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Hydrophobic to hydrophilic surface transformation of nano-scale zinc ferrite via oleic acid coating: Magnetic hyperthermia study towards biomedical applications

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Abstract

Nanoscale spinel zinc ferrite (ZNF) was prepared by sol-gel auto-ignition route and subsequently its surface was modified by oleic-acid (OA) coating. The pristine and surface modified ZNF nanoparticles (UC-ZNF and OA-ZNF) were characterized by standard techniques. XRD patterns of both the samples ensured the nanocrystalline mono-phasic cubic-spinel lattice structure with '*Fd-3m space-group*'. FT-IR spectra revealed the presence of vibrational frequency-modes of spinel structure and successful coating of OA over ZNF. The nano-size spherical grains with some agglomeration and OA coating over ZNF were visualized in FE-SEM images. The hydrophobic-to-hydrophilic surface-transition of ZNF was confirmed by water contact-angle measurements. The BET surface-area and distribution of pore-radius was evaluated by recording N_2-isotherms. The M−H plots confirmed the superparamagnetic nature of both the samples. Optical properties were studied by UV–Vis and PL spectroscopy techniques. The colloidal-stability and distribution of particle-sizes were estimated by zeta-potential and DLS measurements. Magnetic hyperthermia studies were carried out for different concentrations (2, 4, 6, 8 and 10 mg/mL) of both the samples. The biocompatible nature of both the samples was studied by cell-viability studies. All these results ensure the implementation of OA-ZNF nanoparticles with minimum dose rate (8 mg/mL) in magnetic hyperthermia therapies for cancer treatment.

Introduction

The materials and devices derived from the nano-scale have drawn immense interest in creating and developing the cutting-edge technology for real world applications [1,2]. The early developments in nano-scaled materials have already paved the way towards applications in electronic industry and energy sectors [3,4]. Now, the current scientific decade is more inclined towards the application of these nano-scaled materials in biomedical and health care sectors [[5], [6], [7]]. Nano-scale is the favorable scale for biomedical applications as most of the biology occurs at this scale. The other key attributes of the nano-scaled materials are superiority over bulk form, emergence of quantum effects, elevated surface to volume ratio and properties can be tuned effortlessly. Nano-scaled materials with these attributes are primarily implementable in both the '*in-vitro*' and '*in-vivo*' bio-applications such as biological imaging (as contrast enhancer) [8], specified drug release (as drug carriers) [9,10], bio-chemical severance (as a separator) [11], bio-sensing devices (as sensing agents) [12] and magnetic hyperthermia (as heating agents) [13,14].

In the cluster of nano-scale materials, magnetic materials (MM's) with multi-modal dimensionalities have been extremely employed in an assortment of bio-applications due to their superior surface properties, improved colloidal and chemical stability, super-paramagnetic gesture and commandability by exterior guest magnetic field [15,16]. In the current scenario, the extensive efforts are being made on the application of nano-scaled MM's as '*heating agents*' or '*thermal seeds*' in the 'magnetic fluid hyperthermia therapies (MFHT)' of cancerous cells in human body [17,18]. MFHT is a feasible but exigent therapy which is chiefly developed for the destruction of cancerous tumor cells within the precise thermal scope. It is principally dependent on a thermal response of the MM's to the guest magnetic field. MFHT engages the MM's as a heating moderators alleviated by bio-friendly coaters at the cancerous area of the human body which subsequently exposed to appropriate electro-magnetic (EM) field. Highly efficient MM's gains the energy form applied EM field and translates it into a thermal energy. The cancerous cells are more responsive to this generated thermal energy as compared with the healthy cells and thus it gets vanished effortlessly without harming the healthy cells [19].

Amongst the typical MM's, spinel class ferrite materials (SFM's) with general recipe of '$M^{2+}Fe_2O_4$' (in which M^{2+}=divalent metal ion) are extensively employed in the MFHT due to their significant magnetic properties, steady chemical nature, achievable super-para-magnetism and bio-friendly character [20]. The SFM's crystal arrangement consists of a two intrinsic sites namely '*tetrahedral (A)*' and '*octahedral [B]*' respectively over which the M^{2+}, Fe^{3+} and O^{2-} ions distributed as per their site preference energies. The super exchangeable interface between these intrinsic sites gives the foremost contribution towards defining the magnetic properties of SFM's. Iron oxide (Fe_3O_4) is one of the SFM's which widely studied for the MFHT [21]. But it was found unsuitable for the MFHT due its high Curie temperature (T_C) value of the order of ~855 K which is too high than that of requisite T_C value (~315 K) for MFHT. In that comparison, normal spinel structured zinc ferrite (ZNF) is one of

the promising members of SFM's family which possesses lower T_C value and other prerequisite properties for MFHT. The Zn^{2+} ions as the main constituent of ZNF possess toxicity level to the lowermost extent as compared with the other metal ions. The per day reference daily intakes (RDI) limit of Zn^{2+} and Fe^{3+} ion is 15 mg and 18 mg respectively which is much superior as contrast with other materials and this make the ZNF practicable in MFHT [22].

