



**HAL**  
open science

# Tailoring Structure and Surface Chemistry of Hollow Allophane Nanospheres for Optimization of Aggregation by Facile Methyl Modification

Peixin Du, Antoine Thill, Peng Yuan, Shun Wang, Dong Liu, Frédéric Gobeaux, Liangliang Deng, Yaran Song

## ► To cite this version:

Peixin Du, Antoine Thill, Peng Yuan, Shun Wang, Dong Liu, et al.. Tailoring Structure and Surface Chemistry of Hollow Allophane Nanospheres for Optimization of Aggregation by Facile Methyl Modification. *Applied Surface Science*, 2020, 510, pp.145453. 10.1016/j.apsusc.2020.145453 . cea-02454709

**HAL Id: cea-02454709**

**<https://cea.hal.science/cea-02454709>**

Submitted on 24 Jan 2020

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Tailoring Structure and Surface Chemistry of Hollow Allophane Nanospheres for Optimization of  
2 Aggregation by Facile Methyl Modification

3

4 Peixin Du<sup>1,2</sup>, Antoine Thill<sup>3</sup>, Peng Yuan<sup>1,2\*</sup>, Shun Wang<sup>1,2</sup>, Dong Liu<sup>1,2</sup>, Frédéric Gobeaux<sup>3</sup>, Liangliang Deng<sup>1,2</sup>,

5 Yaran Song<sup>1,2</sup>

6

7 1. CAS Key Laboratory of Mineralogy and Metallogeny/Guangdong Provincial Key Laboratory of Mineral

8 Physics and Materials, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street,

9 Guangzhou 510640, China

10 2. University of Chinese Academy of Sciences, 19 Yuquan Road, Beijing 100049, China

11 3. LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, CEA-Saclay, 91191 Gif sur Yvette, France

12

13 \*Email: yuanpeng@gig.ac.cn; Tel: +86 20 85290341

14

15 **Abstract**

16 Allophane, an earth-abundant and easy-to-be-synthesized hollow nanospherical material,  
17 readily loses its unique pore structure via irreversible aggregation of particles upon drying, which  
18 mainly results from capillary stress in the unsaturated inner cavity. To tackle this problem, we  
19 develop a strategy for tailoring the capillary stress and thus the aggregation state of allophane by  
20 introducing methyl moieties onto the inner surface during preparation. Combined spectroscopic  
21 results verified the formation of methyl-allophane with methyl groups only on its inner surface. The  
22 presence of a reflection at approximately 33 Å in the X-ray diffraction pattern, ascribed to the  
23 interference between particles, indicated an increased structural order in methyl-allophane. The  
24 thermal analysis data revealed a decrease of the inner-surface hydrophilicity. The Brunauer-Emmett-  
25 Teller (BET) specific surface area increased from 269 to 523 m<sup>2</sup>/g after methyl modification. An  
26 aggregation model, in contrast with that of allophane, was proposed based on the microscopic and  
27 small-angle X-ray scattering results to explain these observed changes. This work exhibited that  
28 substitution of silanol by methyl on the inner surface of allophane leads to improvement of structural  
29 order by eliminating the presence of oligomeric silicates and decreases the hydrophilicity, resulting  
30 in the reduction of the capillary stress in the inner cavity and thus the inhibition of irreversible  
31 aggregation of particles during drying. The insight into the mechanisms underneath the above  
32 mentioned changes upon methyl modification unraveled in this work is helpful for addressing the  
33 common aggregation issue of other nanomaterials.

34 **Keywords**

35 allophane; hollow nanosphere; structure; surface chemistry; aggregation; methyl.

36

## 37 **1. Introduction**

38       Hollow nanospheres, classified as zero-dimension (0D) nanomaterials, are attracting  
39 increasing research attention due to their unique structures (e.g., an inner cavity for accommodating  
40 guests) and tunable inner/outer surface properties. These materials hold great promise in fields such  
41 as energy storage and conversion [1, 2], drug delivery and controlled release [3], and photo- and  
42 electro-catalysis [4, 5]. To date, a range of hollow spherical materials have been fabricated using  
43 noble metals (e.g., Pt), oxides (e.g., TiO<sub>2</sub>, SiO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>), and carbon materials, among others [6-  
44 8]. However, most such materials have submicron sizes [6, 9, 10] and can only be obtained through  
45 complicated and expensive templating strategies [11]; solid hollow nanospheres with a diameter of  
46 a few nanometres have been rarely reported [12-14]. This largely hinders the potential applications  
47 of hollow spherical materials in dimension-selected areas.

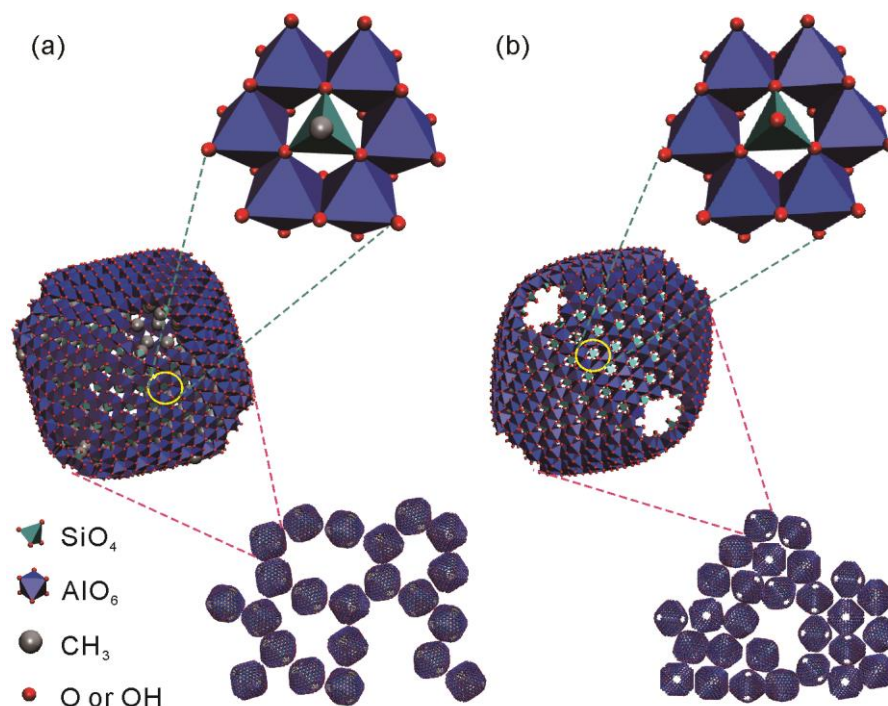
48       Allophane (1-2SiO<sub>2</sub>·Al<sub>2</sub>O<sub>3</sub>·5-6H<sub>2</sub>O, denoted Allo hereafter), a hydroxyaluminosilicate  
49 mineral that is widely distributed in soils of volcanic origin [15], is a naturally occurring hollow  
50 nanospherical material with a diameter of 3.5-5.0 nm and a wall thickness of 0.6-1.0 nm. The wall  
51 of Allo consists of a curved gibbsite-like sheet with Al<sub>2</sub>-μOH groups that are, on the inner side,  
52 substituted by orthosilicate groups. This local structure with a Si/Al molar ratio of 0.5 also occurs  
53 in imogolite (Imo, a nanotubular polymorph of Allo) and thus is called an imogolite local structure  
54 (ImoLS) [16]. Unlike Imo whose Si/Al molar ratio is 0.5, Allo has a Si/Al molar ratio of 0.5-1.0,  
55 and the excess Si is attached to the ImoLS in the form of oligomeric silicate, contributing to the low  
56 structural order of Allo. Several perforations with size of approximately 0.35 nm, formed by  
57 connection of vacancies, exist in the wall of Allo [17, 18] and these perforations serve as passages  
58 for small molecules such as H<sub>2</sub>O.

