doi:10.1246/cl.2010.451
Published on the web March 31, 2010

Single-hole Carbonaceous Microcapsules

Lei Wang,[1] Dezhi Ni,[2] Dan Yang,[1] Kebin Zhou,*[1] and Sen Yang*[2]
[1]*College of Chemistry and Chemical Engineering, Graduate University of the Chinese Academy of Sciences, Beijing 100049, P. R. China*
[2]*College of Resources and Environmental Sciences, China Agricultural University, Beijing 100193, P. R. China*

(Received February 15, 2010; CL-100161; E-mail: kbzhou@gucas.ac.cn, syang@cau.edu.cn)

Single-hole and spherical carbonaceous microcapsules were fabricated via controlling the carbonization, hydrolysis, and bulging force of yeast cells during hydrothermal processing. Moreover, magnetic nanoparticles could be easily coated onto these microstructures, endowing the obtained structures with multifunctionality.

Hollow microcapsules have stimulated great interests due to their promising applications in drug delivery, chemical sensors, enzymatic catalysis, as well as protection of biologically active components.[1] Among them, there is a special category with one large hole in the shell, which has been proposed to be ideal architectures as carriers of guest molecules (i.e., drugs, inks, and proteins) since the channel-like holes could offer target molecules an easier access to the hollow interiors of the microcapsules.[2] Up to now, some representative strategies have been developed to fabricate single-hole microcapsules.[3] Han and co-workers observed the formation of holes on the surfaces of poly(*o*-methoxyaniline) hollow spheres during oxidative polymerization of monomers.[4] Guan et al. used PS beads with surface carboxyl groups as templates and obtained core–shell structures with prepolymer layer.[5] When intensive polymerization/cross-linking reactions took place at a higher temperature, the volume shrinkage of the prepolymer shells resulted in the formation of holes in the shells. Notwithstanding these ingenious strategies, preparation of single-hole microcapsules with well-controlled size and shape is still a great challenge.

Recently, microorganisms have attracted extensive attention as templates to synthesize hollow microcapsules owing to their well-defined morphologies and uniform size distributions.[6] Herein, we report a facile approach to fabricate single-hole carbonaceous microcapsules via careful control of the synergic effects of carbonization, hydrolysis, and the bulging force during hydrothermal treatment of *S. cerevisiae* cells (a kind of yeast). Moreover, a series of magnetic nanoparticles (MFe_2O_4, M = Fe, Co, Mn, and Zn) could be coated onto these synthesized microcapsules which endowed them with magnetic properties.

The single-hole carbonaceous microcapsules were synthesized by hydrothermal treatment of yeast cells in diluted acid solutions. It is known that the yeast cell wall is constructed mainly by polysaccharide frameworks, i.e., glucans.[7] Under hydrothermal conditions, both hydrolysis and carbonization of glucans could take place. And at relatively high temperatures, carbonization could overwhelm hydrolysis, forming the final carbonaceous products.[8] Raman spectrum analysis was carried out to check the carbonization of the yeast cell after hydrothermal treatment.[9] Figure 1 shows the Raman spectrum of the hydrothermal products. The samples exhibit two broad bands at around 1345 (D-mode) (quite weak) and 1590 (G-mode) cm^{-1},

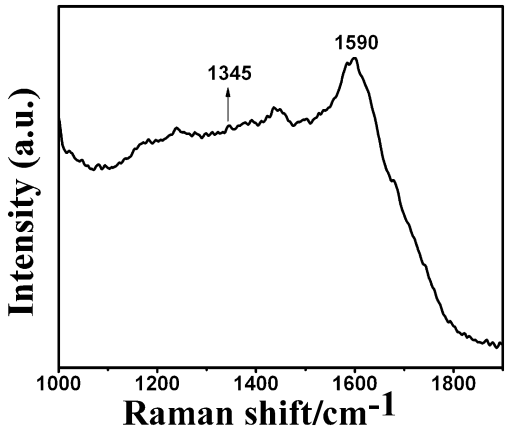


Figure 1. Raman spectrum of obtained carbonaceous products.

