doi:10.1246/cl.2011.159

Surface Modification of Individual Imogolite Nanotubes with Alkyl Phosphate from an Aqueous Solution

Wei Ma,[1] Jungeun Kim,[3] Hideyuki Otsuka,[1,2] and Atsushi Takahara*[1,2]
[1]*Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395*
[2]*Institute for Materials Chemistry and Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395*
[3]*Japan Synchrotron Research Institute, Mikazuki, Sayo-gun, Hyogo 671-5198*

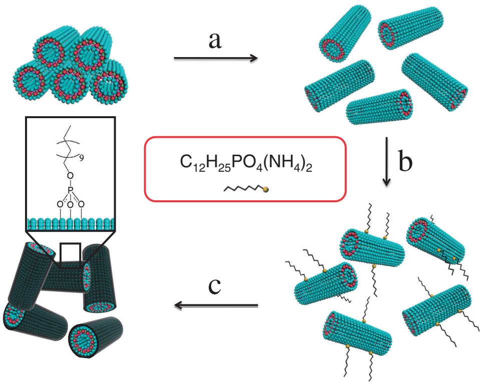
(Received November 8, 2010; CL-100934; E-mail: takahara@cstf.kyushu-u.ac.jp)

Synthetic imogolite surface was modified with alkyl phosphate by covalent bonding from an aqueous solution, and the individual imogolite tubes with a hydrophobic external surface were directly observed with transmission electron microscopy.

Imogolite is a naturally occurring aluminosilicate nanotube which was first discovered in the soil of volcanic ash in 1962.[1] It has a tubular structure, with an empirical formula of $(HO)_3Al_2O_3SiOH$. The internal diameter of imogolite nanotubes is around 1 nm, while the external tube diameter is around 2 nm, and lengths range from several hundred nanometers to micrometers.[2] Since the discovery of a synthetic process for imogolite preparation by Farmer et al.,[3] several applications of this material have been reported,[4–7] and its composition, structure, growth mechanism, and application have been the subjects of research for nearly half a century.[8,9] However, the commercialization of imogolite has been limited by the low abundance of the natural imogolite and the low-yield production of the synthetic imogolite.[10] Nevertheless, research on imogolite has never stopped. Recently, Levard et al. reported a synthetic method leading to a ca. 100-fold increase of the concentration of aluminogermanate imogolite-like nanotubes by partially substituting silicon with germanium.[11] This progress will definitely facilitate the application for this material.

Another important imogolite study area is the introduction of this nanotube into organic systems so that it can be used as nanofillers for conventional polymeric materials and supporter for catalysts.[5,7] Unfortunately, the external surface of imogolite is composed of aluminol groups, making this nanotube quite hydrophilic. Hence, surface modification is of great importance for the application of imogolite nanotubes in organic hybrids. Organophosphonic acids are expected to be useful reagents for the modification of imogolite, since they are commonly used for surface modification of metal oxides.[12] We have reported the modification of imogolite with octadecylphosphonic acid.[13] However, the modification process was carried out in ethanol. Since imogolite can only be dispersed in water because of the hydrophilic surface, it is difficult to achieve the surface modification of individual imogolite nanotubes without water as the reaction media. Hence, a modification method of imogolite in an aqueous solution is necessary for various applications.

In the present paper, such a method toward the modification of individual imogolite nanotubes with alkyl phosphate from an aqueous solution was demonstrated by converting the water-insoluble alkyl phosphate into the corresponding water-soluble ammonium salt. The procedure is shown in Scheme 1. The outer surface of imogolite nanotubes is composed of aluminol groups, thus it can be positively charged and dispersed under acidic conditions by electrostatic repulsion. Hofer et al. have reported the preparation of a self-assembled monolayer onto metal oxide surfaces by using the ammonium salt of alkyl phosphate from an aqueous solution.[14] However, the application of these water-soluble salts in the modification of nanofibers and nanoparticles has not yet been reported. We note that surface modification of such nanostructures in an aqueous solution would be an environmentally friendly method.



Scheme 1. Schematic illustration of dodecylphosphate chemisorbing onto the surface of individually dispersed imogolite nanotubes: (a) dispersion of freeze-dried imogolite powder into weakly acidic water by electrostatic repulsion; (b) chemisorption of dodecylphosphate onto the outer surface of individually dispersed imogolite nanotubes; (c) purifying the product and solidifying it by freeze-drying.

Imogolite was synthesized with the method introduced by Farmer et al.[3] Pure imogolite was collected by freeze drying. The ammonium salt of dodecylphosphate ($DDPO_4(NH_4)_2$) was precipitated from a 2-propanol solution of dodecylphosphoric acid ($DDPO_4H_2$) using ammonia according to a previous report.[14] Freeze-dried imogolite (300 mg) was dispersed in weakly acidic water (100 mL, 0.1 M acetate buffer, pH 5.0) under sonication to get a bluish dispersion, as shown in Figure S3.[17] $DDPO_4(NH_4)_2$ (600 mg) was dissolved in 450 mL deionized water, and then added to the above imogolite dispersion under magnetic stirring at room temperature. After 48 h, the white product was collected by filtration, and rinsed with THF/H_2O (volume ratio of 1:1) repeatedly, followed by freeze-drying to give a white powder of dodecylphosphate-modified imogolite ($DDPO_4$–imogolite).

