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One-step solvothermal approach for preparing soft magnetic hydrophilic PFR coated Fe_3O_4 nanocrystals

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ABSTRACT

The hydrophilic phenol formaldehyde resin coated Fe_3O_4 nanocrystals are prepared via a novel one-step solvothermal approach at 160 °C for 6–9 h without inert gas protection. Water–glycol mixture is used as solvent in common air surrounding. $FeSO_4·7H_2O$, hexamethylenetetramine and phenol are used as resource materials without any others additives or surfactants. The transmission electronic microscope images show the samples are composed of sphere-like particles with sizes about 10–20 nm. The X-ray diffraction data indicate cube-phase Fe_3O_4 nanocrystals are obtained at given conditions. Fourier transform infrared spectra further reveal the samples are consisted of Fe_3O_4 and PFR. Without modified pH and added surfactants, the solubility of the obtained sample is over 1% in water, which is far more than its solubility in toluene. Room-temperature hysteresis loop indicate that the as-obtained nano-crystals possess soft magnetic properties with high saturated mass magnetization (50.6 emu/g) and negligible coercivity.

1. Introduction

Water-soluble soft magnetic or superparamagnetic iron oxide nanocrystals have received wide attention for constructing stable colloid in water solvent [1]. It is benefit to prepare high dispersive and stabile eco-friendly nano-fluid and apply in many fields including biomedical [2], environment [3], magnetic fluid [4]. Up to now, a few of effective solution-phase approaches, typically including co-precipitation methods [5], precipitation-oxidation routes [6], pyrolysis reactions [7,8], or solvothermal/hydrothermal processes [9], have been accomplished for preparing various magnetic iron oxide nanoparticles. The mixture of Fe^{3+} and Fe^{2+} or iron organic compounds are commonly used as iron resource and the hydrophobic Fe_3O_4 nanoparticles are often obtained via the most of above methods. However, the methods are restrained by precisely regulating ratio of two kinds of iron ion resource and high cost of organic ion. Furthermore, for making water-based nano magnetic fluid, the post-processing steps are generally required to transfer the hydrophobic product obtained by the above approaches into the hydrophilic one. Unfortunately, the above methods confront major difficulties on how to facilely transfer the product from oil phase to water phase and keep their dispersive stability in water [10]. Additionally, these methods are almost all performed in inert protective gases for preventing the objective product transformed into Fe_2O_3, so these approaches cannot be applicable to prepare Fe_3O_4 nanomaterials in common atmosphere condition.

For obtaining high hydrophilic Fe_3O_4 nanocrystals via a facile method in usual air setting, we attempt to utilize alcohol–water solvothermal route developed previously for preparing Co_3O_4 and V_4O_7 nanocrystals [11,12]. Here, we firstly demonstrate the one-step solvothermal approach for preparing hydrophilic PFR coated Fe_3O_4 nanoparticles with uniform sizes. In the process, the $FeSO_4·7H_2O$ as single iron precursor reacts with hexamethylenetetramine (HMT), phenol in glycol–water mixed solvent at 160 °C for 6 h without inert gas protection. The major challenge is upon how to control the amount of glycol for forming Fe_3O_4 nanocrystals in the system, because glycol can inhibit the formation of trivalent iron due to its proper reducibility. The low-molecular-weight (LMW) phenol formaldehyde resins (PFR) is an ideal coating agent due to its sufficient –OH groups and three dimensional multi-pored molecular structure. Meanwhile, PFR can be facilely synthesized via the reaction between phenol and formaldehyde in the similar hydrothermal system [13].

Specifically, the as-obtained Fe_3O_4 nanocrystals with narrow size in range of 10–20 nm possess excellent soft magnetic properties with high saturated mass magnetization (Ms) and negligible coercivity (Hc) and retentivity (Mr) at room temperature. So the as-synthesized magnetite nanomaterials can be as an ideal candi-

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date for many applications concerned with water-based dispersion medium, such as magnetic biomedical, efficient bio-separation, and highly stable magnetic water-based nanofluid. The sources materials used in this process are ordinary, simple, inexpensive and eco-acceptable agents, and this approach is preformed in common air. Therefore, compared to reported approaches, this method is particularly valuable to provide a facile, environmentally and economically preferable alternative approach for preparation of organic polymer coated inorganic hybrid nanomaterials.

