A step-heating procedure for the synthesis of high-quality FePt nanostars†

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A step-heating procedure was used to synthesize high quality FePt nanostars by confined decomposition of $Fe(acac)_2$ and reduction of $Pt(acac)_2$.

Chemical prepared FePt nanoparticles have generated great interest recently because of their ease of synthesis, chemical stability, and potential applications in information storage,¹ high performance permanent magnets² and catalysis.³ The surfactants surrounding each FePt nanoparticle can be replaced by other bifunctional stabilizers, rendering the particle water soluble and suitable for bio-applications, such as site-specifc biomolecule attachment, magnetic field-assisted bioseparation, etc.⁴ Furthermore, monodisperse nanoparticles with controlled sizes or shapes are of key importance because their properties depend strongly on the particle size and shape. In the past years, rapid advances have been made in the ability to synthesize matter at the nano-scale with sufficient degree of control over the material shape and morphology.5 By using small nanocrystals as seeds, a two-step procedure was adopted to synthesize nanomaterials with different shape, such as nanorods and cubic nanocrystals. For example, using tetrahedral platinum nanocrystals as seeds, a new shape of Pt nanostar was prepared.⁶ Anisotropic growth of platinum nano-multipods has also been reported by Xia and coworkers, manipulating the reduction kinetics of platinum precursors.7 For FePt nanoparticles, to date, most of the previous researches have focused on the synthesis of FePt nanocrystals with spherical, rodshape⁸ and cubic⁹ structures by using different stabilizers or synthetic procedures. Only very recently, Ung et al.10 have developed a systematic study on the shape growth of different metallic alloys, where other morphologies of FePt have been described.

Here, a step-heating procedure is presented for synthesizing in one pot monodispersed FePt nanostars by confined decomposition of Fe(acac)₂ and reduction of Pt(acac)₂ in benzyl ether. Usually, solvent and ligand selection plays a key role in controlling the shape of the FePt nanocrystal. In this study, the results have demonstrated that the heating procedure can also cause a significant change in particle shape. With a slow step-heating rate, FePt nanostars, but not FePt nanorods or spherical nanoparticles would be prepared.

Furthermore, water soluble FePt nanostars have been prepared by exchanging oleic acid in hexane to 22-mercapto[2,5,8,11tetraoxadocosan]-1-oic acid (HS-C₁₁-TEG-COOH, Fig. S2 \dagger) in water by ligand exchange reaction (Fig. S3 \dagger).

In a typical synthetic process of FePt nanostars, 0.25 mmol $Pt(acac)_2$ was mixed with 20 ml benzyl ether in a 50 ml flask at room temperature under continuous stirring. Once completely dissolved, 0.25 mmol Fe(acac)_2 was added, and the temperature was raised to 120 °C to remove water under vacuum for 30 min. Then, the solution was bubbled with Ar for another 30 min. Then 5 mmol (about 1.6 ml) of oleic acid was injected and 5 min later, 15 mmol (about 7.1 ml) oleylamine was also injected, the last one acting also as a mild reducing agent. The mixture was heated to 270 °C with a heating rate of 15 °C per 5 min, and the reaction continued for 1 h before it was cooled down to room temperature. FePt nanostars were precipitated and washed three times with ethanol. The precipitate was re-dispersed in 10 ml hexane with 0.01 ml oleic acid and oleylamine, respectively.

Fig. 1a shows a TEM image of a FePt nanostar synthesized with a heating rate of 15 °C per 5 min. It can be observed that assynthesized particle is nanostar shaped, which is formed by connecting several short arms of FePt particles. As shown in Fig. 1 and S4[†], FePt nanostars are well dispersed in hexane, and there are few aggregates. For FePt nanostars, the size is about 10-12 nm, the armwidth of the nanostar is 2-5 nm. As reported previously, with different time intervals of injection of the surfactants, FePt particle shape can be controlled to form spherical, rod and cubic nanoparticles.7b We have observed that FePt nanoparticles shape can also be influenced by the heating rate. A slow step-heating rate benefits the formation of FePt nanostars, whereas direct heating to 270 °C provides mainly anisotropic shaped FePt nanoparticles (Fig. S5†). Experiments further demonstrate that slow heating rates are decisive for the growth of the nanostars. With a much slower heating rate of 10 °C per 10 min, FePt nanostars have also been prepared; the size is almost the same as the FePt nanostars synthesized with a faster heating rate, such as 15 °C per 5 min. FePt nanostars were also obtained (Fig. 1b) by incubating the precursory solution first at low



Fig. 1 TEM images of FePt nanostars synthesized (a) with a heating rate of 15 °C per 5 min; and (b) by incubating the solution at 70 °C for one night, and then raising the temperature to 270 °C with a heating rate of 10 °C min⁻¹; for both samples, the reaction time is 1 h. Insert, amplification of TEM images.

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[†] Electronic supplementary information (ESI) available: Chemicals, ligand exchange reaction, synthesis of anisotropic shape FePt nanocrystals, synthesis of HS-C₁₁-TEG-COOH, TEM and STEM images of FePt nanostars, EDX spectra of FePt nanostars and XRD pattern of water soluble nanoparticles (Fig. S1–S10). See DOI: 10.1039/b909022n

temperature for one night and then raising the temperature to 270 °C with a heating rate of 10 °C min⁻¹. Under these experimental conditions, the FePt nanostars formed are similar to those formed in the previous conditions, the size of FePt nanostar being 15–18 nm and the width of the arms 5–7 nm.

