Synthesis of Mesoporous Silica Submicrospheres with High Specific Surface Area via a Modified Octylamine Templating Process

XIANG-FENG WU*, CHANG-RUI WANG, AND YONG-KE ZHAO
School of Materials Science and Engineering, Shijiazhuang Tiedao University, Shijiazhuang 050043, China.
wuxiangfeng@stdu.edu.cn*

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Summary: Mesoporous silica submicrospheres with high specific surface area, 930.9m^2/g, were synthesized without using any acid or alkali as catalyst. Tetraethoxysilane as silica source, octylamine as template and polyoxyethylene (20) sorbitan monolaurate as emulsifier were adopted in this work. The as-prepared spheres were characterized with scanning electron microscopy, energy disperse spectroscopy, thermal gravimetric analysis, small angle X-ray diffraction and nitrogen adsorption, respectively. The results showed that octylamine vesicles were incorporated by silica shell in dilute sodium chloride solution, and the morphology and dispersity of submicrospheres were improved by using polyoxyethylene (20) sorbitan monolaurate. Moreover, the size of as-prepared products was gradually decreased as the amounts of polyoxyethylene (20) sorbitan monolaurate increased. In addition, the shell of the submicrospheres with narrowly distributed nanopores became more and more unordered with the prolonging of the calcinating time.

Keywords: Mesoporous silica submicrospheres; Octylamine; Tween 20.

Introduction

Mesoporous silica submicrospheres (MSS) has received much attention in recent years, because of their broad applications in the fields of catalysis, adsorption, chromatography, controlled release of drugs, hollow glass beads and so on [1-9]. MSS are dominantly produced via chemical routes, in which templates are usually used to form the hollows, and the most templates were solid particles (such as polymer spheres and inorganic particles) or soft entities (such as vesicles) [6-9]. In case of using soft templates, the advantages of this method are that the synthesis is simple and convenient [10-15]. Adapting tetraethoxysilane (TEOS) (as an inorganic framework source) and 1-alkylmine, particularly octylamine (OA) (as a soft template), to synthesize several tens of micro-meters in size of MSS under acidic or alkalic system is popular [16-22]. However, most products prepared with this method, especially under the reaction condition of highly stirring speed, had unsatisfactory morphology and particle size distribution [23, 24].

Polyoxyethylene (20) sorbitan monolaurate (Tween 20) is a water-soluble non-ionic surfactant with relatively low molecular weight. The hydrophile-lipophile-balance value of this surfactant is about 16.7 [25]. Moreover, it is broadly used to lower the interfacial tension at oil–water interface and used to generate monodispersed and nano-sized or submicro-sized droplets or particles [26-29].

Based on our previous report [5], we modified the octylamine templating method, used Tween 20 as the emulsifier, ultrasonics as the driving power and adopted sodium chloride (NaCl) to substitute acid or alkali as the catalyst. The experimental results showed that the as-prepared MSS with relatively high specific surface area and satisfactory dispersity were obtained.

Results and Discussion

SEM Analysis

The dimensions of particles formed without Tween 20 shown in Fig. 1a ranged between 1 and 15 μm. SEM image evidenced their strong aggregation. Moreover, there were some crushed spheres as shown by the black arrows, indicating that MSS were hollow structure. However, as the amount of Tween 20 increased from 0ml to 3.0ml, the average size of MSS was gradually decreased, and the morphology and the dispersity of as-prepared MSS were improved (Fig. 1b-e). However, when the amounts of Tween 20 increased to 4.0ml, there were some agglomerates with irregular shape which were composed of very small spheres.

*To whom all correspondence should be addressed.

