Synthesis of magnetite nanoparticles via a solvent-free thermal decomposition route
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Superparamagnetic nanoparticles have been widely applied in various bio-medical applications. To date, it is still a challenge to synthesize nanosized Fe3O4 particles with controlled size and distribution. In this paper, a novel solvent-free thermal decomposition method is reported for synthesizing Fe3O4 nanoparticles. Size and morphology of the nanoparticles are determined by TEM while the structure of the nanoparticles is identified by FTIR, XPS and TGA measurements. Magnetic properties of the obtained particles are determined using VSM and SQUID measurement. The particle size of the Fe3O4 can be tailored by adjusting either reaction temperature or time. When the reaction temperature is increased to 330 °C and the reaction time is extended to 4 h, the average particle size of the obtained nanoparticles is ~9 nm, while Ms value reaches ~76 emu/g. The as synthesized Fe3O4 nanoparticles show well-established superparamagnetic properties with the blocking temperature at around 100 K.

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1. Introduction
Superparamagnetic nanoparticles have been attracted a great attention in the bio-medical field such as magnetic separation, drug delivery, cancer hyperthermia and magnetic resonance imaging (MRI) enhancement [1–5]. Iron oxides particularly magnetite (Fe3O4) and maghemite (γ-Fe2O3) are very promising candidates in this field due to their nontoxicity and high chemical stability [6]. The major difficulty in the synthesis of ultrafine particles is to control the particle size and its distribution at the nanosized scale. This difficulty arises from the fact that the nanoparticles form aggregates and continuously grow to minimize the overall surface free energy. Therefore, the search for facile and flexible synthetic routes which are able to produce magnetic nanoparticles with the desired size, acceptable size distribution without particle aggregation is of extremely importance to realize the full potential of these materials in biomedicine.

Several synthesis methods have been designed and developed to fabricate superparamagnetic nanoparticles, including co-precipitation method, microemulsion method and thermal decomposition of organometallic compounds. Among these methods, the thermal decomposition method has been well accepted as a promising technique which is able to produce high-quality superparamagnetic magnetite nanoparticles [7,8]. Typically, this method involves several chemical compounds, including organometallic compound Fe(acac)3, high-boiling temperature solvent and stabilizing surfactants such as oleic acid and oleylamine. Nanosized magnetite particles are produced from the thermal decomposition of Fe(acac)3 in the solvent. The newly formed nanoparticles are then stabilized by binding with surfactants. An obvious disadvantage of this method is that the magnetite crystal size is hard to be adjusted due to the fact that the thermal decomposition temperature employed is limited by the boiling temperature of the selected solvent. In this paper, the interest arises from the possibility of synthesizing magnetite nanoparticles by using a solvent-free thermal decomposition method. In this solvent-free method, the thermal decomposition of Fe(acac)3 will be conducted in the presence of stabilizing surfactant only. Without the existence of solvent, the thermal decomposition temperature and reaction time can be varied easily and then the particle size and crystallinity of the magnetite nanoparticles can be tailored more effectively.

2. Experimental section
Absolute ethanol and hexane are used without purification. Oleylamine (OM, ≥ 70%), oleic acid (OA, 90%), iron(III) acetylacetonate (Fe(acac)3, 97%) are purchased from Sigma-Aldrich.

Magnetite nanoparticles are prepared following a modified thermal decomposition method. Generally, 2 mmol of Fe(acac)3 is dissolved in a 20 ml surfactant mixture of oleic acid and oleylamine and magnetically stirred under a flow of argon. The
solution is dehydrated at 120 °C for 1 h, and then quickly heated to a certain temperature and kept at this temperature for a certain time. The black solution is cooled to room temperature by removing the heat source. A total of 20 ml of ethanol is added into the solution and the precipitated particles are collected by centrifugation at 10,000 rpm followed by three times washing with ethanol. The as-prepared nanoparticles are dispersed in hexane. Particle size and morphology of the synthesized nanoparticles are investigated using transmission electron microscopy (TEM, JEOL 2010). The organic coating adsorbed to the particle surface is determined by Fourier transform infrared spectroscopy (FTIR, Varian 3100), X-ray photoelectron spectra (XPS, Kratos AXIS Ultra DLD), and thermogravimetric analysis (TGA, DMSE SHTQ600). Magnetic properties of the nanoparticles are studied by the superconducting quantum interference device (SQUID, Quantum Design, MPMS XL) and vibrating sample magnetometer (VSM, Lakeshore, Model 665) measurement.

