Modified chemical coprecipitation of magnetic magnetite nanoparticles using linear–dendritic copolymers

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ABSTRACT

In this investigation, magnetite nanoparticles (Fe₃O₄ NPs) with a diameter of 5–10 nm were synthesized by coprecipitation from an alkaline solution of ferrous/ferric mixed salt-solution in the presence of copolymers. In this process, linear–dendritic copolymers containing a linear poly(ethylene glycol) core and dendritic poly (citric acid) arms were used as the stabilizer. The Fe₃O₄ NPs were characterized by transmission electron microscopy, energy-dispersive spectra, X-ray powder diffraction, field emission scanning electron microscopy, Fourier transform infrared spectrometer, and vibrating sample magnetometer. Compared to classical coprecipitation, the results showed that uniform, ultrafine, nearly spherical, and high purity nano-magnetite particles with better magnetic properties could be prepared by this method.

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Introduction

Magnetic nanoparticles (NPs), especially magnetite (Fe₃O₄), can be widely used in science, technology, and healthcare in applications such as cell separation (1), microwave absorption (2), magnetic resonance imaging (MRI) techniques (3), recording materials (3), ferrofluids (4), biological sensing (5), bioactive molecule separation (3), catalysis (6–8), and magnetic targeted therapy (9). For future highly sensitive magnetic nanostructures and biological and pharmacological applications, Fe₃O₄ NPs with controlled size, shape, and a narrow size distribution are needed. Recently, research on the synthesis and application of Fe₃O₄ NPs in chemistry and pharmaceuticals has received particular attention (10). Several methods have been developed for the synthesis of magnetic Fe₃O₄ NPs, including chemical coprecipitation (10–14), the hydrothermal process (15), the solvothermal method (16), the sol–gel technique (17, 18), microemulsion (19, 20), etc. Among these, the chemical coprecipitation is considered as the simplest, most economical, and most efficient method (21).

However, the classical coprecipitation method has certain limitations, including insufficient dispersion, broad and uncontrollable particle size distribution, difficulty of mass production, and phase control of NPs. Therefore, achieving uniform-sized Fe₃O₄ particles and high magnetic response is hard; especially when the Fe₃O₄ particle size should be in the nanoscale (12). To overcome these limitations, several coprecipitation techniques were used such as interfacial coprecipitation (12), ultrasonic coprecipitation (11), microwave coprecipitation (22), mechanochemical coprecipitation (13), and coprecipitation with fast stirring (14). Furthermore, other research has utilized surfactants (23), macromolecules (24), or dilute acids (25) to improve the dispersibility of Fe₃O₄ NPs in water. Although several methods have been reported for the synthesis of magnetic NPs, the...
development of a template and stabilizer in water for the synthesis of Fe$_3$O$_4$ NPs is an active, ongoing research area and thus, there is potential for further improvement toward greener conditions, uniform-sized Fe$_3$O$_4$ particles and high magnetic response.

Linear–dendritic copolymers are hybrid macromolecules containing linear polymers and dendrimers (26, 27). Poly (citric acid) (PCA)–poly (ethylene glycol) (PEG)–PCA copolymers containing hyperbranched dendritic citric acid parts (with a large number of OH functional groups in their structures) and linear PEG as flexible part (which enhances the solubility) could be effective as a template and stabilizer in water for the synthesis of NPs (28, 29). In this study, PCA–PEG–PCA dendritic macromolecules have been used to synthesize magnetic NPs. Therefore, this work elucidates the decreased particle size and increased saturation magnetization of Fe$_3$O$_4$ NPs prepared via a modified coprecipitation reaction by PCA–PEG–PCA copolymers.

**Experimental**

**Chemical and apparatus**

Chemical reagents were purchased from the Merck, Aldrich, and Sigma Chemical Companies. Fourier transform infrared spectrometer (FT-IR) spectra were recorded with KBr pellets on a Shimadzu Perkin-Elmer 550 spectrometer. The magnetic measurements of samples were obtained using a vibrating sample magnetometer (VSM) (4 inch, NDKF, Kishan, Iran) at room temperature. Morphological characteristics of the nanostructures were analyzed using field emission scanning electron microscopy (FE-SEM) (MAIA) and transmission electron microscopy (TEM) (Zeiss EM10C). Nanostructures were characterized using a Holland Philips Xpert X-ray diffraction (XRD) diffractometer (CuK$_\alpha$, radiation, $\lambda = 0.154056$ nm), at a scanning speed of 2°/min from 10° to 100° (29).

