ISSN 22846808

Open Access Journal

Letters in Applied NanoBioScience

Volume 1, Issue 2, 031-035, 2012

www.NanoBioLetters.com

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL EVALUATION OF A Fe_3O_4/C_{12} CORE/SHELL NANOSYSTEM

Alexandru Mihai Grumezescu[1*], Ecaterina Andronescu[1], Anton Ficai[1], Dan Eduard Mihaiescu[2], Bogdan Stefan Vasile[1], Coralia Bleotu[3,4]

[1]Department of Science and Engineering of Oxidic Materials and Nanomaterials, Faculty of Applied Chemistry and Materials Science, University Poitehnica of Bucharest, Romania

[2] Department of Organic Chemistry, Faculty of Applied Chemistry and Materials Science, University Politehnica of Bucharest, Romania

[3] Stefan S. Nicolau Institute of Virology, Bucharest, Romania

[4]Department of Microbiology and Imunology, Faculty of Biology, University of Bucharest, Romania

Article info

Received: 15.05.2012
Accepted: 20.06.2012
Published: 30.06.2012

Abstract

Lauric acid (C_{12}) functionalized Fe_3O_4 nanoparticles were fabricated and characterized by XRD, FT-IR, DTA-TG and TEM. Lauric acid was used as a coating agent, controlling particle size and aggregation during the synthesis. XRD confirms the formation of magnetite. FT-IR evidenced the successful surface fictionalization with C_{12}, peaks assigned to lauric acid being identified in the nanopowder. The obtained core/shell nanostructure consists of spherical particles of several nanometers long, according to TEM characterization. The interaction with HEp2 cell line proved that Fe_3O_4/C_{12} nanostructures are biocompatible.

Keywords *Core/shell, magnetite, lauric acid, bioevaluation*

*Corresponding author e-mail address:**grumezescu@yahoo.com**

Introduction

There are a lot studies published involving magnetite (Fe_3O_4), which are of fundamental interest to nanoscience due to their vast applications in controlled drug release [1], drug targeting [2], inhibition of microbial biofilm growth [3], stabilizing volatile organic compounds e.g. essential oils [4], resonance magnetic imaging [5], cancer therapy [6], bone cancer treatment [7] or antimicrobial therapy [8]. Also, Fe_3O_4 is one of the most important magnetic materials and is widely used [9] in numerous industrial processes (printing ink), environmental applications (metal ion removal and magnetic filtration) and also medical applications, some of which being really exciting and under development at the moment [10,11]. To date, various methods for preparing magnetite nanoparticles already have been reported, such as co-precipitation [12], micro-emulsions [13], solvothermal processing [14], and high-temperature organic phase decomposition [15]. However, it has been demonstrated that the physical and chemical properties of magnetite nanoparticles greatly depend upon the synthesis route [16]. In the present work, we report the synthesis, characterization and bioevaluation of nano-sized particles of magnetite using lauric acid (C_{12}) as a coating agent.

Experiment Details

Synthesis. In this present paper, core/shell nanostructure was prepared by a modified precipitation method [17,18]. One gram of C_{12} was solubilized in a known volume of distilled-deionized water,

corresponding to a 1.00% (w/w) solution, under stirring at room temperature. Then, 4 mL of a basic aqueous solution consisting of 28% NH_3 were added to C_{12} solution. Thereafter, 100 mL of $FeSO_4/FeCl_3$ (1.2/0.6 w/w) were dropped under permanent stirring up to pH = 8, leading to the formation of a black precipitate. The product was repeatedly washed with methanol and separated with a strong NdFeB permanent magnet.

Characterization.

FT-IR. A Nicolet 6700 FT-IR spectrometer (Thermo Nicolet, Madison, WI) connected to software of the OMNIC operating system (Version 7.0 Thermo Nicolet) was used to obtain the FT-IR spectra of hybrid materials. The samples were placed in contact with attenuated total reflectance (ATR) on a multibounce plate of ZnSe crystal at controlled ambient temperature (25^{o}C). FT-IR spectra were collected in the frequency range of 4000–650cm^{-1} by co-adding 32 scans and at a resolution of 4 cm^{-1} with strong apodization. All spectra were ratioed against a background of an air spectrum.

