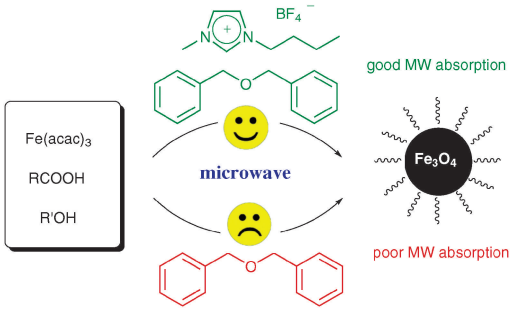

Q1 **Unique role of ionic liquid in microwave-assisted synthesis of monodisperse magnetite nanoparticles**

Hengyao Hu, Hao Yang, Peng Huang, Daxiang Cui,* Yanqing Peng, Jingchang Zhang, Fengyuan Lu, Jie Lian and Donglu Shi*

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Unique role of ionic liquid in microwave-assisted synthesis of monodisperse magnetite nanoparticles†

Hengyao Hu,[a] Hao Yang,[a] Peng Huang,[a] Daxiang Cui,*[a] Yanqing Peng,[b] Jingchang Zhang,[c] Fengyuan Lu,[d] Jie Lian[d] and Donglu Shi*[ae]

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A small amount of ionic liquid [bmim][BF_4] was found to be an efficient aid for microwave heating of nonpolar dibenzyl ether in high temperature solution-phase synthesis of monodisperse magnetite nanoparticles. It was found to act as both microwave absorber and assistant stabilizer in the reactive process and was recovered and reused in successive reactions.

The synthesis of magnetite nanoparticles has been extensively developed, both for the fundamental scientific interest and technological applications, including information storage, electronic devices, medical diagnostics, and drug delivery.[1] Dispersions of properly modified magnetite superparamagnetic nanoparticles can interact with an external magnetic field and be stationary in a specific area, facilitating resonance imaging for medical diagnosis[2] and cancer hyperthermia.[3] Hence, rapid and facile approaches for the production of superparamagnetic nanoparticles are highly desirable. Taking account of facileness and efficiency of the synthetic procedure at the same time, it has consistently been a challenge to produce monodisperse nanoparticles without a further size-sorting process.

In previous reports, several methods of synthesis of magnetite nanoparticles have been developed, among which a common procedure was the coprecipitation of Fe^{2+} and Fe^{3+} ions by a base, usually NaOH or $NH_3{\cdot}H_2O$, in aqueous media.[4] However, the coprecipitation procedure requires the pH of the solution to be carefully adjusted. Moreover, it is difficult to control the size distributions, especially for monodispersed nanoparticles of less than 20 nm. High temperature solution-phase decomposition of the iron precursors has been widely used to synthesize monodisperse iron oxide nanoparticles. For example, direct decomposition of $FeCup_3$,[5] or decomposition of $Fe(CO)_5$ followed by oxidation,[6] offers monodisperse γ-Fe_2O_3. As far as the synthesis of monodisperse Fe_3O_4 nanoparticles is concerned, one of the most important synthesis methods to make monodisperse Fe_3O_4 nanoparticles is the high temperature solution-phase reaction of iron(III) acetylacetonate and 1,2-hexadecanediol in diphenyl ether or dibenzyl ether in the presence of oleic acid and oleylamine.[7] By this route, a series of monodisperse magnetic ferrites, with the diameter of the particles tunable from 3 to 20 nm, could be obtained without a low-yield fractionation procedure. In the high-temperature solution-phase reactions, however, the temperature gradient in the reaction system should be eliminated as far as possible, so that all the nuclei of nanoparticles can form simultaneously according to the LaMer theory.[8] However, it is difficult to achieve a homogeneous temperature distribution by using conventional heating, especially in large-scale preparation. Furthermore, the reaction time at high temperature exceeds an hour, leading to higher depletion of resources and lower synthetic efficiency.

Numerous successful examples with remarkable rate-acceleration have been reported in the synthesis of nanoparticles using microwave irradiation as an alternative thermal energy source to conventional heating.[9] It has been demonstrated that the beneficial effects of microwave irradiation rely on the efficient energy transformation and uniform temperature distribution in the reaction vessel. It must be emphasized that the reaction medium must have an adequately high dielectric constant (ε) for microwave absorption. According to the literature,[7] dibenzyl ether (boiling point: 297 °C) is an appropriate solvent for the synthesis of monodisperse magnetite nanoparticles through a high temperature solution-phase reaction approach. Unfortunately, dibenzyl ether is not preferred for use in microwave-assisted high-temperature synthesis due to its substantially lower dielectric constant (ε = 3.86). Alternatively, room temperature ionic liquids (RTILs) are ideal candidates for making the nonpolar solvent suitable for microwave heating. RTILs have received a great deal of attention in recent years as novel solvent systems for a range of organic reactions due to their polar nature, and attractive properties such as incombustibility, non-volatility, unique phase behavior, and good solubility.[10] The ionic character of ionic liquids provides excellent coupling capability with microwave irradiation. It has been reported that ionic liquids could be used as a microwave-absorbing assistant in organic synthesis.[11] To combine the advantages of the high temperature solution-phase reaction approach and the

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microwave heating technique, ionic liquid [bmim][BF_4] was used as an aid for microwave heating of nonpolar dibenzyl ether in our experiments.

