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Fabrication of iron oxide/silica core–shell nanoparticles and their magnetic characteristics

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ABSTRACT

Magnetic core–shell particles, each with a single iron oxide nanoparticle core, were prepared by the reverse microemulsion method. By using 1-butanol as a co-surfactant, one can effectively control the particle size ranging from 60 to 185 nm. The mechanism of incorporation of the hydrophobic nanoparticles in the center of a colloidal particle was discussed. The magnetic characteristics of the bare iron oxide nanoparticles and core–shell colloidal particles were studied by SQUID measurements. Superparamagnetic behavior has been found, with a blocking temperature of 200 and 100 K respectively. Under an external magnetic field, the as-prepared colloidal particles can assemble along the field direction to form linear structure. These give us a good chance to control the assembly of these colloidal particles by using an external field.

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1. Introduction

Owing to their diverse potential applications, e.g., in biotechnology, data storage, magnetic fluids etc., iron oxide nanoparticles have attracted much study in recent years. In particular, bio-related applications, such as magnetic resonance imaging (MRI) [1,2], hyperthermia [3,4], separation and purification of biomolecules [5], and drug delivery [6] have been of special focused attention. Bare magnetic iron oxide particles can encounter limitations in practical applications, e.g., the hydrophobic surface would mean that the particles cannot disperse well into aqueous solutions, the high chemical reactivity of the nanoparticles' surface can pose health risks, formation of large aggregates would greatly enlarge the effective particle size, and biodegradation when they are directly in contact with the biological systems would mean that such particles can easily lose their original characteristics. To overcome such limitations while retaining the magnetic properties of the nanoparticles, a good choice is the encapsulation of the nanoparticles within silica shells. Silica surfaces are easy to functionalize, nontoxic, and can protect the surface of the core nanoparticle from oxidation. Another advantage of silica coating lies in the enabling the process of transferring hydrophobic iron oxide nanoparticles prepared from non-polar solvents to a hydrophilic system.

A wide variety of silica-coating procedures have been developed for various nanoparticles during the past decade. The most used approaches for covering single nanoparticles with silica can be roughly divided into two types. The first type is based on a sol-gel process first published by Stöber et al. (the so-called “Stöber method”), in which silica was formed *in situ* through the hydrolysis and then condensation of a sol-gel precursor. The Stöber method was usually used to cover nanoparticles that can disperse in polar solvents such as water or ethanol [7–10]. The second type is the microemulsion approach, in which micelles or inverse micelles were used to confine and control the coating of silica on core nanoparticles. Advantages of the microemulsion method are that (1) it is very “robust” against many reaction conditions, the resulting silica nanoparticles have “smooth” surfaces and display good monodispersity, and (2) it can be used for coating nanoparticles dispersed in non-polar solvent [11–13] or polar solvent [14].

However, the maximum particle size that can be achieved by the reverse microemulsion method is usually smaller than 100 nm [12,13]. This size limitation would imply some limitations on the application of superparamagnetic nanoparticles. For e.g., in another interesting application of superparamagnetic nanoparticles, the assembly of magnetic-tunable photonic crystals is also desired to have larger particles with some uniformity in size. Ge et al. reported the assembly of magnetic-tunable photonic crystals using Fe₃O₄ nanocrystal clusters in the liquid medium [15–18]. But it is difficult to obtain Fe₃O₄ nanocrystal clusters with uniform size to ensure that the cluster bear homogeneous force in the magnetic field.

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In this work, we report the preparation of core-shell Fe_3O_4 -silica colloidal particles with size larger than 100 nm using the reverse microemulsion method. The co-surfactant was used to adjust the size of water pool in the reverse microemulsion system. To our knowledge, this is first time to report the preparation of core-shell particles with size over 100 nm by the microemulsion method. The assembly behavior of as-prepared colloidal particles with or without external magnetic field is also studied.

2. Experimental section

The iron oxide nanoparticles were synthesized by the decomposition of home-made iron oleate in 1-octadecene with the presence of oleic acid. A typical synthesis procedure is as follow: 2.068 g iron oleate and 0.5 ml of oleic acid (98%, Aldrich) is dissolved in 40 ml 1-octadecene (90%, Aldrich) in a 100 ml three-necked flask equipped with a condenser. After that, the mixture is heated to reflux for 120 min, and then cooled to room temperature. By adding 40 ml of ethanol, the resultant IONPs are isolated by centrifugation and washed with the mixture of n-hexane and ethanol for three cycles. As-prepared IONPs can re-disperse in cyclohexane or other non-polar solvent easily. About 0.060 g of IONPs is dispersed in 200 ml cyclohexane by ultrasonic treatment to obtain a uniform solution with a concentration of 0.3 mg/ml.

