Fabrication of ordered Nanotubes and Nanowires in a Biopolymer Template

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Introduction

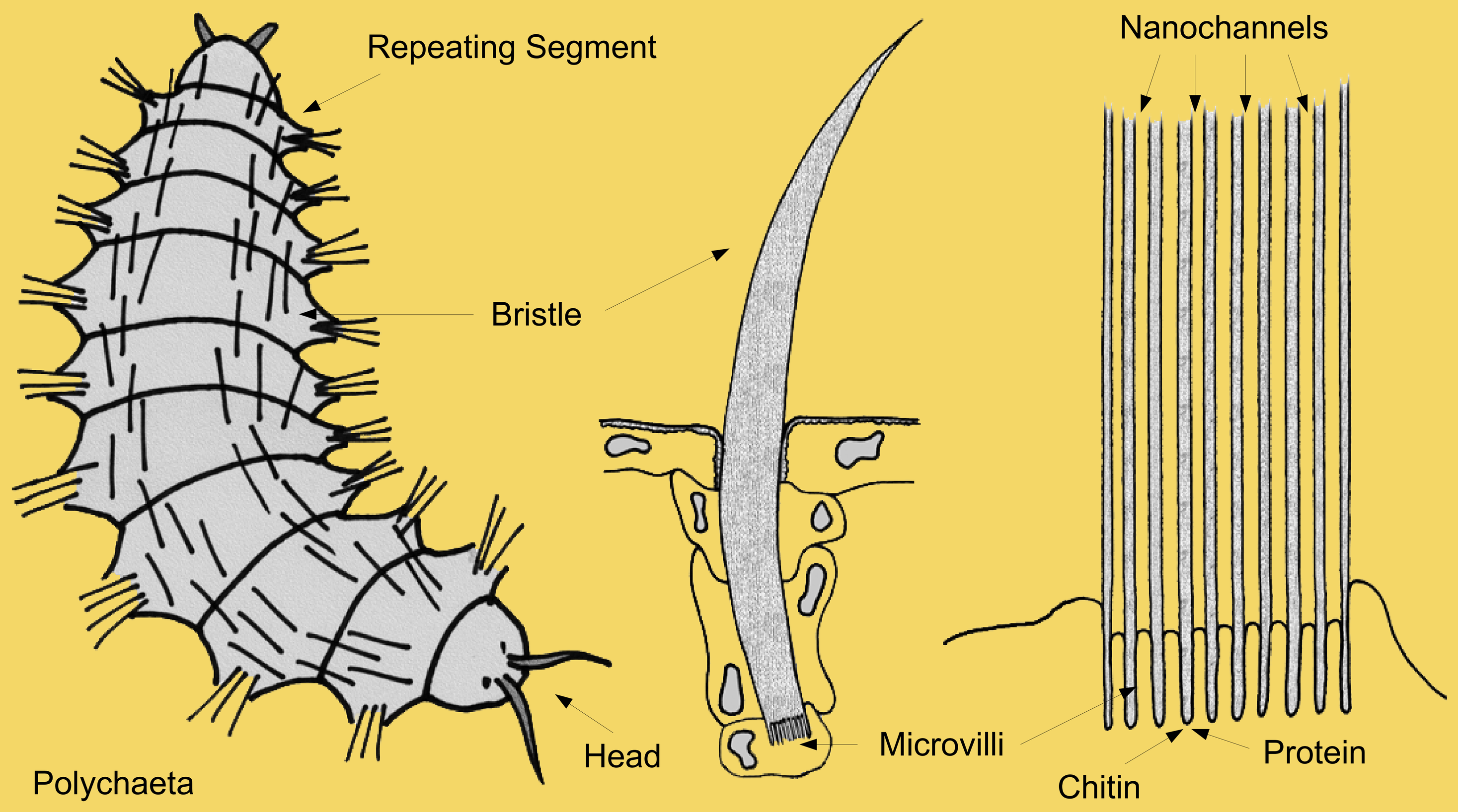
Nanotubes and Nanowires are fabricated in a chitin/protein-template composed of ordered, high aspect ratio nanochannels.

