



Radical guided selective loading of silver nanoparticles at interior lumen and out surface of halloysite nanotubes



Jing Ouyang^{a,b,*}, Binbin Guo^{a,b}, Liangjie Fu^b, Huaming Yang^{a,b}, Yuehua Hu^b, Aidong Tang^c, Hongming Long^d, Yelin Jin^e, Jing Chen^e, Jinlong Jiang^e

^a Centre for Minerals Materials, Department of Inorganic Materials, School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, PR China

^b Key Laboratory for Mineral Materials and Application of Hunan Province, Central South University, Changsha 410083, PR China

^c School of Chemistry and Chemical Engineering, Central South University, Changsha 410083, PR China

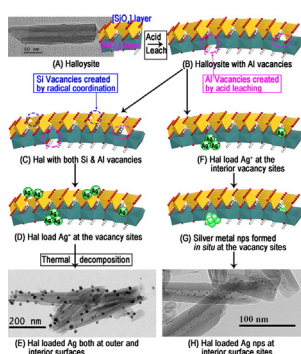
^d School of Metallurgical Engineering, Anhui University of Technology, Ma'anshan 243032, Anhui, PR China

^e Jiangsu Provincial Key Laboratory of Palygorskite Science and Applied Technology, Huaiyin Institute of Technology, Huai'an 223003, PR China

HIGHLIGHTS

- Halloysite nanotubes can be selectively decorated by Ag nps in controlled conditions.
- Ionic radicals of the raw sources guided the absorption behavior of cations.
- Coordination on inert surfaces realized only by negative charged radicals with high activity.
- Electron affinity and ionization energy determines the coordinate performances of radicals.

GRAPHICAL ABSTRACT



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ABSTRACT

Silver nanoparticles (nps) selectively loaded in the lumen cavity and outer surface of halloysite (Hal) nanotubes were realized through the simple impregnation strategy. The Hal mineral was pre-treated through leaching by sulfuric acid followed by calcinations. The silver nps have been loaded on both sides of the Hal nanotubes when nitrate was used as the raw source, while the nps were found only in the lumen cavity when acetate was used. The formation of Ag nps on both sides of the Hal tubes has partially destroyed the wall structures. Those Ag nps at outer surface showed the relatively higher efficiency to the HCOH oxidation, 6.9% of the organic molecular have been oxidized at 125 °C, while Ag nps loaded in the lumen cavity only showed 1.0% in the same conditions. The physico-chemical properties of the two sides of the tubes determined the affordability of acid treatment, which induced the surface defects in the cavity; while the electron affinity, ionization energy and steric configuration of the ionic radical of the raw sources have showed differed coordination manner with outer surface of the Hal tubes, induced the selective adhesion of metal cations, and resulted in the selective formation of Ag nps.

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1. Introduction

Halloysite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, abbreviated as Hal) is a naturally occurred nano-tubular clay mineral [1]. It has been found at many areas in the world, such as the Dragon Mine in USA, Australian, New Zealand,

* Corresponding author at: Centre for Minerals Materials, Department of Inorganic Materials, School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, PR China.

E-mail address: jingouyang@csu.edu.cn (J. Ouyang).

Portugal and China [1–4]. Generally, Hal nanotubes have an average 15–20 nm in inner diameter, 50–80 nm in outer diameter and 100–800 nm in length [5,6]. The composition of Hal is the same with kaolinite and the structure of the two minerals are analogue, with the exception that the Hal is the rolled kaolinite, the silicon-oxygen tetrahedrons [SiO₄] rolled to the outside and the aluminum-oxygen [AlO₆] octahedrons distorted to the inner side, due to the size mismatch of the two kinds of polyhedrons [7,8]. The roll manner of these two kinds of polyhedrons yielded the Hal with different compositions in the interior side and on the outer surface, making the distinctive properties at the two sides of the nanotubes. The Hal has many other properties such as a large aspect ratio, relatively high surface area, good biocompatibility, and excellent stability [6]. Due to the distinctive morphology, unique properties of the nanotubular mineral, researches in the characterization, modification and application of Hal have become a hot spot in material science area. Many reports have declared its suitability for such applications as polymer composite filler [9,10], hydrogen storage matrix [11–13], medicine carrier [14–17] and catalysis supports [18,19]. Some excellent reviews have included the physico-chemical properties, surface as well as structural modification methods, and application techniques to the Hal based materials [1,6,7,20–22].

One of the aspects in the study to Hal is very interesting. Since the Hal is naturally occurred nanotubes, how to effectively take advantage of the pipeline morphology, and what is the key mechanism that will affect the functionalization of the Hal based materials are still in hot debate. In the aforementioned literatures, some of the efforts have focused on the selective modification of interior or outer surface of Hal, such as the modification of Hal lumen by octadecylphosphonic acid have driven the absorption of ferrocene into the pipeline cavity [23], the selective loading of Fe₃O₄ nps into the Hal lumen was realized through liquid impregnation [24], and the fill of Hal cavity with Ag nanorods was conducted through vacuum impregnation [25–27]. But the above literatures did not give the theoretical reason on the topic of why the selective modification or loading can be realized, and what kind of factors are the keys that should be carefully manipulated, especially the effect of ionic radicals on loading manners have not been discussed.