Silica coating is performed through the formation of a water-in-cyclohexane reverse microemulsion. Typically, 8 ml of as-prepared IONPs solution is added to 30 ml cyclohexane in a capped conical flask and treated with ultrasonication, and then 5.0 g of Igepal CO-520 (Aldrich, average Mn~441) or 6.5 g of Igepal CO-720 (Aldrich, average Mn~749), different amount of 1-butanol (Fisher, analytical reagent grade) is added separately and treated using ultrasonication. A total of 600 μl of ammonia solution (29.4 wt.% in water) is added, and the resulting mixture is vortexed to form a transparent microemulsion. Subsequently, 100 μl of tetraethyl orthosilicate (TEOS, 98%, Aldrich) is added and the mixture is vortexed for 2 min, and let stand for 24 h at room temperature. After reaction, 30 ml methanol is added to de-mulsificate the microemulsion; as the mixture separates into two layers, all the formed core-shell particles can be extracted from the lower layer of the mixture. By discarding the upper layer, the core-shell particles can be extracted by centrifuge. The particles are washed by ethanol 3 times. For each washing, ultrasonication is used to completely disperse the nanoparticles in ethanol. As the surfaces of silica shells are negative charged, the core-shell nanoparticles can form very stable dispersions in water without adding other surfactants, owing to the effect of electrostatic repulsion.

TEM samples of core-shell particles were prepared by placing 2–3 drops of water dispersion onto carbon coated copper grid followed by drying at room temperature. Size determinations were performed manually on the TEM images, by measuring at least 10 core-shell particles. The assembly of as-prepared particles was carried out by evaporating a drop of particles dispersion in water on silicon wafer, with or without an externally applied magnetic field. The SQUID samples were prepared by dispersing the IONPs in hexane with a concentration of 0.686 mg/g, and dispersing the core-shell particles in water with a concentration of 8.75 mg/g.

3. Results and discussion

Fig. 1 shows the TEM image of IONPs used for preparing the core-shell particles. The particles have an average size of 14 nm, and are very easy to dissolve in non-polar solvent to form a stable dispersion. The structure of IONPs was characterized by XRD, as shown in the XRD pattern presented in Fig. 2, the main component of IONPs is Fe_3O_4 with an inverse spinel structure.

Microemulsions are characterized as being optically transparent, thermodynamically stable isotropic dispersions with low viscosity. In our reverse microemulsion system, the cyclohexane served as the continuous phase in which TEOS, surfactant (Igeal CO-520 or Igeal CO-720), and hydrophobic-coated iron oxide particles were dissolved. The ammonia solution not only provided water to form the reverse microemulsion, but also catalyzed the hydrolysis and condensation of the silicate species.

Many factors can affect the size of SiO_2 particles prepared by reverse microemulsion, such as the amounts of ammonia solution and TEOS [16–20], the ratios of water to surfactant, the ratio of surfactant to co-surfactant, the ratio of surfactant to organic solvent [16,17], the duration of reaction, and the polarity and viscosity of organic solvent [21,22]. But the SiO_2 particles size can only be tun-

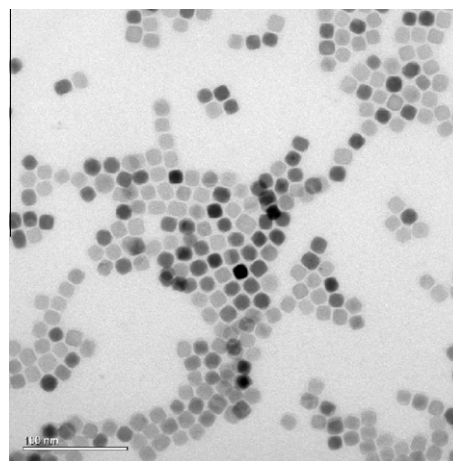


Fig. 1. A TEM image of the IONPs.

able over a range of 20–100 nm by varying the above factors [16–22].

