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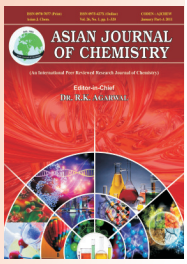

Hydrothermal Synthesis of Magnetic Microspheres Using Pollen Grains as Template†

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Magnetite (Fe_3O_4) microspheres were hydrothermal synthesized by using the rapeseed pollen grains as the template. The as-prepared Fe_3O_4 microspheres were characterized by scanning electron microscopy and X-ray diffraction spectrometer, at the same time its magnetism was verified by a simple observation method. The results indicated that the microspheres had not only the magnetic properties, but also have a hierarchical network surface morphology like the pollen grains. The selective permeation of the pollen wall and the rational designed hydrothermal condition were suggested to be the critical factors for the preparation of this microspheres.

Keywords: Magnetic microspheres, Biotemplate, Hydrothermal synthesis, Pollen grains.

INTRODUCTION

The magnetic microsphere has attracted a lot of attentions in recent years due to its broad range of applications especially in selective separation[1,2], controllable drug delivery system[3,4] and collectable catalyst carrier[5,6]. To improve the performance of the magnetic microspheres in these applications, the well-defined architectures such as hollow structure and porous surface morphology are needed. Despite various methods were developed for synthesis of the magnetic microspheres, the constitution of desired structure and surface morphology in the microspheres is still a challenge for researchers.

Biotemplate is a new concept for synthesis of the nano/micro materials with complex structures and morphologies, in which the biological tissues with the natural designed elaborate structure and morphology are applied as the template. Since its many advantages like easy operation, high efficiency and eco-friendly process, biotemplate method is applied in the preparation of a wild range of materials[7-9]. For the synthesis of microspheres pollen grains have been proved to be a superior template to the artificial ones, due to their homogeneous shape, uniformity in size and desired surface morphology. Several microspheres of different materials have been synthesized by using the pollen grains as template[10,11]. However, few researches on the preparation of the magnetic microspheres by using this biotemplate has been reported so far.

In this work, the rapeseed pollen grains were applied as a biotemplate for the hydrothermal synthesis of the magnetite (Fe_3O_4) microspheres. The iron adsorption of the pollen grains and the influence of the hydrothermal temperature on the microspheres were investigated. The magnetism of the microspheres was verified by a simple observation method. In this work, a possible formation process of the microspheres was proposed.

EXPERIMENTAL

For synthesis of the Fe_3O_4 microspheres, 0.05 mol $FeCl_2{\cdot}4H_2O$ and 0.1 mol $FeCl_3{\cdot}6H_2O$ were first dissolved in 50 mL deionized water. And then 5 mL of 5 M HCl was added into the above solution to avoid the precipitation of the other iron oxide before the hydrothermal process. When the iron salts were dissolved completely, 5 g rapeseed pollen grains were dropped into the solution under constant magnetic stirring. After 2 h, the pollen grains were filtered out and added into a Teflon-lined stainless steel autoclave with 80 mL strong aqueous ammonia. The autoclave was subsequently placed in a furnace for 2 h. To investigate the influence of temperature, the hydrothermal process were performed at 100, 150 and 200 ºC, respectively. After the hydrothermal reaction, the products were collected by pumping filtration and washed with deionized water and absolute ethanol for 3 times, respectively. Finally, all the products were dried in an oven at 50 ºC.