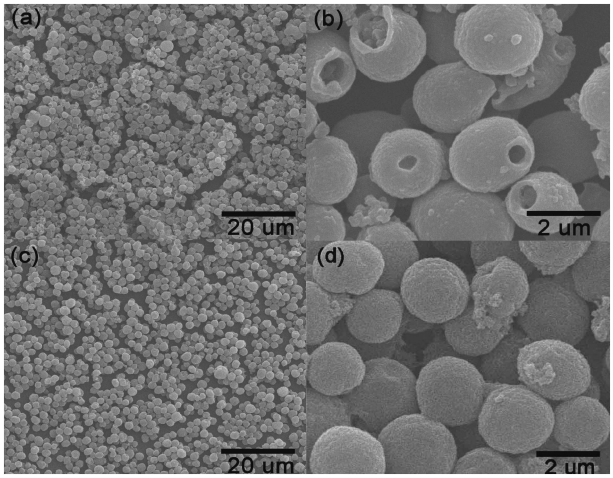


Figure 2. SEM images of carbonaceous (a, b) single-hole microcapsules and (c, d) integral hollow microspheres.

which reveal the presence of C sp^2 atoms in aromatic carbon species,[10] indicating the carbonization of glucan in the yeast cell wall.

Figures 2a and 2b give typical SEM images of the as-formed products. As can be seen from the images, all the microcapsules show nearly spherical shapes with the size in the range of 2.0–3.0 μm. Moreover, it is surprising to find a big hole about several hundred nanometers in diameter, which made the products jar-like and had clear ring-like brims in the shell of each microcapsule. We can also see the hollow cavities of the microcapsules via the opening holes.

To understand the formation of such an interesting structure, recalling the unique structure of the *S. cerevisiae* cell wall would be helpful. Actually, besides glucans, the yeast cell wall is also reinforced with chitin, a component whose content is in positive correlation with the stretching resistance of the cell wall.[7] However, there are some special positions in the *S. cerevisiae* cell wall, such as the base of a growing bud, that usually lacks chitin.[7] Therefore, the glucan network in these areas was supposed to be weaker under external forces. And it is imaginable that the cells, full of water, had to bear great bulging force, which was generated from the heterogeneity between extra and intracellular environments and the relatively enclosed interior space under the hydrothermal conditions. Owing to the bulging force, the buds bulged more sharply like inflating balloons. The overexpansion coupled with hydrolysis resulted in the burst of the bud at last and release the bulging pressure. Therefore, the bulging force, hydrolysis, and carbonization in the hydrothermal conditions, coupled with the lower stretching resistance of those special areas, finally led to the formation of the single-hole carbonaceous microcapsules.

Since the bulging force mainly comes from water expansion inside the cells, it would be weakened correspondingly if the bulging force inside the cells was reduced. It is well known that a large amount of protoplast is contained by the yeast cell wall and that water is the main component. Moreover, the amount of water in protoplast could be easily adjusted through the medium osmotic pressure.[11] If the osmotic pressure of the medium is higher than that of the protoplast, water will pass through the membranes from the cells to the extracellular fluid. Thus, sodium chloride solution was employed to adjust the medium osmotic pressure in the hydrothermal treatment processing. Figures 2c and 2d show images of as-obtained products, from which we can confirm that integral microspheres were obtained successfully. In fact, once sodium chloride was added to the dispersion of yeast, some of the water inside the cells would move out instantly due to the relatively high salt concentration outside. Consequently, the bulging force inside the cells would be weakened under the hydrothermal conditions. Hence, integral carbonaceous microspheres were obtained by hydrothermal treatment.

As mentioned above, water is the main component of protoplast, i.e., the intracellular fluid, of the yeast. And water inside the microspheres could be removed easily by postdrying process. Therefore, the obtained microspheres should have hollow cavities. The carbonaceous microspheres were further characterized with optical microscopy, and the result is shown in Figure 3. An inner void space contained within a shell structure can be observed, indicating hollow carbonaceous microspheres obtained.

Based on the above analysis, we believe it is the synergic effects of hydrolysis, carbonization, and the bulging force during the hydrothermal process that determined the morphology of final products. Through careful control over these forces, both single-hole microcapsules and integral microspheres could be attained. The formation mechanisms are illustrated in Scheme 1.

