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Synthesis and characterization of magnetic nanometer pigment Fe_3O_4

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Abstract

In this paper, nanometer-sized magnetic pigment Fe_3O_4 was prepared by co-precipitation method. The forming mechanism of Fe_3O_4 was investigated and the relationship between the content of Fe^{2+} and the magnetism of Fe_3O_4 was also studied. The color character of Fe_3O_4 was measured and nanometer-sized magnetic pigments Fe_3O_4 were characterized by XRD, IR, TEM and VSM. The results show that the sample is well-proportioned in distribution and small in size (about 10 nm). The shape of the sample particles is spherical. Munsell marking is N1.28/. The specific saturation magnetization intensity is maximal, i.e. 84.03 A m^2 kg^{-1}, when the proportion of Fe^{2+} to Fe^{3+} is 1.6:2. On the other hand, it has certain superparamagnetic properties.

Keywords: Co-precipitation; Nanometer particle; Fe_3O_4; Spinel pigment; Magnetism; Synthesis

1. Introduction

Black pigment Fe_3O_4 is a compound oxide with a non-normal spinel structure which is not only used in the coating industry for qualified covering, coloration and light-resistance, but also widely in the construction industry due to its excellent alkali resistance [1]. Fe_3O_4, as magnetic pigment, also is one of the main materials used to produce copy black powder. Nowadays, Fe_3O_4 is used in more aspects due to the development of preparation technology of nanometer powders. At present, there are many applied reports about nanometer-sized Fe_3O_4 in many different fields such as magnetic absorbing materials [2], magnetic fluid [3] and catalysis [4]. However, the synthesis of nanometer powders with fine granularity, good dispersion and unified size and shapes is critical in the fabrication of nanometer materials. Therefore, the preparation of nanometer materials has attracted great attention and is being extensively studied [5].

Many methods for the preparation of nanoparticles have been reported in the literature such as solid state reactions [6], sol-gel [7], co-precipitation [8] and hydrothermal processes [9,10]. In this work, nanometer-sized powder particles of Fe_3O_4 were successfully synthesized using simple co-precipitation.

2. Experimental

2.1. Preparation of samples

$FeSO_4 \cdot 7H_2O$ and $FeCl_3 \cdot 6H_2O$ were weighed in the required molar proportion, 1:2. Then they were dissolved in deionized water and the mixed solution was obtained. The solution was heated in a water bath. The

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precipitation agent, NaOH (3 mol L^{-1}), was added to the solution with stirring, and the pH for the solution was adjusted to about 11. The reaction was allowed to proceed for 1 h at 70 °C with constant stirring. The precipitate was washed until free of chlorine ions, filtered, dried and ground, obtaining sample 1.

2.2. Change of the proportion of Fe^{2+} to Fe^{3+}

A series of samples were prepared by changing the proportion of Fe^{2+} to Fe^{3+}, which were 1.2:2, 1.4:2, 1.6:2, 1.8:2 and 2.0:2, respectively. The samples were named 2, 3, 4, 5 and 6 correspondingly.

2.3. Characterization of samples

The crystal phase structure of Fe_3O_4 was investigated using an X-ray diffractometer (XRD) (BDX-3300 made by Peking University Instrument Co., China).

An infrared spectroscope (IR) (FTS3000, made by Bio-Bad Exalbor Co., USA) was used to determine information about the structure of Fe_3O_4.

A Transmission Electron Microscope (TEM) (100CX-II made by JEOL, Tokyo, Japan) was used to characterize the Fe_3O_4 powders with respect to their particle size and shape.

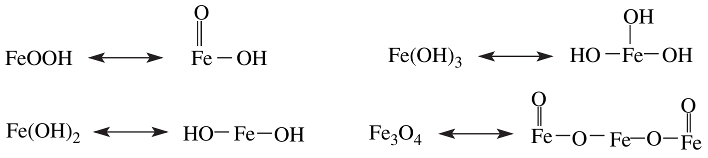
The color characteristics were measured using a JFY-PS color analysis apparatus and D65 illuminant (Tianjin Textile Industry Research Institute).

Magnetic properties were examined at room temperature using a vibrating sample magnetometer (VSM) (9600-1 made by LDJ, USA).

