Hematite nanopowder obtained from waste: Iron-removal sludge

L.Yu. Novoselova

Institute of Petroleum Chemistry, Siberian Branch, Russian Academy of Sciences, pr. Akademicheskii 4, Tomsk 634021, Russia

ARTICLE INFO

ABSTRACT

X-ray diffraction and Fourier-transform IR spectroscopy techniques were employed to confirm that heavy-tonnage iron-removal sludge wastes could be successfully used to synthesize hematite nanopowder (HM NP) with an average particle size of 42 nm. The sizes of the HM NP particles were confirmed from the TEM images. The hematite particles mostly exhibit elongated irregular oval shapes and their sizes vary within 18–74 nm, with a dominant fraction at 42–46 nm. The obtained HM NPs were characterized by a saturation magnetization of ~1.5 emu/g and a remanent magnetization of ~0.9 emu/g. Low-temperature nitrogen adsorption measurements showed that the obtained powder had a large specific surface area ($S = 14$ m^2/g) and well-developed mesoporosity (average pore size, 17.2 nm). A comparison of the obtained results to data from other researchers suggests that this hematite powder has high potential for use in the preparation of sorbents for water purification.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Hematite (α-Fe_2O_3) is the most stable form of ferric oxide (Fe_2O_3) and has drawn considerable attention from researchers around the world. Because of its low cost, effective performance, and environment-friendly properties, hematite is a highly promising material for use in various fields such as environmental protection, catalysis, and energy conversion and storage [1–23]. α-Fe_2O_3 has been used in the development of gas sensors [2,21,24], pigments [25,26], electromagnetic-wave-absorbing materials [27], and electrode materials in lithium-ion batteries and water splitting cells [28–31].

Hematite can have various morphologies, and it shows high activity in adsorption processes. α-Fe_2O_3 is widely used as a desulfurization sorbent to remove sulfur species from gases [3] and to decompose H_2S [4]. 3D flowerlike α-Fe_2O_3 nanostructures could remove various pollutants from water [5], and cauliflower-like α-Fe_2O_3 microstructures could remove Congo red organic dye and heavy metals (chromium and lead) from wastewater [1]. Porous α-Fe_2O_3-based nanomaterials were found to be effective adsorbents for the removal of *p*-nitrophenol from wastewater [6], while low-cost flowerlike α-Fe_2O_3 nanostructures were effective for the removal of As(V) and Cr(VI) from water [7]. The sorption of Se(IV) and Se(VI) on natural hematite has been studied [8], and it has been shown [9] that natural hematite is a suitable sorbent candidate for As(III) and As(V) removal technologies.

At present, a considerable amount of research effort is being devoted to develop nanomaterials. Nanomaterials are of interest, primarily because of the expectations of the so-called "size effect": the properties of well-known materials can be either significantly modified or principally changed when reduced to the nanodimensional state. Furthermore, development of materials and devices based on nanosized elements has opened new research opportunities [32,33]. Nanoscale α-Fe_2O_3 has been obtained in the form of various hierarchical nanoarchitectures, including nanocubes, nanospheres, nanorods, nanoparticles, nanowires, nanobelts, nanotubes, and nanorings [1,5,7,21,27,34–39].

Since the magnetic properties of the nanodimensional hematite are of considerable fundamental interest and are important for applications, some researchers studied these properties in detail [15,36,38,40,41]. In particular, it was reported that hematite nanoparticles with increased saturation magnetization reaching 5.1 emu/g [41] and even 21 emu/g [36] were obtained.

Hematite can be prepared by a variety of approaches, including solution chemistry and vapor-phase and template-assisted synthesis [36]. However, most of these methods are multistage, require numerous reactants (sometimes, rather expensive), and need complicated equipment for large-scale synthesis. Hematite synthesis from waste materials has received limited attention, although effective utilization of anthropogenic wastes is reasonable both economically and environmentally, as it allows the low-cost synthesis of important products and prevents repeated environmental pollution [42–44]. For example, cyanide tailings have been used to prepare nanopowders of iron oxide red pigment by an ammonia process with urea as a precipitant, typically affording α-Fe_2O_3 with particle sizes of 50–70 nm [45]. Powdered α-Fe_2O_3 materials with high surface areas (8.06, 22.5, and 29.6 m^2/g)

Abbreviations: CL, crystal lattice; HM, hematite; ICDD, International Centre for Diffraction Data; IRS, iron-removal sludge; NP, nanopowder; WDP, water deironing precipitate.

E-mail address: novoselova@ipc.tsc.ru.

were successfully prepared through a mild hydrothermal reaction using jarosite waste as a precursor [46]. Mill-scale iron waste has been used to prepare some iron oxide pigments, including hematite powder with surface areas of ~1.0 m^2/g [47].

During the operation of modern municipal water supply systems, deposits are formed in large quantities on the equipment. These deposits precipitate during water conditioning processes that remove undesired and hazardous impurities. Iron-removal sludge (IRS) is a byproduct of the purification of underground (artesian) water from iron by aeration. It is often considered as a heavy-tonnage waste and is discharged onto local terrain or into sewage collection systems, thus creating certain environmental and economic problems. This precipitate has been found to comprise a mixture of compounds, with iron hydroxides and oxides as the major chemical constituents. Its main mineral components are ferrihydrite, goethite, and hematite [44].

Previously, water deironing precipitate (WDP) was separated from IRS and heat-treated under selected conditions to afford a powder-like, large-surface-area, and high-porosity material that could be used as a sorbent for the purification of water from oil [48,49]. It has been also established that both initial and thermally treated WDP is capable of CO sorption [44]. An analysis of the obtained data led to the conclusion that WDP could serve a base for the synthesis of functional materials, particularly CO sorbents.