59       Allo originating from soils possesses a unique pore structure formed by loose stacking of  
60 particles, probably in a configuration of interleaved strings [19], which endows the Allo-rich soils  
61 with a low bulk density ( $\leq 0.85$  g/cm<sup>3</sup>), a high specific surface area (SSA, 15-90 m<sup>2</sup>/g [20]) and a  
62 large adsorption capacity towards guests [17]. However, natural Allo-rich soils are commonly multi-  
63 component, and purification procedures (e.g., removal of organic matter with H<sub>2</sub>O<sub>2</sub> and particle-  
64 size separation by sedimentation/centrifugation) are required to obtain highly pure Allo. During  
65 purification, the unique pore structure of Allo is readily destroyed via irreversible aggregation (also

66 referred to as shrinking [21]) of particles upon drying, which largely decreases the porosity and SSA  
67 of Allo. Synthesized high-purity Allo can be produced in large amounts but readily undergoes  
68 irreversible aggregation during drying even if freeze-drying is used [22, 23]. This irreversible  
69 aggregation results mainly from capillary stress in the inner cavity of unsaturated Allo [21], which  
70 represents the net interparticle stress that tends to pull one particle to another [24]. This capillary  
71 stress mainly results from the ultrasmall particle size of Allo with only short-range order in three  
72 dimensions [15, 25] and the highly hydrophilic inner surface [26] due to the prevailing Si–OH  
73 therein.

74 In this work, tailoring the capillary stress and thus the aggregation state of Allo is achieved by  
75 introducing methyl moieties onto the inner surface during preparation. A combination of techniques,  
76 such as X-ray diffraction (XRD), X-ray absorption near-edge structure (XANES) spectroscopy,  
77 cryo-transmission electron microscopy (Cryo-TEM), small-angle X-ray scattering (SAXS), thermal  
78 analysis and N<sub>2</sub> physisorption, have been used to detect the detailed methyl-modification-induced  
79 changes of structure, surface chemistry, inner-cavity capillary stress and aggregation state in the  
80 products and the mechanisms underneath these changes. This work simply uses  
81 triethoxymethylsilane (TEMS) to replace tetraethyl orthosilicate (TEOS), the most frequently used  
82 Si source for the synthesis of Allo. The hydrolysis and condensation of the Al and methyl-bearing  
83 Si precursors resulted in the formation of nanosized fragments [16, 27, 28] having a general formula  
84 of (OH)<sub>3</sub>Al<sub>2</sub>O<sub>3</sub>SiOCH<sub>3</sub>, and these fragments assembled into methyl-allophane (denoted mAllo  
85 hereafter) via oriented attachment and internal reorganization when they were small enough [29].  
86 Si–CH<sub>3</sub> groups are on the inner surface and Al–OH groups on the outer surface of the resultant  
87 mAllo (Fig. 1a), which differs with the structure of Allo of which Si–OH groups are on the inner  
88 surface (Fig. 1b). Such a change regulates the surface properties of mAllo and effectively inhibits  
89 the irreversible aggregation of mAllo particles during drying.

90



91

92 **Fig. 1** Schematic diagram of the structures of mAllo (a) and Allo (b). Si-CH<sub>3</sub> groups on the inner surface of mAllo  
 93 replace Si-OH groups (and oligomeric silicate at Si/Al molar ratios > 0.5) on the inner surface of Allo, resulting in  
 94 their different aggregation states in dried powder.

## 95 2. Experimental section

### 96 2.1 Materials and methods

97 Orthosilicate sodium (Na<sub>4</sub>SiO<sub>4</sub>) was purchased from Alfa Aesar, USA. Aluminium chloride  
 98 hexahydrate (AlCl<sub>3</sub> · 6H<sub>2</sub>O), TEOS and TEMS were provided by Aldrich, USA. All chemicals and  
 99 reagents used in this study were of analytical grade and used as received. Ultrapure water with a  
 100 resistivity of 18.25 MΩ·cm was used throughout the experiments. Methyl-imogolite (mImo) used  
 101 for comparison in the SAXS analysis is the same as that previously reported [30].

102 The experimental procedure for synthesizing mAllo is as follows: 0.1 M AlCl<sub>3</sub> and TEMS  
 103 were mixed at an initial Si/Al molar ratio of 0.75. To the resulting solution, 0.2 M NaOH was  
 104 added at a rate of 1.0 mL min<sup>-1</sup> until a value of OH/Al = 2 was achieved under continuous  
 105 stirring. After being stirred for another hour, the resulting dispersion was aged for one night  
 106 and then heated to and maintained at 100 °C for 48 h. The dispersion was coagulated by adding  
 107 diluted ammonia to approximately pH 7, centrifuged at 11000 rpm for 5 min, and dialysed for  
 108 4 days to remove the ethanol, Na<sup>+</sup> and Cl<sup>-</sup>. An aliquot of the dispersion was stored for scanning

109 transmission electron microscopy (STEM), atomic force microscopy (AFM), cryo-TEM and  
110 SAXS characterization, and the remainder was freeze-dried. The obtained solids were labelled  
111 as mAllo. For comparison, Allo was synthesized by following the above procedure except  
112 TEOS was used instead of TEMS as a Si source.

