Electronic Supplementary Material (ESI) for Chemical Communications

Supporting information

Single-step formation of micron long $(OH)_3Al_2O_3Ge(OH)$ imogolite-like nanotubes

Mohamed-Salah Amara[1,2], Erwan Paineau[1,2], Maria Bacia-Verloop[3], Marie-Eve M. Krapf[4], Patrick Davidson[2], Luc Belloni[1], Clément Levard[4], Jérôme Rose[4], Pascale Launois[2], Antoine Thill[1*]

1 CEA, IRAMIS, Laboratoire Interdisciplinaire sur l'Organisation Nanométrique et Supramoléculaire 91191 Gif-sur-Yvette, France; 2 Laboratoire de Physique des Solides UMR CNRS 8502, Université Paris Sud 11, 91405, Orsay, France ; 3 CNRS, UMR 5075, Institut de Biologie Structurale, 41, rue Jules Horowitz, 38027 Grenoble, France; *4* CEREGE, UMR 6635 CNRS/Aix Marseille Université, Europôle de l'Arbois, 13545 Aix en Provence, France

Cryo-TEM:

Cryo-TEM observations were performed using a FEI Tecnai G^2 Polara transmission electron microscope operated at 300 kV. The images were acquired under low dose conditions (less than 20 $e^-/Å^2$) using a 4k x 4k Ultrascan 4000 Gatan camera.

A drop (4 μL) of the solution were loaded onto a Quantifoil R2/2 holey grid (Quantifoil Micro Tools GmbH, Germany) made hydrophilic after glow discharging and vitrified using a Vitrobot Mark IV of FEI device.

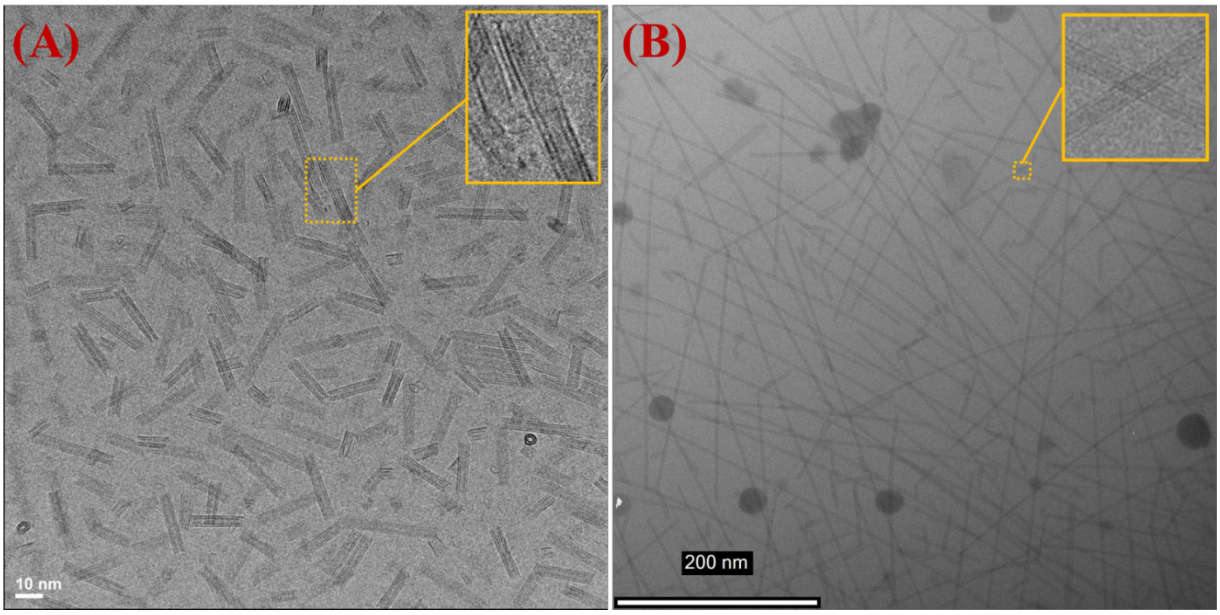

Figure SI_1. (A) Cryo-TEM image obtained with the standard synthesis procedure, using NaOH solution to hydrolyze Aluminum precursors (Image scale = 10 nm) **(B)** Cryo-TEM image of nanotube suspension obtained with the urea-based synthesis procedure (Image scale = 200nm). Insets show a zoom in each image highlighting the Double-Wall (DW) character of the tubes.