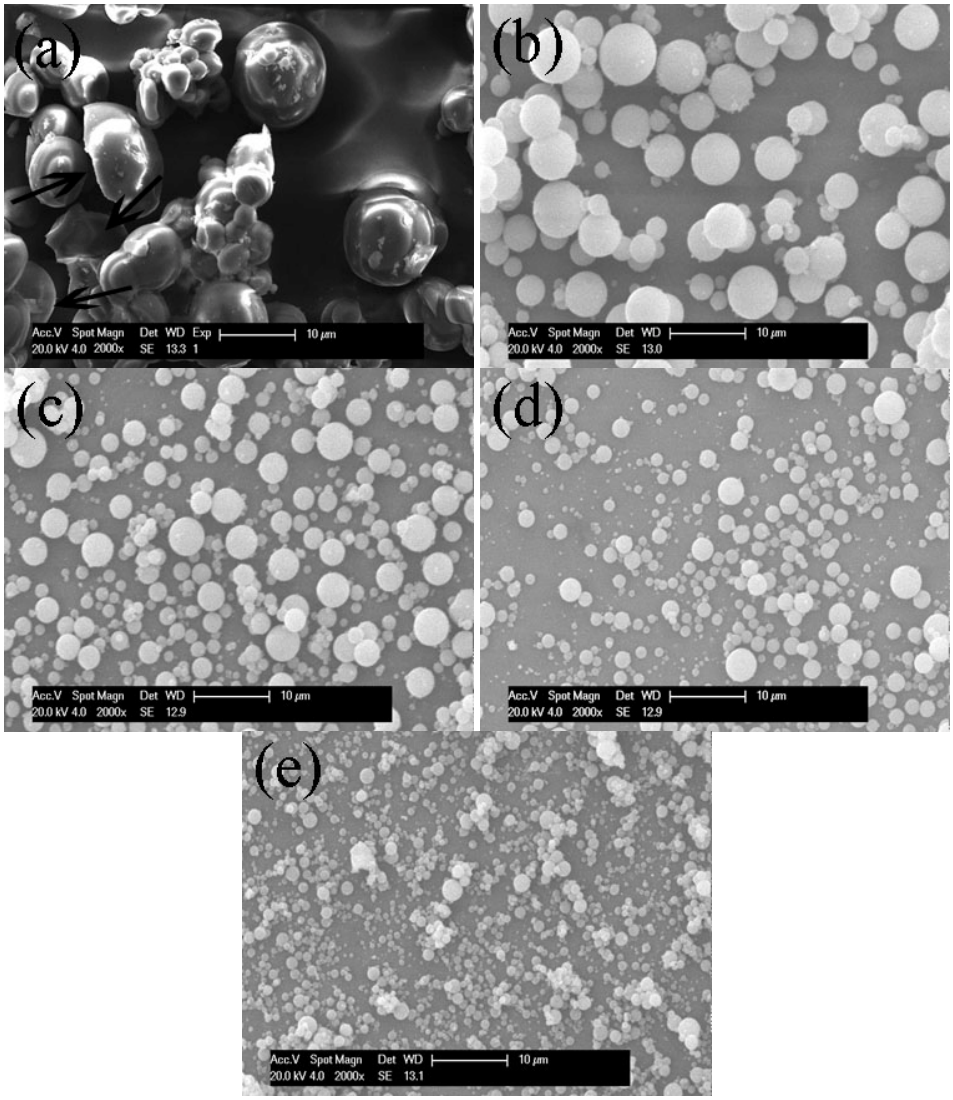

Fig.1 SEM images for MSS which were prepared with different volume of Tween 20, (a): 0ml, (b): 1.0ml, (c): 2.0ml, (d): 3.0ml, (e): 4.0ml.

The possible reasons about this phenomenon were that Tween 20 molecule contained one or several hydrophilic tails (arranged toward aqueous phase) and a hydrophobic head group (tended to go into the oil phase). These head group were very mobile and could rapidly cover the new oil–water interface during emulsion process [30]. Therefore, it was postulated that after the adding of dilute NaCl solution, the OA vesicles were rapidly formed under the stirring of the mixture of TEOS and OA [31, 32]. Moreover, the size of OA vesicles were firstly decreased by collaborative dispersal effects of ultrasonics and Tween 20 molecules. Subsequently, a fast hydrolysis and condensation of TEOS took place around OA vesicles, and the products were then formed, resulting in hollow organic-silica spheres without nanpores in the shell [19, 33]. Simultaneously, the hydrophobic head group of the Tween 20 molecules adsorbed on the surfaces of MSS, while the hydrophilic tails arranged toward aqueous phase. This result might contribute much to avoid the aggregation of the shells with each other during the reaction process [34]. However, if there were too much Tween 20 molecules, typically more than 3.0ml, the products were very small (because of the dispersal effect of Tween 20) to aggregate with each other due to the nanometer effects, and the surplus Tween 20 molecules would scatter in the solution. Finally, all organic matters would be removed by calcinations at high temperature, and MSS with nanoporous shell would be formed, as illustrated in Fig. 2.

