

Synthesis of core-shell structured magnetic nanoparticles with a carbide shell

Shushan Hou , Yue Chi* and Zhankui Zhao*

College of Material Science and Engineering, Key Laboratory of Advanced Structural Materials, Ministry of Education, Changchun University of Technology, Changchun, 130012, China

E-mail: *yuechi@ccut.edu.cn, *zhaozk@ccut.edu.cn

Abstract. Core-shell structured materials combining the functionalities of the core and shell have great application potential in many fields. In this work, by combining solvothermal, polymerization and the high temperature carbonization, we have successfully developed a facile method to generate core-shell structured nanoparticles which possess an internal magnetic nanoparticle with a carbide shell. The thickness of resorcinol formaldehyde resin as intermediate transition shell could be easily adjusted by changing the concentration of the RF precursor. The resulting nanoparticles possess well-defined structure, uniform size and high magnetization. The unique nanostructure of the magnetic core-shell structured nanoparticles could lead to many promising applications in areas ranging from drug delivery to the purification of sewage.

Keywords: solvothermal method, core-shell structure, carbide, magnetic materials

1. Introduction

Multishell composite nanostructure materials, since their discovery [1, 2], have gained global attention because their potential applications in separation [3], catalysis [4], magnetic resonance imaging (MRI) [5], bioseparation [6], drug delivery [7, 8] and sensor [9]. In the other hand, magnetic nanomaterials have recently attracted numerous researchers' interest in catalysis, adsorption and enrichment due to their convenient manipulation, such as magnetic separation and recycling [10-14]. However, magnetic nanoparticles (Fe_3O_4 nanoparticles) are easy to rust corrosion in the water, especially they have a large tendency to aggregate driven by vander Waals forces and high interface energy because of their ultrasmall particle size. Therefore, there is an impending need in developing methods to create a protective shell on the surface to improve its performance and practicability, such as polymer nanoshell, silica nanoshell and so on.

Taking the above considerations into account, there are some experimental reports about preparing magnetic nanoparticles (Fe_3O_4 nanoparticles) with multi-shell structures [15], such as polymer/gold nanoshell [16], Pd/silica [17] and C/silica [18]. Thus it can be seen that it is also very interest and valuable to develop a new method to generate a carbide shell on magnetic nanoparticles.

Herein, we reported a controllable and facile route to fabricate magnetic core-shell structured nanoparticles that comprise Fe_3O_4 core and carbide shell. The introduction of carbide shell and the construction of core-shell structure are considered to improve the potential applications of magnetic nanomaterials, such as separation, drug delivery, bioseparation, sensor and so on.



2. Experimental section

2.1. Chemicals

All chemicals were purchased from Beijing Chemical Corp. Other chemicals were used as received without any further purification. Deionized water was used for all experiments.

