Research articles

# Controllable preparation of iron nanostructures and their magnetic properties

Hongzhe Tang, Dong Han [*]

*Laboratoire International Associé, Beihang University, 100191 Beijing, PR China*
*Ecole Centrale de Pékin, Beihang University, 100191 Beijing, PR China*

A B S T R A C T

Iron nanostructures (chains and particles) were prepared by a simple reduction method. The effects of adding NaOH, PEG or PVP, changing $c(Fe^{2+})$ can lead to different results of microstructure on iron nanochains/nanoparticles. The directional controlled preparation was researched. Their magnetic properties at normal (300 K) and low (5 K) temperatures have been measured, and influences of $OH^-$, polymeric dispersant PEG/PVP, and $c(Fe^{2+})$ have been investigated in detail. The magnetic properties of nanochains/nanoparticles were studied by controllable microstructure through the adjustment of sort of dispersant and ferrous concentration, which can accomplish the fabrication in accordance with magnetism applications.

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## 1. Introduction

Because of its special properties and wide range applications [1–7], ferromagnetic nanostructured materials have attracted the attention and research passion of more and more studies in the past few years. Those excellent performances include high specific surface area, high coercive force, high saturation magnetization, superparamagnetism, and exchange bias effect, which are widely used in catalysis [8], data storage [9,10], therapy purposes [11,12], and spintronic device [13,14].

With the nanotechnology becoming well-considered, the study of controllable morphology and micro-performance of iron nanoparticles turns to increasingly more mature [15]. The nanochains materials, which are orderly formed by nanoparticles, are deemed to have original properties of particle system and wide applications in many areas [16,17]. Because of their strong anisotropism, the magnetic nanochains can improve the magnetic properties of nanoparticles. As the existence of exchange bias effect in ferrimagnetic nanoparticles system [18], chains structure formed by particles can maintain this kind of effect, and then further strengthen the coercive, which makes contributions to high density storage device, and overcomes the superparamagnetism to some extent [19].

The variety intrinsical magnetic properties are directly affected by the uncertainty of iron nanostructures [20,21,22]. In order to study the relationship between the morphology and the magnetic property, to achieve an optimal result, we need to adjust the microstructure, which includes size and arrangement of nanoparticles. A reduction reaction method [23], which is perhaps the simplest, adjustable and environment-friendly mode to obtain monodisperse, controllable size iron nanochains and nanoparticles, was used to study the morphology and magnetic properties.

In this paper, we used the reduction method with addition of dispersants to prepare iron magnetic nanochains and nanoparticles. Different controllable morphologies were obtained via specific dispersants and reactant concentrations. Then, magnetic properties (coercive force $H_C$, remanence $M_R$, saturation magnetization $M_S$, exchange bias field $H_{EB}$) at normal (300 K) and low (5 K) temperatures have been detailedly compared on the basis of their morphologies with respective preparations [24,25]. Finally we achieved different magnetic properties according to the nanostructure via the adjustable preparation.

## 2. Experimental section

### 2.1. Materials

The iron nanochains and nanoparticles were prepared by using commercially available reagents without further purification. $FeCl_2 4H_2O$ (AR, $M$ = 198.81 g mol$^{-1}$, Shantou, China), $NaBH_4$ (AR,

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* Corresponding author at: Laboratoire International Associé, Beihang University, 100191 Beijing, PR China.
*E-mail address:* handong@buaa.edu.cn (D. Han).

$M$ = 37.95 g mol$^{-1}$, Aldrich), NaOH (AR, $M$ = 40.00 g mol$^{-1}$, Beijing, China), PVP (AR, $M$ = 10,000–70,000, Guangdong, China), PEG (CP, $M$ = 1800–2200, Beijing, China), as well as ethanol, acetone, etc.

## 2.2. Fabrication

Iron nanochains and nanoparticles were synthesized by taking FeCl$_2$·4H$_2$O as the source of iron. NaBH$_4$ was used as the reducing agent for ferrous ion. NaBH$_4$ solution (0.05 mol L$^{-1}$) was respectively transferred into FeCl$_2$ solutions (0.005 mol L$^{-1}$ × $N$, '$N$' represents the different multiple of reagent) at room temperature. The mixed solution was then stirred by magnetic stirrer for 10 min. In order to study the role of dispersant, before the mixture, we added respectively different kinds of dispersant in ferrous solutions, as NaOH (wt% = 0.03 g L$^{-1}$), PVP and PEG (both wt% = 0.5 g L$^{-1}$). After the reaction, the black precipitation was obtained, which has been washed three times respectively with deionized water, absolute ethyl alcohol and acetone. Under the protection of nitrogen, the precipitation was dried in a vacuum drying oven at 400 K for 20 min.

## 2.3. Characterization

The crystalline structures of the iron nanostructure samples were investigated by X-ray diffraction (XRD, D/MAX2200pc, 40 kV, 40 mA, Japan). The morphologies of particles were observed by scanning electron microscopy (SEM, JSM7500, 10 kV, Japan). The magnetic properties were measured by Vibrating Sample Magnetometer (VSM7407, America) and SQUID Vibrating Sample Magnetometer (MPMS SQUID VSM, America).

