Nanoparticle Nanotubes (NPNTs): Formation Mechanism and Special Structures

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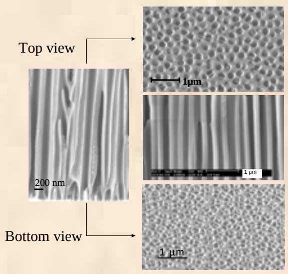
Our group has presented a method for template synthesis of metallic nanotubes using ca. 14 nm citrate-stabilized Au, Ag and Pd nanoparticles (NPs) as building blocks. The nanoparticle nanotubes (NPNTs) are produced by passing a NP solution through the pores of aminosilane-modified nanoporous alumina membranes. Here the mechanism of NPNT formation is investigated by studying the influence of various parameters on tube preparation and properties. The fabrication apparatus was modified to provide better control over preparation parameters, i.e., flow rate, flow direction, and intermittent drying. It was found that periodic intermittent drying of the accumulating NPs facilitates formation of NPNTs with low defect concentration and increases the average length of the free-standing tubes. Decreasing the stability of the initial NP solution allowed preparation of NPNTs using small (ca. 4 nm) Au NPs. Passing of different colloid solutions in series enabled fabrication of core-shell NPNT structures comprising Au NPs of different sizes (4 nm and 14 nm) as well as Au-Pd core-shell tubes.

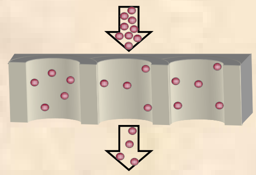
Alumina membrane:

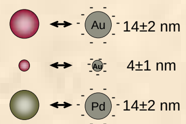


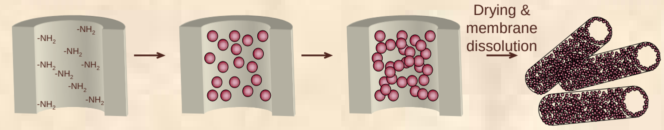
Pore diameter: ca. 220 nm

Membrane thickness: ca. 60 µm

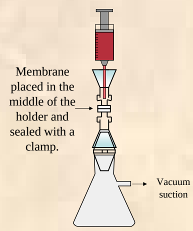
Colloid solution comprising citrate-stabilized metal NPs is passed through alumina membrane







Experimental setup for NPNT preparation:



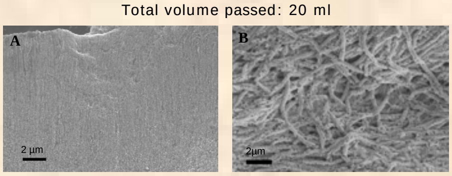
Advantages of the NPNT fabrication apparatus

- Low-vacuum operation possible.
- Flow direction can be reversed.
- Direct control of the flow rate.
- Convenient measurement of solution volume passed.
- Stable and uninterrupted flow of feed solution.
- Air admittance possible between liquid injections.

Influence of the preparation parameters on tube formation – 14 nm Au NPs

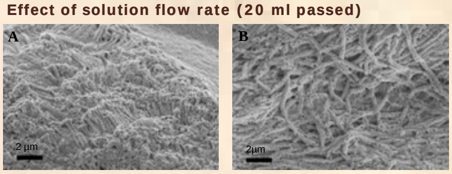
Effect of intermittent drying during NPNT formation

Total volume passed: 20 ml



(A):No intermittent drying. (B): Intermittent drying after every 1 ml of solution passed through the membrane.

Effect of solution flow rate (20 ml passed)

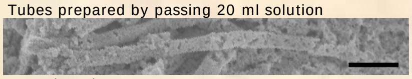


(A): Flow rate: 5 ml/min. (B): Flow rate: 2.2 ml/min

Intermittent drying was applied in both cases.

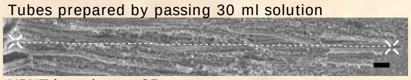
Effect of solution volume (Both bars are 1 µm)

Tubes prepared by passing 20 ml solution



NPNT length: ca. 7 µm.

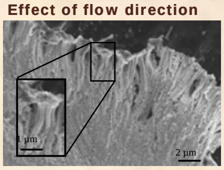
Tubes prepared by passing 30 ml solution



NPNT length: ca. 25 µm

Intermittent drying was applied in both cases.

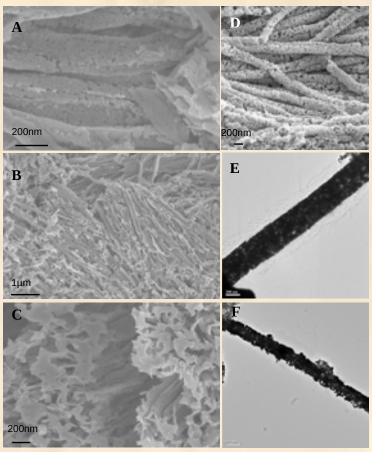
Effect of flow direction



NPNTs prepared by passing 20 ml Au colloid solution with alternating directions every 1 ml and intermittent drying.

