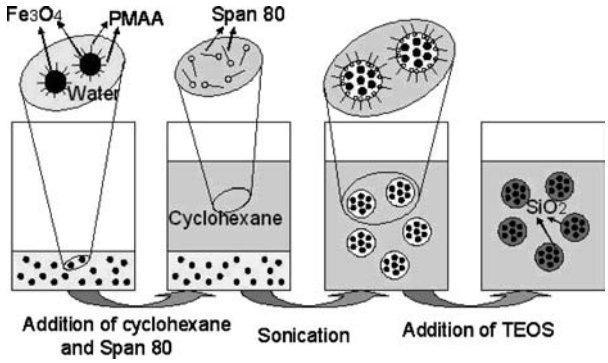
Synthesis of superparamagnetic Fe_3O_4/SiO_2 composite particles via sol-gel process based on inverse miniemulsion

Z. Z. XU, C. C. WANG*, W. L. YANG, S. K. FU
Department of Macromolecular Science and the Key Laboratory of Molecular Engineering of Polymers of Ministry of Education, Fudan University, Shanghai, 200433, People's Republic of China
E-mail: ccwang@fudan.edu.cn

Encapsulating magnetic nanoparticles in silica is a promising and important approach in the development of magnetic nanoparticles for technological and biomedical applications [1–6]. Two different approaches have been explored to generate silica coatings on the surfaces of iron oxides nanoparticles. The first method relied on the well-known Stöber process [7–9], in which silica was formed in situ through the hydrolysis and condensation of tetraethyl orthosilicate (TEOS). The composite particles produced by Stöber process usually contained one core consisted of one magnetic nanoparticle [7] or coagulate magnetic nanoparticles [8, 9]. The other method was based on microemulsion synthesis [10–15], in which inverse micelles or "droplets" were used to confine and control the coating of silica on magnetic nanoparticle cores. In this method, the number of magnetic nanoparticles (about 10 nm) contained in inverse micelles or "droplet" (usually less than 30 nm) of microemulsion were limited by their size. Therefore, these two methods were difficult to produce magnetic composite particles with sub-micron size. We have successfully synthesized magnetic polyacrylamide via inverse miniemulsion polymerization [16]. Now we extended this procedure to produce Fe_3O_4/SiO_2 composite particles with sub-micron size via an inverse miniemulsion method.

Synthesis of Fe_3O_4/SiO_2 composite particles is described in Scheme 1 and details of experiments were as follows: 3.0 g magnetic fluid (Fe_3O_4 content is about 3.0 wt%) was added to 31 ml 0.06 M Span 80 cyclohexane solution under stirring. After 1 h of stirring, the miniemulsion was prepared by ultrasonicating in a Cole-Parner sonifer CP600 and TEOS was added. The system was stirred for 48 h to ensure the complete hydrolysis of TEOS. The magnetic composite particles thus obtained was washed with cyclohexane three times and then with absolute ethanol five times under the help of magnet, and finally dried in a vacuum oven at 50 °C. TEM images were obtained on a Hitachi HU-11B transmission electron microscopy operating at 250 kV. Crystalline structures of the samples were determined by a rotating anode X-ray diffractometer (Rigaku, Japan) using Cu K_α radiation. For magnetic fluid, the sample was dried in a vacuum oven at 50 °C before characterization. A vibrating sample magnetometer (VSM, EG & G Princeton Applied Research Vibrating Sample Magnetometer, Model 155) was used to study the magnetic properties of the Fe_3O_4/SiO_2 composite particles at room temperature.



Scheme 1 The principle of the encapsulation of iron oxide nanoparticles by inverse miniemulsion approach.

Fe_3O_4/SiO_2 composite particles with different amount of TEOS were prepared. Fig. 1 shows the TEM images of the Fe_3O_4/SiO_2 composite particles. When the amount of TEOS is lower than 3.0 ml, individual nanosized Fe_3O_4 particles, which are shown as smaller and darker grains in Fig. 1a–c, can be clearly seen in the composite particles. These composite particles are crumbly and can form Fe_3O_4/SiO_2 nanosized composite particles by ultrasonic treatment. When the amount of TEOS increased to 3.0 ml, the submicrometer composite particles became strong, and the structure of these composite particles can kept perfect shape even under ultrasonic for 30 min in ethanol. Nanosized Fe_3O_4 particles are difficult to be obtained in the composite particles of Fig. 1d. When the external magnet field was applied, the composite particles were enriched quickly. This suggests the composite particles contain Fe_3O_4 nanoparticles. When the amount of TEOS increased to 7.0 ml, no stable composite particles were achieved. These results indicate that the amount of TEOS is very important in synthesis of Fe_3O_4/SiO_2 composite particles. In our experimental conditions, stable magnetic Fe_3O_4/SiO_2 composite particles can be achieved with 3.0 ml TEOS.