2. Experimental

$FeSO_4 \cdot 7H_2O$, hexamethylenetetramine (HMT), phenol and glycol, which were analytical grade, were purchased from Shanghai chemical reagent Ltd., and were used without further purification. The deionized water is self-produced with the electric conductivity round 5 μS.

2.1. Synthesized process

The typical reaction is carried out in a 100 ml capacity Teflon-lined stainless-steel autoclave and the procedures are briefly summarized as follows: Firstly, 1.0 mmol $FeSO_4 \cdot 7H_2O$, 60 ml glycol, 20 ml water 0.025 ml phenol and 0.125 mmol HMT are poured into the autoclave in turn and completely mixed by an ultrasonic instrument. Secondly, the autoclave is sealed and maintained at 160 °C for 6 h in a digital-controlled constant temperature oven, after that the autoclave is cooled to room-temperature naturally. Thirdly, the obtained precipitate is centrifuged and rinsed thoroughly with de-ionized water and absolute ethanol several times in turn. Finally, the as-obtained black sample is dried by a vacuum freeze drying (VFD) instrument for storage and further characterization. The yield of Fe_3O_4 product is beyond 95%.

2.2. Characterized method and instruments

The crystal phase of products are characterized by X-ray powder diffraction (XRD, Rigaku D/MaxgA, Japan) equipped with graphite monochromatized Cu Kα radiation (λ = 1.54056 Å). The XRD patterns are acquired in a 2θ range from 5° to 70° at scanning rate of $0.02° s^{-1}$. The cell lattice constants of samples are calculated and corrected by MDI Jade (5.0 Edition) software. Fourier transform infrared spectra (4000–400 cm^{-1}) are recorded by a Nicolet 5DX FTIR spectrometer equipped with a TGS/PE detector and a silicon beam splitter with 1 cm^{-1} resolution. The micro-morphologies and nanostructure of the as-synthesized products are inspected by transmission electron microscopy (TEM, Hitachi, H800EM, Japan) affiliated a selected area electron diffraction (SAED) at an accelerating voltage of 200 kV. Samples were prepared by dripping sonicated particle suspension on a carbon coated Cu grid for TEM study. The room-temperature M–H curves of typical samples are obtained by vibrating sample magnetometer (VSM, Lake Shore 735VSM, USA) in the range from −8000 Oe to 8000 Oe.

3. Results and discussion

TEM images shown in Fig. 1 indicates the micro-morphology and crystalline status of a sample obtained via the solvothermal approach at the above-mentioned conditions. Fig. 1A indicates that the product is consisted of the nanoparticles with narrow size distribution in the range 10–20 nm. The high magnification micro-image displayed in Fig. 1B further confirms the size and morphology of the nanoparticles. The image shows nanoparticles mainly sphere-like shape, and the surfaces of nanoparticles is coated some material because some film-like matter is found at the interconnections among nanoparticles. Due to the magnetic properties resulting in shifting nanoparticles, the HRTEM image of the samples cannot be obtained. So the thick coated layer of the nanoparticles is not confirmed. The SAED pattern of the typical nanoparticle marked in Fig. 1B is shown in Fig. 1C, it suggests that the particles can be indexed as cube phase crystal structure, because the spatial arrangement of the spots in the SAED pattern reveals the set of lattice planes derived from a single cube crystal with its [0 1 1] direction being oriented toward the direction of the electron beam. The circle diffraction pattern should be attributed to interference came from others same crystal-phase nanoparticles covered by the electron beam.

