Self-rolling of an aluminosilicate sheet into a single walled imogolite nanotube: The role of the hydroxyl arrangement

Citation: AIP Conference Proceedings 1702, 050004 (2015); doi: 10.1063/1.4938786
View online: http://dx.doi.org/10.1063/1.4938786
View Table of Contents: http://scitation.aip.org/content/aip/proceeding/aipcp/1702?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Self-repairing in single-walled carbon nanotubes by heat treatment

Strain-driven self-rolling mechanism for anomalous coiling of multilayer nanohelices

Fabrication of transparent single wall carbon nanotube films with low sheet resistance

Thiolation of single-wall carbon nanotubes and their self-assembly

Role of the metal in contacting Single-Walled Carbon Nanotubes
Self-Rolling of an Aluminosilicate Sheet into a Single Walled Imogolite Nanotube: The Role of the Hydroxyl Arrangement

R. I. González*,†, R. Ramírez**,†, J. Rogan*,†, J. A. Valdivia*,†, F. Munoz*,†, F. Valencia*,†, M. Ramírez*,† and M. Kiwi*,†

*Departamento de Física, Facultad de Ciencias, Universidad de Chile, Casilla 653, Santiago, Chile 7800024
†Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA, Avda. Ecuador 3493, Santiago, Chile 9170124
**Facultad de Física, Universidad Católica de Chile, Casilla 306, Santiago, Chile 7820436

Abstract. Imogolite is an inorganic nanotube, that forms naturally in weathered volcanic ashes, and it can be synthesized in nearly monodisperse diameters. However, long after its successful synthesis, the details of the way it is achieved are not fully understood. Here we elaborate on a model of its synthesis, which starts with a planar aluminosilicate sheet that is allowed to evolve freely, by means of classical molecular dynamics, until it achieves its minimum energy configuration. The minimal structures that the system thus adopts are tubular, scrolled, and more complex conformations, depending mainly on temperature as a driving force. Here we focus on the effect that the arrangement of the hydroxyl groups in the inner wall of the nanotube have on the minimal nanotubular configurations that we obtain are monodispersed in diameter, and quite similar to both from the those of weathered natural volcanic ashes, and to the ones that are synthesized in the laboratory. In this contribution we expand on the atomic mechanisms behind those behaviors.

Keywords: Imogolite, scrolling, Aluminosilicate Nanotubes

PACS: 61.46.+w; 68.35.bt

INTRODUCTION

Imogolite nanotubes (NTs) are especially attractive for several reasons. In the carbon-NT synthesis, the graphitic sheet strain energy required to bend it into a NT decreases monotonically, as the nanotube diameter increases, thus precluding the possibility of tuning the NT diameter. With imogolite, on the contrary, highly monodisperse NT diameters are created, whose diameter can be tuned.

Single walled imogolite is a clay NT with chemical composition Al₂SiO₇H₄. It is found in weathered volcanic ashes [1], whose conformation is illustrated in Fig. 1a. This structure, of basic relevance to the study of imogolite, was put forward in 1972 by Cradwick et al. [2]. It consists of a curved gibbsite cylinder with ortho-silicic acid, coordinated via oxygen with three aluminum atoms. Shortly after the work of Cradwick et al. became known, Farmer et al. [3] published a protocol for the synthesis of imogolite. Independently of the diverse synthesis procedures that have been reported afterwards, the imogolite diameters turned out to be highly monodisperse [3, 4, 5, 6, 7]. Consequently, it is of interest to explain this behavior on the basis of a microscopic model calculation [8], as the one we report here.

In a recent paper we studied a possible process that generates imogolite starting from an aluminosilicate sheet [9]. Here we center our interest on the influence of the inner hydroxyl group arrangement on the imogolite formation. In our calculations we do not include the quantum effects, studied by Demichelis et al. [10]. However, we do include the Coulomb interaction, which is especially relevant for the hydrogen atom arrangement in the inner wall, which competes with these quantum effects.

This paper is organized as follows: after this Introduction we describe the method we used in Section Method. Next the results obtained are given in the Section Results, and the paper is closed with a summary and the drawing of conclusions.

METHOD

The principal tool we use is molecular dynamics (MD) simulations. These MD simulations, as well as the structural relaxations, were carried out using the LAMMPS code [11]. For the atomic interactions the CLAYFF potential [12] is
FIGURE 1. (a) Imogolite unit cell with $N = 12$ repetitions of the 28 atom circular sector, of angle $2\pi/N$. Lateral view of the 28 atom structure that is angularly repeated to form imogolite is shown below. Periodic repetitions of the unit cell are imposed along the axial direction. H: light gray, O: red, Si: yellow and Al: green. b) Energy $E$ as a function of $N$ for imogolite nanotubes. The black circles correspond to the minimal energy configurations with all the Si-O-H angles equally oriented (Inset configuration A), and the red crosses correspond to the minimized configurations with alternating orientation for that angle (inset configuration B).

used, since it has been proven to be adequate to model aluminosilicate (imogolite) nanotubes [8, 9].