Typical X-ray diffraction patterns for the iron oxide nanoparticles before and after coating are shown in Fig. 2. As seen in Fig. 2a, Bragg reflections for the iron oxide nanoparticles have been indexed to a pure

* Author to whom all correspondence should be addressed.

0022-2461

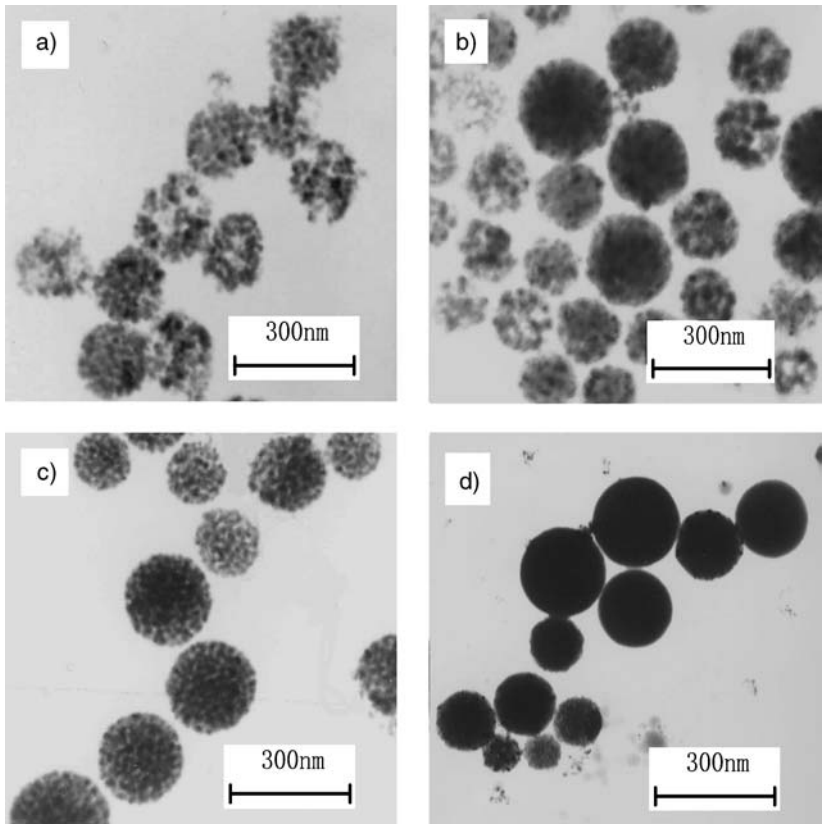


Figure 1 TEM images of Fe_3O_4/SiO_2 composite particles prepared with different amount of TEOS: (a) 0.5 ml , (b) 1.0 ml , (c) 2.0 ml and (d) 3.0 ml.

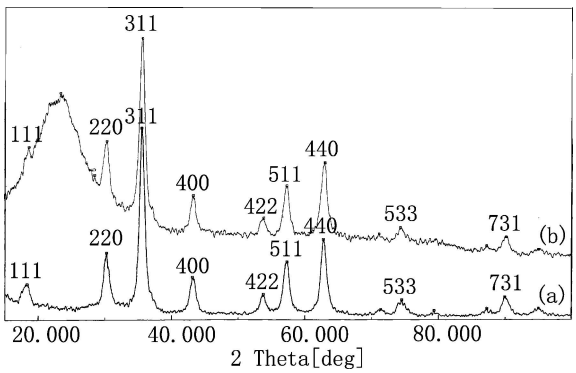


Figure 2 X-ray powder diffraction patterns of (a) Fe_3O_4 nanoparticles and (b) Fe_3O_4/SiO_2 composite particles.

