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Antimicrobial activity of metal-substituted cobalt ferrite nanoparticles synthesized by sol–gel technique

A.H. Ashour[a], Ahmed I. El-Batal[b], M.I.A. Abdel Maksoud[a], Gharieb S. El-Sayyad[b,*], Sh. Labib[c], E. Abdeltwab[d], M.M. El-Okr[e]

[a] Materials Science Laboratory, Radiation Physics Department, National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt
[b] Drug Microbiology Laboratory, Drug Radiation Research Department, National Center for Radiation Research and Technology, Atomic Energy Authority, Cairo, Egypt
[c] Nuclear Chemistry Department, Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt
[d] Physics Department, Faculty of Science (Girls Branch), Al-Azhar University, Cairo, Egypt
[e] Physics Department, Faculty of Science (Boys Branch), Al-Azhar University, Cairo, Egypt

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ABSTRACT

Metal-substituted cobalt ferrites [$M_xCo_{(1-x)}Fe_2O_4$ (M = Zn, Cu, Mn; x = 0.0, 0.25, 0.5, and 0.75)] were synthesized via a sol–gel technique. The ferrite structures were confirmed by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, surface analysis using the Brunauer–Emmett–Teller method, and energy-dispersive X-ray spectroscopy. Antimicrobial activity of these ferrites against selected pathogenic microbes was determined. The structures remained cubic spinel phases after substitution of metals. Substitution strongly influenced the microstructure and homogeneous grain distribution. The particle size of the ferrites increased linearly with increase in their annealing temperature. The surface area of zinc cobalt ferrite nanoparticles (ZCFO) was 52.56 m^2/g, the average pore size was 1.84 nm, and pore volume was 0.136 mL/g. All ferrites showed antimicrobial activity toward all pathogens selected. Of these, the most powerful was ZCFO, showing zones of inhibition of 13.0 mm against *Bacillus subtilis* and *Staphylococcus aureus* and 12.0 mm against *Candida albicans*. Gamma-irradiated ZCFO nanoparticles (150.0 kGy) maintained higher antimicrobial activity than non-irradiated particles, e.g. being active toward *S. aureus* (16.0 mm). ZCFO is proposed as a candidate material for industrial and biomedical purposes.

Introduction

The utilization of metal and metal-oxide nanoparticles for antimicrobial performance is attracting much attention, as several of these suggest superior activity toward resistant microorganisms (El-Batal, El-Sayyad, El-Ghamery, & Gobara, 2017; El-Batal, El-Sayyad, El-Ghamry, Agaypi, et al., 2017; El-Batal, ElKenawy, Yassin, & Amin, 2015; Žalnėravičius, Paškevičius, Kurtinaitiene, & Jagminas, 2016). Ferrites are ferromagnetic compounds that are typically oxides of different transition metals, including iron (Farid et al., 2017); for example, $MnFe_2O_4$ and Zn–Mn ferrite can form unions of the formula $Mn_xZn_{1-x}Fe_2O_4$ (Dar & Varshney, 2017). They are frequently insulators in nature and, similar to most another ceramics, solid and fragile (Amirabadizadeh, Salighe, Sarhaddi, & Lotfollahi, 2017). In phases with magnetic characteristics, ferrites are usually categorized as soft or hard, which leads to respective decreased or increased magnetic coercivity (Pour, Shaterian, Afradi, & Yazdani-Elah-Abadi, 2017).

Spinel ferrite nanoparticles have well-known novel optical, photoelectric, and magnetic features. These nanoparticles possess high permeability, high overload magnetization, and have no preferred route of magnetization (Sharma, Thakur, Sharma, & Sharma, 2017). Spinel ferrites are magnetic semiconductors and are amongst compounds able to generate magnetic nanospheres that are widely accepted because they are non-toxic and simply prepared (Tomitaka, Hirukawa, Yamada, Morishita, & Takemura, 2009).

Ferrites are used in applications such as magnetic ingredients in microelectronics (Alcalá, Briceño, Brämer-Escamilla, & Silva, 2017). Most ferrites used in manufacturing magnetic liquids are of the spinel composition (Sharma et al., 2017; Yan & Luo, 2017). Addi-

* Corresponding author.
E-mail addresses: adham_adham699@yahoo.com, Gharieb.Elsayyad@eaea.org.eg (G.S. El-Sayyad).

