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Short communication

Facile fabrication of ZrO_2 hollow porous microspheres with yeast as bio-templates

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ABSTRACT

ZrO_2 hollow porous microspheres have been fabricated successfully using living yeast cells as bio-templates through a facile ageing process at lower crystallizing temperature. XRD, SEM, FT-IR and N_2 adsorption–desorption were used to characterize ZrO_2 hollow microspheres. The results showed that the inorganic–organic hybrid hollow microspheres were fabricated at 100 °C and ZrO_2 hollow microspheres with tetragonal phase and porous structure were obtained at 300 °C. The crystallization temperature of ZrO_2 decreased obviously due to the inducting of bio-molecules. The as-prepared hollow microspheres are approximately ellipsoid. The shells of these hollow microspheres are porous, which are composed of some nanoparticles with size of ~20 nm. The formation mechanism of ZrO_2 hollow microspheres was proposed and discussed tentatively.

1. Introduction

ZrO_2 is one of the most intensively studied materials owing to its technologically important applications in catalysts, catalytic supports, chromatography, and so on [1,2]. The size and morphology of zirconia are closely related to their properties and influence their potential applications [3–5]. Especially, the micro-/nanostructure ZrO_2 not only has some advantages of conventional size materials but also retains the high surface areas and high activities of nanoparticles [6]. Simultaneously, the double structure of nanometer and micrometer probably produces some new properties and characteristics [7]. Furthermore, ZrO_2 with hollow micro-/nanostructure exhibits even more advantages over their solid counterparts due to lower densities and peculiar cavum structure.

Several methods have been developed for the preparation of zirconia with different sizes and morphologies, including nanoparticles [8,9], wonderful morphologies [10,11], mesoporous [12,13] and hollow spheres [1,14]. Especially, all these methods require higher processing temperature to complete the crystallization of zirconia. Recently, we find that the methods of biological molecules inducing the nucleation and growth would help ameliorate this feature. Bansal et al. [15] had shown that the fungus Fusarium oxysporum secretes proteins which were capable of hydrolyzing aqueous ZrF_6^{2-} ions to form zirconia at room temperature. Jiang et al. [16] also found that lysozyme could catalyze the hydrolysis/condensation of the precursor potassium hexafluorozirconate and induced the formation of zirconia particles at room temperature.

In this paper, we reported a simple and mild method for the synthesis of ZrO_2 hollow porous microspheres using yeast as a bio-template. This method exhibits a number of interesting features: (i) Living yeast cell is the key factor for the preparation of ZrO_2 hollow microspheres. (ii) Hollow structure could be obtained no need to remove templates. (iii) ZrO_2 crystallization temperature is lower than the temperature required for the general template methods. (iv) The resulting wall of hollow microspheres is porous due to the stack of nanoparticles. A formation mechanism is proposed which can explain the porosity and lower crystallization temperature of the products. This bio-template method provides an economical, green, and convenient strategy comparing with the traditional template-directed method, which may open up a new pathway to synthesize porous hollow inorganic spheres by means of a facile bio-assisted method.

2. Experimental procedures

2.1. Preparation of ZrO_2 hollow microspheres

An aqueous solution of $ZrOCl_2{\cdot}8H_2O$ was prepared by mixing the metal salt with distilled water. Acetylacetone solution was added to the solution to control the hydrolysis rate of $ZrOCl_2{\cdot}8H_2O$ [17]. Then ammonia hydroxide was added drop by drop to adjust the pH of solution between 4.5 and 5.0. The reaction system was

