

# Synthesis and characterization of superparamagnetic composite nanorings

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## Abstract

Superparamagnetic nanorings of polystyrene/Fe<sub>3</sub>O<sub>4</sub> composite were synthesized by miniemulsion polymerization. The nanoring structure was characterized by using transmission electron microscopy, scanning electron microscopy, and atomic force microscopy. The results of X-ray diffraction identified the magnetic constituent of as-synthesized composite nanorings as Fe<sub>3</sub>O<sub>4</sub>. The magnetization measurement showed typical superparamagnetic characteristics of polystyrene/Fe<sub>3</sub>O<sub>4</sub> nanorings.

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## 1. Introduction

There is an increasing need to develop new nanostructures with unique properties for both fundamental study and novel engineering applications [1]. In current research of nanotechnology, various methods are being explored for the development of nanoengineered materials utilizing special nanostructures. In particular, the research activities have mainly focused on the self-assembly of nanosize molecular and colloidal building blocks to develop various functional devices [2]. Nanoparticles or hollow nanoparticles [3–5], wires or belt [6] and rings [7] can be synthesized as building blocks for one-, two- or three-dimensional electronic and optical units. Among these building blocks, nano-hollow spheres and nanorings are of particular interest because of their novel geometry and potential practical value. Caruso et al. [8] reported the layer-by-layer assembly procedure that produces hollow polymer/silica composite nanoparticles. Sano et al. [9] developed carbon nanotube nanorings by end-group reactions of short wormlike nanotubes chain. Kong et al. [10] successfully prepared a

freestanding, single-crystal zinc oxide nanoring by spontaneous self-coiling process during the growth of polar nanobelts. As a promising construction material, DNA has already been used to form supermolecular DNA circles recently, which are useful building blocks in biomedical applications [11]. So far, lithography method is the only viable method to generate fine array of rings on the surface of solid substrate, with a necessary uniform inner template. Winzer et al. [12] applied nanosphere lithography method to fabricate arrays of mesoscopic gold rings for the first time and predicted its potential application for persistent current experiment. McLellan et al. [13] obtained uniform mesoscopic gold and silver rings by edge spreading lithography method, which appeared as excellent arrays of rings in scanning electron microscopy. Recently, in order to develop a well organized self-assembly structure of nanocluster and nanorings, block copolymer has been a promising alternative as orderly framework in various architectures. Euliss et al. [14] reported that monodisperse superparamagnetic maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) was combined with the block copolyptide poly (EG<sub>2</sub>-lys)<sub>100</sub>-b-poly (asp)<sub>30</sub> to form uniform magnetic clusters. In the same way, Lecommandoux et al. [15] elucidated that magnetic nanocomposite micelles and vesicles were formed by means of PB-b-PGA block copolymer.

In this letter, we report a novel facile miniemulsion polymerization method to directly synthesize peculiar Fe<sub>3</sub>O<sub>4</sub>/polystyrene (PS) superparamagnetic nanorings. We discuss the

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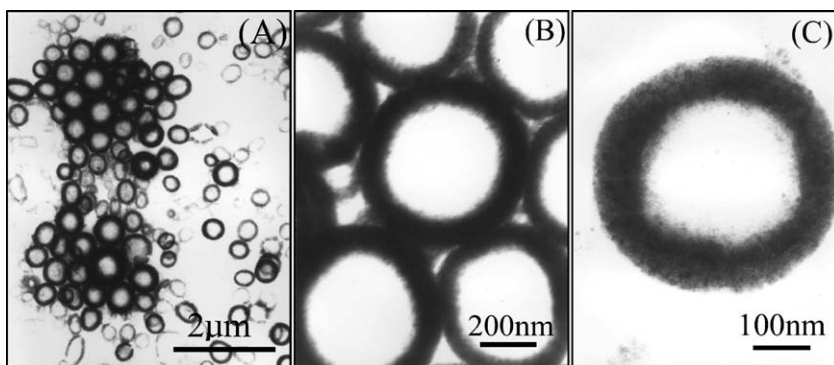


Fig. 1. TEM photographs of superparamagnetic composite nanorings.

formation mechanism of the magnetic composite nanorings during miniemulsion polymerization.