In order to endow the obtained materials with magnetic properties, Fe_3O_4 nanoparticles were loaded onto the products to form magnetic composites by similar hydrothermal treatment, and the obtained microstructures are given in Figure S1.[12] Obviously, the shapes and sizes did not change significantly after the coating procedure, and about 50–100 nm nanoparticles

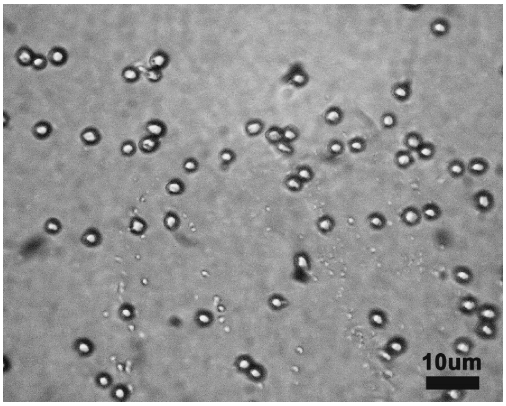
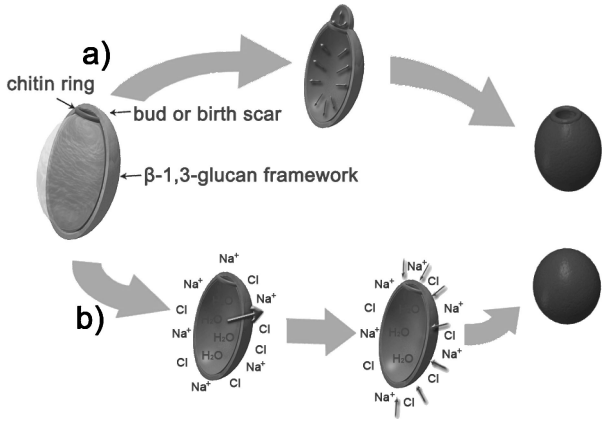


Figure 3. Optical microscopy photo of the hollow carbonaceous microspheres.



Scheme 1. Illustration of the formation of carbonaceous (a) single-hole microcapsules and (b) hollow microspheres from yeast cells.

were coated onto the surface of these hollow structures. X-ray diffraction (XRD) pattern of these obtained composites demonstrated that the nanopaticles were Fe_3O_4 (JCPDS 88-0315). Actually, a series of magnetic materials (MFe_2O_4, M = Co, Mn, and Zn, Figure S2)[12] could also be incorporated into the synthesized microstructures.

The magnetic properties of the obtained magnetic microstructures were investigated with a vibrating sample magnetometer. Figure 4 shows the magnetization curves measured at 300 K for all morphologies decorated with ferrite nanoparticles. The magnetic saturations are 3.623 emu g^{-1} for single-hole microcapsules and 3.546 emu g^{-1} for the microspheres. Upon applying a magnetic field, these microstructures were easily separated from other agents in solution (photos in Figure 4).

In summary, carboneaccous single-hole microcapsules and integral microspheres can be easily fabricated via control over the synergetic effects of hydrolysis, carbonization, and bulging force during hydrothermal treatment of *S. cerevisiae* cells. Through a similar hydrothermal step, a series of magnetic nanoparticles (MFe_2O_4, M = Fe, Co, Mn, and Zn) could be incorporated onto these synthesized microstructures. The obtained microstructures would hold paramount significance in applications such as catalysis, drug delivery, and separations sciences.

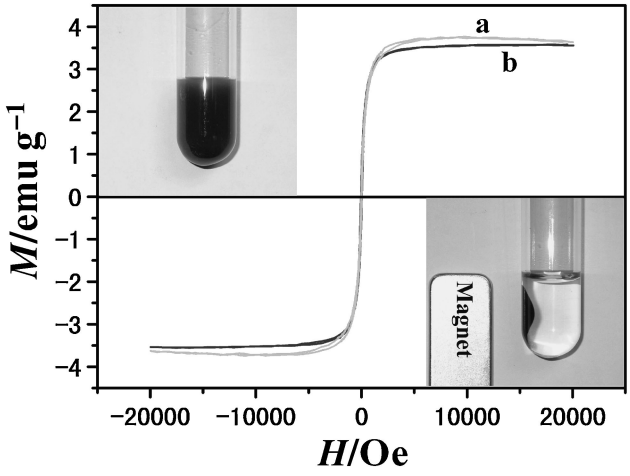


Figure 4. Room-temperature magnetization curves of as-synthesized hollow magnetic microstructures decorated with Fe_3O_4 nanoparticles: (a) single-hole microcapsules and (b) hollow microspheres. Photo images demonstrate the magnetic separation of these composites by an outer magnetic field: upper left is the hollow microcapsules dispersed in water, and the lower right is when a magnetic field gradient presents.