XRD pattern and FTIR spectrum shown in Fig. 2 are used to further demonstrate the crystal structure and the ingredient of the sample, respectively. Fig. 2a reveals the sample belong to cube phase, because all diffraction peaks are easily indexed as cube phase Fe_3O_4 given in JCPDS (65-3107) with lattice constants as 8.383(9) Å except of a peak marked by "*". The signed peak is attributed to trace hexagonal phase α-Fe_2O_3 formed in the procedures. The FTIR spectrum demonstrates characteristic absorbance bands of some groups contained in the samples. The mainly absorbance bands can be divided into four parts including 560–600 cm^{-1}, 1000–1650 cm^{-1}, 2850–3000 cm^{-1}, and 3200–3600 cm^{-1}. The absorbance peak of Fe–O group is mostly shown in firstly part, the peak at 578 cm^{-1} belongs to Fe_3O_4 characteristic absorbance, so the sample includes Fe_3O_4. Some PFR is confirmed in the sample due to its characteristic peaks appeared in the 1000–1650 cm^{-1}, 2850–3000 cm^{-1}, and 3200–3600 cm^{-1}. Among them, the vibrated absorbance bands of OH group appear in region of 3200–3600 cm^{-1} and 1600–1650 cm^{-1}; and C–H vibrated absorbance bands of benzene ring and methylene present in the range of 1000–1600 cm^{-1} and 2850–3000 cm^{-1}. On the other hand, for water show similar absorbance band to OH, tiny H_2O is also contained in the samples by absorbance process [14]. It suggests Fe_3O_4 and PFR are to two mainly components of the product.

The solubility of sample in water and toluene are inspected and some typical photos are shown in Fig. 3. The samples reveal excellent hydrophilic property. In the absence of any regulators or additives, the solubility of the samples obtained at 160 °C for 6 h is over 1.5 mg/ml. In contrast, only trace amounts of samples can be dispersed into toluene. Their corresponding photos are shown in Fig. 3a. The dispersed Fe_3O_4 nanoparticles can be facilely separated from solution by magnets shown in Fig. 3b.

For investigating the effect of some reaction factors and the formation mechanism of PFR coated Fe_3O_4 nanoparticles, a series of experiments are preformed at various conditions. The typical XRD patterns of samples with its given conditions are shown in supporting data (Fig. S1 and S2). They suggest that temperature, time, and components of solvent have all significant influence for preparing product. When the solvothermal systems are done at different temperature, although PFR coated the mixture of Fe_3O_4 and α-Fe_2O_3 nanoparticles is obtained, the relative amount and crystallization of Fe_3O_4 increase with temperature in the system. The reaction time is advantage to obtain PFR coated Fe_3O_4 nanoparticles, the peak of α-Fe_2O_3 is faded away with the time increase, meanwhile, the intensity of wide-peak between 20° and 30° is reinforced due to the increase of producing PFR. With the reaction for 9 h, the pure PFR coated Fe_3O_4 nanocomposites are obtained. If the system is demonstrated in other solvents, the variety of products is prepared including the mixture of α-Fe_2O_3 and FeO(OH) in pure ethanol solvent, the α-Fe_2O_3 in water, the PFR coated Fe_3O_4 nanocomposites in glycol–ethanol (1:3) mixed solvent, the PFR coated the mixture of Fe_3O_4 and α-Fe_2O_3 in glycol–water (1:1) mixed solvent, the mixture of Fe_3O_4 and α-Fe_2O_3 in glycol–water (3:1) mixed solvent without phenol, and a uncertain materials in pure glycol. Compared to the patterns obtained in different solvent, it evidently confirms that the compositions of solvent are a crucial factor for preparing Fe_3O_4 nanoparticles. In water and ethanol system, Fe^{2+} ion all transforms into Fe^{3+} and forms α-Fe_2O_3 and/or alkali type ferric oxide. When pure glycol is used as solvent, the XRD pattern shows the sample is amorphous product. Contrarily, if glycol is used as a part of solvent, the product contained Fe_3O_4 nanoparticle can be obtained. So in the synthesis approach, the glycol is an indispensable component of solvent. Compared with water and ethanol, ethylene glycol, the highest reductive, can inhibit the transformation from divalent iron into trivalent iron. The typical TEM images of as-obtained samples are shown in Fig. 4. The TEM images reveal various morphologies nanoparticles are fabricated via different conditions mainly including nanorods, and different crystallized degree nanoparticles. In particular, the flower-like