In our experiment, with lower TEOS content and short reaction duration, the particle size increases with the increase of TEOS content and the prolonged reaction time. But when the TEOS content exceeds 100 μl and the reaction duration is longer than 24 h, no notable change of particle size can be observed. This implies that the particle size mainly relies on the size of water pool in the reverse microemulsion system. For a given microemulsion system, when the water to surfactant mole ratio lies in the microemulsion region, the increase of surfactant and water content favors the population of reverse micells, rather than increasing the size of water pool. Without 1-butanol as co-surfactant, the content of surfactant has no remarkable influence on the particles size; for e.g., when the Igepal CO-520 amount increase from 2.0 to 5.0 g, the size of obtained core-shell particles remains ca.65 nm; when the Igepal CO-720 increase from 3.0 to 7.0 g, the size of obtained core-shell particles remains ca.90 nm.

In order to control the size of obtained particle, we focus on the variety of surfactant and the content of co-surfactant.

Fig. 3 illustrates the effects of content of co-surfactant 1-butanol on the thickness of SiO_2 shell when using Igepal CO-520 as a surfactant. We can see, with the increase of 1-butanol content, the average size of the core-shell particles increased from 65 to 160 nm in a continuous fashion. When we use Igepal CO-720 as

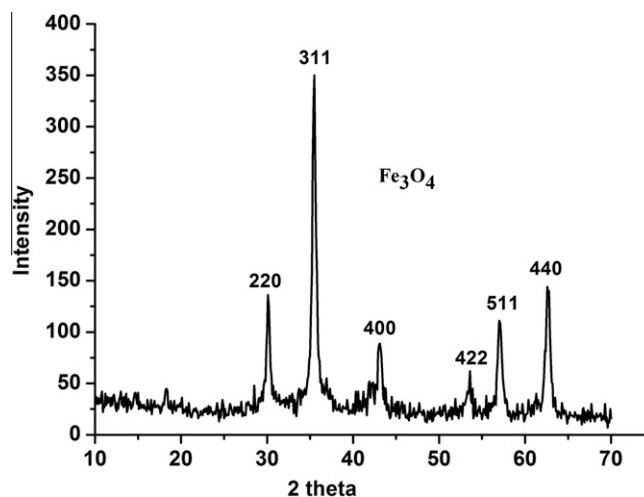


Fig. 2. XRD patterns of bare IONPs.

a surfactant, similar results are observed—the average size of core-shell particles increased from 90 to 185 nm (see Fig. 4). 1-butanol is a short chain monohydric alcohol, which has an amphiphilic structure. When the 1-butanol is added to the microemulsion system, they can wedge themselves into the space between CO-520 (or CO-720) molecules. This can make the surfactant film remain stable with less film rigidity. As a result, a larger water pools can be expected, which in turn can lead to larger colloidal particle size. Big water pools imply an enhanced ability of taking up water under a certain surfactant concentration. Another phenomenon can also support this conclusion. Our experiments indicated that, using 3.0 g of CO-720, with 600 μ l ammonia solution, only a turbid mixture was obtained even after a long duration of vortexing. But when 1.5 ml 1-butanol was added, the turbid mixture turned into a transparent microemulsion only after gentle vortexing. In our

experiment we also found that, with CO-720 as the surfactant, more 1-butanol is allowed to form a transparent microemulsion than that of using CO-520 as the surfactant.

From Figs. 3 and 4, we can see that the hydrophobic-coated iron oxide particles are always in the center of the as-prepared core-shell colloidal particles. This is somewhat surprising because the hydrolysis of TEOS and the subsequent silica nucleation and growth has been expected to occur within the small water pool of the microemulsion, but the hydrophobic-coated iron oxide particles are expected to be present in the continuous phase of the cyclohexane. The mechanism of incorporation of the hydrophobic nanoparticles in the center of a colloidal particle by reverse microemulsion has been studied by many groups [7,11,23,24]. Two different hypothetical mechanisms were suggested: formation of “inverse” surfactant bilayer, or the exchange of the ligands with TEOS and