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tionally, there are different and diverse applications of ferrites in unique technological sectors, such as electronic designs, humidity sensors, microwave reflection, drug-delivery processes, magnetic resonance imaging, and inductors. Ferrites are also used as high-density data-storage materials, converters, catalysts, and antenna bodies (Anupama, Rudraswamy, & Dhananjaya, 2017; El Moussaoui et al., 2016; Niu, Zong, Hu, & Wu, 2017; Patil, Pawar, Tilekar, & Ladgaonkar, 2016; Samoila et al., 2017; Winder, 2016).

The characteristic properties of ferrites can be improved by conjugation of other divalent metallic ions in their chemical structure; for example, the addition of cobalt ions to ferrite improves coercivity, due to enhanced magneto-crystalline anisotropy that results from the coupling of the spins of the cobalt and iron ions (Ghafoor et al., 2016). Cobalt ferrite ($CoFe_2O_4$; CFO) has attracted significant study in the last five decades due to its unique and tunable physical characteristics (Tatarchuk, Bououdina, Paliychuk, Yaremiy, & Moklyak, 2017). These qualities give CFO tremendous potential in several technologies, such as data storage, as a microwave absorber, high-sensitivity sensors, magneto-electronics, optoelectronics, catalyst investigations, and nanobiotechnology (Kumar, Singh, Zope, & Kar, 2017; Samavati & Ismail, 2017; Tatarchuk et al., 2017). Some investigations (Kumar, Reddy, Devi, & Sathiyaraj, 2016) have evaluated dielectric, structural, and gas-sensing performance of metal-substituted spinel (MFe_2O_4; M = Zn, Cu, Ni, and Co) ferrite nanoparticles. $NiFe_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, and $ZnFe_2O_4$ are commercially employed to sense liquefied petroleum gas.

Of the various ferrites, CFO possesses novel fascinating and physical characteristics that have led to extensive attention regarding potential biomedical applications (Sanpo, Berndt, Wen, & Wang, 2016), including its increased drug solubility and stability and decreased side effects (Gupta & Gupta, 2005). It has been used for magnetic orientation in drug delivery (Nasongkla et al., 2006), imaging factors and therapy of brain tumors (Reddy et al., 2006), as a drug-delivery vehicle in biomedical approaches (Byrappa, Ohara, & Adschiri, 2008), for advanced bacterial action of a drug carrier (Sun et al., 2004), and as the vector in drug delivery to the kidney and brain (Buteică et al., 2010; Thankachan, Kurian, Nair, Xavier, & Mohammed, 2014). Conjugation of metals to cobalt ferrite may produce new composite substances with improved antimicrobial action (Samavati & Ismail, 2017). In recent times, experimentation on antibacterial characteristics of ferrites has been very successful (Samavati & Ismail, 2017); most researchers have improved antibacterial quality by replacing copper by cobalt in CFO, manufacturing $Cu_xCo_{1-x}Fe_2O_4$ using a co-precipitation method. Substitution of cobalt by copper in CFO nanoparticles significantly changed the microstructure, crystal composition, and particle diameter and further developed the antibacterial activity (Samavati & Ismail, 2017).

This study investigated the structure of multifunctional nanoferrites with the nominal formula $M_xCo_{1-x}Fe_2O_4$ (M = Zn, Cu, and Mn; x = 0.0, 0.25, 0.5, and 0.75) produced by the sol–gel method to improve their physical characteristics. Moreover, it aimed to recognize the potential of ferrite nanoparticles before and after gamma irradiation on selected pathogenic microbes, as possible candidates in various fields of biomedical applications.

Materials and methods

Materials

All media components were purchased from Oxoid (UK) and Difco (USA). All reagents were of analytical grade. The chemicals used in the manufacture of the ferrites included ferric nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, 98%), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, 99.5%), copper nitrate hexahydrate ($Cu(NO_3)_2{\cdot}6H_2O$), manganese nitrate tetrahydrate ($Mn(NO_3)_2{\cdot}4H_2O$, 98%), zinc sulfate heptahydrate ($ZnSO_4{\cdot}7H_2O$, 99%), citric acid (99.57%), and ethylene glycol ($C_2H_6O_2$, 99.8%).