The interaction between imogolite and $DDPO_4$ is confirmed by IR measurements and X-ray photoelectron spectroscopy (XPS). Figure 1 shows the FT-IR spectra of $DDPO_4$–imogolite,

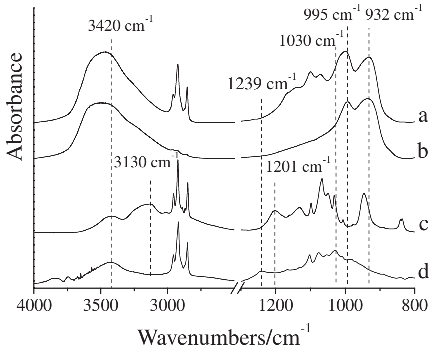


Figure 1. FT-IR spectra of (a) $DDPO_4$–imogolite, (b) pristine imogolite, (c) $DDPO_4(NH_4)_2$, and (d) $DDPO_4H_2$.

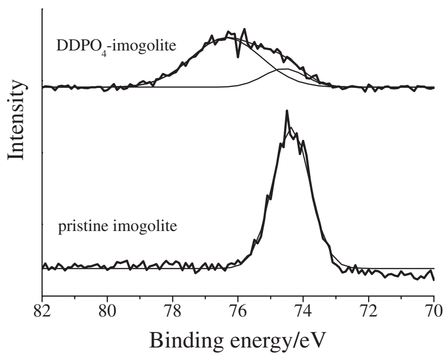


Figure 2. High-resolution XPS spectra for Al_{2p} of the pristine imogolite and $DDPO_4$–imogolite.

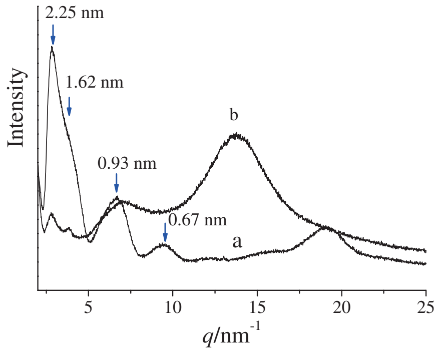


Figure 3. WAXD profiles of (a) pristine imogolite and (b) $DDPO_4$–imogolite.

the pristine imogolite, $DDPO_4(NH_4)_2$, and $DDPO_4H_2$. For $DDPO_4H_2$ the absorption of the PO–H vibration around 3420 cm^{-1}, the absorption of P–O stretching vibration around 1030 cm^{-1}, and the absorption of P=O vibration at 1239 cm^{-1} were observed. The absorption spectrum of $DDPO_4(NH_4)_2$ shows some differences from those of $DDPO_4H_2$, as the absorption band around 1030 cm^{-1} split into several sharp absorptions and the P=O vibration shifts to 1201 cm^{-1} as well. The absorption around 3130 cm^{-1} is attributed to N–H vibration of the ammonium groups. For $DDPO_4$–imogolite, the absence of N–H absorption at 3130 cm^{-1} indicates that ammonium cations do not adsorb on the surface of imogolite. The typical absorption bands of imogolite at 995 and 932 cm^{-1} still exist, suggesting the retention of the Si–O–Al skeleton in imogolite nanotubes, while the absorption at 995 cm^{-1} is strengthened by the coexistent absorption of the phosphate groups. The absorption of P=O at 1239 cm^{-1} for $DDPO_4H_2$ and 1201 cm^{-1} for $DDPO_4(NH_4)_2$ disappears from the spectrum of $DDPO_4$–imogolite presumably due to the condensation between the phosphate groups and the aluminol groups.[15] In Figure 1a, the PO–H vibration around 3420 cm^{-1} still can be found, suggesting there are some POH groups in $DDPO_4$–imogolite. These POH groups might be due to either the unbound $DDPO_4H_2$ or the bound units that still have unreacted POH groups. Since no weight loss for the unbound $DDPO_4H_2$ was observed from the thermal-gravimetric analysis as shown in Figure S2,[17] it is reasonable that those POH groups in $DDPO_4$–imogolite are assignable to the bonded $DDPO_4H_2$. Figure 2 shows the high-resolution XPS spectra of Al_{2p}. For the pristine imogolite, the Al_{2p} signal is found around 74.3 eV with a symmetric peak; while for $DDPO_4$–imogolite, the Al_{2p} peak becomes wide and asymmetric, which can be fit with two Gaussian curves containing a contribution at 74.3 eV and one at 76.3 eV. The second component is ascribed to an increase in the positive charge on Al atoms because of the formation of Al–O–P bonds at the surface of imogolite, while the first indicates the unreacted Al–OH. Thus, it can be concluded that dodecylphosphate attaches to the surface of imogolite through covalent interaction.