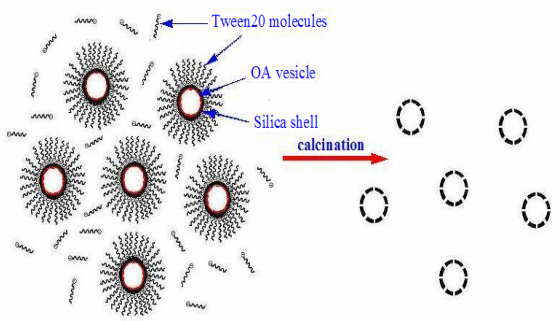

Fig. 2: The schematic illustration for the formation of MSS obtained by using Tween 20.

EDS Analysis

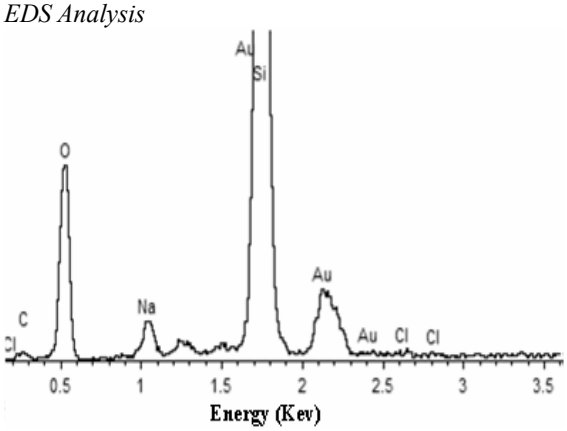

Fig. 3: EDS spectrum for MSS (the same sample as Fig. 1d)

TGA analysis

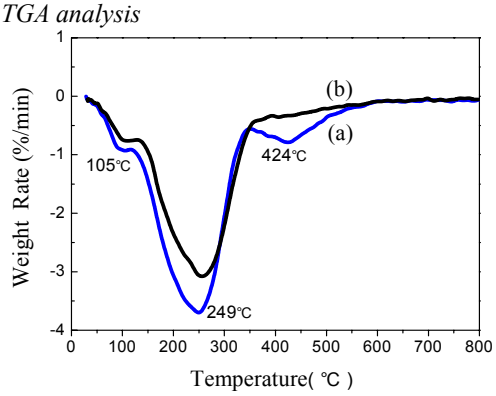

Fig. 4: TGA spectrums for uncalcined MSS which were prepared, (a): using Tween 20 (3.0ml), (b): without using Tween 20.

It can be seen in Fig. 4 that there was a small peak at 105℃, which was due to evaporation of the free water in the specimen, and a very strong peak at about 249℃, which was attributed to the decomposition of OA vesicles. Moreover, there is a peak at 424℃ only in Fig. 4a, which is assigned to Tween 20 in uncalcined samples. The possible reasons were that OA vesicles as the template were incorporated into MSS, while Tween 20 molecules absorbed on the surfaces of the products.

XRD Analysis

It shows that a sharp diffraction peak at 2.36 of 2θ degree in Fig. 5a. This result demonstrated that MSS calcined for 3h were the mesoporous materials [37], which were also in accord with the results of N_2 adsorption (Fig. 6), and the nanopores were randomly distributed in the shell [23]. However, MSS, calcined for 12h, exhibited a pattern with no diffraction peak (Fig. 5b), demonstrating that the nanopore structure in the shell of MSS become more long-range disorder.

