certain molecules, such as lipids,[17,18] peptides,[19] and block copolymers,[20] also exhibit the ability to self-assemble given the right conditions.[21] In this case, many individual, disorganized molecules come together to form highly ordered aggregates. Self-assembly is a very elegant

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approach to nanostructured systems, because the tubes are made from building blocks that already have the required intrinsic structural information. Nature has perfected this principle for the synthesis of complex functional units; material science, on the other hand still has a long way to go. The limitations stem from two different problems: 1) only a small spectrum of materials is suited to self-organizational processes, and 2) while the precursor compounds can be tailored within certain limitations, it is difficult and expensive to then functionalize them as well. Self-assembly processes also offer limited flexibility with respect to the dimensions of the nanotubes.

These restrictions do not apply to template processes. Some materials can be nanostructured in a simple and controlled manner, and are therefore available for the preparation of templates, which can in turn be used for the synthesis of nanotubes from the actual target compound. Martin and co-workers first used nanoporous membranes.[22,23] For instance, when monomers are polymerized within the nanopores, it is possible to tune the wall thickness of the resulting polymers by choosing the right polymerization conditions, particularly the polymerization time.[24] Metallic nanotubes are attainable by electrochemical deposition in aluminum oxide templates with chemically modified pore walls,[25] as well as by electroless deposition.[26] Nanotubes made of inorganic semiconductors and metal oxides can be made by sol–gel processes.[27] Template methods initially yield template–nanotube hybrids. The detached nanotubes are then obtained by selective removal of the template.

Nanotubes with extremely large aspect ratios (the ratio of length to diameter) can be obtained in large quantities in woven or aligned forms by the coating and then selective removal of polymer nanofibers.[28–30] The nanofibers, whose diameters range from a few nanometers to a few micrometers, are formed by electrospinning, in which a strong electric field is used to pull a thin jet out of a drop of polymer solution or melt. The jet then is deposited in the form of a nanofiber.[31] The ability to obtain such high aspect ratios rests on the fact that electrospinning is, like extrusion processes, a continuous process. In addition, it is possible to use this method to obtain nanofibers, and thus nanotubes, with specific surface topologies.[32–34]

3. Nanotubes by Wetting

As versatile as the methods for the preparation of nanotubes described so far may be, two challenges remain: 1) important materials, including numerous high-performance polymers, copolymers, or mixtures of defined composition, cannot be made into nanotubes. 2) For many applications, it is essential to functionalize the nanotube walls by generating a specific fine structure. For example, one important question concerns the course of the crystallization processes within the walls, since the properties of crystalline or partially crystalline materials largely depend on the structure of the crystalline domains. One fascinating possibility for functionalization would be the generation of a

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fiberlike texture, which would bring to mind nanoactuators, piezoelectric actuators, or similar applications.

Composite systems with a highly defined phase morphology and thus a large internal phase interface could make it possible to direct transport processes within the nanotube walls. This is an important prerequisite for the implementation of nanotubes in the area of energy conversion in light-emitting diodes or solar cells, for example. The efficiency of such systems could be considerably increased if the domain structure could be tuned to the diffusion lengths of excitons or light-induced charges. This has already been shown in the case of uniform thin films on even substrates.[35–37] The selective removal of one component should lead to a specific surface roughness or nanoporosity of the tube walls. The surface area of the wall is thus increased further, which is advantageous for applications in catalysis, separation, or sensor technology. The pore size could also be used to modulate the transport of molecules through the wall of the tube.

It is thus necessary to develop a versatile but technically simple process for the preparation of nanotubes, which broadens the spectrum of available wall materials on the one hand, while allowing trouble-free modification for the tailoring of the nanotubes' structure and properties on the other. This could be possible by the controlled induction of phase transitions in the nanotube walls. The key to the solution of these problems is a familiar and thoroughly investigated phenomenon: wetting.[38,39] Complete wetting or spreading occurs when a thin film of liquid in equilibrium covers a substrate. While "soft" materials such as low-melting organic substances mostly have low surface energies (under 100 mNm^{-1}), "hard" inorganic materials with high melting points generally have high surface energies ranging from a few hundred to several thousand mNm^{-1}.[40,41] As a rule, solutions, mixtures, or melts with low surface energies spread over substances with higher surface energies.[42]

The nature of viscous liquids like polymer melts and solutions results in very slow spreading over uniform surfaces, with the frequent formation of precursor films.[43–45] These form around a spreading macroscopic drop of liquid, have thicknesses ranging from a few tens of nanometers down to a few hundred picometers, and cover areas of the substrate on the order of square centimeters (Figure 1). As it spreads,

Figure 1. Spreading drop with precursor film.

more and more material is drawn out of the macroscopic drop (whose height thus decreases) and into the precursor film. Ausserré et al. were the first to prove this experimentally for such cases, in which the nonvolatility of the liquid rules out matter transport via the gas phase.[46] The structure of the precursor film and the dynamics of its spreading cannot be described by macroscopic models. If the film thickness is in the mesoscopic range, then long-range intermolecular interactions, for example, must be taken into account.[43,44,47] It is clear that such wetting phenomena could be the key to a versatile method for the preparation of nanotubes.