In order to obtain further insight into the molecular aggregation state of the $DDPO_4$–imogolite, wide-angle X-ray diffraction (WAXD) measurements were carried out at the BL02B2 beam line of SPring-8 using the white powder product packed in a quartz glass capillary. The WAXD used incident X-rays with a wavelength λ of 0.10 nm. Figure 3 shows WAXD profiles of the freeze-dried imogolite and $DDPO_4$–imogolite. Scattering vector q [nm^{-1}] is defined as $q = (4\pi/\lambda)\sin\theta$, where θ is the scattering angle. The d-spacing was calculated by d [nm] $= 2\pi/q$. The WAXD pattern of imogolite consists of a number of reflections. The reflection peaks at 2.25, 1.62, 0.93, and 0.67 nm for the freeze-dried imogolite can be assigned to the (100), (110), (001), and (211) planes of the monoclinic-like packing of the synthetic imogolite nanotubes.[8] For $DDPO_4$–imogolite, the two broad reflections around $q = 7.1$ and 13.8 nm^{-1} are possibly due to the orientation of the grafted alkyl chains along the long axis and the circumference of imogolite nanotubes, respectively, while the reflections at 2.25 and 1.62 nm suggest the presence of imogolite bundles. On the other hand, however, the intensity of the reflections at 2.25 and 1.62 nm significantly decreased compared with those of the pure imogolite, indicating the efficient exfoliation of the imogolite bundles. Imogolite cylinders may interact through their Al–OH groups, and bundles of imogolite tubes still exist even in weakly acidic water.[16] When dodecylphosphate attaches to the surface of these bundles, one-dimensional core–shell structures with imogolite bundles as the core.

The individual tubular structure of the dodecylphosphate-modified imogolite is directly confirmed by transmission electron microscopic (TEM) observation. The sample for TEM observation was prepared by placing a drop of the $DDPO_4$–imogolite suspension (toluene as the solvent) on carbon-coated copper grid and allowing it to dry in air. Figure 4 shows the TEM image of $DDPO_4$–imogolite, in which fiber-like structures

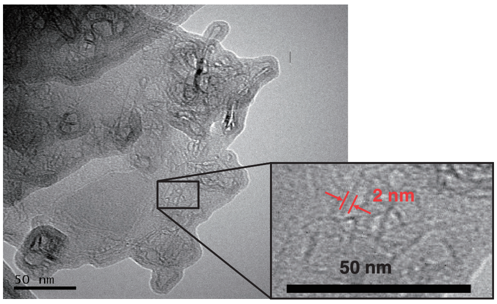


Figure 4. TEM image of $DDPO_4$–imogolite.

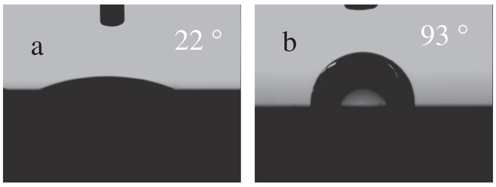


Figure 5. Static contact angle images of water droplets on silicon wafer cast with (a) pristine imogolite and (b) $DDPO_4$–imogolite.

with a diameter about 2 nm were observed. This diameter is similar to that of the individual imogolite nanotubes, indicating that these are individual tubes rather than bundles. To the best of our knowledge, this is the first observation of the individual imogolite nanotubes with a hydrophobic external surface.

The wettability of this dodecylphosphate-modified imogolite nanotube was observed by measuring the water contact angle (CA) of the $DDPO_4$–imogolite film. $DDPO_4$–imogolite was dispersed in ethanol with a concentration of $2\,\mathrm{mg\,mL^{-1}}$, and this dispersion was cast onto a silicon wafer by spin coating. For contrast, an aqueous imogolite solution was also cast onto a silicon wafer by the same procedure. Static contact angle was measured by dropping 1 µL water onto the corresponding surface. As shown in Figure 5, the static contact angle for the pristine imogolite cast surface was 22°. In contrast, for $DDPO_4$–imogolite cast surface, the contact angle increased to 93°. This indicates that the hydrophilicity of the external surface of imogolite is changed by the absorption of $DDPO_4$, which converts the hydrophilic surface of the nanotubes to hydrophobic.

In summary, we modified imogolite nanotubes with alkyl phosphate from an aqueous solution. The absorption of alkyl phosphate onto the external surface of imogolite nanotubes was confirmed by both FT-IR and XPS analysis. The XPS analysis also provided an evidence for the covalent bonding between imogolite surface and the phosphate groups. WAXD study indicates the efficient exfoliation of imogolite bundles with the grafted alkyl chains from imogolite surface. The individual imogolite nanotubes with a hydrophobic outer surface were visualized with TEM observation for the first time. This method will facilitate the development of applications for imogolite nanotubes in organic systems.

The authors gratefully acknowledge the financial support of a Grant-in-Aid for Scientific Research (A) (No. 19205031) from Japan Society for the Promotion of Science. The present work is also supported by a Grant-in-Aid for the Global COE Program, “Science for Future Molecular Systems” from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The synchrotron radiation experiments were performed at BL02B2 in SPring-8 with the approval of the JASRI (Proposal No. 2010A1454).

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