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RESEARCH ARTICLE OPEN ACCESS

Core-Shell Magnetic Mesoporous Silica Microspheres with Small Magnetic Nanoparticle as a Core

Zhouhao Wu, Fang Wang, Ning Wang, Yujiao Li, Cheng-an Tao,Jianfang Wang*
College of Liberal Arts and Science, National University of Defense Technology, Changsha, 410073, China

ABSTRACT:
By the improved Stöber method, a core-shell mesoporous silica microsphere was prepared using Fe_3O_4 nanoparticles with the diameter of nearly 20 nm as the magnetic core, tetraethyl orthosilicate as silica source, polyethylene oxide–polypropylene oxide–polyethylene oxide (P123) and Cetyltrimethylammonium bromide (CTAB) as surfactants, 1,3,5-trimethylbenzene (TMB) as Pore expanding agent. The characterization results show that the morphology is regular, the diameter is about 600 nm, and the mesoporous size is over 8 nm.
Key Words: Magnetic mesoporous silica nanoparticles, Core-shell structure, Stöber method

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I. INTRODUCTION

Magnetic mesoporus silica microspheres(MMSMs) is a kind of mesoporous materials based on silica, which is generally composed of magnetic core, protective layer and mesoporous layer. This material has the advantages of traditional silica-basedmesoporous materials, such as high porosity, high specific surface area, low toxicity, good biocompatibility,andeasy to functionalization,as well as preferable magnetic properties of magnetic nano materials[1-2].Compared with other magnetic mesoporous microspheres coated with organic compounds, silica is more stable under acidic conditions, has better anti-redox properties, and can effectively protect the magnetic cores [3]. Owing to these advantages, MMSMs are widely used in chemical industry, environmental science, life science, and many other fields, such as catalyst carrier [4-5], sewage treatment [6-8], DNA separation, drug carrier, etc. [9-12]. In 2004, Wu et al. [13] reported the preparation of MMSMs for the first time, but the size and shape were not regular enough. After more than ten years of development, synthesis methods of MMSMs are becoming more and more diversified. For the preparation of nano-magnetic nuclei, there are mainly coprecipitation method, hydrothermal method, solvothermal method, micro-emulsion method, pyrolytic carbonyl precursor method, et al. Coating of silica can be achieved by sol-gel method or reversed-phase microemulsion method. While surfactant removal is mainly by calcination or solvent extraction. For the MMSMs with different morphology and pore size, one or more of the cationic or non-ionic surfactants are usually used, and pore-enlarging agents can be added when necessary[14-15].

In practical application, in order to better realize the enrichment and recovery of MMSMs and improve the use efficiency, the size of MMSMs should be greater than 0.5μm, and Fe_3O_4 nanoparticles with a diameter over 100 nmare often used as magnetic core.The size of nano Fe_3O_4 prepared by co-precipitation method is generally small, and the cost is less than 1 % of Fe_3O_4 with a diameter greater than 100 nm. However, it is difficult to prepare MMSMs with regular morphology and diameter greater than 0.5 μm utilizing such small size Fe_3O_4 nanoparticle as magnetic core, and there are few reports about it.Cetyltrimethylammonium bromide (CTAB) is often used in the preparation of mesoporous materials. However, due to the size of its micelles, the pore size of the prepared mesoporous material is very small andgenerally no more than 4 nm.As a triblock copolymer, P123 has a larger micelle size, but its first critical micelle concertration (CMC) is smaller, which makes the mesoporous layer tend to be lamellar in the preparation process.Too small hole and non spherical structure make it have great limitation in practical use.

In this study, a core-shell mesoporous silica microsphere was prepared by the improved Stöber method[16] and characterized, and Fe_3O_4 nanoparticles with the diameter of nearly 20 nm was used as the magnetic core, tetraethyl orthosilicate (TEOS) as silica source, P123 and CTAB as surfactants,1,3,5-trimethylbenzene (TMB) as Pore expanding agent.

II. MATERIALS AND METHODS

2.1. Materials and Instruments

Fe_3O_4 nanoparticles dispersion (10-30 nm, 25wt%,water medium), polyethylene oxide–polypropylene oxide–polyethylene oxide (P123, average molecular weight about 5800). Cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), 1,3,5-trimethylbenzene (TMB) were analytically pure.

