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Research paper

# A structural comparison of halloysite nanotubes of different origin by Small-Angle Neutron Scattering (SANS) and Electric Birefringence

Giuseppe Cavallaro[a,b,*], Leonardo Chiappisi[a,c], Pooria Pasbakhsh[d], Michael Gradzielski[a], Giuseppe Lazzara[b]

[a] Stranski Laboratorium für Physikalische und Theoretische Chemie, Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, Sekr. TC 7, Berlin 10623, Germany

[b] Dipartimento di Fisica e Chimica, Università degli Studi di Palermo, Viale delle Scienze pad 17, Palermo 90128, Italy.

[c] LSS Group, Institut Laue-Langevin, 6 rue Jules Horowitz BP 156, Grenoble F-38042, Cedex 9, France

[d] Advanced Engineering Platform, Mechanical Engineering Discipline, School of Engineering, Monash University Malaysia, Selangor 47500, Malaysia

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ABSTRACT

The structure of halloysite nanotubes (Hal) from different mines was investigated by Small-Angle Neutron Scattering (SANS) and Electric Birefringence (EBR) experiments. The analysis of the SANS curves allowed us to correlate the sizes and polydispersity and the specific surfaces (obtained by a Porod analysis of the SANS data) of the nanotubes with their specific geological setting. Contrast matching measurements were performed on patch Hal (from Western Australia) in order to determine their experimental scattering length density for a more precise analysis. Further characterization of the mesoscopic structure of Hal was carried out by Electric Birefringence (EBR), which allowed to study the rotational mobility of Hal. From the obtained rotational diffusion coefficients of the different Hal we deduced their length via the Broersma theory, which compares well to TEM data. The analysis of both SANS and EBR data provided a bulk average information on the Hal structure in water, which, for instance, documented the markedly higher degree of well-definedness of the PT-Hal and the thinner tube walls present here. The attained systematic structural knowledge represents a step forward for the robust structural description of halloysites selected from four geological deposits and shows that Hal of different origin differ very markedly with respect to their mesoscopic structure.

## 1. Introduction

In recent years, clay nanoparticles have attracted a large and growing interest because their physico-chemical properties may be easily tuned endowing to obtain green nanostructures promising for several biological and industrial applications (Ruiz-Hitzky et al., 2010; Viseras et al., 2010; Lvov and Abdullayev, 2013). Among the nanoclays, halloysite nanotubes (Hal) are a newly emerging nanomaterial as a consequence of their versatile characteristics, such as large specific area, tunable surface chemistry, and especially their hollow tubular morphology, which render them rather unique (Yuan et al., 2015; Churchman et al., 2016; Yang et al., 2016). Halloysite is biocompatible and nontoxic as demonstrated by several in vitro and in vivo studies (Dzamukova et al., 2015; Fakhrullina et al., 2015; Liu et al., 2017). Based on these properties, Hal can be considered proper nanofillers for polymer composites (Liu et al., 2007, 2012; Gorrasi, 2015; Bertolino et al., 2017; Makaremi et al., 2017), and efficient adsorbents for decontamination purposes (Zhao and Liu, 2008; Cavallaro et al., 2014; Owoseni et al., 2014; von Klitzing et al., 2016;). It was proved that the halloysite outer surface represents an efficient catalytic support (Machado et al., 2008; Yuan et al., 2008; Wang et al., 2011; Hong et al., 2014), while the Hal cavity can be employed for the encapsulation and controlled release of antibacterial, (Aguzzi et al., 2013; Wei et al., 2014; Cavallaro et al., 2015) anticorrosive (Abdullayev et al., 2009) and antioxidant (Biddeci et al., 2016) molecules. Chemically, halloysite is composed of gibbsite octahedral sheet (Al–OH) groups on the inner surface and siloxane (Si–O–Si) groups on the external surface. This different chemistry results in a positively charged lumen and a negatively charged shell in the 2–8 pH range as a consequence of different ionization properties of aluminum and silicon oxides (Vergaro et al., 2010). As concerns the Hal sizes, the nanotubes are quite polydisperse, where the polydispersity depends on their geological deposit (Pasbakhsh et al., 2013). Typically, the length of Hal is about 1000 nm, while the external and internal diameters range between 20 and 200 and 10–70 nm, respectively (Pasbakhsh et al., 2013). Patch nanotubes (PT-Hal) from Western Australia represent the purest form of halloysite

* Corresponding author.
*E-mail address:* giuseppe.cavallaro@unipa.it (G. Cavallaro).