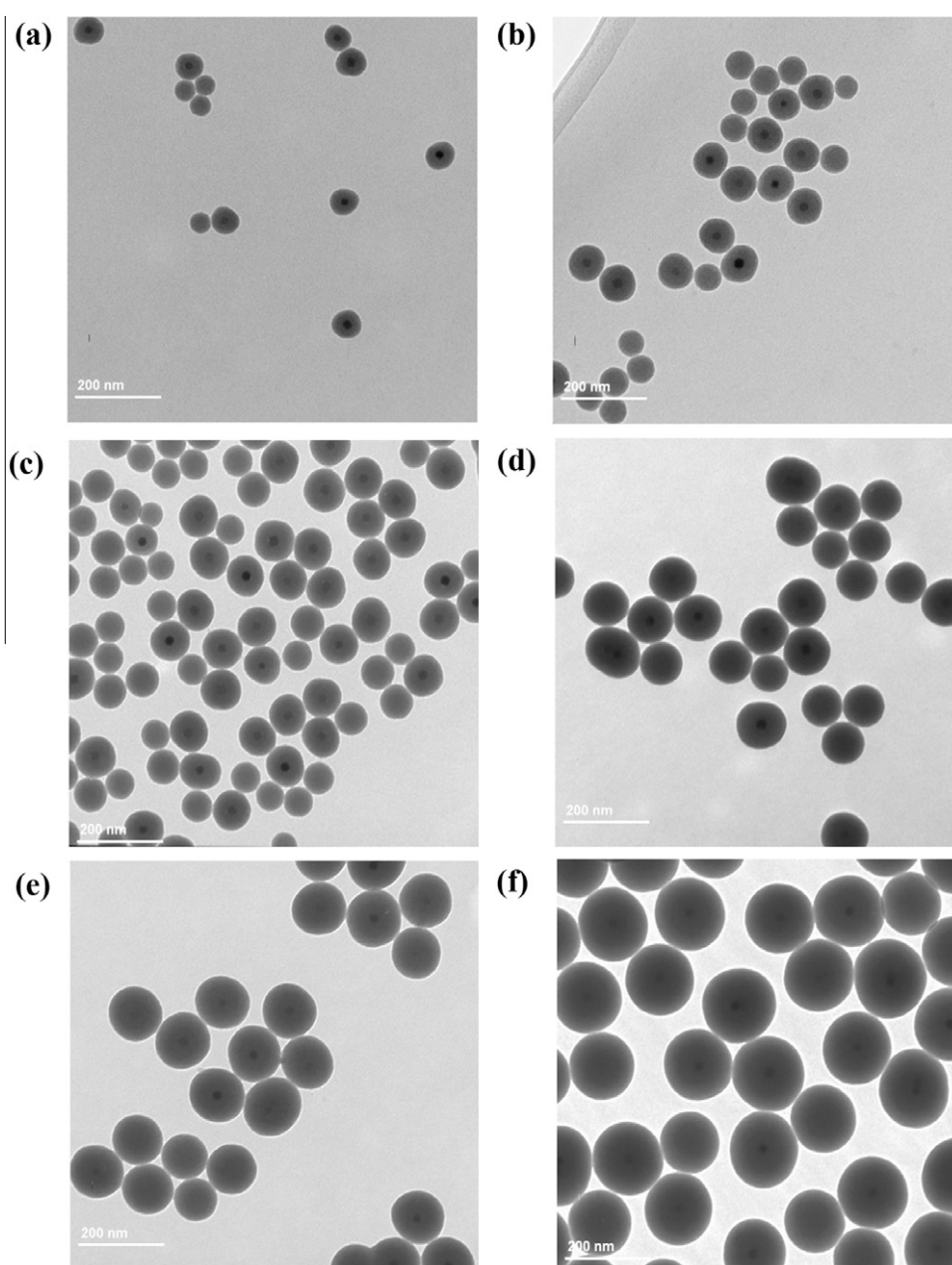


Fig. 3. TEM images of core-shell particles prepared by using CO-520 as the surfactant, with different content of 1-butanol as co-surfactant. (a) particles formed with no 1-butanol, ~65 nm (b) with 0.5 ml of 1-butanol, ~79 nm (c) with 1.0 ml, ~93 nm (d) with 1.25 ml, ~110 nm (e) with 1.5 ml, ~128 nm, and (f) with 1.75 ml, ~160 nm.