### 113 *2.2 Characterization techniques*

114 XRD analysis was performed on a Bruker D8 Advance diffractometer (Manheim,  
115 Germany) with a Ni filter and Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm) generated at 40 kV and 40 mA.  
116 The specimens were scanned from 2° to 70° (2 $\theta$ ) with a step size of 0.02° and a measuring time  
117 of 0.8 s per step.

118 Fourier transform infrared (FTIR) spectra were recorded using a Bruker Vertex 70 IR  
119 spectrometer (Manheim, Germany) at room temperature. The specimens were prepared by  
120 mixing 0.9 mg of sample and 80 mg of KBr, followed by pressing the mixture into pellets. A  
121 pure KBr wafer was measured and used as the background. All of the spectra were collected  
122 over 64 scans in the range of 4000–400 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

123 Solid state <sup>27</sup>Al magic-angle-spinning nuclear magnetic resonance (MAS NMR) and <sup>29</sup>Si MAS  
124 NMR spectra were recorded using a Bruker AVANCE III 600 spectrometer in a static magnetic field  
125 of 14.1 T at resonance frequencies of 156.4 and 119.2 MHz, respectively. <sup>27</sup>Al MAS NMR spectra  
126 were recorded on a 4 mm probe by the small-flip angle technique with a pulse length of 0.5  $\mu$ s ( $<$   
127  $\pi/12$ ), a recycle delay of 1 s and a spinning rate of 14 kHz. <sup>29</sup>Si MAS NMR spectra with high-power  
128 proton decoupling were recorded on a 4 mm probe with a spinning rate of 10 kHz, a  $\pi/4$  pulse length  
129 of 2.6  $\mu$ s, and a recycle delay of 40 s. The chemical shifts of <sup>27</sup>Al and <sup>29</sup>Si were referenced to 1 M  
130 Al(NO<sub>3</sub>)<sub>3</sub> and tetramethylsilane (TMS), respectively.

131 C K-edge XANES spectroscopy was recorded at the soft X-ray spectroscopy (4B7B)  
132 endstation of the Beijing Synchrotron Radiation Facility (BSRF). All the spectra were recorded at  
133 room temperature with a resolution of 0.2 eV in total electron yield (TEY) detection mode. The  
134 spectra were normalized to the incident photon flux.

135 The STEM images were collected on an FEI Talos F200S field-emission transmission  
136 electron microscope operating at an accelerating voltage of 200 kV. The specimens were  
137 prepared by dropping two droplets of the dispersion onto a carbon-coated copper grid.

138 AFM characterization was performed on a Bruker Multimode 8 scanning probe  
139 microscope with a silicon tip on a nitride lever. The ScanAsyst-air mode was used to protect  
140 the samples. To prepare the specimens, a mica sheet was cleaved (yielding a smooth negatively  
141 charged surface) and then dipped into the dispersion for 30 s. Then, two cleaning steps in water  
142 were performed to eliminate the excess materials. All of the specimens were dried in air for  
143 one week before the AFM measurements.

144 Cryo-TEM experiments were performed using a JEOL 2010 FEG microscope operating  
145 at 200 kV at a low temperature ( $-180\text{ }^{\circ}\text{C}$ ). Images were recorded with a Gatan camera. Drops  
146 of the dispersions were deposited on copper grids covered with a holey carbon film (Quantifoil  
147 R2/2) previously treated by glow discharging. The excess liquid on the grids was blotted with  
148 filter paper, and the grids were quickly immersed in liquid ethane to form a thin vitreous ice  
149 film. The whole process was conducted using a Vitrobot apparatus (FEI Company).

150 SAXS analysis was performed using a Xeuss 2.0 apparatus (Xenocs) under vacuum at a  
151 wavelength of  $1.542\text{ \AA}$ . The scattering vector, defined as  $\mathbf{q} = \mathbf{k}_d - \mathbf{k}_i$  (the wave vectors of the  
152 incident and scattered beams) and with a modulus of  $q = 4\pi \sin \theta / \lambda$  ( $\lambda$  is the incident  
153 wavelength and  $2\theta$  is the scattering angle), ranged from  $0.03$  to  $1.2\text{ \AA}^{-1}$  and was attained with  
154 a single sample-to-detector distance. The sample-to-detector distance was calibrated with  
155 tetradecanol and the detector count was normalized by empty beam measurements. Samples  
156 were sealed in glass capillaries (diameter of  $1.5\text{ mm}$ , wall thickness of  $0.1\text{ mm}$ , WJM-Glas).  
157 Standard procedures were applied to obtain the differential scattering cross section per unit  
158 volume (called hereafter intensity in  $\text{cm}^{-1}$ ) as a function of  $q$  [31].

159 Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were  
160 performed using a Netzsch STA 409PC instrument (Selb, Germany). Approximately  $10\text{ mg}$  of  
161 sample was heated in a corundum crucible from  $30$  to  $1000\text{ }^{\circ}\text{C}$  at a rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  in a  $\text{N}_2$   
162 atmosphere ( $60\text{ cm}^3/\text{min}$ ).

163 Nitrogen adsorption-desorption isotherms were measured on a Micromeritics ASAP 2020  
164 system (Micromeritics Co., Norcross, USA) at liquid nitrogen temperature ( $-196\text{ }^{\circ}\text{C}$ ). Before the  
165 measurement, the samples were outgassed at  $200\text{ }^{\circ}\text{C}$  for  $12\text{ h}$ . The specific surface area (SSA) value  
166 was calculated using the multiple-point Brunauer-Emmett-Teller (BET) method, and the total pore



167 volume ( $V_{\text{total}}$ ) was evaluated from the  $\text{N}_2$  uptake at a relative pressure of approximately 0.97. The  
168  $t$ -plot method was used to calculate the microporous specific surface area ( $\text{SSA}_{\text{micro}}$ ) and the  
169 micropore volume ( $V_{\text{micro}}$ ). The pore size distribution (PSD), ranging from 0.45 to 10 nm, was  
170 analysed using non-local density functional theory (NLDFT).