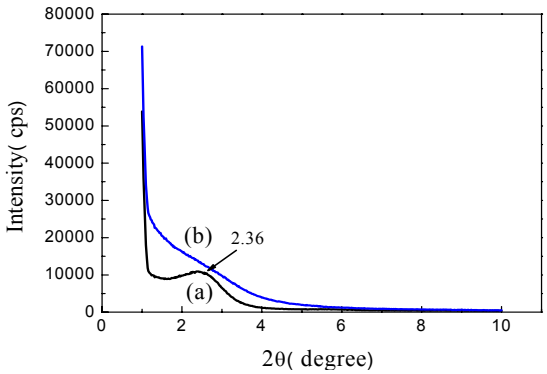

Fig. 5: SXRD spectrums for MSS calcined for different time, (a): 3h, (b): 12h.

The possible reasons about this change might be that the shell of MSS was densified as the prolonging of the calcinating time. The result was in agree with previous works that rising calcinating temperature could also densify the shell of MSS [5, 19], implying that rising temperature and prolonging time have similar effects on the nanopore structure in the shell of MSS.

N_2 Adsorption Analysis

In Fig. 6, it can be seen that a type of IV curve with hysteresis was observed, demonstrating that MSS were amorphous structure [38-40]. In addition, in Fig. 6 (inset), narrowly distributed nanopores width from 0.5-3.0nm, centered at about 1.35nm, was showed. Calculations show that MSS had high specific surface area of 930.9m^2/g and large pore volume of 0.7459 ml/g. This results means using this method could prepare MSS with relative high specific surface area.

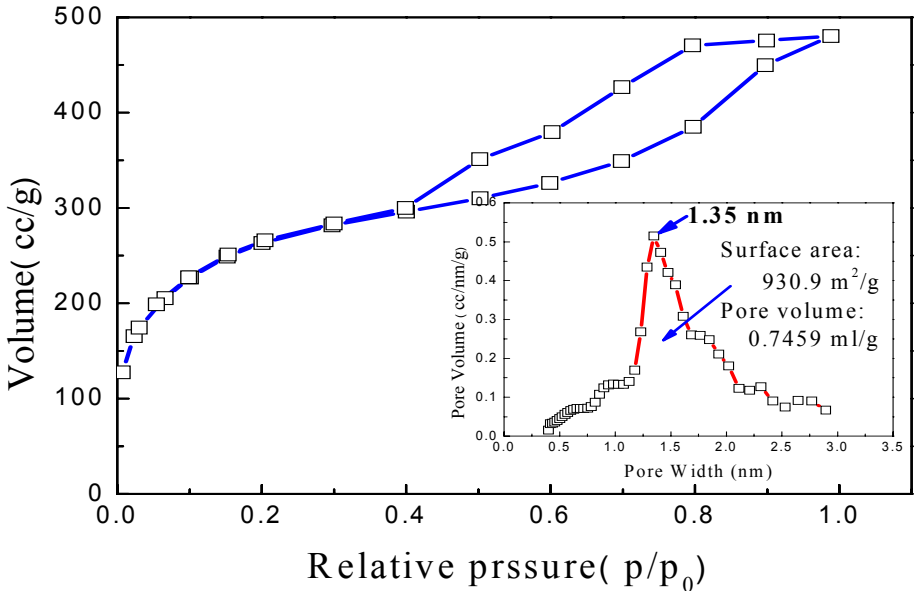

Fig. 6: N_2-adsorption/desorption isotherm and pore-size distribution (inset) for MSS which were prepared with 3.0ml Tween 20 and calcined for 3h.

Experimental

Materials

TEOS, OA and NaCl were purchased from Tianjin Chemical Corporation. Tween 20 was purchased from Beijing Chemical Corporation. All the materials were analytically pure.