## 2. Experimental

### 2.1. Preparation of superparamagnetic composite nanorings

The composite nanorings were synthesized by polymerization involving two miniemulsion systems (A, B). A typical experiment was described as follows:

Miniemulsion (A) was prepared by 2.02 g magnetic fluid (oleic acid coated  $\text{Fe}_3\text{O}_4$  dispersed in octane with 75% magnetic content [16]) and 0.42 g hydrophobic reagent hexadecane mixed in surfactant solution consisting of sodium dodecyl sulfate (SDS: 0.45 g) and distilled water (48 g). The above mixture was stirred for 1 h at 400 rpm, and then adding 20 mg potassium peroxydisulfate (KPS) followed by ultrasonic agitation for 10 min in an ice-cooled bath. Miniemulsion (B) consisting of 4 g styrene, 0.14 g hexadecane, 0.12 g SDS, and 16 g distilled water was prepared by magnetic stirring at ambient temperature for 1 h. Miniemulsions (A) and (B) were mixed in three-neck flask and stirred at 400 rpm for 1 h, then ultrasonically agitated for

5–10 min in ice-water bath. The three-neck flask was removed from ice-water bath to room temperature, finally immersed in water bath at 80 °C. In this case, polymerization reaction was carried out for 17 h to obtain the brown reactive latex, which was bottled for characterization.

### 2.2. Characterization

#### 2.2.1. Size and morphology of magnetic composite nanorings

The morphology and size of as-synthesized magnetic composite nanorings were observed by transmission electron microscopy (a Philips CM 120 keV TEM), scanning electron microscopy (Philips Sirion 200 SEM) and a model AJ-III atomic force microscope (AFM). Preparation of the samples for TEM was straightforward. The distilled reactive latex was dropped into a carbon-coated copper grid and left to dry. For the measurement of SEM, a drop of magnetic nanoring dispersion was spread on the silicon surface and dried in a dust-free environment at room temperature. The dried sample was then sputtered under vacuum with a thin layer of gold before viewing under SEM. With regard to AFM sample, the reactive latex should be distilled and was placed into mica