XRD. X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature. In all the cases, Cu Kα radiation from a Cu X-ray tube (run at 15 mA and 30 kV) was used. The samples were scanned in the Bragg angle 2θ range of 10-80.

HR-TEM. The transmission electron images were obtained on finely powdered samples using a Tecnai^{TM} G2 F30 S-TWIN high resolution transmission electron microscope (HRTEM) from FEI. The microscope was operated in transmission mode at 300kV with TEM point resolution of 2 Å and line resolution of 1 Å. The finely MNPs powder was dispersed into pure ethanol and ultrasonicated for 15 minutes. After that diluted sample was put onto a holey carbon coated copper grid and left to dry before it was analyzed through TEM.

DTA-TG. The differential thermal analysis (DTA) coupled with thermo gravimetric analysis (TGA) was performed with a Shimadzu DTG-TA-50H, at a scan rate of 10^{o}C/min, in air.

Bioevaluation. For quantification of cell viability propidium iodide (PI) and fluorescein diacetate (FdA) stains were used. Briefly, Fe_3O_4/C_{12} nanofluid was coated on glass slides [3]. Each coated slide was transferred into 3,5 Petri dish and 2 ml of complete medium containing 3 x10^5 Hep2 cells were added. The effect of coated substances on cell viability was evaluated after 24h by adding 100 µl PI (0.1mg/ml) and 100 µl FdA (0.1 mg/ml) and fluorescence was quantified using Observer.D1 Carl Zeiss microscope. All cells from several fields were counted and cell viability was established by the ratio between viable cells number (green) and number of total cells (viable cell - green and dead cells - red).

Results and Discussions

A black precipitate was obtained by synthesis under the conditions described above.

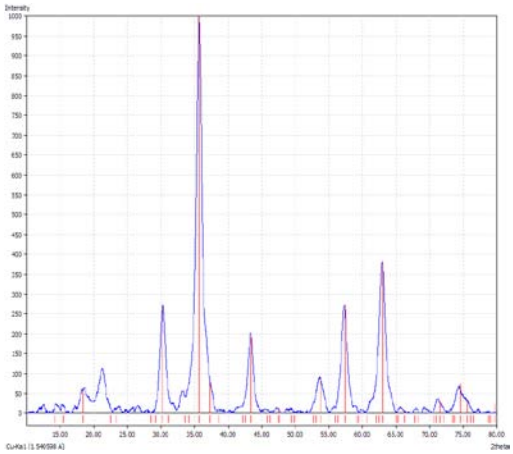

Figure 1: *XRD pattern of the core/shell nanostructure*

The obtained powder was identified as magnetite based on XRD spectrum and confirmed by chemical analysis (Fe^{2+}:Fe^{3+} determination).

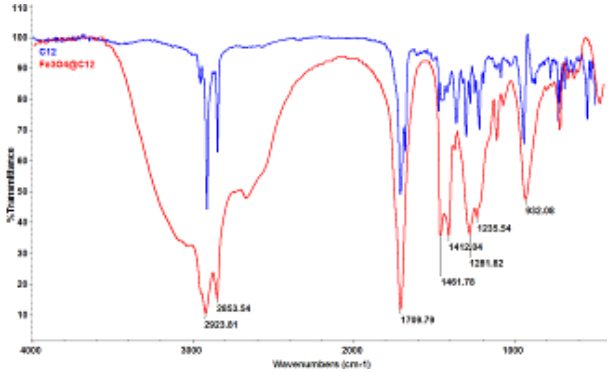

Figure 2: *FT-IR spectra of lauric acid (red line) and of the core/shell nanostructure (blue line)*

Figure 1 shows the XRD patterns of the representative dried powder for the sample. The pattern has

