Electron Microscopy Characterization of Silicon Dioxide Nanotubes

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Received February 19th, 2004.

In memoriam Professor Reginald Gruehn

Abstract. Well-developed crystals of $[Pt(NH_3)_4](HCO_3)_2$ are employed as template for the synthesis of silicon dioxide nanotubes (SiO₂-NTs). Silicon dioxide, which is produced by a sol-gel reaction, coats the surface of these crystals and builds up the nanotube walls. In the final step, the Pt-salt fibers are thermally decomposed and auto-reduced to metallic Pt nanoparticles. Scanning and transmission electron microscopy (SEM and TEM) investigations of the product confirm the formation of silicon dioxide nanotubes in high yield. The tube walls consist of amorphous silicon dioxide. The tube length generally is $0.5 - 3 \mu m$, while the thickness varies in

two distinct ranges: thick tubes have a diameter of 100 - 500 nm and thin ones of approximately 50 nm. Most of the NTs are filled with Pt particles, but others, typically the larger ones with open tube ends, obviously are empty. Presumably, open ends cause the observed Pt loss. In closed SiO₂-NTs, Pt forms as ca. 10 nm large particles in the tube core and as 1 - 2 nm large particles inside the tube walls.

Keywords: Nanotubes; Templates; Electron microscopy; Silicon oxide

Elektronenmikroskopische Charakterisierung von Siliciumdioxid-Nanoröhren

Inhaltsübersicht. Für die Synthese von Siliciumoxid-Nanoröhren (SiO_2-NTs) wurden gut ausgebildete $[Pt(NH_3)_4](HCO_3)_2$ -Kristalle als Template verwendet. Mittels Sol-Gel-Reaktion erzeugtes Siliciumdioxid bedeckt diese Kristalle und bildet die Röhrenwand. Das Pt-Salz wird thermisch zersetzt und metallische Pt-Partikel bleiben zurück. Die Ergebnisse der Untersuchungen im Raster- bzw. Transmissionselektronenmikroskop (REM und TEM) des Produktes zeigen die hohe Ausbeute an SiO₂-NTs. Die Röhrenwand besteht aus amorphen Siliciumdioxid. Die Röhrenlänge beträgt 0.5 – 3 µm,

während die Dicke in zwei Bereichen variiert: Dicke Röhren haben einen Durchmesser zwischen 100 – 500 nm und dünne einen von ca. 50 nm. Die meisten SiO₂-NTs sind mit Pt-Teilchen gefüllt, während andere, insbesondere die grösseren mit offenem Ende, leer erscheinen. Vermutlich führen die offenen Enden zum Pt-Verlust. In geschlossenen SiO₂-NTs bildet sich elementares Platin als ca. 10 nm grosse Partikel im Röhreninnenraum und als 1 – 2 nm grosse Partikel in der Röhrenwand.

Introduction

Although the tubular morphology of asbestos minerals had been known for a long time [1], nanotubes became a major topic of material research not until the discovery of the carbon nanotubes (NT) in 1991 [2]. Since the anisotropic structure of carbon NTs is combined with interesting physical and chemical properties [3, 4], the search for materials with a similar tubular morphology has successfully been extended to other systems, and NTs of boron nitride [5], chalcogenides [6], and various oxidic compounds [7] have been discovered and characterised.

Among the oxidic NTs, those of silicon oxide are outstanding since they appear in different types and sizes. Tube walls consisting of curved crystalline layers occur in the fi-

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Institute for Physical Chemistry and Electrochemistry University of Hanover D-30167 Hanover e-mail: Michael.Wark@pci.uni-hannover.de brous asbestos minerals serpentine and chrysotile. The structural anisotropy that causes the bending of the layers is due to the presence of octahedra MO_6 (M = Mg, Al) on one side and tetrahedra SiO_4 on the other side of the layers. Remarkably, the TEM investigation of various chrysotile samples revealed the co-existence of a variety of structural variations, including spirals and concentric layers [8].

