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Template-assisted synthesis of mesoporous $LiAlO_2$ hollow spheres with high surface area

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Abstract

Mesoporous lithium aluminate (α-$LiAlO_2$) hollow spheres with the diameter of 3–4 μm and the shell thickness of about 500 nm have been successfully synthesized by a hydrothermal method with template-assisted. Many mesopores were found on the surface of the spherical shell. Nitrogen sorption measurement reveals that obtained products exhibited high BET specific surface area up to 322.8 m^2/g and pore volume of 0.72 cm^3/g. The formation mechanism of the mesoporous shell structure was proposed as a core-shell-surfactant-water model.

Keywords: Mesoporous; Lithium aluminate; Hollow spherical shell; Hydrothermal; Specific surface area

1. Introduction

$LiAlO_2$, which presents three different crystalline phases: α-, β- and γ-$LiAlO_2$, is a potential candidate for a tritium breeding blanket of fusion reactor and an electrolyte matrix of molten carbonate fuel cell (MCFC) due to its chemical and thermal stability [1]. The matrix of an MCFC requires high total porosity, stable electrolyte retention and mechanical strength. Furthermore, $LiAlO_2$ particles have a wide application on lithium secondary battery. Firstly, 3 wt% 10 μm γ-$LiAlO_2$ particle is added into polymeric electrolyte of lithium secondary battery to enhance the ionic conductivity [2]. Secondly, because α-$LiAlO_2$ has the same lamellar hexagonal system as $LiCoO_2$, it could be doped into $LiCoO_2$ to form $LiAl_yCo_{1-y}O_2$ solid solution as the electrode of lithium battery, which can raise the voltage and decrease both the density of the material and its cost [3]. For all of these applications, fine lithium aluminate powders with high surface area and homogeneous morphology are desirable. Previously, γ-$LiAlO_2$ was prepared by conventional solid state methods, alkoxide–hydroxide route or sol–gel methods [4–6]. Recently, γ-$LiAlO_2$ particles with a high surface area of 45 m^2/g, have been prepared by an ultrasonic spray pyrolysis from an aqueous solution of aluminum nitrate and lithium salt [7]. Sokolov synthesized γ-$LiAlO_2$ with three dimensional periodic arrays of interconnected macropores by a colloidal crystal templating (PMMA) wet chemical process [8]. The diameter of the macropores was 275–375 nm and the surface area was 48–56 m^2/g. However, the products contained some subsidiary substances. We have reported a hydrothermal synthesis of mesoporous α-$LiAlO_2$ nanosheets using the surfactant hex-adecyltrimethyl ammonium bromide (CTAB) as the template [9]. A high specific surface area up to 124 m^2/g has been obtained. Nevertheless, the surface area is also limited.

Recently, mesoporous materials with well-defined morphologies have attracted much attention. Among many types of mesoporous materials, hollow spheres are of significance for their potential uses in many areas, such as containers for encapsulation, fillers and catalytic supports, because of their low densities, high surface area and excellent optical properties. Large surface area has been found

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in materials with spherical microstructure, such as inverse opal and sphere shell morphology [10–12]. The synthesis of mesoporous microspheres is a major challenge in advanced materials science [13,14]. So far various methods have been employed to explore the preparation of hollow spheres for different inorganic materials, such as CuS, $SrCO_3$, silica spheres [15–17]. However, the synthesis of $LiAlO_2$ hollow microspheres has not been reported.

In this communication, we reported a simple hydrothermal route to synthesize the uniform mesoporous α-$LiAlO_2$ hollow spherical using sulfonated polystyrene (PS) microspheres as the soft template. Meanwhile, a small amount of cationic surfactant CTAB is added into the starting solvent to improve surface characteristic of the PS microspheres. The specific surface area of the product is up to 322.8 m^2/g. To the best of our knowledge, the surface area obtained in this way is higher than any other reported result.

2. Experiment

Sulfonated PS microspheres were employed as a template in the synthesis of mesoporous lithium aluminate hollow spheres, which were synthesized as Yang's method [15]. 1.17 g sulfonated PS powder and 0.2 g CTAB were mixed with 15 ml distilled water under stirring for 30 min to achieve solution A. Then 100 mmol lithium nitrate ($LiNO_3$) (A.R.) and 100 mmol aluminum iso-propoxide (AIP) (A.R.) were added into 10 mmol distilled water to prepare solution B. Solution B was slowly added into solution A under stirring, and the mixture was stirred at least 5 min with ultrasonic irradiation to obtain the homogeneous gel. The gel was put into a Teflon autoclave vessel at 150 °C under autogenous pressure for 48–72 h. Then the precursor obtained after hydrothermal reaction was washed several times by absolute ethanol, dried at 120 °C for 10 h, and calcined at 600 °C for 5 h in air with a temperature ramp of 1 °C/min. The sample after calcination is called "product" next.

