

# Preparation and crystallization of hollow $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> microspheres following the gas-bubble template method



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## HIGHLIGHTS

- Formation of hollow hematite microspheres by the gas-bubble template method.
- This technique does not require hard templates or special conditions of atmosphere.
- Annealing promotes the transition magnetite to maghemite to hematite.
- Crystallization of the hematite shells increase with annealing temperature.

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## ABSTRACT

In this work we report the formation of hollow  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) microspheres by the gas-bubble template method. This technique is simple and it does not require hard templates, surfactants, special conditions of atmosphere or complex steps. After reacting Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and citric acid in water by sol–gel, the precursor was annealed in air at different temperatures between 180 and 600 °C. Annealing at 550 and 600 °C generates bubbles on the melt which crystallize and oxidizes to form hematite hollow spheres after quenching. The morphology and crystal evolution are studied by means of X-ray diffraction and scanning electron microscopy. We found that after annealing at 250–400 °C, the sample consist of a mixture of magnetite, maghemite and hematite. Single hematite phase in the form of hollow microspheres is obtained after annealing at 550 and 600 °C. The crystallization and crystal size of the hematite shells increase with annealing temperature. A possible mechanism for hollow sphere formation is presented.

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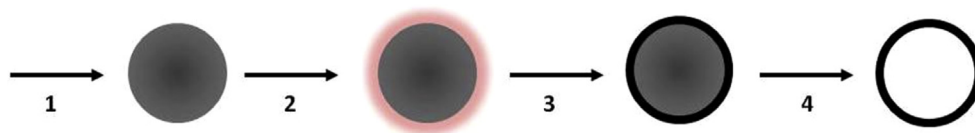
## 1. Introduction

The production of hollow microspheres is of current interest due to their promising applications in photonic crystals, encapsulation, drug delivery, catalysis, chemical storage, light fillers and low dielectric constant materials [1–14]. A variety of hollow spheres such as carbide [15], Ni [16], TiO<sub>2</sub> [17], NiS [18], Bi<sub>2</sub>Te<sub>3</sub> [19] and ZnO/SnO<sub>2</sub> [20] have been successfully fabricated. The most common

techniques to produce hollow spheres are based on the use of core organic/inorganic hard templates such as monodispersed silica spheres [21–23], polymer latex colloids [11,24], carbon spheres [25] and block copolymers [26,27] or soft templates, such as emulsion droplets [28,29], surfactants vesicles [30] and liposome [31]. In general, the template technique involves four major steps (as represented in Fig. 1) [1]: (1) Preparation of the templates; (2) functionalization/modification of the templates surface to achieve favourable surface properties; (3) coating the templates with desired materials or their precursors; and (4) selective removal of the templates in appropriate solvents or calcination to obtain the hollow structures.

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**Fig. 1.** Schematic representation of the process of hollow spheres by using templates. A typical procedure consists of (1) Preparation of the templates (2) functionalization/ modification of their surface, (3) coating them and (4) removal or dissolution of the templates to obtain the hollow structures (Adapted from Reference [11]).

The hard template technique is effective for controlling the morphology of the final product. Nevertheless, this technique requires tedious synthetic procedures such as a careful selection of an affine template and a lot of care to prevent the collapse to affecting the quality of the shell during template removal. Some other drawbacks include limited sphere size, quality, purity, cost of production, and low temperature capability of the produced hollow spheres.

Recently different free-template approaches have been developed to produce hollow spheres. Some of these methods are based on Oswald ripening [32], simultaneous blowing and melting hydrogels [33–35], Kirkendall Effect [36–38], among others. However the average size of the hollow spheres produced by these methods are usually larger than 10  $\mu\text{m}$ . Furthermore, it is difficult to obtain small microspheres having a narrow particle size distribution, and high purity metal oxide composition. Another less explored method for the production of hollow spheres is 'the gas-bubble template method'. This method involves the production of gas microbubbles during the chemical preparation of nanoparticles by using selected ligands. It is believed that the nanoparticles cover the surface and become hollow spheres after calcinations at high temperatures [39–46]. However the exact mechanism for the bubble nucleation and grow is unclear.