Synthesis of nanoferrites

A sol–gel technique was applied to manufacture the spinel nanoferrites. Stoichiometric quantities of the metal salts and citric acid (in a molar ratio of 1:1 to the precursor metal salts) were individually dissolved in the least quantity of deionized water (7.5 mL) for the hydrolysis reaction. The salt solutions were combined and the resultant mixture was heated at 80 °C under continuous magnetic stirring (El-Batal, Farrag, Elsayed, & El-Khawaga, 2016). Citric acid was then added, accompanied by the addition of ethylene glycol (10 mL) as a polymerization promoter to begin the gel formation. The resulting solution was boiled at 120 °C to allow gel formation. The resulting gels were dried and ground to obtain nanoferrite powders. The powders were annealed at 400, 500, 600, and 700 °C for 3 h in a muffle furnace to obtain different degrees of crystallinity.

Characterization of ferrite nanoparticles

The structures of the CFO and metal-substituted CFO nanoparticles were characterized by X-ray diffraction (XRD; Shimadzu XRD-6000, Japan). XRD patterns in the range of 2θ from 4° to 90° were obtained at a scan rate of 2°/min using a Cu Kα radiation source, wavelength of 0.1546 nm, a generator voltage of 50 kV (Arshad, Maqsood, Gul, & Anis-Ur-Rehman, 2017; Bahadur et al., 2017), and generator current of 40 mA at room temperature (Al-Ghamdi, Al-Hazmi, Memesh, Shokr, & Bronstein, 2017). The experimental lattice constants for the cubic system were determined from the inter-planar spacing (d) using the formula described by Musa, Azis, Osman, Hassan, and Zangina (2017). Surface morphology of ferrite nanoparticle structures was examined using scanning electron microscopy (SEM; EVO-MA10, Zeiss, Germany) (El-Batal, El-Sayyad, El-Ghamry, Agaypi, et al., 2017). Energy-dispersive X-ray spectroscopy (EDX; Nano GmbH D-12489, 410-M, Bruker, Germany) was applied to determine the elemental compositions of the ferrite nanoparticles using a mapping technique (El-Batal, El-Sayyad, El-Ghamry, Agaypi, et al., 2017). Fourier transform infrared (FT-IR) analyses were carried out using a FT-IR 3600 infrared spectrometer (Jasco, USA) using KBr pellets (El-Batal, El-Baz, Abo Mosalam, & Tayel, 2013; El-Batal, Haroun, Farrag, Baraka, & El-Sayyad, 2014; El-Batal, El-Sayyad, El-Ghamry, Agaypi, et al., 2017). Spectra were recorded in the wavenumber range of 400–4000 cm^{-1}.

Specific surface areas were determined using the Brunauer–Emmet–Teller (BET) method (Gao, Cui, Zeng, Guo, & Shi, 2010) using a surface analyzer (Nova 3200 nitrogen physisorption apparatus, USA) with N_2 as the adsorbate at −196 °C. Pore size distributions (PSD) were calculated by the Barrett–Joyner–Halenda (BJH) method using the cylindrical pore model (Gao et al., 2010).

Antimicrobial activity of metal-substituted cobalt ferrite nanoparticles

The metal-substituted CFOs (5000 ppm) were investigated for their antimicrobial action prior to gamma irradiation using the agar well diffusion method (El-Batal, El-Sayed, Refaat, & Askar, 2014; El-Batal, Haroun, et al., 2014; El-Batal et al., 2015; El-Batal, El-Sayyad, El-Ghamry, Agaypi, et al., 2017; El-Batal, Hashem, & Abdelbaky, 2013; Ghorab, El-Batal, Hanora, & Mosalam, 2016).

All ferrites were tested against different isolates of Gram-positive (*Bacillus subtilis* ATCC 6633 and *Staphylococcus aureus* ATCC 29213) and Gram-negative, (*Escherichia coli* ATCC 25922 and *Pseudomonas aeruginosa* ATCC 27853) bacteria. Antifungal activity was investigated using the unicellular fungus, *Candida albicans* ATCC

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