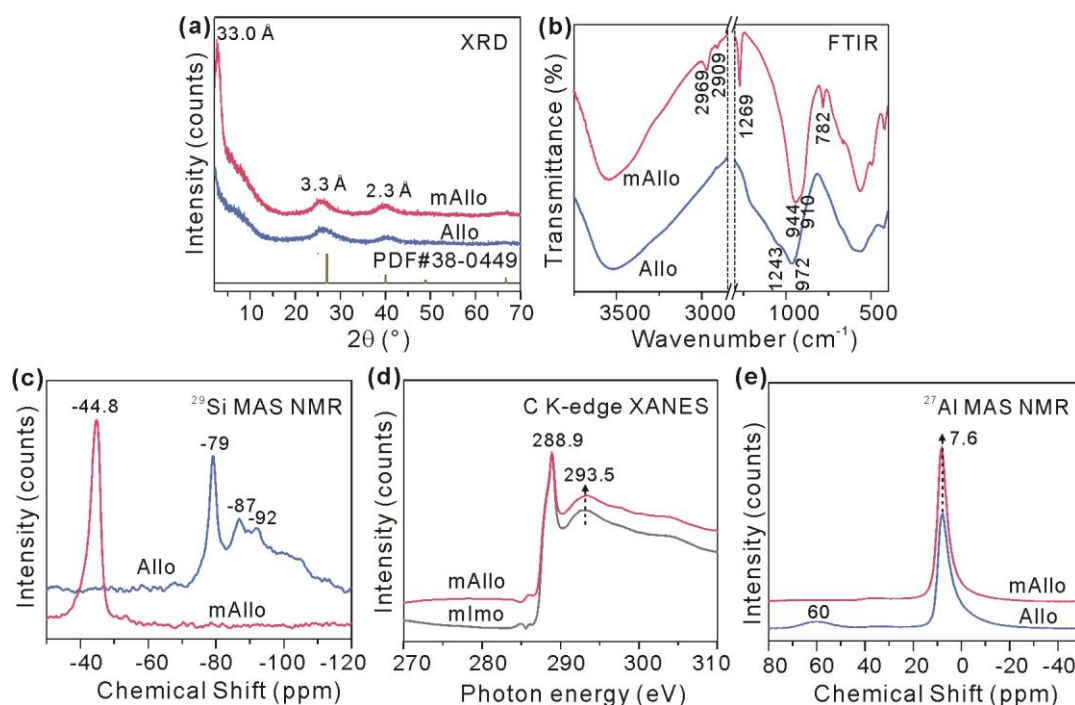
### 171 3. Results and discussion

#### 172 3.1 Structural changes at molecule or local scales

173 The structural changes induced by methyl modification were characterized via a combination  
174 of techniques. Two reflections at 3.3 and 2.3 Å that are characteristic of ImoLS were observed in  
175 the XRD pattern of mAllo (Fig. 2a), and the overall FTIR spectrum of mAllo (Fig. 2b) resembled  
176 that of Allo, both indicating that mAllo has a structure similar to that of Allo. Bands ascribed to Si–  
177  $\text{CH}_3$  [30] (including the asymmetric and symmetric stretching vibrations at 2969 and 2909  $\text{cm}^{-1}$  and  
178 the bending vibration at 1269  $\text{cm}^{-1}$ ) and to –Si–C [32] (bending vibration at 782  $\text{cm}^{-1}$ ) appeared in  
179 the FTIR spectrum of mAllo (Fig. 2b). A new resonance at –44.8 ppm that is ascribed to  
180  $\text{T}^3(6\text{Al})=\text{Si}-\text{CH}_3$  [33], instead of the resonance at –79 ppm that is ascribed to  $\text{T}^3(6\text{Al})=\text{Si}-\text{OH}$  [34]  
181 and is characteristic of ImoLS [16], was observed in the  $^{29}\text{Si}$  MAS NMR spectrum of mAllo (Fig.  
182 2c). Moreover, the C K-edge XANES spectrum of mAllo (Fig. 2d) exhibited peaks at 288.9 and  
183 293.5 eV, which might be attributed to the  $\sigma^*(\text{C}-\text{H})$  and  $\sigma^*(\text{C}-\text{Si})$  resonances, respectively. This  
184 result is almost identical to that for mImo (Fig. 2d), the structure of which has been well  
185 characterized [35], indicating the same chemical environments for C atoms (*i.e.*,  $\text{T}^3(6\text{Al})=\text{Si}-\text{CH}_3$ )  
186 in mAllo and mImo. From these results, methyl groups are assumed to be anchored to the inner  
187 surface of mAllo. The  $^{27}\text{Al}$  MAS NMR spectrum of mAllo (Fig. 2e) was dominated by a resonance  
188 at 7.6 ppm that is ascribed to six-coordinated Al ( $\text{Al}^{\text{VI}}$ ), which is similar to the case of Allo,  
189 indicating the same chemical environments for the Al atoms (*i.e.*, a curved gibbsite-like sheet  
190 serving as the outer framework [26]) in mAllo and Allo. The above mentioned results indicate that  
191 methyl modification occurs only on the inner surface of Allo, exhibiting little effect on the outer  
192 Al–O octahedral sheet.

193 A shoulder band at 1243  $\text{cm}^{-1}$ , which appeared in the FTIR spectrum of Allo and is ascribed to  
194 the oligomeric silicate on the inner surface, was absent in the spectrum of mAllo (Fig. 2b). This is

195 due to the presence of Si-CH<sub>3</sub> groups, which prevents the attachment of oligomeric silicate, resulting  
 196 in a higher structural order in mAllo than in Allo. This assumption is further supported by the change  
 197 of the band at approximately 1000 cm<sup>-1</sup> originating from the framework vibrations, of which the  
 198 high-wavenumber branch was much sharper in mAllo than in Allo (Fig. 2b). Moreover, the  
 199 resonance at 60 ppm in the <sup>27</sup>Al NMR spectrum of Allo, which is ascribed to four-coordinated Al  
 200 (Al<sup>IV</sup>), was absent in the spectrum of mAllo (Fig. 2e). A similar change occurred for the broad  
 201 resonance at approximately -90 ppm in the <sup>29</sup>Si NMR spectra (Fig. 2c), which is ascribed to a  
 202 significant fraction of less ordered Si species with 0–5 next-nearest neighbour Al atoms [28]. These  
 203 changes also indicate the presence of a more ordered structure in mAllo than in Allo.



204

205 **Fig. 2** XRD patterns (a), FTIR spectra (b), <sup>29</sup>Si MAS NMR spectra (c), C K-edge XANES spectra (d) and <sup>27</sup>Al MAS  
 206 NMR spectra (e) of mAllo (a-e) and Allo (a-c, e)/mImo (d).