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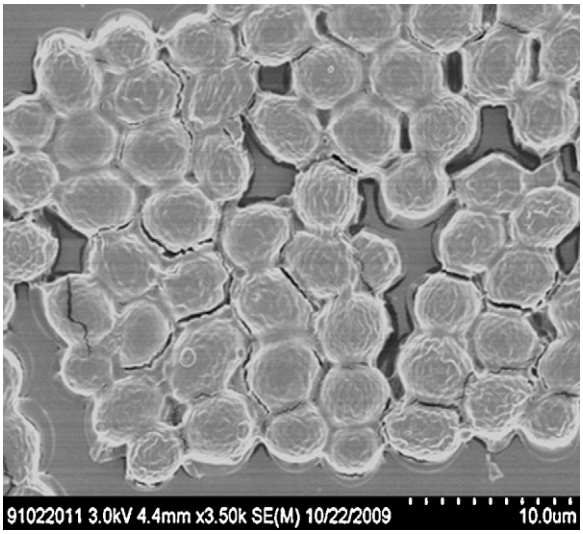


Fig. 1. SEM images of original yeast cell.

continuously stirring for 30 min at 30 °C and still was the solution state. Then yeast-water suspension (1 g yeast/40 ml H_2O) was dropped into the above mixture solution under stirring. After the ultimate solution aged at room temperature for 3 h, the precipitates were filtered, washed with distilled water and then ethanol for several times and dried at 100 °C. Finally, the dried samples were calcined respectively at 300 °C, 500 °C for 2 h to remove organics. Thus, the ZrO_2 hollow microspheres were obtained.

2.2. Characterization

Scanning electron microscopy (SEM) measurement was performed with a Hitachi S-4800 microscope. An X-ray diffraction (XRD) study was carried out using a Bruker D8 ADVANCE X-ray diffractometer with Cu Ka radiation ($\lambda = 1.5418$ Å). Infrared spectra (IR) measurement was carried out on a SHIMADU FIRE-8900 Fourier transform infrared spectrophotometer. The porous structure of the samples was analyzed by N_2 adsorption–desorption in a NOVA4000e nitrogen adsorption apparatus.

3. Results and discussion

3.1. The morphology and structure of ZrO_2 hollow microspheres

3.1.1. The morphology of ZrO_2 hollow microspheres

Fig. 1 shows that the original morphology of yeast is approximately spherical or ellipsoid with the diameter ranging from 4.0 μm to 4.5 μm.

As shown in Fig. 2(a), the hollow microspheres were obtained after the samples were dried at 100 °C. These hollow microspheres should be a kind of organic/inorganic hybrid species and the organics in the inner of living cell are attached to the internal wall of the microspheres. The hollow spheres are ellipsoid with almost