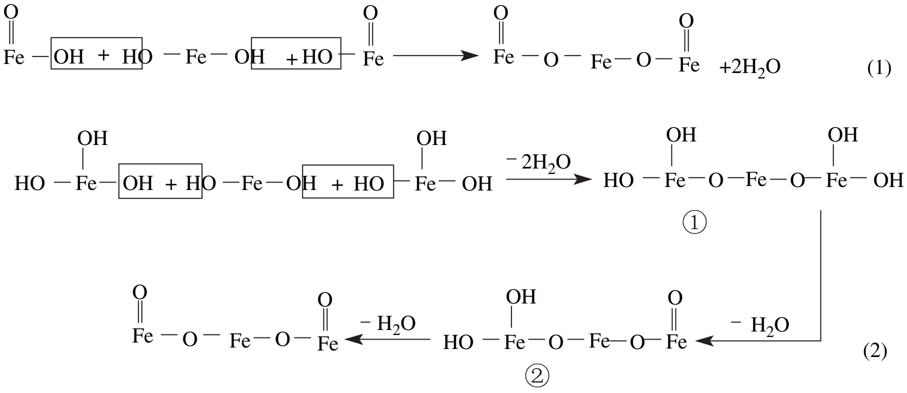
3. Results and discussion

3.1. Forming mechanism discussion on Fe_3O_4

At room temperature, when NaOH was added into the solution containing Fe^{2+} and Fe^{3+} with pH value about 11, Fe^{2+} and Fe^{3+} converted into some responding hydroxide compounds as follows.



With the rise of temperature, the following reactions will take place and the hydroxide compounds crystallize to Fe_3O_4 slowly.



If the sample obtained crystallizes completely, the products would not include −OH, just like the reactions (1) and (2). Conversely, the final products would comprise −OH (such as products 1 and 2).

The IR spectrum of sample 4 is shown in Fig. 1. There is an absorption peak at 3440 cm^{-1}, which is the characteristic peak of −OH. From Fig. 1, it can be seen that the absorption peak is very weak, and it can be concluded that the crystallization is basically entire. In addition, there are two obvious absorption peaks at 565

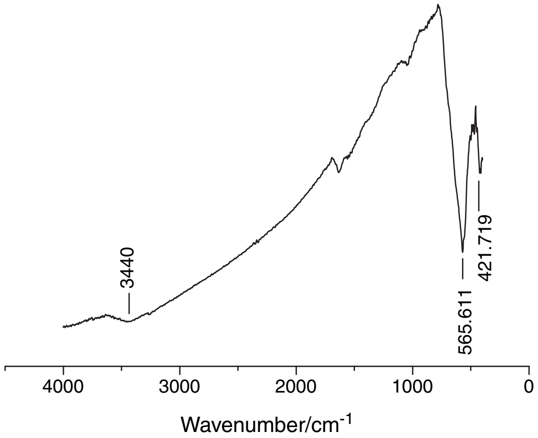


Fig. 1. IR spectra for sample 4.

and 421 cm^{-1}, which are consistent with the reported IR spectra for spinel Fe_3O_4 [11]. The peaks at 565 and 421 cm^{-1} are due to the vibrations of Fe^{2+}–O^{2-} and the vibrations of Fe^{3+}–O^{2-}, respectively. This figure also reveals that the materials have reacted and crystallized spinel Fe_3O_4.

3.2. Crystal phase analysis

Fig. 2 shows the X-ray diffraction pattern for sample 4. All the peak positions are basically consistent with the standard data for Fe_3O_4 structure (JCPDS card file No. 3-863), and no other unexpected peaks are present. The sample powder has an average particle diameter of 12 nm, which was estimated from Scherrer's formula using peak width at half height of the X-ray diffraction. The results show that the sample prepared by this method is pure phase nanometer Fe_3O_4.

3.3. Morphology analysis

Fig. 3 is the TEM photograph of sample 4. It demonstrates that the sample particle size is small and about 10 nm, substantially consistent with the results estimated from Scherrer's formula. The sample is a uniform distribution of spherical particles with no obvious aggregation.

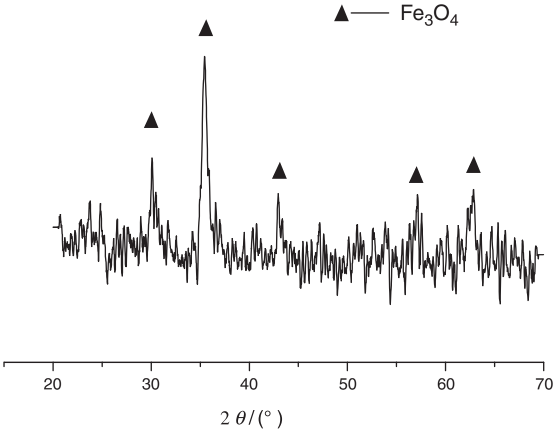


Fig. 2. X-ray diffraction pattern for sample 4.

