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Review article

Properties and applications of halloysite nanotubes: recent research advances and future prospects

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ABSTRACT

Halloysite is a natural nanosized tubular clay mineral that has many potentially important uses in different industrial fields. In this paper, the key structural characteristics and properties of halloysite and their related applications are comprehensively reviewed. Research advances on halloysite, especially those from the past 20 years, are summarized with some critical comments. Attention is mainly paid to the structure and morphology of halloysite and their changes, the formation of tubular structures, the physicochemical properties, the surface chemical modifications, and the halloysite-based advanced materials and some related applications. Additionally, future prospects and key problems to be solved in halloysite studies are discussed. This review shed new light on both fundamental and applied studies that focused on halloysite.

1. Introduction

Nanosized tubular halloysite, also called halloysite nanotube (HNT) in some materials science publications, is the dominant form of naturally occurring halloysite. It was first described by Berthier (1826) as a dioctahedral 1:1 clay mineral of the kaolin group. The multilayer tubular structure of halloysite results from the wrapping of the 1:1 clay mineral layers under favorable geological conditions, driven by a mismatch in the oxygen-sharing tetrahedral and octahedral sheets in the 1:1 layer (Bates et al., 1950; Singh, 1996). Halloysite is chemically similar to kaolinite, but the unit layers in halloysite are separated by a monolayer of water molecules; accordingly, halloysite has a structural formula of $Al_2(OH)_4Si_2O_5 \cdot nH_2O$. The hydrated form of halloysite (when $n = 2$) is named "halloysite-(10 Å)", in which one layer of water molecules is present between the multilayers and where the "10 Å" designation indicates the d_{001}-value of the layers. The dehydrated structure of halloysite (when $n = 0$) is named "halloysite-(7 Å)", and may be obtained through the loss of the interlayer water molecules under mild heating and/or a vacuum environment (Joussein et al., 2005). A schematic diagram of the structure of halloysite-(10 Å) is shown in Fig. 1. In this paper, "halloysite" is used hereafter for simplicity, regardless of hydration or dehydration, unless otherwise noted and will be abbreviated "Hal".

Worldwide, large Hal deposits have been found in Australia, the United States, China, New Zealand, Mexico, and Brazil (Joussein et al., 2005). However, the overall yield of Hal is much lower than the huge production of kaolinite (which will be abbreviated Kaol in this review). Natural Hal often contains impurity phases and varies in morphology and porosity in the different deposits (Pasbakhsh et al., 2013). In general, Hal nanotubes vary in length from the submicron scale to several microns, sometimes even >30 μm (Joussein et al, 2005), in external diameter from approximately 30 to 190 nm, and in internal diameter from approximately 10 to 100 nm (Yuan et al., 2008, 2013).

In the past decade, again Hal became a focus of many studies and patents, although its nanoscale structure had been identified already since few decades (Bates et al., 1950) *via* spectroscopic methods. This renewed interest should be ascribed to the rapid developments of nanoscience and nanotechnology in the past two decades, which drive the increasing interest on naturally occurring nanometric structures. Natural Hal exhibits several advantages in applications over synthetic nanotubes such as carbon nanotube (CNT). According to Lvov et al. (2008), Hal is a low-cost material (at about $4 per kg though the purification process could arise the price of raw ores, and this cost is much less expensive in developed countries) and its global supply exceeds thousands of tons per year, meaning that true mass-scale industrial applications can readily be achieved, unlike the gram-scale yielding of CNT with a very high price ($500 per kg). Furthermore, the advantage

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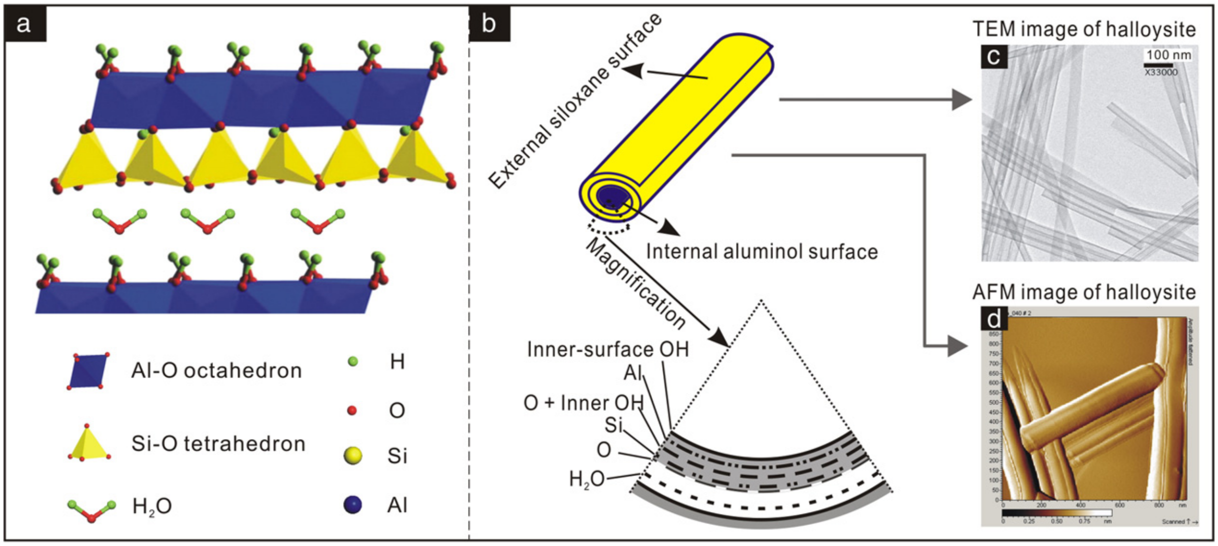

