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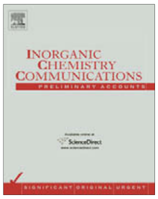

Surface-modified aluminogermanate nanotube by OPA: Synthesis and characterization

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ABSTRACT

In this study, the surface of the synthesized short, single-walled aluminogermanate nanotube was modified by using an amphiphilic molecule, octadecylphosphonic acid (OPA). The synthetic products were characterized by using X-ray diffraction (XRD), Fourier transform infrared (FT-IR), and thermogravimetric analysis (TGA). The obtained evidences indicated that the alkyl chains of OPA were successfully absorbed on the surface of aluminogermanate nanotube. This modification is useful for applying the aluminogermanate nanotube to producing potential polymer nanocomposite.

Aluminogermanate nanotube (AGN) is a nanomineral whose structure is analogous to that of imogolite, a naturally aluminum silicate $(HO)_3Al_2O_3SiOH$ [1,2], with a wall structure of a covered aluminum hydroxide sheet ($Al(OH)_3$) and germanol groups ($(GeO_3)OH$) bound on the inner wall. The length of AGN is only about 20 nm which is considerably shorter than that of imogolite. However, its tube has larger external diameter of about 3.3 nm. The formation of AGN is $(HO)_3Al_2O_3GeOH$ [3,4,6].

Recently, several studies have been reported on AGN [3–7]. Due to its unique properties (e.g., large surface areas on the outside and the inside, tubular hollow structure, short length, and well-defined nanoscale structure), AGN can have various potential applications such as catalysts, membranes, absorbents or use in artificial ion channel devices [4]. Similar to imogolite, the hydrophilic Al–OH groups of the outer surface of AGNs are expected to have strong interaction with the $–PO(OH)_2$ groups. This characteristic can also be used for applying the single-walled aluminogermanate nanotube to polymer nanocomposite. The modified AGNs can improve the effective reinforcement with polymer matrix phase. Regarding to the surface modification of imogolite, several studies recently have been reported [8–12]. However, there is no report on modifying the surface of short, single-walled aluminogermanate nanotube. In this communication, we report the observation of the interaction between the synthesized aluminogermanate nanotube and octadecylphosphonic acid (OPA), a model amphiphilic molecule with a phosphonic group ($–PO(OH)_2$). A simple schematic illustration of the surface modification of aluminogermanate nanotube using octadecylphosphonic acid (OPA) was shown in Scheme 1.

Octadecylphosphonic acid $[CH_3(CH_2)_{17}PO(OH)_2]$ (OPA) was used for modifying the surface of AGNs. The mixture of the synthetic AGN [13] and OPA powder with weight ratios of 1:1 and 1:5 were dissolved in ethanol. The mixed solution was sonicated and then stirred for 24 h. After being stirred, the solution was centrifuged to collect the white precipitate. This product was washed several times to remove the unchemisorbed OPA. The surface-modified AGN powder was obtained after freeze-drying for 2 days. X-ray diffraction (XRD), Fourier transform infrared (FT-IR), transmission electron microscope (TEM) and thermogravimetric analysis (TGA) were used to characterize the synthesized products [14].

Fig. 1a shows the XRD pattern of the synthesized AGN. The remarkable reflection at 8.52 Å was attributed to the (0 0 1) plane, which is consistent with a fiber structure. The remarkable reflection at 32.8 Å was assigned to the overall packed structure (1 0 0). These are typical characteristics of the single-wall synthetic AGN [3–7]. XRD patterns of the surface modified AGNs by OPA (Fig. 1b and c) are generally similar to that of the original AGN except for two new peaks at 16.5 and 4.2 Å. These new reflection lines are different from peaks of OPA (Fig. 1d) and they matched well with XRD patterns observed for lamellar long-chain alkylphosphonate metal oxides [8]. On the other hand, the shifts of the peak at 32.8 Å of the AGN to 35.6 Å and 36.7 Å of the modified AGNs with 1:1 and 1:5 ratios, respectively, in XRD patterns

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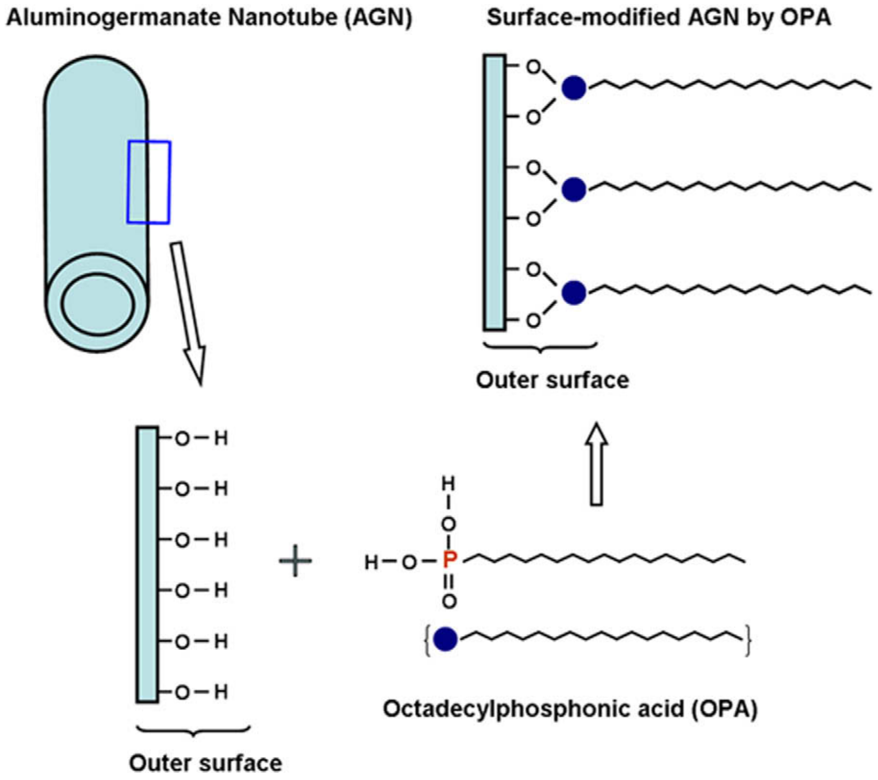