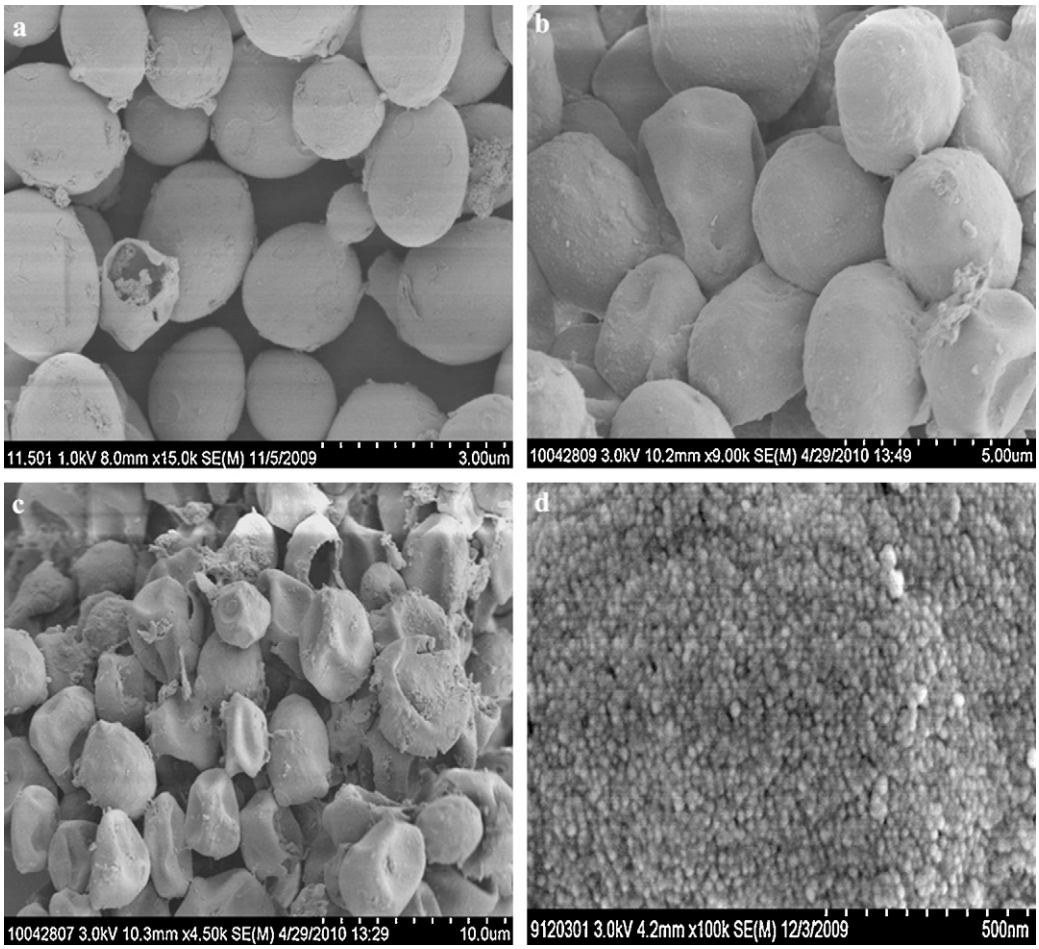


Fig. 2. SEM images of (a) hybrid microspheres, (b) ZrO_2 hollow microspheres calcined at 300 °C, (c) ZrO_2 hollow microspheres calcined at 500 °C and (d) the surface of the hollow microspheres.

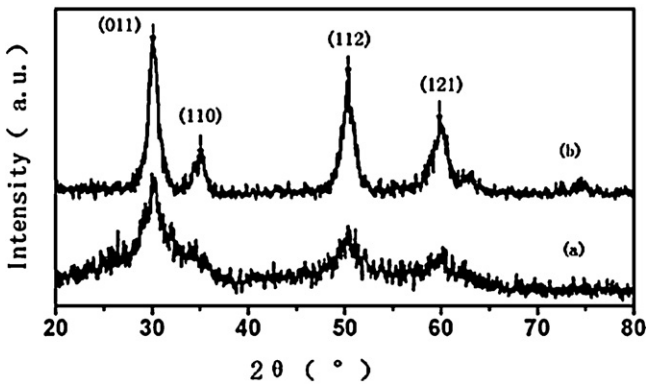


Fig. 3. XRD patterns of ZrO_2 hollow microspheres calcinated at different temperature (a) 300 °C and (b) 500 °C.

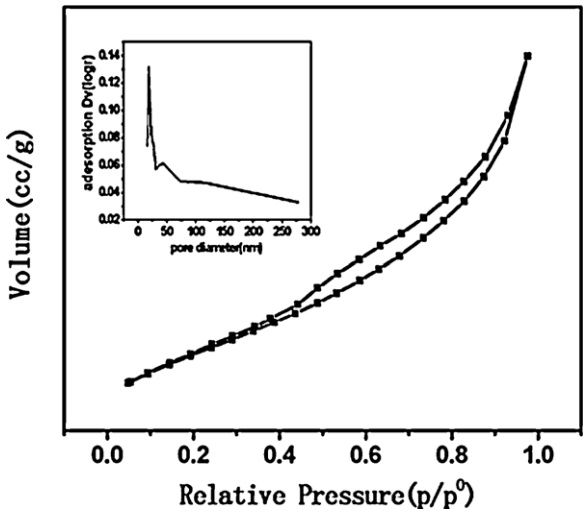


Fig. 4. Nitrogen adsorption–desorption isotherms and the corresponding pore size distribution (inset) for the ZrO_2 hollow microspheres.

