

## Two-dimensional alignment of imogolite on a solid surface†

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Surface modified imogolite fiber, hydrated aluminium silicate that has the shape of a rigid hollow cylinder, was aligned with consistent nano spacing and was visualized by scanning tunneling microscopy.

Imogolite is a natural, hydrated aluminium silicate with a hollow tube structure which was first discovered in the clay of Japanese volcanic ash and which has been found widely distributed in recent volcanic deposits.<sup>1</sup> This aluminosilicate has the shape of a rigid hollow cylinder a few thousand Å long and 15 Å in diameter.<sup>2</sup> The atomic composition of imogolite is  $(\text{OH})_3\text{Al}_2\text{O}_3\text{SiOH}$  from the exterior to the interior of the imogolite tube.  $\text{SiO}_4$  tetrahedrons are isolated and effectively inverted, sharing three oxygen atoms with the gibbsite layer while the other oxygen originates from the silano group.<sup>3</sup> Since the discovery of a synthetic process of imogolite preparation by Wada, several applications have been reported using this hollow nanofiber.<sup>4</sup> The relatively large surface area on the inside and the outside of the imogolite could be used as a catalyst<sup>5</sup> and a gas storage chamber.<sup>6</sup> Imogolite consists mainly of fibers, which are generally aligned in bundles with diameters ranging from 5 to 25 nm and which have typical lengths of at least 0.5 μm. The average diameter of these fibers is ~2.7 nm as determined by a molecular dynamics calculation.<sup>7</sup> The bundling effect of imogolite is typically observed in electron micrographs of natural imogolite.<sup>8</sup> These inorganic fibers of imogolite were used as a filler to make high strength composite materials. PMMA/imogolite nanohybrid and poly(vinyl alcohol)/imogolite nanocomposite, which can make high strength and transparent films, have been introduced.<sup>9</sup>

In spite of the potential applications of imogolite nanofibers due to their CNT (carbon nanotube)-like hollow tube structures, the single molecular structure of imogolite has not been visualized because of the high affinity of the hydroxyl surface.<sup>10</sup> Many researchers can observe only a bundle of imogolites with the diameter of nanometer order. The tubes have curved gibbsite sheets with Al–OH groups on the outer surface, which has a weak interaction with the silanol group of organosilane. Therefore, the outer surface wall can be charged depending on the pH of the solution. Alkyl phosphoric acid was proposed to modify the surface of imogolite.<sup>8</sup> Fig. 1(a) shows the chemical composition and structure of octadecyl phosphonic acid modified imogolite.

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Fig. 1(b) shows the dimension of octadecyl phosphonic acid (ODPA) or tetradecyl phosphonic acid (TDPA)-imogolite on a solid surface.

In a low pH solution, protons presumably adsorb on the outer aluminium hydroxide surface, and we were able to obtain a dispersion of imogolite. Natural imogolites are well dispersed at pH 3.5–4.5, but such a dispersion always displays opalescence, and the imogolites are thought to contain bundles of tubes.<sup>8</sup> Electron microscopy studies have suggested that the imogolite cylinders may interact through their Al–OH groups, which are arranged helically in the cylinder surface leading to cholesteric ordering.<sup>11</sup> A surface modification of the imogolite Al–OH group with phosphonic acid may separate each of the imogolite fibers and prevent raft aggregation.

The synthesis process is as follows: an aqueous solution of aluminium chloride (Aldrich, 99.99%) was slowly added to an aqueous solution of tetraethyl orthosilicate where the Al and Si ratio was 2 : 1. An NaOH solution was added at a rate of 0.5 mL min<sup>-1</sup> until the Al : Si : OH ratio was 2 : 1 : 4. Then the solution was stirred vigorously for 3 h and heated at 97–98 °C for 3 days. Saturated NaCl was added to obtain a white gel, and a pure white gel was obtained by using a low speed centrifuge. A pure imogolite was collected by freeze drying. An aqueous solution of pure imogolite was added to an aqueous solution of octadecyl phosphonic acid (1 : 3.5, weight ratio) to generate ODPA-imogolite. The solution was stirred for 2 days at room temperature and then ODPA-imogolite was washed with ethanol several times. The supernatant was removed by centrifugation and the product was collected after being dried in a vacuum oven. The vibrational band in FT-IR around 1000 cm<sup>-1</sup>, which is usually attributed to the stretching vibration of Al–O and Si–O of imogolite, did not change in the ODPA-imogolite, so the absorption peaks at 2850, 2920 and 2956 cm<sup>-1</sup> were attributed to the symmetric stretching of CH<sub>2</sub>, the antisymmetric stretching of CH<sub>2</sub>, and the antisymmetric stretching of CH<sub>3</sub> of the alkyl chain in the FT-IR spectrum. The