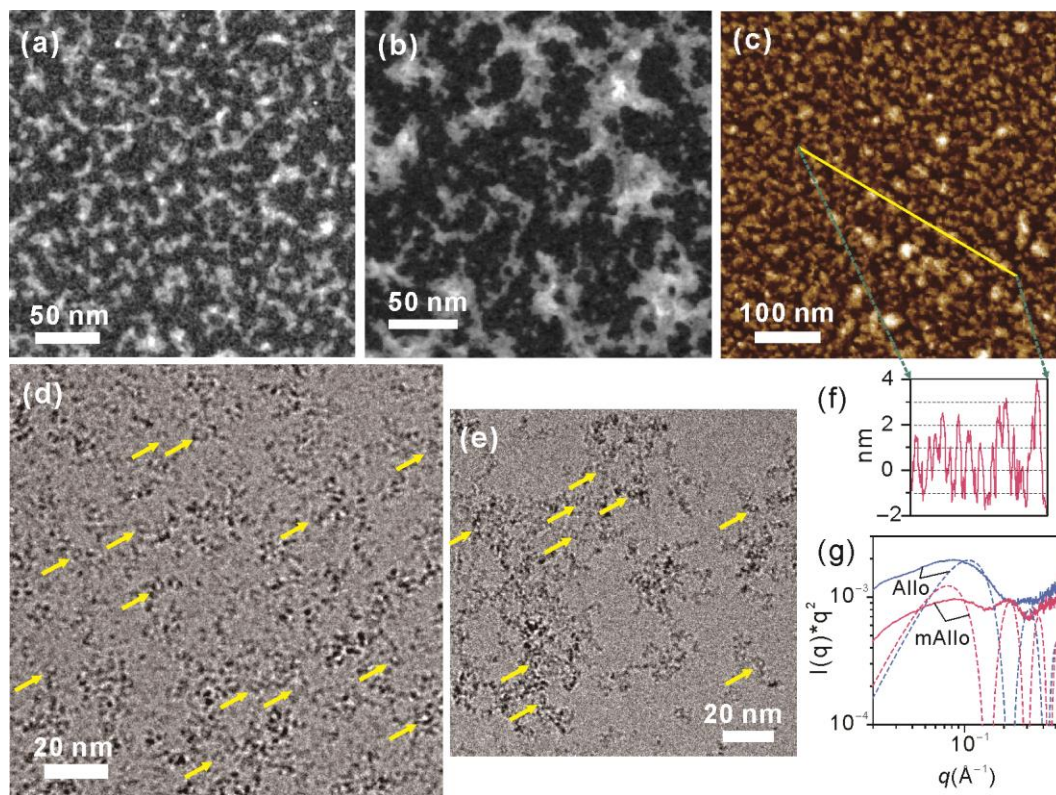
### 207 3.2 Changes of aggregation state and particle size

208 Microscopic observations showed distinct differences in aggregation behaviors between mAllo  
 209 and Allo. Very small nanoparticles were observed in the STEM image of mAllo (Fig. 3a). These  
 210 nanoparticles mainly occurred as interlaced strings, which is in contrast with the case of Allo where  
 211 large aggregates dominated (Fig. 3b). To avoid the possible damage resulting from long-term  
 212 exposure to an electron beam during STEM observation, AFM that operates under ambient

213 conditions was used to further characterize mAllo. A similar configuration of interlaced strings was  
214 shown in the AFM images of mAllo (Fig. 3c), albeit with different specimen preparation methods  
215 for STEM and AFM. This configuration might result from the interaction between particles in the  
216 same string. This assumption was further supported by the XRD and FTIR results. On the XRD  
217 pattern of mAllo (Fig. 2a), a very-small-angle peak was observed. This new reflection is ascribed  
218 to the interference between particles arising after drying, indicating that the particles in the same  
219 string are closely linked to each other. The band at approximately  $1000\text{ cm}^{-1}$  in the FTIR spectrum  
220 of Allo that arose from the Si–O stretching vibration was split into two bands at  $944$  and  $910\text{ cm}^{-1}$   
221 in the spectrum of mAllo (Fig. 2b). This splitting phenomenon into two bands also occurred in a  
222 more pronounced way in the FTIR spectra of Imo and mImo and are characteristic of a tubular  
223 morphology [29, 36]. However, the STEM and AFM results precluded the occurrence of any  
224 imogolite-like nanotubes that were produced as a byproduct (Fig. 3a,c). A possible explanation is  
225 that a moderate interparticle stress in the same string induced by capillary stress makes mAllo  
226 exhibit a similar FTIR adsorption feature as that of tubular Imo, while in the case of Allo, the  
227 presence of a strong interparticle stress prevents the formation of strings.

228 Cryo-TEM and SAXS have been used to characterize mAllo and Allo particles in dispersions  
229 (without potential drying artifacts). The hollow nanospherical structure of these nanoparticles,  
230 which is the most definitive feature of the Allo structure [17], was observed in the cryo-TEM images  
231 (highlighted by arrows in Fig. 3d,e). These hollow nanospheres were better dispersed (some of them  
232 were even isolated) compared to those observed in the STEM or AFM images. Unlike Allo particles  
233 that were gathered in aggregates having an average dimension of appropriately  $100\text{ nm}$  (Fig. 3e),  
234 mAllo particles were homogeneously distributed (Fig. 3d). Notably, some proto-  
235 (methyl-)imogolite-like fragments were probably present in the products (Fig. 3d,e), although they  
236 can hardly be differentiated from the nanospheres (mAllo or Allo) and quantified using cryo-TEM  
237 due to their very small sizes. The SAXS measurements of both Allo and mAllo revealed an increase  
238 of the intensity at the lowest scattering angles (Fig. 3g). The smooth increase of the intensity is  
239 characteristic of disordered (fractal) aggregates in dispersions. This is in good agreement with the  
240 cryo-TEM observations where both samples displayed aggregates (Fig. 3d,e). From these above  
241 microscopic and SAXS results, it is found that hollow nanospheres prevail in both Allo and mAllo

242 and that methyl modification induces changes in the arrangements of these nanospheres in both  
 243 liquid and dried powder.



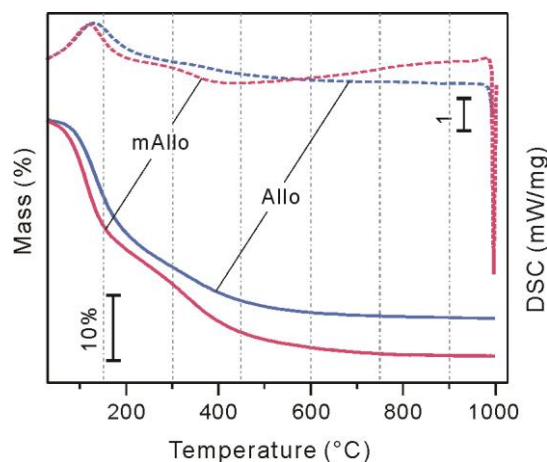
244  
 245 **Fig. 3** STEM images of mAllo (a) and Allo (b), AFM image of mAllo (c) and cryo-TEM images of mAllo (d) and  
 246 Allo (e). (f) Cross-section profile of the yellow line in (c), showing average particle sizes of 3–5 nm. (g) SAXS  
 247 curves of mAllo and Allo. Arrows in (d) and (e) highlight the presence of hollow nanospheres. The dash line in (g)  
 248 represents the expected scattering curves for monodispersed core-shell spheres with external (inner) diameters of  
 249 4.8 (3.6) and 3.6 (2.4) nm, respectively.