The present work aims to develop integrated approaches that allow specific anthropogenic wastes to be treated as renewable sources of raw materials, which can be employed to produce various useful products. An original attempt was made to use heavy-tonnage IRS waste to obtain important useful products such as hematite nanopowder. The aims of this work were: (i) to develop a simple method for HM NP production from IRS (i.e., a method that is not multistage, does not require numerous reactants, and does not need complicated equipment for large-scale synthesis); (ii) to provide useful data on the structure and some magnetic properties for HM NP; and (iii) to elucidate processes that underlie structural formation in nanomaterials synthesized from complex systems (in particular, from various anthropogenic waste products).

2. Experimental

2.1. Synthesis of nanopowder

For this study, WDP samples were separated from the IRS taken from the sludge tank of the water intake system of Tomsk Oblast (Russia) as follows. The IRS was first dried, spreading in a film, at room temperature

Fig. 1. Preparation of the HM NP.

(25 °C) to a constant weight, and the resulting air-dried material was ground to obtain a WDP sample [44]. The WDP was calcined by placing a sample (10 g) into a specially manufactured pyrex crucible and heating in a muffle furnace at 950 °C for 1 h to obtain an HM NP sample. The HM NP preparation scheme is shown in Fig. 1.

2.2. Structural characterization

The phase composition and structural characteristics of the HM NP were studied by X-ray diffraction (XRD) on a Shimadzu XRD-6000 instrument (Shimadzu, Japan) using Cu Kα radiation ($2\theta = 10°$–$70°$ at a step of 0.03°; X-ray tube operating at 40 kV, 30 mA; exposure time, 1 s) in the Bragg–Brentano geometry, with a pyrographite monochromator in the secondary beam. The phase composition, coherent scattering (CSD) size, and internal elastic microstresses were determined using the PCPDFWIN and PDF4+ databases and the full-profile analysis software, POWDER CELL 2.4. The average crystallite size (defined as the CSD size) and crystal lattice (CL) microdistortions (defined from the level of internal elastic microstresses) were determined from the analysis of the physical broadening of diffraction lines.

The particles sizes were confirmed using transmission electron microscopy (TEM); measurements were carried out on a Philips CM 12 instrument (Philips, Netherlands) operated at an accelerating voltage of 120 kV. The sample was prepared by placing a drop of the powder suspension onto a carbon-coated copper grid, followed by drying in air and transferring to the microscope. The size distribution of the HM NP particles was obtained by processing the TEM images with the iTEM 5.1 program (Build 1276, Olympus Soft Imaging Solutions GmbH).

IR spectroscopy was performed in the wavelength range 400–4000 cm^{-1}, using a Nicolet 5700 FT-IR spectrometer (Thermo Electron Corporation, US) with the KBr pellet method.

The obtained HM NP was characterized with respect to some of its magnetic properties. These characteristics were measured at room temperature with the aid of a pulsed field magnetometer [50].

The Brunauer–Emmett–Teller (BET) specific surface area and porosity of the HM NP samples were determined on a TriStar II 3020 automated surface area analyzer (Micromeritics, USA) using a volume variant of the sorption method. Prior to the experiment, a sample was degassed under vacuum at 200 °C for 2 h. The specific surface area was calculated using the low-temperature nitrogen adsorption isotherm, whereas the pore size distribution was calculated from the low-temperature nitrogen desorption isotherm by the Barrett–Joyner–Halenda method [51].

3. Results and discussion

3.1. X-ray diffraction analysis

According to the XRD data, the prepared material is composed of hematite nanopowder with >99.0% α-Fe$_2$O$_3$ content and an average particle size of 42.0 nm. The magnitude of the CL microdistortions (internal elastic microstresses) in the crystallites amounts to 1.5×10^{-3} (Table 1).

The corresponding powder XRD pattern provides phase information for the as-obtained HM NP, as shown in Fig. 2. All the observed diffraction peaks could be readily indexed to α-Fe$_2$O$_3$ (ICDD card no. 01-073-3825).

3.2. TEM

The sizes of the HM NP particles were confirmed by TEM images. These images and the corresponding electron microdiffraction pattern (Fig. 2S.2, Supporting Information) were obtained from the accumulation of nanoparticles.

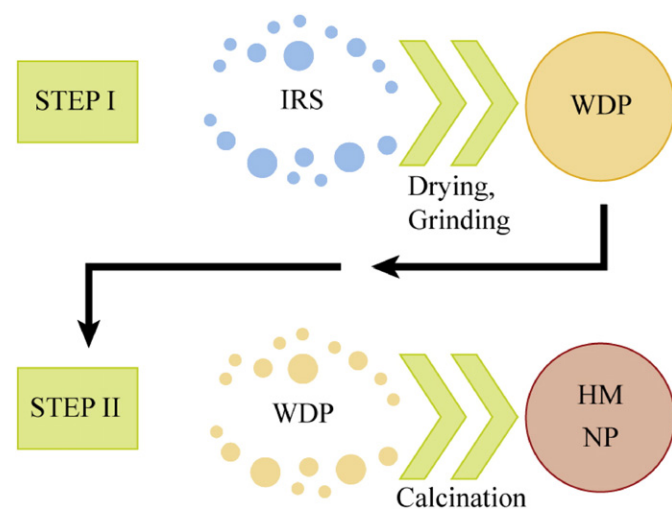Typical TEM images of the HM NP are presented in Fig. 3 (a, b). The hematite particles mostly exhibit elongated irregular oval shapes, and,