The structure was studied by a Fourier transform infrared spectroscopy (FT-IR, PerkinElmer Spectrum Two) from 4000 cm^{-1} to 400 cm^{-1} with an attenuated total reflection (ATR) accessory. Accelerated surface area and porosimetry system (Micromeritics ASAP2460) and small &wide angle X-ray scattering system (SAXSess, mc2) were used for pore analysis. Scanning electron microscope (SEM, Zeiss Gemini 300) and Energy Dispersion Spectrum (EDS) was used for investigating surface topography and Component analysis.

2.2Methods

The preparation process of MMSMs is shown in Figure 1:

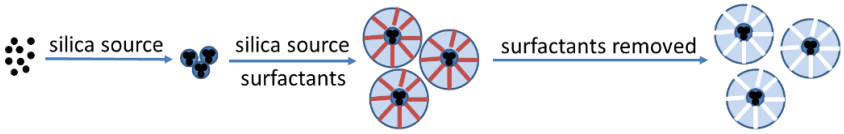

Figure 1 Schematic of the preparation process of MMSMs

2.2.1 Preparation of protective layer

Absolute ethanol (400 mL), deionized water (100 mL) and concentrated ammonia water (about 25~28wt%, 4 mL) were added into the three-neck flask, and Fe_3O_4 nanoparticles dispersion (2 mL) was added under mechanical stirring. After continuous stirring for 15 min,TEOS (5.8 mL) was added within 2min.After stirring for more than 12 hours, the solid materials were separated by magnet, washed with ethanol and deionized water, and then dispersed in appropriate amount of ethanol to prepare the dispersion of magnetic microspheres with silica protective layer(Fe_3O_4@SiO_2).

2.2.2 Preparation of mesoporous layer

Transfer Fe_3O_4@SiO_2 to a three neck flask and add polyether P123 (0.79g), then add CTAB and TMB in sequence according to m_{P123}:m_{CTAB}:m_{TMB} = 0.79:0.16:0.24, 0.79:0.16:0.32, 0.79:0.24:0.24 (recorded as a, b, c, respectively). After that, it was dissolved and dispersed with hydrochloric acid (1.5M, 200 mL). The reactor was placed at 35 ℃ and mechanically stirred at a stirring speed of 450 r/min. TEOS (0.92 mL) was added within 1 min. After stirring for 1 h, the temperature was raised to 75 ℃, the stirring speed was changed to700 r/min. After stirring for more than 12 hours, the temperature was raised to 125 ℃,and the stirring was continued for 4 h. Then, the solid materials were separated by magnet, washed with ethanol and deionized water, dried at 80 ℃, and calcined in resistance furnace (550 ℃) for 6h.Three kinds of MMSMs (MMSMs -a, MMSMs -b and MMSMs -c respectively)were prepared.

III. RESULTS AND DISCUSSION

3.1 Characterization of Fe_3O_4@SiO_2

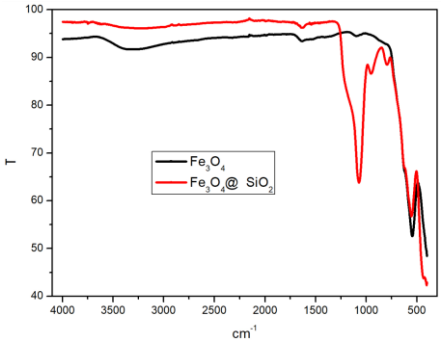

Figure 2 Infrared spectra of Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2

The infrared spectra of Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2 are shown in Fig. 2. The peak at 555cm^{-1} is the infrared characteristic absorption peak of Fe_3O_4. The strong absorption peak at 1073cm^{-1} is caused by the antisymmetric stretching vibration of Si-O-Si bond. The absorption peak at 794cm^{-1} is caused by the symmetric stretching vibration of Si-O-Si bond. The shoulder peak at 436 cm^{-1} may be caused by the bending vibration of Si-O bond. The absorption peak at 953cm^{-1} may be caused by the asymmetry of local defects in SiO_2 skeleton, or the characteristic absorption of stretching vibration of Si-O bond.