Fig. 1. Schematic diagram of (a) crystalline structure of Hal-(10 Å), (b) structure of Hal particle, (c–f) TEM and AFM images of Hal.

of Hal is not limited to its economic viability. Hal possesses a one-dimensional tubular porous structure on the mesoporous (2–50 nm) and even macroporous (>50 nm) scale (Churchman et al., 1995), which is larger than many synthetic porous materials such as CNT. This property enables versatile potential applications such as nanoscale support for the loading of functional guests; for example, a mesoporous lumen may enable Hal availability for the immobilization of large-sized enzymes, *e.g.*, serum albumin and conalbumin, which cannot even be hosted by SBA-15 (Yiu et al., 2001). In addition, the unique tubular structure of Hal is combined with site-dependent aluminosilicate chemistry, *i.e.*, the reactivity of the external surface, the internal lumen surface, and the interlayer surface of Hal is different, thus enabling abundant possibilities for the post-modification of Hal targeted for various applications (Yuan et al., 2008). It is also worth emphasizing that Hal has a high biocompatibility and low cytotoxicity, which promises its safe use in various fields (Vergaro et al., 2010).

Some very interesting research advances focusing on the novel properties and related applications of Hal have been successively reported in the past 20 years. For example, the use of Hal as a viable nanoscale container for the encapsulation of biologically active molecules such as biocides and drugs as well as for their controlled release was first demonstrated by Price et al. (2001), and Hal as a nanofiller in clay–polymer nanocomposites (CPN) was proposed (Du et al., 2006). Concerning the formation of Hal, Gardolinski and Lagaly (2005) proposed a multistep intercalation of Kaol for the transformation of platy Kaol to Hal-like nanotubes and Kuroda et al. (2011) recently proposed a simple one-step preparation of Hal-like nanotube through the delamination and rolling of Kaol. In addition, some key fundamental properties of Hal, such as structural stability under heating (Yuan et al., 2012a) or in acidic/alkaline aqueous dispersions (White et al., 2012) and site-specific availability for surface organosilane grafting modification (Yuan et al., 2008), were comprehensively investigated.

In view of the abovementioned research advances, there are great prospects for Hal-based materials. In this regard, a comprehensive and critical review on previous Hal studies is no doubt necessary and might constitute a premise for a better understanding of the specificity of Hal. Accordingly, the objective of this review is to outline the primary properties of the structure and reactivity of Hal as well as related applications by collating the disparate results from the literature. Moreover, some critical assessments on the collated results or discussions on related prospects are made to initiate possible new ideas in the future. The main focus of this review is directed to the research advances of the past decade because earlier advances have been comprehensively summarized by Joussein et al. (2005). In addition, topics such as the geological genesis and morphology/structure diversity of natural Hal are briefly reviewed because they have already been detailed in the literature.

2. Geological occurrence of halloysite (Hal)

Generally, Hal can be derived by the weathering, pedogenesis or hydrothermal alteration of ultramafic rocks, volcanic glass, and pumice (Joussein et al., 2005). The main geological occurrence of Hal is in weathered or hydrothermally altered rocks, saprolites, and soils. With different genesis, Hal is accompanied by different types of associated minerals. For instance, the Matauri Bay Hal deposit (in Northland, New Zealand), formed by the low temperature hydrothermal alteration of rhyolite and dacite volcanic rocks, is mainly associated with quartz, cristobalite, and feldspar. The Dragon Mine Hal deposit (in Utah, USA), formed by the hydrothermal alteration of dolomite, is associated with Kaol, gibbsite, alunite, and quartz (Pasbakhsh et al., 2013). In addition, the crystallization conditions and geological occurrence of Hal are closely related to its morphology. For example, the Hal exhibits spheroidal morphology when recrystallized from supersaturated solutions of volcanic glass and pumice (Joussein et al., 2005); however, the Hal exhibits a tubular morphology when formed by the hydrothermal alteration of biotite (Papoulis et al., 2009), by the weathering of feldspar in granitic rocks (Adamo et al., 2001), and by the topological alteration of platy Kaol (Singh and Gilkes, 1992). More details concerning the geological genesis of Hal can be found in previous reports (Joussein et al., 2005; Pasbakhsh et al., 2013).

3. Structure and morphology of halloysite (Hal)

3.1. Mechanism of tubular structure formation of Hal

Naturally occurring Hal appears in varied morphologies, such as platy, spheroidal, and tubular. However, the tubular structure is the dominant morphology of Hal in nature. The formation of the tubular structure is triggered by atomic-scaled stress in the unit layer of Hal, which is originally caused by the mismatch in the larger tetrahedral ($a = 5.02$ Å, $b = 9.164$ Å) and the smaller octahedral ($a = 5.066$ Å, $b = 8.655$ Å) sheets (Bates et al, 1950; Bailey, 1990). Because these octahedral and tetrahedral sheets are connected by sharing the apical oxygen of the tetrahedron, the stretched Al–O bond in the octahedron could constrain the shared apical oxygen and induce structural stress