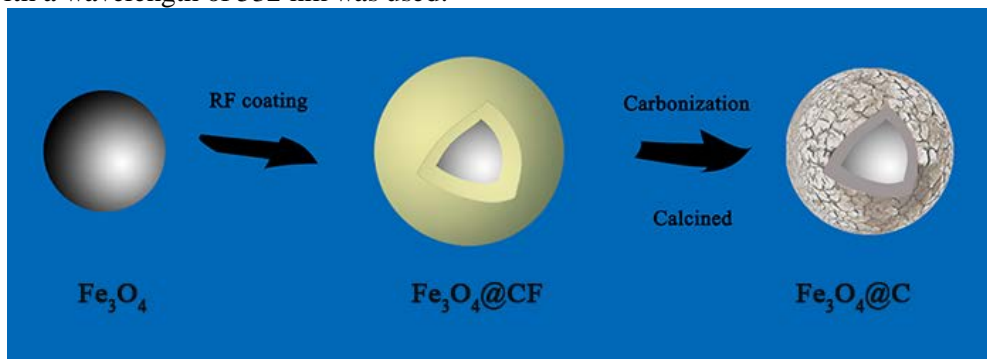
2.2. Materials synthesis

2.2.1. Synthesis of magnetic Fe_3O_4 nanoparticles. The magnetic Fe_3O_4 nanoparticles were synthesized through a solvothermal method according to the method reported previously with some modification [19]. Briefly, 1.08 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL of ethylene glycol with magnetic stirring until the solution became clear. Then 1.8 g of NaAc was added to this solution and stirred for another 1 h. Afterwards, 0.25 g trisodium citrate was added. When the mixed solution was stirred for 10 h to form a homogeneous dispersion, The obtained black solution was then transferred and sealed into a Teflon-lined stainless-steel autoclave (50 mL in capacity), The autoclave was heated at 200 °C for 10 h, and then allowed to cool down to room temperature. The black sample was washing with ethanol and deionized water several times, and then dried under vacuum at 60 °C overnight.

2.2.2. Synthesis of magnetic $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles. 0.1 g of magnetic Fe_3O_4 nanoparticles was dispersed in a mixture solution of ethanol (20 mL) and deionized water (10 mL) by ultrasonication. Into the resulting dispersion, ammonium hydroxide aqueous solution (0.5 g, 28 wt %), resorcinol (0.1 g, 0.09 mM), and formaldehyde (0.1 g, 37 wt %) were added consecutively, and the mixed dispersion was mechanically stirred for polymerization for 2 h at 30 °C, forming a shell of RF resin. After polymerization, the obtained $\text{Fe}_3\text{O}_4@\text{RF}$ nanoparticles were collected by a magnet and washed with deionized water and alcohol several times, respectively. In order to try to adjust the thickness of the RF shell, the concentration of the RF precursor will be appropriate to increase [20]. Finally, the obtained sample was calcined at 500 °C in argon atmosphere for 3 h to form a carbide shell.

2.3. Characterization

Scanning electron microscope (SEM) were measured on JSM-5600. Transmission electron microscopy (TEM) was performed on JEM 2000. Crystal identification was carried out using a Bruker D8 Advance X-ray diffractometer with a Cu K α X-ray source operating at 40 kV and 100 mA. Magnetic measurement of the samples was investigated with a Quantum Design vibrating sample magnetometer (VSM) at room temperature in an applied magnetic field sweeping from - 15 to 15 kOe. Raman data was recorded on a LabRAM HR Evolution using an Ar⁺ laser at ambient temperature. An excitation source with a wavelength of 532 nm was used.



Scheme 1. Schematic representation of synthesis of $\text{Fe}_3\text{O}_4@\text{C}$.

3. Results and discussion

The fabrication of magnetic core-shell structured nanoparticles is illustrated in Scheme 1. Firstly, uniform magnetic Fe_3O_4 nanoparticles were synthesized by the solvothermal method. Secondly, through polymerization of resorcinol and formaldehyde, a controllabe shell (50 ~ 150 nm) can be deposited on the surface of Fe_3O_4 nanoparticles. Thirdly, after calcination in argon atmosphere, $\text{Fe}_3\text{O}_4@\text{C}$ could be obtained. The synthesized nanoparticle is composed of Fe_3O_4 core, and carbide shell.

