Materials Letters 138 (2015) 116–119

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Magnetic needle-like iron oxide particles prepared by microwave-assisted thermal decomposition technique

Zuzana Kozakova *, Ivo Kuritka [1], Pavel Bazant [2], Miroslav Pastorek [3], Vladimir Babayan [4]

Centre of Polymer Systems, University Institute, Tomas Bata University in Zlin, Nad Ovcirnou 3685, 760 01 Zlin, Czech Republic

ARTICLE INFO

Article history:
Received 15 May 2014
Accepted 27 September 2014
Available online 7 October 2014

Keywords:
Magnetic materials
Crystal growth
Phase transformation
Nanocrystalline materials

ABSTRACT

Iron oxide particles were prepared by a simple organic precursor assisted thermal decomposition technique. Microwaves were used as a source of energy for both precursor synthesis and generation of heat required for thermal decomposition. Ferrous oxalate dehydrate prepared within the microwave-assisted solvothermal process possess needle-like particle morphology with the length of about 20 μm and submicrometric diameter. Magnetic iron oxide was formed by a topotactic decomposition of prepared precursor in a microwave reactor thus the final product also preserves needle-like shape and possesses soft ferrimagnetic behavior.

1. Introduction

In recent years, preparation of iron oxide one-dimensional nano- and submicro-structures gets great attention due to their unique properties resulting from the shape anisotropy [1,2]. Especially, spinel ferrites are interesting due to possible utilization for magnetic refrigeration, as a promising component of ferrofluids and materials for the high density data storage [3]. Moreover, they are known for their interesting optical, electron-transport and phonon transport properties as well as for the sensing applications [4]. Furthermore, when these particles are coated by an active substance such as polyaniline, they can serve for the removal of toxic substances like hexavalent chromium or other heavy metals from environment, where magnetic core provides possibility of repeatable use of these particles [5–7]. Furthermore, their incorporation into the polymeric matrix under the influence of an external magnetic field provides the anisotropic reinforced materials [8], materials with tunable elastic modulus [9] or microwave absorbing materials [10].

Among the most common synthesis techniques, hydrothermal and solvothermal methods are most used and there are a number of publications dealing with preparation of magnetic nanostructures; however, these methods predominantly lead to the formation of spherical or polyhedral particles [11–16]. On the other hand, publications devoted to the preparation of magnetic iron oxides with elongated shape are significantly less extensive. As an example, Lian et al. described preparation of single crystalline Fe_3O_4 nanorods from $FeSO_4 \cdot 7H_2O$, NaOH and PEG-1000 at 150 °C in sealed Teflon autoclaves; however, information on the magnetic properties is missing in this publication [17]. Another way to obtain rod-like structures is electrostatic co-assembly, which is a method that utilizes the ability of nanoparticulate suspensions to form elongated structures under certain conditions like ionic strength and pH [18–21].

Another way to obtain magnetic structures is the use of template-assisted synthesis [12]. Methods that utilize organometallic precursors that decompose at relatively low temperature appear to be the most suitable [1]. “Precursor syntheses” are interesting from technological point of view since these methods are simple, cost effective and enable large-scale production [22].

Several types of precursors are commonly used for thermal decomposition techniques. As an example, solution-combustion methods utilize metal nitrates as the source of metal cations and organic compounds such as citric acid, glycine or urea as reducers (fuels). Firstly, the precursor is dissolved in a proper solvent and obtained gel is combusted. Combustion procedure is accompanied by generation of gaseous products which suppress the aggregation of forming metal oxide particles, thus remaining in nanoscale [23,24].

However, these combustion methods do not lead to the formation of elongated rod- or wire-like structures. Another method was proposed by He et al., who performed thermal decomposition of Fe $(CO)_5$ in refluxing PP-g-MA/xylene solution which serves as stabilizer and prevents uncontrollable agglomeration of nanoparticles into the clusters. If the concentration of precursor are low enough and steric repulsion forces of the polymer chains adsorbed on the nanoparticles

* Corresponding author. Tel.: +420 773184823.
E-mail addresses: zkozakova@ft.utb.cz (Z. Kozakova), ivo@kuritka.net (I. Kuritka), bazantik@centrum.cz (P. Bazant), pastorek@ft.utb.cz (M. Pastorek), babayan@ft.utb.cz (V. Babayan).
[1] Tel.: +420 603254579.
[2] Tel.: +420 57 603 8049.
[3] Tel.: +420 57 603 8128.
[4] Tel.: +420 57 603 1451.

http://dx.doi.org/10.1016/j.matlet.2014.09.125
0167-577X/

is higher than the magnetic dipole forces, chain-like structures from these nanoparticles are formed [25,26].

For the purpose of preparation of elongated structures, ferric and ferrous oxalates appear to be proper candidates as precursors for the thermal decomposition due to their preferred growth in one dimension at proper conditions thus forming rod-like structures [1,27–29]. Conversion of precursor into the final product is a topotactic reaction, thus the forming particles preserve the shape given by the precursor [1].

The difficulty in controlling the crystalline phase composition is considered to be the biggest disadvantage of oxidative decomposition techniques and is caused by numerous experimental parameters involved into the oxidative reactions (temperature, time, reaction atmosphere, precursor particle morphology and also thickness of precursor layer). Iron (α-Fe), iron carbide (Fe_3C), siderite ($FeCO_3$), wüstite (FeO) magnetite (Fe_3O_4) and various Fe_2O_3 can be formed within the oxidative decomposition of Fe (II) oxalate precursor [22]. Another disadvantage is the necessity of surfactants which are not only expensive but also can be harmful [30]. According to Zhou et al., controlling the reaction atmosphere of ferrous oxalate thermal decomposition can provide various products: hematite (α-Fe_2O_3) in air, maghemite (γ-Fe_2O_3) in inert atmosphere or magnetite under limited air conditions [1].

