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Accelerated Microwave Assisted Synthesis of Alumino-Germanate Imogolite Nanotubes

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Ge-imogolite nanotubes ($\text{Al}_2\text{GeO}_7\text{H}_4$) can be readily obtained in various lengths, chemical compositions and crystallinities, opening up new perspectives for applications. Their classical synthesis includes the nucleation of roof-tile shaped precursors at room temperature followed by heat promoted growth (typically 95°C) for at least 4 to 7 days. To circumvent this excessively long synthesis duration, we used microwave assisted heating to accelerate the growth. Micron sized tubes were formed from 1hr at 100°C, and best results were obtained for 2 hours at 200°C, i.e approximately 100 fold faster when compared to the conventional heating process. Additionally, tube lengths were shifted towards larger values by one order of magnitude, leading to micron sized Ge-imogolites vs. 100 nm with conventional heating. Specific microwave effects as well as mechanisms leading to these longer tubes are also discussed.

INTRODUCTION

Tubular nanomaterials are increasingly popular in a number of applications e.g. to improve mechanical strength, pack high surface areas in a limited volume... If carbon nanotubes remain the most publicized materials in this category, much of the focus now shifts towards inorganic nanotubes/nanofibers. Among these, imogolites ($\text{Al}_2\text{SiO}_7\text{H}_4$) are nanotubes occurring naturally in volcanic soils, which can be synthesized with simple aqueous sol gel processes.^{1,2} However these protocols have in common very poor yields (millimolar concentrations) and slow kinetics (several days of growth). Yield is no longer an issue, since large quantities of Ge analogues, isostructural to imogolite ($\text{Al}_2\text{GeO}_7\text{H}_4$, hereafter called Ge-imogolites) are readily obtained with initial reagent concentration in the molar range.³ The diameter (3-4.5 nm) is a function of wall multiplicity, which is easily controlled with the initial concentrations.⁴ These hydrophilic tubes can be functionalized on both the internal and external tube surfaces.^{5,6}

Like silicon-based imogolite, the synthesis of Ge-imogolites is an aqueous phase process where the room-temperature based hydrolysis of a mixture of Al and Ge monomers results in the nucleation of roof-tile shaped proto-imogolites (ca. 5nm). Although not entirely elucidated, the mechanisms of tube

growth, during a growth step at moderate temperature for several days, are thought to include the formation of annular structure from proto-imogolite upon heating, followed by tube growth via tip-to-tip collisions.⁷ Under these conditions, average tube length is a few tens of nanometers with a maximum length typically not exceeding 150 nm. Some micro-sized Ge-imogolites were obtained using urea instead of NaOH during hydrolysis.⁸ However the growth still requires a week, and it is unclear to what extent the formation of long tubes is a quantitative process.

Predominantly short tubes (< 200 nm) and long growth duration are detrimental characteristics of all the Ge-imogolite syntheses available in the literature. To overcome these limitations, at least partly, we investigated the improvements that microwave (MW) heating could offer in comparison to conventional heating in an oven. MW is widely used for the synthesis of organic materials and, to a lesser extent, for the synthesis of minerals. Using conventional heating (CH), thermal energy is delivered to the material surface by radiant and/or convection heating and is transferred to the bulk solution via conduction. During MW processing, polar water molecules tend to align with the changing alternating electric field, and energy is transferred by rotation, friction and collision. As a result, heat can be generated homogeneously throughout the volume.⁹ In the literature, MW synthesis have increased reaction rates, improved yield and narrowed nanoparticle size distribution.¹⁰⁻¹⁴ These improvements cannot be explained solely by a rapid heating effect, and therefore various authors postulate the existence of a "specific microwave effect".¹⁵ In the present study, we report the effects of MW heating on the formation of Ge-imogolite as a function of reaction time and temperature.

