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Layered Nanoparticle Nanotubes (NPNTs)

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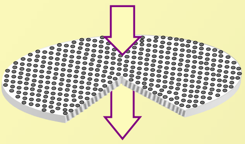
Abstract

Our group recently presented a new method for template synthesis of metallic nanotube structures using citrate-stabilized Au, Ag, and Pd nanoparticles (NPs) as building blocks. The new kind of nanotubes, denoted nanoparticle nanotubes (NPNTs), are produced by passing the NP solution through the pores of aminosilane-modified nanoporous alumina membranes. The NPs bind electrostatically to the pore walls and accumulate as multilayers, followed by spontaneous room-temperature coalescence of the NPs to form solid nanotubes. Single-metal (Au, Ag) and composite (Au-Ag, Au-Pd) NPNTs were synthesized by this method. The NPNTs retain the NP morphology, showing high corrugation, porosity, and electrical conductivity. Detailed structural analysis revealed formation of metallic interfaces between the NPs with lattice continuation.

The above synthetic scheme opens the way to the preparation of a variety of new tubular nanomaterials, some of which are described in the present study. The possibility to vary the size of the NP building blocks, thus controlling the nanotube porosity, was explored by comparing Au NPs of 4±1 nm average diameter to the originally used 14±2 nm Au NPs as the starting colloid. The kinetics of NP accumulation and nanotube formation are different for the two NP sizes tested. The smaller NPs tend to form less dense structures, and the resulting NPNTs are more porous and fragile. Layered NPNT structures were prepared by binding of ca. one monolayer of NPs of one type to the membrane walls followed by accumulation of NPs of another type (size, metal). High-resolution scanning electron microscopy (HRSEM) imaging suggests the formation of core-shell NPNT structures with a radial gradient of properties.

Colloid solution of citrate-stabilized metal NPs

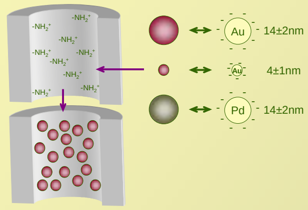


Alumina membrane pre-treated with aminosilane

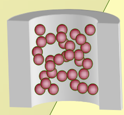
Pore diameter: ca. 220 nm

Thickness: ca. 60 µm

1st NP layer: Electrostatic interaction



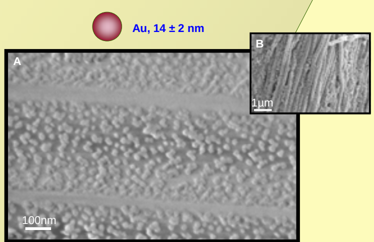
Subsequent NP layers: Aggregation + coalescence



HRSEM Images

A: 1st NP layer on membrane walls
(5 ml of NP solution passed)
NP density: 9.3×10^{10} NPs/cm^2

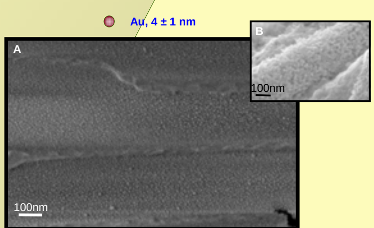
B: Self sustained NPNTs after coalescence and membrane dissolution
(18 ml of NP solution passed)



Using small Au NPs:
Highly porous NPNTs

A: 3.5 ml NP solution passed
NP density: 4.4×10^{10} NPs/cm^2

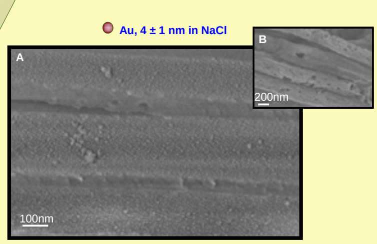
B: 200 ml of NP solution passed



Using small Au NPs, destabilized in 1M NaCl solution:
More uniform NPNTs, due to more facile NP coalescence