the same diameters as original yeast size. Obviously, hydrolysis of zirconium chloride occurred on the surface of the yeast cells and the yeast cells played a role of templates in the process of preparing ZrO_2 hollow microspheres. The morphology of ZrO_2 hollow microspheres change little but the size changed slightly when the dried particles were calcined at different temperature, as shown in Fig. 2(b) and (c). The size of ZrO_2 hollow microspheres is about 2.0–3.0 μm. The shrinkage of the particles is attributed to the removing of organic molecules during heat treatment. The cracked spheres and apparent cavities show the hollow nature of the products. The thickness of ZrO_2 hollow microspheres shell is estimated to be about 100 nm. In addition, it was found that the thickness of the shells of ZrO_2 hollow microspheres can be tuned by the concentration of zirconium chloride rather than reaction time at 30 °C. Careful observation shows that the surfaces of these microspheres are constructed by nanoparticles as shown in Fig. 2(d).

3.1.2. The structure of ZrO_2 hollow microspheres

The XRD patterns of ZrO_2 hollow microspheres synthesized via the yeast bio-template route are shown in Fig. 3.

As shown here, the crystallization of zirconia has been achieved almost perfect at 300 °C (Fig. 3(a)). The crystallization is intensified with the increase of calcinations temperature as shown in Fig. 3(b). Lower crystallization temperature may be confirmed that the yeast cells not only are used templates but also the active bio-molecules of yeast cells take part in the nucleation, growth and crystallization of ZrO_2. All the diffraction peaks can be indexed to the tetragonal phase structure of ZrO_2 (JCPDS 79-1769), and no peaks of other materials or phases are observed, which indicates the high purity of the products. The crystallite sizes, as estimated by Scherrer formula, corresponding to (0 1 1) crystal plane are 6.9 nm (in Fig. 3(a)) and 11.4 nm (in Fig. 3(b)).

3.1.3. The pore structure of ZrO_2 hollow microspheres

The ZrO_2 hollow microspheres are further characterized by nitrogen adsorption and desorption isotherms at 77 K, as shown in Fig. 4.

Fig. 4 shows a type III-like isotherm with H3-hysteresis, indicating the presence of slit-like type porosity in the microspheres. The Barrett–Joyner–Halenda (BJH) method was used to calculate the pore size distribution (as shown in Fig. 4 inset). The result indicates that the specific surface area is 70.322 m^2/g and the pore volume is 0.077 cm^3/g. However, for the solid microspheres, the specific surface area is 57.708 m^2/g and the pore volume is 0.013 cm^3/g. The hollow microspheres have a bimodal pore structure: the smaller pores with a diameter of 18 nm and the bigger pores of approximately 35 nm in diameter. This bimodal pore structure shows benefits not only to the delivery of macromolecules, but also to the shape selectivity of micromolecules.

3.1.4. The infrared spectrogram analysis of hollow microspheres

Fig. 5 shows the FT-IR spectrum of ZrO_2 hybrid microsphere and original yeast templates. On the curve of the original yeast templates, the bands at 1652.9 cm^{-1} could be attributed to the C═O stretching vibration of the amide I band of proteins. The bands at 3419.6 could be ascribed to the O–H, C–H, N–H stretching vibration of the groups which possess hydrogen. On the basis of FT-IR spectrum of original yeast, shows that active components of yeast contain these groups. Compared Fig. 5(b) with (a), we found that the shoulder peak at 1652.9 cm^{-1} in Fig. 5(b) corresponding to the C═O stretching vibration splits to 1593.1 $cm^{-1}$and 1529.4 cm^{-1} in Fig. 5(a) that belong to Zr–O–C deformation vibration. The spectrum of original yeast exhibited clear shifts from 3419.6 cm^{-1}, 2927.7 cm^{-1}, 1456.2 cm^{-1} and 1130.2 cm^{-1}in Fig. 5(b) to 3415.7 cm^{-1}, 2925.8 cm^{-1}, 1425.3 cm^{-1} and 1132.1 cm^{-1} in Fig. 5(a) due to the interaction between reactive functional groups such as carbonyls, hydroxyls, acid amides andZr^{2+} by electrostatic force, hydrogen bond and covalent bond.

