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Synthesis and characterization of nanocrystalline zinc ferrite spinel powders by homogeneous precipitation method

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Abstract

Single-phase nanocrystalline zinc ferrite ($ZnFe_2O_4$) spinel powders have been successfully synthesized by an easy homogeneous precipitation method in short precipitation time at low calcination temperature (250 °C). Characterization of the synthesized samples were carried out by powder X-ray diffraction, thermal gravimetric analysis, Fourier transform infrared spectroscopy, diffuse reflectance spectroscopy, surface area measurements, field emission scanning electron microscopy coupled with energy dispersive X-ray analysis and transmission electron microscopy. The spinel $ZnFe_2O_4$ powders consist of spherical nanoparticles with an average size of 5.2 ± 0.61 nm. The antifungal activity of the nanocrystalline zinc ferrite powders was tested against pathogenic *Candida albicans* using the disc-diffusion susceptibility method. The nanocrystalline zinc ferrite powders exhibit strong antifungal activity against pathogenic *C. albicans*.

Keywords: B. X-ray methods; D. Spinels; Homogeneous precipitation method; Antifungal activity

1. Introduction

Nanocrystalline spinel ferrites are of special interest due to their potential applications in various fields as in magnetic devices, catalysts, pigments, drug delivery systems and highly insulating materials [1–5]. Particularly Zinc ferrite ($ZnFe_2O_4$) possesses unique properties like ferromagnetism, radiation damage resistance, high thermal conductivity, mechanical hardness, excellent chemical stability, energy-transfer efficiency, high electrical resistivity, low eddy current lost and magneto-optical behavior [6–9]. All these properties are affected by particle size, morphology, structure, cation distributions and method of synthesis [2,4]. It is an n-type semiconductor material with small band gap value (1.9 eV) which is used in solar cells, gas sensors, absorbent for hot gas desulphurization and also in photocatalytic applications [10–13] due to its ability to absorb visible light with high efficiency. $ZnFe_2O_4$ nanoparticles are reported [14] as radiosensitizers in radiotherapy of human prostate cancer cells. The catalytic activities of $ZnFe_2O_4$ nanoparticles for O-acylation of alcohol, phenol in acetic anhydride [15] and in oxidative dehydrogenation of n-butene to 1, 3-butadiene [16] are reported. They have been widely adopted as anode materials in commercially available lithium ion batteries [17]. Bulk $ZnFe_2O_4$ has a normal spinel structure of the type $A^{2+}B_2^{3+}O_4$ where A and B refer to the metal ions at tetrahedral and octahedral sites respectively in the oxygen lattice [18]. While nanocrystalline $ZnFe_2O_4$ has a mixed spinel structure with distribution of Zn^{2+} and Fe^{3+} ions over any of the A and B-sites, which are responsible for the enhancement in magnetization compared to normal $ZnFe_2O_4$ [19].

Different processes such as hydrothermal [20], solvothermal [21], thermal decomposition [22], solid-state reaction [23], reverse micelle [24], micro-emulsion [25], sonochemical [26,27], spray pyrolysis [28], combustion [29], mechanochemical [30], citrate precursor [31], electrodeposition [32] and sol–gel [33,34] methods have been used to synthesize nanocrystalline $ZnFe_2O_4$. However, these techniques are difficult to develop in large-scale industrial applications because they are expensive, complicated, require sophisticated apparatus, high reaction temperatures, long production time, toxic

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reagents and producing by-products which are harmful to the environment. Naseri et al. [6] have prepared $ZnFe_2O_4$ nanoparticles by a thermal treatment method using poly (vinyl pyrrolidon) (PVP) as capping agent. Niu et al. [11] have used polyoxyethylene lauryl ether, n-hexanol and n-heptane in a microemulsion method. Yan et al. [21] required polyethylene glycol 200 (PEG 200), teflon-lined stainless steel autoclave and longer reaction time (24 h) in a solvothermal method. The surfactant oleic acid was employed by Yang et al. [22] in a thermal decomposition method and in the other, i.e., in mechanochemical reaction [30] longer time (21 h) and high calcination temperature (600 °C) was needed. Shimada et al. [23] have reported its synthesis by solid phase reaction at high calcination temperature (1000–1154 °C). Among them homogeneous precipitation method has great scope for large scale production of nanoparticles. The advantages of this method are better control on particle size and good textural properties of the materials [16,35–38]. Moghaddam et al. [15] employed the precipitation method for synthesis of $ZnFe_2O_4$ nanoparticles using 2.45 GHz microwave irradiation while Lee et al. [16] synthesized it at high calcination temperature (650 °C for 6 h). In the present work the homogeneous precipitation method is adopted as it is simple and requires low calcination temperature (250 °C for 3 h). Highly pure nanocrystalline $ZnFe_2O_4$ powders are obtained in short processing time without using any surfactant/chelating agent or special condition.