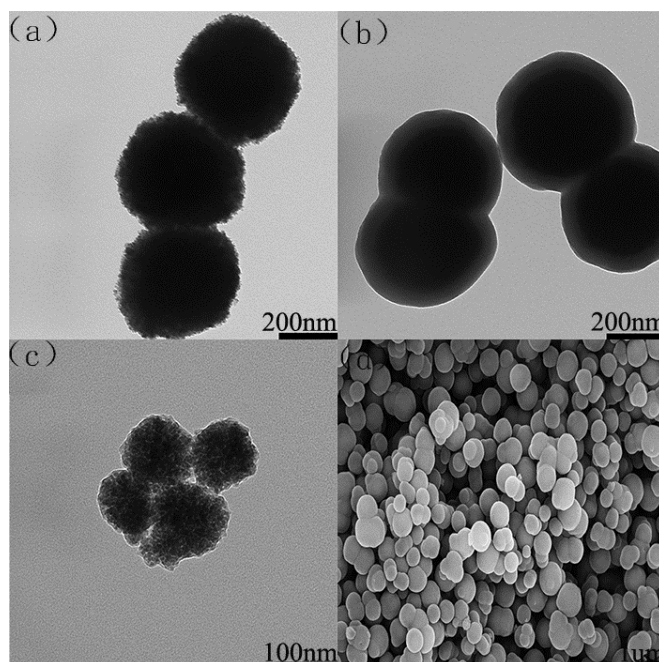


Figure 1. TEM images of (a) Fe_3O_4 , (b) $\text{Fe}_3\text{O}_4@\text{RF}$, (c) $\text{Fe}_3\text{O}_4@\text{C}$, (d) SEM image of $\text{Fe}_3\text{O}_4@\text{RF}$.

As shown in figure 1(a), the obtained magnetic Fe_3O_4 nanoparticles have a mean diameter of ~ 250 nm. After polymerization, a shell of RF of ~ 50 nm in thickness was individually deposited on magnetic Fe_3O_4 nanoparticles, resulting in core-shell structured $\text{Fe}_3\text{O}_4@\text{RF}$ with spherical morphology (figure 1(b) and 1(d)). This RF shell plays some important roles in this process. First, it can prevent the magnetic Fe_3O_4 nanoparticles from being oxidized under some conditions. Second, it can also prevent the magnetic Fe_3O_4 nanoparticles from losing magnetic properties in the final carbonization process. Last, it provides the carbonyl and hydrogen ions^[20], thus providing conditions for the subsequent reaction. After high temperature carbonization in argon atmosphere, magnetic Fe_3O_4 nanoparticles was coated with a carbide shell (figure 1(c)), then core-shell structured nanoparticles with a size of ~ 400 nm were obtained.

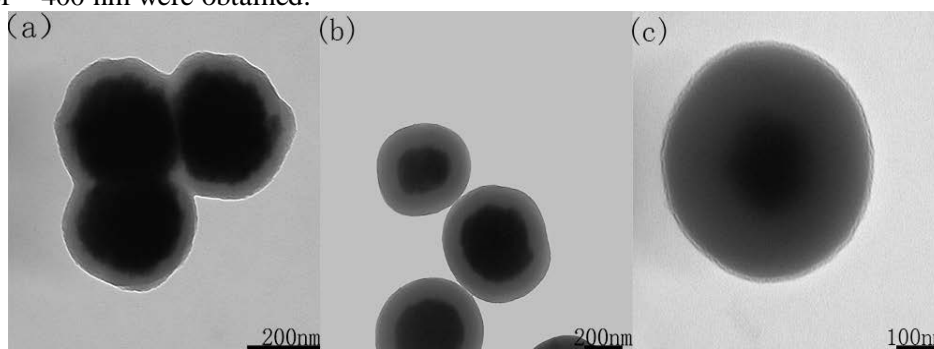


Figure 2. TEM images of $\text{Fe}_3\text{O}_4@\text{RF}$ nanoparticles with different thickness of RF shell.

Under the same conditions except for the concentration of RF precursor, the core-shell structured $\text{Fe}_3\text{O}_4@\text{RF}$, nanoparticles with different thickness of RF shell can be easily adjusted. By increasing the concentration of RF precursor, the thickness of the RF can increase from 50 to 150 nm. As can be seen from TEM images (figure 2(a) and 2(b)), when the concentration of RF precursor is 1:2, the thickness of the RF shell of the resultant core-shell nanoparticles can be easily adjusted from 50 to 100 nm. Further increasing the concentration of RF precursor to 1 : 3 leads to a much thicker shell at ~ 150 nm (figure 2(c)).

