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Synthesis of magnetic nanostructures: Shape tuning by the addition of a polymer at low temperature

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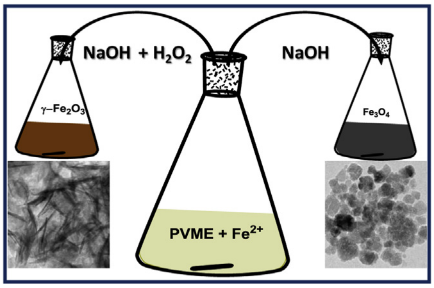
HIGHLIGHTS

- Low-temperature method for iron oxide (Fe_3O_4 and γ-Fe_2O_3) nanostructures is described.
- Shape of iron oxide nanostructures can be tuned by varying the reaction parameter.
- Needle- and flower-shaped iron oxide nanostructures are obtained with polymer.
- HRTEM analysis shows iron oxide nanostructures are crystalline in nature.
- Both γ-Fe_2O_3 and Fe_3O_4 nanostructures shows superparamagnetic behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

We report a simple method for shape-controlled synthesis of iron oxide spinels such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) nanostructures using a thermoresponsive polymer poly(vinyl methyl ether) (PVME) by the alkaline hydrolysis of iron salt at low temperature (20 °C). Microscopic analysis confirmed the formation of needle- and flower-shaped iron oxide nanostructures depending on reaction conditions. High-resolution transmission electron microscopic analysis of the needle- and flower-shaped nanostructures as well as their corresponding selected area electron diffraction patterns revealed that the formed nanostructures are crystalline in nature. X-ray diffraction study reveals the formation of well-crystalline pure Fe_3O_4 and γ-Fe_2O_3 nanostructures under different reaction conditions. Fourier transform Infra-red spectroscopic analysis confirms the adsorption of PVME on the surface of iron oxide nanostructures. Finally, the magnetic properties of γ-Fe_2O_3 and Fe_3O_4 nanostructures is studied that shows the superparamagnetic behavior of the formed iron oxide nanostructures.

1. Introduction

In recent years, magnetic nanomaterials, especially iron oxide spinels such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) stand out for their novel tunable properties [1] and their wide use in catalysis [2], magnetic recording [3], high performance electromagnetic as well as environmental remediation and biomedical applications, such as magnetic resonance imaging (MRI) [4–8], cell and protein separation [9,10] and drug delivery [11,12]. Most of these properties are largely dependent on size and shape [13]. As a result, researchers are focusing more interest in the development of synthetic means to control the size and shape of iron oxide nanoparticles (NPs) [14–22] and thereby control magnetic behavior

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[23], and chemical reactivity [24]. These most commonly used synthetic techniques include vapor solid growth techniques [25], thermal decomposition [15,23], template based synthesis methods [26–28] and sol–gel process [29]. The vapor technique usually requires special equipments and high temperatures. Compared to these high temperature vapor techniques, wet chemical methods are simple, low cost and can be performed at low temperatures even at room temperature. Moreover, simple modifications of the reaction parameters such as temperature, monomer concentration and reaction time serve as a simple way to tune particle size, shape, and therefore magnetic properties of the nanoparticles. To date, various wet chemical methods such as coprecipitation [30], reverse micelle method [31], ultrasound irradiation [32], hydrothermal method [18,21], and thermal decomposition of organometallic compounds [23] have been adopted to synthesize size- and shape-tunable magnetic nanoparticles. However, the problem is that the naked Fe_3O_4/Fe_2O_3 NPs are very sensitive to oxidation for their high chemical reactivity and prone to aggregate for their large ratio of surface area to volume and thus result in poor magnetism and dispersibility [1,33–36]. Those problems limit their further applications. One of the main approaches to overcome these limitations is to protect these naked Fe_3O_4/Fe_2O_3 magnetic NPs with polymers [26–28,34,37,38], long–chain amines [18,21,39], and long–chain acids [15,39] etc. These protective layers not only prevent the iron oxide NPs from aggregation, but also provide a useful platform for further functionalization [28]. Among these coating materials, use of polymers have been received more attention for their capping properties that not only stabilize the particles but also play in most cases a unique role in controlling the size or shape of the formed iron oxide NPs [40].

In this context, poly(vinyl methyl ether) (PVME) is an important thermoresponsive polymer soluble both in polar and nonpolar solvents. PVME is also soluble in water below it's lower critical solution temperature (~34 °C) [41]. But above LCST, PVME forms microscopic precipitates which very much resembles with the denaturation of proteins [42]. Our group have extensively used these properties of the PVME polymer to synthesize thermoresponsive gold NPs [41], amphoteric zinc oxide NPs [43] and solvent adaptable monometallic nickel, cobalt and bimetallic nickel–cobalt alloy [44] NPs in different solvents. In each case, PVME plays an important role during the growth and formation of these nanomaterials and controlled their size and shape. Those results inspire us to use PVME polymer as a capping-cum-shape directing agent to control the size and shape of the iron oxide nanoparticles.