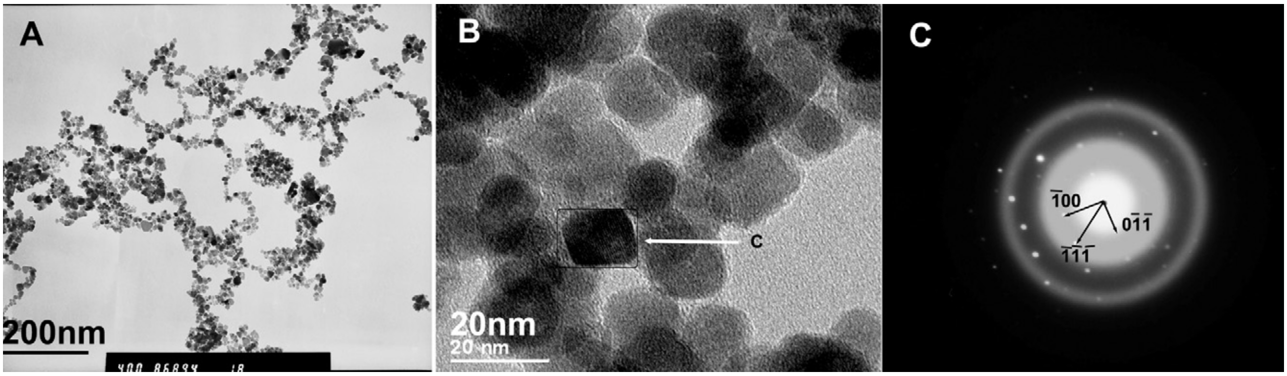


Fig. 1. The TEM images and SAED pattern of the typical sample obtained via solvothermal route with V_{glycol}:V_{water} as 3:1 at 160 °C for 6 h.

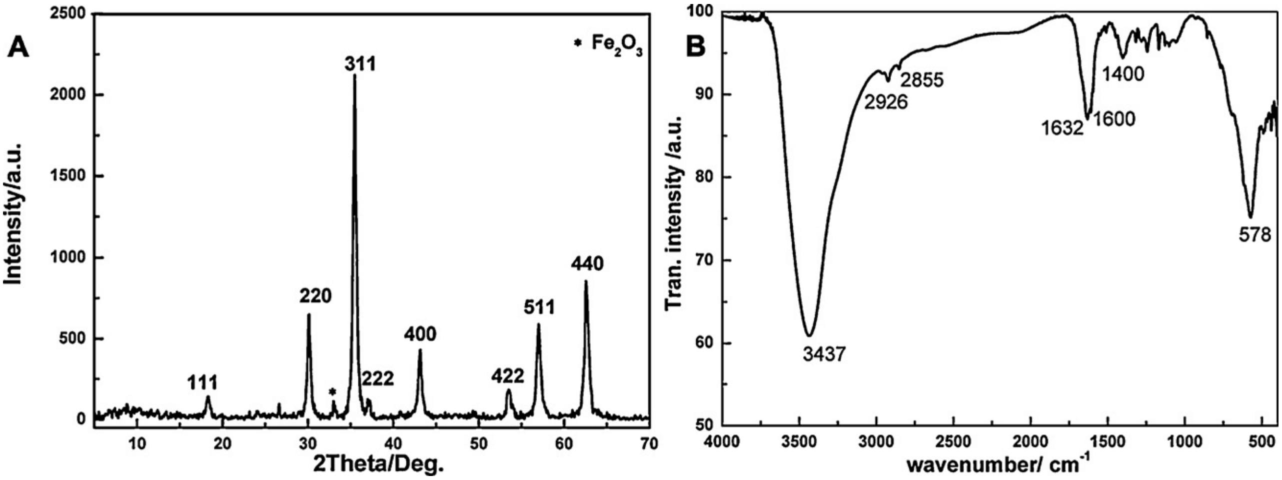


Fig. 2. The XRD pattern (a) and FTIR spectrum (b) of the typical sample obtained via the solvothermal route with V_{glycol}:V_{water} as 3:1 at 160 °C for 6 h.

nanomaterials self-assembled by nanorods is facilely obtained in pure water solvent system; and the size of nanoparticles is directly proportional to reaction times. The size of nanoparticles is decreasing with increasing the concentration of glycol except the samples obtained in pure glycol solvent, it suggest high concentration of glycol is favor to obtain small size mono-dispersive nanoparticles. The PFR synthesized by phenol and formaldehyde is conducive to control the growth of iron oxide nanoparticles, for the as-obtained nanoparticles show wide size distribution without phenol.