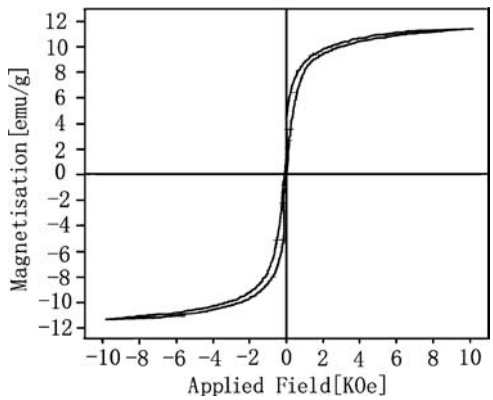


Figure 3 Magnetization vs. applied magnetic field for Fe_3O_4/SiO_2 composite particles at 300 K.

crystal phase of magnetite [16]. A broad band near $2\theta \sim 24^\circ$ was observed (Fig. 2b) when the iron oxide nanoparticles were coated with silica. The broad band demonstrates the existence of amorphous silica shell [17]. The X-ray diffraction pattern remains similar for both Fig. 2a and b, which indicated the crystallinity of the magnetic nanoparticulate core is retained after the coating's procedure.

The superparamagnetic property of magnetic composite particles is critical for their application in academic and biomedical applications, which prevents composite particles from aggregation and enables them to redisperse rapidly when the magnetic field is removed. Dried particles were characterized with a vibrating-sample magnetometer to check for superparamagnetic behavior. Fig. 3 shows the magnetization curve of Fe_3O_4/SiO_2 composite particles. Obvious superparamagnetic properties can be observed for the magnetic composite particles: no remanence was observed when the magnetic field is removed. The saturation magnetization obtains for sample d is 11.6 emu/g, and for pure magnetic particles is 68 emu/g [16]. Consequently, the magnetite concentration in composite particles is 19% (wt/wt). Moreover, the saturation magnetization after keeping the sample in air for about 6 months remained almost invariant (change of less than 5%), similar to the result reported in literature [7].

In conclusion, this paper reported a new synthesis route for preparing Fe_3O_4/SiO_2 composite particles via sol-gel process based on inverse miniemulsion. We have confirmed that the composite particles are superparamagnetic and each composite particle contains multi magnetic particles in the composite cores. Using this method, a variety of composite particles with

various metal and metal oxide nanoparticles could be synthesized.

Acknowledgments

This work was supported by National Science Foundation of China (Grant No. 20374012 and 50173005).

References

1. L. LEVY, Y. SAHOO, K. S. KIM, E. J. BERGEY and P. N. PRASAD, *Chem. Mater.* **14** (2002) 3715.
2. X. LIU, Z. MA, J. XING and H. LIR, *J. Magn. Magn. Mater.* **270** (2004) 1.
3. M. CHASTELLAIN, A. PETRI, A. GUPTA, K. V. RAO and H. HOFMANN, *Adv. Eng. Mater.* **6** (2004) 235.
4. X. ZHAO, R. TAPEC, K. WANG and W. TAN, *Anal. Chem.* **75** (2003) 3476.
5. J. I. TAYLOR, C. D. HURST, M. J. DAVIES, N. SACHSINGER, and I. J. BRUCE, *J. Chromatogr. A.* **890** (2000) 159.
6. Y. S. KIM, K. NAKATSUKA, T. FUJITA and T. ATARASHI, *J. Magn. Magn. Mater.* **201** (1999) 361.
7. Y. LU, Y. YIN, B. MAYERS and Y. XIA, *Nano Lett.* **2** (2002) 183.
8. Y. DENG, W. YANG, C. WANG and S. FU, *Adv. Mater.* **15** (2003) 1729.
9. Q. LIU, Z. XU, J. A. FINCH and R. EGERTON, *Chem. Mater.* **10** (1998) 3936.
10. S. SANTRA, R. TAPEC, N. THEODOROPOULOU, J. DOBSON, A. HEBARD and W. TAN, *Langmuir*, **17** (2001) 2900.
11. P. TARTAJ and C. J. SERNA, *Chem. Mater.* **14** (2002) 4396.
12. D. HOLZINGER and G. KICKELBICK, *ibid.* **15** (2003) 4944.
13. J. XU, S. THOMOMPSON, E. O'KEEFE and C. C. PERRY, *Mater. Lett.* **58** (2004) 1696.
14. P. TARTAJ and C. J. SERNA, *J. Am. Chem. Soc.* **125** (2003) 15754.
15. C. R. VESTAL and Z. J. ZHANG, *Nano Lett.* **3** (2003) 1739.
16. Z. XU, C. WANG, W. YANG, Y. DENG and S. FU, *J. Magn. Magn. Mater.* **277** (2004) 361.
17. X. HUANG and Z. CHEN, *ibid.* **280** (2004) 37.

Received 8 February
and accepted 10 February 2005