We present in this article a theory based on the defect and radical coordination effects, which have been proposed to affect the assembly manners of nanoparticles (nps) onto Hal nanotubes. Silver was chosen as the guest that will be assembled onto the Hal surface, because Ag nps have attracted broad attentions in antibacterial [28], catalysis [28,29], optics [30] and biology [20] due to their distinctive physico-chemical and biological properties. In addition, Ag nps have illustrated the potential applications in oxidizing the indoor pollutant formaldehyde (HCHO) at mild temperatures due to their high activity and large surface area. Although the filling of Ag nanorods into cavity of the Hal have been reported and the antibacterial properties of the Ag nps on surface of the Hal have been realized [31–33], the catalytic performances of decomposing formaldehyde on Ag nps decorated Hal nanotubes have not been studied. So, efforts in this work involved the pretreatment of Hal by acid solvent, careful selection of the silver resources, the vacuum impregnation from aqueous solutions and finally the thermal calcinations to obtain the Ag nps decorated Hal nanotubes. The products showed that the Ag nps uniformly and selectively decorated either on interior lumen surface of the mineral or on both sides of the nanotubes. The ionic radicals in the resources should have affected the selective loading manners of Ag nps, and the catalytic performances showed the relatively higher catalytic efficiency on surface loaded Ag nps thanks to the sufficient contacting of the HCHO molecular with Ag nps on outer surface of the Hal nanotubes.

2. Experimental

2.1. Halloysite minerals

Halloysite nanotubes were obtained from Chenxi, Hunan province in China, due to their relatively high thermal stability [34]. Pre-treatments

were adapted before usage, visible impurities in the raw mineral (such as the brown parts containing too much ferrites) were eliminated by hand-selecting, the blue or white halloysite mineral was milled in an agate mortar before all of the powders passed a 300 mesh sieve. The powder was immersed in water and magnetically stirred for 2 h, then was filtered and washed by ethanol, followed by drying at 60 °C for 2 h, and heated at 500 °C for 2 h to remove the structural hydroxyls. The treated Hal nanotubes were then subjected to the followed lumen expansion and silver nanoparticles loading.

2.2. Expanding the lumen diameter of halloysite

For the purpose of expanding diameter of the lumen and thus facilitating the assembly of metal resources into, an acid leaching to the Hal raw mineral was conducted. In typical procedure, 1.0 g Hal was immersed into 100 ml sulfuric acid (2 M) at 60 °C under severe stirring for 2 h. The treated Hal were filtered and washed with distilled water for 3 times to remove all of the leached Al³⁺ ions, and then the treated mineral was dried at 100 °C for 2 h to obtain the acid treated and expanded Hal nanotubes sample (denoted as A-Hal).

2.3. Synthesis of A-Hal/Ag samples

Silver acetate (C₂H₃O₂Ag) and silver nitrate (AgNO₃) were purchased from Sinopharm Chemical Reagent Co. LTD. China. All of the chemicals were used without further purification. Designed amount of silver nitrate or silver acetate was dissolved in 50 ml distilled water, respectively, then 0.85 g A-Hal was dispersed into the silver solution under ultra-sonication. After the suspension was transferred into a chamber, a pump was used to vacuumize the chamber for 1 h, slight fizzing was heard and bubbles could be observed in the process because the air was removed from lumen of the Hal nanotubes, simultaneously, silver resources were filled into the lumen. Then the chamber was refilled by air and the pressure came back to ambient conditions. The loading process was repeated for three times. After the suspension was filtrated at ambient pressure, washed by de-ionized water, then the solid material was dried at 60 °C for 2 h, and heated at 400 °C for 1 h to decompose silver resources into metallic silver (According to the literatures, silver nitrate will decompose above 400 °C [35], silver acetate will decompose at about 380 °C [36], so the calcinations temperature were all settled to 400 °C). The Hal decorated by silver nps in the lumen or on both sides of the tube walls were obtained. The product obtained from silver acetate as the raw source was denoted as A-Hal-Ag-1, and that from silver nitrate was denoted as A-Hal-Ag-2 in this article.

2.4. Characterizations and catalytic activity tests

Phase of the samples were characterized by a DX-2700 powder diffractometer with CuK α -radiation ($\lambda = 1.541806 \text{ \AA}$). Data were collected from 5° to 80° of 2 θ with a step width of 0.02°. Phases were identified using the Search/Match capabilities of JADE 5.0 program along with ICDD (International Center for Diffraction Data) powder diffraction file (PDF) database. TEM images were collected by a TECHNAI G²-20 transmission electronic microscopy equipped with an energy-dispersive X-ray spectrometer (EDAX) at the accelerating voltage of systematically 200 kV. Before the samples were subjected to the observation, the sample suspensions were dropped onto amorphous carbon coated 300 mesh copper grid and then dried at 80 °C. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5700 spectrophotometer using KBr pellets for samples. Raman spectra were acquired on a LabRAM HR 800 with a laser stimulate at wavelength of 488 nm. Solid state magic angle spinning nuclear magnetic resonance (MAS NMR) spectrum was acquired on a Varian InfinityPlus 300 instrument at a magnetic field of 7.1 T. About 100 mg tested sample was pressed into a ZrO₂ rotor. Spectra of ²⁹Si elements were recorded at room temperature with a Chemagnetic 7.5 mm MAS detector under the following

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