Based on above experimental results and some references, some reactions procedures had to be performed in the synthesis system shown in Scheme 1. HMT is an ideal resource for formaldehyde and ammonia, because it is easily hydrolyzed in warm aqueous solution (see Eq. (1)), so it makes the solution in alkaline environment. In the hydrothermal system, the Fe^{2+} ion may firstly reacts with ammonium hydroxide to form iron (II) hydroxide at initial stage (see Eq. (2)). In alkaline hydrothermal system, the redox potential of Fe^{3+}/Fe^{2+} is low enough to oxidize Fe^{2+} into Fe^{3+} by the dissolved O_2 and water in the solution, so $Fe(OH)_3$ can be successfully formed from $Fe(OH)_2$. And then $Fe(OH)_3$ is changed into Fe_2O_3 and FeO(OH) via dehydration performed in pure water system. However, when the mixture of glycol and water contained a small amount O_2 is used as solvent, the transformation from bivalent to trivalent iron is inhibited by glycol due to its suitable

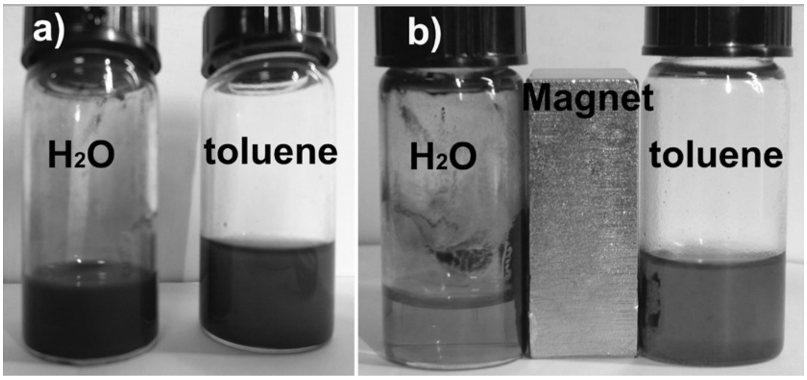


Fig. 3. The photos show the dispersibility and separated ability of the obtained PFR coated Fe_3O_4 nanoparticles in water and toluene. (a) Without magnetic field, and (b) under magnetic field.

