Surface Modification of Aluminosilicate Nanofiber “Imogolite”

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The nanostructure of natural aluminosilicate nanofiber “imogolite” under acidic conditions was directly confirmed by observation with atomic force microscope (AFM) for the first time. The outer surface of imogolite was successfully hydrophobidized by chemisorption of a phosphonic acid derivative with an alkyl chain.

“Imogolite” is a hydrous aluminosilicate material naturally presented in the clay fraction of glassy volcanic ash soil.[1] Figure 1 shows a schematic representation of its structure. Imogolite has the general formula of $Al_2O_3 \cdot SiO_2 \cdot (H_2O)_n$ and a tubular hollow structure with an external diameter of ca. 2.5 nm, an internal diameter of 1 nm[2,3] and lengths from several hundred nanometers to a micrometer. As can be expected from its high aspect ratio, the dispersion of imogolite rods can form space-filling gels with volume fractions as low as 0.2%.[4] Several studies have reported the preparation of an imogolite/polymer hybrid,[5,6] however, effective reinforcement has not been achieved yet due to the lack of the interfacial structure control between imogolite and the polymer matrix. In order to achieve effective reinforcement and apply imogolite to polymer composite, the interaction between organic polymer and imogolite must be enhanced. In this communication, the authors report the direct observation of imogolite nanofiber and the interaction between imogolite and an amphiphilic molecule with a phosphonic group.

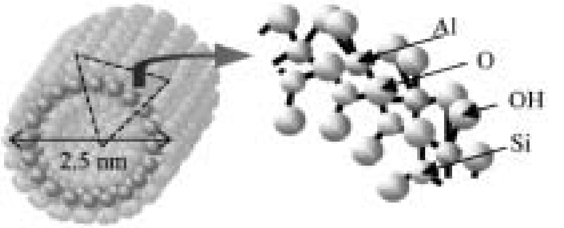

Figure 1. Schematic representation of structure of imogolite.

Since the outer surface of imogolite consists of Al–OH groups, the outer surface wall is charged under acidic conditions (pH below 5) and therefore isolated units form nanofibers because of the electrostatic repulsion. The imogolite[7] dispersed in a low acidic state was observed with AFM. Figure 2 shows the AFM image of the imogolite on a Si wafer prepared from the aqueous dispersion with a concentration of 0.05 wt% at pH = 3.0. The isolated nanofiber structure of imogolite was confirmed by AFM observation. A line-profile of the AFM image of imogolite revealed an imogolite rod with a height of ca. 2.6 nm and a width of 20–30 nm, which is in good agreement[8] with the molecular diameter of imogolite evaluated from X-ray diffraction[9] and molecular dynamics simulation.[3] The shape of imogolite was evaluated three-dimensionally for the first time.

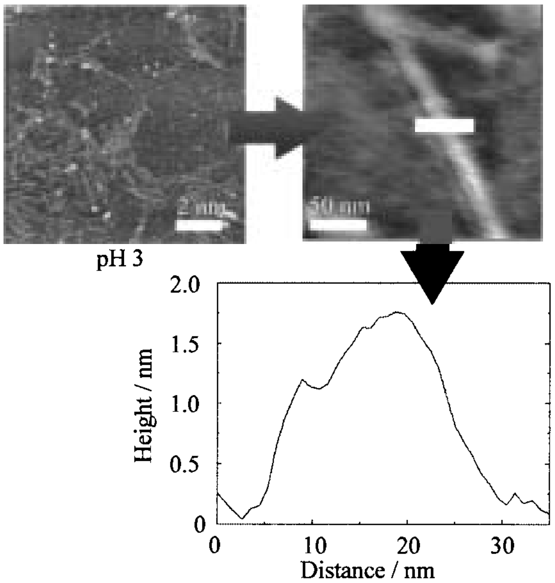

Figure 2. AFM image of the imogolite nanofiber on Si wafer prepared from the aqueous dispersion with concentration of 0.05 wt% at pH 3.0.

Imogolite was modified to investigate the interaction between the imogolite surface and a functional group. An amphiphilic molecule, octadecylphosphonic acid $[CH_3(CH_2)_{17}PO(OH)_2]$ (OPA), was employed for hydrophobidization. Figure 3 shows transmission infrared (IR) spectra of imogolite chemisorbed with OPA prepared from water[10] (a) and unmodified imogolite (b). The absorption peaks at 995 and 935 cm^{-1} were attributed to the stretching vibration of Si–O–Al

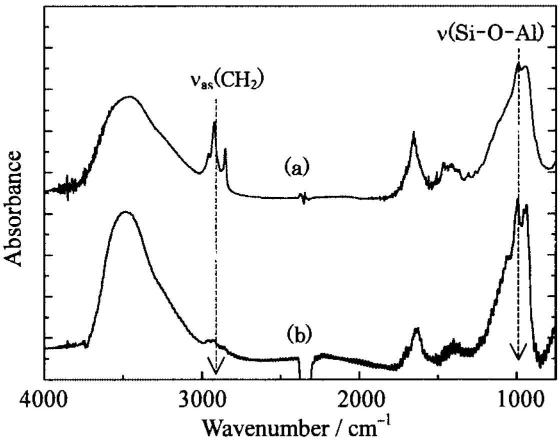

Figure 3. IR spectra of imogolite chemisorbed with OPA(a) from ethanol solution and unmodified imogolite(b).

in imogolite. The absorption peaks at 2850–2853, 2921–2925, and 2956 cm^{-1} can be attributed to the stretching of the alkyl chain, suggesting that imogolite has strong interaction with the phosphonic group.

