Microwave-Assisted Organic-Template Synthesis of Iron Oxide Particles

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Abstract: In this study, $Fe(NO_3)_3.9H_2O$ is used as the Iron source, glycine and ammonium nitrate are co-oxidizers and Xanthan gum is the template. The synthesis of Iron oxide particles and the removal of template are undertaken by microwave radiation. Template synthesis using Xanthan gum and water as the solvent is a green approach. Xanthan gum (XG) is a water-soluble hetero polysaccharide including hydroxyl units along its backbone and branches can provide xanthan gum with capability of forming hydrogel networks. Physical properties of products depend on the power and duration of microwave exposure. The prepared samples are characterized by Fourier-Transform Infrared spectroscopy (FT-IR), powder X-Ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA) and Scanning Electron Microscopy (SEM).

Keywords: Iron oxide, heteropolysaccharide, microwave, organic-template

Introduction

Iron oxide is widely known as a catalyst, pigment and gas sensitive material. There are many developed methods for the synthesis of Iron oxide such as: sol-gel [1], electrochemical techniques [2], sputtering [3], vapor deposition [4] and hydrothermal [5]. Mentioned methods have proven to be advantageous in different aspects, but recently attentions has drawn to methods which are both eco-friendly and commercially feasible.

Organic molecules can produce different interesting arrangements. Using self-assembled systems have drawn a considerable attention because templates can be used to synthesize anisotropic nanostructures and composite materials [6]. The template is defined as a pattern that can be used to reproduce a complementary architecture. The templates can dictate the structure and can be removed after the components have reacted. These whole steps are called transcription [7].

The removal of the organic template can be achieved by heat treatment [8], microwave irradiation [9] or washing [10]. Removal by heat treatment, also known as calcination, needs high temperatures and consumes high amounts of energy. Washing with organic solvents, solely is not effective and does not seem to be green approach. Template synthesis using XG and water as the solvent is a green approach. XG is a water-soluble hetero polysaccharide including hydroxyl units along its backbone and branches can provide xanthan gum with capability of forming hydrogel networks [11] and using MW radiation in has proven to be a fast, effective and reliable means of removing template.

Experimental Section

All chemicals used in this study were bought from Merck Company and used without further purification.

Iron(III)nitrate nonahydrate, $Fe(NO_3)_3.9H_2O$, is used as the iron source, glycine and ammonium nitrate are co-oxidizers and XG is the template. The solvent of the reaction is deionized (DI) water. The stoichiometric proportion of reactants in this study was altered and studied. The ratio of 12:6:1 of glycine: ammonium nitrate: iron nitrate in 5 mL of water and 10:1 w/w of glycine to XG in 10 mL water has shown to be the most favorable conditions for the reaction to take place.

The procedure of the experiment consists of three steps. First, glycine, ammonium nitrate and iron nitrate was dissolved in water and stirred by a magnetic stirrer for 5 min to get an orange-brownish solution. Second, XG, as the template, was added to water and mixed by overhead stirrer to get a transparent and homogeneous gel. In the last step, the first solution was added to the template solution and stirred for 5 min.

The resulting mixture was put into a reaction setup made of an alumina crucible encircled by a jacket of CuO as a MW absorbing layer and was placed in a microwave device with varying power (720-900 W) and times of MW exposure (5, 10, 15, 20 min). The resulting precipitation was washed with Ethanol and distilled water for several times. The products were characterized by XRD, FT-IR, TGA, DTA and SEM.

Characterization

Thermogravimetric analysis (TGA) was carried out on a PerkinElmer Pyris Diamond from room temperature to 800 °C by a ramp rate of 10 °C/min in air. Fourier transform infrared (FT-IR) spectra were recorded on a Shimadzu-8400S spectrometer in the range of 400–4000 cm^{-1} using KBr pellets. The X-ray diffraction (XRD) patterns were recorded by a STOE powder diffraction system using CuKα radiation (wavelength, λ=1.54060 Å). Scanning electron microscopy (SEM) images were taken on VEGA\TESCAN S360 with gold coating.

Results and Discussion

TGA thermogram of product is shown in Fig. 1. As can be seen, a small loss of mass between room temperature and 150 °C is related to physically adsorbed water molecules, which is an endothermic process. The largest weight loss from 180 to 600 °C could be attributed to the degradation of Xanthan. The results show that in order to exterminate the template completely, heating around 600 °C is required.