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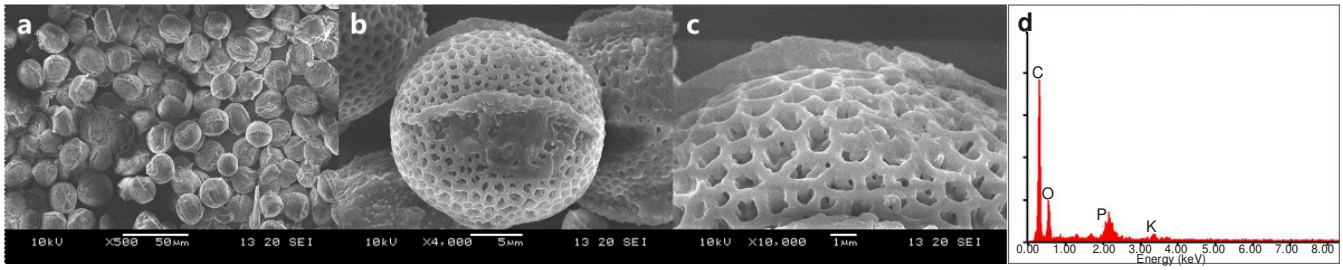

Fig. 1. SEM images (a, b, c) and EDS spectrum of the rapeseed pollen grains (d)

The structure and morphology of the rapeseed pollen grains were characterized by the electron scanning microscopy (SEM, JEOL, JSM-5900) equipped with an energy dispersive spectroscopy system (EDS, NORAN VANTAGE DSI). The structure of the as-prepared Fe_3O_4 microspheres were characterized by the field emission electron scanning microscopy (FESEM, Hitachi S4800). All samples were coated with a gold layer before the observation. The iron adsorption of the pollen grains was investigated by the inductively coupled plasma atomic emission spectrometry (ICP, PerkinElmer, Optima 2000). The crystal structure of the Fe_3O_4 microspheres were measured by an X-ray diffraction spectrometer (XRD, Rigaku, Ultima IV). The magnetism of the Fe_3O_4 microspheres were verified by a simple observational method.

RESULTS AND DISCUSSION

Structure of the rapeseed pollen grains: The typical shape of the rapeseed pollen grain is an ellipsoid of size of 18 mm × 20 mm with the reticular epidermis as the Fig. 1b shown. Under the low magnification image shown in Fig. 1a, it could be found that the rapeseed pollen grains have excellent uniformity in both shape and particle size. While under the high magnification image shown in Fig. 1c, it could be found that the reticular epidermis of the pollen grains is much more than a porous surface. The reticular surface is supported by perpendicular columellae and the entire epidermis of the rapeseed pollen grain is a hierarchical network. The EDS spectrum shown in Fig. 1d indicates the main elements in the pollen grains are carbon and oxygen which attribute to the organic component. And the trace phosphorus and potassium detected in the EDS spectrum may attribute to the inorganic salt which could maintain the biological function of the pollen grains.

Iron adsorption of the pollen grains: Fig. 2 shows the iron adsorption of the rapeseed pollen grains. It could be found that the concentration of iron ion in the iron salt solution decreased significantly when the pollen grains were immersed. In first 3 h a reducing about 25 ppm were detected and the final reduction is about 30 ppm in 12 h. This result suggests a rapid and significant adsorption for iron in the pollen grains. The pollen grain has the natural core/shell structure which is consisted of a tender core called protoplasm[12,13] and a tough shell called pollen wall[14]. This core/shell structure makes the pollen grains promising in template synthesis of the hollow microspheres. And the pollen wall also plays an important role in affecting the morphology of the as-prepared microspheres. In previous investigation[15], the selective permeability of the rapeseed pollen wall were proved and the iron ion was one of

