



Large scale synthesis of Janus nanotubes and derivative nanosheets by selective etching



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ABSTRACT

One-dimensional Janus nanotubes have been successfully synthesized in large quantity by selective etching of the interior Al_2O_3 from hydrophobically modified halloysite nanotube with the exterior surface preserved. By simply tuning the etching time, the colloid shape evolves from nanotubes to partially collapsed nanotubes and porous nanorods. The microstructure and chemical composition of the etched hydrophobically modified halloysite are characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), FT-IR spectrophotometer and nitrogen adsorption–desorption. The results indicate the interior Al_2O_3 can be controlled etched. Labeling experiments demonstrate the hydrophilic nanoparticles are predominantly located onto the coarse region of the etched nanotubes. Selective etching of hydrophobically modified halloysite creates Janus nanotubes with a hydrophobic exterior surface and a hydrophilic interior surface. An enhanced capacity for emulsification of the Janus nanotubes toward immiscible mixture is shown. Furthermore, by a favorable growth of other functional materials, composition of the Janus nanotubes can be further extended, enabling different applications from magnetic separation to water purification, drug immobilization and controlled release. After crushing the Janus nanotubes, derivative nanosheets are derived. The method can be scaled up and economical compared with other method, which is the key to further exploit practical application.

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1. Introduction

Janus colloids have two different compositions or properties compartmentalized onto two sides or surfaces [1,2]. They have gained increasing attention, and are promising in constructing complex hierarchical structures as building blocks, dual-functional devices, optical biosensors, micro/nanoprobes and functional surfactants [3–11]. Various methods have been developed to synthesize Janus colloids with tunable morphology, shape and composition [3–33]. It is straightforward based on mask-protecting assisted site-selective modification of one exposed part of the object while the other part is protected by embedding into a proper medium [12–18]. However, as most interface-based techniques, the synthesis efficiency is low, although this concept has been extended from two dimensional surface to three dimensional Pickering emulsion interface in order to increase yield [19–24]. Microfluidic [25–30] and electrospinning [31–33] methods can be employed to produce Janus colloids in large scale with controlled shapes and size distribution, however their characteristic

size is large in the range of 10–100 μm and microfluidic channels and electrospinning apparatus should be specifically designed [25–33]. Although some other methods such as surface nucleation [34,35], self-organization of block polymers [36,37] and phase separation [38–41] can produce smaller Janus particles, strict synthesis conditions are required. It is urgently required to develop a facile method to large scale synthesis of submicron sized Janus colloids, especially Janus nanotube.

Halloysite is a cheap and abundant natural clay mineral, in the form of hollow nanotubes consisted of two-layered aluminosilicate, chemically similar to kaolin [42,43]. As an economically available nanotubular raw material, it has been widely used as catalyst, in the synthesis of complex structures and as nanoreactors [42–48]. More interestingly, onto their exterior surface SiO_2 is dominant, whilst onto the interior surface Al_2O_3 is dominant. Selective modification between SiO_2 exterior surface and Al_2O_3 interior surface in halloysite is difficult [45,46]. Attempts to use organosilanes for halloysite surface modification resulted in silane binding to both inner and outer surfaces [45]. Octadecylphosphonic acid can be selectively modified the lumen of halloysite, resulting in a hydrophobic aliphatic chain core and a hydrophilic silicate shell [46]. However, the lumen of halloysite nanotube is filled and its uses as nanoreactor or drug delivery system are largely limited

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[47]. Therefore, synthesis of Janus nanotube with the lumen maintained, especially enlarged based on halloysite nanotube is still challenged. Recently, Lvov et al. have demonstrated enlargement of halloysite nanotube lumen by selective etching of Al_2O_3 from interior surface with its external diameter preserved (lumen diameter changed from 15 to 25 nm) [47]. And it proves H_2SO_4 etching of Al_2O_3 takes place in a layer-by-layer fashion; that is, etching starts from the innermost layer and proceeds toward the outermost layer. However both of the interior surface and the exterior surface are SiO_2 , which are hydrophilic, not Janus type nanotubes.

Herein, we present a facile approach to large scale synthesis of Janus nanotubes and their derivative nanosheets by employing the selective etching method on hydrophobically modified halloysite nanotubes. Halloysite clay nanotubes are firstly modified with a silane octadecyltrichlorosilane (C18), resulting in the hydrophobicity of both surfaces. A subsequential selective etching of the interior Al_2O_3 surface allows the exposure of new hydrophilic surface, while the exterior hydrophobically modified SiO_2 surface is not influenced. As a result, a Janus nanotube with hydrophobic C18 modified external surface and a fresh exposed hydrophilic internal surface is resulted. After crushing the Janus nanotube for example by ultrasonication, the Janus nanotubes will be fragmented into scroll like pieces achieving Janus nanosheets. Alternatively, the halloysite can be first modified with a hydrophilic silane such as 3-aminopropyltrimethoxysilane (APS), then etched with HCl, Janus nanotube with amine-terminated external surface and a fresh exposed SiO_2 internal surface are also derived.