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(Pasbakhsh et al., 2013). Compared to the halloysites from different mines, PT-Hal is longer and thinner generating a fibrous structure that is promising for their applications as fillers for polymers. Our recent work (Makaremi et al., 2017) proved that pectin filling with PT-Hal induces a relevant enhancement of the thermal stability of the biopolymer because of the bird nest structure formed by the nanotubes inside the bionanocomposite film. It is interesting to note that the morphological features of PT-Hal were comprehensively investigated in the solid state by X-ray diffraction (XRD) and microscopy techniques, which highlighted that these nanotubes possess the lowest polydispersity in size compared to the other halloysites (Pasbakhsh et al., 2013). On the other hand, so far literature does not report any studies on the structural analysis of PT-Hal in aqueous solution. The characterization of PT-Hal aqueous dispersions can provide a mesoscopic structural picture by the analysis of bulk properties describing how these colloids are present in water (single nanotubes, aggregates, etc), which is crucial for the processing of the nanotubes and their applications within materials science and biotechnology. In that context, small-angle scattering with neutrons (SANS) and X-ray (SAXS) are appropriate techniques to determine the bulk average information on the structure of inorganic tubular nanoparticles, such as halloysite (Cavallaro et al., 2016) and imogolite (Paineau et al., 2016; Taché et al., 2016). The analysis of SANS data provided a straightforward description of the structural properties of Hal/surfactant hybrids (Cavallaro et al., 2016). This work reports the first SANS study of pristine Hal obtained from different sources. The analysis of SANS curves allowed us to estimate the influence of the specific geological deposit on the Hal sizes (and their corresponding polydispersity) as well as on their specific surfaces. The results determined from the analysis of SANS data were correlated to the Hal rotational mobility, which was investigated by Electric Birefringence (EBR) experiments. This paper represents a further step for the complete structural characterization of halloysite nanotubes focusing on the influence of the specific geological deposit toward the mesoscopic structure.

## 2. Materials and methods

### 2.1. Materials

Four halloysite samples from various geological deposits were investigated, details are given in Table 1. DG-Hal and UP-Hal were purchased from Sigma Aldrich and I-Minerals Inc., respectively. MB-Hal were supplied as a "processed product" by Imerys from their Matauri Bay operation, while PT-Hal were a field sample donated by K. Norrish (University of Adelaide). PT-Hal flocculated readily when dispersed in deionized water. Repeated washing and adjustment of pH to 7.5–8, with NaOH, was necessary to achieve a clay suspension. Separation of coarse impurities, including quartz sand and silt, was by gravity sedimentation and size separation following Stokes' Law. Water was of Millipore grade. $D_2O$ was purchased from Eurisotop in 99.9% isotopic purity.

Halloysite samples were preliminarily characterized by X-ray fluorescence (XRF) and X-ray diffraction (XRD) analyses in order to determine their chemical and mineralogical compositions, The analysis of XRF data provided the major oxides chemistry of halloysites from four different sources (Table 2).