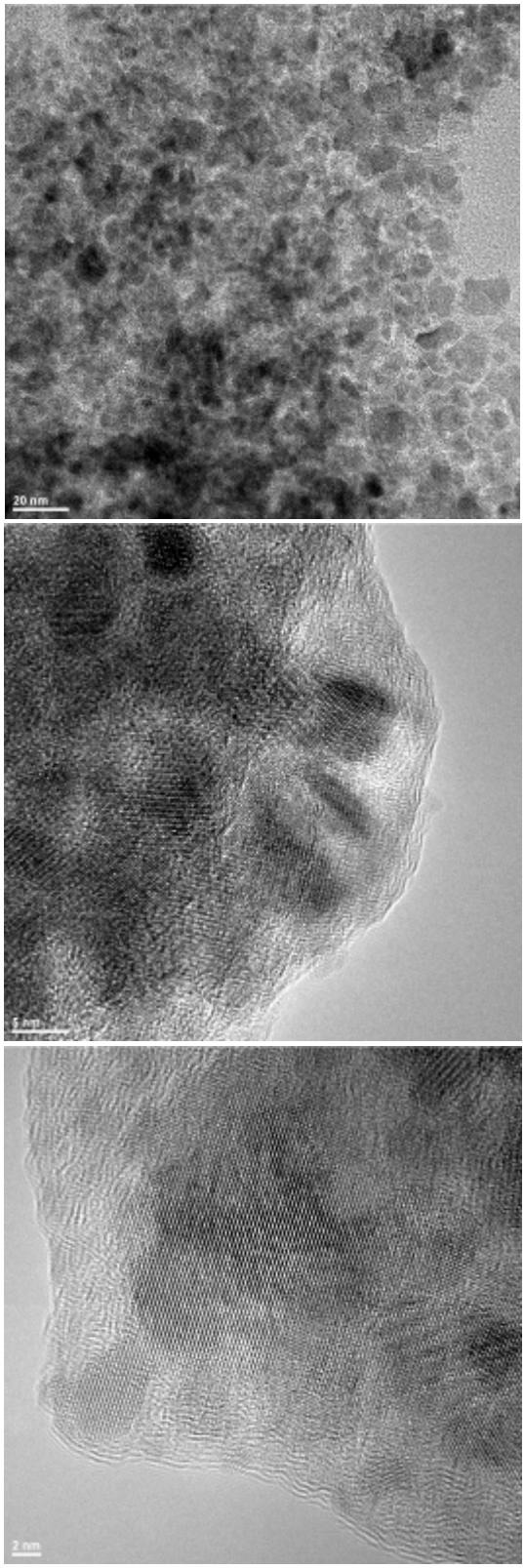

Figure 3: *TEM images of core/shell nanostructure*

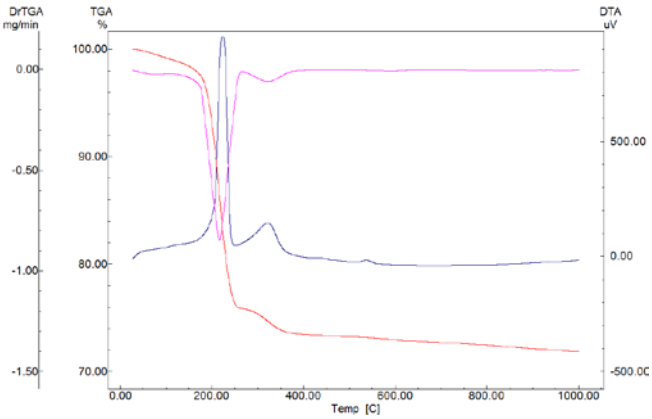

Figure 4: *Thermal analysis of Fe_3O_4/C_{12}*

characteristic peaks (indicated by a circle) at 30.5° (220), 35.9° (311), 37° (222), 43.5° (400), 57.3° (511) and 63.1° (440), which match the standard pattern of Fe_3O_4 well. The FT-IR analysis identified the organic coating on the surface of the magnetite nanoparticles. Figure 2 shows FT-IR spectrum of as-prepared functionalized magnetite nanoparticles. The peak at 2923.81 cm^{-1} was assigned to asymmetrical stretching vibration of C–H. One peak appeared at 1709.79 cm^{-1}, together with the bands at 1281.82 cm^{-1}, attributed to carboxylate group. TEM micrographs of Fe_3O_4/C_{12} nanopowder with different magnifications are shown in Figure 3. Fe_3O_4 particles are observed to have spherical morphology and are aggregated due to the coating agent. The ATD curve presents two exothermic processes at 224 and 322°C, both being accompanied by a weight loss of about 22 and 2.6% respectively. The two exothermic processes can be attributed to the decomposition of the organic shell. The total humidity, as determined as weight loss up to 160°C is 1.88%, the content of lauric acid