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Electronic Supplementary Information (ESI) available: [Figure S1 Repartition in volume percentage of Ge-imogolites nanotube lengths estimated from AFM images. Figure S2 Method for height thresholding used to distinguish proto-imogolites from tubes are presented]. See DOI: 10.1039/x0xx00000x

METHODS

Ge-imogolite precursors (proto-imogolites) were obtained by adding a germanium ethoxide solution to aluminum chloride (0.05 mol.L⁻¹, $n_{Al} / n_{Ge} = 1.75$). The solution was slowly hydrolyzed with a 0.05 mol.L⁻¹ NaOH solution (1ml/min) to a hydrolysis ratio ($R=n_{OH}/n_{Al}$) of 2. Proto-imogolites were refrigerated at 4°C before further use. Tubes growth was performed either under Conventional Heating (CH) in an oven with pressure resistant containers or under microwave (MW) irradiation (Anton Paar Synthos 3000 microwave, 2.45 GHz) under stirring. For both heating regimes, 3 temperatures (100, 150 and 200°C) and 2 durations (1h and 2 h) were tested; CH systems were also heated for 7 days, the CH system at 100°C during 7 days being a reference of current protocols. The final suspensions were dialyzed with a 1kDa pore size membrane against ultra pure water until the conductivity reached 2 μ S.cm⁻¹. AFM images (Bruker INOVA) were obtained in tapping mode. Diluted samples (1mg.L⁻¹) were deposited on a mica sheet and dried several hours at 60°C prior to analysis. AFM images extraction and height profile thresholds were performed using Gwyddion 2.4 software.¹⁶ Particle counting, length and height distributions were extracted using Fiji 2.0 plugin¹⁷ and image J 1.46 software.¹⁸ As opposed to height resolution (0.2 nm), lateral resolution was poor and limited to 25 nm by the dimensions of the AFM tip; therefore proto-imogolites were determined on the basis of their height (ca. 1nm, vs. 3.5 for the tubes) and not their length which is indistinguishable from the shortest tubes. To this end, a threshold of 2.5 nm was applied using the Gwyddion software (cf. Fig. S2 in S.I. for details). X-ray diffraction patterns were obtained on freeze-dried dialyzed samples using an X'Pert Pro diffractometer (PANalytical) equipped with a rotating glass capillary (ϕ 300 μ m) and a mirror as a primary optics to produce a parallel beam. Cobalt K α radiation (1.79Å) was used at 40kV and 40mA. Scans were performed in the scattering angle range $2\theta = 2-55^\circ$ with steps of 0.05° and 15s per step.

RESULTS AND DISCUSSION

The reference sample, i.e. 7 days CH at 100°C, corresponds to the most common protocol described in the literature. The X-ray diffraction patterns of the recovered tubes of this

reference sample (Figure 1) corresponds to the pattern previously observed with Ge-imogolites.^{6,19} As expected, average tube length as determined by Atomic Force Microscopy (AFM) is below 80 nm (Figure 2) and the maximum does not exceed 150 nm (Figure 3(a)). Increasing the temperature to 150°C and 200°C resulted in poorer results. While the diffraction patterns still display the signature of Ge-imogolite (Fig. 1), only very few tubes were detected by AFM (Fig. 2). Instead, the AFM images are dominated by globular structures, presumably aggregates of precursors and/or ill-ordered aluminum (oxy)hydroxides at 150°C, and an additional boehmite contribution (AlOOH; ICDD PDF #74-1895) (Fig.1) at 200°C, possibly resulting from the maturation of the species formed at 150°C.

Figure 4 shows the proportions of proto-imogolite (i.e height <1nm), short tubes (i.e. length < 25 nm) and "long" tubes (i.e. length > 25 nm) as determined from AFM images analysis. Under CH conditions, no tubes are present at 100°C after 1 and 2 hours heating. Above 100°C, the proportion of tubes formed under CH conditions increases with the reaction temperature and reaction time to reach 90% at 200°C after 2 hours, short tubes (<25 nm) being the predominant structure. The X-ray diffraction patterns are consistent with Ge-imogolite formation.¹⁹ (Fig. 1) To the best of our knowledge, this is the first report unequivocally documenting the early formation of Ge-imogolite (i.e. within one or two hours) under hydrothermal conditions. However, it appears that the formed Ge-imogolite cannot withstand prolonged maturation under these conditions since they become undetectable on the AFM images after 7 days (Fig. 2).