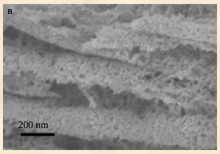
Uniform NPNTs from 14-nm Au NPs

A total amount of 30 ml 14-nm Au NP solution was passed through the silanized membrane at an initial flow rate of 2.2 ml/min: 20 ml in one direction, with air admittance every 1 ml; then 10 ml in the opposite direction, using the same flow rate and drying regimen. The tubes show a uniform structure with relatively few defects.



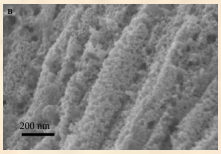
SEM images of uniform NPNTs at different magnifications (A, B); top view, (C); defects along the tube walls, (D); TEM images of uniform NPNTs (E: bar 200 nm, F: bar 0.5 µm).

NPNTs from 4-nm Au NPs



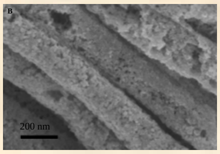
NPNTs prepared from dilute Au NP solution

Total volume passed: 480 ml.



NPNTs prepared from x2 concentrated NP solution

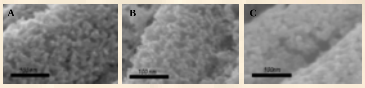
Total volume passed: 190 ml.



NPNTs prepared from 4-nm Au NP solutions destabilized with 1 M NaCl

Total volume passed: 85 ml.

Large magnification of NPNTs made from:

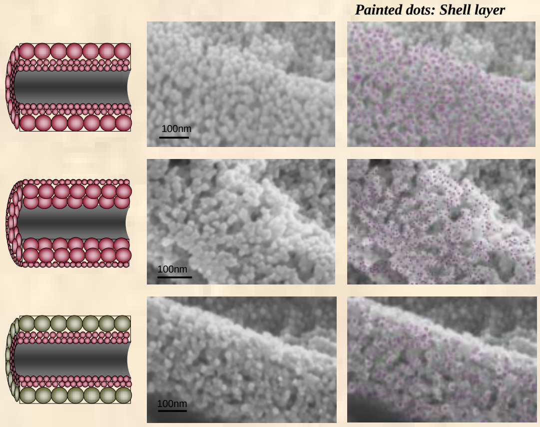


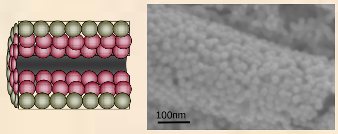
(A): Dilute solution, (B): Concentrated solution, (C): Destabilized solution.

Ideal Core-Shell structure

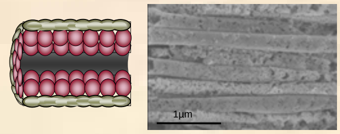
Actual NPNT Core–Shell structure

Painted dots: Shell layer





Core and shell cannot be distinguished by imaging microscopy (same NP size).



14 nm Pd NPs, annealed (17 h, 350ºC) + 14 nm Au NPs.

EDS results for bimetallic core-shell NPNTs

Tube structure		Atomic %	
Shell	**Core**	**Palladium**	**Gold**
14-nm Pd NPs	4-nm Au NPs	45	55
14-nm Pd NPs	14-nm Au NPs	33	67
14-nm Pd NPs (annealed)	14-nm Au NPs	36	64

Conclusions

- Template-synthesis of metallic NPNTs from NP solutions is affected by solution volume, flow rate, flow direction, and intermittent drying. Periodic drying of the accumulating NPs by intermittent air admittance facilitates the formation of stable NPNTs.
- Increase of the average length of the free-standing NPNTs and low defect concentration were achieved by controlling the preparation parameters.
- Stable, self-sustained NPNTs were produced from Au NPs of different diameters, i.e., 14 nm and 4 nm.
- Destabilization by adding NaCl to 4-nm Au NP solution decreased the solution volume needed for NPNT formation and improved the uniformity of the NPNTs, attributed to enhanced NP aggregation and coalescence from the destabilized colloid.
- NPNT synthesis proceeds in two stages: (1) Primary binding of a NP monolayer via electrostatic interactions with the aminosilanized membrane walls; (2) NP aggregation and coalescence, leading to a NP multilayer and a self-sustained tubular structure after membrane drying and dissolution.
- Understanding the two-stage mechanism enabled the formation of core-shell NPNT structures exhibiting radial variation in NP size and composition (core-shell tubes).