Scheme 1. Illustration of surface modification of aluminogermanate nanotube using octadecylphosphonic acid (OPA).

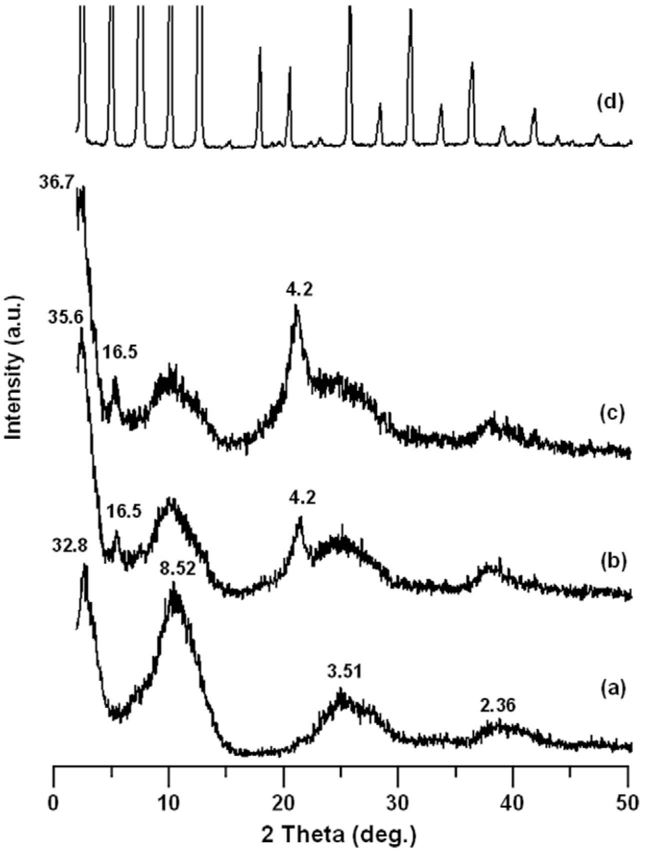

Fig. 1. XRD pattern of the synthesized aluminogermanate nanotube (a), surface-modified aluminogermanate nanotube of ratio 1:1 (b), surface-modified aluminogermanate nanotube of ratio 1:5 (c), and OPA (d).

imply that the surface modified AGNs are attributed to the interdigitated structure of the alkyl chains of OPA lying close to the surface of AGN versus the self-assembled structure of OPA. The interaction between AGNs and the structure interdigitated by OPA molecules would be presented in the shift of the peak in XRD pattern. These evidences firstly indicate that OPA containing phosphonic groups was absorbed on the outer surface of aluminogermanate nanotube.

Fig. 2 shows the FT-IR spectra of the synthesized AGN, the surface-modified AGNs with ratios of AGN:OPA = 1:1 and 1:5 (w/w), and the original OPA. It can be seen that the IR spectrum of the synthesized AGN is quite similar to those of the surface-modified AGNs. The two absorptions at 923 and 815 $\mathrm{cm^{-1}}$ were assigned to the Al–O–Ge and Ge–O–Al stretching vibrations, respectively. These vibrations are attributed to the tubular structure of the synthetic AGN. Other absorptions at 670, 554, 468 and 420 $\mathrm{cm^{-1}}$ were referred to various Al–O vibrations [3,4]. However, there are abnormal differences of new absorption peaks appearing on the IR spectrum of the modified AGNs (small window). The peaks at 2850 and 2921 $\mathrm{cm^{-1}}$ were attributed to the symmetric stretching vibrations of CH_2 and antisymmetric stretching of CH_2 [9,10]. Additionally, the FT-IR spectra of the original OPA (Fig. 2d) were different from those of the modified ones. These indicated that the outer surface of aluminogermanate nanotube was successfully chemisorbed with an amphiphilic molecule, OPA.

Fig. 3 shows the TGA analyses of the synthesized AGN, the surface-modified AGNs with various OPA contents and the original OPA. From the TGA curves, it can be seen that the weights loss from dehydration of adsorbed water on the samples were up to 450 K. The latter weight loss, observed at 900–950 K, is attributed to the weight of the decomposition of OPA. Hence, the weights ratios of the water:AGN:OPA defined in the samples are about 10%:54%:36% and 4%:40%:56% for cases of ratio 1:1 and 1:5, respectively (Fig. 3c and d). It means that the amount of absorbed OPA on