



Research paper

# Magnetic iron nanoparticles prepared by solution combustion synthesis and hydrogen reduction



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## ARTICLE INFO

### Article history:

Received 3 December 2015

In final form 19 May 2016

Available online 20 May 2016

### Keywords:

Magnetic iron nanoparticles  
Solution combustion synthesis  
Hydrogen reduction

## ABSTRACT

A facile and efficient method has been proposed to prepare iron nanoparticles by combining solution combustion synthesis and hydrogen reduction for the first time. A porous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> precursor with high specific surface area of 75 m<sup>2</sup>/g was fabricated by solution combustion synthesis, and then iron nanoparticles with high saturation magnetization of 196.3 emu/g were successfully obtained by hydrogen reduction of the as-synthesized precursor. With the reduction temperature rising from 275 °C to 600 °C, the saturation magnetization of the products increases from 196.3 emu/g to 209.7 emu/g, whilst the coercivity decreases from 611.4 Oe to 98.8 Oe.

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## 1. Introduction

Magnetic nanoparticles have emerged as a promising advanced functional material for a wide field of potential applications such as catalysis, water treatment, environmental remediation, biotechnology/biomedicine, magnetic recording media, electromagnetic wave absorption, magnetic sensors [1–5]. As compared to other magnetic nanoparticles, iron nanoparticles have attracted a great deal of attention due to exceptionally high saturation magnetization, large permeability, superior environmental compatibility and high availability [6–10]. In recent years, multiple techniques have been developed to prepare iron nanoparticles, including thermal decomposition [11,12], sonochemical decomposition [13], vapor phase condensation [14], aqueous reduction of iron salt [15], high-energy milling [16], and hydrogen reduction of nanoscaled iron oxide [17]. Among the above methods, owing to process simplicity, low cost as well as potential high productivity, hydrogen reduction (HR) is utilized to fabricate iron nanoparticles on a commercial basis. Over the past few years, in order to better understand and ameliorate HR, several investigations suggest that the purity and reductive activity of starting materials have great influence on the reduction temperature and microstructure of the as-prepared product [18,19]. Thus, the production of iron oxide with

high purity and reactivity is the prerequisite task required for achieving the successful preparation of iron nanoparticles by HR.

Solution combustion synthesis (SCS) has been demonstrated to be one of the most appropriate methods to produce oxide nanomaterials [20–23]. It is well known that SCS is essentially exothermal redox reaction between an oxidizer (e.g. metal nitrates) and a fuel (e.g. glycine, urea, citric acid, etc.) in a homogenous aqueous solution within several seconds. Simultaneously, the exothermal reaction provides the energy required for sustaining the combustion reaction without adding external energy. The advantages of SCS thus are as follows: (1) the homogeneous mixing of all the components on the molecular level and the evolution of a large volume of gases result in the formation of nanoscaled products with high specific surface area and resultant high reactive activity; (2) inexpensive starting materials, self-sustained instantaneous reaction features, high yield, as well as simple processing and apparatuses render SCS cost-effective and suitable for mass production. In view of these advantages, a large number of efforts have been made to prepare iron oxides by SCS [24–27]. Despite of such fascinating research results, to our knowledge, no research on hydrogen reduction of iron oxides by SCS has been reported.

Hence, in this work, we report a facile and efficient method to prepare iron nanoparticles by combining SCS and HR for the first time. First, by using ferric nitrate as an oxidizer, glycine as a fuel and glucose as an assisted additive and selecting an optimum molar ratio, a porous iron oxide precursor has been fabricated via SCS. Subsequently, iron nanoparticles with high saturation magnetization have been successfully obtained by hydrogen reduction of

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the as-synthesized precursor. Moreover, the whole combustion process and hydrogen reduction process have been investigated, and the influence of reduction temperature on magnetic properties of the products has been discussed in detail.

## 2. Experimental

### 2.1. Synthesis procedure

All the starting materials involving ferric nitrate ( $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , oxidizer and Fe source), glycine ( $\text{C}_2\text{H}_5\text{NO}_2$ , fuel) and glucose ( $\text{C}_6\text{H}_{12}\text{O}_6 \cdot \text{H}_2\text{O}$ , additive), were commercially purchased and of analytical reagent grade. After a series of optimization experiments, the optimal molar ratios of glycine to ferric nitrate and glucose to ferric nitrate were fixed at 2.8 and 1.5, respectively, and the amount of ferric nitrate was 0.1 M.