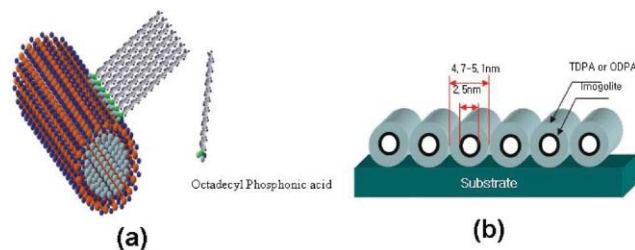


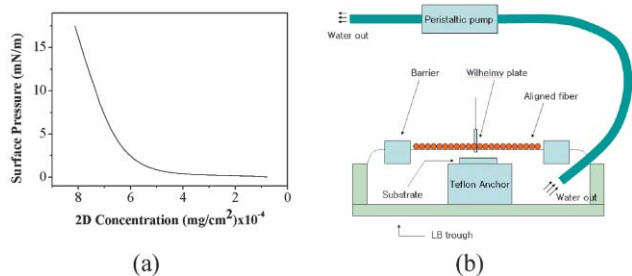
Fig. 1 (a) The chemical structure of octadecyl phosphonic acid modified imogolite (ODPA-imogolite) and (b) the dimension of ODPA- or TDPA-imogolite on a solid surface.

chemical structure of ODP-*imogolite* is shown in Fig. 1(b). A TDPA-*imogolite* was also prepared by the same method. These modified *imogolite*s help dispersion in common solvents such as toluene or chloroform. TEM (transmission electron microscopy) shows a fiber-like structure of *imogolite*, which has a high aspect ratio.<sup>12</sup>

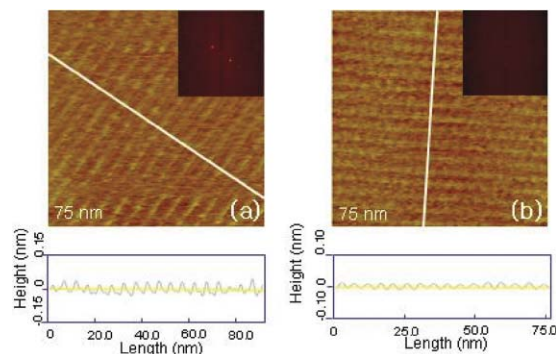
An automatically controlled Langmuir film balance KSV3000 (KSV Instruments Ltd., Finland) equipped with a platinum Wilhelmy plate was used to obtain the surface pressure ( $\pi$ ) vs. surface area (*A*) isotherm of the ODP-*imogolite* at the air/water interface. The synthesized ODP-*imogolite* was dispersed in toluene and spread on the air/water interface. After allowing for solvent evaporation, the ODP-*imogolite* was continuously compressed at a rate of  $7.5 \text{ cm}^2 \text{ min}^{-1}$  to obtain the  $\pi$ -*A* isotherm.

Surface pressure gradually increased from a surface concentration of  $1.0 \times 10^{-4}$  to  $8.0 \times 10^{-4} \text{ mg cm}^{-2}$ . The molecular weight of the *imogolite* fiber could not be determined, so we only defined the *x*-axis of the isotherm as the concentration of the solution. Relatively gradual increments in the surface pressure are due to the long chain flexibility of the ODP-*imogolite*. Fig. 2(a) shows the surface pressure vs. surface area isotherm of the ODP-*imogolite* at the air/water interface at 25 °C. The ODP-*imogolite* was transferred onto a graphite substrate by the surface lowering method in which the  $1 \text{ cm} \times 1 \text{ cm}$  graphite substrate was placed underneath the air/water interface and the water level was slowly lowered by suctioning the subphase water from the other side of the moving barrier. Fig. 2(b) shows the transfer process of the subphase lowering method. Thus, the monolayer was gently placed on the solid substrate.

The graphite substrate was HOPG (highly oriented pyrolytic graphite) ZYH grade that was purchased from Digital Instruments. Before loading the aligned surface modified *imogolite* fibers on the graphite substrate, the uppermost layer of the graphite substrate was peeled off. The transferred monolayer was dried and annealed by letting it stand at room temperature for 3 days and subsequently probed using scanning tunneling microscopy (STM). STM measurements were carried out using a NanoScope E<sup>®</sup> (Veeco Digital Instruments, Santa Barbara, CA) and a commercial Pt/Ir (80 : 20) tip that made mechanical cuts. All STM images were acquired in air by the constant current mode, and imaging conditions were as follows: a bias voltage between 200 and 750 mV (sample positive) and a tunneling current between 0.10 and 0.5 nA. Fig. 3 shows STM images of the transferred ODP- and TDPA-*imogolite* monolayer on the graphite substrate by the Langmuir–Blodgett method.



**Fig. 2** (a) Surface pressure vs. surface area isotherm of the ODP-*imogolite* at the air/water interface at 25 °C. (b) Experimental setting for using the LB technique to get the alignment of surface modified *imogolite*.



**Fig. 3** STM image of (a) ODP-*imogolite* and (b) TDPA-*imogolite* transferred onto graphite by the Langmuir–Blodgett method.