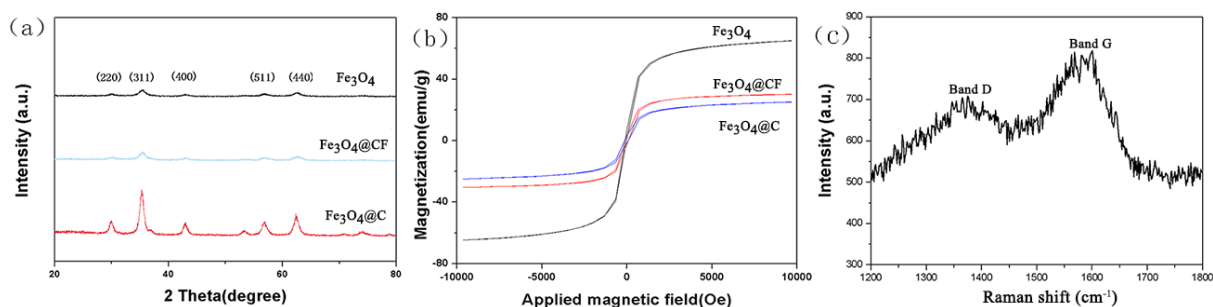


Figure 3. (a) XRD patterns of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{RF}$, $\text{Fe}_3\text{O}_4@\text{C}$, and (b) Magnetization curves of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{RF}$, and $\text{Fe}_3\text{O}_4@\text{C}$ at room temperature. (c) Raman spectrum of $\text{Fe}_3\text{O}_4@\text{C}$.

The phase structures of Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{RF}$, and $\text{Fe}_3\text{O}_4@\text{C}$ were analyzed via XRD (figure 3(a)). For Fe_3O_4 , the characteristic diffractions at 30.0° , 35.5° , 43.1° , 57.0° , and 62.6° of 2θ suggest a face-centered cubic phase structure with the space group of Fd3m according to JCPDS card no. 19-0629. In the case of $\text{Fe}_3\text{O}_4@\text{RF}$ and $\text{Fe}_3\text{O}_4@\text{C}$ composites, the phase structure of Fe_3O_4 core was intact, but the intensity of XRD peaks gradually stronger, when the thickness of shell was increased. This result suggests that the Fe_3O_4 crystal was successfully used as a magnetic center of the $\text{Fe}_3\text{O}_4@\text{C}$. The magnetization curves measured for Fe_3O_4 , $\text{Fe}_3\text{O}_4@\text{RF}$ and $\text{Fe}_3\text{O}_4@\text{C}$ are compared (figure 3(b)). There was no hysteresis in the magnetization for the three tested nanoparticles. Compared with Fe_3O_4 (64.99 emu/g), the saturation magnetization of $\text{Fe}_3\text{O}_4@\text{RF}$ and the $\text{Fe}_3\text{O}_4@\text{C}$ decreased to 29.90 and 24.81 emu/g, respectively. It should be noted that although the magnetization saturation value of $\text{Fe}_3\text{O}_4@\text{RF}$ and the $\text{Fe}_3\text{O}_4@\text{C}$ are lower than that of Fe_3O_4 due to the increase in the mass caused by the surface depositing of Fe_3O_4 , it still shows strong magnetization, which suggests its suitability for magnetic separation and targeting. Raman spectroscopy was used (figure 3(c)). The spectrum consists of two characteristic bands, namely D band at $\sim 1370 \text{ cm}^{-1}$ and G band at $\sim 1580 \text{ cm}^{-1}$, respectively. The D band corresponds to the disordered structure of a carbonaceous solid from an A1g mode, which is attributed to the presence of amorphous or disordered carbon. The G band originates from graphitic lattice vibration mode with E2g symmetry. The disordered D band is weaker than the ordered G band, indicating a substantial coating of definite carbon on the surface of Fe_3O_4 .

4. Conclusions

In conclusion, we have successfully synthesized the $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticles by combining solvothermal, polymerization and the high temperature carbonization. The magnetic Fe_3O_4 nanoparticles with a diameter of ~ 250 nm have been synthesized by solvothermal method. Through adjusting the concentration of RF precursor in the reaction solution, the thickness of RF shell can be adjusted in the range of 50 ~ 150 nm. The transformation of RF shell to carbide protective shell could be implemented by the high temperature carbonization. Considering the facile synthesis method and the useful superparamagnetic properties and unique microstructure, $\text{Fe}_3\text{O}_4@\text{C}$ has promising application in many fields.

