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

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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).

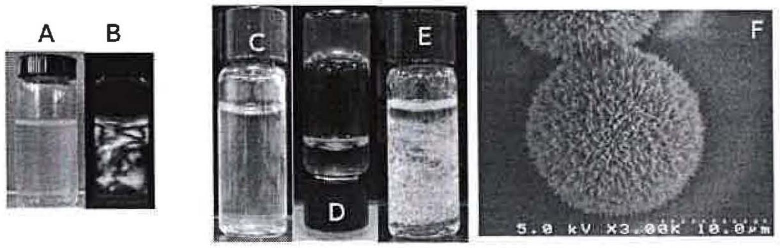

Figure 1: *A) Water suspension of hybrid imogolite nanotubes with internal hydrophobic nanocavity, B) A observed between cross-polarizers, C) encapsulation of pyrene in water through hybrid imogolite, D) oil-triggered hydrogel formation, E) stabilization of an oil-in-water emulsion, F) electronic microscopy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

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