In this study, we report a facile, rapid and reproducible method to prepare monodisperse magnetite nanoparticles ($\sim$6 nm) by the reaction of Fe(acac)$_3$ and 1,2-hexadecanediol in dibenzyl ether in the presence of oleic acid and [bmim][BF_4] at 250 °C, where [bmim][BF_4] acted as both stabilizing agent and microwave absorbing assistant (Scheme 1, See ESI†).

Microwave irradiation can significantly increase the efficiency of nanomaterials synthesis. The efficient in-core volumetric heating with microwave irradiation can evidently reduce the chemical reaction time from hours to minutes. In a typical synthesis procedure, by controlled heating at 220 °C for 5 min and 250 °C for another 5 min under microwave irradiation, monodisperse Fe_3O_4 nanoparticles ($\sim$6 nm) were produced with a small amount of [bmim][BF_4] (IL: dibenzyl ether = 1 : 20 v/v) as stabilizing agent and microwave absorbing assistant. The morphology and structural information of as-synthesized Fe_3O_4 nanoparticles are shown in Fig. 1. Fig. 1a shows transmission electron microscopy (TEM) images of representative Fe_3O_4 nanoparticles. It can be seen that the particles have a narrow size distribution and the diameter is around 6 nm (size variation: ±3.6%, see ESI† Fig S1). Fig. 1b is a high resolution transmission electron microscopy (HRTEM) image of a single nanoparticle. The atomic lattice fringes indicate the nanoparticle to be single crystalline. The interfringe distance is measured to be 0.436 and 0.463 nm, which are close to the lattice spacing of the (021) planes (0.42 nm) and (020) planes (0.47 nm), respectively, in the cubic spinel Fe_3O_4 structure. The power X-ray diffraction (XRD) pattern also shows that the as-synthesized Fe_3O_4 nanoparticles have an inverse spinel type structure (Fig. 1c). The columns at the bottom of Fig. 1c and Fig. S2 (See ESI†) represent the characteristic peaks of the standard magnetite sample from a JCPDS file (89-3854) and maghemite, respectively. As shown in these figures, the position and relative intensity of all peaks can be assigned to the standard magnetite powder diffraction data. The average grain size of the particles calculated by Scherr formula from (220), (311), and (400) was approximately 6 nm which matches well with the TEM data, indicating that each individual Fe_3O_4 particle is single crystalline. These results suggest that the monodisperse Fe_3O_4 nanocrystals can be rapidly produced within 10 min by this approach and the synthetic efficiency of nanoparticles is significantly high since most of the reported Fe_3O_4 nanoparticles synthetic methods need more than an hour.

To investigate the influence of solvents on the synthetic reaction of Fe_3O_4 nanoparticles, Fe(acac)$_3$ was treated with 1,2-hexadecanediol in the presence of oleic acid at the same temperature with thermoregulation using pure [bmim][BF_4] and dibenzyl ether as solvents, respectively. The first model reaction was heated by microwave irradiation because ionic liquid is a good microwave absorber. For the model reaction in dibenzyl ether, an oil-bath was employed as thermal energy source since the dielectric constant of dibenzyl ether is lower (ε = 3.86) and it cannot be heated up to 220 °C by microwave irradiation. Both of these experiments resulted in a viscous red-brown mixture, which was difficult to purify and characterize. These results are consistent with the description in the literature,[12] which has emphasized the crucial role of oleylamine in the high temperature solution-phase decomposition approach to monodispersed magnetite nanoparticles.

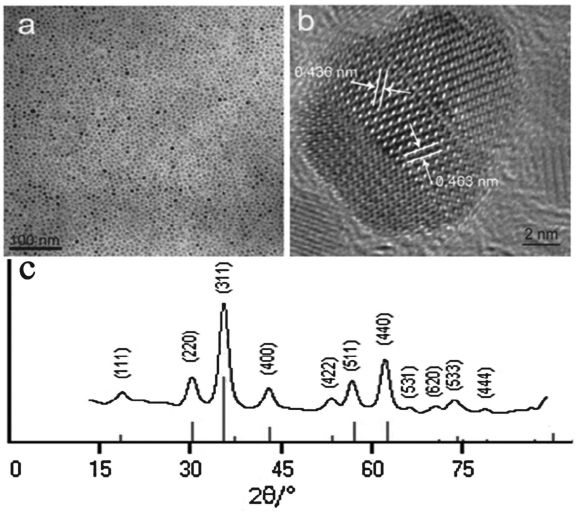

Fig. 1 (a) TEM image, (b) HRTEM image, and (c) XRD pattern of Fe_3O_4 nanoparticles synthesized by typical process and standard JCPDS file (89-3854) of magnetite.

