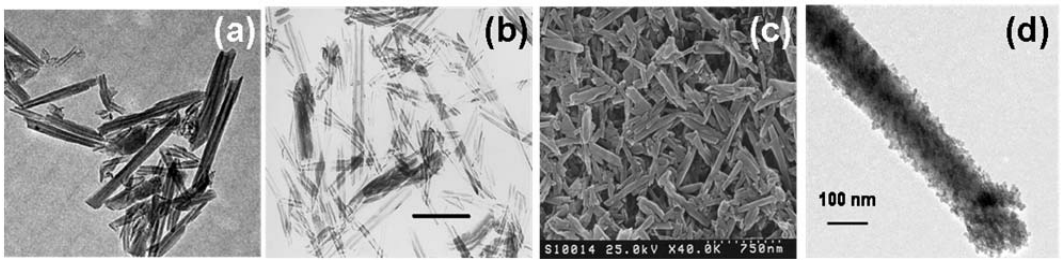
Natural clay nanotubes for sustained release of chemicals

Yuri M. Lvov, Louisiana Tech University, ylvov@latech.edu

Halloysite aluminosilicate nanotubes with a 15 nm lumen, 50 nm external diameter, and length of ca. 1mkm have been developed as an entrapment system for loading, storage, and controlled release of active chemical agents (anticorrosion, antifouling, biocides, flame-retardance). Fundamental research to enable the control of release rates from hours to days and months is being undertaken. By variation of internal fluidic properties, the formation of nanoshells over the nanotubes and by creation of smart caps at the tube ends it is possible to develop further means of controlling the rate of release. Halloysite forms stable aqueous colloids and is well admixable with polar plastics. Anticorrosive, antifouling, flame-retardance halloysite coatings are in development and a self-healing approach has been tested for repair mechanisms through response activation to external impacts



TEM images of halloysite nanotubes dispersed in water (a-b), SEM image of layer-by-layer nanocoating with halloysite multilayer (c), and halloysite nanotube coated with polyelectrolyte + 7 nm diameter silica

Doping loaded clay nanotubes into polymeric matrix (polyurethane, siloxane, epoxy, etc.) provides sustained inhibitors' release and ceramic "skeleton" is enhancing the composite strength. Doping clay nanotubes into paint formulations at 5-8 wt % provides sustained release of anticorrosion agents resulting in 2-times longer term metal protection as well as in 50-100 % increase in the coating strength and adhesivity. Such enhanced coating is especially important for operations in extreme conditions (like marine operations).

Petroleum-related studies: 1) halloysite is good spill-oil sorbent; 2) "inorganic micelles" made by hydrophobization of the tube inner lumens allow for fine water purification; 3) An efficient catalyst based on blending of tubule halloysite and Y-zeolite has been developed for the fluid catalytic cracking of heavy vacuum gasoil and its mixtures with vegetable oils (significantly increasing the yield of branched hydrocarbons); 4) time-controllable gels are under consideration.

Applications of halloysite as nanometer-scale containers are discussed including the use of halloysite clay tubes for sustained drug release, for bone implant composites, and for chemical separations. Halloysite nanotubes are available in thousands of tons, and remain sophisticated and novel nanomaterials which can be used as smart nano-containers. Halloysite is also a "green" material and due to the fact that it is a natural product will not add risk to the environment.

References

1. E. Abdullayev, K. Sakakibara, K. Ariga, Y. Lvov, ***ACS Applied Mater. Interfaces,*** v.3, 4040-4048, 2011, "Natural Tubule Clay Template Synthesis of Silver Nanorods for Antibacterial Composites"
2. W-O. Yah, A. Takahara, Y. Lvov, ***J. Am. Chem. Soc.***, v.134, 1853-1859, 2012, "Selective Modification of Halloysite Lumen with Octadecyl Phosphonic Acid: New Inorganic Tubular Micelle"
3. E. Abdullayev, W. Wei, Y. Lvov, ***ACS Nano,*** v.6, 7216-7226, 2012, "Enlargement of Clay Nanotube Lumen by Selective Etching of Aluminum Oxide"
4. Y. Lvov, E. Abdullayev, ***Progress Polymer Sciences,*** will be issued in June 2013, "Functional Polymer - Clay Nanotube Composites with Sustained Release of Chemical Agents"