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Benzoic acid-functionalized α -Fe₂O₃ nanoparticles: synthesis, characterization, magnetic and optical properties

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ABSTRACT

In this work, a new iron precursor was prepared, calcinated at 500 °C and 600 °C. The final α -Fe₂O₃ products (named Fe-500 and Fe-600) were characterized using the Fourier transformed infrared spectroscopy (FT-IR), UV-Vis, X-ray diffraction (XRD), transmission electron microscopy (TEM) and vibrating sample magnetometer (VSM) analysis. The results of the FT-IR analysis demonstrated that the sharp peaks at wavenumbers 450-650 cm⁻¹ confirmed the stretching vibration of Fe-O. The XRD results revealed that the product prepared at 500 °C was a mixture of 59% rhombohedral and 41% cubic phases of Fe₂O₃ with only 11% of cubic phase Fe₂O₃ in the sample processed at 600 °C. TEM images showed a slight increase in particle size by increasing the calcination temperature. The magnetic properties of the products depicted a weak ferromagnetic behavior.

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Graphical Abstract

Introduction

In recent years, there has been an increasing interest in the preparation, characterization and application consideration of various transition metal oxides including NiO [1], CuO/Cu₂O [2], Mn₃O₄ [3], Co₃O₄ [4], and Fe₃O₄ [5, 6] and Fe₂O₃ [7–9], not only for morphological diversity but also for good properties and applications. For these reasons, several research groups worked on this subject and annually published a fair number of papers [1–9]. Iron oxide has two main types, including magnetite Fe₃O₄ [5, 6] and hematite Fe₂O₃ [7–9]. Fe₂O₃ nanoparticles are considered to be of great interest because of their physical properties [7–9] and variety of applications such as photocatalytic degradation of bisphenol A [10], H₂S removal at low temperature [11], as anode materials in Li-ion batteries [12], photoelectrochemical water splitting [13], adsorption capability towards acid-dyes [14], photocatalytic degradation towards RhB [15]. Until now, iron oxides with various sizes, shapes

and morphologies have been prepared *via* hydro- and solvothermal [5, 6], co-precipitation ultrasonic irradiation [16], conventional solid-phase [17], electrospray [13] and green chemistry [18–21].

In continuation of our works [22–28], in this paper, prepared iron oxide nanoparticles using a simple, low-cost and convenient method.

Experimental

Materials and methods

All chemical used in this research study including FeCl₃·6H₂O, and benzoic acid were purchased from the Merck company, and used without any further purification.

Characterization

Fourier transform infrared (FT-IR) spectra were recorded as a KBr disk on an FT-IR Perkin–Elmer spectrophotometer. Optical absorption measurements were done using a UV-Vis Perkin Elmer-UV/VIS-Lambda 950

spectrophotometer in the wavelength ranges of 200–800 nm at room temperature. The photoluminescent (PL) emission spectra were performed using Hitachi F4500 spectrofluorimeter. XRD pattern of the complex was obtained on Empyrean powder diffractometer of PANalytical in Bragg-Brentano configuration equipped with a flat sample holder and PIXCel3D detector (Cu K α radiation, $\lambda = 1.5418 \text{ \AA}$). TEM images of the nanoparticles were recorded on transmission electron microscope Philips CM120 with a LaB $_6$ cathode operating at 120 kV and equipped with CCD camera Olympus Veleta. The magnetic properties were investigated by Vibrating sample magnetometer

Preparation of iron oxide nanoparticles

A mixture of ferric chloride hexahydrate (1 gr) and benzoic acid (1 gr) in the solid state was substantially ground for about 10 min and then put into a quartz crucible. Then about 5 mL of distilled water was added to obtain a uniform mixture, the solvent was decanted and the precipitate was kept in a tube furnace and calcined for 1.5 h at 500 and 600 °C, respectively, a heating rate of 20 °C/min under an air atmosphere. As a result, two iron oxide samples were obtained and named as Fe-500 and Fe-600.

