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Redox-Active Nanotubes of Vanadium Oxide

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Martin Müller, F. Krumeich, and Hans U. Nissen

Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday

Nanoporous materials (nanostructures), which are considered as intermediates between classical molecular scale and microsized entities, constitute a rapidly growing field of scientific interest and industrial applications. Well-defined structures of this length scale are difficult to obtain because neither typical physical tailoring techniques nor planned chemical syntheses are very applicable in this size domain. Since chemical reactivity and physical properties in the nanoregion are strongly dependent on the size of the structures, such materials are very interesting in many respects, particularly for the production of highly functional, finely dispersable, and resource-saving base materials for "nanodevices". Nanoparticles may be of quite different shapes such as spheroids, mushrooms,[1] platelets, rods, or tubes; the form adopted plays a large role in determining the basic properties, for example, isotropic or anisotropic behavior and region-dependent surface reactivity.

The tubular form is particularly attractive since it provides access to three different contact regions: inner and outer surface as well as the tube ends. Carbon nanotubes[2, 3] establish such singly or multiwalled entities that consist of graphite-like sheets depending on the synthesis conditions.[4, 5] They have already attracted a great deal of interest because they might turn out to become very useful in future nanodevice technology. Another very interesting family are the nanoporous MCM-aluminosilicates[6, 7] with continous framework structures that have tunnel dimensions between 3 and 10 nm, extending the range of zeolite-like materials. The synthesis of these mesostructured molecular sieves relies on surfactant micelles or liquid-crystal arrays of micelles as structure-directing agents for the assembly and subsequent polymerization of inorganic alumosilicate precursors at the surfactant-solution interface. The application of complementary electrostatic interactions between surfactant molecules and charged or polarized metal oxy precursors as the inorganic component has opened a way to new metastable modifications of metal oxides.[8] Quite recently it has been shown that hydrogen bonding[9] or real coordinative interactions[10–12] between the ligand liquid crystal template and the metal center offer new perspectives for the controlled synthesis of surfactant-based periodic inorganic structures.

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One of our aims in this area is to produce specialized nanostructures from transition metal oxides for potential applications in electrochemical devices and for catalytic applications, and in appropriate template syntheses we have used neutral surfactant molecules such as primary aliphatic amines, together with vanadium alkoxide precursors to generate a novel nanotubular redox-active form of vanadium oxide. The hydrolysis of a solution of vanadium (*V*) triisopropoxide in hexadecylamine gave, after aging, a yellow, lamellar-structured composite of surfactant and hydrolyzed vanadium(v) oxide (Figure 1). The layer distance of this homogeneously periodic vanadium oxide surfactant assembly is about 3 nm. Treatment of this hydrolysis product under hydrothermal conditions yielded a product of isolated and starlike grown-together nanotubes with the nominal composition $VO_{2.40}(C_{16}H_{33}NH_2)_{0.34}$.[14, 15]

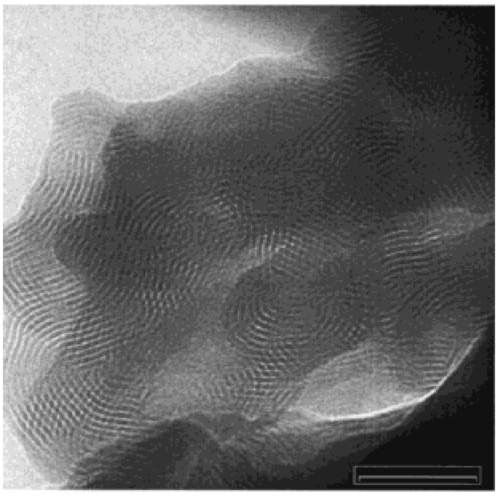

Figure 1. TEM image of the lamellar-structured, periodic assembly of surfactant and vanadium(v) oxide obatined after hydrolysis of the vanadium alkoxide in the presence of the surfactant templates. Layer thicknesses in the range of about 2.8 to 3.0 nm are observed. The bar shown in the box (bottom right) denotes 50 nm.