4. Wetting of Porous Membranes

Organic polymers are among the materials with low surface energy.[40,42] Polymer melts are molten onto templates in excess, whereas wetting with polymer solutions occurs dropwise under ambient conditions (Figure 2a). It is to be
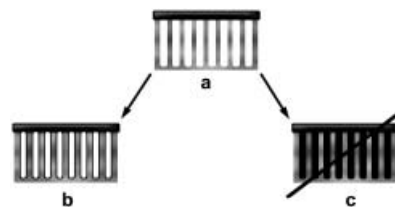

Figure 2. Wetting of porous templates with polymer melts or polymer-containing solutions: a) The fluid is brought in contact with the template. b) Within seconds, the pore walls are covered with a mesoscopic film of the liquid. c) Complete filling of the pore interior, if it occurs at all, happens on a completely different time scale.

expected that a mesoscopic film wets the walls of the pores in a manner analogous to the formation of precursor films on flat substrates (Figure 2b). As a prerequisite, the pore walls must have a high surface energy. The processes discussed here are microscopic in nature, in contrast to phenomena such as the Lotus effect,[48] which are associated with the macroscopic wettability of structured surfaces.

We can only speculate as to whether the equilibrium state corresponds to complete filling of the pore volume (Figure 2c and if it does, how this state is reached. On the one hand, the interface between the air and the inner shell surface would disappear, and cohesive energy might be gained. In that case, the state in which the pore walls are only wetted by a mesoscopic film would be kinetically stable (development toward equilibrium hindered or very slow)—because the adhesive forces between the polymer-containing liquid and the pore walls, which drive the spreading, would be neutralized—but not in equilibrium. On the other hand, as a result of the spatial limitations and the different interface energies of the outer shell surface (pore wall/nanotube wall) and the inner shell surface (nanotube wall/air), the molecules in the vicinity of pore walls may have a higher degree of order than those in the bulk. This would allow the formation of a phase boundary between those molecules in contact with the pore wall and those farther from the pore walls, that is, in the bulk. Phenomena such as autophobicity may also have to be taken into consideration. Autophobicity means that a droplet of a liquid shows nonwetting behavior on a thin surface layer of the same liquid. This would argue for the fact that equilibrium is already reached as soon as the pore walls are wetted by a mesoscopic film.

It remains unknown why low molecular weight fluids fill the entire pore space differently than polymers do. We presume that the polymer layer on the pore walls is particularly stable. Because of the unusually large dimensions of polymer molecules, the region near the pore wall, in which attractive interactions are in effect, is covered by a monolayer, so that most of the molecules are in direct contact with

the pore wall. However, in the case of nonpolymeric materials, the influence of long-range intermolecular interactions could allow for a coating made of multiple layers of molecules. In those layers that are not in direct contact with the pore wall, the molecules could be relatively mobile; this could trigger the occurrence of instabilities, which could lead to the formation of a meniscus, and finally the complete filling of the pore.

With polymer melts as well as polymer solutions the pore walls are completely wetted, with complete reproduction of the pore structure and even to a pore depth (T_p) of 100 µm, within seconds.[49] The liquid film solidifies when cooling or evaporation of the solvent lead to crystallization or vitrification. Figure 3a depicts a pore opening from the top of a macroporous silicon membrane that has been wetted with polymethylmethacrylate (PMMA). It is clear that the interior of the pore has not been completely filled. The underside of a polyvinylidene fluoride (PVDF) wetted membrane of porous aluminum oxide (Al_2O_3) is shown in Figure 3b. The aluminum substrate that was bound to the membrane has been selectively etched away. The exposed tips of the PVDF nanotubes, which replicate the closed ends of the pores, are visible within the pores. As can be seen in Figure 3c, the thickness of the walls is typically about 10 nm. Pictured is a TEM image of an ultrathin section of an Al_2O_3 membrane wetted with a ten percent solution of polystyrene (PS). The dark region in the lower portion of the picture is the Al_2O_3 pore wall. In the upper portion of the picture, the cavity inside a PS nanotube appears light. In between the two is the roughly 10 nm nanotube wall, dyed with osmium tetroxide.