250 Thanks to the high  $z$ -axis resolution of AFM, an average particle size of 3–5 nm (with  
 251 appropriately 3 nm being dominant) of the mAllo particles was recorded (Fig. 3f). This average size  
 252 agrees with the previously reported values of Allo obtained by electron microscopy [17]. This result  
 253 indicates that the overall particle size of Allo remained in the same range upon methyl modification.  
 254 Similar SAXS curves with weak oscillations were observed for both samples (Fig. 3g). The  
 255 positions of these oscillations enable to access the average characteristic dimensions of mAllo and  
 256 Allo through comparison with the oscillation positions of modeled core-shell particles [30, 36]. The  
 257 dimensions that yield oscillations at the closest positions indicate an inner/external diameter of  
 258 3.6/4.8 nm for mAllo and 2.4/3.6 nm for Allo (Fig. 3g). Notably, in addition to mAllo particles with

259 sizes of 3–5 nm, a few of particles with  $z$ -scans of less than 1 nm were observed (Fig. 3f). It is likely  
260 that these particles are proto-methyl-imogolite-like fragments that adsorb flat on mica sheets, as  
261 previously reported [16]. Despite not being fully quantitative, the proportion of the particles with  
262 different sizes, summarized from the repeated section analyses of the AFM images, indicates that  
263 hollow nanosphere is the dominating morphology of the nanoparticles.

### 264 3.3 Changes of surface hydrophilicity

265 These structural changes result in modification of the inner-surface hydrophilicity of the  
266 products. As exhibited in the TG curves (Fig. 4), for the mass loss below 150 °C, which is mainly  
267 attributed to the desorption of physisorbed water [26], a lower temperature was required for mAllo  
268 than for Allo to lose the same mass. The corresponding endothermic peak in the DSC curves also  
269 occurred at a lower temperature for mAllo than for Allo (Fig. 4). These results indicate that the  
270 physisorbed water in mAllo is removable at a lower temperature than that in Allo; that is, the inner  
271 surface of mAllo is less hydrophilic than that of Allo.



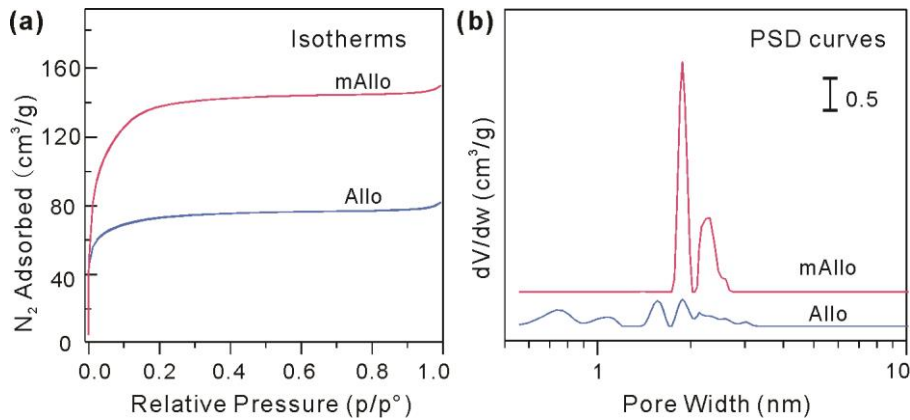
272

273 **Fig. 4** TG-DSC curves of mAllo and Allo.

### 274 3.4 Changes of porosity and specific surface area

275 According to the International Union of Pure and Applied Chemistry (IUPAC)  
276 recommendation [37], the  $N_2$  physisorption isotherms of mAllo and Allo are characterized as type I  
277 (Fig. 5a), indicating that both materials are dominated by micropores. The SSA and  $V_{\text{total}}$  of mAllo  
278 ( $523 \text{ m}^2/\text{g}$  and  $0.2273 \text{ cm}^3/\text{g}$ ) were much higher than those of Allo ( $269 \text{ m}^2/\text{g}$  and  $0.1222 \text{ cm}^3/\text{g}$ )  
279 (Table 1). As discussed above, methyl modification results in limited changes in the particle sizes

280 and outer structural framework of Allo. The high SSA and porosity of mAllo arise from the  
 281 configuration of interlaced strings. In addition, the PSD curves derived using a NLDFT method (Fig.  
 282 5b) exhibited a distinct difference. Specifically, micropores with wide-ranging diameters were  
 283 observed in Allo, while pores with diameters of approximately 2 nm dominated in mAllo. This  
 284 difference might be because the pores in Allo originated from cavities between aggregates formed  
 285 by the irreversible aggregation of particles, while the pores in mAllo arose from the network formed  
 286 by the interleaving of strings of particles (as schematically shown in Fig. 1).



287

288

**Fig. 5** N<sub>2</sub> adsorption/desorption isotherms (a) and PSD curves (b) of mAllo and Allo.

289

**Table 1** Textural data of mAllo and Allo obtained from N<sub>2</sub> adsorption analysis.

	SSA (m <sup>2</sup> /g)	SSA <sub>micro</sub> (m <sup>2</sup> /g)	V <sub>total</sub> (cm <sup>3</sup> /g)	V <sub>micro</sub> (cm <sup>3</sup> /g)
Allo	269.5	267.2	0.1222	0.1156
mAllo	523.1	519.6	0.2273	0.2191

290

### 3.5 Mechanisms underneath the above mentioned changes

291

As discussed above, the introduction of Si-CH<sub>3</sub> to the inner surface of mAllo makes this  
 292 surface less hydrophilic than that of Allo. The weakened surface hydrophilicity decreases the  
 293 capillary stress in the inner cavity of mAllo and thus inhibits the irreversible aggregation of particles  
 294 during drying, resulting in higher SSA and porosity values. On the other hand, the absence of Si-  
 295 OH on the inner surface of mAllo prevents the formation of oligomeric silicate therein and thus  
 296 increases the structural order and total pore volume of this material. Notably, the simultaneous  
 297 absence of oligomeric silicate and Al<sup>IV</sup> in mAllo might provide insight into the probable location of  
 298 Al<sup>IV</sup> in the Allo structure; *i.e.*, Al<sup>IV</sup> might be mainly located in oligomeric silicate by substituting Si

299 on the inner surface, which sheds light on the long-standing question of whether Al<sup>IV</sup> is located  
300 around the perforations on the wall [38] or in the oligomeric silicate upon substituting Si atoms [39]  
301 in the Allo structure. This assumption is further supported by the fact that scarcely any Al<sup>IV</sup> occurs  
302 in Imo consisting of only ImoLS [28].