**Procedure for preparation of Fe$_3$O$_4$ NPs by PCA–PEG–PCA**

PCA–PEG–PCA macromolecules (Mw \(\approx\) 2000) were prepared according to the reported method in literature (29). Copolymers were synthesized following the procedure shown in Scheme 1. Fe$_3$O$_4$ NPs were prepared via the Massart’s processes as a simple chemical coprecipitation technique (11) in the presence of PCA–PEG–PCA. Typically, 20 mmol of FeCl$_3$·6H$_2$O, 10 mmol of FeCl$_2$·4H$_2$O and 0.1 g of PCA–PEG–PCA were dissolved in 80 ml of distilled water in a three-necked bottom (250 ml) under Ar atmosphere for 1 h. Next, a certain amount of NH$_4$OH (28% (w/w)) was added into the solution within 30 min until the pH value was titrated to 11.0 under continuous Ar atmosphere bubbling. Once the NH$_4$OH solution was added into the reaction flask, the color of the mixture turned from orange to black immediately. The reaction mixture was rapidly stirred for 1 h. Then, the resultant black dispersion was heated to 85°C for 1 h. Fe$_3$O$_4$ NPs were isolated by magnetic decantation, exhaustively washed with double-distilled water until neutrality, and dried at 60°C overnight under vacuum tray drying.

**Results and discussion**

The chemical coprecipitation of Fe (III) and Fe (II) salts in alkaline solutions was used as a traditional method of preparing Fe$_3$O$_4$ NPs:

\[
\begin{align*}
\text{Fe}^{3+} + 3\text{OH}^- & \rightarrow \text{Fe(OH)}_3, \\
\text{Fe(OH)}_3 & \rightarrow \text{FeOOH} + \text{H}_2\text{O}, \\
\text{Fe}^{2+} + 2\text{OH}^- & \rightarrow \text{Fe(OH)}_2, \\
2\text{FeOOH} + \text{Fe(OH)}_2 & \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O}.
\end{align*}
\]

However, the Fe$_3$O$_4$ NPs synthesized by classical procedure shared some flaws and deficiencies such as poor dispersity, impurity of production, nonuniform particle size, and so on. To overcome these limitations, in this paper, the PCA–PEG–PCA copolymers were used to modify the classical coprecipitation technique to synthesize the uniform-sized Fe$_3$O$_4$ particles and high magnetic response of Fe$_3$O$_4$ NPs.

The proposed mechanism for the modified preparation of Fe$_3$O$_4$ NPs was shown in Scheme 2. In the first stage, the Fe$^{2+}$ and Fe$^{3+}$ ions and the carboxylic acid functional groups of PCA–PEG–PCA copolymers formed a complex structure. After the NH$_4$OH solution was added, carboxylic acid groups on the surface of...
PCA–PEG–PCA promoted the nucleation of Fe$_3$O$_4$ NPs. Because the PCA–PEG–PCA macromolecules acted as the support for Fe$_3$O$_4$ nucleation, the growth of NPs was hindered by the copolymers and the size of the Fe$_3$O$_4$ NPs was about 5–10 nm, which was smaller than the traditional method. The addition of the PCA–PEG–PCA with a hyperbranch structure during the reaction process provided steric repulsion to improve the quality of the dispersion of particles. These effects of polymeric stabilizers in the synthesis of metallic nanoparticle were also discussed in previous research. Thus, the PCA–PEG–PCA copolymers acted as templates and steric stabilizers that reduced the intrinsic particle size of Fe$_3$O$_4$ NPs and aggregation of particles.

The properties of Fe$_3$O$_4$ NPs with an average size of 5–10 nm were investigated. Figure 1(a) shows the FE-SEM image of Fe$_3$O$_4$ NPs prepared by modified coprecipitation. The average size of Fe$_3$O$_4$ NPs was approximately 10 nm, and the particles are spherical shaped, uniform, and monodispersed. Figure 1(b) shows a SEM image of magnetic NPs under classical conditions. It is worthwhile to note that the size distribution is 15–30 nm.