In contrast to the silicon dioxide minerals with crystalline characteristics, the walls of artificial silicon dioxide nanotubes (in the following abbreviated as SiO_2 -NTs) are all amorphous. SiO_2 -NTs, which are partly filled with elemental silicon, can be obtained by a high temperature approach involving the pyrolysis of mixed SiO_2 and Si powders [9]. A widely applicable route to inorganic nanotubes is the use of other anisotropic nanostructured materials as structure-directing templates [10]. For example, coating carbon NTs with a thin film of silicon dioxide generates tubular SiO_2 [11, 12]. Besides that, large organic molecules can also be applied as templates, which have the advantage that they can easily be removed afterwards [13]. Well-developed SiO_2 -NTs with quite large diameters (up to 200 nm) and thin tube walls are formed from xerogels that consist of tubular structures [14]. These xerogels are prepared by gelatinising organic solvents with cholesterol derivates, and, after a sol-gel polymerization of tetraethoxysilane on their surface, the calcination results in SiO_2 -NTs. In a novel approach, fibers of V_3O_7 ·H₂O were coated with silicon dioxide, and, after removal of the core by H₂O₂, SiO₂-NTs were obtained in an excellent quality [15, 16].

Recently, NTs of silicon dioxide were obtained by coating needle-like crystals of $[Pt(NH_3)_4](HCO_3)_2$ with Si(OEt)₄ followed by a calcination [16, 17]. On an analogous synthesis path, NTs of titania are accessible [17]. A comprehensive structural characterisation of the SiO₂-NTs obtained in this way will be given in this paper.

Results and Discussion

According to the results of the electron microscopy investigations, the reaction product comprises nanotubes of silicon dioxide in high purity. The tubular morphology is



Figure 1 Scanning electron microscopy (SEM) images of the synthesis product. Rectangular silicon dioxide nanotubes (SiO_2 -NTs) of different sizes are present.

clearly visible in the SEM images (Fig. 1). Surprisingly, the SiO_2 -NTs have diameters in different ranges of size. In their basal plane, larger tubes have an edge length in the range of 100 - 500 nm while their length is in between $0.5 - 3 \mu$ m. Apparently all of these large tubes have open tube ends. The smaller SiO₂-NTs, which appear in a higher number, are about as long as the rectangular ones but have significantly smaller diameters, typically around 50 nm. Only a small part of the tips of the thin NTs appears to be open.

The TEM images (Figs. 2, 3) give further information about the inner structure of the SiO_2 - NTs. Obviously, the cores of most tubes are filled with Pt particles. Because of the high electron scattering potential of platinum, Pt par-



Figure 2 Transmission electron microscopy (TEM) images of the synthesis product. (a) Overview image. Most NTs are filled with Pt particles, which can be recognized by their black contrast. Besides that, a thick NT in the centre appears empty. (b) Pure SiO_2 -NTs, i.e., without any filling. (c) SiO_2 -NTs filled with Pt particles. The SiO_2 -NTs on the lower left side contains a Pt nanowire that is about 0.5 µm long and has a diameter of about 10 nm. On the top, two NTs are grown together, forming a unique arrangement.



Figure 3 Cross-sectional TEM images of SiO_2 -NTs. (a) Tubes containing Pt particles. The circular diameter of two tubes is due to small tilts of the tube axes with respect to the direction of observation.(b) An empty and a filled SiO_2 -NT.

ticles appear with black contrast under the selected imaging conditions (close to Scherzer focus), whereas the regions containing SiO_2 are grey. The presence of Pt and Si in the NTs was moreover confirmed by EDS analysis.

Most of the tube ends are closed (Fig. 2). If both ends are closed, the tubes contain Pt particles as a rule. On the other hand, some NTs are empty (Figs. 2b, 3b), and no Pt particles could be detected in their core. Since these empty SiO₂-NTs have generally a diameter of 200 nm or more (Fig. 2a,b), they obviously correspond to the large rectangular tubes as observed in the SEM images (Fig. 1). Since the TEM images in the longitudinal projection (Fig. 2) cannot provide an unambiguous characterization of the cross-sectional structure, it is necessary to view along the tube axis in order to gain this information. The cross-sectional TEM images (Fig. 3) corroborate that both types, filled as well as empty SiO2-NTs, occur simultaneously. The inner surface of the SiO₂-NTs is rectangular in most cases since the structure of the templating crystals is preserved during the coating with silicon dioxide. On the other hand, this occurs to a lesser extent at the outer surface so that the edges are smooth. Due to this, small SiO₂-NTs even appear to have circular cross-sections (Figure 3a). Other NTs have evidently been embedded in a tilted position, resulting in an elliptically shaped cut. Two rectangular NTs are intergrown (Fig. 3a). Such features can sometimes also be observed in the longitudinal TEM images as well (e.g., Fig. 2c, top).



