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Direct synthesis of Fe_3O_4 nanopowder by thermal decomposition of Fe–urea complex and its properties

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ABSTRACT

An easy synthesis route of magnetite (Fe_3O_4) nanopowder is developed by using thermal decomposition of Fe–urea complex ($[Fe(CON_2H_4)_6](NO_3)_3$). The formation of Fe_3O_4 is confirmed from X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. The morphological properties and magnetic properties of the Fe_3O_4 are characterized by transmission electron microscopy (TEM) and magnetic measurements, respectively. By an increase in reaction temperature from 200 to 300 °C, the average crystallite size of the Fe_3O_4 nanopowder increases from 37 to 50 nm. Room temperature magnetization hysteresis curves show that the Fe_3O_4 nanopowder possesses ferrimagnetic characteristics. The saturation magnetization of the Fe_3O_4 nanopowder increases from 70.7 to 89.1 emu/g when the reaction temperature increases from 200 to 300 °C.

1. Introduction

Among several iron oxides, magnetite (Fe_3O_4) is a ferrimagnetic material with the highest saturation magnetization (Ms) of 92.0 emu/g. It is readily available and relatively stable under ambient conditions. Owing to these excellent properties, the Fe_3O_4 has been widely used in many applications such as magnetic recording, ferro-fluids, magnetic separation, magnetic resonance imaging, and catalysis for a long time [1–6]. When the particle size of Fe_3O_4 is decreased to nanoscales, it exhibits superparamagnetic behavior [7,8]. This nanosize effect together with biocompatible properties of the material are considered of great potential for applications in biotechnology and biomedicine including bio-assays, magnetic resonance imaging (MRI), magnetically guided drug delivery, and hyperthermia [9–11]. In recent years, the Fe_3O_4 attracts much attention from environmental applications in which it is used as an adsorbent, due to its high adsorption capacity for heavy metals and organic pollutants [12]. Iram et al. reported that Fe_3O_4 hollow nanospheres showed enhanced removal abilities for neutral red dye in wastewater [13]. Mahdavian et al. prepared polymeric-modified Fe_3O_4 nanopowder, and found that this nanopowder possessed large adsorption capacities for heavy metal cations, Cu^{2+}, Pb^{2+}, Ni^{2+}, and Cd^{2+} [14]. Due to its excellent magnetic properties, the Fe_3O_4 is also widely used as a magnetic support of catalysts. For example, it has been demonstrated that Ag/Fe_3O_4 nanocomposite has high catalytic activities for degradation of rhodamine B and epoxidation of styrene [15,16]. The most important advantage of using Fe_3O_4 as adsorbents or magnetic support of catalysts is that it can be easily separated from reaction system with an external magnetic field. For many applications, high quality Fe_3O_4 nanopowder with different properties is required to satisfy individual demand. For example, for biomedical applications, the Fe_3O_4 nanopowder is required to be biocompatible and should possess superparamagnetic characteristics to prevent agglomeration of the particles. For applications in water treatment, however, it is desirable that Fe_3O_4 nanopowder has ferrimagnetic characteristics with a high Ms and high specific surface area.

In response to the many potential applications for Fe_3O_4 nanopowder, various preparation methods have been developed, such as co-precipitation, microemulsion, hydrothermal method, sonochemical approach, mechanochemical approach, and non-aqueous synthetic method, etc. [17–22]. Most of the previously developed methods involve multiple steps and use multi-reagents, which will lead to the large wastage of energy and material. Among these methods, the nonaqueous synthetic method attracts much attention; and, it has been extensively demonstrated that Fe_3O_4 nanopowder with rather narrow size distribution can be obtained by using this technique [23–25]. However, the use of multi-reagents including organometallic compound of iron, organic solvents and some stabilizers are still required in this method. In addition, in most case, iron pentacarbonyl ($Fe(CO)_5$), an extremely toxic and unstable chemical, is commonly used as a precursor, which may

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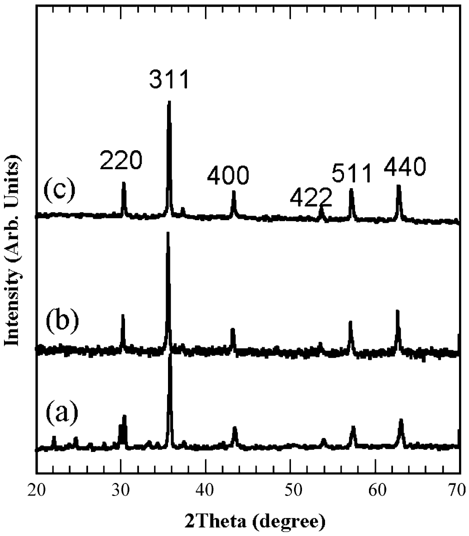

Fig. 1. XRD patterns of the samples prepared by the direct thermal decomposition of $[Fe(CON_2H_4)_6](NO_3)_3$ in a closed container at (a) 200 °C, (b) 250 °C, and (c) 300 °C.

limit the usage of this method for the mass production of Fe_3O_4 nanopowder.