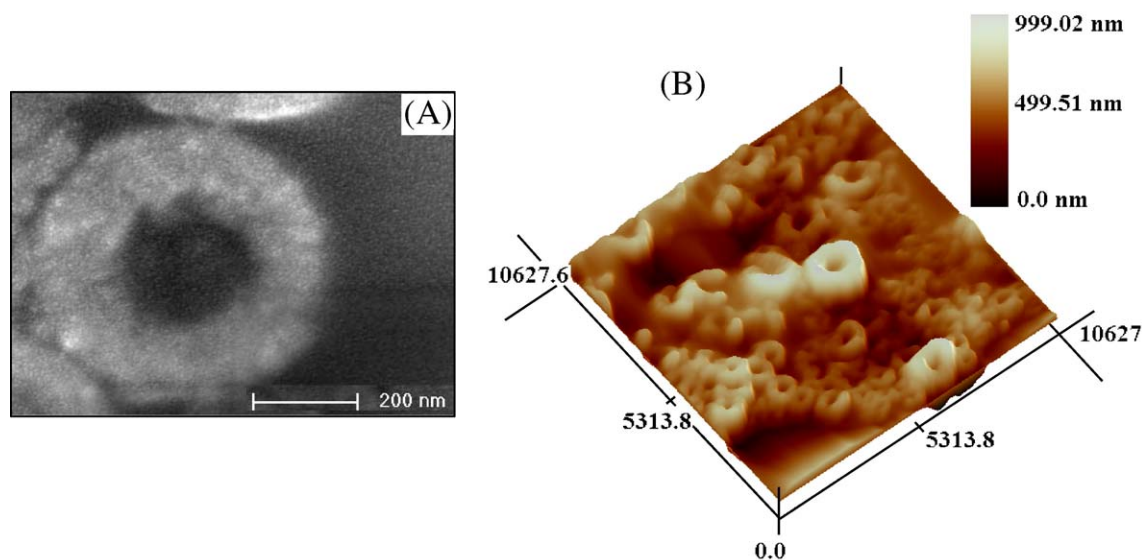


Fig. 2. (A) SEM photographs of superparamagnetic composite nanorings. (B) 3D view built from AFM picture of superparamagnetic composite nanorings.

slice to form monolayer array of as-synthesized magnetic nanorings.

### 2.2.2. X-ray diffraction analysis

The crystallographic results were acquired from a rotating anode X-ray diffractometer (BRUKER D8 ADVANCE) using Cu K $\alpha$  radiation ( $\lambda=1.540598$  Å). Samples for XRD measurements were solid powder prepared using the following operation. The reactive latex was washed several times with ethanol by magnetic separation to remove excess surfactants, and then the purified product was dried under vacuum.

### 2.2.3. Magnetic properties measurement

Magnetization curves were obtained by using a Quantum Design Physical Property Measurement System (PPMS) at 300 K temperature. The sample was prepared by encapsulating the brown reactive latex with known magnetic content into a cylinder plastic capsule.

## 3. Results and discussion

The TEM images of nanorings are shown in Fig. 1(A)–(C). As can be seen in this figure, the as-synthesized composites exhibit nanoring structure with a diameter of about 500 nm. The wall thickness is on the order of 100 nm. The images of the sample observed from both SEM (Fig. 2(A)) and AFM (Fig. 2(B)) give a three-dimensional view of nanoring structure, which is consistent with the TEM observation. However, the inner diameter of the ring, observed in AFM, appears to be slightly larger compared to that seen in the TEM and SEM. This may result from the different operating environment in these three characterization methods. TEM and SEM were carried out under vacuum, while AFM was performed at atmospheric pressure.

Fig. 3 shows XRD results of magnetic composite nanorings and the location of expected, indexed Bragg reflections of face-centered cubic Fe<sub>3</sub>O<sub>4</sub> crystal (marked with solid lines). It is found from the pattern that the magnetic composite nanorings have the typical Fe<sub>3</sub>O<sub>4</sub> crystal diffraction peaks, which can be well indexed with the standard X-ray diffraction pattern. The corresponding diffraction peaks reflect the (220), (311), (400), (422), (511), and (440) planes of the face-centered cubic structure of Fe<sub>3</sub>O<sub>4</sub> powder according to

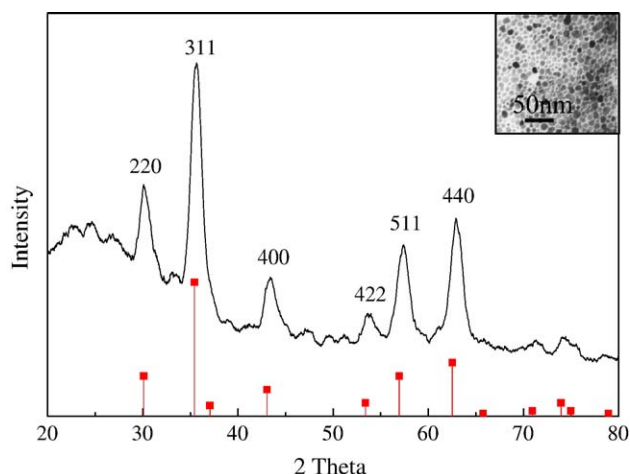


Fig. 3. X-ray diffraction pattern of the magnetic nanorings.