A: 6 ml NP solution in NaCl passed
NP density: 7.7×10^{10} NPs/cm^2

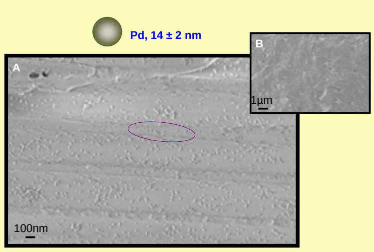
B: 75 ml of NP solution passed



Formation of low-quality Pd NPNT fractions

A: 5 ml NP solution passed
NP density: Not determined, due to NP detachment

B: 18 ml of NP solution passed

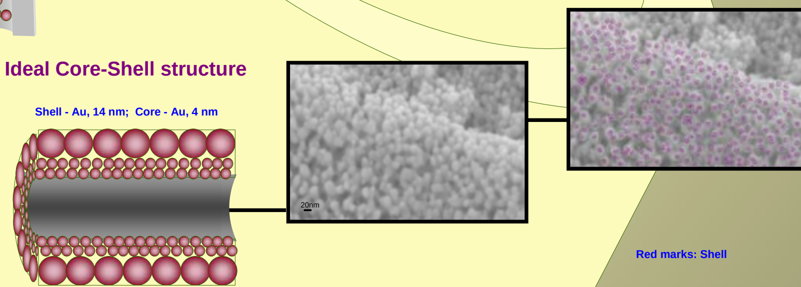


Ideal Core-Shell structure

Actual NPNT Core–Shell structure

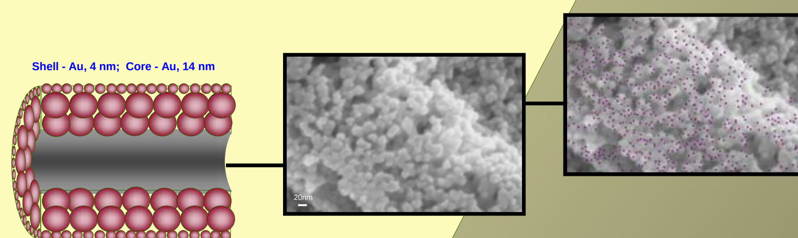
The two-stage mechanism enables to combine different kinds of NPs to form self-sustained core–shell NPNTs

Shell - Au, 14 nm; Core - Au, 4 nm

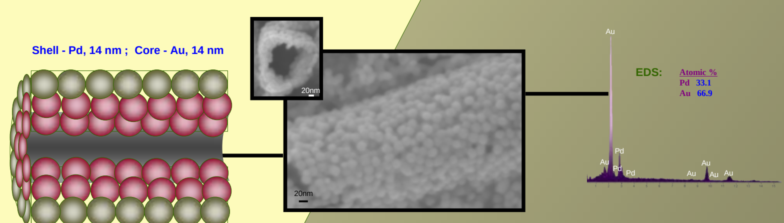


Red marks: Shell

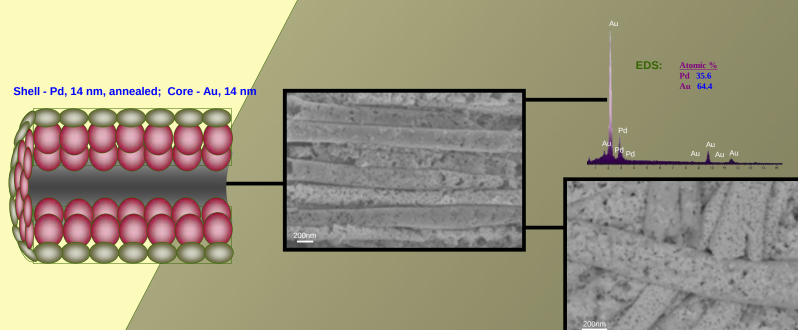
Shell - Au, 4 nm; Core - Au, 14 nm



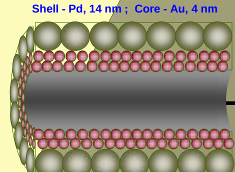
Shell - Pd, 14 nm ; Core - Au, 14 nm

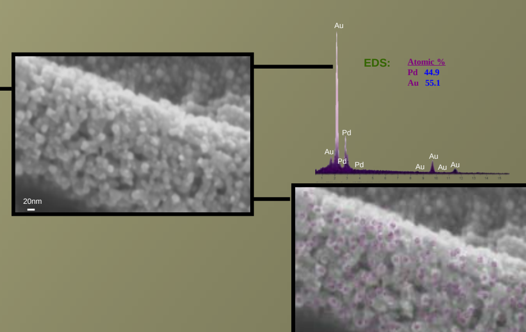


Shell - Pd, 14 nm, annealed; Core - Au, 14 nm



Shell - Pd, 14 nm ; Core - Au, 4 nm





Conclusions

- **Au nanoparticles (NPs) of different diameters can be used to form self-sustained nanoparticle nanotubes (NPNTs). Use of Pd NPs results in poor coalescence and sporadic tubular fractions.**
- **NPNT synthesis proceeds in two stages: 1) Primary binding of a NP monolayer via electrostatic interactions with the modified membrane walls, with a NP density comparable to citrate-stabilized NP films on surfaces; 2) NP aggregation and coalescence, leading to a NP multilayer and a self-sustained tubular structure after membrane dissolution.**
- **Addition of electrolyte (NaCl) to the 4 nm Au NP solution decreases the solution volume needed for NPNT formation, and improves the uniformity of the NPNTs obtained. This is attributed to destabilization of the NPs in solution and enhanced coalescence.**
- **The two-stage mechanism enables formation of core-shell NPNTs showing radial gradients of NP size and composition.**