IR spectroscopy:

Infrared spectra were recorded using a Bruker Vertex 70 Fourier Transform IR spectrometer in transmission mode. Samples were prepared in transparent KBr pellets (1.5 mg of dried imogolite for 150 mg of KBr). Spectra were obtained by averaging 200 scans at a resolution of 4 cm^{-1} in the 1000-400 cm^{-1} range in order to assess the structure of the nanotubes.

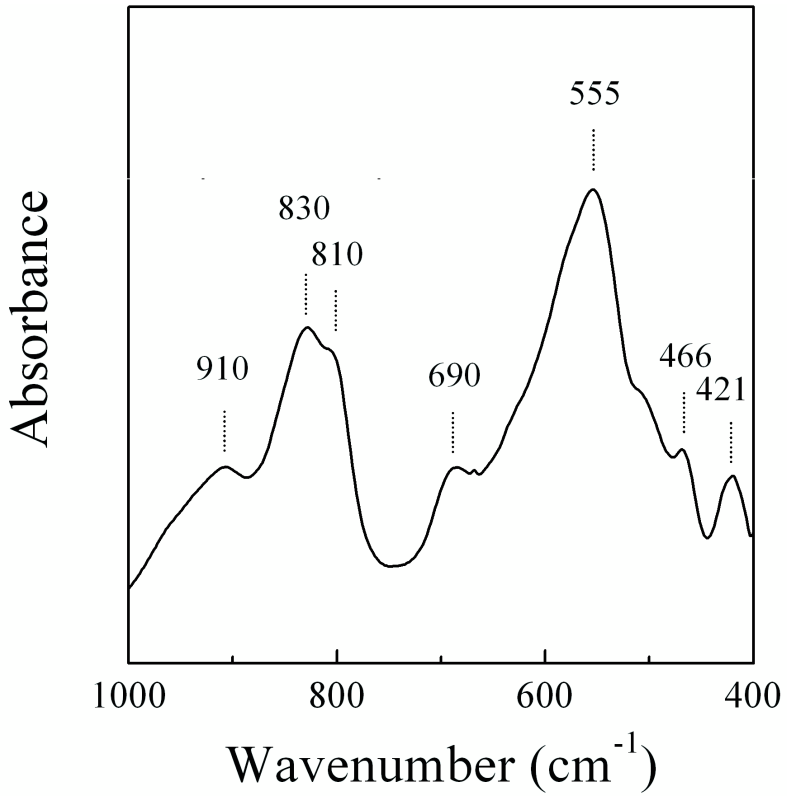

Figure SI_2. Transmission IR spectrum of imogolite nanotubes obtained with the urea-based synthesis after heating the pellet at 140°C. The bands located at 910 and 810 cm^{-1} are attributed to the stretching vibrations of Ge-O while the 830 cm^{-1} band is related to OH vibrations, in agreement with previous studies. [S1,S2] Bands located at 555 and 420 cm^{-1} correspond to the stretching vibrations of Al-O. Finally, the two absorption bands at 690 and 466 cm^{-1} are closely related to Al-O stretching vibrations arising from a DW structure, as shown recently.[S2]

SAXS treatment:

The scattering diagram obtained from the imogolite suspension has been fitted using relative weight fractions of 96.5 % of DW nanotubes and 3.5 % of proto-imogolites. A homogeneous thick cylinder is used to represent the nanotube wall. Internal tube radius is found to be R_1 = 7.7 Å, walls thickness e = 6 Å and interstitial space between walls is equal to 2 Å. The external radius is thus equal to 21.7 Å. Figure SI_3B shows the refined electronic density profile. The internal and external densities of the imogolite tube walls are respectively equal to 0.91 and 0.92 e/Å^3, which corresponds to 12 (±1) Ge atoms in the inner tube circumference and 22 (±1) in the outer one, within the *c* axis repeat distance T ~ 8.5 Å. Water density is taken equal to that of bulk water ρ_w (ρ_w = 0.334 e/Å^3). This assumption does not take into account the small variations (compared to the wall electronic density) of the water electronic densities close to the imogolite walls. These variations do not have significant effects especially at small angles.