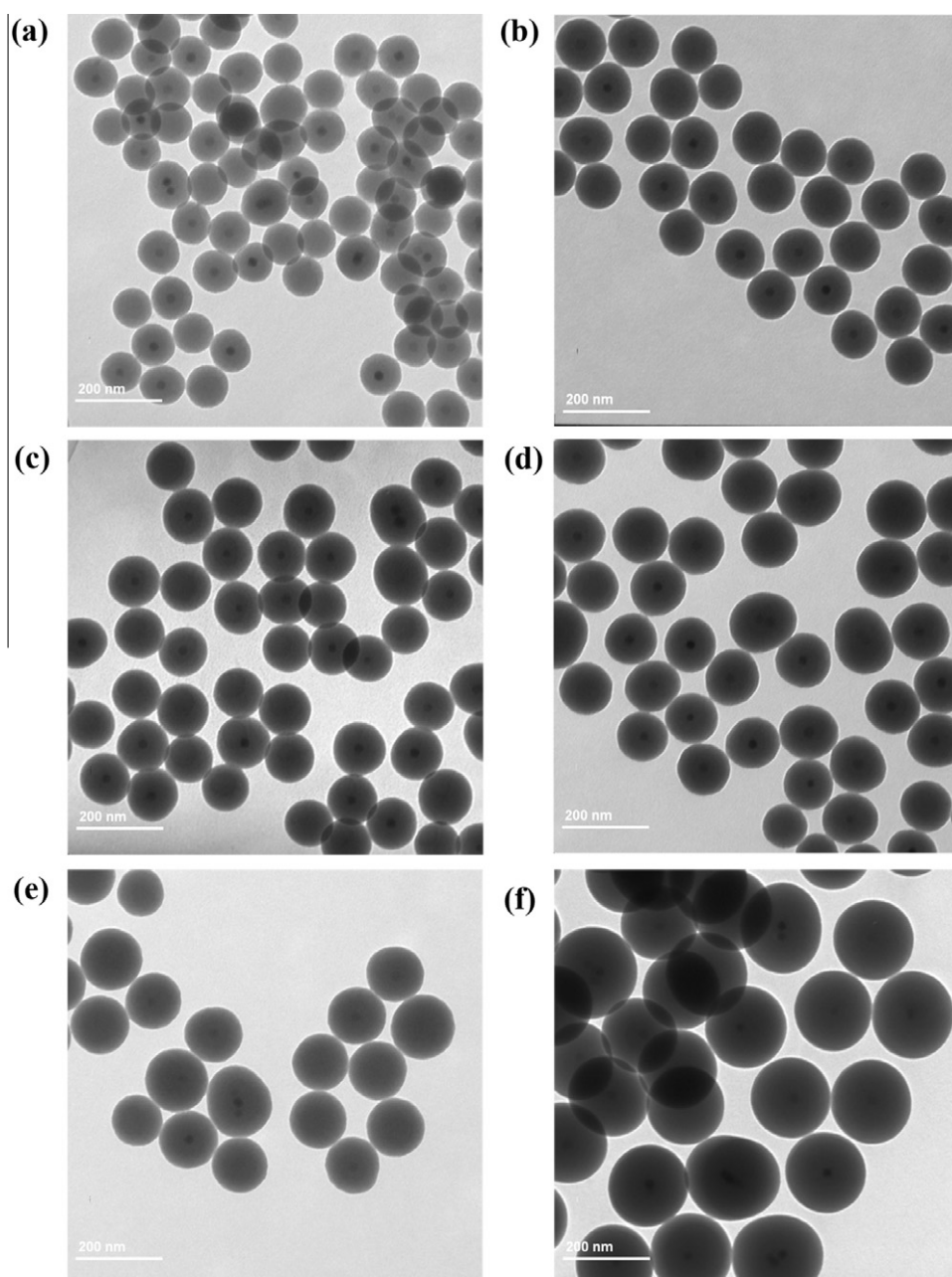


Fig. 4. TEM images of core-shell particles prepared using CO-720 as the surfactant, with different contents of 1-butanol as co-surfactant: (a) with no 1-butanol, ~90 nm (b) with 1.0 ml of 1-butanol, ~111 nm (c) with 1.5 ml, ~117 nm (d) with 2.0 ml, ~122 nm (e) with 2.5 ml, ~137 nm, and (f) with 3.0 ml, ~185 nm.

surfactant. Based on the ligands exchange mechanism [11], we would like to present a new hypothetical mechanism as follows (Fig. 5).

In our experiment, the IONPs were synthesized by the decomposition of iron oleate with the presence of oleic acid. One can expect that the surface of IONPs were covered by oleic ligands. The oleic ligands shells around the nanoparticles are not densely packed, and therefore permit diffusion of water molecules to the surface. With the addition of ammonia solution, a small amount of water will diffuse to the surface of iron oxide or captured by the hydrophilic group of oleic acid ligands. With the addition of TEOS, part of the oleic acid ligands will be exchanged by TEOS, and the TEOS will hydrolysis and condense on the surface of the IONPs to form a thin layer of silica. Because the silica surface is negatively charged, the oleic acid (anionic surfactant) will no longer

prefer to adhere on the surface of the particles after the formation of silica layer. This makes the particle very unstable in the oil phase, so the particles can be easily captured by the neighboring water pool. This process is hypothesized to finish in the early stage of the reaction. The process of the IONPs transfer from oil phase to water pool is schematically shown in Fig. 5.