is 24.6% while the content of magnetite is 73.6%. Figure 5 and 6 show the morphology of HEp2 cell line grown with and without core/shell nanostructure. Cytotoxic effects of Fe_3O_4/C_{12} treatment for 24 h on the HEp2 cell line were evaluated by double fluorescent staining with PI and FDA. Fe_3O_4/C_{12} showed no toxicity on the tested eukariotic cell line. These results suggest the possibility of the *in vivo* use of this nanostructured system for biomedical applications with minor risks for the occurrence of side effects.

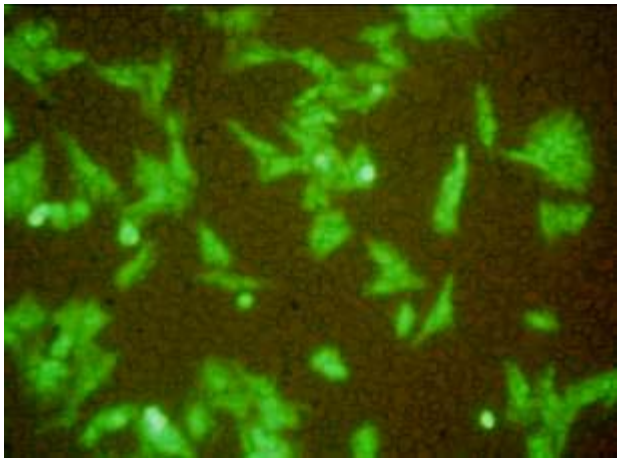

Figure 5*: The aspect of HEp2 in the presence of Fe_3O_4/C_{12} nanostructure*

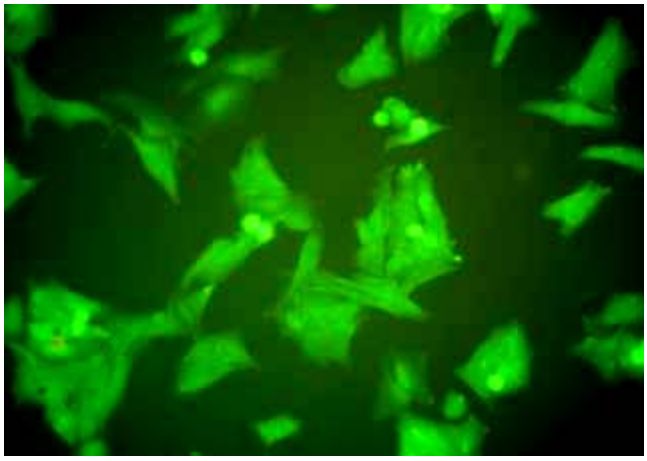

Figure 6: *The aspect of HEp2 cells (control*)

Conclusions

We have successfully fabricated and characterized a core/shell nanostructure by XRD, TGA, TEM and FT-IR. Lauric acid coated magnetite nanoparticles with a primary particle size of approximately 5 nm were successfully produced by precipitating iron salts ($FeSO_4x7H_2O$ and $FeCl_3$) in the presence of C_{12}/NH_3 in aqueous solution. The cytotoxicity assay revealed that Fe_3O_4/C_{12} have no toxicity, recommending this powder for biomedical applications.

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