Figure 4 (a) HRTEM image of a tube wall. Small Pt particles appear not only at the inner surface (top) but also inside the silicon dioxide wall. (b) Further magnified Pt particle, with the lattice fringes corresponding to crystal planes of the type {111}. (c) Selected area electron diffraction pattern of Pt-containing SiO₂-NTs. The reflections are generated by polycrystalline Pt and are indexed accordingly. The measured d-values (d₁₁₁ = 2.28 Å; d₂₀₀ = 1.95 Å; d₂₂₀ = 1.37 Å; d₃₁₁ = 1.18 Å) agree well with the theoretical ones for fcc Pt (a = 3.924 Å).

This is certainly caused by coating two adjacent template crystals of $[Pt(NH_3)_4](HCO_3)_2$ at the same time, so that a corresponding shape of the resulting NT is obtained after removal of the templating crystals. This cross-sectional views show that the Pt particles are located at the inner surface of the tubes and that the centre is still open and thus represents a possible container for further materials. In figure 3b, an empty NT is present.

The thickness of the silicon dioxide walls is in the range 20 - 50 nm. Whereas the silicon dioxide is amorphous, the Pt particles are crystalline, as it can be seen in HRTEM images (Fig. 4a, b). Close to the inner surface of the NT, rather large Pt particles (diameter approximately 5 - 15 nm) appear. The single-crystalline characteristic of several particles is indicated by the presence of lattice fringes. The crystallinity of Pt is confirmed by the electron diffrac-



Figure 5 SEM image of $[Pt(NH_3)_4](HCO_3)_2$ template crystal. The size varies significantly. Besides mm-sized crystal, there are smaller needle-like crystals with a high aspect ratio.

tion pattern as well (Fig. 4c). The observed reflections agree perfectly with those of face-centred cubic platinum metal. Smaller Pt particles (diameter approximately 1 - 2 nm) are embedded in the silicon dioxide matrix and distributed inside the whole tube wall. Pt particles on the outer surface of SiO₂-NTs have been scarcely observed. It should be noted that the particle size could be up to about 100 nm (Fig. 2c). Furthermore, the Pt particles are sometimes quite well aligned in a row, resulting in wire-like arrangements (Fig. 2c).

A SEM investigation of the templating $[Pt(NH_3)_4]$ -(HCO₃)₂ crystals showed that the morphology of the obtained SiO₂-NTs indeed reflects that of the starting material (Fig. 5): rectangular large crystals and small needles are present. However, there are very large crystals with length up to some 10 µm while tubes that large cannot be found in the product. Such crystals might be destroyed or partly dissolved during the coating step.

For the formation of silicon dioxide nanotubes around $[Pt(NH_3)_4](HCO_3)_2$ nanofibers, acting as templates, a coating mechanism, comparable to that given by Caruso et al. for the coating of polystyrene spheres with SiO₂ or TiO₂ [18], can be discussed. Under the basic conditions present during the synthesis, the silicon dioxide species are partly deprotonated and negatively charged. It is assumed that an exchange of $(HCO_3)^-$ ions with silicate anions takes place at the surface of the precipitated needle-like $[Pt(NH_3)_4](HCO_3)_2$ crystals. The arrangement of the silicate anions around the metal salt fibers is, besides the electrostatic interaction, attracted by the formation of hydrogen bonds with the NH₃ ligands of the $[Pt(NH_3)_4]^{2+}$ complex cations [19].

The SiO_2 walls are built up by condensation processes, for which the anchored silicate species act as nucleation points. The enrichment of the oxide at the templating crystals occurs by an Ostwald ripening mechanism; the particles grow in size at the tube walls and highly soluble very small silicon dioxide particles re-dissolve to the reaction solution.

