Template Synthesis of Nanoparticle Nanotubes

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Abstract

A method is presented for template synthesis of metallic and composite nanotubes using citrate-stabilized Au, Ag and Pd nanoparticles (NPs) as building blocks. The nanoparticle nanotubes (NPNTs) are prepared by passing a NP solution through the pores of ammine-modified nanoporous alumina membranes. The NPs bind to the exposed amine groups and aggregate on the pore walls. Upon drying the aggregated NPs undergo spontaneous room-temperature coalescence to form solid, porous, multi-layered nanotubes. The alumina membrane template can be dissolved, to yield self-sustained NPNTs. The NPNTs comprise a new class of template-synthesized, NP-based nanotubes possessing unique features such as room-temperature preparation, mechanical stability, highly corrugated wall structure, and electrical conductivity. Composite NPNTs were synthesized using mixed Au-Pd colloid solutions.

The NPNT preparation scheme was also combined with sol-gel synthesis of TiO2-composite NPNTs are produced by passing a citrate-stabilized Au, TiO2-metal NTs are thus prepared and structurally characterized. The composite TiO2-metal NTs are of interest as components of photochemical and photoelectrochemical systems.

Conclusions

A novel kind of Au, Ag nanotubes (nanoparticle nanotubes, NPNTs) were synthesized by passing a citrate-stabilized metal colloid solution through the pores of ammine-modified nanoporous alumina membranes.

† The Au, Ag nanoparticles (NPs) stick to the pore walls and undergo spontaneous coalescence to form solid, multi-layered nanotubes.

‡ Self-sustained NPNTs are obtained by dissolution of the membrane template.

‡ Pd NPs do not form solid NPNTs using the same methodology. However, self-sustained 1:1 composite Au-Pd NPNTs are readily obtained.

‡ TiO2 nanotubes can be prepared by sol-gel-template synthesis.

‡ Oxide-metal NTs were prepared by applying the NPNT synthetic scheme to previously prepared TiO2 NTs.

‡ The NPNTs are highly porous, mechanically stable, electrically conducting.

‡ The mechanism of NPNT formation involved removal of stabilizer molecules and actual room-temperature coalescence of adjacent NPs to form metallic interfaces. The process is assisted by the drying step.

References


SEM images (different magnifications) of nanotubular titania structures prepared by surface sol-gel template synthesis in NAMs. TiO2 precursor solution and 0.15 M HCl were alternately passed through the membrane for one minute, followed by ethanol wash. The solutions were repeatedly passed 5 times (A) or 8 times (B).

SEM images showing top view (A) and cross-section (B) of a silanized nanoporous alumina membrane (Whetman, 200 nm).

ESEM images showing top view (A) and cross-membrane (Whatman, shown at different magnifications. The nanoparticle nanotubes (NPNTs) are seen clearly in (B).

HRTEM images showing Au NP interfaces, obtained by drying a drop of NPNT (A, B) or NP (C) solution on a carbon-coated TEM grid. Formation of metallic interfaces with lattice continuity is seen.

HRTEM images showing Au NP interfaces, obtained by applying a drop of NPNT solution on a carbon-coated TEM grid.

HRTEM image showing Pd NP interfaces, obtained by applying a drop of NPNT solution on a carbon-coated TEM grid.

HRTEM image showing Au NP interfaces, obtained by applying a drop of NPNT solution on a carbon-coated TEM grid.

HRTEM image showing Au NP interfaces, obtained by applying a drop of NPNT solution on a carbon-coated TEM grid.

TEM image of the TiO2-Pd interface, showing the TiO2 outer layer and the Pd NP morphology.

Energy-Filtering TEM (EFTEM) (A) zero-loss image of the NPs in Au-Pd NPNT fragment. (B) Pd map (385-405 eV) of the same fragment: Pd NPs appear bright. (C) HRTEM magnified image of the area marked in A and B, showing Au and Pd NPs and emphasizing NP coalescence.