Effect of glycine on one-step solution combustion synthesis of magnetite nanoparticles

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ABSTRACT

Magnetite (Fe_3O_4) nanoparticles have been readily prepared via a one-step solution combustion synthesis (SCS) method by designing a simple airless device: a beaker with perforated rubber plug could not only separate the outside air but also release the gases generated during the combustion reaction, which could ensure an air free condition in the SCS process. The whole process did not involve any toxic or unavailable reagents, and could be finished in a few minutes by its self-generated energy derived from the redox reaction between glycine (fuel) and ferric nitrate (oxidizer). Innovatively, the combustion reaction mechanism, morphology and microstructure, phase composition and magnetic properties of SCS products in relation to the glycine have been systematically investigated. The results revealed that with the increasing molar ratio (ϕ) of glycine to ferric nitrate, the combustion mode varied from self-propagating combustion to smouldering combustion and the average grain size of SCS products increased in nanometer scale. On the contrary, the iron oxidation state of SCS products decreased with the increase of ϕ value, and the oxide phase changed from α-Fe_2O_3 to Fe_3O_4 and then to FeO sequentially. It was noteworthy that when $\phi = 0.7$, we could easily obtain pure phase Fe_3O_4 nanoparticles with the highest saturation magnetization of 89.17 emu g^{-1} and small average grain size of 57.3 nm, which would have great potential for various applications, such as magnetic drug delivery, magnetic data storage and novel ferrofluids.

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1. Introduction

Magnetite (Fe_3O_4) has long been attractive material owing to its distinct physical and chemical properties [1—3]. Because of the low toxicity, high conductivity, good biocompatibility and excellent magnetic properties [4—7], nanostructured Fe_3O_4 has potential applications ranging from medical diagnostics and drug delivery to information storage and electronic devices [8], for example, magnetic resonance imaging [9], targeted drug delivery [10], magnetic recording media [11] and lithium ion batteries [12]. In recent years, multifarious methods have been developed to synthesize Fe_3O_4 nanoparticles with appropriate features (small particle size, good dispersibility, high purity and crystallinity, etc.), including high-energy ball milling [13], co-precipitation [14], micro-emulsion [15], hydrothermal synthesis [16], sol-gel method [17] and so on.

However, these synthetic processes often confront the disadvantages of complicated equipment, long preparation time, multiple processing steps or environmental pollution. Besides, in the binary phase diagram of iron and oxygen, Fe_3O_4 is formed only in a very narrow stoichiometric range [18], leading to a requirement of inert-gas atmosphere, high-temperature treatment and precise controlled ratio of ingredients in the synthetic process [19—22]. Therefore, it is highly desirable to explore time- and energy-saving method for the simple and scalable preparation of Fe_3O_4 nanoparticles in an environmental-friendly way.

During the past few decades, solution combustion synthesis (SCS) has emerged as an extensive employed technique to fabricate nanomaterials, especially for nano-oxides, due to its attractive advantages of simplicity, scalability, non-pollution, time- and energy-efficiency [23—25]. It is well known that a typical SCS is substantially an exothermic redox reaction between a soluble oxidizer (e.g. metal nitrates) and an organic fuel (e.g. urea, glycine, citric acid, etc.) derived from a homogenous aqueous solution within a short

time (on the order of seconds) without any additional external energy input (in a self-sustained manner), coupled with copious gas evolution (e.g. H_2O, CO_2, N_2, etc.) [26−28]. Obviously, such SCS characteristics will endow the synthesized product with some unique properties [29,30]. Firstly, the initial aqueous solution allows all the raw materials to mix on molecular level, permitting the homogenous distribution of desired composition and the precise formulation of synthesized product. Secondly, the ignition temperature needed for SCS is merely adequate triggering the combustion reaction, instead of providing the sustaining energy input (additional high-temperature calcination step) to form crystal lattice just like some traditional preparation methods, thus the high self-generated energy derived from exothermic redox reaction ensures the high purity and crystallinity of synthesized product. Thirdly, the short process duration could inhibit the growth of particle size and the formation of various gases could fragment some large agglomerates, thus leading to a fine and dispersed morphology of synthesized product. In light of the above outstanding features, a growing number of useful nano-oxides have been prepared by SCS method over the past few decades [25,27,31−33]. However, as far as we know, there are few reports on the fabrication of nanostructured Fe_3O_4 via SCS, heretofore, not to mention the direct synthesis of Fe_3O_4 nanoparticles, in a pure, crystalline state via a single SCS route.

Hence, in this work, we reported a one-step SCS method by designing a simple air exhausting device for the preparation of pure phase Fe_3O_4 nanoparticles just by tuning the molar ratio (ϕ) of fuel (glycine) to oxidizer (ferric nitrate). The whole process did not involve any toxic or unavailable reagents, and could be finished in a few minutes by its self-generated energy derived from redox reaction between glycine and ferric nitrate. In addition, the effects of ϕ value on the combustion reaction mechanism and phenomenon, morphology and microstructure, phase composition and saturation magnetization of the synthesized SCS products have been investigated systematically.

