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Review article

Applications and interfaces of halloysite nanocomposites

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ABSTRACT

Halloysite nanotubes (HNTs) showed natural nanotubular structures with similar chemical composition to kaolin. This paper reviewed the exciting applications of HNTs due to their abundantly deposit, nanoscale lumens, high length-to-diameter ratios, and relatively low surface hydroxyl group density. HNTs have been used as ideal templates for conveniently immobilizing nanoparticles, which could enable the construction of designed nano-architectures that are extremely attractive as supports for heterogeneous catalysts and for use in the fuel cells and related technologies that exploited the inherent 'smallness' and hollow characteristics of the nanoparticles. The recent developments in this area by exploring the various techniques with which HNTs could be functionalized with metal nanoparticles, and the diverse applications of the resulting materials overviewed in detail. The corresponding interfacial characteristics of the nanocomposites were emphasized.

1. Introduction

Halloysite ($Al_2Si_2O_5(OH)_4 \cdot nH_2O$) was first described by Berthier (1826) as a dioctahedral 1:1 clay mineral of the kaolin group (Fig. 1), which contains octahedral gibbsite $Al(OH)_3$ and tetrahedral SiO_4 sheets (i.e., halloysite nanotubes, HNTs), and consists of hollow cylinders formed by multiple rolled layers (Joussein et al., 2005; Guimarães et al., 2010). Layered halloysite occurs mainly in two different polymorphs, the hydrated form (with interlayer spacing of 10 Å) with the formula $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ and the anhydrous form (with interlayer spacing of 7 Å) with the formula $Al_2Si_2O_5(OH)_4$. Tubular halloysite was rolled from platy kaolinite due to the action of either weathering or hydrothermal processes (Zhou and Keeling, 2013). Many countries, such as China, France, Belgium and New Zealand, have deposits of natural HNTs. Unlike other tubular materials (such as boron nitride, metal oxide (MO), and carbon nanotubes), halloysite is an abundantly available natural nanomaterial, which makes it attractive and convenient for technological applications. Halloysite-based nanocomposites have been studied for several decades due to their physicochemical properties, including their tubular structures, ion exchange, and hydrophobicity (Rozynek et al., 2013). These materials have been commonly used for antibacterial (Zhou, 2010; Abdullayev et al., 2011; Rao et al., 2014), catalytic (Machado et al., 2008; Zieba et al., 2014), optical (Prashantha et al., 2013), electrical (Rozynek et al., 2013), magnetic (Zhang and Yang, 2012b) and energy storage (Yang et al., 2010; Mei et al., 2011) applications.

Studies on halloysite act as containers for drug delivery have been performed by several researchers (Shchukin et al., 2005, 2008; Lvov et al., 2008; Fix et al., 2009; Abdullayev and Lvov, 2010; Shchukin and Möhwald, 2011; Yah et al., 2012a, 2012b; Abdullayev and Lvov, 2013; Konnova et al., 2013; Wei et al., 2014), who observed the cytocompatibility and chemical stability of HNTs, and noted that these nanotubes can be used for the loading and sustained release of drugs. Additionally, Guimarães et al. (2010) presented a systematic theoretical investigation on the structure and electronic properties of single-walled halloysite nanotube models using self-consistent charge density-functional based tight-binding calculations (SCC-DFTB). The results have helped improve the knowledge about HNTs at the molecular level. A number of researchers paid significant attention to the thermal transformation of halloysite and the interfacial relationships between halloysite and organics (Annabi-Bergaya, 2008; Yuan et al., 2008, 2012, 2013; Tan et al., 2013). Based on their results, organosilane-modified halloysite appears to be a versatile host for loading various functional guests, e.g., bio-molecules and drugs. Furthermore, halloysite could be developed as a metal complexing agent by surface modification with sulfhydryl silane to load transition metal ions (e.g., Ag^+, Cu^{2+}, and Zn^{2+}) (Mellouk et al., 2009; Kiani, 2014) for antimicrobial agent applications in the medical or coating fields (Carli et al., 2014). The applications of HNTs in the fabrication of polymer nanocomposites were emphasized (Du et al., 2006, 2008, 2010). The unique structures and performance of HNT-incorporated polymer nanocomposites synthesized by various methods have been described. The functionalization of clays with organosilanes has been explored as a way to improve clay dispersal in a polymer matrix, thus increasing the mechanical properties of the resultant polymer–clay nanocomposites. These nanocomposites

