TiO₂ Nanotubes Encapsulating Silver Nanoparticles

B.M. Rabatic,*** Z.V. Saponjic,** A. Petford-Long,*** and T. Rajh**

- * Center for Nanoscale Materials, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439
- ** Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439 *** Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439

Heterogeneous nanoscale inorganic-inorganic materials provide the opportunity to study a wide range of physical, electrical and optical properties, not commonly accessible with their bulk counterparts. Unfortunately, producing a nanoscale system to confine nanometer scale materials within discrete structures poses a considerable synthetic challenge. Carbon nanotubes have historically been the material of choice for encapsulating metallic and semiconductive inorganic materials to form heteronanostructures. Here, we report a method of incorporating metallic nanostructures within a high dielectric material consisting of one-dimensional titanium dioxide (TiO₂) nanotubes. Our methodology uses a liquid diffusion, template-based approach to generate binary inorganic 1-D nanostructures consisting of a scrolled tube of TiO₂ containing particles of Ag metal within its central core.

We find that the addition of the low bidentate molecule (L-ascorbic acid 6-palmitate) to the surface of the TiO_2 nanotubes is sufficient to act as a phase transfer agent. Upon binding of this amphiphilic molecule to TiO_2 , dispersion of the inorganic/organic hybrid from water into hexane is possible. As this occurs, water becomes trapped within the interior (hydrophilic) region of the TiO_2 . To this, we use mixed phase agitation process to deliver silver ions to the central core of the nanotube. After diffusion of ions into the hydrophilic core, light is used to induce the reduction of the ions into silver metal resulting in a plug of material confined to the interior core of the TiO_2 tube. From our studies we have found an indirect correlation between the amount of organic modifier added to the TiO_2 tube surface and the efficiency of filling.

We utilized electron energy loss spectroscopy (EELS) to image the interaction of silver surface plasmon resonances with TiO₂. Interesting optical phenomena become accessible when the conductive metal is present within the interior of the scrolled TiO₂ tubes. We find a pronounced dampening of the silver surface plasmon takes place as the metal is encapsulated within the TiO₂ template. We postulate that the observed dampening is an effect of polarization coupling between the silver metal and surface modified TiO₂. We envision this hybrid binary nanocomposite consisting of semiconductor wrapped metal nanoparticle could have influences in the field of nanophotonics.

[1] Supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Science, under contract W-31-109-Eng-38.

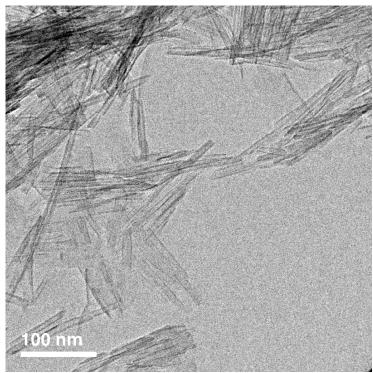


Fig. 1. TEM image of the TiO₂ nanotubes template.

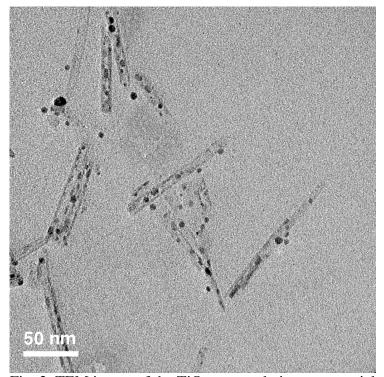


Fig. 2. TEM image of the TiO₂ encapsulating nanoparticles of silver metal.