

# Pt Nanoshell Tubes by Template Wetting

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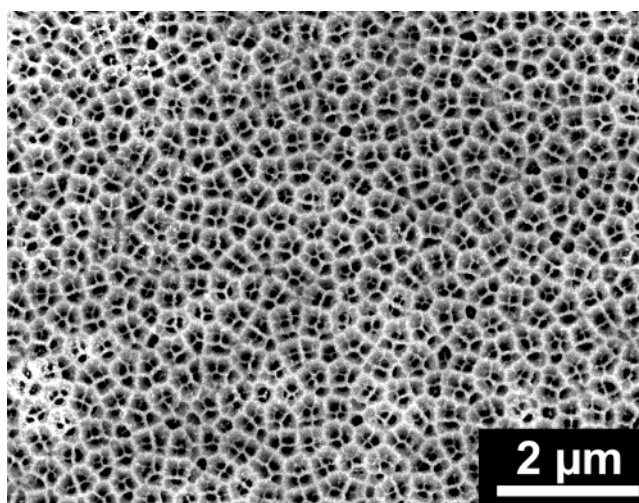
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## ABSTRACT

Large-scale fabrication of platinum (Pt) nanoshell tubes has been accomplished via a simple and convenient method: porous templates are wetted at ambient conditions with a polymer/Pt precursor solution. Annealing yields functionalized membranes having Pt-coated pore walls. Unsupported Pt nanoshell tubes are accessible by selectively removing the template. We have also synthesized composite tubes having an outer Pt shell and an inner polymer core by performing consecutive wetting steps. The tube diameter is adjustable by using templates with respective pore diameters. We demonstrate that “giant” nanoshell tubes with a diameter of 1  $\mu\text{m}$  can be fabricated. They exhibit nanostructured walls consisting of sintered crystallites extending approximately 10 nm and can thus be considered as a hierarchical system combining nano- and microscale features.

Platinum is commonly used as a catalyst and as an electrode material. For these applications it might be advantageous to employ Pt nanoparticles<sup>1–5</sup> and nanotubes<sup>6,7</sup> with a considerably enhanced surface-to-volume ratio compared to bulk Pt. Particularly interesting are Pt nanoshell tubes within the pores of a membrane acting as a support. Such hybrid systems may exhibit channels with diameters ranging from a few tens of nm to several microns and depths up to hundreds of microns with Pt-coated walls. The advantages compared to dispersed systems are obvious: no precipitating and flocculating of the Pt species reducing its activity occur. Pt-coated porous membranes are easy to handle, and no tedious recovering procedures are necessary as in the case of dispersed Pt nanoparticles. They are ideal building blocks for miniaturized flow reactors. Discrete Pt nanoparticles attached to the pore walls may be removed by the flowing medium. However, the leaching should not occur if the Pt forms a stable microtubular structure within the pores. Aligned pores within a membrane having blind ends, whose walls are coated with Pt, may allow performing Pt catalyzed reactions within their interior. Such hybrid systems containing functionalized microcavities could be promising materials for the “lab on a chip” technology. Furthermore, Pt coated porous materials may be used as nanostructured electrodes.<sup>8</sup>

Sun et al.<sup>6,7</sup> recently reported on an elegant method to prepare Pt nanotubes involving the reductive deposition of a Pt salt on a silver nanowire along with the oxidation of silver. However, one obtains dispersed nanotubes that are difficult to align or to attach to a support. Alternatively, the



**Figure 1.** Scanning electron microscopy (SEM) image of a Pt-coated, commercially available porous alumina membrane (Whatman, Anodisc).

tubes may be synthesized directly within the pores of a meso- or macroporous material. This approach has extensively been investigated by Martin and others.<sup>9–13</sup> Here, we report on a simple procedure that allows the large-scale production of Pt nanoshell tubes either aligned within a template or without support as a powder, for which only a syringe and a furnace are required. As an example, a commercially available circular alumina membrane<sup>14</sup> with a diameter of 25 mm and pores having a diameter of 200 nm, which was functionalized by coating the pore surfaces with Pt, is shown in Figure 1.