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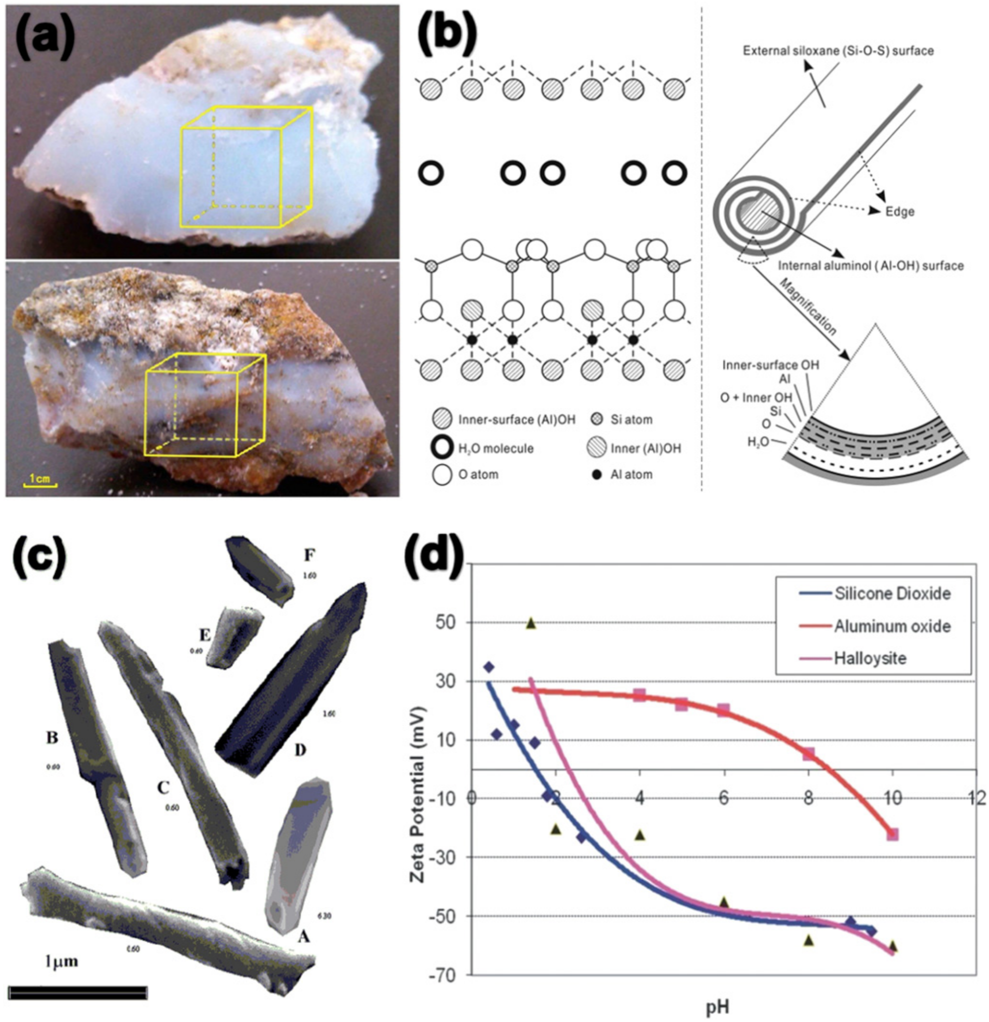

Fig. 1. (a) Photos of the raw mineral, top is the blue colored block, which is high purity and crystallized halloysite, bottom is brown colored block containing impurities. (b) Schematic diagrams of the crystalline structure of halloysite, and the structure of a halloysite nanotube. (c) Observed morphological changes in the halloysite particles: Tubes (A), tubes with planar faces with internal cylindrical holes (B), tubes with internal and external planar faces (C), unrolling tubes (D,E,F). (d) Comparison of zeta-potential curves for halloysite nanotubes (violet), silica (blue), and alumina (red) nanoparticles.
Reprinted with permission from Ref. Oliveira et al. (2007), Yuan et al. (2008), and Vergaro et al. (2010).

exhibit remarkable characteristics such as strengthening effects, enhanced flame retardancy, and reduced thermal expansion.

After a brief introduction to the application of HNTs in medication, modeling, the interfacial relationships between halloysite and organics, and the fabrication of polymer nanocomposites, this review emphasizes the interfacial characteristics between metal nanoparticles and halloysite in addition to the application of halloysite–metal nanocomposites.

2. Applications of HNTs-supported nanocomposites

Multiple nanocomposites provide an excellent platform for the integration of different functional nanocomponents into a single entity to exhibit multifunctional properties. Most studies on metal nanoparticle deposition on HNTs are predominantly focused on transition metals, such as Pt, Pd, Ru, Ag, and Au. The catalytic, magnetic, antibacterial and other applications of HNT-supported metal nanoparticles are described in the following sections.

2.1. Dye degradation

Halloysite has mostly been investigated for use in new advanced materials because of its availability, ease of functionalization, and well-defined structures. Its structures have been modified to yield specific chemical and physical properties, particularly for their use as adsorbents, photocatalysts or photocatalyst supports. In the field of environmental catalysis, HNTs-based nanocomposites offer various advantages, such as the use of catalytic amounts, simple recovery and high turnover rates, ease of set-up and work-up, mild experimental conditions, and high yields and selectivities, making them useful foundations in the establishment of environmentally friendly technologies (Zhou, 2011a, 2011b).

Using clays with tube morphology was beneficial to the improvement of the dispersibility and photocatalytic activity of TiO_2 nanoparticles (Papoulis et al., 2010). HNTs act as a clay stabilizer to prevent the aggregation of nanoparticles due to their tube structure and large specific surface area (the S_{BET}, pore volume and average pore diameter of HNTs were estimated to be 78.6 m^2/g, 0.21 cm^3/g, and 3.9 nm, respectively.) (Fig. 2a). These researchers prepared HNTs–TiO_2 nanocomposites using a sol–gel method with titanium isopropoxide as the precursor under hydrothermal treatment at 180 °C. The clay–titania samples exhibited significantly higher activity in decomposing NOx gas under visible-light irradiation ($\lambda = 510$ nm) and UV light irradiation ($\lambda = 290$ nm) compared with that of the standard commercial titania, P25 (Fig. 2b). Intercalation of TiO_2 nanoparticles in the clay mineral structure could prevent their aggregation due to the TiO_2 powders