Just like the typical experimental procedure for SCS, the above starting materials were dissolved in 200 ml deionized water under thoroughly stirring to obtain a rufous homogeneous starting solution at room temperature. Subsequently, the resultant solution was poured into a 2000 ml beaker and heated in a temperature-controlled muffle furnace in air. As heating continued, the solution evaporated and gradually developed into a viscous gel. Then, the gel began to swell and a smoldering combustion reaction occurred, coupled with the evolution of a large volume of gases. The whole process of swelling and combustion seemed to undergo a self-propagating and nonexplosive exothermic reaction and lasted only a few minutes, resulting in the generation of a gray porous foam. Upon further heating, the foam was ignited and the carbon was completely removed, leading to the formation of a loose reddish precursor. Hereafter, hydrogen reduction of the precursor was conducted in a tube furnace. A strict temperature program was followed in all runs, with heating up to the plateau temperature, 150–600 °C, at a constant heating rate of 10 °C/min. The as-synthesized precursors were reduced at various temperatures for 2 h in a flowing hydrogen atmosphere at a flow rate of 1 L/min. Finally, when cooled naturally to room temperature, the reduction products were obtained.

### 2.2. Characterization

Thermal behavior of the formed gel sample was investigated by thermal gravimetric analysis (TG) and Differential Scanning Calorimetry (DSC) using a Netzsch 409PC thermal analyzer. The TG and DSC curves were recorded over the temperature range of 25–600 °C at a heating rate of 10 °C/min in air at a constant flow rate of 20 ml/min. The phase composition of the foam, precursor and reduction products was determined by X-ray Diffraction (XRD), using a TTRAX III diffractometer with monochromatic  $\text{Cu K}\alpha$  radiation. The average crystallite size was calculated according to the Scherrer's equation. The presence of  $\text{Fe}_3\text{O}_4$  was studied by X-ray photoelectron spectroscopy (XPS), using a ESCALAB 250 Xi spectrometer. The morphology and particle size of the precursor and reduction products were observed by scanning electron microscopy (SEM, JSM-6510) and field emission scanning electron microscopy (FE-SEM, ZEISS ULTRA 55), respectively. The reduction products were further observed and the associated selected-area electron diffraction images were captured by transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN). The specific surface area (SSA) of the precursor was examined by BET method using an Automated Surface Area & Pore Size Analyzer (QUADRASORB SI-MP, Quantachrome Instruments, Boynton Beach, FL). The magnetic properties were measured by vibrating samples magnetometry (VSM) at room temperature, using a Lake Shore 7307 magnetometer.

## 3. Results and discussion

### 3.1. Solution combustion synthesis

As described in detail in the experimental section, under continuous heating conditions, the homogeneous starting solution containing ferric nitrate, glycine, and glucose gradually developed into a viscous gel, and the succeeding thermal behavior of the gel was investigated. Fig. 1 depicts the TG and DSC curves of the formed gel. It is clear that the whole process is composed of three major stages with the two dash lines as division marks. In the initial stage (below 136 °C, dehydration), the gel sample undergoes a rapid mass loss of around 40% on the TG curve. On the same temperature interval, a roughly V-shaped endothermic peak at 110 °C is presented on the DSC curve, which can be attributed to the evaporation of remaining water and the desorption of chemically absorbed water in the gel. For the second stage (136–330 °C, smoldering combustion), as compared to the previous stage, the mass decreases by approximately 30% at a relatively gentle rate, accompanied by a wide and weak exothermic peak. The characteristic profile of the DSC curve suggests the low exothermic effect, which is in good agreement with the observed slow smoldering combustion phenomenon. It is well known that, after the removal of the various types of water, the formed gel becomes far more reactive with further heating, and then is closely followed by the vigorous initiation of the combustion reaction. Actually, in this stage the exothermic combustion reaction between ferric nitrate (oxidizer) and glycine (fuel) is conducted [Eq. (1)]. Simultaneously, after absorbing the heat released from combustion reaction, the decomposition of glucose (additive) occurs [Eq. (2)], resulting in the generation of a gray porous foam [Fig. 2(a)]. Thus, it is the superposition of the exothermic combustion and endothermic decomposition reaction that is responsible for the total low exothermicity and smoldering phenomenon. With respect to the last stage (above 330 °C, decarbonization), as the temperature continues to rise, the sharp exothermic peak, located at approximately 393 °C, corresponds to the complete removal of carbon in the foam [Eq. (3)], leading to the formation of a loose reddish precursor [Fig. 2(b)]. In addition, when the temperature surpasses 450 °C, the mass of the sample keeps almost constant.

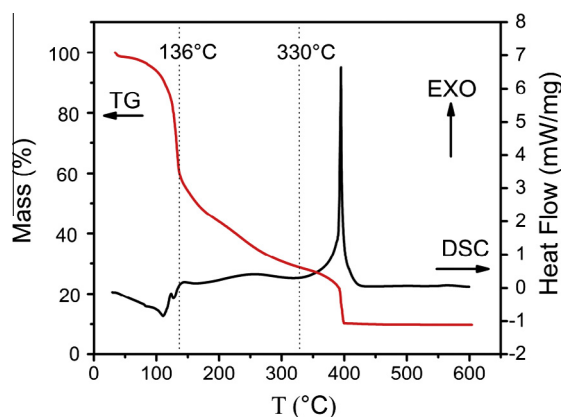
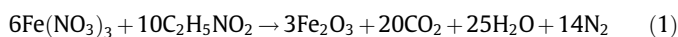


Fig. 1. TG and DSC curves of the formed gel.

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