The method is based on the exploitation of the wetting phenomena.<sup>15–17</sup> A polymeric melt or solution that is allowed

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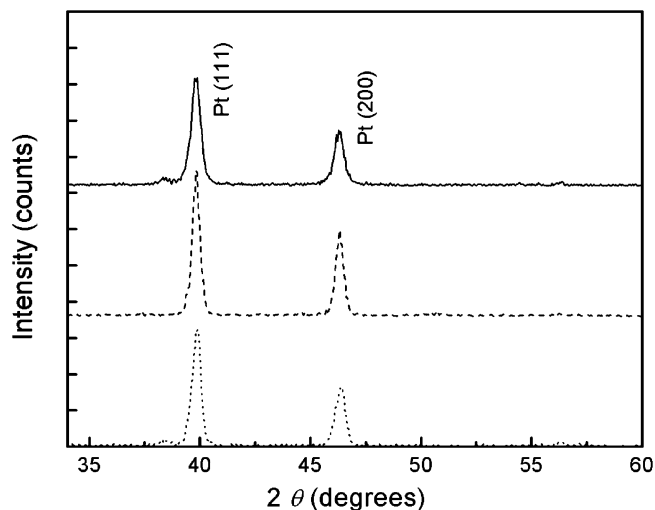
to spread on a meso- or macroporous material having a high surface energy will form a mesoscopic wetting layer on the pore walls. The strong adhesive forces<sup>18</sup> acting between the template material and the wetting liquid drive this process. A complete filling of the pore volume may occur due to cohesive forces. However, they are relatively weak, and they have to overcome the viscous forces of the wetting liquid. Consequently, this requires much more time than the rapid wetting of the walls. Quenching in order to preserve tubular structures within the pores might be accomplished by cooling below the solidification temperature of the polymer, or by the evaporation of a volatile solvent.

The polymeric liquid can be loaded with considerable proportions of low molar mass compounds. Metal tubes may be accessible via composite tubes containing a metal precursor. For example, we prepared palladium nanotubes with adjustable porosity<sup>19</sup> using polylactide (PLA)/palladium(II) acetate solutions that were originally introduced by Hou et al. to fabricate PLA/palladium composite nanofibers by electrospinning.<sup>20</sup> PLA completely degrades at elevated temperatures, and it can be removed by pyrolysis conveniently.<sup>21</sup> Template wetting with solutions containing PLA and a low molar mass compound acting as a metal source should be a promising and general route toward metallic tubes. First, the solutions are dropped on the template at ambient conditions. Subsequent annealing transforms the precursor into the respective metal and removes PLA. As a result, metal tubes remain within the template pores.

We have used both ordered porous alumina<sup>22–24</sup> and macroporous silicon (Si)<sup>25–28</sup> as templates to prepare the Pt nanoshell tubes. These two material systems have a high surface energy as required to conduct the wetting process. In contrast to commercially available disordered porous membranes, they feature a sharp pore size distribution, and the pore diameter is constant over the entire pore depth. Moreover, the pores are arranged in a regular lattice. Currently, the pore diameters of ordered porous alumina are adjustable to any value between 25 and 400 nm, while macroporous silicon covers the diameter range from 370 nm up to few microns.

