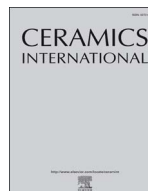




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# Solution combustion synthesis of nanostructured iron oxides with controllable morphology, composition and electrochemical performance

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## ABSTRACT

Nanostructured iron oxides have emerged as promising materials for electrochemical energy storage and conversion devices due to their high theoretical capacity, eco-friendliness and earth abundance. Particularly, the morphology- and composition-controllable synthesis of nanostructured iron oxides is extremely important to optimize their electrochemical performance. However, the development of facile and effective synthetic method is still a great challenge. In this paper, we demonstrated a one-pot solution combustion synthesis (SCS) approach for the time- and energy-effective preparation of nanostructured iron oxides with controllable morphology and composition just by tuning the molar ratio ( $\varphi$ ) of fuel (glycine) to oxidizer (ferric nitrate). Innovatively, the effects of  $\varphi$  value on the control of combustion reaction mechanism, morphology and composition of SCS products, and the electrochemical properties in relation to the morphology and composition have been systematically investigated. The results revealed that with the increase of  $\varphi$  value, the reaction mechanism varied from pyrolysis to combustion and the combustion phenomenon changed from volumetric mode to self-propagating mode. Correspondingly, the morphology of products evolved from uniform nanoneedles to porous nanosheets, and finally into aggregated nanoparticles. Meanwhile, the phase composition of these products changed from amorphous  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> to crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and eventually into  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> composites. When evaluated as lithium ion battery anode, the as-prepared  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>/Fe<sub>3</sub>O<sub>4</sub> porous nanosheets ( $\varphi = 1.0$  product) exhibited the best electrochemical properties (a high reversible capacity of  $\sim 1200 \text{ mA h g}^{-1}$  and an excellent rate capability) among all the SCS products, which may be attributed to its mesoporous structure (supply favorable accessibility for electrons), nanosheet morphology (shorten the transport length of Li<sup>+</sup>) and appropriate proportion of Fe<sub>3</sub>O<sub>4</sub> phase (enhance the electronic conductivity). Consequently, the facile SCS method demonstrated here might provide a new methodology for the morphology and composition-controllable synthesis of nanomaterials, for which a number of prospective applications in electrochemical fields can be envisioned.

## 1. Introduction

Iron oxides, such as hematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and magnetite (Fe<sub>3</sub>O<sub>4</sub>), have received steadily growing attention during the past few decades owing to their earth abundance, low toxicity and peculiar physicochemical properties [1–4]. As compared to the corresponding bulk counterparts, nanostructured iron oxides exhibit enhanced properties, such as good biocompatibility, superior magnetic properties, excellent gas and light sensing properties, which make them attractive for various applications including biomedicine, magnetic recording media, gas sensors and photocatalysts [5–8]. Besides, in recent years, with the rapid development of electrochemical energy storage and conversion devices, nanostructured iron oxides have also attracted considerable

interest in the electrochemical area due to their low cost, environmental benignity, high theoretical capacity and good chemical stability [9–12]. In spite of these distinct advantages, the electrochemical performance of nanostructured iron oxides is still strongly dependent on their morphology and composition, which are generally believed to have significant influences on the diffusion kinetics of ions, transport rate of electrons and structural stability of electrodes in energy conversion and storage systems [13–16]. Therefore, the morphology- and composition-controllable preparation of nanostructured iron oxides is of great importance to explore their optimal electrochemical performance.

As is well known, the wet chemical methods, including hydrothermal, micro-emulsion, co-precipitation and sol-gel method, can easily prepare uniform nanomaterials with controllable morphology and

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**Table 1**  
Reaction systems of different molar ratios ( $\varphi$ ) of glycine to ferric nitrate.

$\varphi$	Glycine (mol)	Ferric nitrate (mol)	Reaction condition
0	0	0.025	fuel-free
0.5	0.0208	0.025	fuel-lean
1.0	0.0417	0.025	stoichiometric
1.5	0.0625	0.025	fuel-rich

composition just by tuning the reaction conditions due to their unique advantage, that is, they own the ability to fabricate nanomaterials through molecular precursors in aqueous solution, permitting rigorous control of the entire process and allowing the tractable synthesis of “tailor-made” nanomaterials [17–20]. However, these synthetic approaches generally confront the disadvantages of complex apparatus, long duration, elaborate procedure or environmental pollution, which would limit their massive production and practical applications to some extent. Therefore, it is imperative to explore time- and energy-saving method for the simple and scalable preparation of nanostructured iron oxides with controllable morphology and composition in an environmental-benign manner.

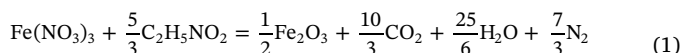
During the past few decades, solution combustion synthesis (SCS) has emerged as an extensive employed wet chemical method to fabricate diverse nanomaterials, especially for nano-oxides and composites, due to its obvious advantages of nonpollution, simplicity, scalability, time- and energy-efficiency [21,22]. To be specific, 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.) dissolved in a homogenous aqueous solution (molecular precursors) within a short duration (on the order of seconds) without any additional energy input (in a self-sustained manner) [23,24]. Apparently, the raw materials are non-toxic, low-cost and available, meanwhile, the experimental apparatus and preparation procedures are simple and straightforward. Once the redox reaction occurs, the high self-generated

energy derived from combustion could convert metals into the corresponding oxides directly in a few seconds without the requirement of external energy. The short processing duration and energy saving feature make SCS method suitable for the massive production in practical applications [25–27]. Hence, in the present work, we synthesized nanostructured iron oxides with controllable morphology and composition via SCS method just by tuning the molar ratio ( $\varphi$ ) of fuel (glycine) to oxidizer (ferric nitrate). The effects of  $\varphi$  value on the control of combustion reaction mechanism, morphology and composition of SCS products, and the electrochemical properties in relation to the morphology and composition have been systematically investigated.