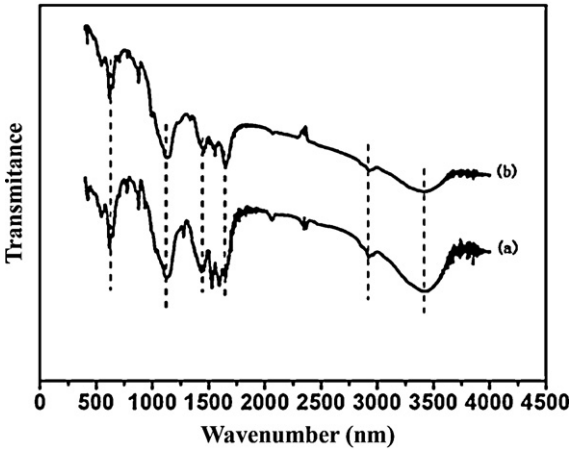


Fig. 5. FT-IR spectrum of (a) ZrO_2 hollow spheres without the calcined and (b) original yeast templates.

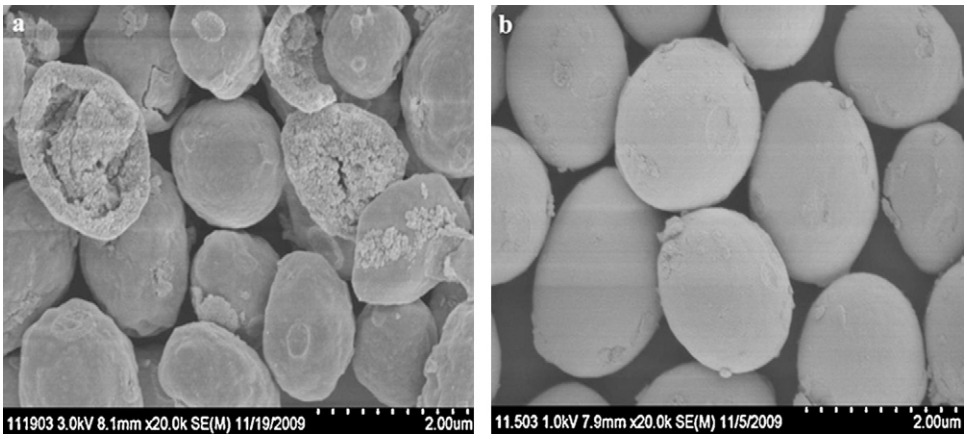


Fig. 6. SEM images of (a) ZrO_2 core–shell microspheres and (b) ZrO_2 solid microsphere.

3.2. The mechanism for the formation of ZrO_2 hollow microspheres

The influences of experimental parameters on the morphology of products, such as the reaction temperature, the reaction time, the concentration of zirconium chloride and pH of the solution, were investigated. It was found that the hydrolysis of zirconium chloride was accelerated with increasing the reaction temperature. However, when the temperature was higher than 30 °C, the mixture of hollow and core–shell microspheres were obtained because yeast cells were deactivated and the walls of the yeast cells became loose and porous. At 80 °C, ZrO_2 core–shell microspheres and solid microspheres were synthesized following different reaction time, as shown in Fig. 6.