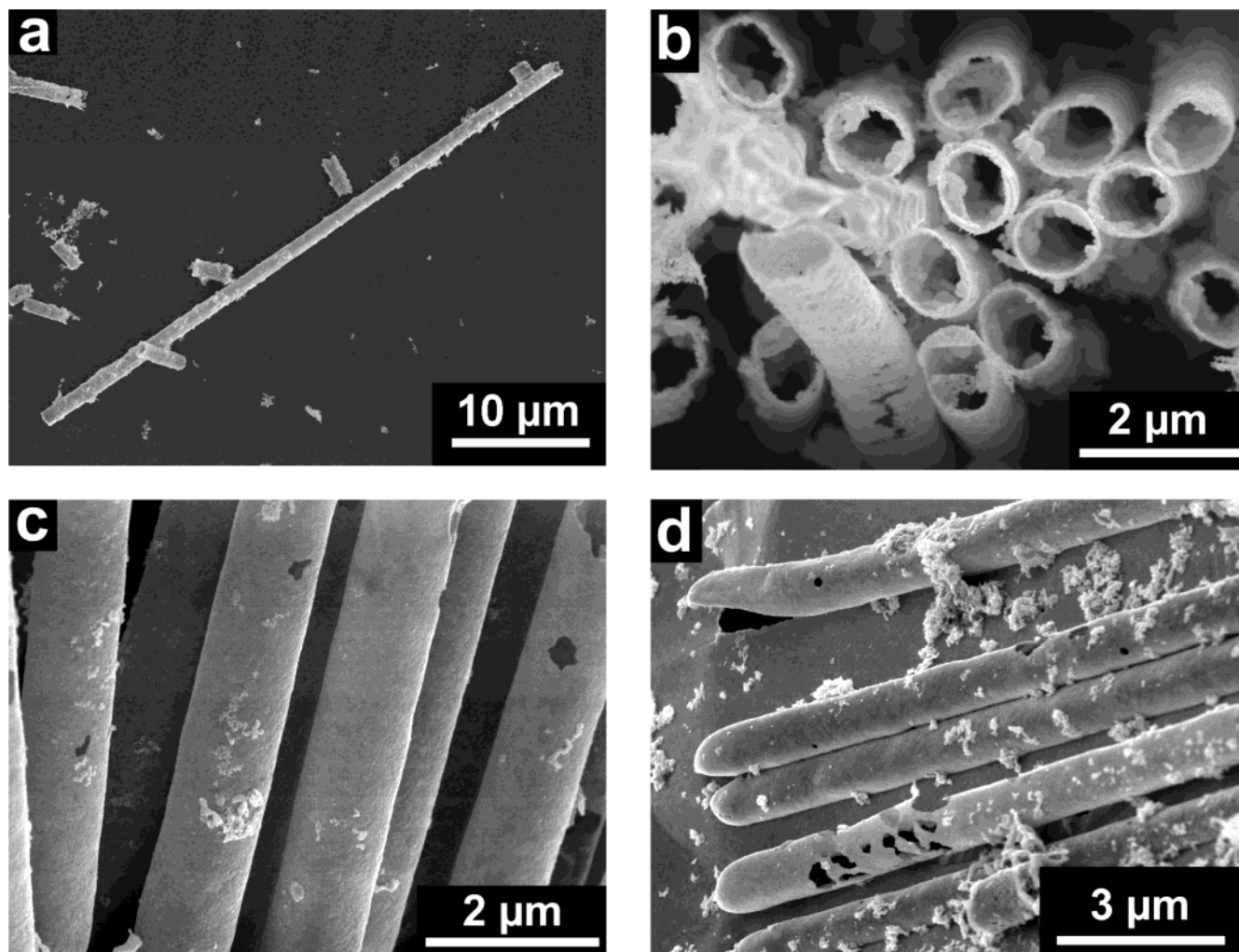
In the frame of this work, we will demonstrate that even “giant” Pt nanoshell tubes with a diameter of a micron can be made. Tubes having such dimensions are of particular interest for applications involving the flow of a medium through their interior. This is obvious from Hagen-Poiseuille’s law: the volume flow of the mobile medium depends on the fourth power to the tube radius. If Pt coated template pores having blind ends are employed as microreactors, it might be useful to have pore diameters in the micron range. This facilitates, for instance, the addressing of individual reactors, and the readout of the desired information. However, only smaller diameters are accessible with established preparation methods.

As Pt source, we used platinum bis(pentanedionate) (Pt-(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>2</sub>, Pt(acac)<sub>2</sub>) from Alfa Aesar. It was mixed with poly(D,L-lactide) (PDLLA) from Sigma-Aldrich at a ratio of 3:1, and dissolved in freshly distilled CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. The light yellow solutions were then dropped onto a macroporous silicon template at ambient conditions. After the solvent had



**Figure 2.** X-ray diffraction (XRD) pattern of macroporous silicon containing Pt nanoshell tubes that was annealed at 200 °C for 24 h, then at 350 °C for 1 h and finally at 600 °C for 1 h, measured at room temperature. The solid line denotes the diffractogram obtained after the first annealing step at 200 °C. The dashed line corresponds to the diffractogram obtained after the second annealing step at 350 °C, and the dotted line to that obtained after the third annealing step at 600 °C. One scale division on the intensity axis corresponds to 200 counts.