Detailed X-ray scattering calculations are developed below. The Fourier transform of a cylinder of a radius ρ and a length L writes:

$$F_\rho(\vec{Q}) = \int_{V_{cyl}} e^{i\vec{Q}.\vec{r}} d^3\vec{r} \qquad [1]$$

Notations used are explicated in fig. SI_3(A). One finds:

$$F_\rho(\vec{Q}) = 2\pi L.sinc\left(Q_z \frac{L}{2}\right).\frac{\rho J_1(Q_{/\!/}\rho)}{Q_{/\!/}} \qquad [2]$$

where $Q_{/\!/}$ and Q_z are the projections of the scattered vector $\vec{Q} = \vec{k}_d - \vec{k}_i$ on the (xOy) plan and the (Oz) axis.

The electronic densities of the internal and external walls of the imogolite nanotube, denoted ρ^i_{imo} and ρ^e_{imo} respectively, are calculated as a function of the tube dimensions and the number of Ge atoms in the inner and outer tube circumferences ($N^i \wedge N^e$), over the period T ~ 8.5 Å.

$$\rho_{imo}^{i} = \frac{N^{i} \times Z_{imo}}{\pi \frac{T}{2}[(R_1+e)^2 - R_1^2]} \quad [3a]$$

$$\rho_{imo}^{e} = \frac{N^{e} \times Z_{imo}}{\pi \frac{T}{2}[(R_1+2e+2)^2 - (R_1+e+2)^2]} \quad [3b]$$

Z_{imo} is the number of electrons associated to one Ge atom, which is calculated from the chemical formula of a Ge-Imogolite nanotube. It is equal to 118. At small wave vectors, one can consider electronic densities instead of atomic X-ray scattering factors. The scattered X-ray intensity of the imogolite suspension of volume V and containing N Double-Wall (DW) nanotubes writes:

$$I(\vec{Q}) = \frac{N}{V} V_{tube}^2 2\pi \int_0^{\pi} d\theta_{\vec{Q}} sin(\theta_{\vec{Q}}).\left(P(\vec{Q})\right)^2 \quad [4]$$

$$P(\vec{Q}) = (\rho_w - \rho_{imo}^{i}).[F_{R_1} - F_{R_1+e}] + (\rho_w - \rho_{imo}^{e}).[F_{R_1+e+2} - F_{R_1+2e+2}] \quad [5]$$