The amount of adsorbed OPA on the imogolite surface was estimated by thermogravimetric analysis (TGA). Figure 4 shows TGA curves of imogolite chemisorbed with OPA. There is a weight loss of 5–10 % up to 523 K and 40–65 % up to 823 K. The former weight loss is attributed to the dehydration of weakly adsorbed water, and the latter to the bound water and the decomposition of OPA. The amount of adsorbed OPA increased with an increase in the OPA/imogolite ratio. An equilibrium was attained at OPA: imogolite = 5:1 (w/w). The amount of adsorbed OPA estimated at the equilibrium adsorption corresponded to the complete coverage of imogolite surface with an OPA monolayer.[11]

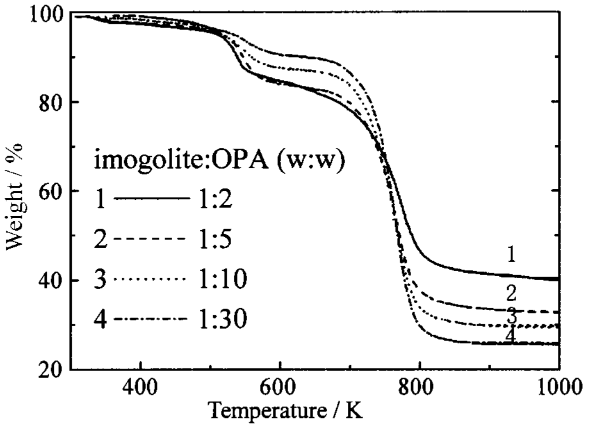

Figure 4. TGA curves for imogolite chemisorbed with OPA from water and ethanol (water:ethanol = 2:3,vol:vol) mixed solution.

The force-distance curve measurement between the cantilever tip and the imogolite surface was carried out before and after the adsorption of OPA. The adhesion force was estimated from the maximum attractive force observed as a minimum in the force-distance curve. Figure 5 shows the histograms of adhesion force observed on the surface of imogolite and OPA-adsorbed imogolite. The adhesion force between imogolite and the cantilever tip is larger than that between OPA-chemisorbed imogolite and the cantilever tip. Although there is a strong adhesion force between Al–OH and hydrophilic SiO_2 of the cantilever tip, the adhesion force is weak in the case of OPA-chemisorbed imogolite. The adsorption of OPA onto imogolite changed the surface hydrophilicity, since the hydrophobic alkyl groups cover the imogolite surface. Furthermore, the hydrophobidized imogolite thus prepared was successfully dispersed in organic solvent such as hexane.[12]

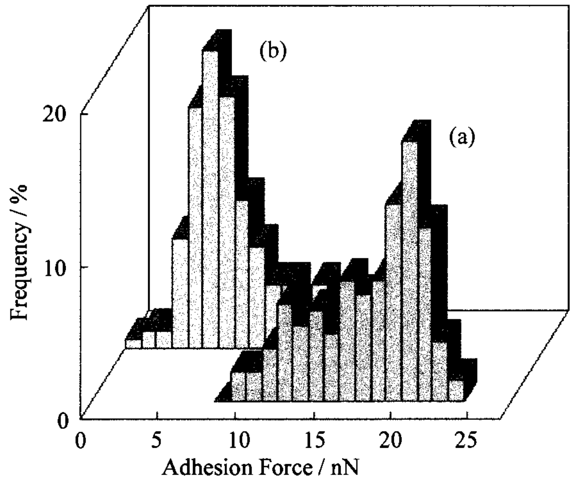

Figure 5. Histograms of adhesion force observed on the surface of imogolite (a) and imogolite chemisorbed with OPA from ethanol and water solution (b).

In conclusion, the authors directly observed and effectively modified aluminosilicate nanofiber. The present method can be applied to the preparation of a novel organic/inorganic nanohybrid system.

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References and Notes

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7 Raw imogolite material (from Kitakami Area, Iwate, Japan) was purified by the similar method reported in ref 1.
8 The average height of imogolite rod determined from the line-profile of AFM image was 2.6 ± 0.5 nm. The convolution effect of the AFM tip overestimates the nanofiber width. In the case of tip radius of 20 nm, the deconvolution of the observed diameter with the tip radius gives the nanofiber width of about 2–3 nm.
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10 Modification of imogolite was carried out by the following method: imogolite and OPA powder (1:5,w/w) were added in ethanol. This solution was sonicated and stirred for 24 h, then centrifuged, decanted, and rinsed with ethanol three times to remove the unchemisorbed OPA.
11 The amount of adsorbed OPA of imogolite prepared by OPA: imogolite = 5:1 (w/w) was 1.55 mg per mg of imogolite. The calculated amount of adsorbed OPA at the complete monolayer coverage of imogolite surface with OPA was estimated to be 1.69 mg. The calculated value is in good agreement with the experimental value at OPA: imogolite = 5:1 (w/w).
12 The concentration of OPA chemisorbed imogolite solution was 0.1 wt%.