Progress in Preparation of Cr2O3 Hollow Micro/Nano-Sphere

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Abstract. The preparation methods of Cr2O3 hollow micro/nano-spheres are summarized. The preparation methods are mainly divided into hard template method, soft template method and template-free method. The advantages and disadvantages of different methods are introduced and discussed. At the same time, the preparation methods of Cr2O3 hollow micro/nano-spheres are prospected.

1. Introduction

In recent years, nano-materials with different morphologies and structures have attracted considerable interests. Inorganic hollow micro/nano-spheres is one of the most important ones. The hollow sphere has a large specific surface area and low density. Hollow structures can accommodate a large number of molecular objects or serve as carriers of materials. Through chemical modification of hollow structure or physical doping in micro/nano-hollow spheres, the properties of hollow spheres materials can be controlled, making micro/nano-hollow spheres materials widely used in chemical catalysis [1], rechargeable batteries [2] and so on. Cr2O3 is a p-type semiconductor (bandwidth 3.4 eV). It has a similar crystal structure with corundum, has high chemical stability, corrosion resistance, high hardness, high near infrared reflectance, and is widely used as catalyst [3](Abu-zied 2000), green pigments and protective coatings [4], gas sensors [5-6] and so on [7]. Combining the hollow structure with the characteristics of Cr2O3, micro/nano-Cr2O3 hollow spheres will have great application prospects.

At present, the synthesis of nano-Cr2O3 hollow structure are hard template method, soft template method and template-free method. In this paper, the research progress of Cr2O3 hollow micro/nano-spheres prepared by these methods at home and abroad is reviewed.

2. Hard Template Method

Hard template method is widely used in the synthesis of inorganic hollow spheres. Typical methods for fabricating hollow structures from hard templates usually include four steps [8]: 1) preparing hard templates 2) modifying the surface of the template 3) covering the hard template surface with the target materials or the precursors, and making the formed structure absorbable on the board surface 4) choosing the appropriate way to remove the template to obtain the hollow structure. The shape and size of the hollow structure depend on the shape and size of the template.

Many materials have been used as templates to prepare hollow structures: organic polymers, silica, metal particles and so on [9]. In recent years, carbohydrates (such as glucose and fructose) have been successfully used as templates to synthesize hollow inorganic metal oxides [10-11]. Carbohydrates are...
considered as good templates for the synthesis of hollow spheres because of their low cost and easy availability. Its surface contains lots of -C=O and -OH functional groups. These functional groups make the material easy to be adsorbed by the template surface and cover the template surface better and more stably [12]. Taking the work of Haitham Mohammad Abdelaal [13-15] as example, the general step of preparing micro/nano-Cr$_2$O$_3$ hollow spheres using carbohydrates as template (Fig. 1) is to dissolve carbohydrates (fructose or glucose) and reactants into solvents and transfer them to a closed reactor. During heating, carbohydrates in the solution form carbon pellets with rich-C=O and -OH functional groups by polymerization and carbonization. In the reaction system, chromium ions and functional groups on the surface of carbon spheres are connected by mutual coordination or electrostatic interaction, so that chromium ions react with oxygen functional groups in situ to form product particles, and a core-shell structure with carbon spheres as products is obtained. The intermediate template is removed by calcination at high temperature. The Cr$_2$O$_3$ hollow spheres or ball in ball (bnb) hollow structure without template supporting is obtained by ion interaction and hardening.

Wang [16] successfully prepared the hollow nanospheres of Cr$_2$O$_3$ with glucose as a template and obtained bnb and single hollow spheres by controlling the heating rate at the time of roasting. Zhang [17], Li [18], Sun [19] used carbohydrates as template to successfully prepare Cr$_2$O$_3$ hollow micro/nano-spheres by a similar method and explored the factors and principles of the reaction.

