



Research paper

Aqueous dispersion state of amphiphilic hybrid aluminosilicate nanotubes

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ABSTRACT

Imogolite is known to form bundles when dried; but these nanotubes can also be perfectly dispersed in water. When the silicon precursor in the synthesis of imogolite nanotubes is changed from tetraethoxysilane (TEOS) to methyltriethoxysilane (TEMS), internal wall hydroxyls are replaced with methyl groups. This chemical modification also happens to change their dispersion properties; the nanotubes then form small bundles in solution. In this work, we explore modifications of the synthesis procedure in order to enhance the dispersion of such hybrid nanotubes. The study focuses on the effects of [Al]/[Si] ratio, acid types, ethanol addition or choice of silicon precursor. Using small-angle X-ray scattering (SAXS), infra-red spectroscopy (IR) and cryo-TEM, we show that it is possible to improve yield and length. However, none of the tested modifications allowed the prevention of bundle formation in solution.

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1. Introduction

Imogolite was discovered in volcanic Japanese soil in 1962 (Yoshinaga and Aomine, 1962). The natural form of imogolite has the general chemical formula $(\text{OH})_3\text{Al}_2\text{O}_3\text{Si}(\text{OH})$. It forms nanotubes with an external diameter of 2 nm and length of up to microns. Soon after their discovery, synthesis procedures to obtain artificial imogolite were published (Farmer et al., 1977). The first synthetic imogolite had a slightly larger diameter of 2.4 nm and can be obtained using rather mild synthesis conditions in several days.

Many physico-chemical modifications of imogolite have been published. It is possible to modify the diameter and length of imogolite nanotubes through the replacement of silicon with germanium atoms (Wada and Wada, 1982). In this case, diameter increases from 2.4 to 3.5 nm and length reduces down to about 20 nm. In the case of germanium based imogolite, the obtained nanotubes can be single-walled or double-walled depending on synthesis conditions (Thill et al., 2012). According to Yucelen et al. (2012), it is also possible to control the diameter between 2.2 and 2.8 nm of synthetic silicon based nanotubes through the use of different acids. The external surface of synthetic nanotubes can be modified. Yamamoto et al. (2005) show that it is possible to bind phosphonic acid compounds on the external surface of nanotubes without destroying their structure. Hydrophobic imogolite can also be obtained in a single step using biosurfactant (Thomas

et al., 2012). Bac et al. (2009) successfully applied the same chemical method to modify the surface of germanium based imogolite nanotubes. Ma et al. (2011) used the Reversible Addition-Fragmentation Chain Transfer (RAFT) method to grow polymer from the imogolite surface. The surface modified nanotubes can be dispersed in transparent polymer films such as polyvinylalcohol (PVA) (Barona et al., 2012) or polyacrylic acid (PAA) (Lee et al., 2013) and can significantly modify the mechanical properties of the obtained films. These methods and others have been used to prepare many different hybrid materials based on imogolite [9,11–19].

A recent and very interesting aspect on imogolite-like material physico-chemical modification is the possible production of hybrid nanotubes with modified internal surface. Indeed, it has also been shown that internal modifications are possible first through post-synthesis treatment (Kang et al., 2011) or even in single step synthesis (Bottero et al., 2011; Kang et al., 2014). In this article, we explore several synthesis modifications for the production of imogolite with a methylated cavity (CH3-imo). We particularly look at the liquid state behavior of these hybrid nanotubes.

2. Experimental

2.1. Preparation of the samples

CH3-imo are synthesized following the general recipe published by Bottero et al. (2011). In a glove box under nitrogen atmosphere, an acidic solution of Aluminum tri sec-Butoxide (ASB) is prepared with a molar

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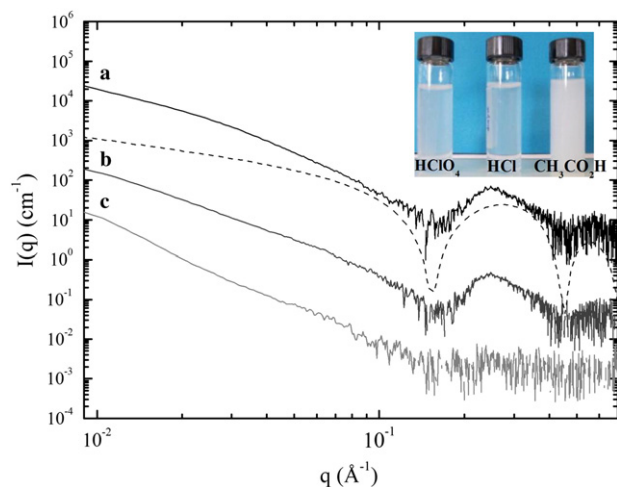


Fig. 1. Variation of the scattered intensity as a function of q for hybrid $\text{Si}(\text{CH}_3)$ imogolite nanotubes obtained using different acid types. (a) HCl , (b) HClO_4 , (c) CH_3COOH . The dotted line corresponds to the scattering form factor of core-shell cylinder model. For clarity, an offset has been applied for each curve. A picture of the corresponding samples is also presented in inset.

ratio $[\text{ASB}]/[\text{acid}]$ of 2 and an initial aluminum concentration of 0.2 M. The synthesis was performed with different acids (HCl , HClO_4 , CH_3COOH) to assess a possible control of the nanotube diameter (Yucelen et al., 2012). A silicon precursor is added under vigorous stirring at $[\text{Al}]/[\text{Si}]$ ratio from 1.5 to 2.5 in this acidic solution of ASB. Two different silicon precursors were used (methyltriethoxysilane (TEMS), methyltrimethoxysilane (TMMS)). The solution is then stirred at room temperature for 20 h. After this aging stage, the solution is diluted to an $[\text{Al}]$ concentration of 0.05 M, transferred in a closed Teflon bottle and placed for five days in an oven at 90°C . Finally, the dispersion is cooled down and dialyzed against demineralized water until conductivity of dialyzing water drops below $1\ \mu\text{S}\cdot\text{cm}^{-1}$.