In our previous studies, we found that the direct thermal decomposition of $[Fe(CON_2H_4)_6](NO_3)_3$ in an open container can produce maghemite (γ-Fe_2O_3) nanopowder [26,27]. We also found that Fe_3O_4 nanopowder with superparamagnetic properties can be prepared by a solvothermal method using the iron urea complex as a precursor [28]. In comparison with organic iron complexes (e.g., $Fe(CO)_5$, iron acetylacetonate, iron cupferronates) that are currently used as precursors in thermal decomposition process, the $[Fe(CON_2H_4)_6](NO_3)_3$ is a nontoxic, stable inorganic complex, as has been evidenced from its application in agriculture where it is used as a fertilizer [29]; hence, it can safely be used as a iron oxide precursor. In the present work, we show that Fe_3O_4 nanopowder with ferrimagnetic characteristics can be prepared via the direct thermal decomposition of $[Fe(CON_2H_4)_6](NO_3)_3$ in a closed container. The main advantages of this method are: (i) the preparation procedure involves only one-step, (ii) only one reagent (i.e., $[Fe(CON_2H_4)_6](NO_3)_3$) is used. Accordingly, these advantages are very promising for the large scale production of Fe_3O_4 nanopowder when taking the production cost and the influence of production on environment into consideration.

2. Experimental

2.1. Synthesis

2.0 g of the $[Fe(CON_2H_4)_6](NO_3)_3$, which was synthesized using previously reported method [26], was added to a 45-mL stainless autoclave with a Teflon liner. Then the autoclave was heated in an oven at a predetermined temperature for 2 h, resulting in the formation of a black fine powder.

2.2. Characterization

X-ray diffraction patterns (XRD) were recorded on a Philips PW 1830 diffractometer using CuKα radiation. X-ray photoelectron spectroscopy (XPS) spectra were measured using an AXIS-Ultra instrument from Kratos Analytical with a monochromatic Al Kα radiation source; in this case, peak positions were calibrated using the C 1s peak position. TEM measurements were carried out using a JEOL JEM-2200FS transmission electron microscope. Magnetic measurements were performed using a Lake Shore 7407 vibrating-sample magnetometer (VSM) at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the samples prepared by the direct thermal decomposition of $[Fe(CON_2H_4)_6](NO_3)_3$ at different temperatures for 2 h. The diffraction patterns match well with the Joint Committee on Powder Diffraction Standards (JCPDS) file of Fe_3O_4. In iron oxides, both Fe_3O_4 and γ-Fe_2O_3 have a same cubic spinel crystalline structure, and it is very difficult to differentiate them with XRD patterns. But they can be distinguished using *d*-spacing values. The *d*-spacing values of the sample which was obtained at 250 °C together with the JCPDS files of Fe_3O_4 and γ-Fe_2O_3 are listed in Table 1. It can be seen that experimental data match with the *d*-spacing values of Fe_3O_4 better, indicating the formation of Fe_3O_4. For the samples prepared at 200, 250 and 300 °C, the average crystallite sizes of Fe_3O_4, which were calculated from the half-width of diffraction lines by using Scherrer's equation, were estimated to be 37, 42 and 50 nm, respectively, indicating that Fe_3O_4 crystallite size increased with the increase of reaction temperature. Although the crystallite size could be controlled by varying reaction temperature, the controllable range was relatively narrow. One advantage of this method is that the Fe_3O_4 nanopowder with a relatively large particle size can be prepared in a short time as compared with our previously reported method [28].

Table 1
d-Spacings of the sample prepared by the direct thermal decomposition of $[Fe(CON_2H_4)_6](NO_3)_3$ in a closed container at 250 °C and those of Fe_3O_4 and γ-Fe_2O_3 from JCPDS files.

d (Å)	Fe_3O_4 (Å)[a]	γ-Fe_2O_3 (Å)[b]	*h k l*
2.9541	2.9670	2.9530	2 2 0
2.5226	2.5320	2.5177	3 1 1
2.0923	2.0993	2.0866	4 0 0
1.7102	1.7146	1.7045	4 2 2
1.6121	1.6158	1.6073	5 1 1
1.4812	1.4845	1.4458	4 4 0

[a] JCPDS file No. 19-629.
[b] JCPDS file No. 39-1346.

As reported in literatures [30], XPS has also been proven to be a powerful tool for the discrimination of Fe_3O_4 and γ-Fe_2O_3. Therefore, the XPS spectra of the sample have been measured in order to further confirm the formation of Fe_3O_4. Fig. 2 shows XPS spectrum in the Fe 2p region for the sample prepared by the direct thermal decomposition of $[Fe(CON_2H_4)_6](NO_3)_3$ at 250 °C for 2 h (spectrum a). For comparison, the spectrum for γ-Fe_2O_3, which is prepared by previously reported method [26], is also shown in the figure (spectrum b). For present sample, the peak positions of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ were observed at 710.7 and 724.2 eV, respectively, which agree well with those for the Fe_3O_4 reported in literature [31]. On the other hand, the peak positions of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ for γ-

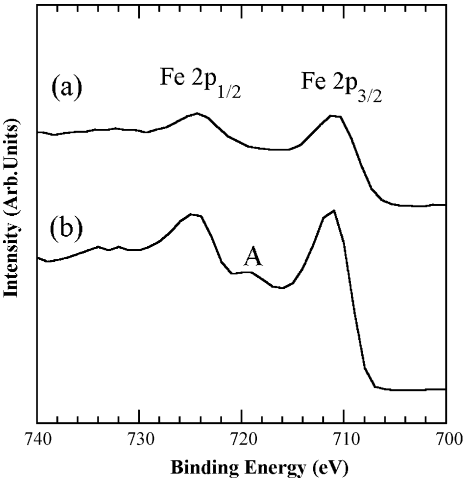

Fig. 2. XPS spectra: (a) for the sample prepared by the direct thermal decomposition of $[Fe(CON_2H_4)_6](NO_3)_3$ in a closed container at 250 °C for 2 h, and (b) for γ-Fe_2O_3.