As a control experiment, the whole heating process was carried out in the absence of Fe reagent, then only spherical Pt nanoparticles were obtained (Fig. S6†). We can conclude that Fe(II) species alter the growth of Pt-rich initial nuclei into branched morphologies. On the other hand, the TEM image of an aliquot taken at 240 °C (1 min) and purified magnetically shows a heterogeneous sample where nanostars and spherical particles are observed (Fig. S7†). Probably the spherical particles are Fe based nanoparticles obtained by partial decomposition of Fe(acac)₂ at temperature < 240 °C. Finally, the slow heating process (10 °C per 10 min or 15 °C per 5 min) from 240 to 270 °C allows the complete diffusion of Fe conserving the branched nanostructure to obtain fcc FePt nanostars. More efforts will be made to elucidate deeply the mechanism of nanostar formation.

In Fig. 2, we present results obtained for XRD measurements from hexane soluble FePt nanostars. The XRD pattern shows that as-synthetised nanocrystals posses a chemically dissordered fcc crystaline structure. An estimation of the crystalline domain size from the full width at half maximum (FWHM) of the most intense peak (111) and the peak (220) was performed using the Debye–Scherrer formula, and indicates the average size of the crystallites as close to 4.5 (111) and 4.4 (220) nm, respectively. These values are slightly smaller than the corresponding dimensions of the nanocrystal arms length as determined by TEM.

By ligand-exchange followed by magnetic sorting, water soluble FePt nanostars have been prepared (Fig. S3[†]). Thiol molecule binds weakly to iron oxide or iron; but the bond between thiol and Pt is stronger than that between oleic acid (or oleylamine) and Pt. Thus, the by-products of free iron oxide or iron particles during the synthesis of FePt nanostars, can not be transferred into the water phase. In this study, HS-C₁₁-TEG-COOH (S2[†]) has been used as a water soluble surfactant to transfer FePt particles from hexane into water. In fact, after ligand exchange, the hexane solution is very clear (Fig. S3[†]), which demonstrates that few iron oxide or iron particles are presented in the final solution of FePt nanoparticles. Furthermore, with magnetic sorting, the free Pt particles can be removed from the thiol capped FePt particle aqueous solution.



Fig. 2 XRD spectra of hexane soluble FePt nanostars.

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Fig. 3a, S8a† and S8b† show TEM images and a STEM image of particles dispersed in water. Multi-armed and well dispersed particles can be observed. Compared with the image shown in Fig. 1a, there is no change in the shape or size of particles after ligand exchange and magnetic sorting. EDX analysis (Fig. 3b, Fig. S9†, Table S9) showed a 1 : 1 molar ratio of Fe and Pt for the nanostars. In the corresponding HRTEM image of FePt nanostars (Fig. 3c), a good cubic *Fm3m* crystalline structure is observed. Most nanostar particles grow along (111) and (200) directions and their corresponding lattice distances of (111) and (200) are 0.20790 and 0.18000 nm, and for Pt *Fm3m* crystal, their corresponding values are 0.22650 and 0.19616 nm, respectively. Iron oxide and iron impurities in hexane and water soluble nanostars are present as <1% in accordance with XRD data (Fig. 2, Fig. S10†).

The magnetic properties of water soluble FePt nanostars were examined and were in accordance with the chemically disordered fcc structure of FePt, with low magnetic anisotropy. The saturation magnetization, coercivity, and susceptibility are determined from SQUID measurements. Fig. 4a shows hysteresis loops of as-synthesized FePt nanostars measured at 300 K. It can be noted that the FePt nanostars mainly display superparamagnetic properties with a very slight remanence of 0.2 emu g⁻¹ and a low coercivity of 32 Oe at room temperature. The temperature dependence of magnetization of FePt nanostars was measured with zero-field cooling (ZFC) and field cooling (FC) procedures. Fig. 4b shows the plot of magnetization (*M*) versus temperature (*T*) for FePt nanostars with a measuring field of 100 Oe between 5 and 300 K (Fig. 4b). The blocking $T_{\rm b}$ observed in the ZFC curve is 24 K. This value is below the usual



Fig. 3 TEM (a), EDX pattern (b) and HRTEM (c) images of FePt nanostars dispersed in water.



Fig. 4 (a) Magnetization *versus* applied field curve measured at 300 K; (b) temperature dependence of field-cooled (FC) and zero-field-cooled (ZFC) magnetization of FePt nanostars at H = 100 Oe.



Fig. 5 FTIR spectra of FePt nanostars in hexane (black) and water (red).

values for spherical FePt nanoparticles of comparable sizes.⁸ In general, the magnetic properties are highly dependent not only on the size but also on the shape of nanoparticles.¹⁰ The decrease in blocking temperature may be attributed to a decrease in dipolar interactions between magnetic nanoparticles.

In the FTIR spectra (Fig. 5) the characteristic peaks of oleic acid¹¹ (near 2854 and 2924 cm⁻¹) disappear after the ligand exchange, which demonstrates that oleic acid is removed from the FePt nanostar surface. The strong peak at ~1700 cm⁻¹ in spectrum (a) corresponds to the COOH group of ligand HS-C₁₁-TEG-COOH on the FePt surface.

In summary, with a step-heating procedure, high-quality FePt nanostars were synthesized by confined decomposition of $Fe(acac)_2$ and reduction of $Pt(acac)_2$ in benzyl ether. With a slower step-heating rate than 15 °C per 5 min, FePt nanostar can also be synthesized. Water soluble FePt nanostars were prepared by ligand exchange for its potential bio- and chemical applications. Furthermore, the magnetic properties of as- synthesized FePt nanostars were investigated in this paper.

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