



A universal biological-materials-assisted hydrothermal route to prepare various inorganic hollow microcapsules in the presence of pollens

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ABSTRACT

A universal bio-economical hydrothermal route has been developed to prepare various inorganic hollow microcapsules with the help of rapeseed pollens for the first time. The pollens were used without any modifications. TiO_2 , ZnO , zeolite ZSM-5, BaTiO_3 and ZnS were prepared by this route using the regular synthesis solutions added with rapeseed pollens. The obtained products were examined by scanning and transmission electron microscopy, X-ray diffraction, FT-IR, N_2 adsorption and thermogravimetric analysis. The hollow microcapsules are composed of inorganic particles around the derivations of pollens. And the diameter of the hollow has been demonstrated almost the same size as the derivations microspheres. The derivations were decomposed in high temperature crystallization procedure; therefore, no additional procedure is needed to remove the templates for the hollow structure. The hollow microcapsules prepared with rapeseeds have much higher specific surface area. The formation mechanism can be ascribed to the template effect of derivative microspheres formed from decomposition of these pollen grains. Furthermore, other pollens are also used in the preparation by the universal hydrothermal route. Still, inorganic hollow microcapsules but with different hollow diameters were obtained probably resulting from the different size of the derivations.

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1. Introduction

Inorganic hollow microcapsule possessing a micro-scale thick shell and a hollow interior have attracted great attention because of the special properties, such as low density, high surface area, thermal insulation, high loading capacity, etc. [1]. Thus, they can be used in drug delivery [2–4], catalysis [5–10], material encapsulation [11,12], energy storage and conversion [13–15], gas sensing [16–19], photovoltaic materials [20,21], etc. Therefore, various techniques have been developed to prepare such microcapsules, which can be simply categorized as the template method [22,23] and template-free method [24–27]. The template based method is always an active research in this field. Until now, many organic [28], inorganic [29,30] and even biological materials [31–34] have been used as template. In addition, template-sacrifice method has been employed to prepare some hollow microcapsules, for instance hollow ZnO nanospheres [35]. Compared to the other templates, natural biological materials provide a relative facile and economical route. By biological pollen as template, some metal oxide nanostructures with special morphologies have been prepared, such as highly crystalline SnO_2 motifs with porous and hollow structures [31], TiO_2 hollow spheres [32,36,37] etc. Besides, some hollow zeolite

materials also have been prepared in the presence of biological materials [32,34]. However, most of these template materials have to be pre-prepared before the templating process. Furthermore, some of the templates are to be selectively removed via chemical etching or thermal decomposition, along with potential problems on the product quality and process cost. In addition, even if the same templates are used, different strategies have to be developed to deposit the shell on the template to prepare different kinds of inorganic hollow microcapsules. Therefore, the synthesis strategy for hollow structure inorganic microcapsules still has some limitations on the universality and production of materials with hollow structure. A general, a universal and no-need-to-be-removed template method is expected to be developed to prepare various kinds of inorganic hollow microcapsules.

Synthesis of TiO_2 with different morphologies and unique physical texture is considered especially attractive due to efficient photocatalysis [36–38]. Our group has also developed a technique to prepared hollow TiO_2 microspheres by using pollen grain as template [32]. As introduced above, in that hydrothermal route, the hollow structure only can be obtained after removing the pollen template by calcination. Herein, after the development of the synthesis strategy, a one-step, simple and general method to prepare several oxides hollow microcapsules, zeolite microcapsules, titanates and sulfides hollow microcapsules is presented. All of hollow microcapsules can be prepared by just adding rapeseed pollen grains in the synthesis solutions, which have been used to

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synthesize these oxides, zeolites, titanates and sulfides as nano- or micro-sized particles by hydrothermal treatments. After synthesis, no further procedure is needed to remove the template. It has been demonstrated that this method can be successfully applied to synthesize a variety of inorganic hollow microcapsules. To the best of our knowledge, this is the first report of a general synthesis of inorganic hollow microcapsules.

2. Experimental

The rapeseed pollen template was purchased for using directly. No pre-preparation of the template is needed. All the chemicals in the experiments were of analytical grade and no further purification was done. Two common oxides, TiO_2 and ZnO , one commercially used ZSM-5 zeolite, BaTiO_3 and ZnS as the target materials were chose to confirm the feasibility of this general method for the synthesis of hollow microcapsules. The preparation was conducted by adding a certain amount of rapeseed pollen grains (generally, 3 wt% of the solution) in the regular synthesis solutions of the five kinds of materials. Afterward, the solutions were hydrothermally treated in autoclaves. Finally, all of the obtained powder was dried at 80 °C for 8 h. After trial and error, the following recipes were used for synthesis hollow microcapsules, the details were shown below.

2.1. Synthesis of TiO_2 and TiO_2 hollow microspheres

TiO_2 were prepared as follows: First, 4.8 g of titanous sulfate was dissolved into the 18 ml distilled water with vigorous stirring. After that, 2 ml fluosilicic acid was added into the beaker. The mixture was stirred for 2 h to ensure the intensive mixing. The resultant solution was transferred into the hermetic 100 ml Teflon-lined stainless steel chamber and 180 °C hydrothermal treated for 24 h. The preparation of TiO_2 microspheres was executed with the same procedures just with 0.3 g rapeseed pollen added. After the hydrothermal reaction, the resultant powder was washed and centrifuged with distilled water continuously.