Synthesis of MSS

MSS were synthesized by using TEOS, OA and Tween 20 in dilute NaCl solution. In a typical preparation, firstly, 4ml OA, 10ml TEOS and a given amount of Tween 20 were mixed in a 300ml beaker at ambient temperature. A mechanical stirrer was used and the stirring speed was kept at 1300r/min. Secondly, 0.2g NaCl was dissolved in 150ml distilled water, and rapidly poured into to the mentioned beaker. 5min later, the white products was formed. They were filtrated and repeatedly washed with ethanol to remove the impurity. Thirdly, the products were dried in a vacuum oven at 90℃ for 2h. Finally, the products were calcined in a muffle furnace at 600℃ for several hours to remove the organic substances.

Characterization

The morphology of the specimens was observed by environmental scanning electron microscopy (SEM, Model: Philips XL-30, Netherlands). The elemental composition was characterized by energy disperse spectroscopy (EDS, Model: EDAX Genesis, USA). The thermal behavior was studied by a thermal gravimetric analyzer (TGA, Model: Netzsch STA449C, Germany) at a heating rate of 20℃/min in nitrogen atmosphere. The structural identification was characterized by small-angle x-ray diffraction (SXRD, Model: Rigaku D/max 2500v, Japan). The specific surface area and pore size distribution were carried out by an automated gas sorption instrument at 77K (Model: Quantachrome NOVA 2000, USA).

Conclusions

It was presented a pathway for preparation of MSS with the specific surface area of 930.9m^2/g and large pore volume of 0.7459ml/g without using any acid or alkali as the catalyst. The experimental results showed that in the NaCl solution Tween 20 could improve the dispersity of MSS and lower the size of products. Moreover, the shell of MSS with narrowly distributed nanopores range from 0.5-3.0nm, centered at about 1.35nm, became more and more unordered with the prolonging of the calcinating time.