3. Results and discussions

The first batch of magnetite nanoparticles are synthesized at the temperature of 300 °C with various reaction times of 0.5, 2 and 24 h, respectively. The TEM images of the resultant magnetite nanoparticles are shown in Fig. 1. When the reaction time is 0.5 h, the magnetite nanoparticles have average size around 5 nm in diameter with a very narrow size distribution, as shown in Fig. 1(a). The obtained magnetite nanoparticles are well dispersed, indicating that the surfactants have been attached on surface of the nanoparticles successfully. With increasing the reaction time
to 2 h, the average particle size is increased to \( \sim 6 \text{nm} \) slightly while the size distribution of the nanoparticles is kept narrow, as shown in Fig. 1(b). The average particle size of the magnetite can be further increased to \( \sim 11 \text{nm} \) when the reaction time is prolonged to 24 h. More interestingly, the size distribution of the magnetite nanoparticles synthesized at 330 \( ^\circ \text{C} \) for 2 h was recorded using SQUID under an applied field of 100 Oe between 5 and 300 K, as shown in Fig. 3(b). Both ZFC and FC curves coincide at high temperature and begin to separate when the temperature was decreased to \( \sim 100 \text{K} \). For the ZFC curve, a maximum was also shown at \( \sim 100 \text{K} \). It is generally assumed that the temperature at the ZFC maximum depends on the average particle size, while the temperature at which the FC and ZFC curves start to separate corresponds to the blocking temperature of the largest particles. The very small difference between these two temperatures suggests that the magnetite nanoparticles are quite uniform in size distribution and they are well dispersed. This statement is also supported by the TEM result of the sample, as shown in Fig. 1(c). The \( M(H) \) curves of the sample at 300 and 10 K are shown in inset of Fig. 3(b). Again, the zero coercivity and zero remanence indicating that the particles are superparamagnetic at the room temperature (300 K) while the particles exhibit ferromagnetic behavior at 10 K.

The chemically adsorbed organic coating on the particle surfaces can be further recognized by FT-IR and XPS measurements. Fig. 4 shows the FT-IR spectrum of the sample synthesized at 300 \( ^\circ \text{C} \) for 2 h. Generally, the absorption peaks below 800 cm\(^{-1}\) belong to the Fe\(_3\)O\(_4\) particles while the peaks above 800 cm\(^{-1}\) are due to the chemically adsorbed OA and OM coatings on the particle surfaces [9–11]. The broad band between 3600 and 3000 cm\(^{-1}\) centered at 3410 cm\(^{-1}\) is due to the O–H stretching vibration arising from surface adsorbed water. The peaks at 2926 and 2854 cm\(^{-1}\) are assigned to the C–H stretching vibration arising from the surface adsorbed OA and OM coatings. Further, the peaks at 1562 and 1440 cm\(^{-1}\) are due to the COO\(^{-}\) stretching vibration and the peak at 1411 cm\(^{-1}\) is due to the C–N bending vibration arising from the surface adsorbed OA and OM coatings, respectively. In addition, the strong absorption band at 584 cm\(^{-1}\) is due to the Fe–O stretching vibration of Fe\(_3\)O\(_4\) nanoparticles.

Fig. 5a depicts the wide scan XPS spectrum of the Fe\(_3\)O\(_4\) nanoparticles synthesized at 300 \( ^\circ \text{C} \) for 2 h. The corresponding deconvoluted O(1s) and C(1s) spectra are shown in Fig. 6b and c. The magnetite nanoparticles synthesized at 300 \( ^\circ \text{C} \) for 2 h was measured as 58 emu/g at 300 K. When the reaction time is increased to 24 h, the saturation magnetization is increased to be 71 emu/g. The saturation magnetization was further increased to be 76 emu/g when the reaction condition is adjusted to 330 \( ^\circ \text{C} \) for 4 h. The obvious increase in the saturation magnetization with reaction temperature and time is attributed to the increase in the crystallinity of the resultant magnetite nanoparticles. The temperature dependence of the zero-field cooled/field cooled (ZFC/FC) magnetization of the magnetite nanoparticles synthesized at 330 \( ^\circ \text{C} \) for 4 h was shown in Fig. 3(a) and (b), respectively. Hysteresis loop of the magnetite nanoparticles synthesized at 330 \( ^\circ \text{C} \) with various reaction times. At 300 K, all nanoparticles were characterized by using vibrating sample magnetometer and superconducting quantum interference device, as shown in Fig. 2 shows the TEM images of the magnetite nanoparticles synthesized at 330 \( ^\circ \text{C} \) with various reaction times. At 300 \( ^\circ \text{C} \), the average particle size can be adjusted from \( \sim 7 \) to \( \sim 10 \text{nm} \) when the reaction time is increased from 30 min to 4 h.

