TUNING THE PROPERTIES OF IRON OXALATE PRECURSOR FOR ELONGATED MAGNETIC PARTICLES

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Abstract

Iron (II) oxalate dihydrate was investigated as a possible candidate for the preparation of elongated magnetic particles. In order to prepare 1-dimensional nanostructures with high aspect ratio, three kinds of synthesis were employed for the preparation of this precursor. It was shown that microwave solvothermal synthesis utilizing pressurized reactor provides desired structure without the use of any surfactant in short synthesis times and uses low cost and relatively low toxic reactants.

Keywords: Magnetic materials, Solvothermal synthesis, Microwave synthesis, Thermal decomposition,

1. INTRODUCTION

Preparation of iron oxide nano- and submicro-structures with prolonged shape gets great attention due to their unique properties resulting from the shape anisotropy [1,2]. However, most of the methods proposed for nanostructures synthesis, such as solvothermal and hydrothermal, results in the formation of spherical or polyhedral shaped particles [3-8]. Among the synthetic routes that support growth in a certain direction, “precursor syntheses” are interesting from technological point of view since these methods are simple, cost effective and enable large-scale production [9]. Methods that utilize organometallic precursors that decompose at relatively low temperature appear to be the most suitable for both, laboratory and practical use [1]. For this purpose, ferric and ferrous oxalates seem to be proper candidates due to their preferred growth in one dimension at suitable conditions thus forming rod-like structures [1,10-12]. Conversion of precursor into the final product is a topotactic reaction thus forming particles preserve the shape given by the precursor [1]. However, tuning the shape of particles and obtaining of particles with high aspect ratio is usually conditioned by the use of surfactants [1]. We performed a synthesis of iron oxalates by various routes and showed that particles aspect ratio can be tuned without a use of any surfactant. Iron(II) oxalate was prepared by a conventional heating, microwave-assisted synthesis at atmospheric pressure utilizing external cooler and also microwave solvothermal synthesis utilizing pressurized reactor.

2. EXPERIMENTAL PART

Iron(II) oxalate was prepared by conventional heating, with the assistance of microwaves as a source of energy at atmospheric pressure and by solvothermal method utilizing microwave pressurized reactor.

2.1. Materials and Methods

All the chemicals used within experiments were purchased from Penta Ltd. and were used as-received without further purification. Ammonium iron(II) sulfate (Mohr's Salt) served as a source of Fe^{2+} ions. 20 mmol of $(NH_4)_2.Fe(SO_4)_2.6H_2O$ (or alternatively 2 mmol) was dissolved in mixed solvent consisted of ethylene glycol and deionized water in a ratio 3:1. Similarly, 20 mmol (or 2 mmol) of oxalic acid were dissolved in a mixed solvent of the same composition. After the complete dissolution, two prepared solutions were mixed together and the synthesis was performed immediately. The first synthesis was performed by a conventional heating on a hot plate at 100 °C and the duration of half an hour. The second type of the synthesis utilized microwaves as a source of energy. The synthesis was performed at 100 °C for 30 minutes and atmospheric

pressure. For this reaction, common domestic microwave oven (Hyundai) was used; however, the top of the oven was modified in order to enable the insertion of an external cooler. The last kind of synthesis proceeded also due to the action of microwaves; however, pressurized reactor was used instead of open-vessel system. Total volume of reaction mixture (60 mL) was sealed into a PTFE liner of a volume 100 mL and heated at 100 °C for 30 minutes in CEM MARS 5 microwave reactor. After the synthetic steps, obtained yellow precipitate was filtered and washed with deionized water several times and obtained precursor was dried before the thermal decomposition. Synthetized oxalate precursor was sealed into the glass tube in order to provide stoichiometric amount of oxygen involved in the system. Glass tubes were inserted into the Muffle oven and heated at 400 °C for 60 minutes. After the cooling down, black powder was collected.