Polymers with ultrahigh molecular weights between 10^6 and 10^7 g mol^{-1}, such as polytetrafluoroethylene or polyethylene, which do not have the ability to flow viscously, owing to their extraordinarily high melt viscosity, will also spread on the pore walls if they are lightly pressed against the surface of the template. This indicates that the expansion of the polymer melt or solution over pore surfaces occurs by surface diffusion. The chain conformation would thus strongly deviate from the equilibrium conformation in the resting melts. The thicknesses measured for precursor films of polymers spreading on flat surfaces are in the subnanometer range, and are thus considerably smaller than the correspond-

ing gyration radii (The gyration radius is a characteristic constant for polymers that take the form of statistical coils, and gives the average distance of the chain segments from the center of the molecule).[50] The polymer chains must thus lie flat on the substrate. If precursor films evolve on even substrates, it can be assumed that a limited amount of liquid spreads over an "infinite" substrate, whereas the surface of a single pore is finite and the reservoir of liquid with which it is in contact is "unlimited". In the wetting of pore walls, it is thus possible for a kinetically or thermodynamically stable state to form, which is distinguished by a wetting layer thickness of about 10–30 nm. When the diameters of the template pores become smaller than the wall thickness of the nanotubes, massive nanowires should form instead. Indeed, the pore volume of porous matrices with pore diameters in the subnanometer range can be completely filled by polymer melts.[51]

5. The Modular Assembly System

5.1. Ordered Porous Membranes as Templates

In order to be suitable as templates for the preparation of nanotubes, porous membranes must have pore walls with a high surface energy. Inorganic oxides meet this requirement. Since the mid 1990s, two materials that are particularly interesting for this purpose and have practically monodisperse pore diameter distributions in the nanometer and micrometer range have become the focus of much interest: porous aluminum oxide and macroporous silicon. These materials cover the pore diameter range from about 15 nm up to several micrometers (Figure 4). The pores can be arranged in a very regular fashion, and such templates are thus considered to be ordered.

Disordered porous aluminum oxide has been used for the eloxation of aluminum for over 100 years. In this process, the aluminum is potentiostatically anodized in diprotic acids (mostly sulfuric acid, oxalic acid, phosphoric acid, or chromic acid). Under certain conditions, a film of aluminum oxide with relatively even pores forms along the current lines. A detailed discussion of the pore formation process can be
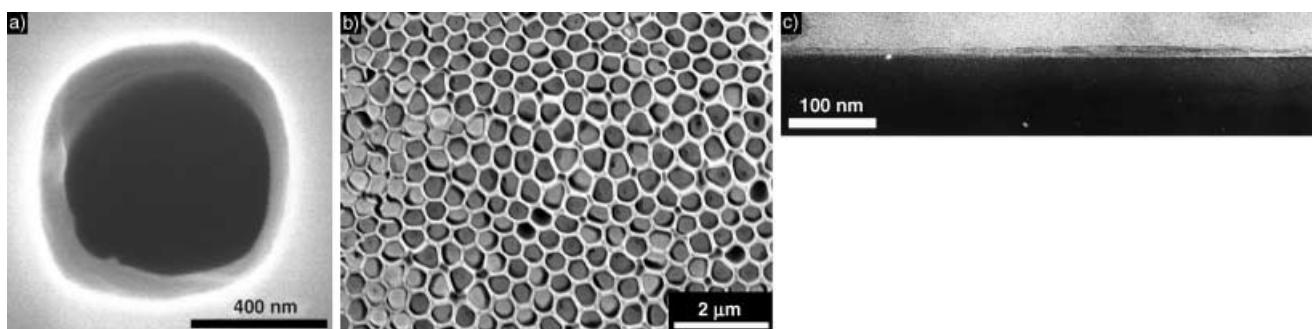

Figure 3. Wetted porous membranes: a) Scanning electron microscopy (SEM) image of a pore opening in macroporous PMMA-wetted Si. b) SEM image of the underside of a PVDF-wetted membrane of porous Al_2O_3 after selective etching of the aluminum substrate to which the membrane was bound. c) Transmission electron microscopy (TEM) image of an ultrathin section of a porous Al_2O_3 membrane wetted with a PS solution. The lower portion of the picture shows the Al_2O_3 pore wall, the middle portion depicts the wall of a PS nanotube, and the upper portion shows the cavity inside the nanotube.
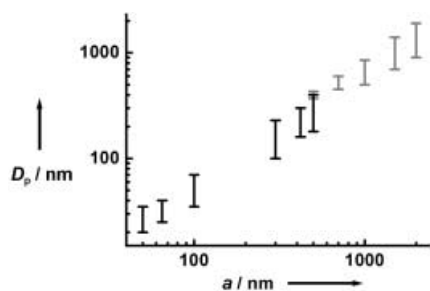
Figure 4. Overview of the pore diameters (D_p) and lattice constants (a) of the currently available highly ordered templates of aluminum oxide (black bars) and silicon (grey bars). Taken from reference [39].