In this manuscript, we report the synthesis of different shaped γ-Fe_2O_3 and Fe_3O_4 NPs in aqueous medium using Fe^{2+} ions, NaOH, poly(vinyl methyl ether) (PVME) and with/without the addition of H_2O_2 at 20 °C. X-ray diffraction studies showed that the formed iron oxide nanoparticles are pure and crystalline in nature. Microscopic measurement showed that we were able to synthesize needle- and flower-shaped iron oxide nanostructures with controllable sizes. The adsorption of PVME on the surface of the iron oxide NPs were confirmed by the FTIR spectroscopic measurements. The magnetic properties of the synthesized iron oxide nanostructures were obtained from direct current (dc) magnetometry measurements.

2. Materials and methods

2.1. Materials

Poly(vinyl methyl ether) (PVME) was obtained from Sigma–Aldrich, USA as 50 wt% aqueous solution and was purified prior to use. NaOH and H_2O_2 (30% aqueous solution) were purchased from E–Merck, India. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) was purchased from Loba Chemicals, India. All the chemicals were used as received. All solutions were prepared in triple distilled water.

2.2. Purification of poly(vinyl methyl ether) (PVME)

The as-received 50 wt% aqueous PVME solution was diluted to 10 wt% with double distilled water and was heated to 50 °C to precipitate out. The supernatant was discarded and the residual solid was re-dissolved in cold water. This process was repeated twice and finally the isolated PVME was dried in a vacuum oven at 60 °C for 2 days.

2.3. Synthesis of γ-Fe_2O_3 nanoparticles

The synthesis of γ-Fe_2O_3 NPs involves the alkaline hydrolysis of ferrous salt in the presence of PVME followed by the addition of hydrogen peroxide. In a typical synthesis, 10.0 mL of an aqueous PVME solution (5 wt%) was taken in a conical flask maintained at 20 °C with constant magnetic stirring. The overall concentration of PVME in the reaction mixture was 1 wt%. To this stirring solution, 25.0 mL of an aqueous $FeSO_4$ solution (0.1 M) was added and the reaction mixture was homogenized for 30 min via magnetic stirring. 15.0 mL of an aqueous NaOH solution (0.5 M) was then added drop-wise to the above reaction mixture to make it alkaline (pH of the reaction mixture ~12–12.5). Immediately, 1.0 mL of H_2O_2 (30%) solution was added to the resulted greenish suspension, and the stirring was further continued for 3 h. This resultant brown product was isolated from the suspension by centrifugation at 9500× *g* for 15 min and was labeled as FeO-1 (see Table 1 for the details of reaction recipe). The isolated brown mass was further purified from any trace of physically adsorbed PVME and un-reacted reactants by three cycles of washing, centrifugation and re-dispersion in cold water. Finally, the collected mass was dried under vacuum at 60 °C for 24 h. This dry powder samples were used for X-ray diffractometric, magnetometric and spectroscopic analysis and the alcoholic suspension of these samples was used for microscopic analysis.

We have also carried out two similar sets of reaction by varying the concentration of PVME to study the effect of concentration of PVME on the morphology or size of the formed NPs keeping the other reaction parameters same as mentioned earlier for sample FeO-1. The purified and dried samples are designated as FeO-2 and FeO-3 and the details are provided in Table 1.

2.4. Synthesis of Fe_3O_4 nanoparticles

The synthesis of Fe_3O_4 nanoparticles was carried out by following the same procedure as discussed above for γ-Fe_2O_3 except the addition of hydrogen peroxide. In a typical synthesis, 15.0 mL of an aqueous PVME solution (5 wt%) was taken in a conical

Table 1
Synthesis parameters and morphology of γ-Fe_2O_3 nanostructures prepared at 20 °C. All the samples are prepared in water.

Sample ID	PVME (wt%)	[$FeSO_4$] (M)	[NaOH] (M)	H_2O_2 (M)	Composition	Morphology	Yield (%)
FeO-1	1.0	0.05	0.15	0.2	γ-Fe_2O_3	Needle	~100
FeO-2	1.5	0.05	0.15	0.2	γ-Fe_2O_3	Needle	~100
FeO-3	0.5	0.05	0.15	0.2	γ-Fe_2O_3	Needle	~100