Hematite is the most stable iron oxide. It is *n*-type semiconductor ( $E_g = 2.2$  eV) under ambient conditions and it is easy to synthesize. Due to its magnetic properties, corrosion-resistance, low cost and low toxicity it is widely used in catalysis [47–50], environmental protection [51–57], sensors [58–61], magnetic storage materials [62] and clinic diagnosis and treatment [63]. To date, the preparation of a variety of hematite morphologies such as rhombohedra [64], particles [65–68], nanocubes [69,70], rings [71], wires [72,73], rods [74,75], fibers [76], flakes [77], cages [78], airplane-like structures [79] and hierarchical structures [80–82] have been reported. Recently, some works have reported the production of crystalline hematite hollow spheres through various methods. Some of the approaches are listed in Table 1. Note that most of the existing methods for obtaining the hematite hollow spheres involve templates, surfactants, toxic organic solvents, or complex steps. Among them, the hydrothermal/solvothermal method has some advantage over the rest due to its fast reaction time, effective control of particle shape, and low incorporation of impurities into the products. However, this technique requires of steel pressure vessels or autoclaves during preparation to apply high pressure and thus to achieve the formation of the hollow spheres [88–96]. In contrast, in this work we report the preparation of hematite hollow spheres by the gas-bubble template technique in which no high pressure or any special conditions of atmosphere are required. Here, the hollow hematite microspheres are formed by annealing sol–gel iron oxide precursor in air. We propose a mechanism for the hollow formation based on the condensation, crystallization and oxidation of bubbles shells at high temperatures. This method is reproducible, simple, cheap, environmental friendly and it allows good control of the size, crystallization and oxidation of the product.

## 2. Experimental

Hollow hematite microspheres were produced by a modified gas-bubble template method following annealing in air an iron oxide precursor obtained by sol–gel [98]. For the precursor, 200 ml of colloidal ferric nitrate nine-hydrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) particles and mono hydrated citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , 0.2 M) were dissolved in 800 ml of de-ionized. The solution was vigorously agitated in a magnetic stirrer at 350 rpm (70  $^\circ\text{C}$ ) for a period of 48 h to form  $\text{Fe}(\text{OH})_3$ . The citric acid was used as ligand, to promote hydrolysis and to balance any difference of ions in the solution. A gel is formed by the hydrolysis of the ferric nitrate to iron oxohydrate  $\text{FeOOH}$  polymer [99].

The gel was then dried for two days at 40  $^\circ\text{C}$  to evaporate the acid, water residuals and other possible impurities formed during hydrolysis. This sample precursor was then introduced in a tubular furnace (LENTON LTF-PTF Model 16/610) for annealing in air at different temperatures, from 180 to 600  $^\circ\text{C}$ . The furnace was programmed to increase the temperature at  $2 \pm 1$   $^\circ\text{C}/\text{min}$ , to remain constant for 12 h, and finally to cool down at a rate of  $2 \pm 0.5$   $^\circ\text{C}/\text{min}$ . This step has two purposes. First, to thermally oxidize the gel to obtain pure hematite; and secondly, to form bubble structures via boiling in air from which the hollow spheres are formed after quenching. Remarkably, the solution precursor, is stable in air and has a shelf life longer than two years. After reacting with water and following the same annealing process, similar hollow spheres can be obtained, confirming the reproducibility of the results.

The characterization of the sample was performed by X-ray diffraction (XRD). The data was collected from 20 $^\circ$  to 65 $^\circ$  (0.02 $^\circ$  steps) using a powder universal diffractometer Bruker D8 Focus with  $\text{Cu-K}\alpha$  radiation (1.5406  $\text{\AA}$ ). The diffractograms corresponding to the single hematite phase were refined using the Rietveld method and the peaks shape was modelled with a Pseudo-Voigt function (a combination of Gaussian and Lorentzian functions). The average crystallite size for the single-phase hematite samples was estimated with the Scherrer equation [100]. During Rietveld refinement,  $R_{\text{wp}}/R_{\text{exp}}$  (the rate of the parameters *R*-weighted and *R*-expected) was used to observe the convergence of the cell parameters and to obtain a good fitting [101]. The shape of the hematite crystallite was modelled by using the program Vesta v.3.2.1 [102] and their strain were calculated with the Williamson-Hall method [103]. The morphological analysis was performed using a scanning electron microscope (SEM–XL30 SFEG). With the help of the Image-J software, several SEM images have been used to count  $N \sim 1000$  particles. Subsequently, particle size histograms have been mounted using the Sturges method [104,105].

## 3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of the samples after annealing at different temperatures from 180 to 600  $^\circ\text{C}$ . Initially, after annealing at 180  $^\circ\text{C}$ , the sample consists of an amorphous solid with no preferred reflections in the XRD. After annealing at 250  $^\circ\text{C}$ , magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) coexisting with a

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