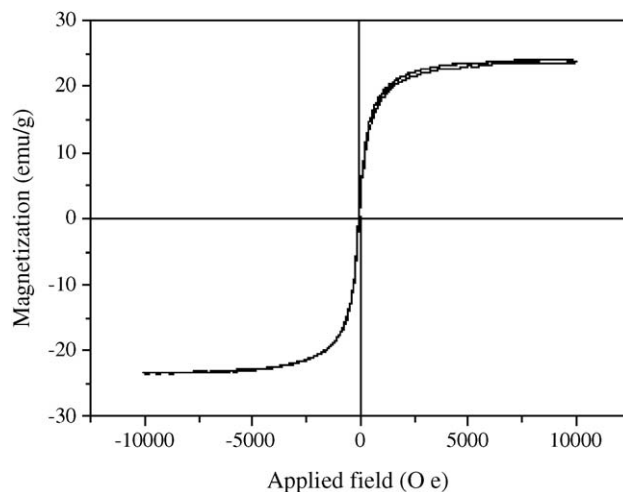


Fig. 4. Magnetization vs. applied magnetic field for magnetic nanorings at 298 K.

the standard Fe<sub>3</sub>O<sub>4</sub> XRD data card. This result indicates that Fe<sub>3</sub>O<sub>4</sub> is the major magnetic component in the composite with polystyrene. The crystallite size is calculated to be 11.6 nm using the Scherrer's formula, and the averaged crystallite size is in good agreement with mean diameter in the range of 7–12 nm, determined from TEM imaging (see inset of Fig. 3).

Fig. 4 shows the typical magnetization curves of the magnetic composite nanorings by the PPMS magnetometry measurements. The saturation magnetization of composite nanorings is 23.46 emu/g. There appears a reversible hysteresis curve and both remanence and coercivity are zero, suggesting that these nanorings are superparamagnetic at ambient temperature.

The previous studies have mainly focused on the formation mechanism of composite microsphere prepared by miniemulsion

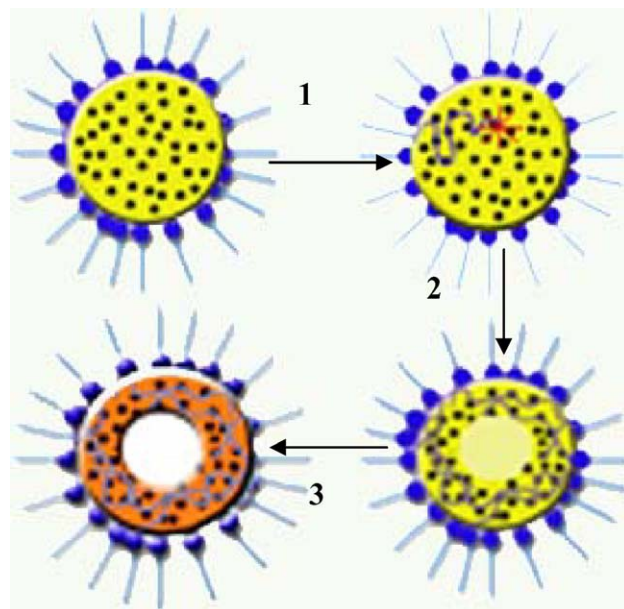


Fig. 5. Schematic illustration of miniemulsion polymerization process to form superparamagnetic nanorings: (1) initiating stage; (2) as polystyrene chain length increases, microphase separation occurs and hexadecane is at the center of the vesicle; (3) because vaporizing of octane gives the hole, polystyrene shell coil forms a swimming-like composite rings.