2. Experimental

2.1. Materials

Halloysite (HA) is obtained from Imerys Tableware Asia Limited [48]. Octadecyltrichlorosilane silane (C18) is obtained from Aldrich. 3-Aminopropyltrimethoxysilane (APS) is purchased from Alfa. Toluene is dried over CaH_2 and distilled prior to use. Unless specified otherwise, all other reagents are used as received.

2.2. Synthesis of C18-modified halloysite nanotubes (HA-C18)

Halloysite nanotube is first activated by H_2O_2 . Then the sample is washed with water and freezing dried for further use. 12 g of the halloysite nanotube is dispersed into 120 mL of anhydrous toluene, and 12 g of C18 is added. The system is heated at 120 °C and hold for 24 h under stirring. Then, the C18 modified halloysite nanotube is washed repeatedly with toluene and ethanol and dried.

2.3. Synthesis of Janus nanotubes and nanosheets

A typical process of synthesis of Janus nanotubes is as follows: in a flask, C18-modified halloysite nanotube (HA-C18, 1.25 g) is dispersed into 5 mL of ethanol, and then 70 mL of aqueous HCl is added. After further dispersion under ultrasonication, the flask is placed in 80 °C oil bath to selectively remove Al_2O_3 . At specific time intervals, some samples are withdrawn and washed repeatedly with water to neutral. The selective etching conditions of halloysite are the same with that of HA-C18 without adding ethanol and halloysite nanotubes are used directly. After the Janus nanotubes being further crushed by ultrasonication, derivative nanosheets are derived.

2.4. Labeled Janus nanotube

Au nanoparticle with an average diameter of 3 nm is synthesized as follows: 720 μL of 0.1 M NaBH_4 is added into 60 mL of

aqueous solution containing 2.4×10^{-4} M of trisodium citrate and HAuCl_4 , and stirred for 2 h. 0.01 g of Janus nanotube is dispersed into 1 mL of 1 wt% APS ethanol solution under stirring for 12 h. The APS modified Janus nanotube is separated by centrifugation and washed with ethanol and then re-dispersed in water. 1 mL of Au nanoparticles aqueous dispersion is added under sonication. The Au absorbed Janus nanotube is collected by centrifugation. Along the similar approach, anionic sulfonated polystyrene nanoparticles about 30 nm labeled Janus nanotubes are prepared. The nanoparticles labeled Janus nanotube is dispersed into ethanol and dropped onto silicon and carbon-coated copper grid for SEM and TEM characterization.

2.5. Performance of the Janus nanotubes

About 0.05 g of the Janus nanotube is added in a glass tube containing 5 mL of water and decane. A trace of methylene orange is introduced into water only for the guidance of eyes. After the mixture is slightly shaken, a stable mixture stands there. 0.01 g of the Janus nanotube and 0.5 g of paraffin is added into 5 g of water. The mixture is heated to 80 °C for 1 h. After being vigorously stirred, an emulsion formed. Afterwards, the system is dropped into ice water to solidify the emulsion structure. Fe_3O_4 nanoparticles are synthesized by coprecipitation of FeCl_3 and FeCl_2 aqueous solution. 5 mL of 1 M aqueous mixture solution of $\text{FeCl}_3/\text{FeCl}_2$ (molar ratio 2/1) is added into 50 mL of 5 M NaOH solution after degassing with N_2 for 30 min. After stirring for 30 min, the system is heated to 85 °C and stirred for 1 h. 1 g of PVP is added into the mixture and the temperature is kept at 85 °C for 30 min. The resultant sample is cooled down to room temperature and the Fe_3O_4 nanoparticles are collected by a magnet and washed with water. 0.025 g of APS modified Janus nanotube is dispersed into 4 mL of Fe_3O_4 aqueous dispersion under stirring for 2 h. Then the dispersion moves towards a magnet and the separation of Janus nanotubes from dispersion is demonstrated.

2.6. Characterization

Morphology observation of the samples is preformed with a HITACHI S-4800 scanning electron microscope (SEM) operated at an accelerating voltage of 15 kV. All samples except Au-labeled, Fe_3O_4 -labeled Janus nanotubes are vacuum sputtered with Pt for observation. The samples are dispersed into ethanol and dropped onto carbon-coated copper grids for transmission electron microscope (TEM) characterization (JEOL 100CX operated at 100 kV). The as-prepared emulsion is observed under a phase-contrast microscope Olympus BX51. The emulsion conductivity is measured using a DDS-307A digital conductivity meter. The dried samples are pressed into pellets with potassium bromide (KBr) for characterization by BRUKER EQUINOX 55 FT-IR spectrophotometer. Nitrogen adsorption-desorption is performed on a Micromeritics ASAP 2020 M Surface Area and Porosity Analyzer. XRD patterns are recorded on a Rigaku, DMAX-2400 powder X-ray diffractometer by using Cu Ka radiation (60 kV, 200 mA).

3. Results and discussion

Janus nanotubes having different chemical properties on the exterior surface and the interior surface are synthesized in large scale by selective etching and derivative nanosheets are prepared by crushing the Janus nanotubes. As demonstrated in Scheme 1, after a hydrophobic modification with a silane octadecyltrichlorosilane (C18), both surfaces of halloysite nanotubes are synchronously modified and hydrophobic. A subsequential selective etching of the interior Al_2O_3 surface allows the exposure of new

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