been evaporated, the solidified PDLLA/Pt(acac)<sub>2</sub> mixture formed a thin film covering both the pore walls and the surface of the template. The residual material on the template surface was carefully removed with a sharp scalpel. SEM investigations confirmed that the pore openings were uncovered. Pt(acac)<sub>2</sub> degrades at 200 °C along with a reduction of Pt(II) to Pt(0). Ostwald ripening results in the growth of Pt crystallites within the liquid PDLLA matrix. Eventually, the crystallites sinter and form a tubular structure that is stable even after the removal of the PLA and the template. To investigate the formation of the Pt crystallites, we annealed wetted macroporous Si (pore diameter = 1 μm) first at 200 °C for 24 h, then at 350 °C for 1 h, and finally at 600 °C for 1 h.  $\theta/2\theta$  scans (Figure 2) were performed in the reflection mode with a  $2\theta$  resolution of 0.05° and an integration time of 1 s subsequently to each annealing step. The sample was placed in the diffractometer in such a way that the aligned nanoshell tubes within the template were oriented parallel to the plane defined by the incident and the reflected X-ray beams. For all the XRD diffractograms shown in Figure 3, the reflections of platinum were assigned by using the JCPDS card No.04-0802. The first annealing step at 200 °C led to the formation of polycrystalline platinum within the PDLLA matrix. The (111) and the (200) reflections of face-centered cubic Pt occurred at  $2\theta = 39.88^\circ$  and  $2\theta = 46.38^\circ$ , respectively. Assuming a spherical shape of the crystallites, we estimated their size from the full widths at half-maximum of both reflections using the Debye–Scherrer method.<sup>29</sup> The diameter of the particles was of the order of 8 nm (Table 1). The subsequent annealing at 350 °C for 1 h removed the PDLLA completely. Moreover, the crystallite size increased significantly to 10 nm. For both diffractograms measured after annealing at 200 °C and 350 °C, the values of the crystallite sizes estimated from the two evaluated



**Figure 3.** SEM images of Pt nanoshell tubes prepared by annealing at 200 °C for 24 h and at 350 °C for 1 h. (a) Unsupported Pt nanoshell tube on a silicon substrate. (b) Top view of the openings of Pt nanoshell tubes emanating from a partially etched silicon template. The sample is contaminated with KOH. (c) Middle section of some aligned Pt nanoshell tubes. (d) Tips of Pt nanoshell tubes that are replicas of the blind ends of the pores.

**Table 1.** Crystal Sizes of Pt Nanoparticles within the Walls of Pt Nanoshell Tubes Obtained after the Successive Annealing Steps Estimated by Using the Debye–Scherrer Method

reflection	annealing temperature		
	200 °C	350 °C	600 °C
(111)	8.1 nm	10.0 nm	9.2 nm
(200)	7.7 nm	10.0 nm	8.0 nm

reflections coincide well. Contrary to our expectations, further annealing at 600 °C led to a decrease in crystallite size. We obtained values of 9.2 nm by evaluating the (111) reflection and 8 nm by evaluating the (200) reflection. We speculate that mechanical stress occurring during cooling to room temperature could have disturbed the crystal structure.

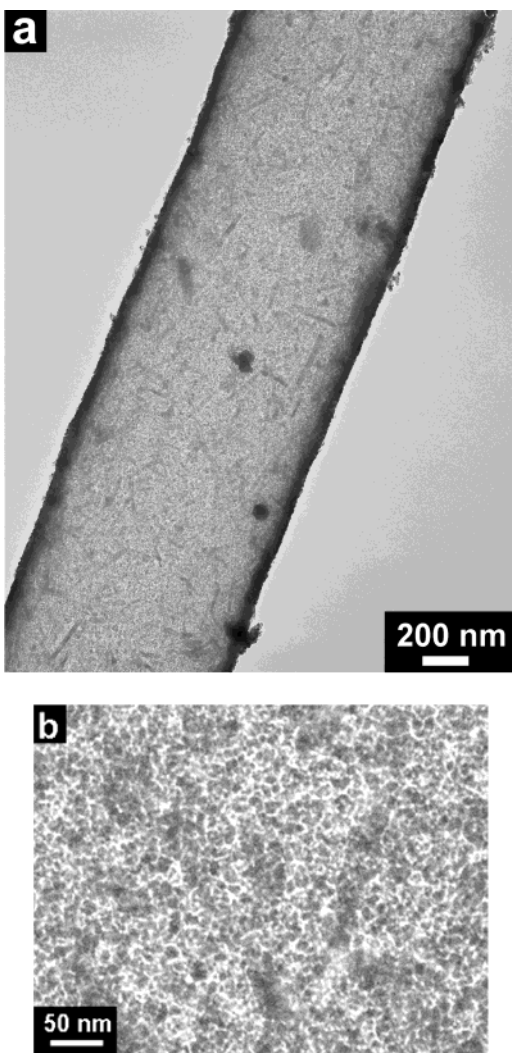
To investigate the morphologies of the Pt nanoshell tubes, we removed the silicon templates selectively by treating them with 30 wt % aqueous KOH at 90 °C. They formed a black precipitation, which was carefully washed with diluted HCl and deionized water for several times. Eventually, the Pt nanoshell tubes were suspended in water by sonification. The suspension was then dropped onto a highly conductive silicon

wafer for SEM investigations or onto copper grids coated with a thin carbon film for transmission electron microscopy (TEM) investigations. Note that KOH contaminations are still present, despite the applied cleaning protocol. This is particularly obvious from Figure 3b.