2.2. Synthesis of ZnO and ZnO microspheres

In a typical process for the production of ZnO , 1 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 1 g NaOH and 1 g citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) were weighed respectively and mixed by 40 ml distilled water for 1 h. After the uniform mixing, this compound was transferred into a hermetic Teflon-lined stainless steel chamber with 100 ml volume and heated at 180 °C for 12 h. As a comparison, another hydrothermal system was executed in the meanwhile with the same reactive materials just with 0.8 g rapeseed pollen added. After the hydrothermal reaction, the resultant powder was washed and centrifuged with distilled water continuously.

2.3. Synthesis of ZSM-5 and ZSM-5 microspheres

A typical synthesis procedure involves the admixing of NaOH , NaAlO_2 and distilled water. Then, a certain amount of Ludox colloidal silica (HS-40, 40 wt% silica) was trickled into solutions drop by drop. The final molar composition of the synthesis mixture was $4.4\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:68\text{SiO}_2:845\text{H}_2\text{O}$. After the uniform mixing, the resultant gel was treated at 180 °C in the hermetic Teflon-lined stainless steel chamber with 100 ml volume for 96 h. As a comparison, another hydrothermal system was executed in the meanwhile with the same reactive materials just with 0.3 g rapeseed pollen added. At the end of the treatment, the solid product obtained was collected by filtration, washed with deionized water and dried.

2.4. Synthesis of BaTiO_3 and BaTiO_3 microspheres

First, tetrabutyl titanate (TBOT, 0.34 g) and barium hydroxide ($\text{Ba}(\text{OH})_2$, 0.387 g) were added into distilled water (20 ml) and the mixture was stirred for 2 h. Second, ammonium hydroxide was added to solution and aged for 2 h. BaTiO_3 was then synthesized by hydrothermal treatment at 180 °C for 72 h. The same procedure was carried out to prepare BaTiO_3 microspheres just with 0.6 g rapeseed pollen added. The final products were obtained after filtered and dried.

2.5. Synthesis of ZnS and ZnS microspheres

For typical synthesis, sodium thiosulfate (1.01 g) and zinc acetate (1.76 g) were mixed with deionized water (20 ml), forming settled solution at room temperature. Then, the obtained solution was transferred into Teflon-lined steel autoclaves for hydrothermal treatment at 180 °C for 16 h. For comparison, the ZnS microspheres were also synthesized following the above produces with 0.4 g rapeseed pollen added. The final products were filtered, washed with deionized water and dried.

2.6. Characterization

The morphology and microstructure of the obtained materials was observed by a scanning electron microscope (SEM, Hitachi S-4800) and a transmission electron microscope (TEM, JEL-200CX). X-ray diffraction (XRD) patterns collected on a Rigaku SmartLab powder diffractometer using a Ni-filtered $\text{Cu-K}\alpha$ radiation source at 40 kV and 40 mA. The Fourier transform infrared (FT-IR) spectra were obtained on a Nexus 870 FT-IR spectrometer. Samples mixed and ground with KBr in mass ratio of 1:10 were measured in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. N_2 adsorption-desorption isotherms measurements were performed at 77 K on a BELSORP-max instrument. The samples were all outgassed at 200 °C overnight before measurement. Thermogravimetric (TG, Netzsch STA 409)

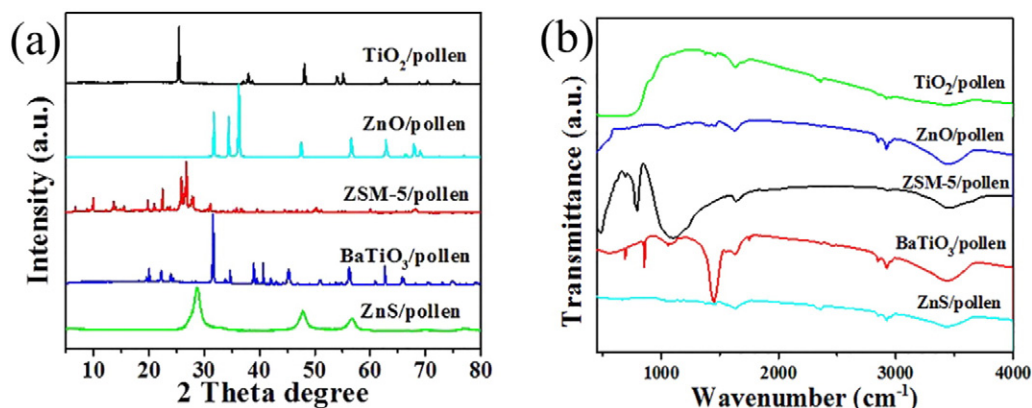


Fig. 1. (a) XRD patterns and (b) FTIR spectra of the products prepared by adding 3 wt% rapeseed pollen grains in the synthesis solutions of TiO_2 , ZnO , zeolite ZSM-5, ZnS and BaTiO_3 .

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