polymerization [17–19]. As for nanorings, however, we propose a different formation mechanism based on the experimental observations in this study. In the original stage of polymerization, styrene monomer is initiating in water phase of the system. The short polystyrene oligomer chain enters the inner-interface of miniemulsion droplet. Inside the droplets, microphase separation will occur as the polystyrene chain length increases. Polystyrene departs from the mixture of *n*-octane and hexadecane. Meanwhile, Fe<sub>3</sub>O<sub>4</sub> nanoparticles, attached with polystyrene, are moved outward. In this situation, polystyrene vesicles are formed with the shell of Fe<sub>3</sub>O<sub>4</sub> nanoparticles embedded inside the polystyrene. At the temperature of 80 °C, octane is evaporated slowly from the center of miniemulsion colloid inducing double opening oppositely in the thin magnetic composite shell, thus a new interface of composite shell and hexadecane with high energy is exposed. In order to reduce the newly formed interface energy, the shell film coil develops from two openings, leading to ring formation. This polymerization process can last about 17 h. A schematic illustration of the magnetic nanoring formation during miniemulsion polymerization process is shown in Fig. 5.

#### 4. Conclusion

In summary, we have developed a simple approach to obtain magnetic composite nanorings of polystyrene/Fe<sub>3</sub>O<sub>4</sub>. The as-synthesized nanoring structure is an ideal elementary building block in nanoscale architecture technology. Compared to other literature that reported method for synthesizing nanorings, the reactive self-assemble procedure employed in this study is a unique approach, which will not only simplify the steps of forming hybrid nanorings but also control the component ratio of composite nanorings. Further study on the synthesis mechanisms and physical property characterization is under way.

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#### References

- [1] M.C. Roco, *Am. Inst. Chem. Eng.* 50 (2004) 890.
- [2] C.M. Niemeyer, *Angew. Chem., Int. Ed. Engl.* 40 (2001) 4128.
- [3] M.S. Wong, J.N. Cha, K.S. Choi, T.J. Deming, G.D. Stucky, *Nano Lett.* 2 (2002) 583.
- [4] Z.F. Dai, H. M $\ddot{O}$ hwald, *Langmuir* 18 (2002) 9533.
- [5] M. Okubo, H. Minami, T. Komura, *J. Appl. Polym. Sci.* 88 (2003) 428.
- [6] Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* 291 (2001) 1947.
- [7] V.S. Murthy, J.N. Cha, G.D. Stucky, M.S. Wong, *J. Am. Chem. Soc.* 126 (2004) 5292.
- [8] F. Caruso, R.A. Caruso, H. M $\ddot{O}$ hwald, *Science* 282 (1998) 1111.
- [9] M. Sano, A. Kamino, J. Okamura, S. Shinkai, *Science* 293 (2001) 1299.
- [10] X.Y. Kong, Y. Ding, R. Yang, Z.L. Wang, *Science* 303 (2004) 1348.
- [11] C.M. Niemeyer, M. Adler, S. Gao, L. Chi, *Angew. Chem., Int. Ed. Engl.* 39 (2000) 3055.
- [12] M. Winzer, M. Kleiber, N. Dix, R. Wiesendanger, *Appl. Phys., A Mater. Sci. Process.* 63 (1996) 617.
- [13] J.M. McLellan, M. Geissler, Y.N. Xia, *J. Am. Chem. Soc.* 126 (2004) 10830.
- [14] L.E. Euliss, S.G. Grancharov, S. O'Brien, T.J. Deming, G.D. Stucky, C.B. Murray, G.A. Held, *Nano Lett.* 3 (2003) 1489.
- [15] S. Lecommandoux, O. Sandre, F. Chécot, J. Rdriguez-Hernandez, R. Perzynski, *Adv. Mater.* 17 (2005) 712.
- [16] L.P. Ramirez, K. Landfester, *Macromol. Chem. Phys.* 204 (2003) 22.
- [17] M. Antonietti, K. Landfester, *Prog. Polym. Sci.* 27 (2002) 689.
- [18] F. Tiarks, K. Landfester, M. Antonietti, *Langmuir* 17 (2001) 908.
- [19] D.C. Sundberg, A.P. Casassa, J. Pantazopoulos, M.R. Muscato, *J. Appl. Polym. Sci.* 41 (1990) 1425.