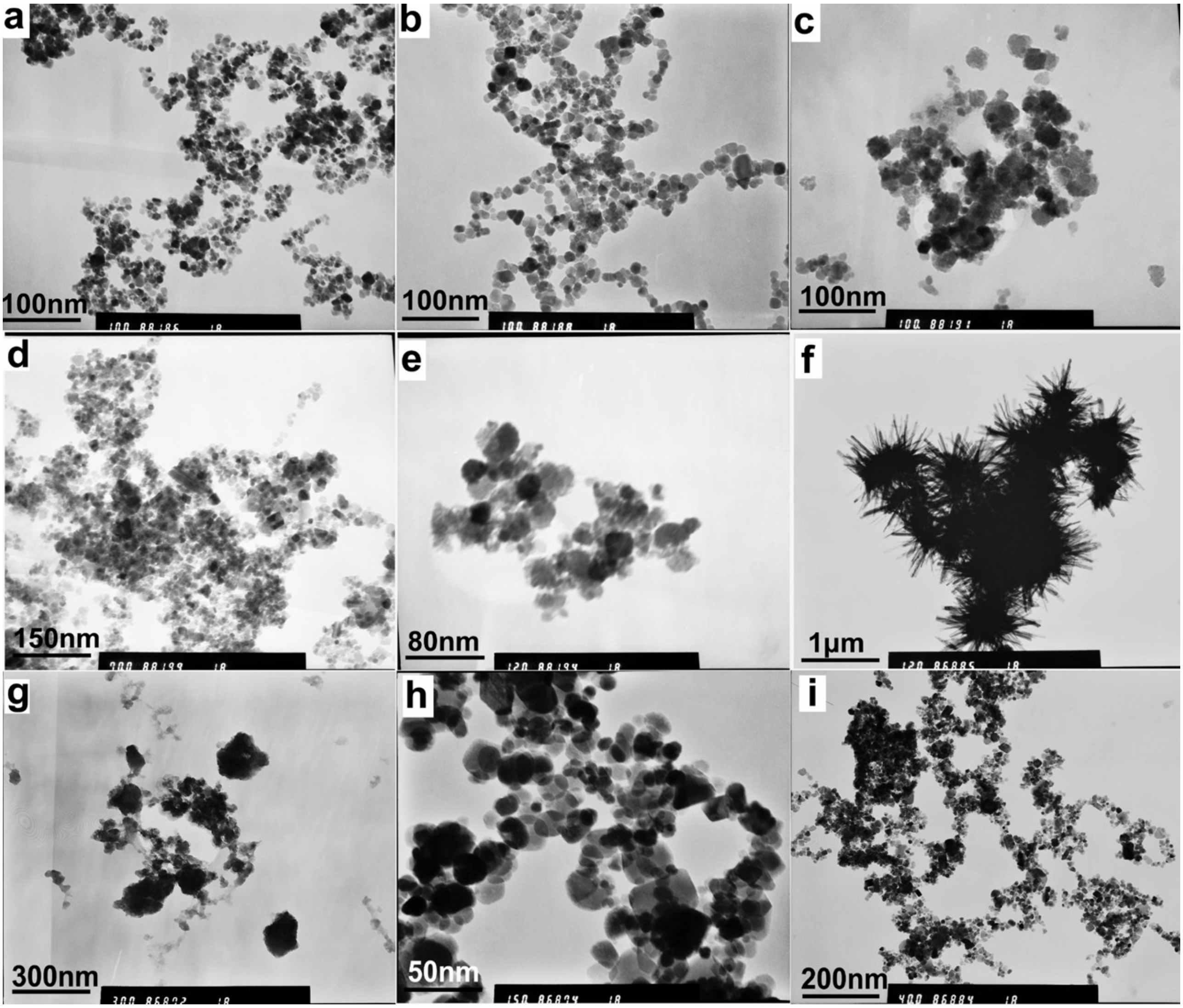
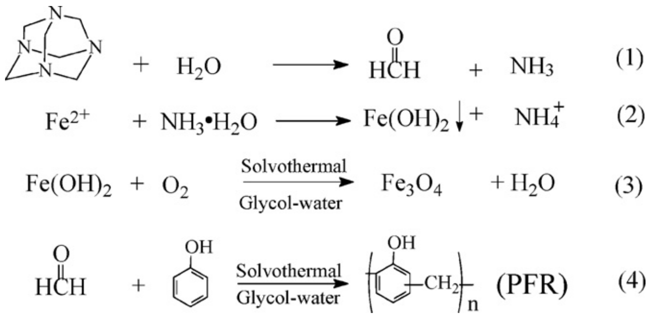


Fig. 4. (a) 3 h, V_{glycol}:V_{water} = 3:1, (b) 9 h, V_{glycol}:V_{water} = 3:1, (c) 120 °C, V_{glycol}:V_{water} = 3:1, (d) 180 °C, V_{glycol}:V_{water} = 3:1, (e) no-phenol 160 °C, 6 h, (f) pure water,160 °C, 6 h, (g) pure glycol, 160 °C, 6 h, (h) V_{glycol}:V_{water} = 1:1, 160 °C, 6 h, and (i) adding PEG 4000, V_{glycol}:V_{water} = 3:1, 160 °C, 6 h.

reducing capacity, so only a part of divalent iron turns into trivalent iron, which results in forming ferriferrous oxide contained two kinds iron ion (shown in Eq. (3)). The amount of O_2 is an important factor for successfully obtaining Fe_3O_4 nanomaterial. If the solvent is not pretreated via ultrasonic processing to decrease the loading of O_2, Fe_2O_3 nanoparticles are more appeared in the obtained samples. During the procedures, the phenol is polymerized into PFR with formaldehyde (see Eq. (4)). PFR is absorbed on the surface of the nanoparticles because iron oxides nanograins are more preferentially formed than it. With reaction time lasted, the thick of shell is obviously increasing due to accumulation amount of PFR.