2.2. **Characterization Techniques**

Crystalline composition of prepared precursor and magnetic particles were was confirmed by X-ray diffraction (XRD, PANalytical X'Pert PRO) with CuKα1 radiation (λ=1.540598 Å). Particle size and morphology were studied by scanning electron microscopy (SEM, VEGA\\LMU, Tescan).

3. RESULTS AND DISCUSSION

Crystalline composition of prepared precursor as well as of a final product was studied by X-ray diffraction and resulting diffraction patterns can be seen in Fig. 1. The crystalline phase of precursor was determined as ferrous oxalate dihydrate. Material obtained after the decomposition step has all of the diffraction peaks attributed to magnetite (or maghemite, difficult to distinguish by XRD). For clear arrangement, only one material was chosen for representation before and after the decomposition step, concretely material prepared by reaction in pressurized microwave reactor at a reactants dosage of 20 mmol. However, the crystalline composition of other precursors were confirmed as iron oxalate dihydrate and the final product as magnetite or maghemite, too.

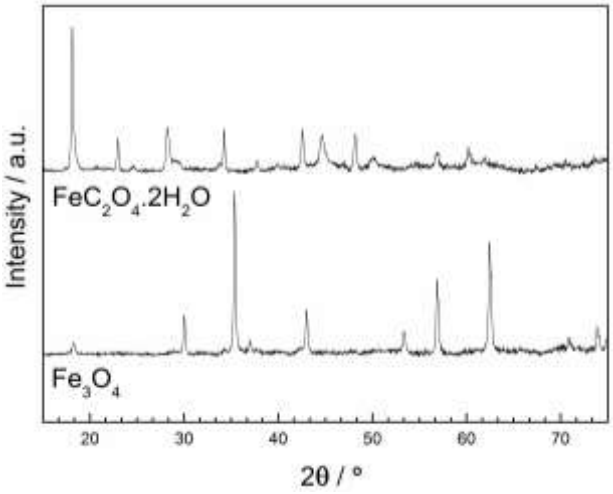

Fig. 1 XRD patterns of prepared iron(II) oxalate dihydrate precursor and magnetite obtained by its decomposition.

Morphology of iron(II) oxalates prepared by different methods were studied by scanning electron microscopy and resulting images can be seen in Fig. 2. First of all, the variation of particle size and, especially, of the aspect ratio can be observed for materials prepared at different conditions. The conventional synthesis without the use of microwaves led to the formation of irregular shaped particles at lower concentration of Mohr salt and oxalic acid (Fig. 2a); however, if the concentration was increased by 10 times, rod-like particles started to form although it is evident that the sample homogeneity is not sufficient (Fig. 2b). Similar results were obtained also after the application of microwaves at atmospheric pressure at lower

concentration of reactants (Fig. 2c), nevertheless, at higher reactants dosages, rod-like particles with an average size of 5 μm and diameter of about 1-2 μm were obtained (Fig. 2d). When pressurized reactor was used instead of the system with reflux cooler, the needle-like particles were formed (Fig. 2 e, f). These particles are quite uniform in shape and size, their length reaches several tens of micrometers and their diameter is in nano-dimensions. Moreover, lover concentration of reactant provides particles with clearly higher aspect ratio (Fig. 2 e).

