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Studies on the microwave assisted and conventional combustion synthesis of *Hibiscus rosa-sinensis* plant extract based $ZnFe_2O_4$ nanoparticles and their optical and magnetic properties

K. Kombaiah[a], J. Judith Vijaya[a,*], L. John Kennedy[b], M. Bououdina[c,d]

[a]*Catalysis and Nanomaterials Research Laboratory, Department of Chemistry, Loyola College, Chennai 34, India*
[b]*Materials Division, School of Advanced Sciences, Vellore Institute of Technology (VIT) University, Chennai Campus, Chennai 127, India*
[c]*Nanotechnology Centre, University of Bahrain, PO Box 32038, Bahrain*
[d]*Department of Physics, College of Science, University of Bahrain, PO Box 32038, Bahrain*

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Abstract

Nanocrystalline $ZnFe_2O_4$ samples were synthesized by both conventional combustion method (CCM) and microwave assisted combustion method (MCM) using *Hibiscus rosa-sinensis* plant extract for comparison purpose. The prepared $ZnFe_2O_4$ samples were characterized by X-ray diffraction (XRD), Rietveld analysis, Fourier transform-infrared spectrophotometer (FT-IR), high resolution scanning electron microscopy (HR-SEM), energy dispersive X-ray analysis (EDX), diffuse reflectance spectroscopy (DRS), photoluminescence (PL) spectroscopy, and vibrating sample magnetometer (VSM). The formation of single phase $ZnFe_2O_4$ was confirmed by XRD and FT-IR. The lattice parameter was calculated by Rietveld analysis. The change in the particle size ranges from 372.0 to 541.7 nm and 23.4 to 48.5 nm respectively for the conventional and microwave methods and has been clearly shown by HRSEM. UV–visible diffuse reflectance spectroscopy is used to measure the band gaps of $ZnFe_2O_4$, which is about 2.1 eV. Single phase $ZnFe_2O_4$ emits the photoluminescence bands at 486, 530, 542, and 566 nm. The magnetic properties of the synthesized $ZnFe_2O_4$ nanoparticles were investigated by VSM studies and the hysteresis loops were studied at room temperature. The saturation magnetization (M_s) of $ZnFe_2O_4$-CCM (63.61 emu/g) is lesser than that of $ZnFe_2O_4$-MCM (255.7 emu/g). $ZnFe_2O_4$ nanoparticles prepared by the microwave assisted combustion method were found to have higher surface area and lower crystallite size than $ZnFe_2O_4$ nanoparticles prepared by the conventional combustion method.

Keywords: A. Microwave processing; B. Nanocomposites; C. Magnetic properties; D. Ferrites; Plant extracts

1. Introduction

In recent years, preparation of transition metal oxides based ferrites (MFe_2O_4) (M = Cu, Co, Ni and Zn) has gained substantial interest [1]. Among them, zinc ferrite ($ZnFe_2O_4$) is the most extensive semiconductor material with a direct bulk band gap of 1.9 eV [2]. $ZnFe_2O_4$ bears a normal spinel structure with Zn^{2+} ions residing in the tetrahedral sites (A sites) and Fe^{3+} ions in the octahedral sites (B sites) and this arrangement can be commonly represented using the formula $(Zn^{2+})[Fe_2^{3+}]^{-}O_4^{2-}$. Remarkable magnetic properties are shown by the nanometer-sized $ZnFe_2O_4$ compared to the bulk form [3]. For example, high Curie temperature and large magnetization at room temperature (RT) have been observed in $ZnFe_2O_4$ nanoparticles and films [4]. Because of their distinct properties, a variety of high-quality $ZnFe_2O_4$ nanostructures are renowned to acquire an extensive range of potential applications in microelectronics [5], magnetic behavior [2], electrical characteristics [6], semiconductor photocatalysis [7], high-density data storage, ferrofluid technology, magneto caloric refrigeration, magnetic resonance imaging, heterogeneous catalysis [8], gas sensors [9], and magnetically guided

*Corresponding author. Tel.: +91 44 28178200; fax: +91 44 28175566.
E-mail addresses: jjvijayaloyola@yahoo.co.in, jjvijaya78@gmail.com (J.J. Vijaya).

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drug delivery [10]. $ZnFe_2O_4$ nanoparticles are prepared by various methods, such as, sol–gel [11] and [12], co-precipitation [13], microemulsion [14], pulsed laser deposition [15], hydrothermal method [16], and ultrasonic cavitation approach [17,18]. Of those methods mentioned, the combustion method [19] is commercially the most successful and it is used to speed up the synthesis of complex materials. This method is a time- and energy-saving technique, when compared to the traditional methods, and results into smaller crystallite size. Conventional combustion methods involve high sintering temperatures and longer annealing times to attain a homogeneous composition. Unfortunately, this preparation method prevents the optimization of physical properties of these materials required for numerous advanced technological applications, due to the poor homogeneity, undesirable phase formation and irregular grain growth [20,21].