Scheme 1. The reaction equations in the solvothermal process.

The room-temperature magnetization curve (Fig. 5) of the obtained PFR and Fe_3O_4 composited nanoparticles is measured by cycling the field between −8000 Oe and 8000 Oe. The nanocomposite displays soft magnetic characteristic with relatively high saturated mass magnetization (Ms) value of 50.6 emu/g. The hysteresis loop shows almost negligible coercivity (Hc) and retentivity (Mr) value of 34.4 Oe and 3.42 emu/g, respectively. The small Hc value properties should be attributed to PFR coated on the surface of Fe_3O_4, which hampers the movement of magnetic core in the external magnetic field. With the reaction time prolonged to 9 h, the saturated mass magnetization, coercivity value and retentivity (Mr) value all increase to 59.8 emu/g, 35.5 Oe and 4.35emu/g, respectively (see Fig. S3). The obviously higher magnetization should be attributed to the improved crystallites of Fe_3O_4 nanostructure. On the other hand, PFR is more synthesized and inhibits the growth of nano-grains size and results into its coercivity and retentivity just a slight increasing. The magnetic of Fe_3O_4 nanomaterials could be controlled by adjustment of reaction time and coated content of PFR polymer.

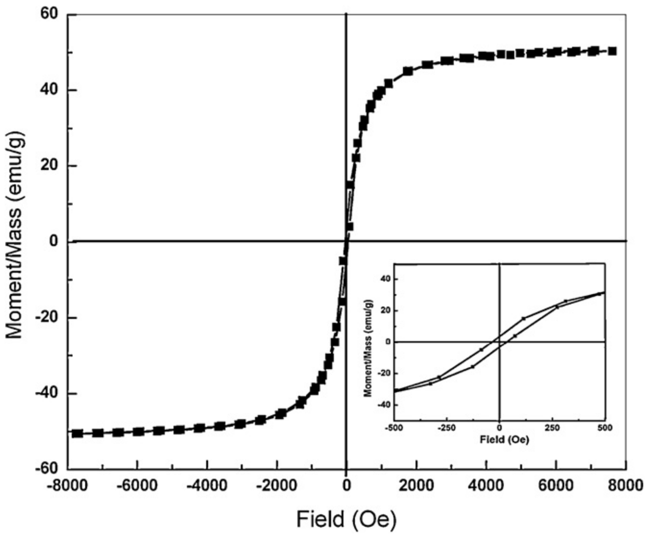


Fig. 5. The magnetization curve of the PFR coated Fe_3O_4 nanoparticles obtained at 160 °C for 6 h. The inset shows the data around zero fields with an expanded scale ranging from −500 Oe to 500 Oe.

4. Conclusion

In summary, a novel one-step solvothermal process is achieved to synthesize PFR coated Fe_3O_4 nanocrystals with a narrow size distribution in the range of 10–20 nm, high crystallinity and high water solubility, in the presence of common air. Some simple, inexpensive, eco-friendly materials are utilized as precursors without any surfactants assistance or precise control of pH value of system, which replaces expensive, toxic, and complex reagents used in solvothermal. Furthermore, the high hydrophily is accomplished by using a low-molecular-weight PFR as capping agent, which is produced via polymerization of phenol and formaldehyde. The water-soluble soft magnetic PFR coated Fe_3O_4 nanocrystals can be conveniently produced in one step in the presence of air. The one-step solvothermal approach is tried to apply for preparing other PFR coated nanomaterial.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jallcom.2011.05.008.

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