Fig. 3 shows a perfect alignment of ODP-*imogolite* and TDPA-*imogolite* on the graphite substrate. The insets of Fig. 3 are the Fourier transformed images of the STM images, and the height profiles are shown at the bottom of the Figures. A wider range for the alignment is available in the Supporting Information. We observed an *imogolite* alignment of several hundred nanometers in width. The *imogolite* part, which is the bright part in the STM image, is 2.5 nm in horizontal width and 0.7 nm in height, on average, for the ODP-*imogolite*. A molecular dynamic simulation showed that the optimum diameter of the pure *imogolite* is 2.6–2.9 nm.<sup>7</sup> The average length scale in the STM observations was obtained after monitoring the cross sectional intensity distribution with a standard deviation of  $\pm 0.3 \text{ nm}$ . The *imogolite* fibers were aligned with a spectral period of 5.14 nm whose interval must be the alkyl chain of octadecyl phosphonic acid. Alkyl chains are intercrossed with each other since the expected periodicity without intercrossing is 7.2 nm. When we compressed further to reach  $0.2 \text{ mN m}^{-1}$ , a thicker *imogolite* fiber was observed. This fiber is thought to be an aggregation between the *imogolite* fibers and forms a thick bundle. The ODP-*imogolite* showed a clear separation between the tubes. This was due to the interconnection between the side chains. Octadecyl hydrocarbons are more strongly interconnected to each other than are the tetradecyl chains. So the diameter of the ODP-*imogolite*, 5.1 nm, is similar to the diameter of the TDPA-*imogolite*, 4.7 nm, even though ODP-*imogolite* has longer alkyl chains than those of TDPA (Fig. 1). Hydrophobic inter-digitation and aggregation of the long alkyl chains are the driving forces that cause separation between the *imogolite* fibers. The direction of alignment is perpendicular to the compressed direction, which could be observed in the X-ray diffraction pattern with a multi-layer deposition.<sup>‡</sup>

In summary, we modified the surface of the inorganic nanofiber, *imogolite*, with octadecyl phosphonic acid. The hydrophobic nature of the surface modified *imogolite* aids dispersion in organic solvents and the *imogolite* fibers aligned themselves at the air/water interface. The surface modified *imogolite* fibers were aligned with constant nano spacing, which was caused by tight molecule contact. The aligned structure was clearly visualized for the first time by STM and the dimension of the nanofiber was proposed.

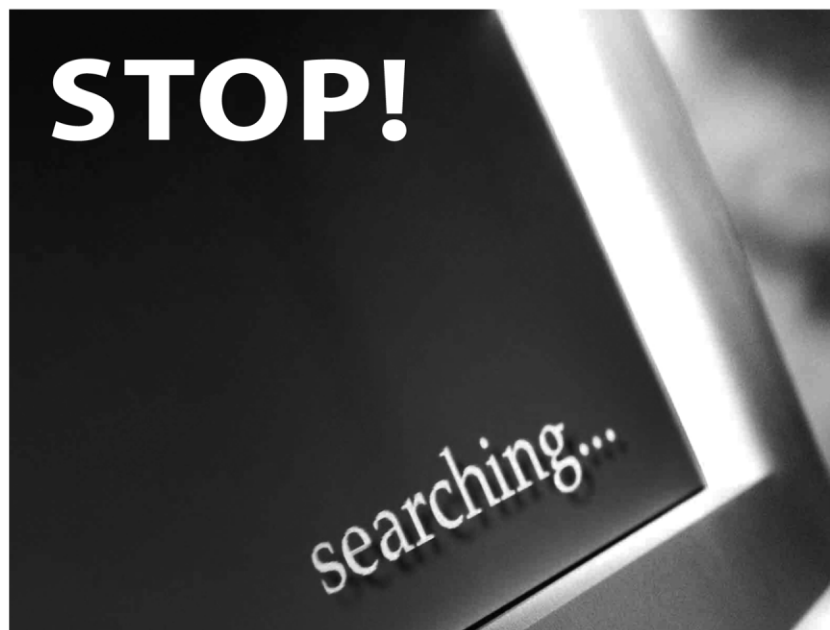
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## Notes and references

‡ X-ray diffraction: ODPa-imogolite multilayer was prepared by the vertical dipping method of the Langmuir–Blodgett technique for 30 times. In this case the surface of Si-wafer was treated with dimethylchlorosilane to give hydrophobic nature. An X-ray diffraction pattern for pure imogolite in bulk was obtained in a previous study. Aligned ODPa-imogolite showed peaks of  $7.81^\circ$ ,  $10.05^\circ$ ,  $11.93^\circ$ ,  $14.84^\circ$ ,  $17.07^\circ$  while pure imogolite in bulk shows  $6.99^\circ$ ,  $7.72^\circ$ ,  $13.68^\circ$ ,  $18.53^\circ$ , and  $26.85^\circ$ . This shows that the surface modified imogolite has more tube-like characteristics than the pure imogolite.

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