Recently, the use of microwave treatment has emerged as an efficient technique and it has many advantages compared to the conventional heat treatments [22]. Microwave heating is basically different from the conventional heating, because microwaves can penetrate deeper into the sample. It is more environment friendly, cost effective, and requires less energy than the other conventional methods [23]. In the microwave, the sample heating is to be initiated volumetrically, as opposed to the conventional thermal processing, which heats the sample from inward via the standard heat transfer mechanisms, i.e., through convection, conduction, and radiation [24]. Also microwave method is preferred, because of non-contact heating, energy transfer rather than heat transfer, rapid heating, material selective heating and volumetric heating [25,26].

Bhattacharaya et al. [27] have reported the use of biological organisms, such as, microorganisms, plant extract or plant biomass, which could be an alternative to chemical and physical methods for the production of nanoparticles in an eco-friendly manner. In addition, Bhainsa et al. [28] reported that without the use of toxic chemicals or the need for high pressures, energy and temperatures, the use of plants can be easily scaled up for large-scale synthesis. Plant extracts are used as both reducing and capping agents for the synthesis of nanoparticles [30]. The plant extract plays the dual role of a fuel with a coordinating action, thus occupying the metal ions in the amylose helix of the extract through the transparent sites. It also impedes the separation of the metal oxides. An interesting topic of this research field is the non-polluting and controlled synthesis of oxide materials, which involves the natural compounds of low cost as raw materials and also as active ingredients for the nanosized metal oxide particles [29].

Hibiscus rosa-sinensis is an herbaceous plant and it is a well known member of the family Malvaceae. The bio-chemical constituents of the plants are taraxerol acetate, β-sitosterol, campesterol, stigmasterol, cholesterol, ergosterol, lipids, citric, tartaric and oxalic acids, fructose, glucose, sucrose, flavonoids and flavonoid glycosides [30]. The leaf extract of *H. rosa-sinensis* has been used as the reducing as well as the surface stabilizing agent for the synthesis of nanoparticles. Hence, it is of great interest to make an energy efficient, new and simple route towards the preparation of $ZnFe_2O_4$ using the plant extract. Although, synthesis of $ZnFe_2O_4$ nanoparticles using the plant extracts like aloe vera is reported [26,31], studies on the synthesis of the same under microwave assisted combustion method is not reported. Also, there is a literature available for the preparation of metal oxides using *H. rosa-sinensis* [32]. But to the best of our knowledge, no literature is found on the synthesis of nano-zinc ferrites by a microwave assisted combustion method using metal nitrates and *H. rosa-sinensis* extract solution as the precursors. The structure, phase, and morphology of the synthesized products are investigated by the standard characterization techniques in the present study in order to have the comparative investigation of the prepared samples.

2. Experimental section

2.1. Materials

Zinc nitrate (99% purity) and ferric nitrate (99% purity) were used as the starting materials. All the metal salts were obtained from Merck, India (analytical grade) and were used without further purification. *H. rosa-sinensis* leaves were collected from the local fields in Chennai, Tamilnadu.

2.2. Preparation of Hibiscus rosa-sinensis plant extracts

A 25 g portion of thoroughly washed *H. rosa-sinensis* leaves was finely ground and the obtained gel was dissolved in 100 ml of double distilled water. It was stirred for 45 min to obtain a clear solution. The resulting extract was named as *H. rosa-sinensis* plant extract.

2.3. Preparation of zinc ferrite by conventional combustion method (CCM)

2.974 g of zinc nitrate and 8.08 g of ferric nitrate were dissolved separately in 10 ml of double distilled water and then both the solutions were mixed and stirred for about 30 min until a homogeneous mixture was obtained. *H. rosa-sinensis* plant extract was mixed with the homogeneous metal nitrate solutions with constant stirring at room temperature for 5 h, until a clear solution was obtained. The molar ratio of Zn/Fe was kept as 1:2. *H. rosa-sinensis* plant extract served as a fuel, while the nitrates in the precursors served as the oxidizers. The resulting solution was dried in a hot air oven at 180 °C for 3 h. The powders were then sintered at 900 °C with a heating rate of 5 °C/min for 3 h in the muffle furnace and the obtained solid powder is washed with ethanol and dried in an oven at 100 °C for 1 h. The obtained powder was labeled as sample A (prepared by CCM).

2.4. Preparation of zinc ferrite by microwave assisted combustion method (MCM)

The clear solution prepared as mentioned in the earlier section was then transferred into the silica crucible and placed in a domestic microwave-oven for irradiation. Microwave irradiated the precursors for 15 min at 850 W output power,