found in the literature.[52,53] The pore diameters (D_p) typically lie between 15 and 400 nm, with a dispersity (calculated by dividing the standard deviation by the mean pore diameter) of at most 20% (Figure 5a). One hundred years after the first
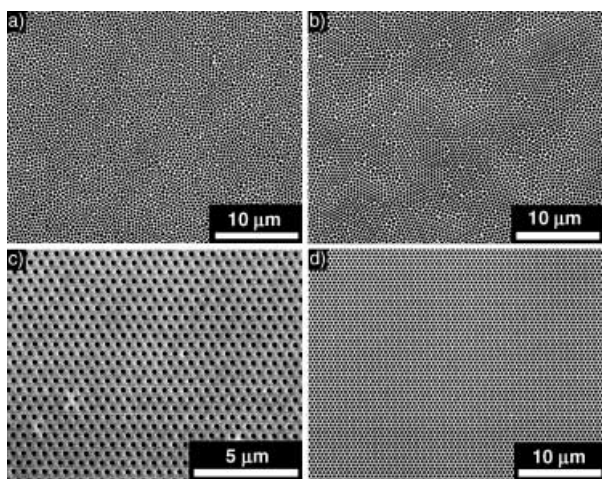

Figure 5. SEM images of porous membranes: a) disordered porous Al_2O_3, b) porous Al_2O_3 obtained by self-organized growth, c) Al_2O_3 prepared by a combination of nanoimprint lithography and self-organization, d) highly ordered macroporous Si. In all four systems $a = 500$ nm.

patent for disordered porous aluminum oxide,[54] Masuda and Fukuda were able to produce self-organized pore structures.[55] The self organization is induced during pore growth by lateral forces resulting from the expansion in volume on the conversion of aluminum to aluminum oxide.[56] In a two-step process,[55] self-organized pore structures can be produced, in which the pores form a hexagonal lattice with a porosity (fraction of the whole membrane surface taken up by pore openings) of 10% (10% porosity rule).[57] The distances between the centers of the pores a (the lattice constants) can be controlled by the conditions of the process. The domains typically stretch over 10–20 pore intervals and the dispersity of the pore sizes is 8%. The initial porosity of 10% can be increased by wet chemical processes after anodization. For example, the pore diameter for porous aluminum oxide with $a = 500$ nm after anodization can be increased from $D_p =$

180 nm to 400 nm in a controlled manner by means of isotropic etching (Figure 5b). While self-organization allows access to pore structures with a polycrystalline degree of order, combination with lithographic methods makes it possible to produce extensive monodomains of pores with lateral dimensions ranging into the square centimeter range. Owing to its nanoroughness, direct electron beam lithography on aluminum gives unsatisfactory results, whereas nanoimprint processes are proving to be highly promising.[58] In this process it is necessary to match the lattice constants of the stamp to the correlation distances that result from the self-organized pore growth. Attainable pore diameter dispersities are below 2% (Figure 5c).

In parallel to this work, Lehmann developed an electrochemical method, also based on anodization, for the formation of ordered pore structures in silicon.[59] In this process, the silicon oxides or fluorides formed in the oxidation of silicon dissolve in an electrolyte containing hydrofluoric acid.[60] The processes involved are relatively complex and are extensively discussed in the literature.[59–61] Three growth processes can be distinguished, which lead to microporous ($D_p < 4$ nm), mesoporous ($4 < D_p < 100$ nm), and macroporous ($D_p > 100$ nm) silicon. The growth conditions for both n-silicon[59] and p-silicon[62] have been extensively investigated in recent years. The etch pits for the nucleation of the pores are as a rule generated lithographically. This process also results in extensive pore monodomains with lateral dimensions reaching the square centimeter range. The distance between pores can be set anywhere from $a = 500$ nm (Figure 5d) to $a = 20$ μm by variation of the process conditions. The pores are nearly perfectly vertically aligned, and can attain aspect ratios over 250.[63]

5.2. Wall Materials

Wetting of porous templates succeeds through contact with both polymer melts and polymer solutions under ambient conditions, which gives rise to the versatility of the method. The wetting step is preparatively simple and requires little effort. The fact that this process is based on a fundamental physical phenomenon, wetting, is the reason for the first major advantage of this method: practically all polymer-containing liquids with a low surface energy can be processed in this way. Aside from structural polymers like PS and PMMA, this particularly applies to high-performance polymers, which have been impossible or very difficult to nanostructure by conventional methods because of their unusual characteristics, such as insolubility in conventional solvents. High-performance polymers include technical plastics with outstanding mechanical, optical, or electronic properties; a high elasticity modulus; high impact strength; negligible cold flow; high continuous heat resistance, or particular biocompatibility.[64] Such materials are naturally also of considerable interest in nanotechnology, as minireactors, in the area of material separation, or for applications that require particular chemical or heat resistance. Polyether ether ketone (PEEK) and polytetrafluoroethylene (PTFE) are two such materials.