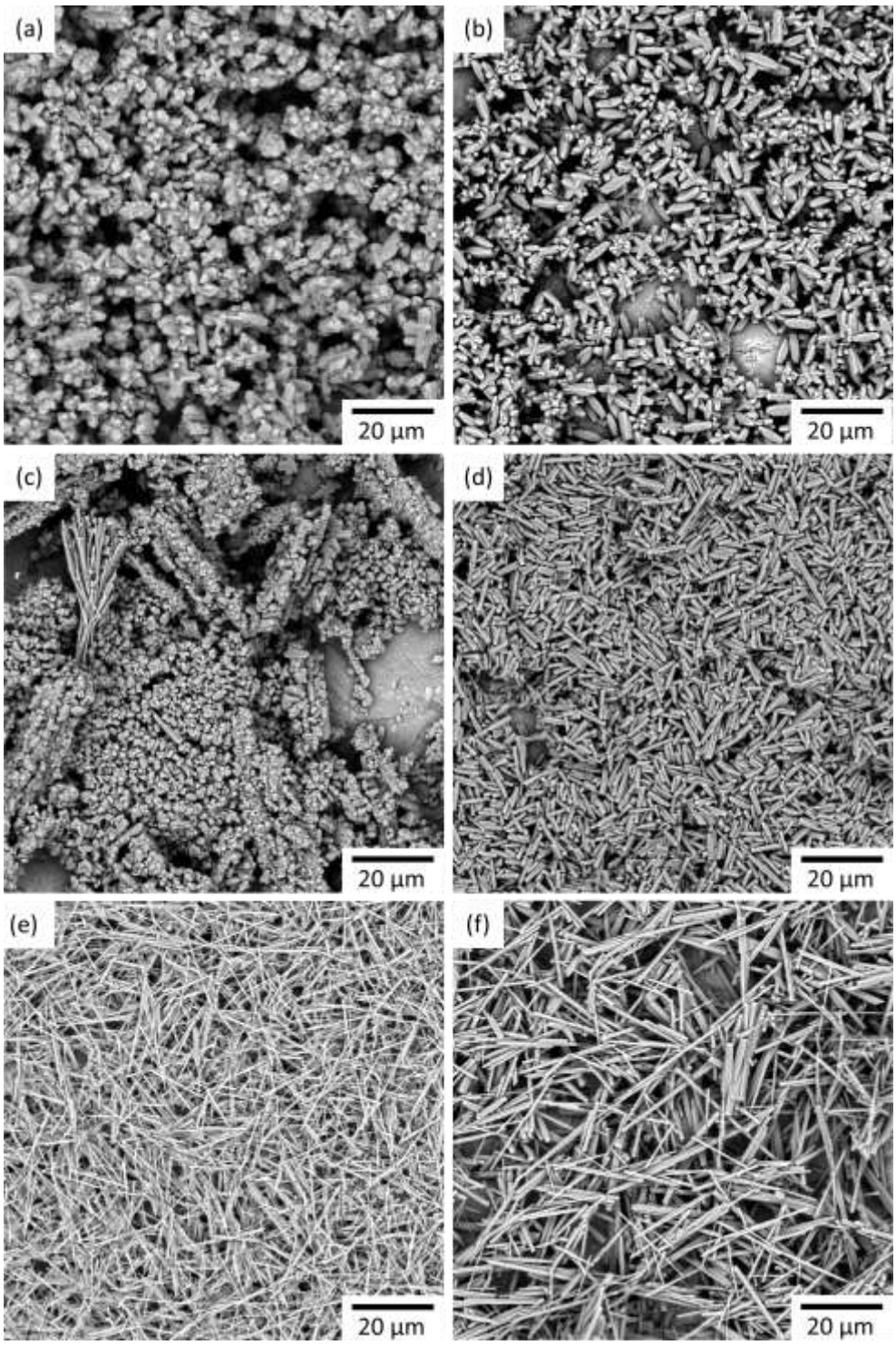

Fig. 2 SEM images of prepared iron(II) oxalate dihydrate precursors.

4. CONCLUSION

Iron (II) oxalate dihydrate serving as a precursor for magnetic particles was prepared by various synthetic routes. The firs type was conventional method when the reactants were heated on a hot plate at 100 °C for 30 minutes. This type of synthesis led to the formation of quasi rod-like shape particles with irregular size and organization. Second type of synthesis was performed with the assistance of microwaves; other reaction conditions were kept unchanged. At the higher dosage of reactants, quite uniform rod-like particles were formed, however, the diameter of these particles was in submicrometric dimensions instead of nano-dimensions. Third type of synthesis was also microwave assisted, however this procedure employed pressurized reactor instead of the atmospheric-pressure system with a reflex cooler. Obtained oxalates have needle-like shape with nano-sized diameter and they are uniform in size and shape. Moreover, at low concentrations, particles with high aspect ratio are formed without the use of any surfactants.

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