#### 303 **4. Conclusion**

304 Tailoring the structure and surface chemistry and thus the aggregation state of hollow Allo  
305 nanospheres has been achieved by a simple strategy of methyl modification. The as-obtained mAllo  
306 is a novel hollow nanospherical material with a higher structural order, a much less hydrophilic  
307 inner surface and a larger porosity and SSA than Allo, which allow its promising applications in a  
308 variety of fields such as selective gas adsorption. This facile inner-surface methyl-modification  
309 method and the basic knowledge on the mechanisms underneath the changes of the structure, surface  
310 chemistry, inner-cavity capillary stress and aggregation state of Allo nanospheres reported in this  
311 work is of great significance for dealing with the common aggregation issue of other nanomaterials.

#### 312 **Conflicts of interest**

313 There are no conflicts to declare.

#### 314 **Acknowledgements**

315 This work is supported by the Science and Technology Planning Project of Guangdong Province,  
316 China (2017B020237003), the National Natural Science Foundation of China (41672042 and  
317 41972045), Youth Innovation Promotion Association CAS for the excellent members (2016-81-01),  
318 the China Postdoctoral Science Foundation (2018M640831) and the Open Funds of the Beijing  
319 Synchrotron Radiation Facility (2017-BEPC-PT-001065). Cryo-TEM observations were made,  
320 thanks to “Investissements d’Avenir” LabEx PALM (ANR-10-LABX-0039-PALM). This is a  
321 contribution (No. xxxx) from GIGCAS.

#### 322 **References**

323 [1] M. Sasidharan, K. Nakashima, N. Gunawardhana, T. Yokoi, M. Inoue, S.-i. Yusa, M. Yoshio, T.  
324 Tatsumi, Novel titania hollow nanospheres of size  $28 \pm 1$  nm using soft-templates and their application  
325 for lithium-ion rechargeable batteries, *Chem. Commun.*, 47 (2011) 6921-6923.

- 326 [2] M.Q. Zhu, S.M. Li, J.H. Liu, B. Li, Promoting polysulfide conversion by V<sub>2</sub>O<sub>3</sub> hollow sphere for  
327 enhanced lithium-sulfur battery, *Appl. Surf. Sci.*, 473 (2019) 1002-1008.
- 328 [3] Y. Hu, Y. Ding, D. Ding, M. Sun, L. Zhang, X. Jiang, C. Yang, Hollow chitosan/poly (acrylic acid)  
329 nanospheres as drug carriers, *Biomacromolecules*, 8 (2007) 1069-1076.
- 330 [4] H.P. Liang, H.M. Zhang, J.S. Hu, Y.G. Guo, L.J. Wan, C.L. Bai, Pt hollow nanospheres: facile  
331 synthesis and enhanced electrocatalysts, *Angew. Chem. Int. Edit.*, 43 (2004) 1540-1543.
- 332 [5] M. Tian, X.L. Cui, C.X. Dong, Z.P. Dong, Palladium nanoparticles dispersed on the hollow  
333 aluminosilicate microsphere@hierarchical gamma-AlOOH as an excellent catalyst for the hydrogenation  
334 of nitroarenes under ambient conditions, *Appl. Surf. Sci.*, 390 (2016) 100-106.
- 335 [6] F. Xu, Z. Tang, S. Huang, L. Chen, Y. Liang, W. Mai, H. Zhong, R. Fu, D. Wu, Facile synthesis of  
336 ultrahigh-surface-area hollow carbon nanospheres for enhanced adsorption and energy storage, *Nat.*  
337 *Commun.*, 6 (2015) 7221.
- 338 [7] W.J. Wu, W.T. Qi, Y.F. Zhao, X. Tang, Y.F. Qiu, D.W. Su, H.B. Fan, G.X. Wang, Hollow CeO<sub>2</sub> spheres  
339 conformally coated with graphitic carbon for highperformance supercapacitor electrodes, *Appl. Surf.*  
340 *Sci.*, 463 (2019) 244-252.
- 341 [8] A.E. Awadallah, W. Ahmed, M.R.N. El-Din, A.A. Aboul-Enein, Novel aluminosilicate hollow sphere  
342 as a catalyst support for methane decomposition to CO<sub>x</sub>-free hydrogen production, *Appl. Surf. Sci.*, 287  
343 (2013) 415-422.
- 344 [9] G. Zheng, S.W. Lee, Z. Liang, H.-W. Lee, K. Yan, H. Yao, H. Wang, W. Li, S. Chu, Y. Cui,  
345 Interconnected hollow carbon nanospheres for stable lithium metal anodes, *Nature Nanotechnology*, 9  
346 (2014) 618-623.
- 347 [10] Z. Zhou, J. Gu, X. Qiao, H. Wu, H. Fu, L. Wang, H. Li, L. Ma, Double protected lanthanide  
348 fluorescence core@shell colloidal hybrid for the selective and sensitive detection of ClO<sup>-</sup>, *Sensors*  
349 *Actuators B: Chem.*, 282 (2019) 437-442.
- 350 [11] X.W. Lou, L.A. Archer, Z. Yang, Hollow micro-/nanostructures: synthesis and applications, *Adv.*  
351 *Mater.*, 20 (2008) 3987-4019.
- 352 [12] B.H. Bac, Y. Song, M.H. Kim, Y.-B. Lee, I.M. Kang, Single-walled hollow nanospheres assembled  
353 from the aluminogermanate precursors, *Chem. Commun.*, (2009) 5740-5742.
- 354 [13] M.B. Tahir, G. Nabi, N.R. Khalid, W.S. Khan, Synthesis of Nanostructured Based WO<sub>3</sub> Materials  
355 for Photocatalytic Applications, *J. Inorg. Organomet. P.*, 28 (2018) 777-782.
- 356 [14] Y. Wu, H. Wang, W. Tu, Y. Liu, Y.Z. Tan, X. Yuan, J.W. Chew, Quasi-polymeric construction of  
357 stable perovskite-type LaFeO<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> heterostructured photocatalyst for improved Z-scheme  
358 photocatalytic activity via solid p-n heterojunction interfacial effect, *J. Hazard. Mater.*, 347 (2018) 412-  
359 422.
- 360 [15] C. Levard, E. Doelsch, I. Basile-Doelsch, Z. Abidin, H. Miche, A. Masion, J. Rose, D. Borschneck,  
361 J.Y. Bottero, Structure and distribution of allophanes, imogolite and proto-imogolite in volcanic soils,  
362 *Geoderma*, 183 (2012) 100-108.
- 363 [16] P. Du, P. Yuan, A. Thill, F. Annabi-Bergaya, D. Liu, S. Wang, Insights into the formation mechanism  
364 of imogolite from a full-range observation of its sol-gel growth, *Appl. Clay Sci.*, 150 (2017) 115-124.
- 365 [17] R. Parfitt, Allophane and imogolite: role in soil biogeochemical processes, *Clay Miner.*, 44 (2009)  
366 135-155.
- 367 [18] B. Creton, D. Bougeard, K.S. Smirnov, J. Guilment, O. Poncelet, Structural model and computer  
368 modeling study of allophane, *J. Phys. Chem. C*, 112 (2008) 358-364.
- 369 [19] Y. Adachi, J. Karube, Application of a scaling law to the analysis of allophane aggregates, *Colloid*



