# Imogolite and imogolite-like tubular nanocrystals. Formation mechanism, properties and applications

Antoine Thill

▶ **To cite this version:**

Antoine Thill. Imogolite and imogolite-like tubular nanocrystals. Formation mechanism, properties and applications. 16th International Clay Conference, Jul 2017, Granada, Spain. cea-02340826

**HAL Id: cea-02340826**
**https://cea.hal.science/cea-02340826**

Submitted on 31 Oct 2019

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Imogolite and imogolite-like tubular nanocrystals. Formation mechanism, properties and applications.

Antoine Thill*

*CEA Saclay, UMR 3685 CEA/CNRS, DSM/IRAMIS/NIMBE/LIONS, 91191 Gif-sur-Yvette, France*

Imogolites are aluminosilicate nanotubes naturally occurring in volcanic soils (Yoshinaga and Aomine, 1962) and even found on Mars recently (Bishop and Rampe, 2016). Getting inspiration from this natural clay, it is possible to prepare synthetic aluminosilicate or aluminogermanate nanotubes of formula $(OH)_3Al_2O_3Si_xGe_{(1-x)}(OH)$ which are perfectly monodisperse in diameter (from 2 to 4 nm depending on composition) and polydisperse in length from several tens of nanometers up to several microns (Thill et al. 2012, Amara et al, 2013). The formation mechanism of these nanotubes has been the subject of recent discoveries especially for the aluminogermanate nanotubes. The existence of Double-walled nanotubes has been discovered and their formation mechanism has been explained. A better understanding of the imogolite precursors (proto-imogolite) has been achieved and the growth kinetic of the nanotubes has been studied *in situ* and modelled. It has recently been discovered that it is possible to prepare hybrid nanotubes having coexisting hydrophobic and hydrophilic surfaces (Bottero et al. 2011, Bac et al. 2009). These hybrids inside/out janus nanotubes can be prepared in two symmetric configurations. Through the grafting of phosphonic acids bearing an aliphatic carbon chain on the outside aluminol surface, nanotubes dispersed in apolar solvents, are obtained. Alternatively, by replacing the tetraethoxysilane precursor by methyltriethoxysilane, nanotubes possess a hydrophobic nanocavity covered with Si-$CH_3$ groups instead of Si-OH (Figure 1A,B). These nanotubes are easily dispersed in aqueous solutions and are able to trap poorly soluble organic molecules (Figure 1C) (Amara et al. 2015).

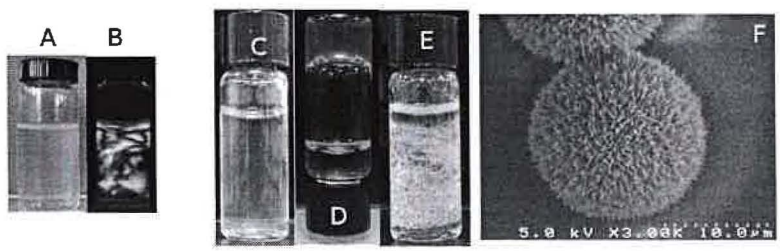


***Figure 1:*** *A) Water suspension of hybrid imogolite nanotubes with internal hydrophobic nanocavity, B) A observed between cross-polarizers, C) encapsulation of pyrene in water through hybrid imogolite, D) oil-triggered hydrogel formation, E) stabilization of an oil-in-water emulsion, F) electronic microscopy image of a dried water-in-oil emulsion droplet.*

We believe that their very original structure brings new and fascinating properties to these nanoparticles. In particular, we are currently studying the behaviour of such hybrid inside/out janus nanotubes at oil/water interfaces (Picot et al., 2016). Addition of oil to water containing hydrophilic/hydrophobic nanotubes or water addition to oil containing hydrophobic/hydrophilic nanotubes without mixing led into the formation of a gel (Figure 1D). When water and oil are mixed in the presence of the nanotubes, stable emulsions are obtained whose size is controlled by the concentration of particles (Figure 1E). After drying, a very original hedgehog-like structure is observed with electronic microscopy, (Figure 1F). Therefore, such an oil/water-triggered gel formation signs for a very specific and original behaviour of these hybrid nanotubes originating from their inside/out janus functionality.

In this mini-lecture, a review of the recent discoveries on imogolite formation mechanism will be made. We will also present the synthesis of the hybrid janus nanotubes. These hybrid nanotubes have promising properties. We will illustrate their behavior in contact with an oil/water interface.

**References:**


- Yoshinaga, N. and Aomine, S., 1962. Imogolite in some andosoils. Soil Science and Plant Nutrition, 8:3, 22-29.

- Bishop, J. and Rampe, E.B., 2016. Evidence for a changing Martian climate from the mineralogy at Mawrth Vallis. Earth and Planetary Science Letters, 448, 42-48.

- Thill, A., Maillet, P., Guiose, B., Spalla, O., Belloni, L., Chaurand, P., Auffan, M., Olivi, L., Rose, J., 2012. Physico-Chemical Control over the Single-or Double-Wall Structure of Aluminogermanate Imogolite-like Nanotubes. J. Am. Chem. Soc. 134, 3780– 3786.

- Amara, M.-S., Paineau, E.; Bacia-Verloop, M.; Krapf, M.-E., Davidson, P. Belloni, L., Levard, C., Rose, J., Launois, P., Thill, A., 2013. Single-step formation of micron long $(OH)_3Al_2O_3GeOH$ imogolite-like nanotubes. Chem. Commun. 49, 11284-11286.

- Bottero, I., Bonelli, B., Ashbrook, S. E., Wright, P. A., Zhou, W., Tagliabue, M., Armandi, M., Garrone, E., 2011. Synthesis and characterization of hybrid organic/inorganic nanotubes of the imogolite type and their behaviour towards methane adsorption. Phys. Chem. Chem. Phys. 13, 744-750.

- Bac, B.H., Song, Y., Kim, M.H., Lee, Y.B., Kang, I.M., 2009. Surface-modified aluminogermanate nanotube by OPA: synthesis and characterization, Inorg. Chem. Comm. 12, 1045-1048.

- Amara, M.-S., Paineau, E., Rouzière, S., Guiose, B., Krapf, M.E.M, Taché, O., Launois, P., Thill, A., 2015. Hybrid Tunable-Diameter Metal-Oxide Nanotubes for Organic Molecules Trapping. Chem. Mater. 27, 1488-1494.

- Picot, P., Taché, O., Malloggi, F., Thibaud, C., Thill, A., 2016. Behaviour of hybrid inside/out janus imogolite nanotubes at an oil/water interface. A route to self-assembled nanofluidic?. Faraday Discussions, DOI: 10.1039/C6FD00034G