There are also some evidences in our experiments to support the above proposed mechanism. From Figs. 3 and 4 it can be seen that there are some pure silica spheres, without the IONP core, present in the product and the pure silica spheres without a core are dramatically smaller than the core-shell particles. This can be explained by the capture of IONPs by water pool which would make the water pool with an IONP larger than that without an IONP. Whether a hydrophobic IONP can capture a small amount of water on its surface is crucial for its eventual transfer into the

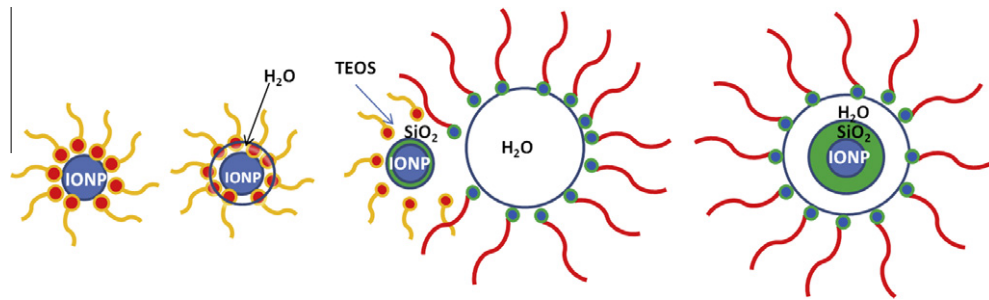


Fig. 5. Schematic of the proposed incorporation mechanism of hydrophobic IONPs in silica spheres by the reverse microemulsion method.

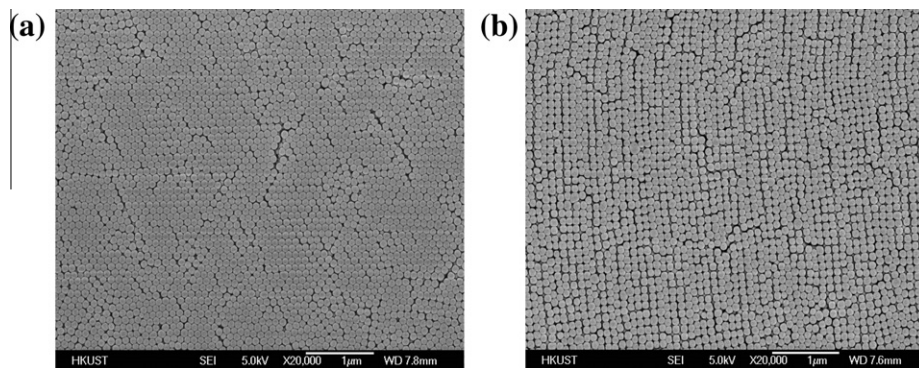


Fig. 6. SEM images of the core-shell particles self-assembly. (a) In the absence of externally applied field, a tight packing of the particles is seen. (b) Under an externally applied magnetic field, a chain pattern is evident.

water pool; hence not all the hydrophobic IONPs can be transferred into the water pool. When we terminate the reaction by adding methanol, there are also some IONPs remaining in the oil phase, which is responsible for a light brown color of the oil layer. The adding of alcohol as a co-surfactant not only improves the size of colloidal particles, but also favors the transfer of hydrophobic IONPs into the water pool. In the situation of adding 1-butanol, when the reaction is terminated by adding methanol, the ratio of core-shell particles to pure silica sphere improved dramatically (see Figs. 3 and 4). The color of the oil phase is also lighter than that without the addition of 1-butanol. The above observations indicate that more IONPs have been transferred into the water pool with the help of 1-butanol.