The black powdered material is paramagnetic, and shows a semimetallic conductivity presumably due to mixed-valent vanadium centers. Electron microscopic investigations show nearly exclusively isolated starlike or grown-together nanotubes up to 2000 nm long (Figure 2a). The scanning electron microscope image in Figure 2b illustrates the cylindrical open-ended shape of the tubules. The high-resolution transmission electron microscopy (TEM) photographs (Figures 2c and 2d) show that the walls are formed of several concentric shells each of about 3 nm. In fact, this corresponds to the most pronounced 2Θ value found in the very broad X-ray powder patterns shown in Figure 2e. The tube diameters range from 15 to 100 nm and have tunnel openings between 5 and 50 nm (cf. Figure 2a). In accordance with the general practice for zeolite-like and mesoporous materials we call this product ETH1. Under slightly different conditions tubes with closed ends can also be obtained (Figure 2f).[14]

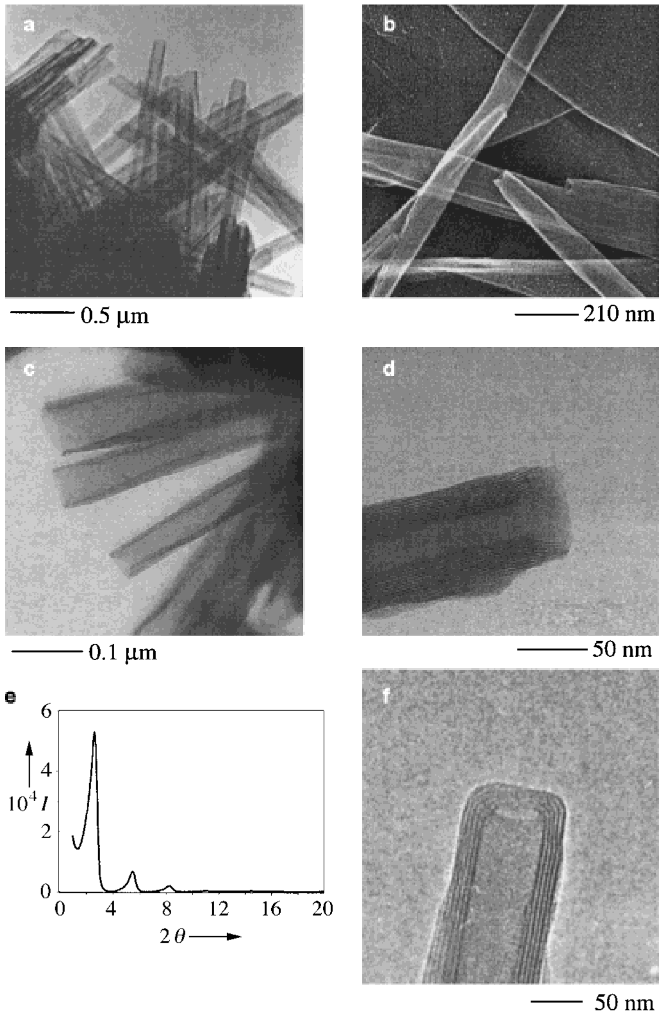

Figure 2. ETH1: a) Scanning electron micrograph of the open-ended vanadium oxide nanotubes that are up to 2000 nm long. b) Low-resolution TEM images of the hydrothermal reaction product, indicating isolated or grown-together vanadium oxide nanotubes as the main product. c and d) High-resolution TEM images of the vanadium oxide nanotubes, indicating the multishell structure of the tube walls with an average layer thickness of about 3 nm. The free inner diameter of the tubes range between 25 and 35 nm and the total tube diameters are between 50 and 70 nm. e) Powder X-ray diffraction pattern of the vanadium oxide nanotube material. The peak with the highest intensity at $2\Theta = 2.66°$ corresponds to a *d*-value of 3.3 nm, and reflects the layer distance of two concentric single shells of the multi-shell structure of the tube wall. f) Closed multiwalled vanadium oxide nanotube generated at alkoxide to template ratio of 1:1.