Main components of the template are readily available from nature as part of the bristles of the marine worm *Aphrodita Aculeata* (class polychaeta, common name: sea mouse).

Bristle Formation in Polychaetes

Polychaetes are widespread marine worms covered with many bristles (called chaetae, thus the name). These bristles are formed by secretion of chitin and protein at the base of cylindrical cell membrane extensions called microvilli.

During growth, the bristles are pushed upwards by newly secreted material, leaving behind empty nanochannels in those regions, which were prior adopted by the microvilli [1].



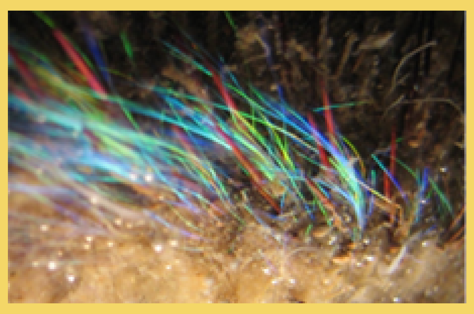
The Sea Mouse Spine

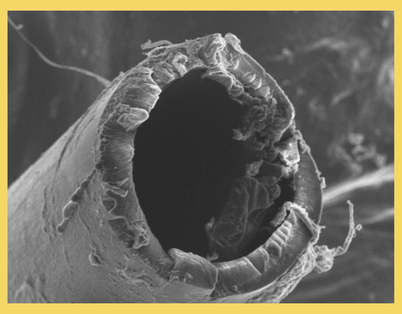
The polychaete we use is the sea mouse. It is covered with two types of bristles: spines and hairs. The spines consist of a hollow core with a varying diameter surrounded by a wall, which is permeated by the nanochannels. These are ordered in a densely packed, hexagonal array. They have a diameter of about 150 nm with a length of up to 2 cm.

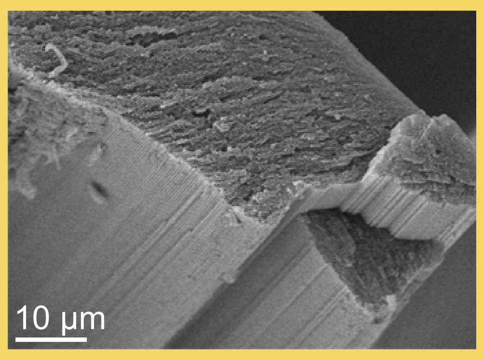
The precise order of the channels is necessary, as the sea mouse uses their arrangement to produce a photonic crystal effect, which creates the red, iridescent appearance of the spines [2].

The hairs are composed of even narrower nanochannels, but in contrast to the stiff spines, they are very thin and flexible and, thus, hard to handle, so this work is focused on the spines.

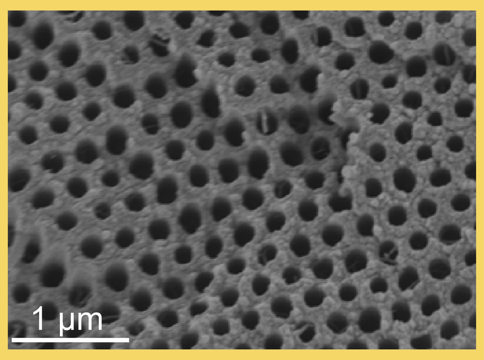

Sea Mouse


Spines (red) and hairs (blue / green)