Synthesis results obtained with MW contrast sharply their CH counterpart. The most striking result is that micron-sized tubes are detected at the lowest temperature and shortest time (100°C, 1 h) (Fig. 2). At this stage, there is still a majority of proto-imogolite present in the sample. Increasing the temperature and duration causes this proportion to gradually decrease, mainly to the benefit of long (> 25 nm) tubes, which are the only detected structures after 2 h at 200°C (Figs. 3 and 4).

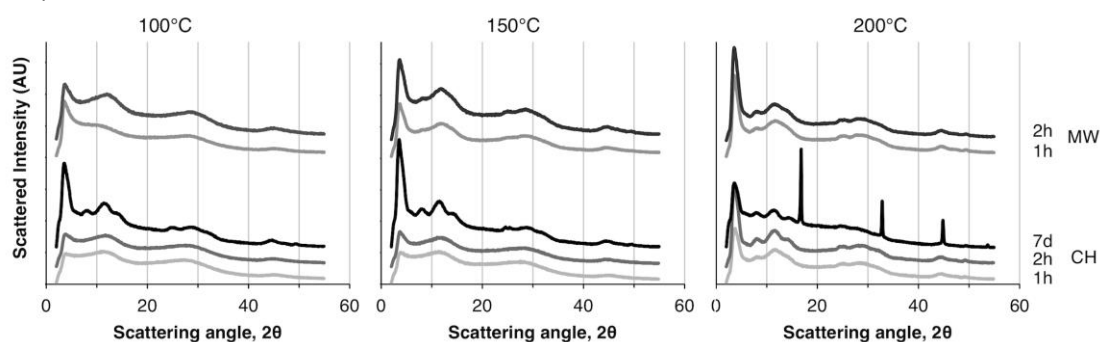


Figure 1: X-ray diffraction patterns of samples grown at 100, 150 or 200°C under conventional heating (CH) or microwave (MW) irradiation for 1h, 2h or 7 days.

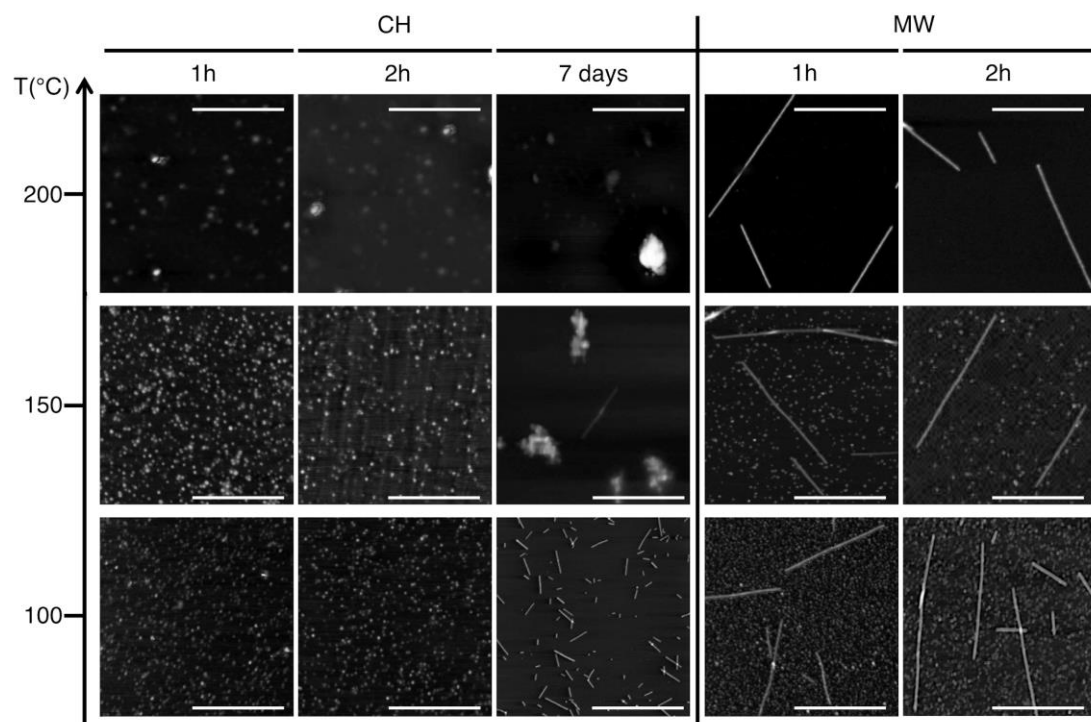


Figure 2: AFM images under tapping mode for samples synthesized under conventional heating (CH) or microwave (MW) irradiation, at 100, 150 or 200°C. Scale bar = 500nm. Grey level is related to the height of the particles.