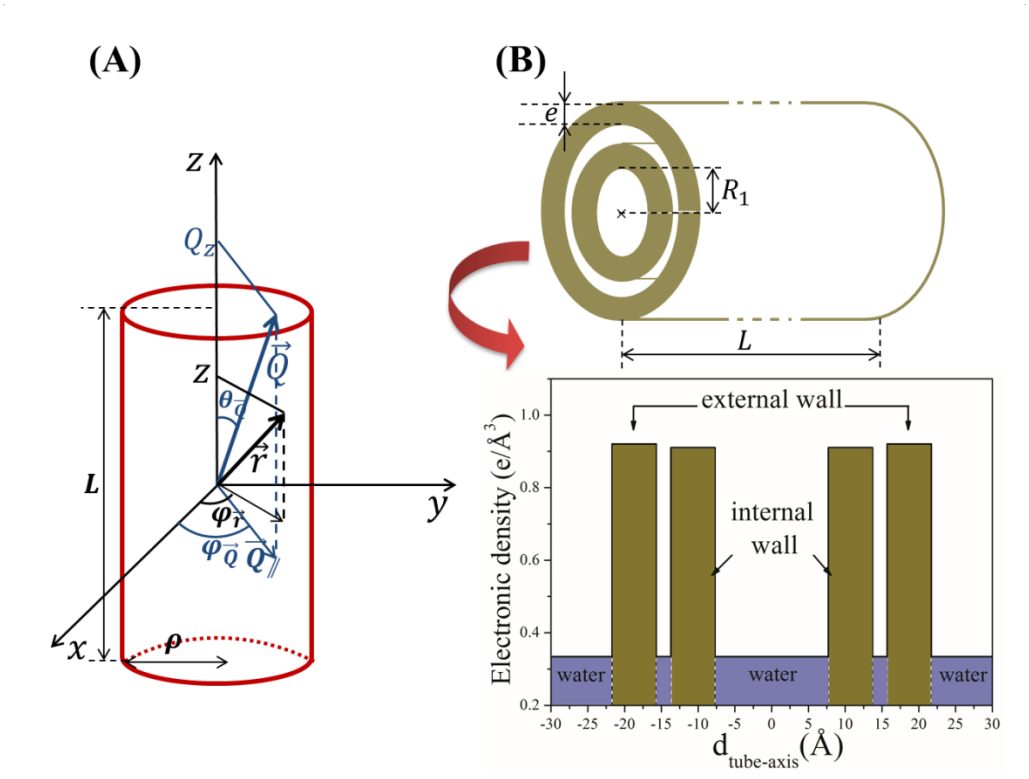

Figure SI_3. (A) Notations used in the calculation of the scattered intensity (B) Model of a double-

walled imogolite nanotube and corresponding electronic density profile.

AFM size distribution:

AFM images were obtained in tapping mode prepared from a very dilute solution of dialyzed Ge-Imogolite suspension deposited on mica sheets. Figure SI_4 shows a typical AFM image (scan size 5 µm × 5 µm) and the length distribution of the nanotubes. The lengths of all the fully visible imogolite tubes were measured. Note that the proportion of large nanotubes is most probably underestimated due to the adsorption kinetics on the substrate, which favors the small nanotubes.

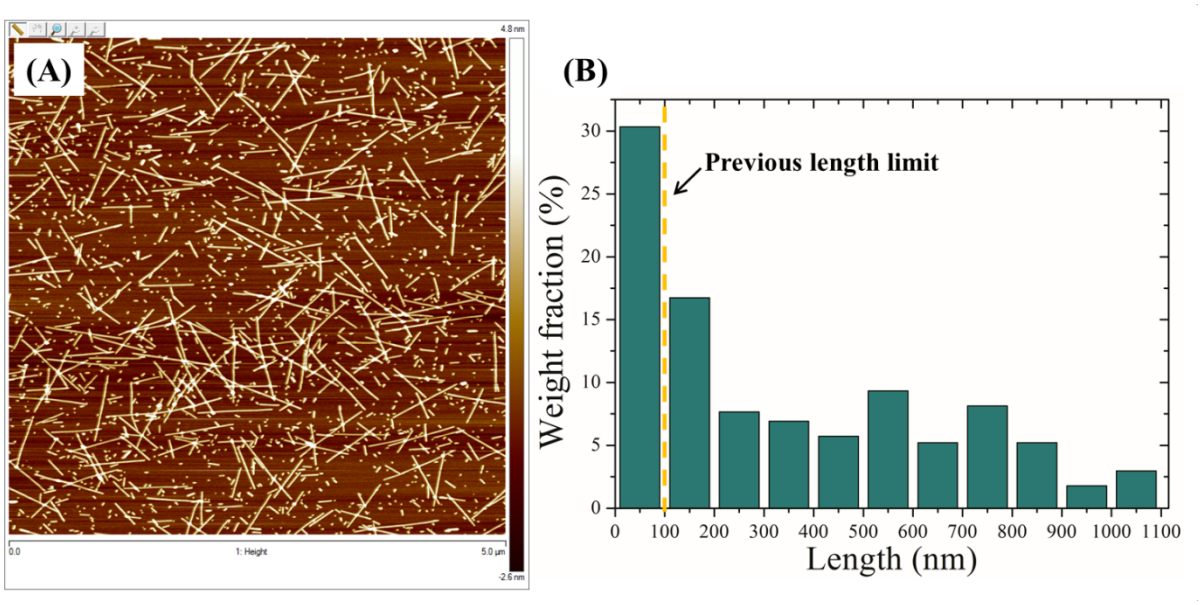

Figure SI_4. (A) AFM picture of the imogolite nanotubes obtained with the urea-based synthesis and further chemically adsorbed on a mica sheet (B) Weight fraction of their length distribution. For previous synthesis procedures, the DW length was always less than 100 nm (limit indicated with a dashed line).

References

S1. Wada S.; Wada K., Clays and Clay Minerals 1982 (30) 123-128.

S2. Thill, A.; Maillet, P.; Guiose, B.; Spalla, O.; Belloni, L.; Chaurand, P.; Auffan, M.; Olivi, L.; Rose,

J. J. Am. Chem. Soc. 2012 (134) 3780-3786.