Though it has been reported that numerous nanomaterials including iron oxide nanocrystals have been prepared by using RTILs as solvents or co-solvents,[13] few reports are on the synthesis of Fe_3O_4 nanoparticles. In our experiments using pure ionic liquid as solvent, Fe_3O_4 nanoparticles could also be obtained from the reaction mixture of [Fe(acac)$_3$] and 1,2-hexadecanediol in [bmim][BF_4] in the presence of oleic acid and oleylamine by controlled microwave heating at 220 °C and 250 °C each for 5 min, respectively. The reaction produces an upper black dispersion and a red-brown precipitation in the bottom of the vial. The precipitation was difficult to purify and characterize. The samples for the TEM and HRTEM images were obtained from the upper black dispersion. Fig. 2a shows a TEM image of the nanoparticles with a rather wide diameter distribution. Fig. 2b and c show HRTEM images of two single Fe_3O_4 nanoparticles with different zone axes. The atomic lattice fringes indicate that the Fe_3O_4 nanoparticle is single crystalline. As the upper black dispersion only contains a small amount of Fe_3O_4 nanoparticles, this method is not suitable to produce mass Fe_3O_4 nanoparticles because of the very low productivity.

Having established the practicability of this procedure, attention was next focused on the recycling of ionic liquid [bmim][BF_4] for environmental and economic reasons. After the resulting product was separated with a magnet, the remaining liquid was then added to diethyl ether to form a bi-phase mixture. The upper layer was decanted and the ionic layer was washed repeatedly with diethyl ether. The ionic liquid was then recovered after being dried *in vacuo* at 100 °C for 1 h. The same batch of ionic liquid could be reused more than six times in successive reactions without further purification, affording similar results in comparison with fresh ones. Fig. 2d shows the TEM image of Fe_3O_4 nanoparticles synthesized by the sixth recycled ionic liquid.

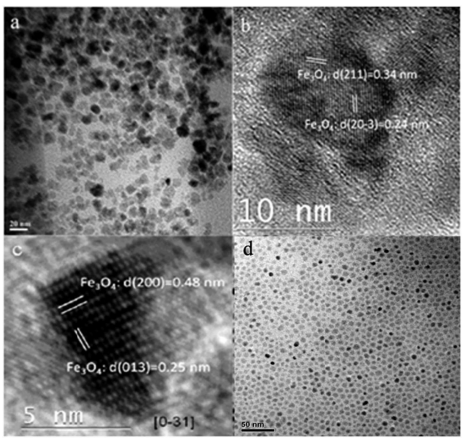

Fig. 2 (a) TEM image, (b) and (c) HRTEM images of Fe_3O_4 nanoparticles synthesized in pure [bmim][BF_4], (d) TEM image of Fe_3O_4 nanoparticles synthesized by typical process using the sixth recovered [bmim][BF_4].

An interesting observation in our experiments is that the traditionally used oleylamine could be replaced by ionic liquid. Namely, ionic liquids might play a dual role as microwave absorber and assistant stabilizer. Although the distinct effect of oleylamine as a partner of oleic acid in the synthesis of magnetite nanoparticles was reported several years ago, the unique stabilizing mechanism of oleylamine is still unclear nowadays. Because the ionic liquids could be recovered and reused in a simple fashion, the replacement of oleylamine with an ionic liquid is favourite from the viewpoints of environmental protection and economy, especially in large-scale synthesis.

Magnetic measurements of Fe_3O_4 nanoparticles were performed by using a Quantum design superconducting quantum interface device (SQUID) magnetometer (Model PPMS-9, USA). Fig. 3 shows the hysteresis loops of as-synthesized nanoparticles measured at both 10 K and 300 K, respectively. It can be seen that the particles are ferromagnetic with a coercivity of 503 Oe at 10 K (Fig. 3a). At room temperature, as shown in Fig. 3b, Fe_3O_4 nanoparticles exhibit superparamagnetic behavior with a saturation moment of 71.6 emu g^{-1}, which is lower than the value of commercial magnetic fine powder. This may be attributable to the surface spin canting of small magnetic nanoparticles.[14]

In conclusion, we have reported a rapid and facile process for preparing monodisperse magnetite nanoparticles by using a small amount of ionic liquids as microwave absorber and assistant stabilizer. The diameter of the particles is around 6 nm. The reaction time is as low as 10 min due to the high efficiency of microwave heating. The ionic liquid can be recovered and reused in successive reactions for many times. Hence this method might be suitable for economical mass-synthesis of monodisperse magnetite nanoparticles.

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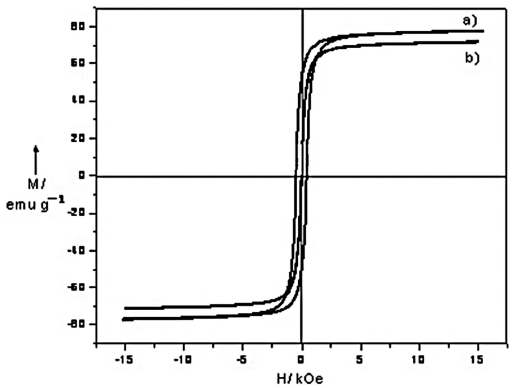

Fig. 3 Hysteresis loops of the Fe_3O_4 nanoparticles measured at (a) 10 K and (b) room temperature.

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