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A novel method for synthesizing well-defined boehmite hollow microspheres

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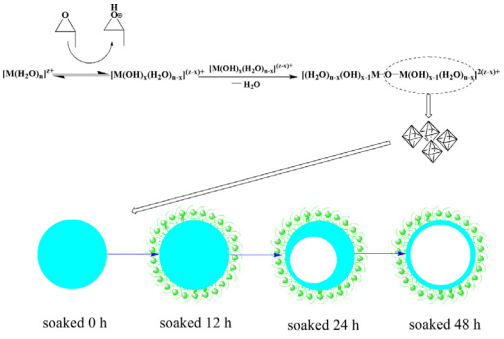
GRAPHICAL ABSTRACT



General reaction scheme for the epoxide-driven sol-gel and chemically induced self-transformation process

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ABSTRACT

A novel and effective synthesis route has been developed to fabricate γ-AlOOH (boehmite) hollow microspheres (diameter in 1–2 μm) with urchin-like shell structures. The external surface of the hollow microspheres was constructed by randomly aggregated and interconnecting nanoplatelets (length in 50 nm). The method involves two processes: (1) solid spherical particles can be obtained by an epoxide-driven sol-gel process in several seconds, (2) solid spheres particles transform into urchin-like hollow spheres through chemically induced self-transformation process. Formation of the γ-AlOOH hollow microspheres was strongly dependent on the amount of propylene oxide, the volume ratio of solvents, as well as the kinds of anion. γ-AlOOH hollow microspheres could only be obtained in a particular situation that $AlCl_3{\cdot}6H_2O$ acts as salt precursor and the volume between H_2O and ethanol were defined as 4 ml, 6 ml and 6 ml, 4 ml. In general, the described method is efficient and environmentally benign, and has significant advantages over traditional template approaches to the large-scale production of hollow inorganic materials.

1. Introduction

Recently, the fabrication of hollow microspheres has attracted intense interest because of their well-defined structure, large specific surface area, low density, and high mechanical stability. These characteristics endow this kind of material various potential applications, such as in catalyst supports [1], drug delivery systems [2], adsorption [3], biomaterials [4], sensors [5,6], as well as lightweight adiabatic materials [7]. By varying its morphological characteristics (particl/pore size, shape, structure et al.), γ-AlOOH (boehmite) could be widely used as catalyst supports, absorbents,

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ceramics, abrasives and fibers [8–10]. Also, as a kind of aluminum oxyhydroxide, γ-AlOOH is the main precursor for production of γ-Al_2O_3. However, the synthesis of well-defined γ-AlOOH hollow spheres has rarely been studied.

According to previous reports, the fabrication of γ-AlOOH hollow spheres are mostly based on the colloid template. However, the selected template materials are usually expensive. Besides, this approach is rather laborious and time-consuming. Therefore, it is urgent to find a facile and simple method for the synthesis of γ-AlOOH hollow microspheres.

Nowadays, the most widely used methods for the fabrication of γ-AlOOH or γ-Al_2O_3 hollow microspheres are sol-gel process [11], nanocasting on soft or hard templates [12–14], hydrothermal synthesis [15] and chemically induced self-transformation [16,17]. Dilsiz et al. [11] has ever synthesized uniform and size controlled γ-Al_2O_3 hollow microspheres by combining a drop-generation technique with sol-gel processing. The sol-gel process consists of two steps: (1) forming a concentrated colloidal sol of the metallic oxides or hydroxides, (2) converting this sol to a semi rigid gel. However, the preparation of hollow microspheres via sol-gel chemistry is limited due to the low product yields and complicated process. Comparatively speaking, nanocasting on soft or hard templates is considered as one straightforward and effective approach. The inner structural arrangement, outer morphology and the surface characteristic can be tailored easily. For example, γ-AlOOH/γ-Al_2O_3 hollow microspheres could be prepared by carbon spheres solid template (prepared in high temperature carbonization using mesoporous silica SBA-15), as is illustrated by Xia et al. [12]. Different from the complex template preparation process, Sun et al. [13] has also demonstrated the feasibility that the carbon spheres solid template could be fabricated by hydrothermal synthesis method. But this synthetic method is not suitable for mass industrial production because of the expensiveness of the selected template materials. Chemically induced self-transformation method successfully avoids the expensive template materials and related complex manipulation process, which is a simple and effective method for the preparation of various kinds of hollow spheres. The intermediates and/or final product with hollow sphere structure can be collected via the chemically induced self-transformation. However, the crystal structure transformation process needs complex external environment and a long time. Therefore, taking these issues into consideration, it is still a challenge to develop a facile and environmentally friendly method for obtaining uniform γ-AlOOH hollow microspheres.