## 2. Experimental section

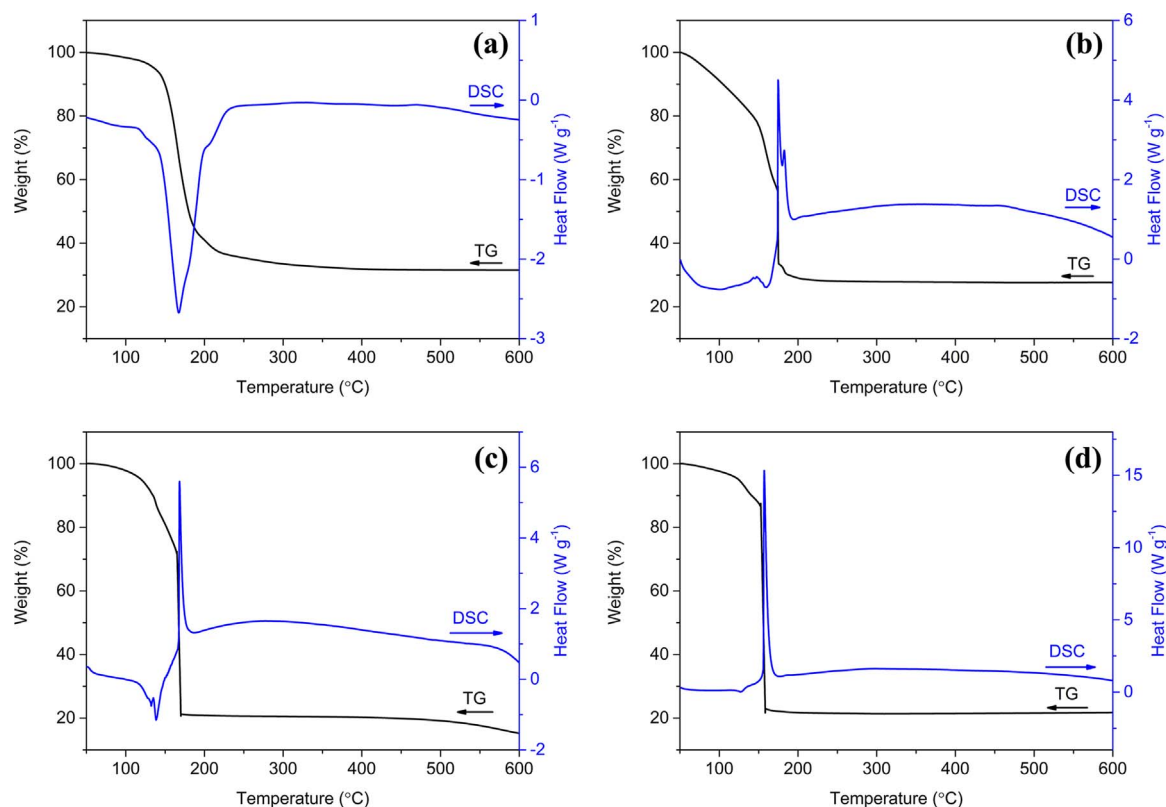
### 2.1. Synthesis

The nanostructured iron oxides were prepared via SCS method by using ferric nitrate [ $\text{Fe}(\text{NO}_3)_3$ ] as the oxidizer and glycine ( $\text{C}_2\text{H}_5\text{NO}_2$ ) as the fuel. The stoichiometric equilibrium combustion reaction could be represented as follow:



Among the various tunable parameters in SCS process, the amount of fuel has been verified to play a crucial role in altering the morphology, composition and properties of final products [28]. Thus, in this work, the molar ratio of glycine (variate) to ferric nitrate (constant), denoted as  $\varphi = \frac{3}{5} \times n_{\text{Gly}}/n_{\text{Fe}}$ , was taken to be a key tunable parameter, which varied from 0 (fuel-free condition) to 1.5 (fuel-rich condition), as specified in Table 1.

In a typical SCS procedure,  $\text{Fe}(\text{NO}_3)_3$  and  $\text{C}_2\text{H}_5\text{NO}_2$  were first mixed under appropriate molar ratio and then dissolved in 50 mL deionized water to get a homogeneous solution. The obtained solution was poured into 500 mL beaker and put on a pre-heated electric furnace (300 °C). As heating continued, the solution boiled with the evolution of a large



**Fig. 1.** TG-DSC curves of gel originated from different  $\varphi$  reaction systems: (a)  $\varphi = 0$ ; (b)  $\varphi = 0.5$ ; (c)  $\varphi = 1.0$ ; (d)  $\varphi = 1.5$ .

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