Materials Chemistry and Physics 194 (2017) 153–164

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Studies on *Opuntia dilenii haw* mediated multifunctional $ZnFe_2O_4$ nanoparticles: Optical, magnetic and catalytic applications

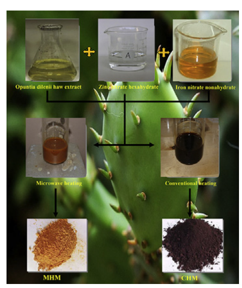
K. Kombaiah [a], J. Judith Vijaya [a, *], L. John Kennedy [b], M. Bououdina [c, d], Hamad A. Al-Lohedan [e], R. Jothi Ramalingam [e]

[a] *Catalysis and Nanomaterials Research Laboratory, Department of Chemistry, Loyola College (autonomous), Chennai, 600034, India*
[b] *Materials Division, School of Advanced Sciences, Vellore Institute of Technology, (VIT) University, Chennai Campus, Chennai, 600127, 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*
[e] *Surfactant Research Chair, Chemistry Department, College of Science, King Saud University, Riyadh, 11451, Saudi Arabia*

HIGHLIGHTS

- Microwave method is an efficient route to synthesize nanoparticles.
- Plant extracts could be an alternative to chemical reagents.
- Plant extracts play the role of a fuel with a coordinating action.
- High purity single-phase cubic $ZnFe_2O_4$ was reported.
- $ZnFe_2O_4$ prepared by MHM showed small particle size and high catalytic activity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 January 2017
Received in revised form
7 March 2017
Accepted 14 March 2017
Available online 21 March 2017

Keywords:
Green synthesis
Nanoparticles
Microwave processing
Catalytic activity
Glycerol
Magnetic properties

ABSTRACT

The sustainable and eco friendly green synthesis report on the use of plant extract alternate to chemicals has been discussed. In this work, opuntia plant extract is used as a natural reagent to synthesize nanoparticles. Herein, we demonstrate two methods namely, conventional and microwave method for the synthesis of nanoparticles using plant extract, due to its easy handling and bio-compatibility. Both the methods were carried out under the same conditions to explore the comparison of the data. Various characterization techniques were used to determine the crystallinity, crystallite size, lattice parameter, morphology, elemental composition, band gap energy, emission, saturation magnetization, and coercivity of the as-synthesized nanoparticles. A brief discussion about the importance of using the plant extract as well as the importance of microwave heating were discussed and summarized. The phase identification was examined using XRD analysis, which showed the formation of single and pure phase without any post annealing in microwave heating method. The formation of pure phase ferrites is also confirmed by Fourier Transform Infrared Spectroscopy (FTIR). The surface morphology of $ZnFe_2O_4$ nanoparticles showed spherical shape and the size difference depends upon the method of synthesis. EDX analysis confirms the phase-purity of the as-synthesized nanoparticles. UV–Vis DRS of the as-obtained nanospheres exhibited the absorbance in the visible region. VSM analysis showed that the sample prepared by microwave technique exhibited better magnetic behaviour at room temperature than that of the ones prepared by the conventional heating method. The microwave heating technique produces nano-ferrites with high yield, low crystallite size, uniform morphology, and good absorption properties than the conventional heating method. Zinc ferrites were used in the catalytic reaction for the

* Corresponding author.
E-mail addresses: jjvijayaloyola@yahoo.co.in, jjvijaya78@gmail.com (J.J. Vijaya).

http://dx.doi.org/10.1016/j.matchemphys.2017.03.020

oxidation of glycerol into formic acid. The catalyst exhibit good catalytic performance and better selectivity of formic acid throughout the reaction. The plausible mechanism has been proposed.

1. Introduction

The nanoparticles have enticed a great interest among the scientific researchers, due to their complex structure, and chemical stability. They completely exhibit new and novel properties, when compared to their bulk materials. A variety of applications were carried out in medicine, solar cells, environment, energy, agriculture, information, communication, consumer goods, electronics, and catalysis using nanoparticles [1,2]. Ferrites are ceramic ferromagnetic materials. The general formula of the spinels is MFe_2O_4, where M represents Cu, Ni, Co, Zn etc. Among these, $ZnFe_2O_4$ has attracted much interest, due to its intriguing magnetic properties [3]. All the non-magnetic Zn^{2+} cations are located at A sites and magnetic Fe^{3+} cations are located at B sites. Bulk $ZnFe_2O_4$ commonly shows an antiferromagnetic behaviour at a Neel temperature of 10.5 K. But, nanosized ferrites often display the ferromagnetic behaviour below a blocking temperature (TB) as it has a mixed spinel structure and it strongly depends on the synthesis conditions [4].