Acknowledgements

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References

1. K. Kosuge and P. S. Singh, *Microporous and Mesoporous Materials*, **44**, 139 (2001).
2. M. E. Davis, *Nature*, **417**, 813 (2002).
3. A. Stein, *Advanced Materials*, **15**, 763 (2003).
4. Y. Chen, Y. J. Wang, L. A. Yang and G. S. Lu, *Alche Journal*, **54**, 298 (2008).
5. X. F. Wu, H. R. Lu, Z. Q. Wang and X. H. Xu, *Journal of Sol-Gel Science Technolo*gy, **54**, 147 (2010).
6. M. Dams, L. Drijkoningen, B. Pauwels, T. G. Van, D. E. De Vos and P. A. Jacobs, *Journal of Catalysis*, **209**, 225 (2002).
7. Q. Y. Hu, J. B. Pang, N. Jiang, J. E. Hampsey and Y. F. Lu, *Microporous and Mesoporous Materials*, **81**, 149 (2005).
8. J. B. Pang, J. E. Hampsey, Z. W. Wu, Q. Y. Hu and Y. F. Lu, *Applied Physics Letters*, **85**, 4889 (2004).
9. S. Tanaka, F. Mizukami, S. Niwa, M. Toba, K. Maeda, H. Shimada and K. Kunimori, *Applied Catalysis* A-*General*, **229**, 165 (2002).
10. D. E. Lynch, Y. Nawaz and T. Bostrom, *Langmuir*, **21**, 6572 (2005).
11. K. P. Velikov and A. van Blaaderen, *Langmuir*, **17**, 4779 (2001).
12. C. Z. Yu, B. H. Tian, J. Fan, G. D. Stucky and D. Y. Zhao, *Chemistry Letters*, **31**, 62 (2002).
13. P. S. Singh and K. Kosuge, *Chemistry Letters*, **27**, 101 (1998).
14. K. J. C. Van Bommel, J. H. Jung and S. Shinkai, *Advanced Materials*, **13**, 1472 (2001).
15. A. Galarneau, J. Iapichella, K. Bonhomme, F. D. Renzo, P. Kooyman, O. Terasaki and F. Fajula, *Advanced Functional Materials*, **16**, 1657 (2003).
16. K. Kosuge, T. Murakami, N. Kikukawa and M. Takemori, *Chemistry of Materials*, **15**, 3184 (2003).
17. M. T. Bore, S. B. Rathod, T. L. Ward and A. K. Datye, *Langmuir*, **19**, 256 (2003).
18. N. Shimura and M. Ogawa, *Bulletin of the Chemical Society of Japan*, **78**, 1154 (2005).
19. X. Cheng, S. Q. Liu, L. C. Lu, X. Sui, V. Meynen, P. Cool, E. F. Vansant and J. Jiang, *Microporous and Mesoporous Materials*, **98**, 41 (2007).
20. L. Li, C. K. Tsung, T. Ming, Z. H. Sun, W. H. Ni, Q. H. Shi, G. D. Stucky and J. F. Wang, *Advanced Functional Materials*, **18**, 2956 (2008).
21. T. H. Zheng, J. B. Pang, G. Tan, J. He, G. L. McPherson, Y. Lu, V. T. John and J. Zhan, *Langmuir*, **23**, 9, 5143 (2007).
22. X. L. Ji, Q. Hu, J. E. Hampsey, X. Qiu, L. Gao, J. He and Y. Lu, *Chemistry of Materials*, **18**, 9, 2265 (2006).
23. S. Q. Liu, J. C. Rao, X. Y. Sui, P. Cool, F. E. Vansant, V. G. Tendeloo and X. Cheng, *Journal of Non-Crystalline Solids*, **354**, 826 (2008).
24. S. Q. Liu, M. Y. Wei, X. Y. Sui, X. Cheng, P. Cool and V. G. Tendeloo, *Journal of Sol-Gel Science Technolo*gy, **49**, 373 (2009).
25. J. V. L. Henry, P. J. Fryer, W. J. Frith and I. T. Norton, *Journal of Colloid and Interface Science*, **338**, 201 (2009).
26. S. Kerstens, B. S. Murray and E. Dickinson, *Journal of Colloid and Interface Science*, **296**, 1, 332 (2006).
27. I. T. Norton, F. Spyropoulos and P. W. Cox, *Food Hydrocolloids*, **23**, 1521 (2009).
28. L. Yobas, S. Martens, W. L. Ong and N. Ranganathan, *Lab on a Chip*, **6**, 1073 (2006).
29. G. T. Vladisavljević, I. Kobayashi and M. Nakajima, *Powder Technology*, **183**, 37 (2008).
30. S. M. Jafari, Y. H. He and B. Bhandari, *Eurpean Food Research Technology*, **225**, 733 (2007).
31. P. T. Tanev and T. J. Pinnavaia, *Science*, **271**, 1267 (1996).
32. L. X. Zhang, P. C. Li, X. H. Liu, L. W. Du and E. Wang, *Advanced Materials*, **19**, 4279 (2007).
33. J. Z. Du and Y. M. Chen, *Macromolecules*, **37**, 6322 (2004).
34. M. M. Wu, G. G. Wang, H. F. Xu, J. B. Long, F. L. Y. Shek, S. M. F. Lo, I. D. Williams, S. H. Feng and R. R. Xu, *Langmuir*, **19**, 4 (2003).
35. R. Ryoo and S. Jun, *the Journal of Physical Chemistry* C, **101**, 317 (1997).
36. K. Flodstrom, V. Alfredsson and N. Kallrot, *Journal of the American Chemical Society*, **125**, 4402 (2003).
37. S. A. Bagshaw, E. Prouzet and T. J. Pinnavaia, *Science*, **269**, 1242 (1995).
38. L. M. Yang, Y. J. Wang, Y. W. Sun, G. S. Luo and Y. Y. Dai, *Journal of Colloid and Interface Science*, **299**, 823 (2006).
39. X. L. Ji, Q. Y. Hu, J. E. Hampsey, X. P. Qiu, L. X. Gao, J. B. He and Y. F. Lu, *Chemsitry of Materials*, **18**, 2265 (2006).
40. P. S. Singh, *Journal of Colloid and Interface Science*, **325**, 207 (2008).