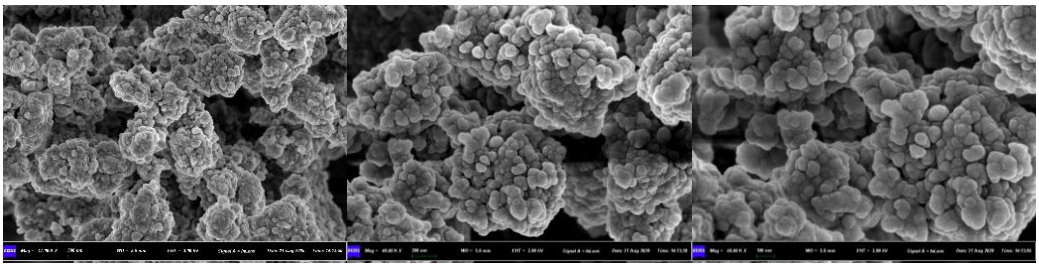

Figure 3 SEM images of Fe_3O_4@SiO_2indifferent magnification

The SEM of Fe_3O_4@SiO_2 is shown in Fig. 3. Serious agglomeration and irregular morphology appear after coating the surface of small-sized Fe_3O_4 nanoparticles with silica, which size is about 70nm. Therefore, the synthesis of regular MMSMs needs to choose an appropriate method for mesoporous layer preparation.

3.2 Characterization of MMSMs

3.2.1Nitrogen adsorption and desorption of MMSMs

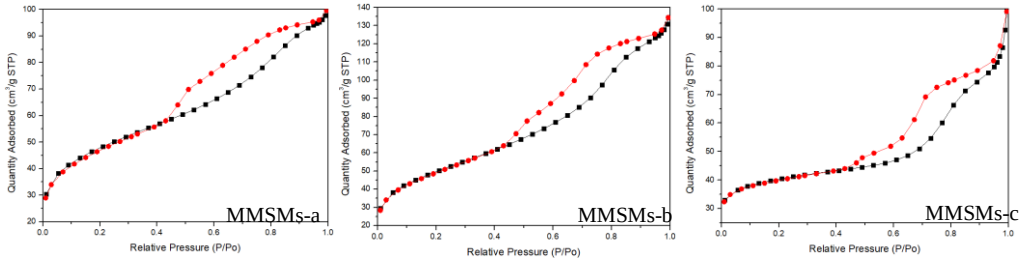

Figure 4 Adsorption and desorption isothermsof MMSMs

The adsorption and desorption isothermsof the three preparedMMSMs (MMSMs-a,MMSMs-b,MMSMs-c) are shown in Fig. 4.Hysteresis loops appear in all the three, indicating that there are mesoporous structures. BET specific surface areas are 169.5m^2/g、177.9 m^2/g 和 160.3 m^2/g respectively.According to the definition given by the International Union of theoretical and Applied Chemistry (IUPAC), there are some spherical particles with uniform distribution and slit structure formed between particles, because the adsorption isotherms are all close to type IV and the hysteresis loops are close to the mixed type of H1 and H4.

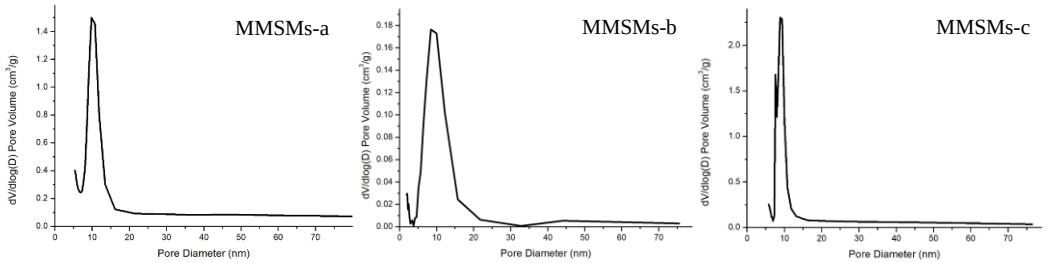

Figure 5 BJH pore size distribution of MMSMs

Fig. 5 shows that the most probable pore sizesof the three MMSMs are 9.1 nm, 10.2nm and 8.8 nm, respectively. Compared with MMSMs-a, the pore size of MMSMs-b increase slightly and the pore size distribution range also increases with the amount of TMB increasing, which does not meet the preparation expectation. With the amount of CTAB increasing, the pore size of MMSMs-c is slightly reduced much compared with MMSMs-a, but it is still above 8 nm, and the pore size distribution range does not change much.