In the past, some of the active researchers have made efforts to study the ZNF nanoparticles for bio-medical applications. Recently, Kerroum et al. (2019) [23] reported the impact of solution pH on the structural, magnetic and self heating properties of ZNF prepared by co-precipitation route. Their results showed a linear rise in SAR values with incrementing EM field. A. Manohar et al. (2019) [24] presented the physicochemical and hyperthermia properties of ZNF prepared by solvothermal route. They have estimated the heating efficiency and rate of heat generated via EM field of ZNF for 1 mg/mL particle concentration. Lima Tenório et al. (2016) [25] reported the recent developments and comparison in between the ZNF and COF (cobalt ferrite) properties for application in bio-medical sectors. Their results show the superiority of ZNF over COF for bio-applications. Hoque et al. (2016) [26] studied the self heating and contrast enhancing properties of ZNF prepared by soft chemistry approach. Their results showed the efficient heating properties and enhanced contrast images obtained from *in-vitro* MR imaging. Kharat et al. (2019) [27] investigated the magnetic nanofluids of nickel ferrite based on water as fluidic media. In another work (2018) [28] they reported the thermal studies of ethylene glycol based cobalt ferrite nanofluids. In the excellent review, Hedayatnasab et al. (2017) [29] demonstrated the MFHT applications of magnetic nanofluids based on ferrites. Although, these literature reports are focused on hyperthermia properties of ZNF, the more addressing on fluidic colloidal stability and requisite biocompatibility is lacking in these reports. Apart from this, the systematic investigations on role of surface analysis in defining the fluidic stability and magnetic heating efficiencies by appropriate coating of ZNF core are rarely reported.

It is prerequisite to coat the core of ZNF by bio-friendly agent for their adequate implementation in '*in-vivo*' and '*in-vitro*' fields. The past studies revealed that the superior SAR values can be effortlessly accomplished by averting the 'aggregation' or 'agglomeration' of nano-scaled ZNF in fluidic media [29]. Amongst the available coating entities, oleic acid (OA) with chemical recipe of '$C_{18}H_{34}O_2$' is a potential coater because of its hydrophilic behaviour, non-toxic character and non immunogenic environment. In addition to this, OA helps to diminish the inflammation in human cells and have enhanced effect on genes allied with the cancerous cells. Apart from the surface modifications, the synthetic routes also play a major role in governing the physicochemical and magnetic properties of ZNF. Number of synthetic routes such as sol-gel, hydro-thermal, co-precipitation, high energy milling, micro-emulsion etc was derived for the preparation of ZNF. In this range, the sol-gel auto-ignition route was found a better place due to low thermal requirement, uniform and high yielded product, non-complicated setup and reasonable expenditure [30].

In accordance with the above facts, we report herein, the sol-gel auto ignition synthesis of ZNF

nanoparticles and its surface transformation (hydrophobic to hydrophilic) by OA coating over ZNF core. The impact of the surface transformation on the structural, morphological, surface, magnetic, optical, fluidic stability, hyperthermia and cytotoxicity properties of ZNF nanoparticles were investigated systematically.

Section snippets

Synthesis and surface modifications of ZNF nanoparticles

The reliable and novel sol-gel auto ignition route formulated by citric acid chelating was employed for preparation of ZNF nanoparticles. In brief, the mixed uniform solution of nitrates of the relevant metal ions (i.e. Zn^{2+} and Fe^{3+}) and citric acid was prepared by continuous stirring for the period of 1.5 h. The adjustment in the initial pH of the mixed uniform solution was formulated by drop-by-drop addition of liquid ammonia. The pH adjusted solution was magnetically stirred and heated at…

Thermal analysis (TG-DTA)

The thermal behaviour and spinel phase transformation in prepared UC-ZNF and OA-ZNF samples was examined by recording TG-DTA curves. In the typical procedure, both the UC-ZNF and OA-ZNF samples were exposed to a thermal heat treatment in the scope of R_{Temp} to higher temperature (850 °C) under continuous N_2 flow atmosphere and the loss in the weight was noted. Fig. 2(a–b) displays the TG-DTA curves for prepared UC-ZNF and OA-ZNF samples. It is observed from the TG curves shown in Fig. 2(a–b)…

Conclusions

The hydrophobic-to-hydrophilic surface-transformation of sol-gel synthesized zinc ferrite nanoparticles was successfully achieved by oleic acid (OA) coating. The XRD results confirmed the nanocrystalline formation of both the samples (UC-ZNF and OA-ZNF) with mono-phasic cubic spinel (F.C.C.) structure. FT-IR spectra revealed the presence of vibrational frequency-modes of spinel structure and successful coating of OA over ZNF core. The spherical grain like structure and the presence of OA over…

Declaration of competing interest

There are no conflicts of interest connected with the present work.…

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