The magnetic properties of the obtained magnetite nanoparticles were characterized by using vibrating sample magnetometer and superconducting quantum interference device, as shown in Fig. 3(a) and (b), respectively. Hysteresis loop of the samples is registered at room temperature of 300 K as the magnetic field is cycled between –2 and 2 kOe. At 300 K, all samples exhibited superparamagnetic characteristics, including zero coercivity and remanence. The saturation magnetization of the magnetite nanoparticles synthesized at 300 \( ^\circ \text{C} \) for 2 h was measured as 58 emu/g at 300 K. When the reaction time is increased to 24 h, the saturation magnetization is increased to be 71 emu/g. The saturation magnetization was further increased to be 76 emu/g when the reaction condition is adjusted to 330 \( ^\circ \text{C} \) for 4 h. The obvious increase in the saturation magnetization with reaction temperature and time is attributed to the increase in the crystallinity of the resultant magnetite nanoparticles. The temperature dependence of the zero-field cooled/field cooled (ZFC/FC) magnetization of the magnetite nanoparticles synthesized at 330 \( ^\circ \text{C} \) for 4 h was recorded using SQUID under an applied field of 100 Oe between 5 and 300 K, as shown in Fig. 3(b). Both ZFC and FC curves coincide at high temperature and begin to separate when the temperature was decreased to \( \sim 100 \text{K} \). For the ZFC curve, a maximum was also shown at \( \sim 100 \text{K} \). It is generally assumed that the temperature at the ZFC maximum depends on the average particle size, while the temperature at which the FC and ZFC curves start to separate corresponds to the blocking temperature of the largest particles. The very small difference between these two temperatures suggests that the magnetite nanoparticles are quite uniform in size distribution and they are well dispersed. This statement is also supported by the TEM result of the sample, as shown in Fig. 1(c). The \( M(H) \) curves of the sample at 300 and 10 K are shown in inset of Fig. 3(b). Again, the zero coercivity and zero remanence indicating that the particles are superparamagnetic at the room temperature (300 K) while the particles exhibit ferromagnetic behavior at 10 K.

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respectively. The O(1s) peak components at about 531.4, 532.4 and 533.9 eV are assigned for the O–H, C=O and C–O bond, while the C(1s) peak components at about 285.3, 286.6, 288.9 and 289.4 eV are assigned for the C–C/C–H, C–N, C=O and C–O bond, respectively, arising from surface adsorbed OA and OM coatings and water [11–15]. In addition, the Fe(3p3/2), O(1s), Fe(2p3/2) and Fe(2p1/2) peak components at around 55.2, 530.2, 710.8 and 724.4 eV are attributed to the Fe–O bonds [11,12]. The XPS results further confirm the absorption of the OA and OM on the surface of the Fe3O4 nanoparticles.

Fig. 6 shows the TGA curve of nanoparticles representing a two-stage weight loss in the temperature ranges 25–200 °C and 200–800 °C. The first slight amount of weight loss is due to the evaporation of water and the second major weight loss is due to the decomposition of chemically adsorbed organic coating from the particle surface. It is estimated from the TGA result that the amount of the absorbing surfactants on the surface of the Fe3O4 nanoparticles is ~6 wt%.

Fig. 7 shows a photograph of the dispersion of the obtained Fe3O4 nanoparticles in an organic solvent and illustrates the magnetic manipulation ability. When an external magnetic field is placed beside the glass vial, the whole solution is attracted by the magnet, suggesting a stable ferrofluid has been successfully formed. There is no agglomeration formed in the obtained ferrofluid.

4. Conclusions

In summary, a novel solvent-free thermal decomposition method has been developed to synthesize high-quality Fe3O4 nanoparticles. Reaction temperature of this method can be easily adjusted due to the absence of solvent. By using this method, the Ms value of the synthesized Fe3O4 nanoparticles can reach 76 emu/g, while the superparamagnetic property of the Fe3O4 nanoparticles is well retained. The obtained Fe3O4 nanoparticles can be well dispersed in organic solvent and form stable ferrofluid.

References