## 3. Results and discussion

### 3.1. Morphology and microstructure of iron nanochains/nanoparticles

The X-ray diffraction pattern of the simples (none dispersant, addition of PVP, addition of PEG, addition of NaOH, respectively) is shown in Fig. 1A–D. Three major diffraction peaks at 44.64° 65.24° and 82.43° (standard: 44.76°, 65.16° 82.53°), which has been assigned to the (1 1 0), (2 0 0) and (2 1 1) planes of a cubic structure (JCPDS No. 05-0696), can be seen in each figure. Thus, the nanochains fabricated by reduction reaction method are considered to consist of iron chains/particles.
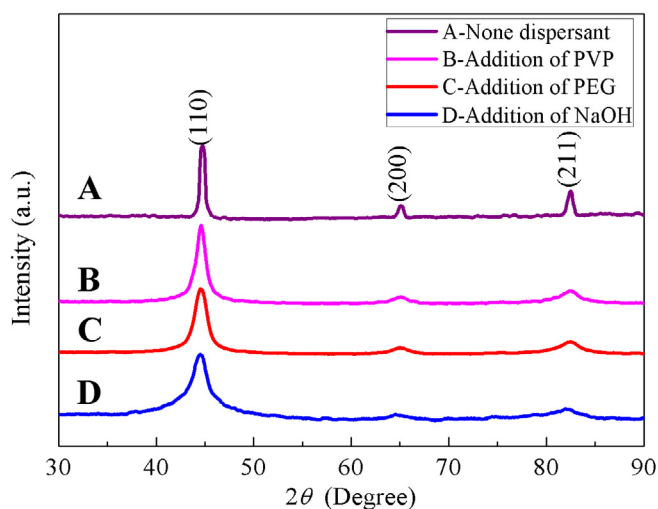


**Fig. 1.** XRD patterns of iron nanochains/nanoparticles.

Shown in Fig. 1, compared to three others, the peak width of α-Fe under NaOH treatment (pattern D) is wider, indicating that the iron atom has relatively low crystallinity, and the internal atomic arrangement is loosely to some extent. Its magnetic properties can be affected which will be discussed.

### 3.2. Influence of dispersant

The SEM images below indicate the microstructure of iron nanochains and nanoparticles which are influenced by diverse dispersants. Fig. 2A–D represents the results of dispersants (None dispersant, addition of NaOH, PEG, and PVP, respectively) in the condition with c(Fe$^{2+}$) = 0.015 mol L$^{-1}$.

None dispersant in the system, iron particles can spontaneously form a chain structure with average diameter 95 nm (shown in Figs. 2A and 3A). When the alkaline dispersant NaOH (0.03 g L$^{-1}$) is added, it presents a globular structure (in Fig. 2B). In the process of polymerization of iron atoms, a large number of OH$^-$ are adsorbed on the surface of iron particles.

According to previous studies, we have concluded that the surface roughness of iron particles can be affected by c(OH$^-$) [26]. If the concentration is deficient, the electrostatic attraction between the iron atom which has been reduced and the local ferrous ion in the surrounding liquid phase is not enough. In an unstable crystallization process, the iron particles are shriveled. If the concentration is superfluous, the iron atoms and ferrous ions in the liquid phase are reduced to a state of excessive electrostatic attraction. An excessive expansion of the iron particles is obtained.

In consideration of electric double layer theory, with an appropriate concentration of OH$^-$ (the ratio of c(Fe$^{2+}$) and c(OH$^-$) is 10: 1), the nanoparticles are fabricated with smooth surface, and the repulsive force between OH$^-$ leads to dispersion of particles. Those OH$^-$ can enhance isotropic and destroy the previous chains structure, which makes iron atoms gather in larger particles.

As shown in Fig. 2C, the organic dispersant PEG can reduce the size of the generated particles, and the nanochains are elongated. Each unit of PEG has its own hydroxyl, which can wrap up the iron atoms [27,28]. At the same time, the randomness of polymer PEG in the system can provide iron atoms with different existence environments, which enhances the anisotropism of iron atoms to form a chain-like structure. Due to the effect of the PEG chains and its regular distribution of hydroxyl groups, the agglomeration of iron atoms is hindered to some extent, and the diameter of the particles decreases.

PEG is a nonionic surfactant molecule. Although the presence of OH$^-$, it only exists at both ends of the chain molecule. Its adsorption on the particle surface can not only prevent the development of particle, but also play a role in connecting between two particles. The effect of PEG on iron particles can be attributed to the aggregation effect and steric hindrance effect. In the anhydrous state, PEG is usually serrated. However it has a zigzag shape under hydration and can be adsorbed on the surface of particle and bind forming polymer network. In the process of reaction, the continuing development of particle is prevented by the steric hindrance effect of PEG.

The addition of PVP increases particle size, shown in Fig. 3D. The ring structure of PVP strengthens the steric effect [29], which can raise the repulsion between iron particles. Meanwhile, the hydrogen bond is easily formed between the amide group and the hydroxyl group. The thickness of the adsorbed layer is increased, so that the diameter is enlarged.

In order to investigate the influence of dispersant on magnetic properties, the magnetization versus magnetic field (M-H) curves (c(Fe$^{2+}$) = 0.015 mol L$^{-1}$ fixed) with the addition of different dispersants are shown in Fig. 4A.