This work was supported by National Key Technologies R & D Program of China (No. 2006BAD07A01), National Science Foundation of China (Nos. 20703065, 20806089, and 20877097), and the Ministry of Science and Technology of China (863 Program No. 2008AA06Z324).

References and Notes

1 a) T. Levy, C. Déjugnat, G. B. Sukhorukov, *Adv. Funct. Mater.* **2008**, *18*, 1586. b) G. Sukhorukov, L. Dähne, J. Hartmann, E. Donath, H. Möhwald, *Adv. Mater.* **2000**, *12*, 112. c) L. Duan, Q. He, K. W. Wang, X. H. Yan, Y. Cui, H. Möhwald, J. B. Li, *Angew. Chem., Int. Ed.* **2007**, *46*, 6996.
2 S. H. Im, U. Y. Jeong, Y. N. Xia, *Nat. Mater.* **2005**, *4*, 671.
3 a) F. Caruso, *Chem.—Eur. J.* **2000**, *6*, 413. b) X. M. Sun, J. F. Liu, Y. D. Li, *Chem.—Eur. J.* **2006**, *12*, 2039. c) Y. T. Lim, J. K. Kim, Y.-W. Noh, M. Y. Cho, B. H. Chung, *Small* **2009**, *5*, 324.
4 J. Han, G. P. Song, R. Guo, *Chem. Mater.* **2007**, *19*, 973.
5 G. Guan, Z. Zhang, Z. Wang, B. Liu, D. Gao, C. Xie, *Adv. Mater.* **2007**, *19*, 2370.
6 a) T. Douglas, M. Young, *Nature* **1998**, *393*, 152. b) B. Wang, P. Liu, W. G. Jiang, H. H. Pan, X. R. Xu, R. K. Tang, *Angew. Chem., Int. Ed.* **2008**, *47*, 3560.
7 a) X.-Y. Liu, Q. Wang, S. W. Cui, H.-Z. Liu, *Food Hydrocolloids* **2008**, *22*, 239. b) J. A. Shaw, P. C. Mol, B. Bowers, S. J. Silverman, M. H. Valdivieso, A. Duran, E. Cabib, *J. Cell Biol.* **1991**, *114*, 111. c) G. Lesage, H. Bussey, *Microbiol. Mol. Biol. Rev.* **2006**, *70*, 317.
8 a) X. M. Sun, Y. D. Li, *Angew. Chem., Int. Ed.* **2004**, *43*, 597. b) T. Sakaki, M. Shibata, T. Miki, H. Hirosue, N. Hayashi, *Bioresour. Technol.* **1996**, *58*, 197. c) D. Z. Ni, L. Wang, Y. H. Sun, Z. R. Guan, S. Yang, K. B. Zhou, unpublished results. d) M. Sevilla, A. B. Fuertes, *Chem.—Eur. J.* **2009**, *15*, 4195. e) M. Sevilla, A. B. Fuertes, *Carbon* **2009**, *47*, 2281.
9 a) Q. Wang, H. Li, L. Q. Chen, X. J. Huang, *Carbon* **2001**, *39*, 2211. b) C. Sheng, *Fuel* **2007**, *86*, 2316. c) A. Cuesta, P. Dhamelincourt, J. Laureyns, A. Martínez-Alonso, J. M. D. Tascón, *Carbon* **1994**, *32*, 1523.
10 a) J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt, S. R. P. Silva, *J. Appl. Phys.* **1996**, *80*, 440. b) A. C. Ferrari, J. Robertson, *Phys. Rev. B* **2000**, *61*, 14095.
11 M. M. Alemohammad, C. J. Knowles, *J. Gen. Microbiol.* **1974**, *82*, 125.
12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