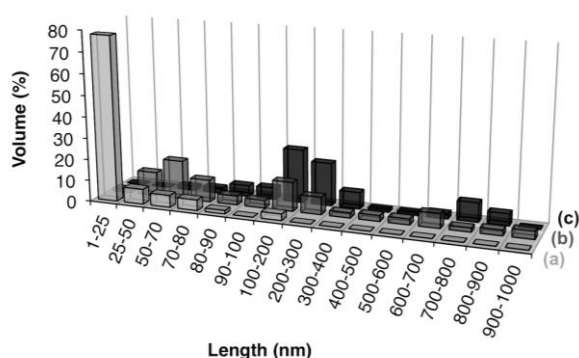


Figure 3: Repartition in volume percentage of the length of Ge-imogolites nanotube measured from AFM images. At least 500 particles were considered excluding aggregates. Growth stages were performed under (a) conventional heating at 100°C for 7days or under microwave irradiation at 200°C (b) 1h or (c) 2h.

Using MW, the reaction rate is accelerated by a factor close to 100 compared to CH protocols. This is accompanied by a shift in the tube length by approximately one order of magnitude (Fig. 3). To the best of our knowledge, there is no previous evidence of the synthesis of micron-sized Ge-imogolite in such a short time frame.

Micron-sized Ge-imogolite was also obtained previously using urea as hydrolysis agent with considerably slower kinetics than the present study, i.e. 5 days of heating.⁸ The maximum lengths measured under these conditions were around 1 μm , which is also the case with our MW based protocol. This length

might correspond to an "equilibrium" value since two different growth procedures lead to the same maximum value. The systems hydrolyzed with urea was described as very polydispersed in length.⁸ In the present case, the particle size distribution can be termed as bimodal with maxima around 300 and 800 nm (Fig. 3 and Fig. S1 in Supporting Information (S.I.)), and may be an improvement in term of length selectivity compared to the urea based protocol. However, a particle size distribution of the solids formed following this procedure is required to confirm this hypothesis.

Amara et al. hypothesize an urea mediated modification of the interactions between the tips of the tubes to explain the increased length, but did not give further details on the nature of the mechanisms involved.⁸ The present results are consistent with a structuring role of urea during tube formation. Indeed, when the growth is conducted under similar conditions (viz. CH, 150°C for 7 days vs. 140°C for 5 days for the urea based protocol), only negligible amounts of tubes are produced from NaOH hydrolyzed systems (Fig. 2), thereby suggesting that urea and/or its decomposition by-products not only promote tube lengthening, but also prevent the decomposition/destruction of the short tubes formed in the initial stages of heating. In the present study, it is obvious that the enhanced tube growth under MW heating is the result of a different mechanism.