Results and Discussion

FT-IR spectra

The FT-IR spectrum is one of the important analytical techniques. It was used to consider various metal-oxygen bond vibrations. Also it was used to assess changes between different samples (reactants and products) before and after calcination. The FT-IR spectra of row materials (the mixture of ferric chloride and benzoic acid) and of the as-prepared samples Fe-500 and Fe-600 are demonstrated in Figure 1. There are several stretching bands in iron precursor such as at 3360 cm^{-1} (–OH), 3050 cm^{-1} (C–H aromatic), 2957 (C–H aliphatic), 2677 and 2560 cm^{-1} (CH $_3$), 1686 cm^{-1} (C=O) and 1422, 1496, 1583 cm^{-1} (C=C aromatic), 1292, 1326 (C–O). These bands indicated presence of the benzoic acid in the iron precursor. The characteristic peaks of the benzoic acid disappeared by the calcination of the iron precursor into iron oxide at 500 and 600 °C. In the FT-IR spectra of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, there are four bands at 461, 475, 551 and 632 cm^{-1} for Fe-500 while there are two bands at 472 and 543 cm^{-1} for Fe-600, which are assigned to the vibration of Fe–O and Fe–O–Fe and confirm the presence of Fe_2O_3 nanoparticles [14, 29, 30].

Figure 1. FT-IR spectra of a) iron precursor, b) Fe-500 and c) Fe-600

UV-vis spectra

The optical properties of the as-prepared iron oxides (Fe-500 and Fe-600) were carried out by UV-Vis, as shown in Figures 2 and 3, respectively.

The absorption band at 578 nm is considered to be the result of pair excitation process and the charge-transfer band tail [27]. The optical absorption band gap E_g of the prepared samples can be calculated by the Tauc equation: $(\alpha h\nu)^n = A (h\nu - E_g)$, where A is a constant that is determined by the valence and conduction

bands of particular materials, $h\nu$ is the photon energy, α is the absorption coefficient, and n is a constant depending on the nature of electron transition, hematite has a direct band gap then $n=2$ [31, 32]. Figures 2 and 3 demonstrates the $(\alpha h\nu)^2 \sim h\nu$ curves of as-prepared α -Fe₂O₃ samples. The band gap energies of Fe-500 and Fe-600 are 1.63 and 2.19 eV, respectively, which is in the range of the indirect band gap of α -Fe₂O₃ (1.9 ~ 2.2 eV) [31-33]. The difference in the energies of the band gaps can be caused by the size and morphology of the α -Fe₂O₃ nanoparticles.

Figure 2. UV-Vis spectrum and tauc plot of the Fe-500

Figure 3. UV-Vis spectrum and tauc plot of the Fe-500

XRD patterns

XRD patterns of the as-prepared samples Fe-500 and Fe-600 are presented in Figure 4. The diffraction peaks at $2\theta \approx 24.15^\circ(012)$, $33.15^\circ(104)$, $35.63^\circ(110)$, $40.86^\circ(113)$, $49.46^\circ(024)$, $54.06^\circ(116)$, $57.59^\circ(018)$, $62.38^\circ(214)$, $64.01^\circ(300)$, $71.93^\circ(1010)$ and $75.45^\circ(220)$ imply rhombohedral $\alpha\text{-Fe}_2\text{O}_3$ phase (JCPDS card 00-024-0072) [14, 33]. The other diffraction peaks at $2\theta \approx 23.14^\circ(211)$, $32.96^\circ(222)$, $38.24^\circ(400)$, $45.17^\circ(332)$, $55.19^\circ(440)$ and $65.80^\circ(622)$ can be indexed as cubic Fe_2O_3 phase (JCPDS card 00-032-0469) [7-9]. The structure was refined by Rietveld fit in crystallographic program Jana2006 [34]. The Rietveld analysis revealed that sample Fe-500 consist of 59% rhombohedral and 41% cubic Fe_2O_3 . The lattice constants were found $a=5.03519(18) \text{ \AA}$ and $c=13.7515(6) \text{ \AA}$ for rhombohedral phase and $a=9.4061(3) \text{ \AA}$ for cubic phase. In the sample Fe-600 the content of the cubic phase decreased to 11%. The lattice constants were found $a=5.03548(13) \text{ \AA}$ and $c=13.7507(4) \text{ \AA}$ for rhombohedral phase [31] and $a=9.4081(6) \text{ \AA}$ for cubic phase. The size of crystallites was calculated using fundamental parameter approach [35] integrated in Jana 2006, which removes the instrumental part of