The CLAYFF potential, developed by Cygan et al. [12], incorporates the charges of every single atom, the Van der Waals interaction, and an harmonic potential for the O-H group stretching. Analytically it is given by

$$E = \frac{e^2}{4\pi\varepsilon_0} \sum_{i
eq j} \frac{q_i q_j}{r_{ij}} + \sum_{i
eq j} \varepsilon_{ij} \left[ \left( \frac{R_{0,ij}}{r_{ij}} \right)^2 - 2 \left( \frac{R_{0,ij}}{r_{ij}} \right)^6 \right] + k_{ij}(r_{ij} - r_0)^2,$$

where the $q_i$ are the partial charges, obtained by means of quantum mechanics calculations, $e$ is the electron charge, and $\varepsilon_0$ is the dielectric vacuum permittivity. The second summation is the Van der Waals contribution, where $R_{0,ij}$ and $\varepsilon_{ij}$ are empirical parameters derived by fitting to bulk structural and physical properties, and $r_{ij}$ are the distances between atoms $i$ and $j$. The last term in Eq. 1 describes the O-H bond stretch energy by means of a simple harmonic interaction, where the $k_{ij}$ are the stretching constants, and $r_0$ is the equilibrium O-H distance. The values of the parameters of the potential and further details on the methods used (included MD details) can be found in our previous work [9]. The Ovito code is used for the graphics and for post-processing of the results [13].

RESULTS

As we mentioned above, this work is focused in the role played by Si-O-H angles on the inner wall structure of the imogolite. In Fig. 1b we show the imogolite energy that we obtain for tubular initial condition (TIC) as a function of $N$, and two possible configurations are compared. After the nanotubes are relaxed with the FIRE [14], damped dynamics method included in LAMMPS, the configuration B with alternating angles turns out to be of larger energy (see inset in Fig. 1b). Moreover, for values $N \geq 13$ all the final configurations have the inner angles with the same orientation. In other words they take the configuration A. Although the opposite angle configuration is energetically unfavorable, we will see later that the temperature may lead to configurations with opposite orientation.

To study the kinetics effects during the formation of imogolite nanotubes, we start with Planar Initial Conditions (PIC) and let the system evolve at a fixed temperature. In this way, an aluminosilicate sheet is allowed to evolve freely in 2D, to seek its minimum energy conformation. Periodic boundary conditions are adopted along the rolling axis. Once this putative minimal energy is reached for the 2D structure, a 3D Gaussian velocity distribution, consistent with the given temperature (10 or 300 K in the present work) is applied to the system, which is allowed to evolve for 200 ps, and we use a time step of 1 fs in all our calculations. This procedure is carried out for a large number of randomly different Gaussian distributions. In all these cases the aluminosilicate sheet rolled up, adopting a variety of shapes, but
mainly forming nanotubes and nanoscrolls. The average total energy of the configurations was calculated for at least 50 different initial velocity realization on the planar sheet, and the lowest energy configuration was kept.

In Fig. 2 we plot the average total energy per circular sector structure of the minimal energy conformation we obtain, for temperatures of 10 and 300 K for both PIC and TIC. The latter correspond to the perfect imogolite NT. For both temperatures final configurations of representative $N$ values are shown. To facilitate the analysis and visualization, only the inner oxygen atoms are shown, and the color coding represents the angle between Si-O-H. If a red atom is next to a blue one it implies opposite orientation of the OH bonds. The 10 K structure was investigated to keep the thermal effects low, and in this way we also avoided defects along the NT seam. Furthermore the 300 K results, correspond to imogolite at room temperature, and it turns out to be stable even at higher temperatures. Previously we have shown [9] that when the simulations are started with PIC we obtain several possible rolled conformations as the end result: nanotubes, nanoscrolls, and double nanotubes and nanoscrolls, depending on diameter and temperature. In Fig. 2a it is apparent that at 10 K parallel bond orientation is dominant, while in Fig. 2b (at 300 K) regions of opposite Si-O-H angle orientation (red and blue) are abundant. At 10 K the conformations of Fig. 2a are almost all tubular, and only for $N > 19$ we obtain other kinds of configurations. On the opposite, in Fig. 2b we notice that only a few conformations are tubular.

Finally, as an example in Fig. 3 we show two final configurations for $N = 12$ at 300 K, which differ by $\approx 0.15$ eV/N.
In Fig. 3a, which is the higher energy structure, there are two seams along the NT, while the lower energy configuration has just one seam, but adopts a less tubular shape.

**SUMMARY AND CONCLUSIONS**

The main objective of this contribution is to study the possible imogolite configurations as a function of temperature, and of the kinetic effect on the angles of the inner wall of the nanotube. In a first stage we study the minimal energy configurations of imogolite for two different conformations as a function of the number of angular repetitions ($N$). The only difference between both conformations is in the inner angles of the Si-O-H. The minimum energy trend is for all the interior angles to adopt the same orientation. In the other case, were we optimize for $N \geq 13$ conformations with alternating orientation of Si-O-H angles, the initial configuration is unstable against the lower energy parallel bond structure.

We discuss the conformations of the interior angles of the imogolite due to Coulomb interactions which are dominant [12], and they do lead to a qualitative agreement with the quantum mechanical calculations, as performed by Demichelis et al. [10]. Moreover, our results are in agreement with the experimental findings reported by Lee et al. [15] who determined that by varying the temperature the diameter of the NTs can be tuned. We suggest that a possible explanation could be related with the inner angle conformations as the one presented here.

**ACKNOWLEDGMENTS**

We gratefully acknowledge valuable discussion with Drs. Nicolás Arancibia and Mauricio Escudey. This work was supported by the Fondo Nacional de Investigaciones Científicas y Tecnológicas (FONDECYT, Chile) under grants #11110510 (FM), #3140526 (RG), #1110630 (RR), #1110135 (JAV), #1120399 and 1130272 (MK and JR), and Financiamiento Basal para Centros Científicos y Tecnológicos de Excelencia (RR, JR, JAV, FM, FV, MR and MK). FV was supported by CONICYT Doctoral Fellowship grant #21140948.

**REFERENCES**