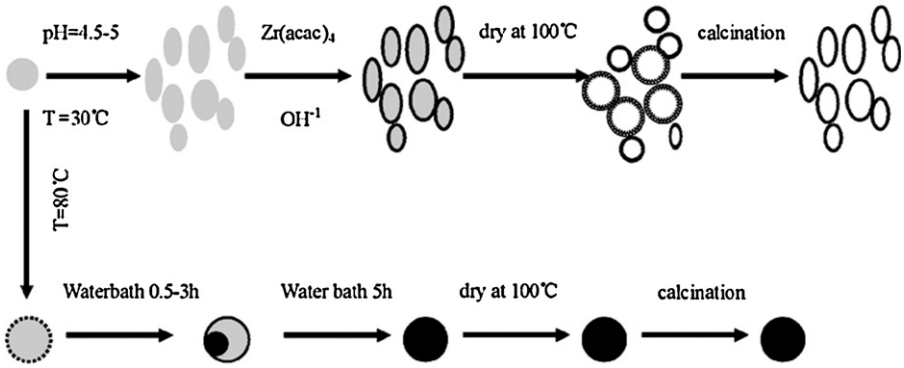
When the initial temperature was 80 °C and the reaction times were between 0.5 h and 3.0 h, ZrO_2 core–shell microspheres were synthesized (as shown in Fig. 6(a)). When the reaction time was longer than 5.0 h, solid microspheres were synthesized (as shown in Fig. 6(b)). The main reason for such results might be that yeast cells are deactivated at 80 °C and the longer reaction time the more serious inactivation. At the same time the walls of the yeast cell become loose and porous. The inorganic salt or ions enter to the inner of cell through these porous and combine with some biomolecules. At this point, nucleation and growth of ZrO_2 occur not only in the surface of yeast cell, but also in internal. Core–shell structure comes into being. With the reaction time extension, solid microspheres are finally formed. The living yeast cell with a dense wall is the necessary condition for the formation of hollow microspheres.

The mechanism model for the formation of ZrO_2 hollow microspheres is tentatively proposed as shown in Scheme 1.

The whole process can be described as: (i) the yeasts keep characteristic of unicellular eukaryotic microorganism and would reproduce prolifically at appropriate environment, such as pH 4.5–5.0, T = 30 °C. The wall of the living cell of yeasts can prevent inorganic salt or ions from entering the inner of the cells. (ii) The cell wall of yeast is primarily made up of mannan and glucan [18]. Thus, there are many reactive functional groups on the cell wall, such as hydroxyls, acid amides and carbonyls (as shown in Fig. 5(b)) which are able to bind mental ions through coordination or electrostatic attractions. Consequently, tens of thousands of the cells provide nucleate sites for ZrO_2 crystals and ZrO_2 crystals will grow in the surfaces of the cells when the concentration of $ZrOCl_2{\cdot}8H_2O$ is fixed. These groups not only have interaction with crystal element but also guide nucleation, growth and crystallization of ZrO_2. It results in the crystallization temperature of ZrO_2 inclining to drop obviously as shown in Fig. 3(a). (iii) The yeast cell is dead when it is dried at 100 °C. Then, the hydration water in the inner cell is escaped and the free water is evaporated together. Other compositions (such as cell nucleus, mitochondria and so on) adhere to inner wall of cytomembrane to form inorganic–organic hybridization precursors of ZrO_2 hollow microstructure. The organics is volatilized and precursors of ZrO_2 hollow microstructure are crystallized at different calcinations temperature. At the end, ZrO_2 hollow microspheres with the porous shell are formed.

4. Conclusions

In summary, a facile technique for synthesizing ZrO_2 hollow porous microspheres was developed using living yeast cells as biotemplates. It was demonstrated that the dense wall of living yeast cell is the necessary condition for the formation of hollow microspheres. The structure of ZrO_2 hollow microspheres could be obtained only when pH 4.5–5.0, T = 30 °C of the solution, while other conditions will lead to the formation of core–shell or solid



Scheme 1. Schematic illustration of ZrO_2 hollow microspheres formation.

microspheres. The obvious decreasing of the crystallization temperature was attributed to the interaction between the inherent functional groups on the cell wall and the reactants. The mechanism model proposed provided a fundamental understanding for the yeast cells used as bio-templates to control the product structure. This bio-template strategy can be generally extended to the synthesis of other inorganic hollow microspheres.

Acknowledgement

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