370 Surface A, 151 (1999) 43-47.

371 [20] S. Filimonova, S. Kaufhold, F.E. Wagner, W. Häusler, I. Kögel-Knabner, The role of allophane nano-  
372 structure and Fe oxide speciation for hosting soil organic matter in an allophanic Andosol, *Geochim.*  
373 *Cosmochim. Ac.*, 180 (2016) 284-302.

374 [21] T. Woignier, J. Primera, L. Duffours, P. Dieudonné A. Raada, Preservation of the allophanic soils  
375 structure by supercritical drying, *Micropor. Mesopor. Mater.*, 109 (2008) 370-375.

376 [22] F. Ohashi, S.-I. Wada, M. Suzuki, M. Maeda, S. Tomura, Synthetic allophane from high-  
377 concentration solutions: nanoengineering of the porous solid, *Clay Miner.*, 37 (2002) 451-456.

378 [23] J. Castello, J.J. Gaumet, J.F. Muller, S. Derousseaux, J. Guilment, O. Poncelet, Laser ablation of  
379 aluminosilicates: Comparison between allophane and mixed alumina/silicas by Fourier Transform-Ion  
380 Cyclotron Resonance-Mass Spectrometry, *Appl. Surf. Sci.*, 253 (2007) 7773-7778.

381 [24] W.J. Likos, N. Lu, Hysteresis of capillary stress in unsaturated granular soil, *J Eng Mech-Asce*, 130  
382 (2004) 646-655.

383 [25] D. Wang, A. Fernandez-Martinez, Order from disorder, *Science*, 337 (2012) 812-813.

384 [26] P. Du, P. Yuan, D. Liu, S. Wang, H. Song, H. Guo, Calcination-induced changes in structure,  
385 morphology, and porosity of allophane, *Appl. Clay Sci.*, 158 (2018) 211-218.

386 [27] V. Farmer, A. Fraser, J. Tait, Synthesis of imogolite: a tubular aluminum silicate polymer, *J. Chem.*  
387 *Soc., Chem. Commun.*, (1977) 462-463.

388 [28] G.I. Yucelen, R.P. Choudhury, A. Vyalikh, U. Scheler, H.W. Beckham, S. Nair, Formation of single-  
389 walled aluminosilicate nanotubes from molecular precursors and curved nanoscale intermediates, *J. Am.*  
390 *Chem. Soc.*, 133 (2011) 5397-5412.

391 [29] A. Thill, P. Picot, L. Belloni, A mechanism for the sphere/tube shape transition of nanoparticles with  
392 an imogolite local structure (imogolite and allophane), *Appl. Clay Sci.*, 141 (2017) 308-315.

393 [30] Y. Liao, P. Picot, J.-B. Brubach, P. Roy, S. Le Caër, A. Thill, Self-supporting thin films of imogolite  
394 and imogolite-like nanotubes for infrared spectroscopy, *Appl. Clay Sci.*, 164 (2017) 58-67.

395 [31] P. Lindner, T. Zemb, *Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed*  
396 *Matter*, Elsevier, 2002.

397 [32] M. Boyer, E. Paineau, M. Bacia-Verloop, A. Thill, Aqueous dispersion state of amphiphilic hybrid  
398 aluminosilicate nanotubes, *Appl. Clay Sci.*, 96 (2014) 45-49.

399 [33] D.-Y. Kang, N.A. Brunelli, G.I. Yucelen, A. Venkatasubramanian, J. Zang, J. Leisen, P.J. Hesketh,  
400 C.W. Jones, S. Nair, Direct synthesis of single-walled aminoaluminosilicate nanotubes with enhanced  
401 molecular adsorption selectivity, *Nat. Commun.*, 5 (2014) 3342.

402 [34] P.F. Barron, M.A. Wilson, A.S. Campbell, R.L. Frost, Detection of imogolite in soils using solid-  
403 state Si-29 NMR, *Nature*, 299 (1982) 616-618.

404 [35] I. Bottero, B. Bonelli, S.E. Ashbrook, P.A. Wright, W.Z. Zhou, M. Tagliabue, M. Armandi, E.  
405 Garrone, Synthesis and characterization of hybrid organic/inorganic nanotubes of the imogolite type and  
406 their behaviour towards methane adsorption, *Phys. Chem. Chem. Phys.*, 13 (2011) 744-750.

407 [36] M.S. Amara, S. Rouzière, E. Paineau, M. Bacia-Verloop, A. Thill, P. Launois, Hexagonalization of  
408 aluminogermanate imogolite nanotubes organized into closed-packed bundles, *J. Phys. Chem. C*, 118  
409 (2014) 9299-9306.

410 [37] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.  
411 Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size  
412 distribution (IUPAC Technical Report), *Pure Appl. Chem.*, 87 (2015) 1051-1069.

413 [38] H. Shimizu, T. Watanabe, T. Henmi, A. Masuda, H. Saito, Studies on allophane and imogolite by

414 high-resolution solid-state  $^{29}\text{Si}$ - and  $^{27}\text{Al}$ -NMR and ESR, *Geochem. J.*, 22 (1988) 23-31.  
415 [39] B. Goodman, J. Russell, B. Montez, E. Oldfield, R. Kirkpatrick, Structural studies of imogolite and  
416 allophanes by aluminum-27 and silicon-29 nuclear magnetic resonance spectroscopy, *Phys. Chem.*  
417 *Miner.*, 12 (1985) 342-346.  
418