![Figure 1. Schematic diagram of the fabrication of Cr$_2$O$_3$ hollow micro/nano-spheres with carbohydrates as template.](image_url)
At present, there are also other materials as hard template for the preparation of Cr$_2$O$_3$ hollow micro/nano-spheres. Bai[20] used yeast as a template to obtain a hollow structure of micro/nano-Cr$_2$O$_3$ through a similar procedure. The innovation of the method is that the reaction is carried out at a relatively mild temperature (30 °C). The experiment obtained hollow Cr$_2$O$_3$ spheres with a diameter of 2.5~2.8 μm and a wall thickness of about 300 nm.

It is very suitable to prepare micro/nano-Cr$_2$O$_3$ hollow spheres with hard template. Because the size and quantity of precursor and template can be strictly controlled so as to direct the cavity size and shell thickness of the hollow spheres of Cr$_2$O$_3$. The experimental device for preparing hollow spheres with hard template is relatively simple. However, the hard template method also has some inherent shortcomings, requiring additional template additives and steps to remove the template, and may cause varying degrees of impact on the Cr$_2$O$_3$ hollow structure when calcined at high temperature. For example, the emergence of bnb-type Cr$_2$O$_3$ hollow structure. In addition, the key applications of hollow structure, such as drug and therapeutic delivery, need to easily enter the central control space. It is a challenging task to use hard template method to fill the hollow structure with functional materials in shell-forming devices or to encapsulate the shell-forming molecules in situ by guest molecules.

3. Soft template method

Soft templates typically have a surfactant, long chain polymer or a structure formed by a virus, and these structures are usually amphiphilic molecules containing a hydrophilic group and a hydrophobic group. Under certain conditions, these materials self-assemble into aggregated entities, such as positive and negative micelles, emulsions, vesicles or liquid crystal phases, which constrain and guide the growth of the guest structure. The precursor reacts on the confined or outer surface of the soft template to produce a bubble or tubular structure similar to the original shape of the template. The template can be dissolved in the reaction solvent after the reaction or can be removed by a simple washing step. For example, Wan[21] prepares a SiO$_2$ hollow spheres using a polyelectrolyte as a soft template, and the template is removed by water washing after the reaction.

Jiang [22] used PEG as a soft template to react with acetaldehyde by adding Cr(NO$_3$)$_3$·9H$_2$O and urea in a closed hydrothermal autoclave at 180 °C for 5 h. Two types of Cr$_2$O$_3$ materials, the Cr$_2$O$_3$–C composite nanospheres with a novel hierarchical core/shell structure, and pure mesoporous Cr$_2$O$_3$ spheres have been obtained by using a certain thermal treatment without adding more carbon precursor. It is also proved by experiments that PEG and acetaldehyde are essential in the synthesis of Cr$_2$O$_3$ mesoporous structure and Cr$_2$O$_3$–C nanospheres.
Figure 3. (i) SEM images of (a) Cr$_2$O$_3$ precursor, (b) mesoporous Cr$_2$O$_3$. (c) TEM, and (d) HRTEM images of mesoporous Cr$_2$O$_3$. The inset in (b) shows the SEM image of a broken sphere indicating its inside structure. (ii) SEM images of (a) Cr$_2$O$_3$–C, (b) TEM images of Cr$_2$O$_3$–C; and (c, d) HRTEM images of Cr$_2$O$_3$–C. The inset in (a) shows the SEM image of a broken sphere indicating its core-shell structure.

In a soft template method for synthesizing micro/nano-hollow spheres, do not require additional steps to remove the templating agent, since the template is usually in the form of emulsion droplets, vesicles/micelles and bubbles, etc. Compared to hard templates, soft template preparation of hollow spheres offers more possibilities for adjusting the interior and modifying the external structure, resulting in a more complex layered structure, and the modification or doping of the shell molecules remains the structure of the hollow sphere is maintained. However, soft templates are often difficult to control the uniformity of the size of the hollow structure compared to the hard template method. The self-assembly of templates and the complexity of the related steps of shell growth make the preparation of hollow microspheres by soft template a challenging task.