2.2. Characterization of the nanotube dispersions

2.2.1. IR spectroscopy

Part of the sample is dried at room temperature and the powder is used to perform IR measurements. Infrared spectra were recorded using a Bruker Vertex 70 FTIR spectrometer with a resolution of $4\ \text{cm}^{-1}$ at

room temperature. About 1 mg of dried sample was mixed with 100 mg of potassium bromide powder and then pressed into a transparent disk. IR spectra were collected by averaging 100 scans in the range $4000 - 400\ \text{cm}^{-1}$.

2.2.2. Small angle X-ray scattering

The experimental set up for Small Angle X-ray Scattering (SAXS) experiments includes a rotating anode and collimating optics providing a monochromatic beam ($\lambda = 0.1548\ \text{nm}$) of $2 \times 2\ \text{mm}^2$ at the sample position with a total incident flux of 80 million photons per second. The transmitted flux is measured continuously with a photo-diode placed on the beam stop. A MAR research X-ray sensitive 300 mm plate detector is placed after the output window of the vacuum chamber at a distance of 1200 mm from the sample. A ratio $q_{\text{max}}/q_{\text{min}}$ of 34 is reached with $q_{\text{max}} = 0.5\ \text{\AA}^{-1}$ and $q_{\text{min}} = 0.015\ \text{\AA}^{-1}$. The scattering vector q is defined as $q = k_d - k_i$ (the wave vectors of the incident and scattered beams) and has a modulus of $q = 4\pi \sin(\theta) / \lambda$ where λ is the incident wavelength and 2θ is the scattering angle. The samples are introduced in kapton cells. The counting time is 3600 s and the signal is corrected for background. Standard procedures are applied to obtain the differential scattering cross section per unit volume (called hereafter intensity in cm^{-1}) as a function of scattering vector q (Lindner and Zemb, 2002).

2.2.3. Cryo-TEM observations

Some samples have been observed using high resolution cryo-TEM observations. Cryo-TEM experiments were undertaken using a FEI Tecnai G2 Polara device operated at 300 kV. The images have been collected using a $4\ \text{k} \times 4\ \text{k}$ Ultrascan Gatan camera. A drop ($4\ \mu\text{l}$) of the solution is deposited on a R2/2 Quantifoil grid made hydrophilic after glow discharging. A fully automated Vitrobot (FEI) device was used to blot the grid and rapidly plunge and freeze aqueous films of the nanotube suspensions into liquid ethane cooled by liquid nitrogen to prevent the formation of ice crystals.

3. Results and discussion

3.1. Impact of the acid type

It is known that ions and especially anions can induce significant modification of the morphology of precipitated oxides. In the case of imogolite, Yucelen et al. (2012) recently published an article showing a significant impact of the type of acid used on the imogolite nanotube

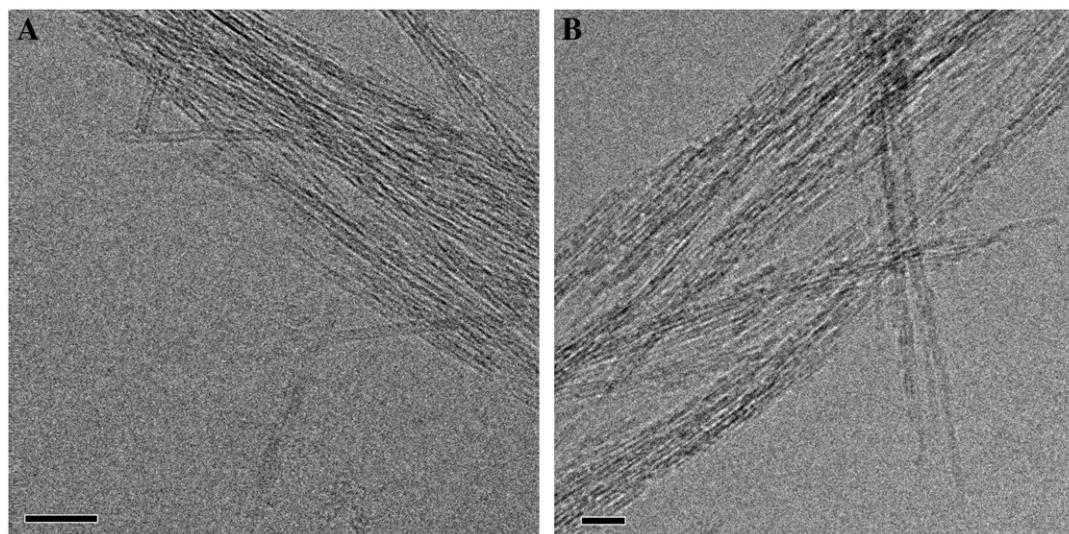


Fig. 2. Cryo-TEM observations of the nanotubes synthesized with (A) HCl or (B) HClO_4 . The scale bar is 20 nm.

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