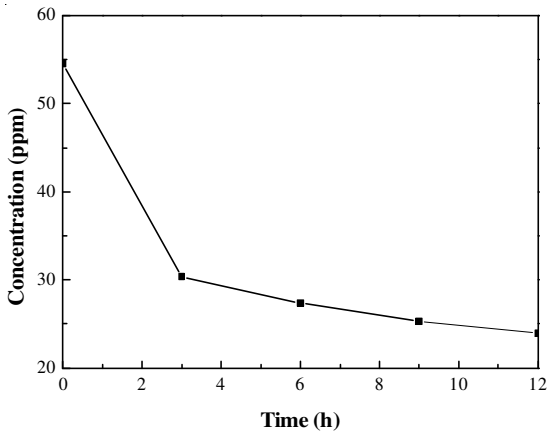

Fig. 2. Iron adsorption by the rapeseed pollen grains

the chemicals can penetrate the pollen wall. As shown in Fig. 3a, the pollen grain shows little change in shape and size after 2 h immersion in the mixture solution of the iron salt. The EDS spectrum of the surface of pollen wall shows only weak signals of iron and chlorine (Fig. 3b). While the EDS spectrum was taken from the protoplasm as the section shown in Fig. 3c, the signals of iron and chlorine were much stronger (Fig. 3d). This result indicates that iron ion were adsorbed on the protoplasm and the precipitation of the Fe_3O_4 would be deposited in the pollen grains.

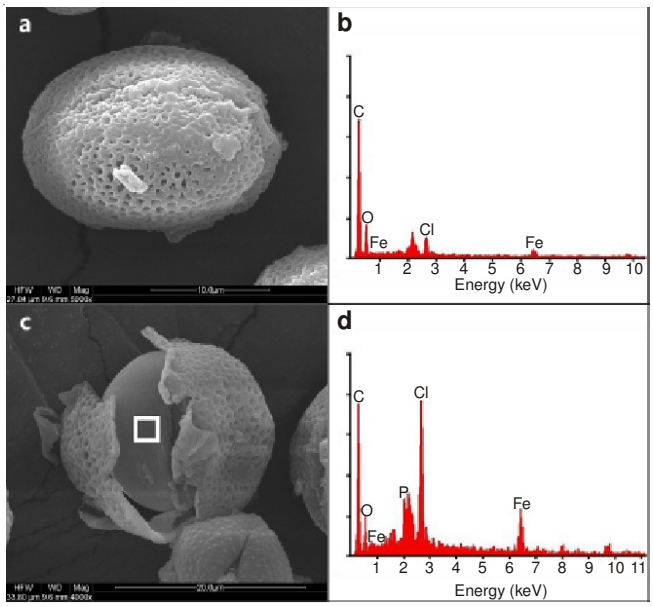

Fig. 3. SEM images and EDS spectra of the pollen wall (a, b,) and protoplasm (c, d,)