Herein, a new facile sol-gel synthetic route accompanied with chemically induced self-transformation to prepare γ-AlOOH hollow microspheres was proposed. Propylene oxide was used as the gelation initiator to induce the gelation of aluminum chloride hexahydrate solution. This approach is quite different from the traditional sol-gel process, which requires a long reaction time in sol-gel process and complex external environment. In this method, the gel can be obtained within several seconds. Soaking the gel in the oven at 60 °C, the γ-AlOOH hollow microspheres can be obtained in a chemically induced self-transformation process. Therefore, it is a facile, efficient and environmentally friendly method. In this work, one interesting phenomenon has been found that the anion of the Al(III) salt used in the sol-gel reaction appears to have a significant impact on the structure and morphology.

2. Experimental

2.1. Synthesis of γ-AlOOH hollow microspheres

All the analytical grade chemicals including Aluminum chloride hexahydrate, Aluminum nitrate nonahydrate, Propylene oxide, and anhydrous ethanol (purchased from Sinopharm Chemical Reagent Co., Ltd.,) were used without further purification. Distilled water was used in all experiments. Aluminum chloride hexahydrate (20 mmol, 4.83 g) was first dissolved in the mixture solvent of distilled water and anhydrous ethanol (4 ml of distilled water, 6 ml of anhydrous ethanol) to form a clear solution, and then the resultant homogeneous solution was sealed and maintained at 60 °C. Finally, propylene oxide (0.05–0.15 mol, 3.5–10.5 ml) was rapidly added into the mixture solution. Then the resultant homogeneous solution was sealed and maintained at 60 °C for gelation. To help determine the role of the anion and solvent in this system, hollow microspheres were also prepared from different salts and solvent systems using a procedure similar to the one described above. In those experiments, different volume ratio between water and ethanol (the real volume of H_2O and ethanol are 0 ml, 10 ml; 2 ml, 8 ml; 4 ml, 6 ml; 6 ml, 4 ml; 8 ml, 2 ml and 10 ml, 0 ml) were adopted. To elucidate the role of anion in hollow microspheres formation, Aluminum nitrate nonahydrate was used as the Al(III) salt precursor. For example, propylene oxide (7 ml, 0.1 mol) was added to solutions of (1) $Al(NO_3)_3{\cdot}9H_2O$ (6.75 g, 20 mmol) in the mixture solvent (H_2O and ethanol is 4 ml and 6 ml); (2) $Al(NO_3)_3{\cdot}9H_2O$ (6.75 g, 20 mmol) in the mixture solvent (H_2O and ethanol is 2 ml and 8 ml); and (3) $Al(NO_3)_3{\cdot}9H_2O$ (6.75 g, 20 mmol) in the mixture solvent (H_2O and ethanol is 0 ml and 10 ml). After this gelation reaction, the obtained samples were soaked in anhydrous ethanol at 60 °C for various time. In the soaking process, the anhydrous ethanol was replaced every 12 h.

2.2. Characterization

The phase compositions of the samples which sintered at different temperatures were detected by X-ray diffraction (X'per MPD Pro System, Holland) using Cu (Kα) radiation source (λ = 1.54178 Å) in the 2θ range of 10–80. SEM (JSM-5610LV, JEOL, Japan) was used to observe the morphology of the hollow microspheres. A thin layer of Pt was sputtered on the surface before SEM characterization. TEM analysis was performed in bright-field mode using an EM-1200EX at 120 keV (JEOL Japan). Fourier transform infrared (FTIR) spectra were recorded with a Shimadzu IRAffinity-1 FTIR spectrometer within the range of 4000–400 cm^{-1}. Thermogravimetric and differential thermal analyses (TG/DTA, STA449c/3/G, NETZSCH, Germany) were used to examine the decomposition behavior of the microspheres at elevated temperatures. The samples were heated to 700 °C at a constant heating rate of 10 °C/min in flowing air. The Brunauer-Emmolett-Teller (BET) surface area of the powders was analyzed by nitrogen adsorption-desorption isotherms at 77 K using a Micromeritics Model ASAP 2020 analyzer. All the samples were degassed at 300 °C for a certain time prior to nitrogen adsorption measurement. The BET surface area was determined by a multipoint BET method using the adsorption data in the relative pressure (P/P_0) range of 0.05–0.3. The pore size distribution, average pore diameter and pore volume were calculated by using the adsorption branch of the isotherm.

3. Results and discussion

3.1. Formation and characterization of γ-AlOOH hollow microspheres

The γ-AlOOH hollow microspheres were synthesized by using a very convenient procedure based on the epoxide-driven method. The advantages of this straightforward method for the preparation of γ-AlOOH hollow microspheres is efficient, environmentally friendly and ease manipulation. Previous works indicated that the propylene oxide acts as an irreversible proton scavenger can induce hydrolysis and condensation of the hydrated metal cations