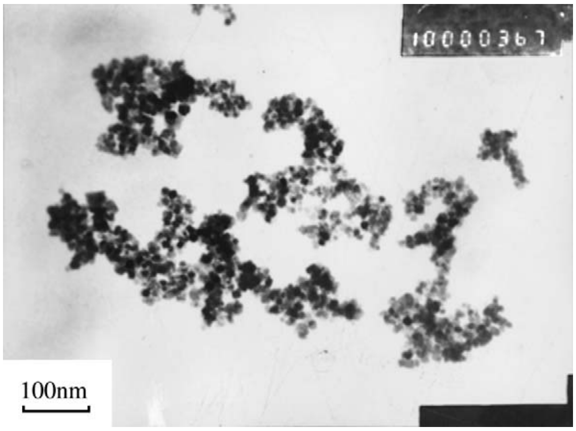


Fig. 3. TEM image for the sample 4.

3.4. Properties analysis

3.4.1. Color characteristics of pigment

We measured the color's tri-stimulus values (X,Y,Z) and chromaticity coordinate (x,y) of the pigment using JFY-PS color analysis apparatus, and then calculated the lightness value and Munsell marking. The results are shown in Table 1.

Fig. 4 shows the spectral reflectivity curve for sample 4. It can be seen that it does not exit reflecting from 400 to 700 nm. This shows that the sample is a better black pigment.

3.4.2. Magnetic properties

The magnetism of Fe_3O_4 is related with the content of Fe^{2+} in the structure. According to Ref. [12], Fe_3O_4 possesses a non-normal spinel structure. Half of Fe^{3+} takes up the tetrahedron cavity (site A) in the spinel structure. Half of Fe^{3+} and Fe^{2+} occupy the octahedron cavity (site B). On the basis of the ferrimagnetism theory, the direction of magnetic moment of any ion occupying the same type position is the same. However, the direction of magnetic moment of site A is contrary to site B, and the total magnetic moment is determined by the magnetic moment vector sum of the two kinds of magnetism ions. As a result, the increase of net magnetic moment is in accordance with the content of Fe^{2+}.

Table 1
The characteristics of color for sample 4

Tri-stimulus values			Chromaticity coordinate		Lightness value	Munsell marking	
X	Y	Z	x	y	V_Y	N	$V/$
1.641	1.633	1.337	0.3559	0.3541	1.28	N	1.28/

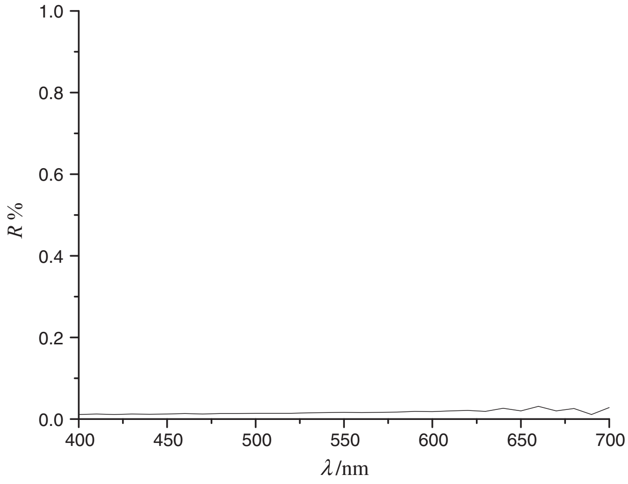


Fig. 4. Spectral reflectivity curve for sample 4.

Theoretically, the rate of Fe^{2+}–Fe^{3+} in structure Fe_3O_4 is 1:2. However, Fe^{2+} is easily oxidized in the actual reaction, hence, the content of Fe^{2+} in the sample obtained is less than the theoretical value. The reaction would be underway in theoretical percentage in the first stage, but the rate of Fe^{2+}–Fe^{3+} in the prepared sample would deviate from the theoretical value. For this reason, the content of Fe^{2+} in the solution is increased appropriately in practice, which has an effect upon the magnetism of the sample.

A series of samples were prepared by changing the content of Fe^{2+} in the solution. The magnetic parameters are given in Table 2.