The magnetization curves of Fe$_3$O$_4$ NPs are shown in Figure 2. As demonstrated in Figure 2, magnetic performance of the modified NPs is better than NPs without modification. Because the remanence ($M_r$) value of unmodified Fe$_3$O$_4$ is about 1.25 emu/g; while, that of the modified Fe$_3$O$_4$ NPs is less than 0.65 emu/g that this could be attributed to the fact that, the NPs with modification were so small that they might be considered to have a single magnetic domain. From the magnetization curve, we can also see that the saturation magnetization ($M_s$) of the NPs increase from 62.76 to 66.54 emu/g when the sizes of Fe$_3$O$_4$ increase from...
15–30 to 5–10 nm, which can be attributed to the increase of crystallinity of the modified NPs.

Figure 3 presents the XRD powder diffraction patterns of the magnetic modified Fe$_3$O$_4$. The position and relative intensities of all peaks confirm well with the standard XRD pattern of Fe$_3$O$_4$ (JCPDS card No. 01-1111). The data for the Fe$_3$O$_4$ NPs at 2$\theta$ = 30.66, 36.06, 43.72, 54.22, 57.68, 63.18, 74.85 corresponded to (2 2 0), (3 1 1), (4 0 0), (3 3 1), (4 2 2), (5 1 1), and (5 3 1) respectively. The crystallographic parameters calculated using software provided by Panalytical company (Holland) are: $a = b = c = 8.3941$ Å, $\alpha = \beta = \gamma = 90.0000^\circ$, they are indexed to the crystalline cubic spinel structure of modified Fe$_3$O$_4$ NPs.

Elemental components of Fe$_3$O$_4$ are calculated from energy-dispersive spectra (EDS) in Figure 4. The elemental compositions of magnetic iron oxide particles are 24.90% and 75.10% for Fe and O, respectively. According to this analysis, it could be concluded Fe$_3$O$_4$ have been successfully synthesized.

Figure 5 shows the FT-IR spectrum of Fe$_3$O$_4$ NPs synthesized with PCA–PEG–PCA. This sample exhibits a strong absorption peak around 3417 cm$^{-1}$, corresponding to

Quantitative Results

| Elt | Line | Int  | Error | K    | Kr   | W%  | A%  | HConf | Cat# |
|-----|------|------|-------|------|------|-----|-----|-------|------|
| O   | Ka   | 683.7| 8.4769| 0.2019| 0.1775| 24.90| 53.64| 25.18  | 0.00 |
|     |      |      |       |      |      |     |     |       |      |
| Fe  | Ka   | 1555.2| 1.6069| 0.7981| 0.7020| 75.10| 46.36| 75.67  | 0.00 |
|     |      |      |       |      |      |     |     |       |      |
|     |      | 1.0000| 8.795 | 1.0000| 1.0000|     |     |       |      |

Figure 4. EDS of modified Fe$_3$O$_4$ NPs.
to the stretching mode of OH group adsorbed on the surface of the Fe₃O₄ NP while the peak appearing at approximately 1630 cm⁻¹ was associated with the bending vibration of the O–H group. These peaks were owing to the adsorbed water on the surface of Fe₃O₄. The peak at 574 cm⁻¹ corresponds to the Fe–O bond NPs (7, 8).

**Conclusion**

We have reported an efficient coprecipitation for the synthesis of Fe₃O₄ NPs in the presence of dendritic macromolecules as the stabilizer. The obtained iron oxide NPs can be promising as a potentially suitable magnetic support to be employed in different branches of magnetic technology with good biocompatibility, good economic aspects, and good magnetic quality.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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**Notes on Contributors**

**Zohre Zarnegar** received her BS (2002) in Pure Chemistry from University of Kashan (Iran). Next, she studied her MS (2008) in Organic Chemistry at the Lorestan University. She performed her MS research in the field of nanochemistry which included synthesis of novel dendrimers under the supervision of Prof. Mohsen Adeli. She obtained her PhD degree in Organic Chemistry at University of Kashan (2014) which included development of magnetic nanoparticles and their application in host-guest systems and some of the organic reactions under the supervision of Dr Javad Safari. She added a postdoctoral stage from the Iran Nanotechnology Initiative Council (INIC) in 2016.

**Javad Safari** was born in Kashan, Iran in 1965. He obtained his B.Sc. degree in Chemistry at the University of Kashan in 1989. He received his M.Sc and Ph.D. degrees in Organic Chemistry at the University of Isfahan in 1992 and 2002. He is teaching as associate professor of Chemistry at the University of Kashan. His research interests focus on heterocyclic chemistry, spectroscopy, catalysis and organic methodology.

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