Figure 3 shows SEM micrographs of Pt nanoshell tubes lying on silicon substrates prepared by annealing the Pt/PDLLA composite tubes at 200 °C for 24 h and subsequently at 350 °C for 1 h. The silicon template was etched either partially or completely. An individual Pt nanoshell tube with an aspect ratio of 50 is depicted in Figure 3a. The openings of Pt nanoshell tubes that are partially embedded in the macroporous silicon matrix are shown in Figure 3b. Using the image analysis program DIPS we estimated the thickness of the pore walls to approximately 40 nm. Figure 3c shows the middle sections of some aligned Pt nanoshell tubes. Figure 3d represents their capped tips, which are exact replicas of the blind ends of the template pores. The Pt nanoshell tubes have smooth walls showing only few defects.

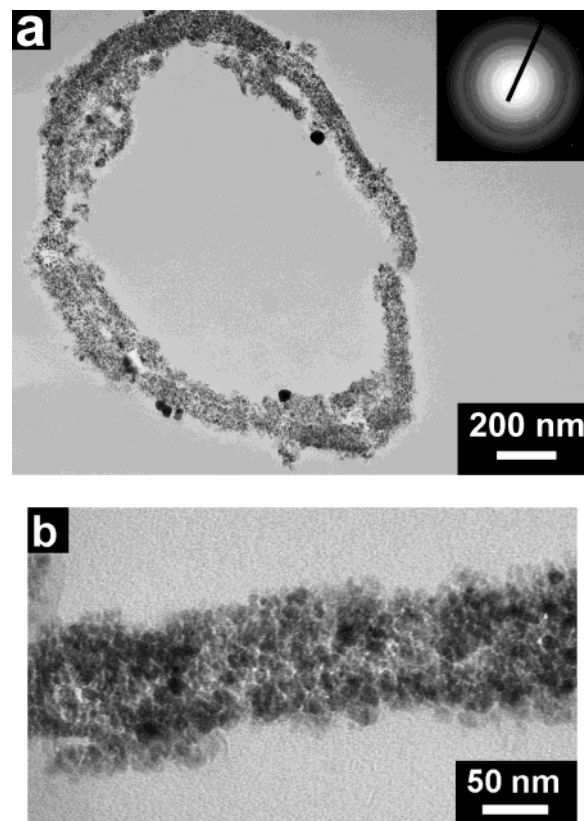
Whereas SEM yields information on the surface topology, TEM allows gaining information on the internal wall