PEEK[65] has a continuous service temperature of 250°C, is insoluble in practically all common solvents, and demonstrates excellent chemical resistance. The melting point of the partially crystalline material is at about 340°C. PEEK nanotubes have been produced by melting a film of the polymer on a template surface at 380°C and subsequent removal of the Al_2O_3 template (Figures 6a, b).
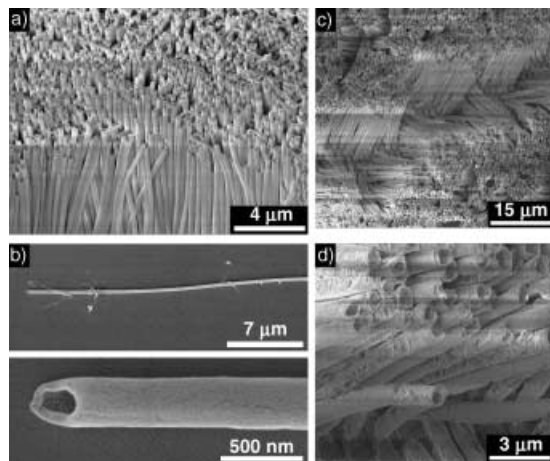

Figure 6. SEM images of nanotubes made from high-performance polymers: a) Array of PEEK nanotubes, b) individual PEEK nanotube, c, d) nanotubes made of ultra-high molecular weight PTFE.

An even larger challenge is the production of nanotubes from PTFE ("Teflon"). There has long been doubt about whether this would be possible at all, since commercially used PTFE has an extremely high molecular weight of 10^6 to 10^7 g mol^{-1}, is practically not flowable, and cannot be processed by the usual plastic molding techniques like extrusion or injection molding. The preparation of molded PTFE parts has thus fallen back on sintering. PTFE has highly interesting properties; it is insoluble, is stable toward nearly all chemicals, and has a very low surface energy as well as extreme toughness.

Experiments with Teflon CN (Dupont, Wilmington), a commercially available material, showed that wetting of pore walls occurs at a temperature of 400°C when the polymer is gently pressed against the template surface. The walls of the resulting Teflon nanotubes (Figure 6c, d) are slightly ribbed. This could possibly be a result of the strongly divergent thermal expansion coefficients of the template and PTFE, as well as the large difference between the wetting and room temperatures, which leads to mechanical tension while cooling.

Multicomponent systems and composites with a defined composition can also be made into nanotubes. Thus polymers, which act as carriers in the wetting process, can be mixed with large proportions of inorganic components, which can then be chemically transformed within the walls of the composite nanotubes. One example of this is the formation of palladium nanotubes.[66] Palladium is of particular interest as a wall material, since nanoparticles or nanowires of this metal are used in catalysis,[67–70] sensors,[71] and hydrogen storage,[72] as well as other applications.

The preparation of Pd nanotubes occurs by wetting of porous templates with a mixture of palladium(II) acetate and a polymer in a solvent common to both. The polymer of choice was polylactide (PLA), first because, in the presence of polymers like PLA, which act as reducing agents, Pd^{II} is reduced to Pd^0 within seconds at only 160°C; and second because PLA can be directly and easily removed by further tempering of the wetted templates at 350°C, so that pure Pd nanotubes remain. Examples are shown in Figure 7, in which porous Al_2O_3 with pore diameters of 400 nm (a, b) and 55 nm (c) was used. The wall thickness of the Pd nanotubes is about 10 nm (Figure 7a). Their outer diameter corresponds to those of the template pores, either 400 nm (Figure 7b) or 55 nm (Figure 7c). It is also possible to fabricate nanotubes from ferroelectric and piezoelectric oxides such as lead zirconate titanate (PZT, $PbZr_{0.52}Ti_{0.48}O_3$) and barium titanate ($BaTiO_3$) in a similar manner.[73] In this case, precursor compounds that contain stoichiometric ratios of the metal cations are used for the wetting process.

5.3. Nanotube Powders and Organized Superstructures

Aside form their possible use as templates, materials with highly ordered pores are of interest in a wide spectrum of applications, including areas such as material separation, sensor technology, or photonics. The pores can either be open at both ends, or can have one end closed off. Wetting of the pore walls results in hybrid systems that contain nanotubes within the porous matrix. In this way, it is possible to tune the properties of the pore surface, such as the optical density, polarity, reactivity, and biocompatibility. Their use as functionalized photonic crystals, catalytic systems, or components in model systems for the investigation of the blood-brain barrier, have been discussed.
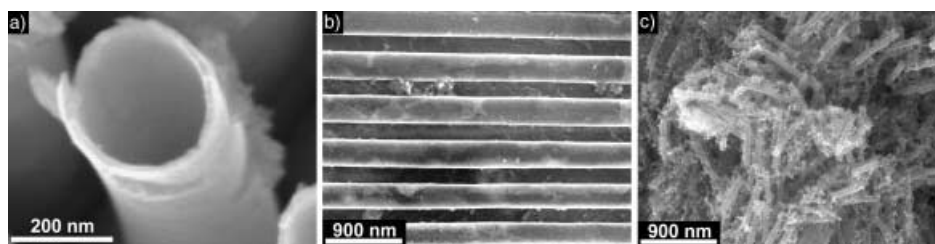

Figure 7. SEM images of Pd nanotubes: a) Cross-section of a Pd nanotube with a 400 nm diameter, b) parallel Pd nanotubes with a 400 nm diameter, c) powder of Pd nanotube segments with a 55 nm diameter.