To gain information about the structure development during the synthesis, we also investigated the intermediate product, obtained after drying the coated sample but before



Figure 6 Intermediate reaction product before calcination. (a), (b) SEM and (c), (d) TEM images.

the final calcination. The SEM images (Fig. 6a,b) demonstrate that the tubular morphology has already been evolved and is very similar to that of the final product. As expected, most of the tubes are still completely filled with the templating material. This is clearly the case at the rectangular solids in figure 6a. However, a few tubes, e.g., the large rectangular SiO₂-NT on the central right side of figure 6b, appear with open ends, indicating that a part of the forming nanotubes is broken possibly due to mechanical stress. The TEM images (Fig. 6c,d) show that the decomposition of the $[Pt(NH_3)_4](HCO_3)_2$ crystals has yet not taken part at this step. The tube cores are almost homogeneously filled with material, and distinct Pt particles are not recognizable. Areas with brighter contrast inside the tube cores point at the presence of gas bubbles, caused by the starting decomposition of the Pt complex. However, since such bubbles are already generated by the strong electron irradiation during the TEM investigation, this might be an artefact.

Conclusions

The following strategy for the synthesis of Pt-filled silicon dioxide nanotubes has been selected:

- 1. Preparation of well-developed template crystals of [Pt(NH₃)₄](HCO₃)₂.
- 2. Coating of the template crystals by silicon dioxide.

3. Thermal decomposition of the template into gaseous products and metallic Pt, which remains inside the tube corres.

The results presented confirm that this synthesis indeed generates highly pure SiO_2 -NTs in an excellent yield. However, SEM and TEM investigations of the product have unexpectedly uncovered the existence of distinct tube variants, which differ with respect to size and morphology as well as to the filling with Pt particles. While most of the NTs are filled with Pt particles, some obviously contain none, typically the larger ones. Furthermore, the ends of the filled SiO_2 -NTs are mostly closed, whereas the large tubes are open and contain no Pt particles. Presumably, crystals open ends are responsible for the observed Pt loss of the large tubes. Apparently, the [Pt(NH₃)₄](HCO₃)₂ forms gaseous compounds that leave the tube and decompose on the outside. If SiO₂-NTs stay completely closed during the heat treatment, the gaseous components are forced to diffuse through the porous silicon dioxide forming the tube walls. Consequently, the largest amount of the Pt will remain in the tube core, and indeed a precipitation of about 10 nm large Pt particles occurs there. Nevertheless, a part of the decomposition of the Pt complexes occurs inside the silicon dioxide walls as indicated by 1 - 2 nm large Pt particles detected there.

To get a better control of the tube morphology and a more regular filling of the tube cores with Pt are important goals for an optimisation of the synthesis. A higher amount of Pt nanowires inside silicon dioxide nanotubes would be desirable since this would open perspectives towards an application as electronic nano devices.

Experimental Section

Synthesis: After dissolving 0.0193 g [Pt(NH₃)₄](HCO₃)₂ (Chempur) in 2.15 ml water, it is reprecipitated by adding 40 ml ethanol. 111.8 μ l tetraethylorthosilicate (TEOS, Fluka) and 2.15 g 0.4 N NH₃ is dropwise added to the precipitate at room temperature. After stirring this mixture for 12 h, the solvent is slowly evaporated at room temperature. A dry, white product is obtained which afterwards is calcined in a stream of Ar (20 l/h) at 773 K for 5 hours. Finally, the sample appears as a black powder.

Electron Microscopy: Transmission electron microscopy (TEM) investigations were performed on a Philips CM30 microscope at 300 kV (LaB₆ cathode, SuperTwin lens). For the investigation of the longitudinal structure of the SiO₂-NTs, a suspension of the material in ethanol was deposited onto a perforated carbon foil supported on a copper grid. To observe the structure along the axis of the nanotubes, the material was embedded in a resin between two silicon wafers. The resulting sandwich was cut in slices, which were subsequently thinned by mechanical grinding and finally by

ion milling. Details of this modified cross-sectional preparation technique are given elsewhere [20]. An energy dispersive X-ray spectrometer (EDS) is attached to the CM30, allowing us to analyse the elemental composition. Scanning electron microscopy (SEM) was performed on a LEO 1530 Gemini microscope with field emission gun. Secondary electron images of the as-synthesized, uncoated samples were recorded at low voltage (1 kV).

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