**Figure 4.** (a) TEM micrograph of a Pt nanoshell tube. (b) Detail of the tube wall.

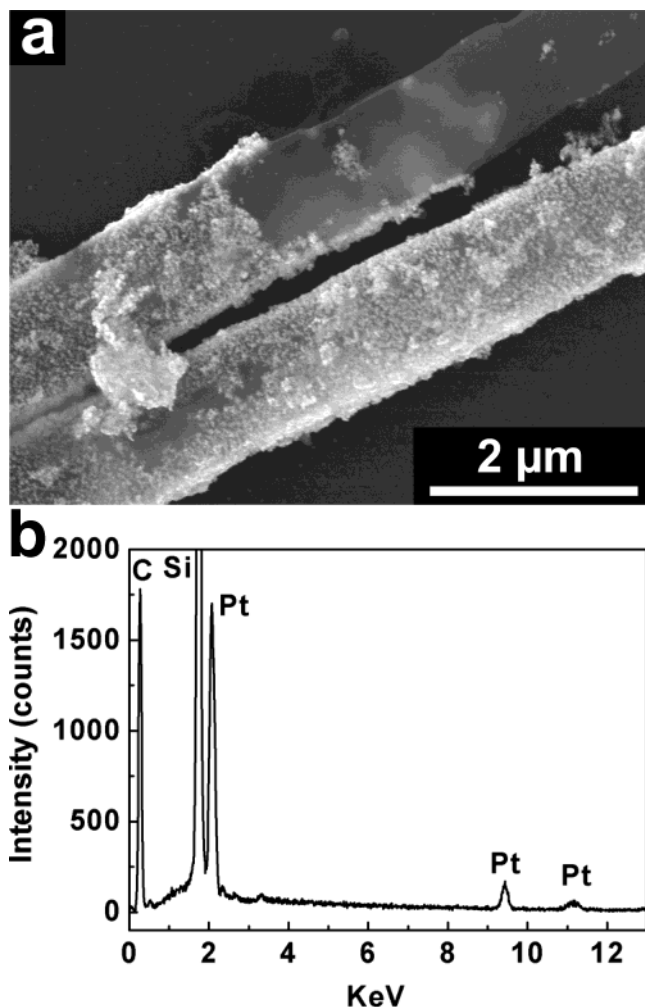
structure. A TEM micrograph of a Pt nanoshell tube at low magnification is shown in Figure 4a. Figure 4b depicts a part of the wall at a higher magnification. It is composed of nanoparticles with a size of the order of 8–10 nm, which is in line with the data obtained by evaluating the XRD measurements with the Debye–Scherrer method. Furthermore, we have investigated sections of Pt nanoshell tubes embedded in epoxy resin. Slices measuring 70 nm or thinner were prepared using an ultra-microtome equipped with a diamond knife. The slices were transferred onto carbon-coated copper TEM grids. Figure 5a shows the bright field TEM micrograph of a cross-section of a Pt nanoshell tube. The corresponding selected-area electron diffraction yielded multiring patterns (inset of Figure 5a), confirming the polycrystalline nature of the nanoshell tubes. Figure 5b displays the tube wall at a higher magnification. It is obvious that it consists of sintered Pt nanoparticles. However, the wall thickness cannot be estimated from Figure 5 since the shape of the nanoshell tube was considerably deformed during preparation. Moreover, for a precise measurement of the thickness, the angle between the plane of the section and the long axis of the tube had to be adjusted to 90°. Since



**Figure 5.** (a) TEM micrograph of an ultrathin slice showing the cross-section of a Pt nanoshell tube embedded in epoxy resin. The inset displays the corresponding selected-area electron diffraction pattern. (b) Detail of the tube wall at higher magnification.

the Pt tubes having diameters in the micron range have a nanostructured wall, they represent a hierarchical system that combines features in the 10 nm and in the micron range.

To improve the mechanical properties of the Pt nanoshell tubes and to reduce their tendency to precipitate, a second reinforcing layer consisting of a material having a lower density than Pt can be added. Pt has a surface energy that is sufficiently high to secure the wettability of templates having Pt-coated pore walls by polymeric liquids. We dropped a solution of polystyrene (PS) dissolved in chloroform on a macroporous silicon template containing Pt nanoshell tubes within its pores. The sample was then annealed for 1 h at 100 °C to accomplish the formation of a defect-free PS wetting layer on the inner surface of the Pt nanoshell tubes. As a result, we obtained core/shell tubes consisting of a Pt shell and a PS core (Figure 6a). This architecture might be advantageous for unsupported nanoshell tubes, because the Pt shell is exposed to the surrounding medium. Sonification resulted in the partial removal of the Pt shell, so that the PS core was partially uncovered (the upper tube in Figure 6a). Energy-dispersive X-ray microanalysis (EDX) was used to verify the presence of Pt and PS. As expected, the  $K_{\alpha}$  carbon peak at 0.3 keV indicating the presence of PS and three Pt peaks (2.1 keV:  $M_{\alpha}$ ,  $M_{\beta}$ ; 9.4 keV:  $L_{\alpha}$ ; 11.2 keV:  $L_{\beta}$ ) were detected. The most intensive silicon peak (1.7 keV:  $K_{\alpha}$ ,  $K_{\beta}$ ) originates from the silicon wafer on which the core/shell tubes were placed.



**Figure 6.** (a) SEM image of core/shell nanoshell tubes composed of an inner PS core and an outer Pt shell. Top right, the PS core is partially uncovered. (b) Corresponding EDX spectrum.

In conclusion, we have presented a simple and convenient preparation method for platinum nanoshell tubes with nanostructured walls consisting of sintered Pt nanoparticles. It involves wetting ordered porous templates exhibiting a high surface energy with solutions containing PDLLA as a sacrificial polymer and the Pt precursor  $\text{Pt}(\text{acac})_2$ . Both porous membranes having Pt coated pore walls and unsupported Pt nanoshell tubes are accessible. They may have large diameters of the order of 1 micron. Such tubes should be of considerable interest for applications in the fields of catalysis or electrochemistry.

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