For the preparation of freestanding or powdered nano-tubes, the templates are then dissolved. Since there are a large number of different formulations available for both acid and alkaline environments, the matrix can mostly be removed selectively and without damage to the nanotubes, even in the presence of sensitive polymeric components. With a 4 inch wafer, a single preparation can produce more than one hundred billion nanotubes.

By using stiff polymers or otherwise non-elastically deformable substances as wall materials and templates with thin pore walls, the degree of order of highly ordered template structures can be reproduced when these are wetted and selectively removed. For this, the highly ordered nanotubes must be attached to a substrate on at least one side. As a rule, some excess of the wetting fluid remains on the surface of the template after the wetting process. Mechanical removal of this excess fluid then frees up the openings of the coated pores. However, a film that has the same thickness as the nanotube walls and wets the upper surface of the pore walls will remain and bind the individual nanotubes together. These then form a highly ordered foil. An example of this with Pd as the wall material is depicted in Figure 8a. The excess wetting fluid that remains on the surface of the template can also act as the substrate to which the highly ordered nanotubes are fastened. In Figures 8b, and c, PMMA tubes bound by a 1 mm thick PMMA film are shown as an example.

5.4. Wall Morphologies

The functionality of nanotubes does not only stem from their dimensions and the type of wall material, but also from the inner structure of the nanotube walls. Specific wall morphologies can be generated by phase transitions or phase-separation processes in the nanotube walls.[66,74] The hollow cylinder geometry of the walls imposes a spatial confinement on the system: whereas the length of the nanotubes can be considered as infinite, the wall thickness and circumference are finite. In contrast to thin flat films, which have been intensively studied as model systems for spatially limiting geometries,[75–77] a curvature occurs, which is naturally highly significant for the evolution of the wall morphology.

An important phase transition in one-component systems is crystallization. The structure of crystalline domains to a large extent determines the mechanical, electrical, optical, and chemical properties of crystallizable substances. This is

the case for actuators or sensors made of piezoelectric materials (coupling of mechanical deformation and electrical fields), pyrolectric materials (coupling of temperature changes and electrical fields), and ferroelectric materials (in which there can be spontaneous electrical polarization). As a rule, only certain crystal forms have the desired properties.

Particularly pronounced changes of corresponding material properties resulting from an interaction with an external electrical field will be attainable if the material is single-crystalline, or if is polycrystalline exhibiting a distinct crystalline texture. An investigation of crystallization in nanotube walls is thus of high interest. As a first step, it is necessary to determine if a crystalline texture is induced by the hollow-cylinder geometry. The partially crystalline poly-mer PVDF was chosen as a model system, because some of its crystal forms exhibit piezo-, pyro-, and ferroelectricity. In addition, it has extremely high chemical resistivity and biocompatibility, as well as a low surface energy, and is used in materials separation and in filter membranes.

Porous Al_2O_3 with $D_p = 400$ nm was wetted with a PVDF melt and thermally treated so that a well-formed and well characterizable crystalline phase, consisting only of α-PVDF, should be present in the nanotube walls. X-ray diffraction experiments were carried out on PVDF nanotubes that were perfectly aligned in the template. These experiments, in which the surface of the template was perpendicular to the plane formed by the incoming radiation beam and the detector, demonstrate the existence of a pronounced crystalline texture in the nanotube walls (Figure 9).[74] The diffractogram in Figure 9a is from an isotropic reference sample from melted PVDF pellets, which were otherwise prepared identically. It shows all of the reflections expected for α-PVDF,[78,79] with no
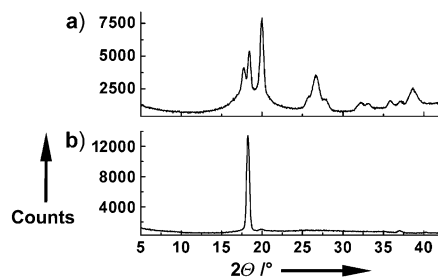
Figure 9. Diffractograms a) of an isotropic PVDF reference sample and b) of PVDF nanotubes ($D_p = 400$ nm) in a template, where the template surface is perpendicular to the plane formed by the primary beam and the refracted beam.
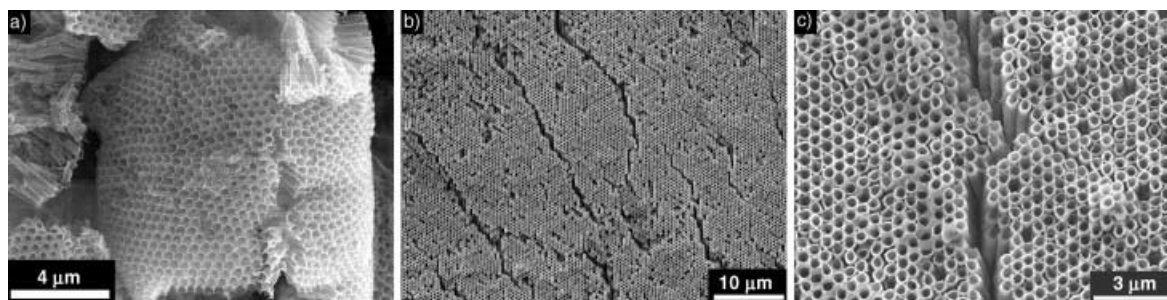
Figure 8. SEM images of highly ordered nanotube arrays made of Pd (a) and PMMA (b, c).