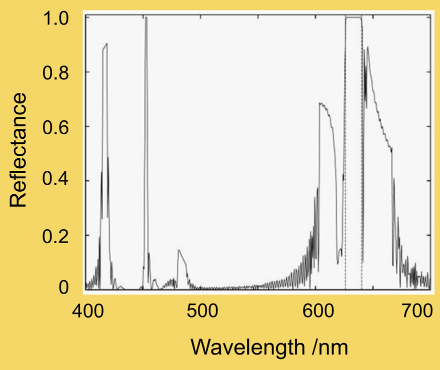

Spine closeup



Spine Wall



Channel Allignment



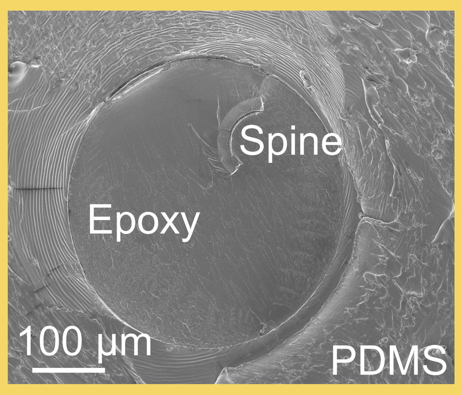
Photonic Crystal Effect [2]

Template Fabrication

The spines are embedded in epoxy which is surrounded by poly(dimethyl siloxane) (PDMS). To avoid filling problems in the hollow core, split spines, which were cut along their length-axis, were used.

The resulting biocomposit/silicone polymer templates are about a few millimeter in length, width, and height.

After nanostructure fabrication, the templates are removed mechanically and by heat decomposition.

