Materials Chemistry and Physics 182 (2016) 219–230

Contents lists available at ScienceDirect

Materials Chemistry and Physics

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

Synthesis of nanocrystalline cobalt ferrite through soft chemistry methods: A green chemistry approach using sesame seed extract

Dana Gingasu [a], Ioana Mindru [a, *], Oana Catalina Mocioiu [a], Silviu Preda [a], Nicolae Stanica [a], Luminita Patron [a], Adelina Ianculescu [b], Ovidiu Oprea [b], Sultana Nita [c], Ileana Paraschiv [c], Marcela Popa [d], Crina Saviuc [d], Coralia Bleotu [e], Mariana Carmen Chifiriuc [d]

[a] Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy, 202 Splaiul Independentei, 060021, Bucharest, Romania
[b] Politehnica University of Bucharest, Faculty of Chemistry, 1-7 Polizu Street, 011061, Bucharest, Romania
[c] National Institute for Chemical Pharmaceutical Research and Development, 112 Calea Vitan, 031299, Bucharest, Romania
[d] University of Bucharest, Faculty of Biology, Microbiology Department, Research Institute of the University of Bucharest-ICUB, Life, Environmental and Earth Sciences Division, 91-95 Splaiul Independentei, Bucharest, Romania
[e] Stefan S. Nicolau Institute of Virology, Cellular and Molecular Pathology Department, 285 Mihai Bravu Avenue, Bucharest, Romania

HIGHLIGHTS

- $CoFe_2O_4$ were obtained by two chemical synthesis methods.
- Sesame seed extract was used as gelling or chelating agent.
- The morphological features of $CoFe_2O_4$ nanoparticles were evaluated.
- $CoFe_2O_4$ exhibited good microbicidal and anti-biofilm features.

ARTICLE INFO

Article history:
Received 22 February 2016
Received in revised form
6 July 2016
Accepted 10 July 2016
Available online 8 August 2016

Keywords:
Oxides
Chemical synthesis
Fourier transform infrared spectroscopy (FTIR)
Powder diffraction

ABSTRACT

The nanocrystalline cobalt ferrites ($CoFe_2O_4$) were obtained through self-combustion and wet ferritization methods using aqueous extracts of sesame (*Sesamum indicum* L) seeds. The multimetallic complex compounds were characterized by Fourier transform infrared spectroscopy (FTIR), UV-VIS spectroscopy and thermal analysis. Phase identification, morphological evolution and magnetic properties of the obtained cobalt ferrites were investigated using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), FTIR and magnetic measurements. FE-SEM investigations revealed the particle size of $CoFe_2O_4$ obtained by wet ferritization method ranged between 3 and 20.45 nm. Their antimicrobial, anti-biofilm and cytotoxic properties were evaluated.

1. Introduction

Spinel ferrite nanoparticles have attracted considerable interest in the last decades for their potential applications in different fields, as high frequency magnets, information storage systems, microwave absorbers etc. In the biomedical field, they are used to induce magnetic hyperthermia, for drug delivery, as biosensors and in magnetic resonance imaging [1–5].

Among the spinel ferrite families, one of the most important is the inverse spinel cobalt ferrite ($CoFe_2O_4$) which possesses large anisotropy and saturation magnetization, as well as tunable coercivity [2,6–8]. These properties make it a suitable candidate for different biomedical applications [1,7,9]. Recent studies revealed the antibacterial properties of the cobalt ferrite nanoparticles on multidrug resistant bacterial strains [7,9,10].

It is well known that the synthesis method has a crucial influence on the composition, structure and morphology of the spinel

* Corresponding author.
E-mail address: imandru@yahoo.com (I. Mindru).

http://dx.doi.org/10.1016/j.matchemphys.2016.07.026
0254-0584/

ferrites. Various strategies have been developed to obtain cobalt ferrite nanoparticles, such as sol-gel technique [2,11], solvothermal/hydrothermal method [12–14], microemulsion routes [15], microwave synthesis [16,17] and the precursor method [6,18–21].

In the recent years, there is increased emphasis on the biosynthesis of nanoparticles, also known as green synthesis methods [22,23] – green chemistry – which tends to become an important alternative to chemical procedures.

The biogenic routes are environmentally friendly methods as they do not use toxic or expensive chemicals [24]. The green chemistry draws its inspiration from nature through yeast, fungi, bacteria and plants [25].

The use of plant extracts offers the possibility of preparing nanostructured spinel ferrites *via* several chemical pathways using benign reagents thus reducing the risk of hazardous substances [17,26–29].

The plant extracts contain and can therefore release a variety of metabolites including carbohydrates, aminoacids, vitamins, enzymes, etc, which can be used as capping agents, reducing agents, stabilizing and/or, even, chelating agents for "capturing" the metal ions. Therefore, the plant extracts can influence the size, the shape and the morphology of the nanoparticles. They generate nanoparticles with high dispersity, high stability and narrow size distribution [30,31].

Nowadays, a variety of plant extracts such as sesame leaves, aloe vera leaves, hibiscus flowers/leaves, ginger roots, etc. are used to obtain metal oxide nanoparticles. Some of the most important studies in this field belong to the Indian researchers [17,27,28,32–35]. C. Ragupathi et al. published in recent years the first studies on the synthesis of $CoAl_2O_4$ and $NiAl_2O_4$ spinel oxides using sesame (*Sesamum indicum* L) leaves as plant extract [32,33].