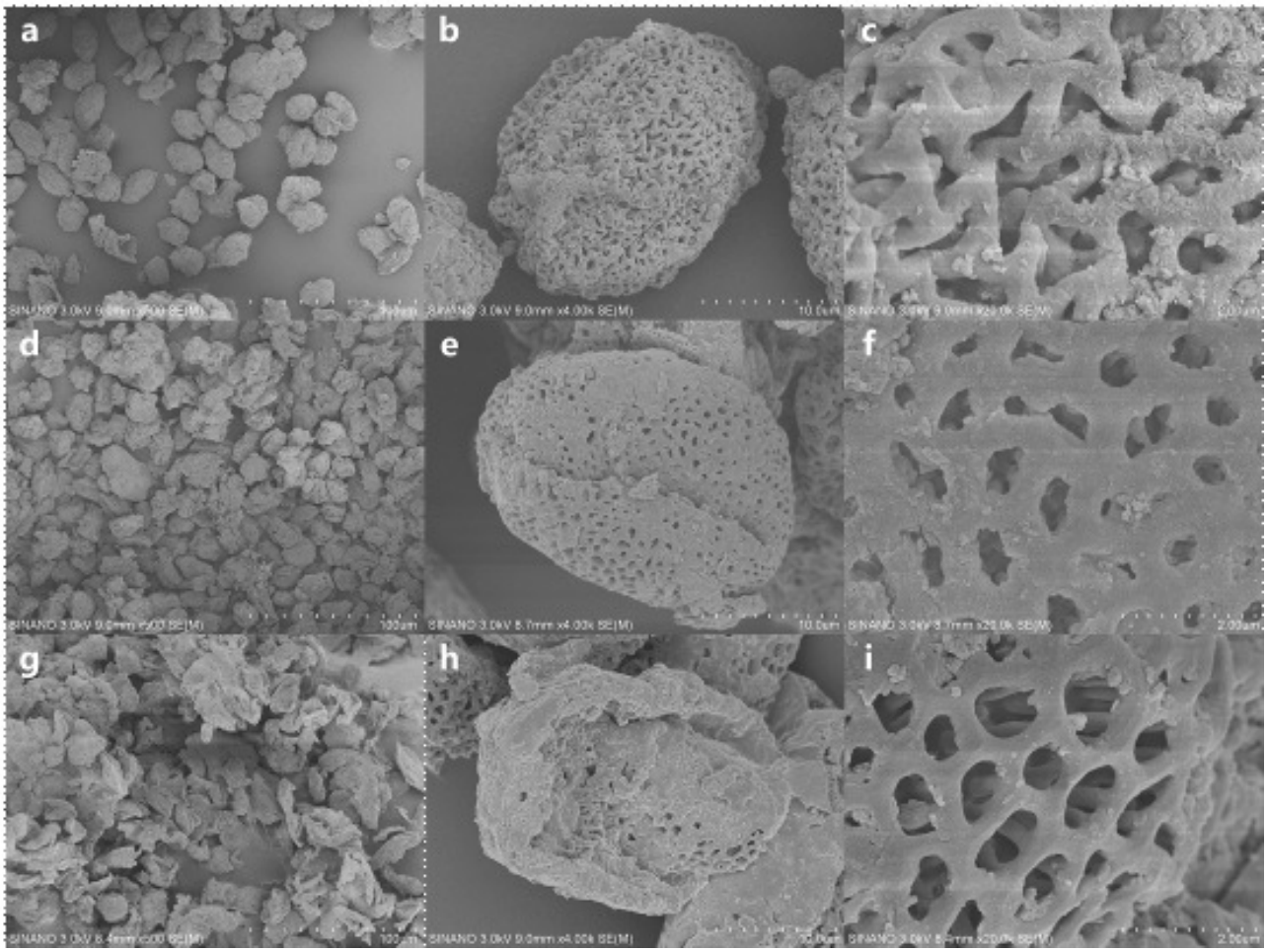

Fig. 4. SEM images of Fe_3O_4 microspheres prepared at different temperatures (a, b, c-100 ºC, d, e, f-150 ºC, g, h, i-200 ºC)

Characterization of the Fe_3O_4 microspheres: Fig. 4 shows the SEM images of the Fe_3O_4 microspheres prepared at different temperatures, from which the difference of the structure and morphology bewteen these samples could be found clearly. Through the low magnification images it could be found that the fragment and the aggregation in the microspheres were increased as the temperature increased. As shown in Fig. 4a, the monodispersion and uniformity of the pollen grains were kept in the microspheres prepared at 100 ºC and few fragment and aggregation were turned up. Whereas the microspheres prepared at 200 ºC shown in Fig. 4g were seriously broken, barely integrate microsphere could be found. Despite the pollen-like appearance were observed in both microspheres prepared at 100 and 150 ºC, some difference between these samples still could be identified. For the microspheres prepared at 100 ºC, a shrinkage in particle size (Fig. 4b) and a distortion in epidermis (Fig. 4c) were found. In contrast, the microspheres prepared at 150 ºC showed a more similar appearance to the pollen grains (Fig. 4e-f). It is worth noting that the porous epidermis without distortion could be found in the microspheres prepared at 200 ºC (Fig. 4i), although the most microspheres were collapsed and twisted (Fig. 4h).