The phase structure of the as-prepared sample was characterized by a Bruker D8 advance X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å). A JEM-2011 transmission electron microscopy (TEM) with acceleration voltage of 200 kV and a JEOL JSM-6460LV scanning electron microscopy (SEM) were used to observe the morphology of the samples. TG-DTA analysis was taken on Setaran 92–16.18 thermal analyzer in air with a heating rate of 20 °C /min. The special-surface area was estimated by the Brunauer–Emmett–Teller (BET) four points method, on the basis of the nitrogen gas adsorption isotherm (77.4 K) with a NOVA4000 high gas sorption analyzer. The pore size distribution was also analyzed with the same apparatus.

3. Results and discussion

The XRD patterns of the precursor and product are given in Fig. 1, which indicate that, the precursor is a mixture of PS microspheres, α-$LiAlO_2$ (JCPDS 44-0224), $LiAl_5O_8$ (JCPDS 38-1425), and $LiNO_3$ $(H_2O)_3$ (JCPDS 77-1364). After heat treatment at 600 °C, $LiAl_5O_8$ phase disappears and only characteristic peaks of hexagonal ($R\bar{3}m$) α-$LiAlO_2$ phase with lattice constants $a = 2.799$ Å and $c = 14.18$ Å can be observed. This demonstrates that the crystallization transition process of the precursor completes at 600 °C, and pure α-$LiAlO_2$ phase has been obtained at this temperature. The weak and broad diffraction peaks for the product suggests that the products might be composed of very small crystals with the size in nanoscale. The grain size for [1 0 4] orientation is calculated to be 6.3 nm based on the Scherrer's formula. The inserted small-angle diffraction patterns do not show any resolved diffraction peak, which imply absence of mesostructure order in the pore arrangement.

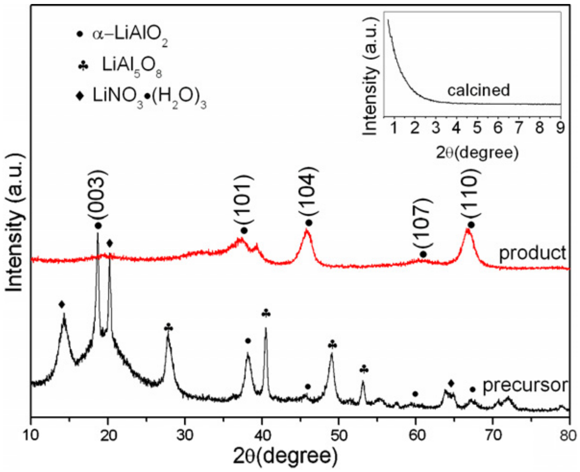

Fig. 1. XRD patterns of the precursor and the product. Insert is the small-angle diffraction pattern of the product.

The decomposition of the precursor can be seen from the TG-DTA curves in Fig. 2. The first weight loss of 17.8% can be attributed to desorption of dissociated water on the surface of the powder, corresponding to the endothermic peak at 357 °C. While the temperature increasing, the removal of the template takes place. The exothermic peak at 357–477 °C is caused by the decomposition of the organic template and desorption of water in the mesoporous framework, corresponding to a weight loss during this step of 38%. In the temperature region between 510 and 620 °C, the weight loss was extremely small. Meanwhile, a significant exothermic peak could be found at 581 °C, which can be attributed to the crystallization transition process from the precursor to the pure α-$LiAlO_2$.

SEM morphology of sulfonated PS microspheres is shown in Fig. 3a, which suggests that the PS microspheres with average diameter of 3 μm form an almost opal structure. From the SEM image for the lithium aluminate precursor in Fig. 3b, spheres also could be observed, which size is about 3–4 μm, a little larger than PS microsphere. The enlargement in diameter could be due to the coating of precursor of $LiAlO_2$ and surfactant on the surface of PS microsphere, which indicates that the core-shell struc-