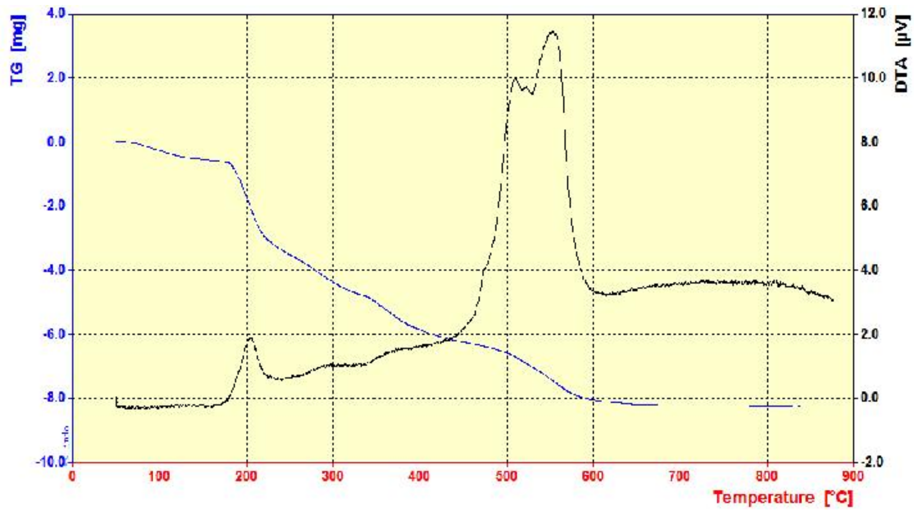

Figure 1 TG-DTA diagrams of product

Fig 2. illustrates the IR spectrum of precursor and product, before and after the removal of the template. The observed broad peak around 3400 cm^{-1} is related to O-H bond. The appeared peak at 2900 cm^{-1} is assigned to the stretching vibration of C-H bond. The peak near 600 cm^{-1} belongs to Fe-O bond [12]. These two analyses along with each other show that the MW radiation is an effective way for template synthesis of inorganic materials.

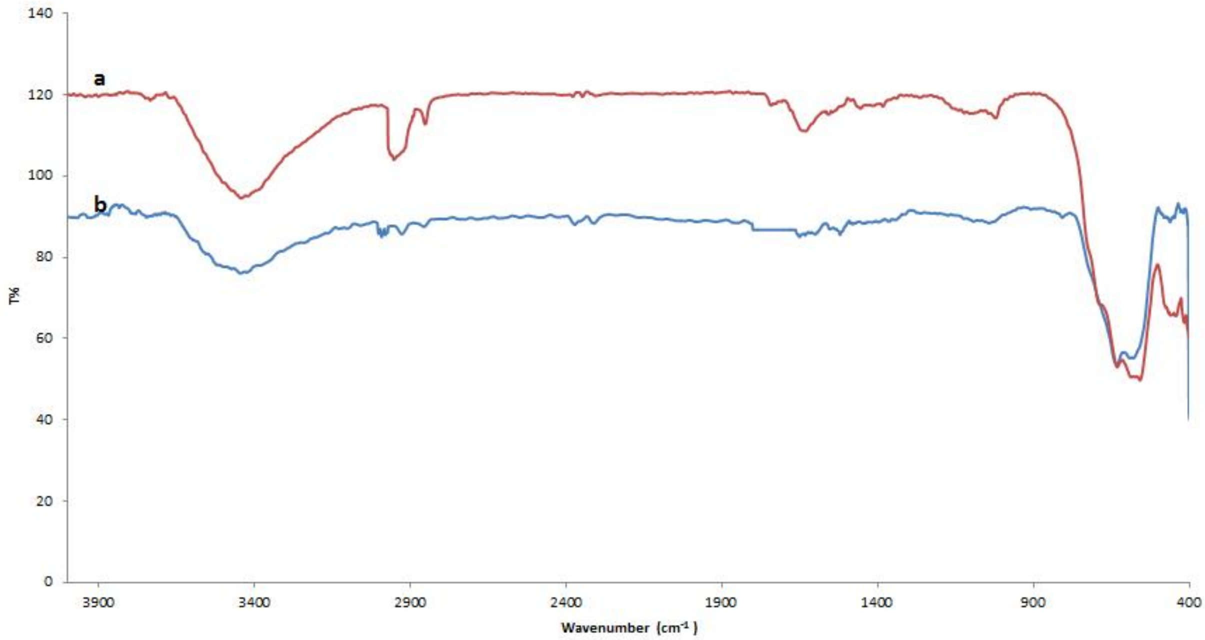

Figure 2 IR spectrum of a) before and b) after the removal of template

XRD pattern of synthesized product shows similar cubic pattern of Fe_3O_4 pertaining to JCPDS card No. 01-076-1849 (Fig.3). Diffraction peaks at 2θ values of 18.278°, 30.066°, 35.413°, 37.044°, 43.038°, 53.391°, 56.914°, 62.497° and 73.931° are matching with 111, 220, 311, 222, 400, 422, 511, 440 and 533 planes of Fe_3O_4 cubic phase in Fd-3m space group. The sharp diffraction peaks confirm the formation of a pure phase of Fe_3O_4 with excellent crystallinity. No other peaks for impurities were detected.