3.2.2SEMimages of MMSMs-a and MMSMs-c

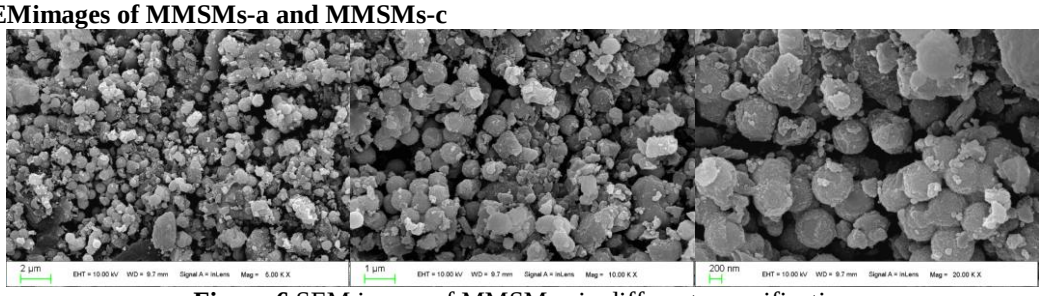

Figure 6 SEM imagesof MMSMs-ain different magnification

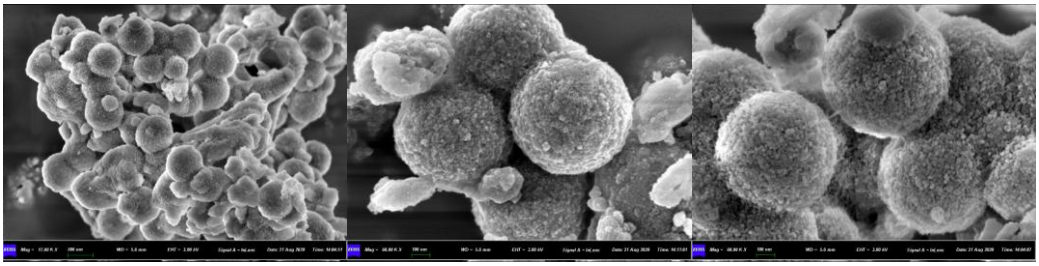

Figure 7 SEM imagesof MMSMs-cin different magnification

The SEM images of MMSMs-a and MMSMs-c are shown in Fig. 6 and Fig. 7, respectively.It can be found that the spheroidization of MMSMs-a is slightly poor, and there are more flake or irregular shaped nanoparticles in MMSMs prepared with less CTAB.On the other hand, the spheroidization of MMSMs-c is better, the size of the ball is uniform, and the particle size is about 600 nm.The reason may be that the critical micelle concentration of polyether P123 is different from that of CTAB, and different aggregation micelles are producedand different templates are formed by changing the ratio between them. It indicates that the mesoporous materials tend to be spherical when the amount of CTAB is increased in a certain proportion. The pore size and particle size of the three kinds of MMSMs are in accordance with the requirements, and MMSMs-chas more concentrated pore size distribution and more regular morphology.

3.2.3SAXS of MMSMs-c

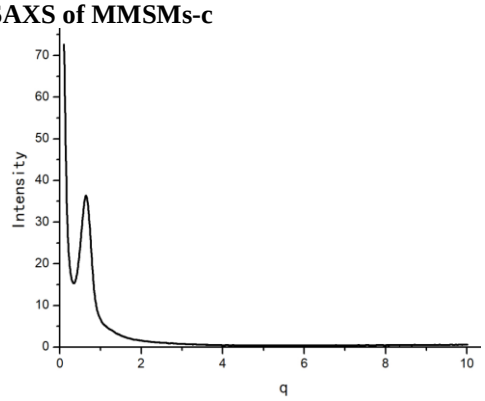

Figure 8 SAXS of MMSMs-c

Fig. 8 shows the Q-I curve of SAXS of MMSMs-c, with q = 0.7107 at the extreme point.According to formula (1), (2):

$$q = 4\pi sin\theta/\lambda \quad (1)$$

$$2dsin\theta = n\lambda \quad (2)$$

It can be seen that d=2π/q=8.84 nm at the extreme point, which is consistent with the most probable pore sizes measured by BJH method. There is only a single scattering peak, which indicates the existence of mesoporous structure,but the long-range order of the poresis not good.