Sesame is considered to be the oldest oilseed crop known to humanity. It is a survivor crop, due to its resistance to very difficult conditions such as drought and/or high heat [36–38]. Sesame seeds contain high levels of oil (52%), proteins (24%), ash (5%), fibers and carbohydrates (~13.5%). The chemical composition varies with the variety, origin, color and size of seed.

The current study has the following goals: (i) the synthesis of cobalt ferrites ($CoFe_2O_4$) by self-combustion and wet ferritization methods using an aqueous extract of sesame seed (*Sesamum indicum* L) (ii) the physico-chemical characterization of multimetallic complex compounds; (iii) the physico-chemical characterization of cobalt ferrites; (iv) the investigation of the antimicrobial activity of cobalt ferrites against some Gram-positive, Gram negative bacterial and fungal strains; (v) *in vitro* assay of cobalt ferrites biocompatibility.

2. Experimental

All chemicals used: the iron nitrate ($Fe(NO_3)_3\cdot 9H_2O$), the cobalt nitrate ($Co(NO_3)_2\cdot 6H_2O$) were of reagent quality (Merck). *Sesamum indicum* L white seeds were from the health food store originated in India.

2.1. Preparation of the plant extract

The sesame extracts were prepared in three concentrations, as follows: 5 g of sesame seeds in 10 ml, 20 ml and 40 ml distilled water, respectively, were left in an ultrasonic bath at 40 °C/1 h. The emulsions were separated by centrifugation (E1, E2, E3).

2.2. Synthesis of cobalt ferrites

The cobalt ferrites were obtained by green chemistry approach using aqueous extracts of sesame seeds as gelling/chelating agent.

2.2.1. Self-combustion method

The metal nitrates ($2Fe^{3+}$:$1Co^{2+}$) were added slowly in the sesame emulsion (E1, E2, E3). This precursor mixture (pH = 2) was brought to a gel-like concentration in an oven at 80 °C (**C1**, **C2**, **C3**). Then the red-brown gel was placed on a heater at 250–300 °C. Initially, the viscous solution melted, and then decomposed by spontaneous self-ignition, leaving behind a voluminous powder. This self-combustion reaction is a redox process in which sesame extract plays the role of the reducing agent. These voluminous powders (**S1**, **S2**, **S3**) were calcined at 800 °C/1 h in order to obtain well-crystallized cobalt ferrites (**S1-800, S2-800, S3-800**).

2.2.2. Wet ferritization method

The metal nitrates were added under stirring to the sesame emulsion (E1, E2, E3) and the pH was raised to 10 by adding NH_4OH 25%. A dark brown precipitate was separated. This suspension was maintained at 80 °C/8 h. After 8 h, the dark precipitate became magnetic. It was filtered and dried on P_4O_{10}. A good crystallinity of these samples (**S4, S5, S6**) was obtained after a thermal treatment at 800 °C/1 h (**S4-800, S5-800, S6-800**). A $CoFe_2O_4$ sample (**S0**) was synthesized in same manner, without sesame extract.

2.3. Characterization techniques

The composition of the aqueous emulsion of sesame seeds was carried out by gas chromatography (GC) on the methyl esters of the fatty acids. For the gas chromatographic analysis, one microliter of the ester solution was analyzed on a GC (GC 6890N Agilent Technologies) equipped with an Agilent HP 88 (60 m × 0.25 mm) column with a stationary phase: poly(cyanopropyl)(88)(methyl) siloxane (film thickness of 0.2 μm) at a split ratio of 1:10 with a temperature scheduled in two steps. The sample was analyzed by GC after extraction in *n*-heptane and derivatisation to methyl esters of fatty acids by fast transesterification with KOH 0.2 M methanolic solution. For the identification of fatty acids it used a solution containing standards of methyl esters of the fatty acids (Fluka) in *n*-heptane. The composition of fatty acids is determined by normalization procedure, calculating the percentage of each component from the test solution chromatogram. The identification of fatty acids is done using the retention times of methyl esters from reference solution. FTIR spectra were recorded on KBr pellets, between 4000 and 350 cm^{-1}, with a sensitivity of 4 cm^{-1}. The Nicolet 6700 apparatus with OMNIC soft were used for characterization. Absorption measurements were recorded with a JASCO V-670 spectrophotometer in the domain 200–1800 nm. The thermal analysis TG-DSC for the multimetallic complex compounds was performed with a Netzsch STA 449C Jupiter apparatus. The samples were placed in an open crucible made of alumina and heated with 10 $K\cdot min^{-1}$ from room temperature up to 900 °C, under the flow of 20 mL min^{-1} dried air. An empty alumina crucible was used as reference. Powder X-ray diffraction patterns were recorded using Rigaku's Ultima IV multipurpose diffraction system. The diffractometer was set in parallel beam geometry, using Cu Kα radiation (λ = 1.5406 Å), CBO optics and graphite monochromator, and operated at 40 kV and 30 mA, 0.02° step size and 5°min^{-1} scan speed. Phase identification was performed using Rigaku's PDXL software, connected to ICDD PDF-2 database. The lattice constants were refined using Whole Powder Pattern Fitting (WPPF) and crystallite size was calculated by Williamson-Hall method. The morphology of the cobalt ferrite nanoparticles was assessed using a FEI QUANTA INSPECT F scanning electron microscope with field emission gun. The magnetic measurements were performed at room temperature on a Lake Shore's fully integrated Vibrating Sample Magnetometer (VSM) system 7404. In interpretation of magnetic data were used hysterezis curve (ferromagnetic phase)