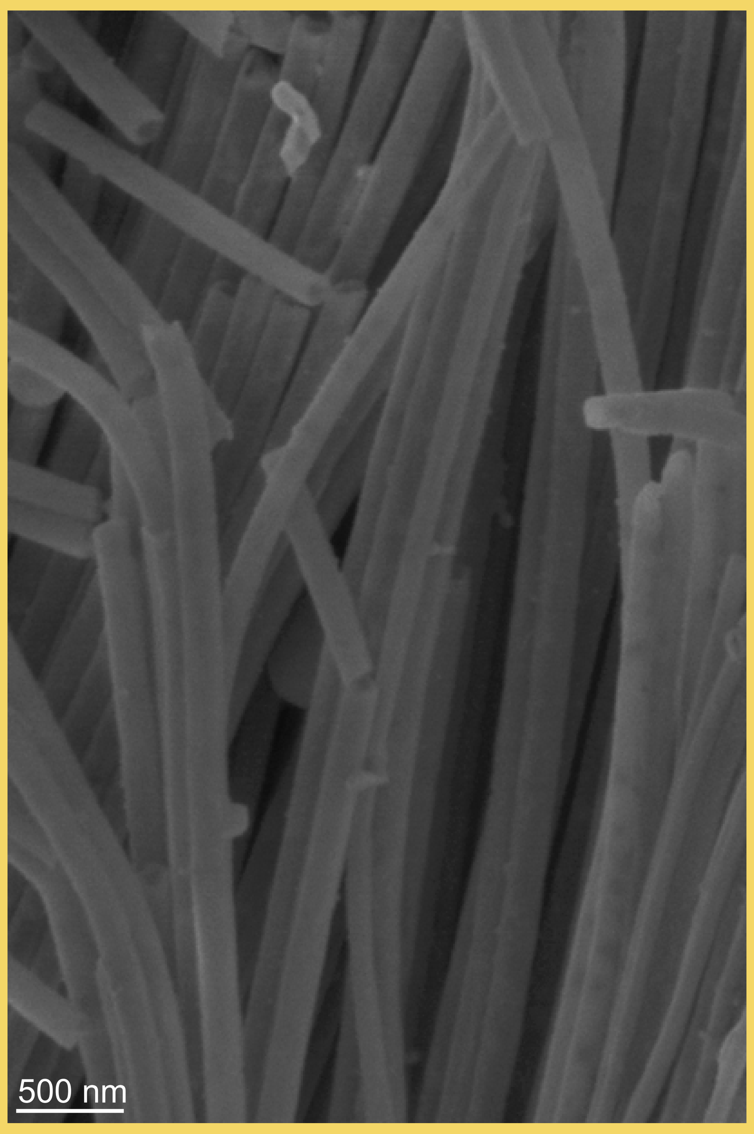


Nanotubes

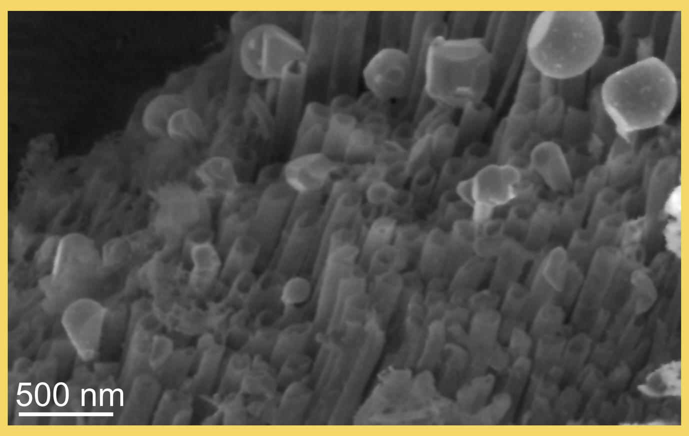
Nanotubes were fabricated in the templates using atomic layer chemical vapour deposition.

To produce Al_2O_3 nanotubes with 20 nm wall thickness, 250 deposition circles were conducted at 150 °C using trimethylaluminium and water as precursors. Pulse and purge durations of 0.2 s and 60 s, respectively were used.

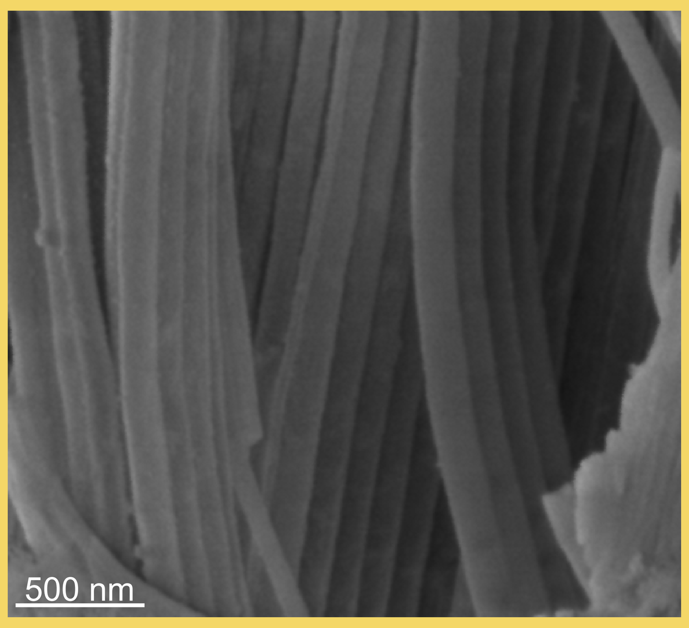
This part is a cooperation with the department of inorganic chemistry at the university of Helsinki.