**Table 1**
Sources of halloysite samples in this study.

| Sample code | Geological deposit | Locality |
|---|---|---|
| DG-Hal | Dragon Mine | Utah, North America |
| UP-Hal | Latah County | NW Idaho, North America |
| MB-Hal | Matauri Bay | Northland, New Zealand |
| PT-Hal | Siberia, 85 km NW of Kalgoorlie | Western Australia |

**Table 2**
Major oxides chemistry by X-ray fluorescence (XRF) analysis.

| | DG-Hal | PT-Hal | MB-Hal | UP-Hal |
|---|---|---|---|---|
| $Na_2O$ % | 0.012 | 0.07 | 0.063 | 0.060 |
| MgO % | 0.039 | 0.21 | – | 0.179 |
| $Al_2O_3$% | 38.7 | 36.86 | 35.786 | 36.2 |
| $SiO_2$% | 46.4 | 45.64 | 50.136 | 47.4 |
| $P_2O_5$% | 0.106 | 0.01 | 0.277 | 0.032 |
| $SO_3$% | 0.1 | 0.22 | 0.080 | 0.102 |
| $K_2O$ % | 0.036 | 0.02 | 0.019 | 0.400 |
| CaO % | 0.17 | 0.8 | 0.012 | 0.070 |
| $TiO_2$% | 0.025 | 0.08 | 0.114 | 0.384 |
| MnO % | 0.001 | 0.02 | – | 0.017 |
| $Fe_2O_3$% | 0.5 | 0.65 | 0.384 | 1.630 |
| ZnO % | 0.002 | – | – | 0.005 |
| SUM % | 86.165 | 84.82 | 86.87 | 86.48 |
| LOI % | 13.835 | 15.18 | 13.13 | 13.52 |

The results are consistent with a kaolin group mineral of theoretical composition $SiO_2$ 46.5%, $Al_2O_3$ 39.5% and $H_2O$ 13.95%. Hal-MB and Hal-UP showed higher silica content, indicative of a fine-grained silica impurity. Higher $Fe_2O_3$ concentration was detected in UP-Hal and PT-Hal as expected by the reddish/brownish colour of the initial collected samples. UP-Hal had the highest amount of $TiO_2$. The presence of $K_2O$ and $SO_3$ in DG-Hal and UP-Hal can reflect some traces of alunite (Pasbakhsh et al., 2013). Lowest $Fe_2O_3$ content was recorded for MB-Hal. We observed that DG-Hal possesses the highest alumina content and also comparatively high phosphorus, possibly from the remains of the pyrophosphate dispersant that may have been used in its preparation, along with a minor contribution from the phosphate mineral woodhouseite (Pasbakhsh et al., 2013).

XRD patterns of the four different types of halloysites are illustrated in Fig. 1. It should be noted that the XRD spectrum for PT-Hal was

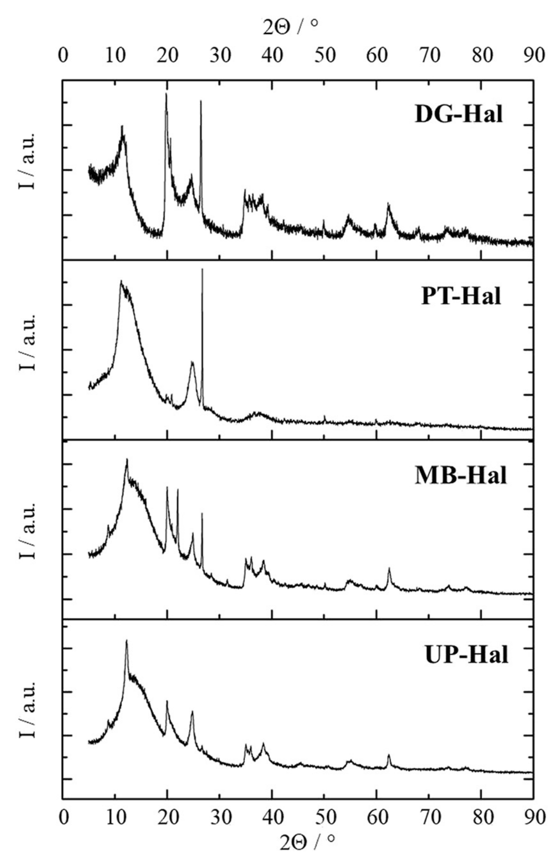


**Fig. 1.** X-ray diffraction (XRD) patterns of halloysite nanotubes.