The pathogenic *Candida albicans* is the most common microorganism implicated in fungal infection [39]. Candidiasis is caused by overgrowth of fungal species in the genus *Candida* and it creates several types of infections in mouth, skin, blood stream, throat, intestines, heart valves and genital regions of both men and women [40,41]. Currently, the fungal infection candidiasis has significantly increased and in its treatment only a small number of antifungal drugs are available such as polyenes (amphotericin B), triazoles (fluconazole, itraconazole, voriconazole, posaconazole) and echinocandins (caspofungin) [42]. However, candidiasis has developed resistance, side effects, toxicity and interactions with these drugs. Hence, it is necessary to search other novel antifungal agents to avoid the above-mentioned adverse effects. This encouraged the authors to synthesize nanocrystalline $ZnFe_2O_4$ which is characterized by different techniques and its antifungal activity is explored against *C. albicans.*

2. Experimental

2.1. Materials

The chemicals Zinc acetate dihydrate (MERCK®), ferrous oxalate dihydrate (ALFA AESAR®) and ammonia solution (25%, RANKEM®) were of analytical grade and were used as reagents as received without further purification. For testing antifungal activity *C. albicans* strain (MTCC 221) was purchased from the Culture Collection, Chandigarh, India and potato dextrose broth (PDB) medium for fungus cultures was purchased from SRL®. Millipore® water was used for the preparation of aqueous solutions.

2.2. Synthesis

In this paper nanocrystalline $ZnFe_2O_4$ spinel powders were prepared using suitable precursors by the homogeneous precipitation method. The details of procedure are as follows.

80 mL aqueous solution of zinc acetate (4 mmol) and 80 mL aqueous solution of ferrous oxalate (16 mmol) were taken in a 250 mL beaker. To this mixture 15 mL of 25% ammonia solution (ammonium hydroxide) was added drop wise and the contents were heated to ~75 °C with continuous stirring for 3 h. During the reaction a dark brown precipitate formed which was centrifuged, washed with water several times to remove the impurities and further washing with ethyl alcohol dried in an oven at 80 °C for 8 h. The as-prepared sample was grounded to fine powder with the help of a mortar and pestle and then calcined in air at 250 °C and 350 °C for 3 h at a heating rate of 1 °C min^{-1} inside a muffle furnace. The colors of the samples before and after calcination were brown.

2.3. Characterization

Powder XRD patterns were recorded using a Bruker AXS-D8 Advance diffractometer operating with Cu-Kα radiation (λ=0.15406 nm) at 40 kV and 40 mA in the 2θ range from 10–70° with a scanning speed of 2°/min. Thermo gravimetric analysis (TGA) was carried out on a PerkinElmer Thermal Analyzer (Pyris Diamond) in air at a heating rate of 5°/min in the temperature range 25–600 °C. Optical absorption spectra of the samples were obtained with the help of a Shimadzu UV-2450 UV–visible spectrophotometer in the wavelength range 200–800 nm along with a diffuse reflectance accessory using $BaSO_4$ as the reference for the reflectance measurements. IR spectral analysis of the samples was performed with a Thermo Nicolet Nexus Fourier FT-IR spectrometer in the range 4000–400 cm^{-1} employing a KBr disk method. The specific surface area of the as-prepared and calcined samples was measured with a Brunauer–Emmett–Teller (BET) instrument (Micromeritics Chemisorb 2720) using nitrogen physisorption. Morphology of the samples along with elemental analysis (EDXA) data was investigated with a field emission scanning electron microscope (FE-SEM, FEI Quanta 200F) operating at an accelerating voltage of 20 kV. A FEI TECNAI G2 electron microscope operating at an accelerating voltage of 200 kV was used to record TEM images of the nanocrystalline powders. For TEM measurements the nanocrystalline zinc ferrite powders were dispersed in ethanol using a low power sonicator and a few drops of this solution were allowed to dry on the carbon coated copper grids at room temperature.

2.4. Antifungal activity test

The antifungal activity of the synthesized nanocrystalline $ZnFe_2O_4$ powders were tested against *C. albicans* using the disc-diffusion susceptibility method. The medium of potato dextrose broth (PDB) (~50 mL) was prepared by dissolving proper amount of potato dextrose powder (39 g/L) in Millipore water and mixing it well. The final volume of 50 mL was made