indications of other modifications, as expected. In contrast, the oriented nanotubes with $D_p = 400$ nm generate only the (020) reflection of the α-form (Figure 9b). The PVDF crystallites in the nanotube walls must thus be oriented so that the crystallographic $\langle 0k0 \rangle$ direction, their main direction of growth,[80] is parallel to the long axis of the nanotube. This is thus the only direction in which the wall curvature equals zero, which is why this phenomenon can be described as curvature-directed crystallization.[74]

Although the nonpolar α-modification of PVDF does not yet demonstrate the desired piezoelectric properties, other systems have already shown that nanotubes that act as nanoactuators are attainable through template wetting. The nanotubes of ferroelectric and piezoelectric oxides, such as the PZT and $BaTiO_3$ discussed in Section 5.2, demonstrate piezoelectric hysteresis.[73]

An interesting expansion of the wetting concept is based on the use of multicomponent systems. Induction of decomposition processes by a leap in temperature, or the evaporation of a volatile solvent allows the generation of a specific phase morphology in the walls of the nanotubes. The ripening of the resulting phase morphology begins as soon as the phase separation starts. As well as the previously mentioned geometric limitations, wetting phenomena could also play a large role in this process. The ripening process occurs as long as the material forming the nanotube wall remains fluid, either because it is being annealed at correspondingly high temperatures or because it contains a sufficient quantity of a solvent. The driving force for ripening is the reduction of the originally large interface between the coexisting phases. This was examined in the case of Pd/PLA composite tubes, for example.[66] Figure 10 shows a TEM image of an ultrathin section of an Al_2O_3 template ($D_p = 400$ nm), whose pore walls (below, dark area) are covered with a 10 nm thick Pd/PLA composite layer (middle of picture). This contains Pd nanoparticles, visible as dark spots, with diameters of about 5–
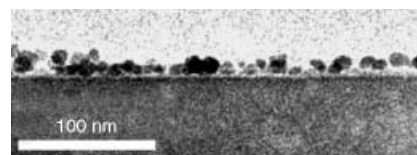

Figure 10. TEM image of an ultrathin section of an Al_2O_3 template (the pore wall is the dark area in the lower half of the picture) wetted with a PLA/Pd mixture. The wall of the PLA/Pd composite tube in the center of the picture contains Pd particles of about 10 nm.

10 nm. Their morphology corresponds to an advanced state of ripening, as the palladium was originally finely dispersed.

Selective removal of PLA and the template leads to structured Pd nanotubes with walls consisting of sintered Pd nanoparticles. SEM and TEM images of Pd nanotubes with a 400 nm diameter and a morphology corresponding to a relatively early ripening stage are shown in Figures 11a and b. The rough, fine, and netlike structure of the walls can be discerned. In contrast, Figures 11c and d depict SEM and TEM images of Pd tubes with the same diameter but a wall morphology corresponding to a late ripening stage. The walls in this case are smoother and the Pd crystallites are larger. Figures 11e and f contain TEM images of Pd tubes with a 55 nm diameter after varying ripening times. These clearly show that the size of the Pd particles can be controlled by the duration of the ripening process. Larger Pd crystallites, such as those in Figures 11c, d, and f, correspond to a longer ripening time.[66]