From Table 2, it can be seen clearly that the specific saturation magnetization intensity (σ_s) is enhanced gradually with the increase of Fe^{2+}. When the ratio of Fe^{2+} to Fe^{3+} in the solution is 1.6:2, i.e. 60% of excessive Fe^{2+}, specific saturation magnetization intensity is maximal. Henceforth, the magnetization intensity begins to reduce due to the following three reactions:

$$2FeOOH + Fe(OH)_2 \rightarrow Fe_3O_4 + 2H_2O \qquad (1)$$

$$2Fe(OH)_3 + Fe(OH)_2 \rightarrow Fe_3O_4 + 4H_2O \qquad (2)$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \qquad (3)$$

In the solution, Fe^{2+} and Fe^{3+} react as eqs. (1), (2) and (3). Certainly, the reaction velocities are different from each other, and the three reactions consume the Fe^{2+} according to their respective velocities. On increasing the content of Fe^{2+} in the solution, the amount of Fe^{2+} participating in the reaction and entering into Fe_3O_4 crystal configuration augments gradually. Therefore, the magnetism also is enhanced correspondingly. When the ratio of Fe^{2+} to Fe^{3+} reaches 1.6:2, the specific saturation magnetization intensity is at its largest. That is to say, in such conditions the amount of Fe^{2+} satisfies the need of the reaction, and is used effectively. After that, the specific saturation magnetization intensity decreases due to the surplus of Fe^{2+}, namely a shortage of Fe^{3+} correspondingly, thus ending reactions (1) and (2). Finally, excessive Fe^{2+}, as a result of oxidization, converts into $Fe(OH)_3$. This leads to a drop in the Fe_3O_4 content.

Table 2
Impacts on magnetism of the samples from Fe^{2+} ion

Sample no.	$n(Fe^{2+})$/ $n(Fe^{3+})$	σ_s (A m^2 kg^{-1})	H_c (Oe)	σ_r (A m^2 kg^{-1})
1	1:2	59.12	6.843	0.5597
2	1.2:2	73.58	12.69	1.333
3	1.4:2	81.40	13.65	1.604
4	1.6:2	84.03	15.48	1.851
5	1.8:2	69.74	17.13	1.757
6	2.0:2	67.85	14.96	1.518

3.4.3. Superparamagnetism analysis

The origin of superparamagnetism can be explained as follows. Due to small particle size, anisotropy energy is less than heat disturbance energy of the ions, so magnetized direction is no longer fixed in an easy magnetized direction, and the movement of the ions is random [13]. Consequently, the sample would display a superparamagnetic nature like a paramagnetic body. When the particle size of the sample powder is less than the superparamagnetic critical size of the material, magnetic particles would lose ferrimagnetic or subferrimagnetic properties which are inherent in the bulk materials, and exhibit a remanent superparamagnetic state with no magnetic hysteresis. When this occurs, the values of the magnetizability (σ_r) and coercivity (H_c) of the sample are zero. The magnetization curve of the sample reversibly goes through the zero point.

Table 2 shows that σ_r and H_c are very small. These data mean that the sample is superparamagnetic. This can also be concluded from Fig. 5. The two magnetization curves go through the zero point and overlap together. All manifest the superparamagnetic nature of the sample.

Nanometer-sized Fe_3O_4 finds usage in synthesizing magnetic fluid for the properties of superparamagnetism, which is being researched constantly [14,15].

4. Conclusion

By a co-precipitation method, nanometer-sized magnetic pigment Fe_3O_4 was prepared. The sample particles have a uniform distribution and the size is small (about 10 nm). The shape of the sample particles is nearly spherical. Munsell marking, N1.28/, is determined through color analysis. The specific saturation magnetization intensity is maximal, i.e. 84.03 A m^2 kg^{-1}, when the proportion of Fe^{2+} to Fe^{3+} is 1.6:2. At the

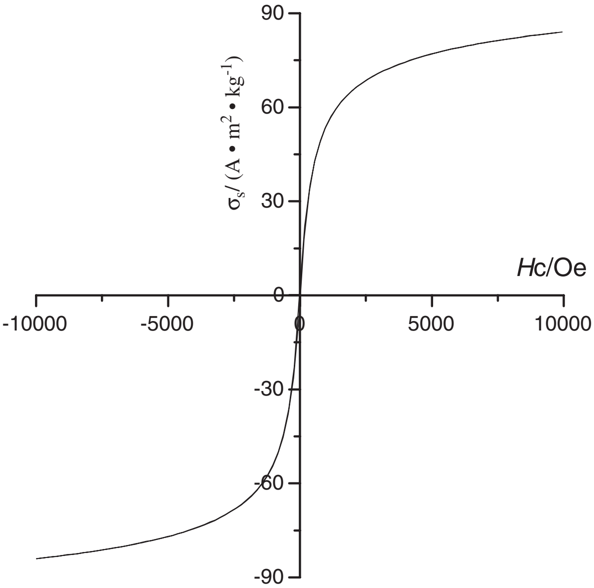


Fig. 5. The magnetization curve for sample 4.

same time, it harbors properties of superparamagnetism. This opens up more applied areas for Fe_3O_4.

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Jianhua Meng, as a graduate student, is studying at the Department of Chemistry, College of Science, Tianjin University. Her subject of interest is nanometer pigments.