In recent years, the catalytic conversion is in demand among the industries and researchers. There are various routes available on the catalytic reactions; etherification [5], dehydration [6,7] and hydrogenolysis [8,9]. Oxidation reaction [10–13] is more favourable, due to its environmental concern, economical benefit, clean, non-hazardous and safety issues. Glycerol is one of the most important renewable resources and oxidation of glycerol is extensively studied for sustainable number of products formation, such as glyceraldehyde, glyceric acid, oxalic acid, acetic acid, Dihydroxyacetone, formic acid, etc. Several literature are available on the catalytic conversion of glycerol to variable products by varying the supported metal catalysts, such as Pt, Pd, Au, Cu, TiO_2 [14–16]. Also few literature are available on the conversion of glycerol to formic acid products [17–19]. The main aim of preparing formic acid is because it is a non-toxic and renewable reagent, biodegradable, and used in energy storage for green chemical synthesis.

Nanoparticles have been synthesized using sol gel technique [20], ball milling [21], sonochemical [22], co-precipitation [23], hydrothermal [24], reverse micelle [25], mechanical alloying [26], and citrate precursor technique [27]. Among these methods, combustion synthesis has attracted many researchers, due to its energy and time-saving process [28]. The combustion method has also emerged as an attractive technique for the production of unstable powders, forming hard agglomerates with excellent chemical stability, uniform distribution of the metal ions and nanosized particles [29]. Different fuels, such as urea, citric acid, glycine, N-methylurea, hexamethylenetetramine, N,N diformylhydrazine, L-alanine, starch, and L-arginine are used for the combustion reactions along with the metal precursors to synthesize undoped and doped zinc ferrites. The nanoparticles synthesized by conventional heating method have several limitations compared to microwave heating method [30].

Recently, microwave (in situ heating) is used for the synthesis of ferrites as an efficient method. The popularity of this method is because of the friendly method and its outstanding ability to reduce the reaction time by superheating and produce products with high yield. In contrast to classical heating, microwave generate the heat within the material on a molecular level by the interaction of microwaves, and the heat will be evenly and rapidly distributed from inside and outside (no wall heating), instead of originating from the external sources, which leads to a homogeneous and quick reaction. This method requires shorter time periods and it is more efficient in terms of using less external energy, producing homogeneity, small particle size and highly pure sample [31]. On the other hand, in conventional heating, the materials surface is first heated followed by the movement of heat inward via radiation, conduction and convection [32]. To overcome the limitation of these methods, there is a growing need to develop the clean, non-toxic and environment-friendly procedures for the synthesis of nanoparticles.

Nowadays, synthesis of metal nanoparticles using microorganisms, fruits, marine algae, plant parts, such as, leaf, roots, latex, seed and stem plants as simple and viable alternative techniques is highly preferred [33]. Hence, growing environmental concerns motivated the researchers to avoid the use of toxic chemicals. Consequently, the focus on the innovative green approach, (i.e) the use of plants in the 'green synthesis' or 'sustainable synthesis' of nanoparticles was found to be more attractive and shows better advancement over other chemical and physical methods [34]. There is no more high energy and high pressures requirements, thus causing significant energy saving [35–37].

Opuntia dilenii haw is found mainly in the southern parts of India. It consists of 8–10% hexoses and 0.98% pentoses. The major components of *Opuntia dilenii haw* are mucilage and pectin. Plant mucilage contains D-glucose, D-galactose, L-arabinose, D-xylose, L-rhamnose D-galacturonic and glucuronic acids [38]. Pectin is the most abundant polysaccharide present in *Opuntia dilenii haw* [39]. It also has vitamin A and E in major amounts and succinic acid, oxalic acid, sucrose, malonic acid, maleic acid and tartaric acid in appreciable amounts [40]. Prior to this study, no attempt was made to prepare zinc ferrites by a simple and efficient microwave heating method using plant extracts. Various literature reported the preparation of metal ferrites using *aloe vera plant extract* [41,42]. But in this present investigation, we discuss the preparation of zinc ferrite nanoparticles and compare their optical, magnetic and catalytic properties.

2. Experimental section

2.1. Materials

$Zn(NO_3)_2 \cdot 6H_2O$, (Merck) and $Fe(NO_3)_3 \cdot 9H_2O$, (Merck) act as the oxidizing agents. Both the chemicals were used without any additional refinement, due to the analytical grade of the products. *Opuntia dilenii* haw plant extract is used as the reducing agent. All the solutions were prepared using deionised water.

2.2. Preparation of the plant extract

Opuntia dilenii haw extract was prepared by using 5 g portion of leaves which were thoroughly washed and was used in the present study instead of toxic organic compounds. The upper part of the leaves is removed and the inner part is finely cut, and mixed with 30 ml of deionised water. The combination was stirred thoroughly