Acknowledgements

This work was supported by the Natural Science Foundation of Jilin Province of China (20150520020JH), National Natural Science Foundation of China (grant nos. 51608050 and 51601018) and Jilin Provincial Science & Technology Department (Grant nos: 20160519020JH).

References

- [1] Kresge C T *et al.* 1992 Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism *Nature* **359**(6397) 710–712
- [2] Che S *et al.* 2004 Synthesis and characterization of chiral mesoporous silica *Nature* **429**(6989) 281–284
- [3] Vinu A *et al.* 2004 Adsorption of cytochrome c on mesoporous molecular sieves: Influence of pH, pore diameter, and aluminum incorporation *Chemistry of materials* **16**(16) 3056–3065
- [4] Alayoglu S *et al.* 2008 Ru-Pt core-shell nanoparticles for preferential oxidation of carbon monoxide in hydrogen *Nature materials* **7**(4) 333–338
- [5] Shin J *et al.* 2009 Hollow manganese oxide nanoparticles as multifunctional agents for magnetic resonance imaging and drug delivery *Angewandte Chemie* **121**(2) 327–330
- [6] Chen O *et al.* 2013 Compact high-quality CdSe-CdS core-shell nanocrystals with narrow emission linewidths and suppressed blinking *Nature materials* **12**(5) 445–451
- [7] Melancon M P, Zhou MIN and Li C 2011 Cancer theranostics with near-infrared light-activatable multimodal nanoparticles *Accounts of chemical research* **44**(10) 947–956
- [8] Kam N W S *et al.* 2005 Carbon nanotubes as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction *Proceedings of the National Academy of Sciences of the United States of America* **102**(33) 11600–11605
- [9] Reiss P, Protiere M and Li L 2009 Core/shell semiconductor nanocrystals *Small* **5**(2) 154–168
- [10] O'handle R C 2000 *Modern magnetic materials* (Wiley)
- [11] Miller J S and Epstein A J 1994 Organic and organometallic molecular magnetic materials-designer magnets *Angewandte Chemie International Edition in English* **33**(4) 385–415
- [12] Standley K J 1972 *Oxide magnetic materials* (Oxford University Press)
- [13] Spaldin N A 2010 *Magnetic materials: fundamentals and applications* (Cambridge University Press)
- [14] Hu M *et al.* 2012 Tailored design of multiple nanoarchitectures in metal-cyanide hybrid coordination polymers *Journal of the American Chemical Society* **135**(1) 384–391
- [15] Park H *et al.* 2009 Multifunctional nanoparticles for combined doxorubicin and photothermal treatments *ACS nano* **3**(10) 2919–2926
- [16] Wan Y *et al.* 2009 Ordered mesoporous Pd/silica-carbon as a highly active heterogeneous catalyst for coupling reaction of chlorobenzene in aqueous media *Journal of the American Chemical Society* **131**(12) 4541–4550
- [17] Han S and Hyeon T 1999 Simple silica-particle template synthesis of mesoporous carbons *Chemical Communications* **19** 1955–1956
- [18] Fuertes A B, Valle-Vigón P and Sevilla M 2012 One-step synthesis of silica@resorcinol-formaldehyde spheres and their application for the fabrication of polymer and carbon capsules *Chemical Communications* **48**(49) 6124–6126
- [19] Chi Y *et al.* 2012 Synthesis of Fe₃O₄@SiO₂-Ag magnetic nanocomposite based on small-sized and highly dispersed silver nanoparticles for catalytic reduction of 4-nitrophenol *Journal of colloid and interface science* **383**(1) 96–102
- [20] Yue Q *et al.* 2015 Magnetic yolk-shell mesoporous silica microspheres with supported Au nanoparticles as recyclable high-performance nanocatalysts *Journal of Materials Chemistry A* **3**(8) 4586–4594