Attempts to release the template from the material by calcination were unsuccessful because of the thermal lability of the nanotubes above 250 °C; however, the surfactant could be partially extracted under mild acidic conditions without structural damage. According to a recent publication by Antonelli and Ying,[13] protonation of the alkylamine by alcoholic NH_4Cl solutions and subsequent replacement by OH groups should lead to a template exchange. Although we were able to exchange the template molecules by using NH_4Cl in ethanol we believe that this mechanism is not applicable in our case because reactions with nonhydrolyzing salts, such as NaCl, CsCl, $CoCl_2$ and even $[Co(NH_3)_6]Cl_3$, also gave rise to a complete exchange of the templates, while solutions of LiCl and $CuCl_2$ did not show a significant removal of the templates. Thus, we believe that the alkylamine is already protonated during the synthesis and that the resulting ammonium ion is then replaced by a cation exchange for a sufficiently large M^{n+}. This is supported by EDX analyses which, for example, for the Co-exchanged samples clearly reveal considerable cobalt but no chlorine content in the tubes.

Interestingly, the layer distances change from about 2.8 to 3.0 nm for the templated (ETH1) to 0.86 nm for the template-exchanged material (formation of ETH2; Figure 3 top left). As the majority of the tubes are preserved, this exchange is presumably based on a cooperative mechanism. Notably, the crystallinity of the template-exchanged product is considerably better than that of the primary tubes ETH1; for some tubes even contrasts of about 0.65 nm are observed, which are indicative of an ordered structure within and between the individual shells of the tube walls (see arrows in center of Figure 3). This is supported by the fact that the vanadium oxide tubes exhibit a much better stability in the electron beam after the template exchange. We call this template-exchanged material ETH2.

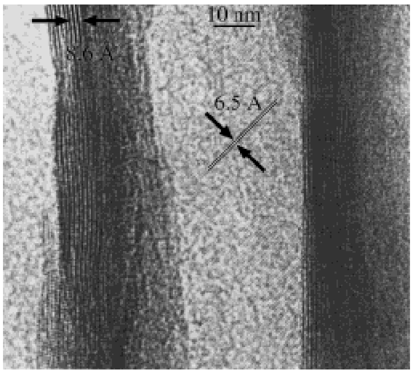

Figure 3. ETH2: High-resolution TEM image of a cation template-exchanged multiwalled vanadium oxide nanotube. The contrasts along the walls exhibit a distance of about 0.86 nm (see arrow top left). Several regions show a fine structure with contrast distances of about 0.65 nm (see arrow in the center), which are indicative of an ordered structure within and between the individual shells of the tube wall.

To our knowledge, the vanadium oxide materials reported herein are the first redox-active transition metal oxide nanotubes prepared and characterized.[15] In contrast to the much smaller carbon nanotubes, the vanadium oxide tubes are obtained as the main product by a direct chemical synthesis at relatively low temperatures. Here, unlike other nanoporous oxidic materials such as MCM41 and MCM48 isolated tubes are present. The MCM-type nonredox-active aluminosilicates have only been synthesized with somewhat smaller tunnel diameters (roughly by a factor of ten) in the form of condensed extended structures but not as isolated tubes. Furthermore, no multishelled walls are present in the MCM materials. This might be the reason that isolated tubular aluminosilicate intermediates have not yet been observed.

The novel vanadium oxide nanotubes open fascinating possibilities for further chemical and physical explorations of nanostructures and hold promise for possible applications. The cooperative cation exchange behavior between the layers may allow incorporation of numerous functional cations or cation complexes. Although the tubes are interesting in terms of the high surface area, we believe that even more interest lies in their potential for hosting functional molecules and for combining inorganic material and polymer organic compounds or even biological entities.

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[14] In a typical reaction procedure, a solution of vanadium(v) triisopropoxide (15.75 mmol) and hexadecylamine (7.87 mmol) in a molar ratio of 2:1 in ethanol (5 mL) was stirred under inert atmosphere for 1 hour. Hydrolysis of the reaction mixture with H_2O (15 mL) under vigorous stirring followed by the aging of the hydrolysis product for a few hours to a full day leads to a yellow, lamellar-structured composite of surfactant and hydrolyzed vanadium oxide component. The hydrothermal reaction of this hydrolysis product in an autoclave at 180 °C afforded after about a week black, isolated or starlike grown-together nanotubes with open ends as the main product. A molar ratio of 1:1 afforded predominantly nanotubes with closed ends.

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