Al_2O_3 Nanotubes, side view



Al_2O_3 Nanotubes, top view

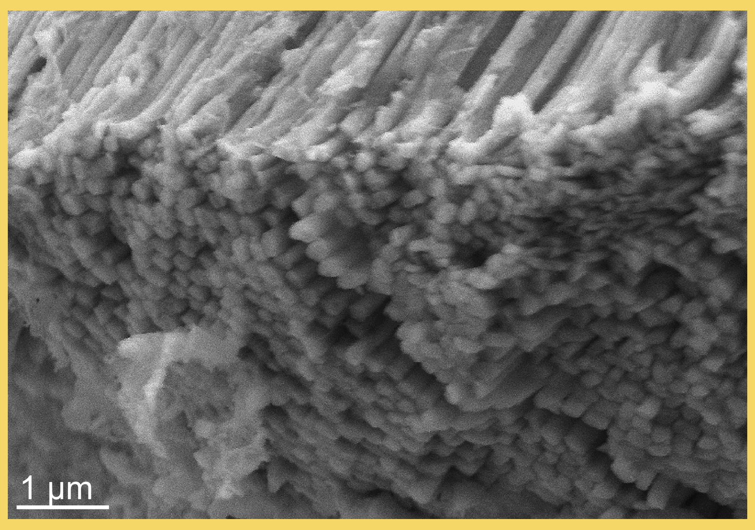


Al_2O_3 Nanotubes, side view

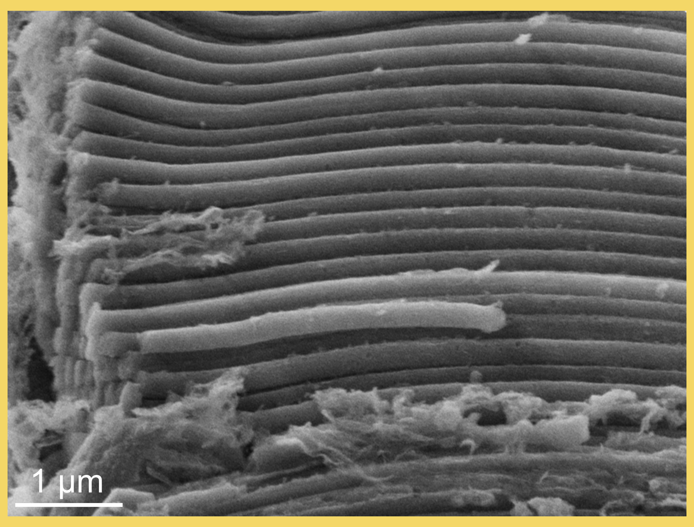
Nanowires

Nanowires were produced by electrodeposition, for which a thin platinum film was sputtered on one side of the template. The film was connected to an electrode by conductive silver-epoxy and isolated with silicone.

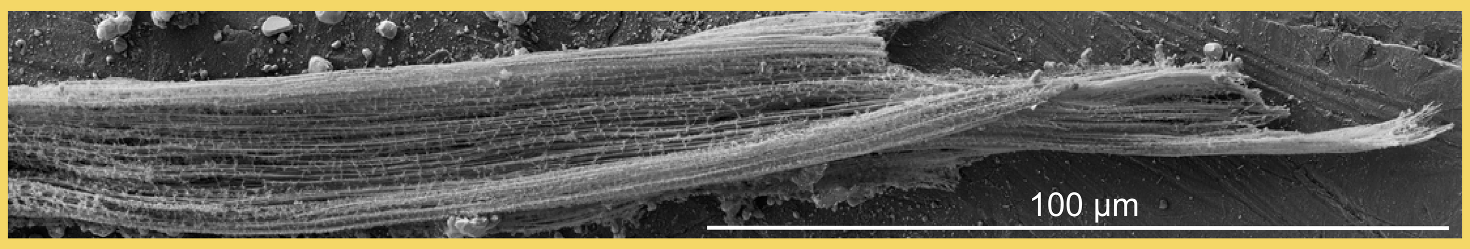
$CuSO_4$ and H_2SO_4 at 50 °C as well as $ZnCl_2$ and KCl in combination with bubbling air at 80 °C were used as electrolytes to deposit copper and ZnO.



ZnO Nanowires, top view



ZnO Nanowires, side view



Cu Nanowires in a partially decomposed template

Conclusions and Outlook

It is possible to use the chitin/protein structure, which is naturally formed in the spines of sea mice, as key component in a nanofabrication template. As the channels in the spines are up to two centimetre in length, this might be a way to fabricate high aspect ratio nanotubes and nanowires.

The main challenge at this point is the total removal of the template, without loosing or destroying the produced nanostructures.

Acknowledgments

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References

1. Hausen, H. *Hydrobiologia* **535**, 37-52 (2005).
2. Parker, A. R., McPhedran, R. C., McKenzie, D. R., Botten, L. C., and Nicorovici,N. A. P. *Nature* **409** (6816), 36-37 (2001).

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