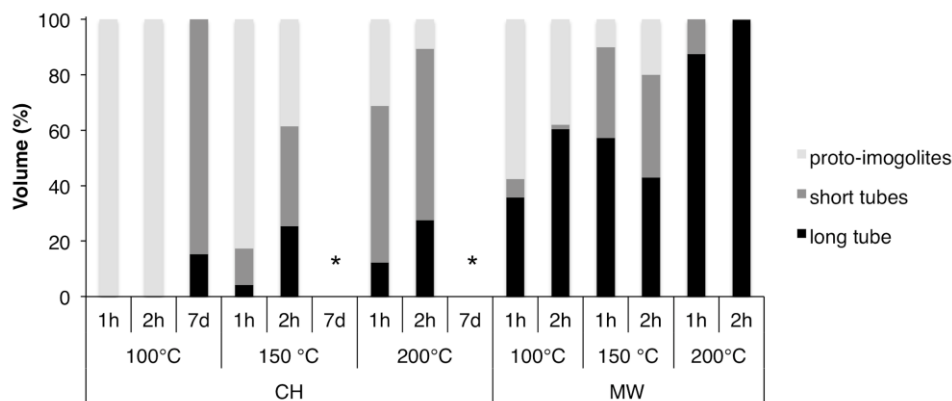


Figure 4: Repartition in volume percentage and type: proto-imogolites, short tubes (length <25nm) or long tubes (length >25nm) measured from AFM images, for various temperatures, growing durations and the two heating conditions. CH: Conventional Heating, MW: MicroWave irradiation *: samples dominated by large aggregates preventing the determination of tube proportions.

The MW induced molecular motion of polar species causes homogenous heating throughout the sample volume,²⁰ but increased molecular mobility is not necessarily linked to thermal effects.²¹ The fast and homogeneous increase in temperature under MW irradiation certainly increases the kinetics of tube formation. However this faster molecular motion is not sufficient to explain the observed enhancement of the tube length. As a matter of fact, it appears that prolonged heating at temperature above 100°C has even adverse effects on tube growth as shown by the quasi-absence of Ge-imogolites for the systems that underwent CH at 150 and 200°C during 7 days (Fig.2). Interestingly, this temperature dependent destructuring of short Ge-imogolite tubes is not observed when MW are applied, and increasing proportions of long tubes are formed instead (Figs. 2 and 4).

Improvement of the tube growth could be achieved by favoring tip-to-tip collisions, since this has been hypothesized as major growth mechanism.⁷ The most obvious way to accomplish this, is to restrict, at least partly, the randomness in particle collisions, i.e. promoting the alignment of the tubes within the sample, which equates to eliminating 2 degrees of liberty and thus a theoretical increase of the probability of effective collisions by 4 to 5 orders of magnitude depending on symmetry.

In this context, a specific MW effect could be the alignment of imogolites tubes along the MW electric field streamlines. Recent experiments, carried out with polarized light extinction spectroscopy,^{22,23} have clearly demonstrated that in the 0.3-6 MHz range, where the electrical properties of water are expected to be comparable to the GHz range, electric field gradients of 50V/mm are sufficient to align aqueous suspensions of imogolites nanotubes of a few tens of nanometers. On the other hand, for such moderate electric

field gradients, electromagnetic calculations show that the induced dielectric force and dielectric moment are directly proportional to the particle electrical polarisability and thus, to the square of their length in the case of elongated particles such as nanotubes. As a consequence, the effect of the dielectric force induced by MW increases quadratically with the length of nanotubes, limiting their rotation induced by the Brownian motion and thus, to some extent, thermal effects. It is believed that such a mechanism would be most effective in promoting the tip-to-tip collisions between long tubes (and thus rare at the beginning of the process), leading to the formation of micrometer-long tubes rather than nanometer of a few tens nanometers long.

For the MW systems at 100°C, proto-imogolite and long tubes are the major species while the proportion of short tubes is surprisingly low. This suggests an additional growth mechanism, according to which tubes grow from the addition of proto-imogolite. Since Ge is a good MW absorber (i.e. high equivalent electrical permittivity),²⁴ hotspots are likely to occur where Ge atoms are concentrated, i.e. the tubes and precursors, thus creating a favorable environment from an energy standpoint.

Obviously, these two mechanisms probably take place simultaneously. They are also not fully inconsistent since, for instance, the forced orientation of the largest nanotubes should also promote the assembly at their tips of proto-imogolites (which are probably less sensitive to the MW electrical field).

Conclusions

The use of MW is a significant step forward in the synthesis of Ge-*imogolite* (100 times faster and tubes 10 times longer than with CH), and could be the key to commercial applications of this material. A better control over the tube length might be required to tailor tubes to specific uses. This means a more in-depth investigation of the mechanisms involved, their relative importance during the entire process. Here, it would be a matter of determining at which stage precursor addition or tube-tube collision are the predominant mechanism. To do so, monitoring particle orientation during the entire process is an essential piece of information. This aspect, which is far from being straightforward, is currently under investigation.

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