Fig. 6 shows the SEM images of self-assembly of as-prepared colloidal particles, with the silica shell. The magnetic particles tend to orient their dipoles opposite to each other so as to attract each other via the magnetic dipole-dipole interaction. This can lead to some special patterns, such as the rings in the absence of external magnetic field [25]. In our experiment the particles tend to form a hexagonal close-packed structure in the absence of external magnetic field (Fig. 6a). This implies that the as-prepared core-shell particles have no obvious dipole-dipole interaction in the absence of external magnetic field, indicating a superparamagnetic behavior. Under an external magnetic field, the magnetic field forces the particle dipoles to orient along the field, leading to a linear structure along the magnetic field direction (Fig. 6b). This phenom-

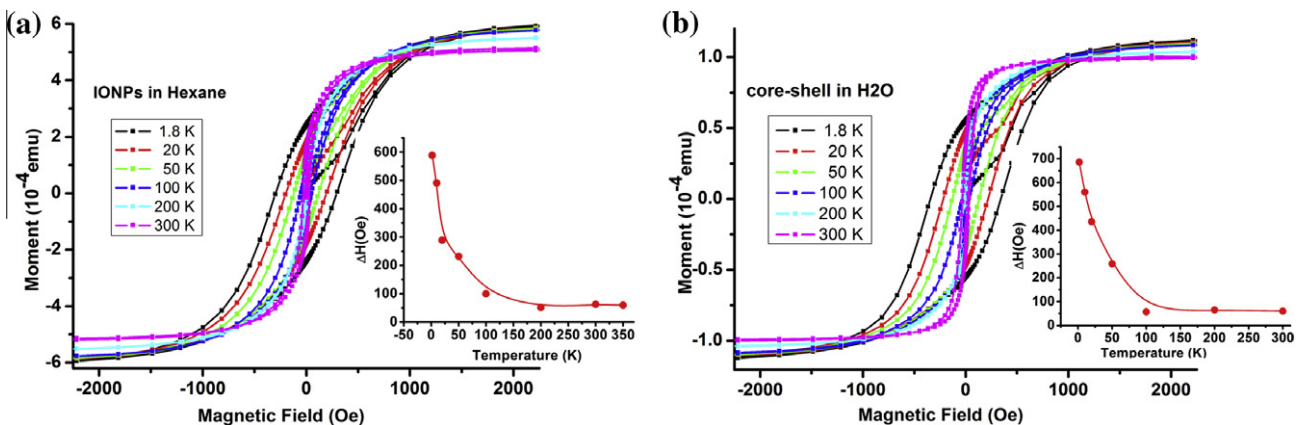


Fig. 7. Field-dependent magnetization at different temperature. (a) For the IONPs dispersed in hexane. (b) For the core-shell particles dispersed in H₂O. In each figure, the inset indicates the variation of the coercivity value, measured as the width of the hysteresis at zero magnetization, plotted as a function of temperature. The point at which the coercivity vanishes is the blocking temperature. The IONPs have a blocking temperature of 200 K, whereas the core-shell particles have a blocking temperature of 100 K.

enon implies that we can control the assembly structure of those core-shell particles by altering the external magnetic field.

The magnetic properties were studied using superconducting quantum interference device (SQUID). Fig. 7 shows the field-dependent magnetization plots at different temperatures. Fig. 7(a) is for the IONPs, without the silica shells, disperse in hexane. Fig. 7(b) is for the core-shell colloidal particles dispersed in H₂O. Insets are the relationship between the coercivity values (ΔH) and the temperature. The plots indicate that the coercivity values decrease with increasing temperature as expected. For the IONPs, the hysteresis disappears at 200 K, i.e., anisotropy energy is overcome by thermal entropy at this temperature, interpreted as the blocking temperature. For the core-shell particles dispersed in H₂O, the blocking temperature is 100 K. This can be due to the decrease of “effective” size of the IONP core after the coating of silica. The reduction of blocking temperature may also indicate a decrease of magnetic interactions, as a result of the existence of a homogeneous silica coating layer [26]. The magnetic properties of as-prepared core-shell nanoparticles are similar as that reported in references [10,27,28].

4. Concluding remarks

Core-shell colloidal particles, each with a single iron oxide nanoparticle core, have been prepared by the reverse microemulsion method. The size of as-prepared core-shell particles are mainly determined by the size of the water pools in the reverse microemulsion system. The particle size can be tuned from 65 to 185 nm by using 1-butanol as the co-surfactant. The as-prepared core-shell particles can be aligned into a linear structure under an external magnetic field. Magnetic characterization of the IONPs and the core-shell particles indicate that they are superparamagnetic with blocking temperatures of 200 and 100 K, respectively.