5.5. Core-Shell Systems and Quantum-Dot-Containing Nanotubes

The highly variable principle of template wetting makes it possible to provide the nanotube walls with additional
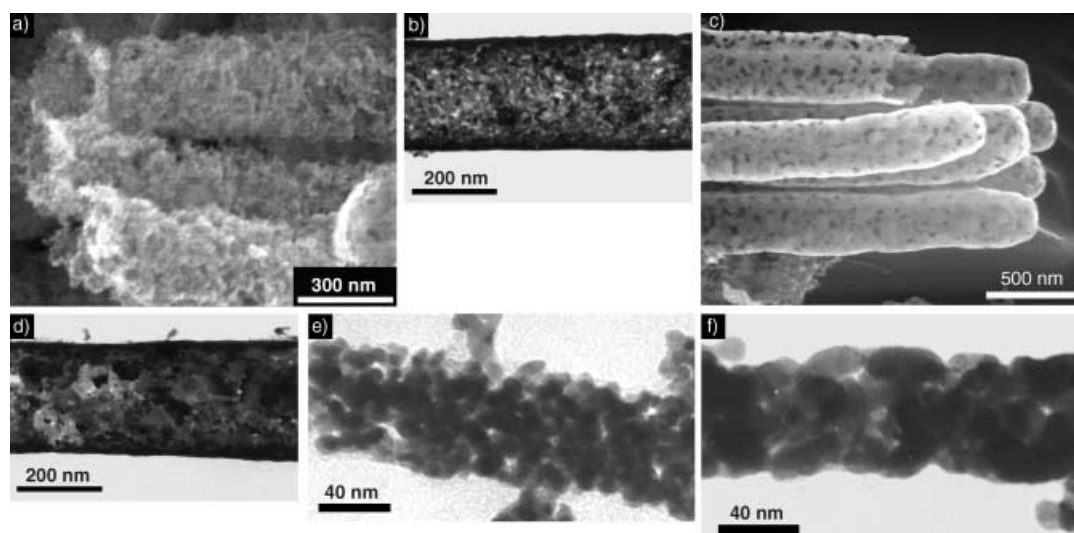

Figure 11. Pd nanotubes with structured walls: SEM (a) and TEM (b) images of nanotubes with a 400 nm diameter and a morphology corresponding to an early ripening state. SEM (c) and TEM (d) images of nanotubes with a 400 nm diameter and a morphology corresponding to a late ripening state. e,f) TEM images of Pd nanotubes with a 55 nm diameter and morphologies corresponding to early (e) and late (f) ripening state. Figure 11c was taken from reference [66].

functionalities. If the wall material is transformed after template wetting, as described in Section 5.2, such that it has a high rather than a low surface energy, the nanotube walls can be coated through a second wetting step. It should thus be possible to increase the wall thickness in successive 10 nm steps, or to generate hybrid nanotubes with a core-shell morphology.[39] As an example, macroporous silicon was first coated with Pd, which was subsequently wetted with a PS melt in a second step. The resulting microtubes have a core-shell structure in which the PS core is surrounded with a Pd shell (Figure 12). In this way it is possible to produce polymer-metal hybrid nanotubes in which the metal layer's morphology is controllable.[39] This could result in hybrids that have higher mechanical stability than pure metal nanotubes, for example.

Figure 12. TEM image of a tube with a core-shell morphology, which was prepared by consecutive wetting steps. The outer shell is a network of Pd, the inner core consists of PS.

Another interesting possibility for functionalization is the embedding of semiconductor quantum dots in the nanotube walls. Such composite tubes should have interesting optical properties. Their preparation results from the dissolution of a carrier polymer in a colloid suspension of the quantum dots and subsequent template wetting. Light-emitting nanotubes are accessible in this way.[83] This process is particularly attractive because a regular arrangement of these tubes within a two-dimensional photonic crystal may result in hybrid systems, which could have specific emission properties.

6. Potential Applications

If it is possible to produce nanotubes with specific wall morphologies from a large spectrum of materials, very highly promising systems will be available for a plethora of very different applications. These lie in the areas of medicine and pharmaceuticals (tissue engineering, galenics, antifouling), packaging (high-thermal insulation), transport and separation, sensors (gas-, moisture-, and biosensors), chromatography, microreaction technology (nanotubes as microcavities, reaction chambers, and nanopipettes), storage of substances (fuel cells), microelectronics (interlayer dielectrics), electronics (nanocircuits, nanocables, nanocapacitors), and optics (light conduction, nanocapillaries for optical near-field microscopy). The nano- and mesoscale tubes could themselves be used as templates for the preparation of biomimetic nanostructures of a quality that would otherwise not be obtainable by artificial means. Examples of this would be hydroxyapatite, the basis for the formation of hard tissues in mammals (bones,

teeth), protein storage, or artificial viruses. Nanotubes with dimensions into the 10 nm range open up undreamed of possibilities as functional units for steering physical and chemical phenomena. Quantum effects can occur, and transport processes and the speed of signal transmission could be controllable on a nanoscale. The concept of template wetting could be an important step toward tailored nanotubes for fundamental research as well as nanotechnology.

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