2. Experimental section

Ferric nitrate nonahydrate [Fe $(NO_3)_3\cdot 9H_2O$] and glycine ($C_2H_5NO_2$) were supplied by Sinopharm Chemical Reagent Co., Ltd., China. Both chemicals were of analytical grade, commercially available and used as received without further purification. As shown in Fig. 1, Fe $(NO_3)_3$ and $C_2H_5NO_2$ were first dissolved in 150 mL deionized water under stirring to get a homogeneous solution. Then, the solution was poured into 1000 mL beaker with a perforated rubber plug (not only separated outside air but also released gases derived from reaction) and heated on a temperature controlled hot plate. With continuous heating, the solution evaporated and evolved into a viscous gelatinous mass. In a few minutes, a violent combustion reaction suddenly took place among or along the edge of gelatinous mass, accompanied by the liberation of voluminous gases. Noteworthily, the whole SCS process seemed to undergo a self-propagating and non-explosive combustion reaction, which took short time and resulted in the formation of fluffy nanosize powder.

Thermal analysis of the gelatinous mass was characterized in argon atmosphere from 50 °C to 600 °C at a constant heating rate of 10 °C min^{-1} by using a thermal analyzer (TG-DSC, TA Q600). Surface morphology of the SCS products was observed using field emission scanning electron microscopy (FE-SEM, Quanta FEG-450) at 30 kV. Phase analysis of the SCS products was performed on an X-ray diffractometer (XRD, Ultima IV) equipped with graphite monochromatized Cu Kα radiation as the X-ray source. The average grain size of SCS products was calculated according to the Debye-Scherrer formula [34], D = Kλ/βcosθ, where D was the average

grain size, K was a constant related to the shape of grain, λ was the wavelength of employed radiation, β was the peak width (full width at half maximum, FWHM) in radians, and θ was the Bragg diffraction angle. The surface composition of SCS products was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo EscaLab 250Xi) at a background pressure of about 10^{-9} Torr using Al Kα X-rays as the excitation source (1486.6 eV). Magnetic measurements were carried out using the physical properties measurement system (PPMS) in a vibrating sample magnetometer (VSM, BKT-4500) with a magnetic field varied in the ± 6000 Oe range.

3. Results and discussion

In SCS process, the fuel to oxidizer molar ratio has been previously shown to alter the thermal behavior, oxidation state, morphology and properties of products [35,36]. Thus, in this work, the molar ratio of glycine (variate) to ferric nitrate (constant), denoted as $\phi = (n_{Gly} - n_{Fe})/n_{Fe}$, was taken to be 0.5 (fuel-lean condition), 0.7 (stoichiometric equilibrium), 1.2 and 1.6 (fuel-rich condition), according to the propellant chemistry theory proposed by Jain et al., [37] as described in Eq. (1).

$$54Fe(NO_3)_3 + 92C_2H_5NO_2 = 18Fe_3O_4 + 184CO_2 + 230H_2O + 127N_2$$

$$(1)$$
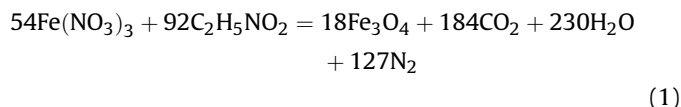
In order to explore the combustion reaction mechanism in SCS process, the gelatinous mass obtained from different ϕ reaction systems were heated from 50 °C to 600 °C in argon atmosphere at a heating rate of 10 °C min^{-1} by using thermogravimetry (TG)-differential scanning calorimetry (DSC). The resulting TG-DSC curves are presented in Fig. 2. According to the shape of curves, the whole reaction procedure can be clearly divided into three temperature stages. In the first stage (100−150 °C), Fig. 2 (a, b) show a weak and wide endothermic peak accompanied by a major weight loss of ~30%, while Fig. 2 (c, d) display a relatively distinct and narrow endothermic peak at around 130 °C coupled with a minor weight loss of ~10%. The observed ~10% weight loss in $\phi = 1.2$ and 1.6 reaction systems can be ascribed to the vaporization of residual water and desorption of chemically absorbed water in the gelatinous mass. By comparison, the observed ~30% weight loss in $\phi = 0.5$ and 0.7 reaction systems can be attributed to the superposition of the removal of various types of water and the partial decomposition of excessive ferric nitrate in fuel-lean condition. In light of the corresponding weak and wide endothermic characteristic on DSC curves (Fig. 2 a and b), it is a reasonable inference that the decomposition of ferric nitrate is a slow and moderate process. In the second stage (150−200 °C), all the reaction systems undergo an abrupt weight loss on the TG curves and a drastic exothermic peak at ~160 °C is presented on the DSC curves, which are in relation to the thermally induced redox reaction between ferric nitrate and glycine. As depicted in Fig. 2(a−d), it is apparent that with the increase of ϕ value, the position of exothermic peak seems immobile while its shape changes from sharp to a little wide, especially in $\phi = 1.6$ reaction system, the exothermic peak become bimodal, which may be attributed to the synergy effects of the combustion reaction between ferric nitrate and glycine and the reduction reaction of ferric ions. Actually, glycine can not only serve as a fuel during the combustion reaction, but also act as a reducing agent being oxidized by nitrate ions, at the same time, the ferric ions in ferric nitrate will be reduced by amino group in glycine. It is well known that the more reducing agent exists in reaction system, the stronger reduction ability it owns. Thus, in this ferric nitrate-glycine