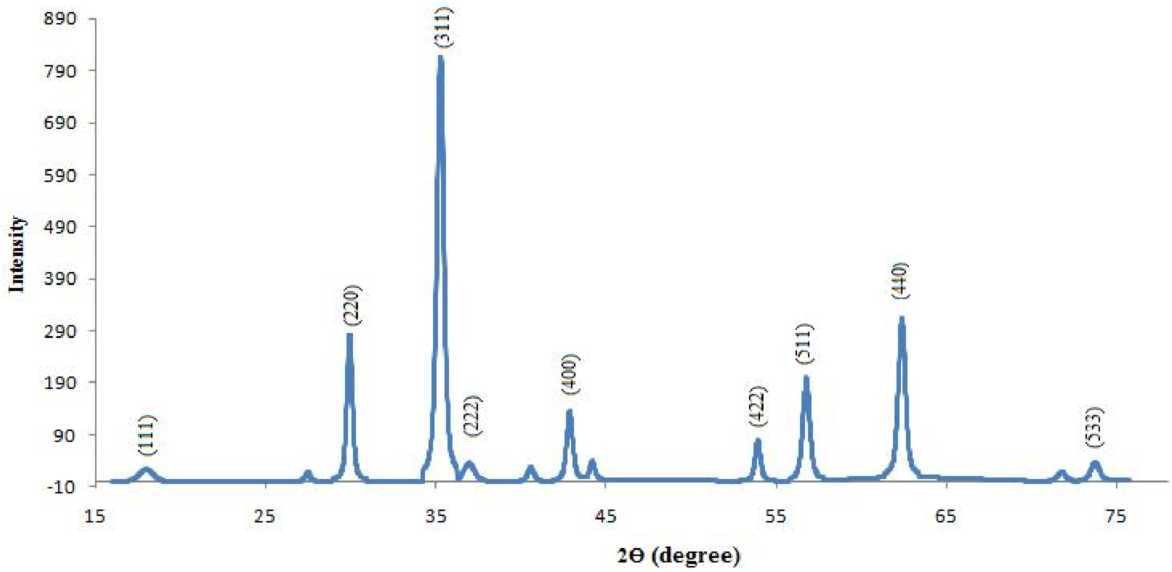

Figure 3 XRD pattern of prepared sample after the removal of template

Fig. 4 reveals SEM image of product. It seems that agglomeration of particles was happened in samples because of very high temperature of reaction. MW irradiation has been caused to sinter the nanoparticles.

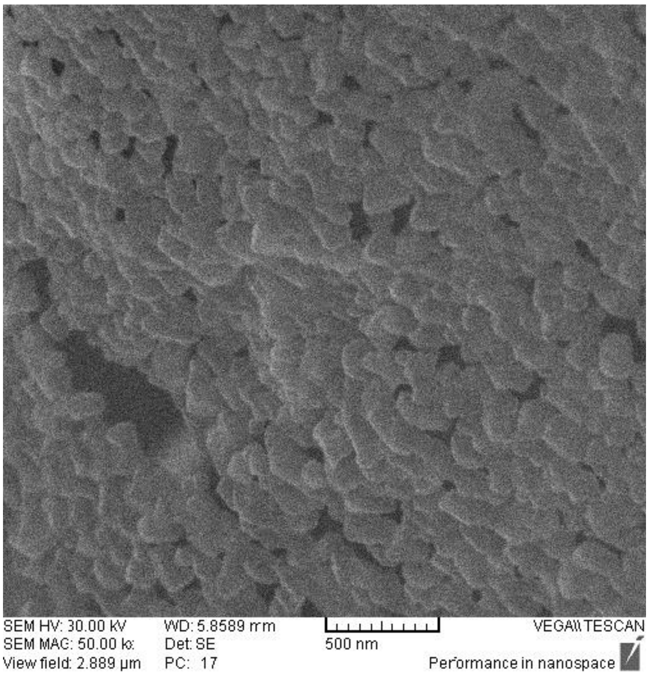

Figure 4 SEM image of product

Conclusion

In this study a natural polysaccharide gel template which is a driving force to dictate different morphologies is used. Utilizing templates in supramolecular chemistry, especially those which are biodegradable has shown to be useful and eco-friendly. Templates found to be essential for construction of complex molecular architectures that would otherwise have been impossible. The removal of template is achieved by MW radiation which is economical, fast and efficient approach.

Acknowledgements

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