In order to achieve uniform elongated precursor particles with high aspect ratio in short synthesis times we developed a microwave-assisted procedure providing material with such properties. Moreover, we showed that the desired product can be prepared in a good quality without the use of surfactants. To minimalize the synthesis time and maximize efficiency of synthesis procedure, the process of thermal decomposition of the precursor was performed in a microwave oven in a ceramic kiln having a microwave absorbing layer on the inner wall. This two-step setting enables to reach high temperature in short times and thus performing rapid conversion of precursor into the desired product. Limited amount of air involved in the reaction system was provided through the sealing of precursor into glass tubes.

2. Materials and methods

Magnetic needles based on iron oxides were prepared by a thermal decomposition of organometallic precursor. Microwaves were used in both steps of procedure: they served as a source of energy for the formation of precursor and for generation of heat required for the thermal decomposition.

Precursor synthesis: The organometallic precursor was prepared by a microwave-assisted solvothermal method. All of the chemicals used within the synthesis were purchased from Penta Company (Czech Republic) in an analytical purity and were used as-received without further purification. Iron(II) sulfate heptahydrate (20 mmol) and oxalic acid dihydrate (20 mmol) were dissolved separately in a mixed solvent containing water and ethylene glycol in a ratio of 1:3. Prepared solutions were filtered off and then a solution of oxalic acid was added into the solution of iron(II) sulfate slowly with constant stirring. As-prepared solution was then transferred into the Teflon liner, sealed and placed into the cavity of a pressurized microwave reactor CEM Mars 5 (USA). The solution was then treated for 30 min at 100 °C and the obtained yellow precipitate was filtered-off and rinsed with distilled water.

Thermal decomposition of organometallic precursor: Magnetic needles were prepared by the thermal decomposition of organometallic precursor obtained by the described solvothermal procedure. A small amount (10 mg) of precursor was sealed into the glass tubes with the total volume of about 2 ml. Tubes were then placed into the ceramic kiln equipped with the microwave absorbing layer and the kiln was heated in the cavity of a common domestic microwave oven (Hyundai, MWM 1417 W) at 750 W for 15 min. This setup enables reaching of high temperature in short times, and therefore the decomposition of precursor was complete after 15 min. Temperature measured immediately after the decomposition using the contactless pyrometer was found to be of about 450 °C.

Characterization of prepared materials: First of all, macroscopic appearance of prepared powder was observed by naked eye and by a digital microscope DVM 2500 (Leica Microsystems, Germany). Crystalline composition of prepared materials was studied with the help of X-ray diffraction (XRD, PANalytical X'Pert PRO) with Cu Kα1 radiation ($\lambda = 1.540598$ Å). Particle size and morphology were investigated with the help of scanning electron microscopy (SEM, VEGA\\LMU, Tescan). Magnetic properties were measured by a vibrating sample magnetometer (VSM, VSM 7400, Lake Shore) at the room temperature and air conditions.

3. Results and discussion

Crystalline composition of prepared magnetic particles was determined by XRD. Fig. 1 shows XRD patters of precursor and the final product obtained by its thermal decomposition.

The prepared precursor is composed solely of the ferrous oxalate dehydrate with monoclinic crystal system (ICDD-JCPDS PDF-2 entry 01-072-1305). All peaks that were observed in the XRD pattern of the decomposition product can be attributed to the spinel cubic structure of magnetite (or maghemite). Even if the distinction of magnetite and maghemite by XRD method is not explicit, one can expect the prepared black powder to contain magnetite phase majority due to the limited air conditions within the decomposition of precursor. To investigate the structure of prepared oxalate precursor and final product, the crystallites size was calculated from the broadening of the diffraction peaks from XRD diffractograms according to Schrerer's equation and was estimated to be about 40 nm in both cases.

Morphological investigation was performed with the help of SEM. A representative captured image of the product can be seen in Fig. 2.

Prepared precursor particles have the shape of long needles and their diameter is less than 1 μm. Due to the topotactic character of the decomposition process, the shape of the converted product remains preserved. The length of about 20 μm and diameter less than 1 μm give to our product a uniquely high aspect ratio, although it can be seen that there is apparent

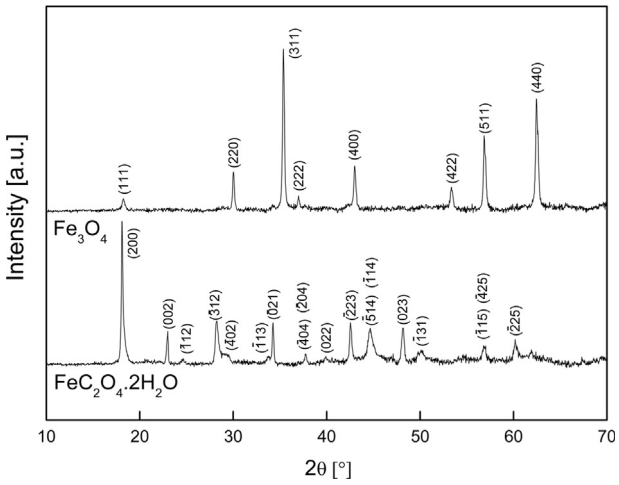

Fig. 1. XRD patterns of precursor and product of the thermal decomposition.