the diffraction pattern by means of known geometry of the diffractometer. The maximum peaks (104) in rhombohedral phase and (222) in cubic phase of the nanoparticles prepared at 500°C , are approximately equal, while these peaks in the XRD pattern of nanoparticles prepared at 600°C are different. The maximum peak of Fe_2O_3 cubic phase corresponding to (222) is comparable with the maximum of rhombohedral phase corresponding to (113). These results demonstrated that the cubic phase was decreased by increasing the temperature. The size of nanoparticles can be calculated based on the Scherer Equation (1) [31] according to the full width at half maximum (FWHM) of the strongest peak. The (104) and (222) planes were selected to calculate the crystal sizes of rhombohedral and cubic phases, respectively.

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

The average crystallite sizes determined for the as-prepared product at 500°C are 56 nm for rhombohedral phase and 32 nm for cubic phase. In the as-prepared product at 600°C , the average crystallite size for rhombohedral phase increases to 49 nm, while for cubic phase decreases to 25 nm.

Figure 4. XRD patterns of a) Fe-500 and b) Fe-600. In a), the maximum (222) of Fe₂O₃ cubic phase ($2\theta=32.96^\circ$) is comparable with maximum (104) of rhombohedral phase ($2\theta=33.15^\circ$)

TEM analysis

The TEM images of the Fe-500 and Fe-600 are revealed in Figures 5 and 6, respectively. Particle size distribution indicated that the calcination of the iron precursor at 500 and 600 °C produces the particles with size ranging from ≈ 20 nm to hundreds of ≈ 120 nm. In the particle

size distribution diagrams of the products, two different ranges are seen for the average particle size (25 and 58 nm for Fe-500 and 21 and 40 nm for Fe-600), confirmed the presence of two different phases (rhombohedral and cubic) in the samples. These results are approximately equal to the average of the particles obtained with the Scherrer equation.

Figure 5. TEM images of a, b) Fe-500 and c, d) Fe-600 at two different scales

Figure 6. Particle size distribution of a) Fe-500 and b) Fe-600

TEM images indicate that the prepared nanoparticles do not have the same shapes and the globular, truncated cube or cube particles can be found in both samples. However, higher calcination temperature appears to lead to slight decrease in particle size.

VSM analysis

The magnetic properties of the as-prepared Fe₂O₃ nanoparticles at 500 °C and 600 °C were studied as a function of applied magnetic field (Figure 7). It was observed that the M vs. H graphs is linear and no saturation magnetization can be seen even at high magnetic field [36], indicating paramagnetic behavior while bulk Fe₂O₃ is antiferromagnetic [36].

Figure 7. VSM of the as-prepared Fe₂O₃ nanoparticles at a) 500 °C and b) 600 °C

Conclusions

Two Fe₂O₃ nanoparticles (named as Fe-500 and Fe-600) were prepared using the thermal decomposition of new iron precursor at two different temperatures 500 and 600 °C for 1.5 h and were characterized using the FT-IR, UV-Vis,

XRD and TEM. The XRD results revealed that the Fe-500 is a mixture of 59% rhombohedral and 41% cubic phases of Fe₂O₃, while Fe-600 is a mixture of 89% rhombohedral and 11% of cubic phase Fe₂O₃. TEM images demonstrated a slight decrease in particle size as the calcination temperature was increased.

Disclosure Statement

No potential conflict of interest was reported by the authors.

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