The difference between the Fe_3O_4 microspheres prepared at different temperatures could also be found in the XRD characterization. Fig. 5 showed the XRD pattern of the microspheres prepared at 100 ºC exhibits only one weak characteristic peak

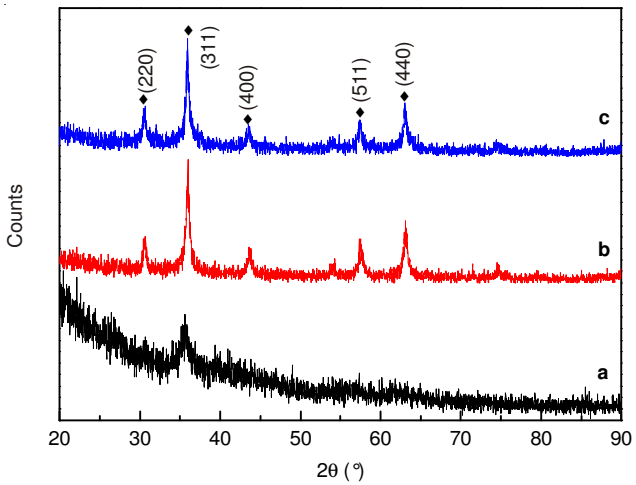

Fig. 5. XRD patterns of Fe_3O_4 microspheres prepared at different temperature (a-100 ºC, b-150 ºC, c-200 ºC)

which suggested a low crystallinity in this sample. In contrast the microspheres prepared at 150 and 200 ºC exhibit identical strong characteristic peaks in their XRD patterns. All recorded peaks could be assigned to the cubic Fe_3O_4 (JCPDS No. 75-449), which indicating no impurity crystal phase was contained in these samples. And the strong and narrow peaks suggest the Fe_3O_4 microspheres prepared at 150 and 200 ºC have a high crystallinity.

Considering the characterization of the Fe_3O_4 microspheres and the iron adsorption of the pollen grains a possible formation mechanism of the microspheres were proposed. Since both the iron ion and the OH^- could penetrate the pollen wall, the precipitation of the Fe_3O_4 would be deposite in the pollen grains to be a magnetic core. At the same time the porous pollen wall with the thermal stability was maintained as the epidermis of the microspheres. when the synthesis process was carried out at a relative low temperature like 100 ºC. The low production of the crystal provided the less support to the pollen wall and the shrinkage were turned up. Furthermore, the microspheres would be no magnetism since the low crystallinity. However, when the synthesis process was carried out at 200 ºC, partly decompostion of the pollen wall resulted in the broken of the microspheres.

To verifiy the magnetism of the as-prepared Fe_3O_4 microspheres, a simple observational method was applied. In berif, 1 g Fe_3O_4 microspheres prepared at 150 ºC were dispersed in deionized water by ultrasonication in a beaker. And then a magnet was placed nearby the beaker as the Fig. 6b shown. As a result, the microspheres could be separated to the beaker wall in 30 s and once the magnet was removed, they could be re-dispersed easily with a slight shake. The magnetic property and the porous surface make this microsphere promessing in various fields.

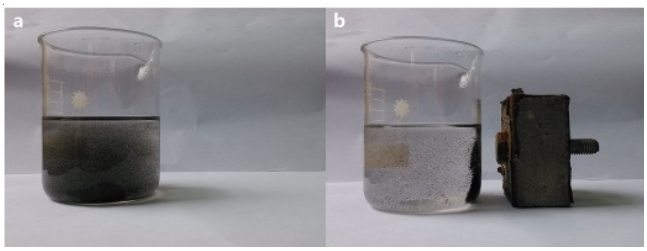

Fig. 6. Photographs for the magnetism verification of the Fe_3O_4 microspheres (a-dispersed microspheres, b-separated microspheres)

Conclusion

In this study, the Fe_3O_4 magnetic microspheres were synthesized through a hydrothermal process by using the rapeseed pollen grains as the template. The influence of the temperature on the microspheres was also investigated. As a result the microsphere prepared at a suitable temperature were proved to be magnetic, at the same time the hierarchical network morphology of the pollen wall was kept on its surface. The formation of this microsphere was attributed to the coaction of the selective permeation of the pollen wall and the suitable hydrothermal condition. This magnetic microsphere with the porous surface could be a good candidate for many applications such as catalyst carrier, biomacromolecule separation and controllable drug carrier.

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