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References

- [1] E.H. Kim, Y. Ahn, H.S. Lee, *J. Alloys Compd.* 434–435 (2007) 633–636.
- [2] S.T. Selvan, T.T.Y. Tan, D.K. Yi, N.R. Jana, *Langmuir* 26 (2010) 11631–11641.
- [3] S. Mornet, S. Vasseur, F. Grasset, E. Duguet, *J. Mater. Chem.* 14 (2004) 2116–2119.
- [4] D.L. Zhao, X.X. Wang, X.W. Zeng, Q.S. Xia, J.T. Tang, *J. Alloys Compd.* 477 (2009) 739–743.
- [5] C. Xu, K. Xu, H. Gu, R. Zheng, H. Liu, X. Zhang, Z. Guo, B. Xu, *J. Am. Chem. Soc.* 126 (2004) 9938–9939.
- [6] T. Neuberger, B. Schopf, H. Hofmann, M. Hofmann, B. von Rechenberg, *J. Magn. Magn. Mater.* 293 (2005) 483–496.
- [7] L.Y. Chen, Z.X. Xu, H. Dai, S.T. Zhang, *J. Alloys Compd.* 497 (2010) 221–227.
- [8] M.P.S. de Almeida, K.L. Caiado, P.P.C. Sartoratto, D.O. Cintra e Silva, A.R. Pereira, P.C. Morais, *J. Alloys Compd.* 500 (2010) 149–152.
- [9] J. Kim, H.S. Kim, N. Lee, T. Kim, H. Kim, T. Yu, I.Ch. Song, W.K. Moon, T. Hyeon, *Angew. Chem. Int. Ed.* 47 (2008) 8438–8441.
- [10] D.L. Ma, T. Veres, L. Clime, F. Normandin, J.W. Guan, D. Kingston, B. Simard, *J. Phys. Chem. C* 111 (2007) 1999–2007.
- [11] M. Darbandi, R. Thomann, T. Nann, *Chem. Mater.* 17 (2005) 5720–5725.
- [12] D.K. Yi, S.S. Lee, G.C. Papaefthymiou, J.Y. Ying, *Chem. Mater.* 18 (2006) 614–619.
- [13] Y. Han, J. Jiang, S.S. Lee, J.Y. Ying, *Langmuir* 24 (2008) 5842–5848.
- [14] Y.H. Yang, M.Y. Gao, *Adv. Mater.* 17 (2005) 2354–2357.
- [15] J.P. Ge, Y.X. Hu, T.R. Zhang, T. Huynh, Y.D. Yin, *Langmuir* 24 (2008) 3671–3680.
- [16] J.P. Ge, Y.X. Hu, M. Biasini, W.P. Beyerermann, Y.D. Yin, *Angew. Chem. Int. Ed.* 46 (2007) 4342.
- [17] J.P. Ge, Y.X. Hu, Y.D. Yin, *Angew. Chem. Int. Ed.* 46 (2007) 7428.
- [18] J.P. Ge, Y.D. Yin, *Adv. Mater.* 20 (2008) 3485–3491.
- [19] R.P. Bagwe, C. Yang, L.R. Hilliard, W. Tan, *Langmuir* 20 (2004) 8336–8342.
- [20] C. Chang, H. Fogler, *Langmuir* 13 (1997) 3295–3307.
- [21] F. Arriagada, K. Osseo-Asare, *Colloids Surf.* 154 (1999) 311–326.
- [22] Y.P. Fang, W.S. Loc, W.G. Lu, J.Y. Fang, *Langmuir* 27 (2011) 14091–14095.
- [23] Y.H. Jin, S. Lohstreter, D.T. Pierce, J. Parisien, M. Wu, C. Hall, J.X. Zhao, *Chem. Mater.* 20 (2008) 4411–4419.
- [24] R. Koole, M.M. Schooneveld, J. Hilhorst, C.M. Donegá, D.C. Hart, A. Blaaderen, D. Vanmaekelbergh, A. Meijerink, *Chem. Mater.* 20 (2008) 2503–2512.
- [25] S.L. Tripp, S.V. Puzstay, A.E. Ribbe, A.J. Wei, *Am. Chem. Soc.* 124 (2002) 7914–7915.
- [26] M. Mikhaylova, D.K. Kim, N. Bobrysheva, M. Osmolowsky, V. Semenov, T. Tsakalagos, M. Muhammed, *Langmuir* 20 (2004) 2472–2477.
- [27] D.K. Yi, S.T. Selvan, S.S. Lee, G.C. Papaefthymiou, D. Kundaliva, J.Y. Ying, *J. Am. Chem. Soc.* 127 (2005) 4990–4991.
- [28] M. Stjerndahl, M. Andersson, H.E. Hall, D.M. Pajeroski, M.W. Meisel, R.S. Duran, *Langmuir* 24 (2008) 3532–3536.