3.2.4 EDS and mapping analysis of MMSMs-c

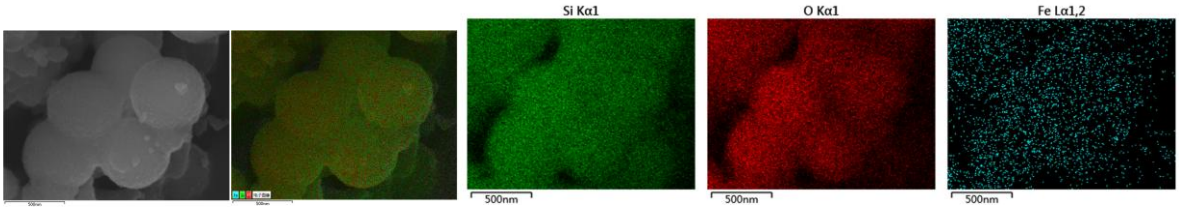

Figure 9 EDS mappings of MMSMs-c

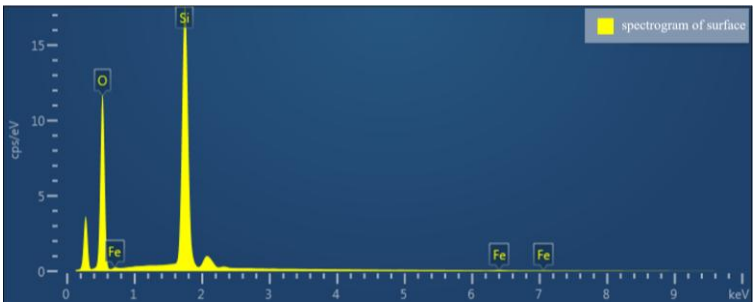

Figure 10 Surface scanning EDS-Mapping of MMSMs-c

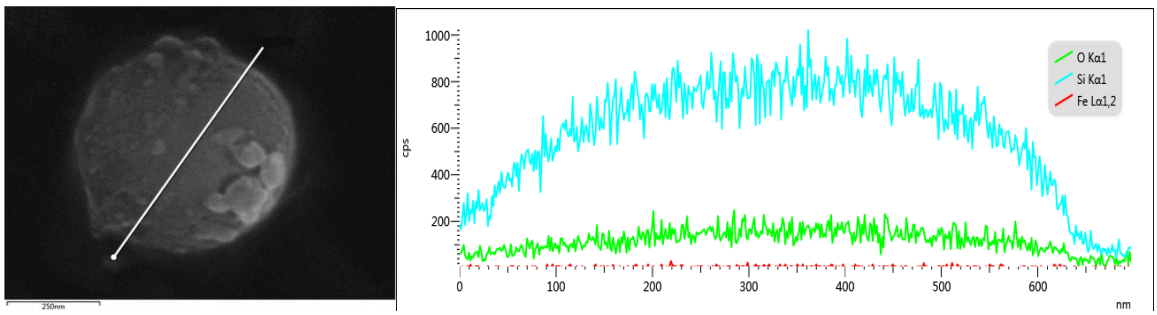

Figure 11 Line scanning EDS-Mapping of MMSMs-c

EDS mappingsof MMSMs-c (Fig. 9) show that the microspheres contain O, Si and Fe, and the distribution of O and Si is dense and consistent with themicrospheres morphology, while the distribution of Fe is dispersed. According to the surface and line scanning EDS-Mapping of MMSMs-c (Fig. 10, Fig. 11), it can be concluded that the surface of microspheres contains O, Si and no Fe, which indicates that Fe_3O_4 nanoparticles are completely coated by silica and not exposed to the surface of the microspheres.The results show that diameter of the sphere is about 600 nm, which is consistent with the SEM data.

IV. CONCLUSIONS

A kind of core-shell mesoporous silica microspheres with small magneticFe_3O_4 nanoparticles core were successfully prepared, whose morphology was regular, with a particle size of about 600 nm and a pore size of more than 8 nm. The effects of CTAB and TMB on the morphology and pore size of MMSMs were studied by comparison experiments. The results show that increasing CTAB dosage in a certain range can make MMSMs closer to the sphere shape.Meanwhile, the control of TMB dosage can keep the MMSMswith larger pore size without widening the pore distribution range.

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