### 4. Template-free method

Template-free method is also called self-template method. Hollow micro/nano-spheres were prepared by direct reaction without additional template. At present, many self-template methods for hollow spheres have been developed based on different principles, including Ostwald ripening, Kirkendall effect, current substitution, surface protection etching and so on. Generally, self-template synthesis involves two steps: (1) synthesis of nanomaterials template (2) template transformation to hollow structure. Unlike the traditional template methods (including hard and soft templates), the template used in the self-template method is not only used as a template to generate internal hollow structure, but also used to react to generate a shell layer or to form a shell layer. At present, template-free methods for preparing Cr$_2$O$_3$ hollow micro/nano-spheres are mainly based on Ostwald ripening. Sun$^{[23]}$ by dissolving Cr(NO$_3$)$_3$.9H$_2$O in deionized water, adding acrylic acid and ammonia water, and reacting at 120°C for 24 h. After calcining at 500°C for 4 h, porous Cr$_2$O$_3$ hollow spheres having an average diameter of 2.2 μm was obtained. In the initial stage of the reaction, chromium hydroxide nanoparticles begin to form through heat treatment in the hydrothermal process, and a large number of acrylic anions and chromium ions are adsorbed by strong interaction between the carboxyl groups $^{[24]}$. Subsequently, these newly formed colloidal nanoparticles aggregate into spheres to minimize total surface energy. Because of the inherent density change in the solid sphere, the hollow effect begins in a specific area below the direct surface layer. Smaller particles in solid spheres with higher surface energy and solubility are dissolved and merged with hydrothermal processes on the outermost surface. Mass transfer first produces a shell-core structure, and then a well-defined hollow microsphere structure is obtained due to the continuous dissolution of the core and longer reaction time. By changing the reaction time, the products with different reaction time were collected for characterization and microstructure observation. The experiment explored the formation mechanism of Cr$_2$O$_3$ hollow spheres (Fig. 4).
Figure 4. (a)-(e) TEM images of Cr₂O₃ precursors at different reaction time

(f) Formation mechanism of Cr₂O₃ hollow spheres

Bai [25] directly synthesized Cr(OH)₃ hollow hexagonal by chemical reaction at room temperature with CrCl₃·H₂O and NaBH₄. The product was calcined at 450°C for 30 minutes to obtain Cr₂O₃ dark green hollow hexagonal. Through experimental sampling observation, the hexagonal structure is completed by nanoparticle oriented self-assembly and selective etching. Later Owstwald ripening makes the hexagonal structure develop toward the hollow structure of larger and better crystalline forms (H⁺ enters into the pore of hexagonal structure in the reaction system, etches Cr(OH)₃, and the Cr³⁺ produced will continue to hydrolyze to produce more H⁺, which makes the concentration of H⁺ in the middle of the hexagonal structure higher than that in the outside, and the etching speed is faster, eventually leading to the formation of the hollow structure).

Template-free route has several advantages: 1) The synthesis process is relatively simple, the hollow structure can be obtained by one-step reaction of reactants, and the experiment has a relatively high reproducibility. 2) There is no need for additional template additives and no need for additional template removal steps. The process of surface modification of the template is omitted, which reduces the production cost. 3) The shell thickness and particle uniformity can be well controlled by the reaction. 4) Template-free hollow structure can also be modified by adding other reagents in the reaction, giving more excellent properties to the hollow structure. For example, Lei [26] prepared Ni-Cr₂O₃ hollow structure by template-free method. However, there are some shortcomings of template-free method, which cannot adjust the size of hollow structure very well. It takes a relatively long reaction time to synthesize hollow structure based on Owstwald ripening mechanism.

5. Conclusions

Cr₂O₃ hollow microspheres have broad application prospects. At present, the preparation of hollow chromium oxide micro/nano-spheres has been successful. However, there are some shortcomings in the current schemes, the preparation of hollow chromium oxide microspheres by hard/soft template method requires template additives and additional template removal steps, while the template-free method requires relatively long reaction time, which need further optimization or design of new synthetic schemes by scientific researchers. The existing preparation schemes of chromium oxide hollow microspheres are the precursors of chromium oxide obtained by reaction, and the final products need to be calcined at high temperature. The preparation of hollow chromium oxide microspheres by one-step synthesis without high temperature roasting and jumping chromium peroxide precursor is worth further exploration.

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