



Original Research Paper

Impact of acidic catalyst to coat superparamagnetic magnesium ferrite nanoparticles with silica shell via sol–gel approach



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ABSTRACT

This paper describes a simple way for the coating of superparamagnetic magnesium ferrite (MgFe_2O_4) nanoparticles with amorphous silica layer. First, core MgFe_2O_4 nanoparticles were synthesized by ultrasonic spray pyrolysis (USP) technique from the aqueous metal nitrate precursor solution. Afterward, silica was coated on the obtained particles surface by a sol–gel approach. In this reaction, tetraethyl orthosilicate (TEOS) were used as precursor of silica and HCl as a catalyst, and it has been found that acidic catalyst plays an important role to form amorphous silica layer on nanoparticle surface without formation any core-free silica particles. The composition, morphology and structure of the products were characterized using different analysis technique such as X-ray diffraction (XRD), field emission electron microscopy (FESEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), electrophoretic scattering photometer, Fourier transform infrared (FT-IR) spectroscopy and thermogravimetric analysis (TGA), respectively. The results indicate that the product has a core–shell structure, which is combined through the chemical bond of Fe–O–Si. The silica thickness lies in the range of 30–50 nm with overall dimension of the resulting nanospheres 200–300 nm. Magnetic measurement were carried out on a vibrating sample magnetometer (VSM), and the measurement results indicate that MgFe_2O_4 nanoparticles remain superparamagnetic after coating with silica although their Ms values is significantly less than uncoated samples. This core/shell nanocomposite can be used for several applications especially in the biomedical field due to having superparamagnetic property of core and unique properties of silica.

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1. Introduction

Superparamagnetic ferrite nanoparticles have become exceptionally popular for a wide variety of applications in biomedical fields such as contrast agent in magnetic resonance imaging, carriers for targeted drug-delivery technology, heating agent of hyperthermia treatment, cell separation and biochemical sensing, especially for their unique magnetic properties [1–4]. It has been demonstrated that magnesium ferrite (MgFe_2O_4) are the best studied candidate particles for use in magnetic hyperthermia treatment in human cancer therapy which exhibit greater magnetic heating

ability than do other ferrite [5,6]. In addition, the elements present in MgFe_2O_4 are nontoxic and biologically compatible for use in human body [6]. Due to the potential applications, MgFe_2O_4 nanoparticles have been investigated by using various synthetic methods included coprecipitation [7], sol–gel [8], mechanochemical [1], combustion synthesis [9], microwave hydrothermal [10] and polymerization method [11]. Some of this solution based methods have complicated steps and unfortunate grain growth with necking of particles can usually occur during the synthesis step or post-annealing process in atmospheric environment [12,13]. In this case, we have synthesized MgFe_2O_4 nanoparticles by using one-step ultrasonic spray pyrolysis technique, which could produce as-dried spherical particles in superparamagnetic limit with controlled composition, high purity, good crystallinity and morphology in short reaction time [14].

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However, the specific biological applications of these nanoparticles are greatly restricted because of their poor dispersibility in aqueous solutions; tend to agglomeration and oxidation with possible decomposition induced by the surrounding environment [15–17]. A nonmagnetic shell encapsulating the surface of the nanoparticles can provide new opportunities for improving their performance with prevent such limitations. Nanoparticles are often coated with high bio-compatible organic surfactants, gold, SiO₂ and polymers, etc. Among this component, it is well-admitted that silica is probably the best described coating material because it is non-toxic, easily water-dispersible, thermally stable and more biocompatible to coat core structure of the nanoparticles [15,18]. SiO₂ shell also provides a chemically inert surface which protects the nanoparticles from leaching in an acidic environment. Due to the existence of abundant silanol groups on the silica layer, it allows to conjugate its surface with various functional groups by formation of –Si–O–Si– covalent bonds in biological systems [19]. Various Synthetic route to coat magnetic nanoparticles with silica that have been reported over the past decade such as sol–gel [17], Stöber process [19] and microemulsion synthesis [15]. In the last few years, formation of silica layer on nanoparticle surface by sol–gel method has been widely used, because it has a series of advantages such as high purity, homogeneous layer and controlled thickness through systematic monitoring of the reaction parameters [17,20]. Furthermore, sol–gel processes utilize chemicals that are harmless to the environment such as water, ethanol and silica particulates. A number of modification/developments have been reported in sol–gel process like reaction temperature, varieties in precursors with molar ratios, type of catalyst, etc [20–22]. Amorphous SiO₂ layer were mostly formed through hydrolysis and condensation of alkoxysilanes such as tetraethyl orthosilicate (TEOS) with addition of acid or base catalyst. The physical and chemical properties of the resultant materials largely depend on the type of catalyst used in the reaction. Since acid catalysis was proposed to form linear polymers. On the, other hand, formation of highly branched clusters takes as a result of base catalysis [22,23]. For high biocompatibility, its need to coated amorphous dense silica layer on nanoparticle surface. To obtain the desired microstructure, at first choose catalyst that is to favor formation of homogeneous amorphous silica. Acidic catalyst allows us to prepare such gel-like structure.

Therefore, in this study, we report on preparation of single core magnesium ferrite – silica shell nanoparticles. The synthesis is based on a two steps method: (i) synthesis of superparamagnetic MgFe₂O₄ nanoparticles by ultrasonic spray pyrolysis technique and (ii) silica coating on these obtained nanoparticles by the sol–gel method using acidic catalyst in order to systematically investigate the core–shell structure and the influences of the silica coating on the structural and magnetic properties with various characterizations.

2. Materials and methods

2.1. Materials

In this work, analytical-grade magnesium nitrate hexahydrate (Mg(NO₃)₂·6H₂O, purity 99%), iron (III) nitrate nonahydrate (Fe(NO₃)₃·9H₂O, 99%) were selected as a precursor chemicals because of their relative high solubility in water. 1 M concentration hydrochloric acid (HCl, 99.9%) and tetraethyl orthosilicate (TEOS, 99.9% as a precursor for SiO₂) were used for coating process. All chemicals were procured from Kanto Chemical Co. Tokyo, Japan without any further purification. Deionized water was used as a solvent and also all experimental step.

2.2. Synthesis of MgFe₂O₄ nanoparticles

Initially, the magnesium and iron nitrate were dissolved separately in distilled water at concentration of 0.04 and 0.08 M respectively to consideration the Mg/Fe molar ratio 1:2. The resultant nitrate solution was obtained by mixing these two solutions together in 1:1 volumetric proportion. The final solution was continuously stirred for 12 h using a magnetic stirrer which was used as the precursor solution for MgFe₂O₄ nanoparticles synthesis via ultrasonic spray pyrolysis technique. The schematic diagram of this system is given elsewhere [14]. The prepared precursor solution was atomized in the three neck round flask by ultrasonic vibrator with selected resonant frequency of 1.6 MHz and the resulting droplets are then carrying into the tubular quartz reactor (length and diameter are 1500 mm and 31 mm, respectively) by a carrier gas. N₂ was used in this experiment as the carrier gas and the total carrier gas flow rate was controlled at 3 l/min by using a mass flow controller. The dynamic (continuous) reduction took place in the quartz tube reactor which is located in the three zone electrical heated tubular furnace (ASH, Model ARF-50KC, Kobe, Japan). The droplet evaporated, decomposed and/or crystallized to form product particles in the quartz reactor [13]. The product particles are deposited on the filter paper as substrate which is placed in the funnel at the outlet of the reactor, while the water vapor and off-gases are discharged through an exhaust line. A vacuum pump (having a capacity of 15 m³/h) was used to put the reactor under slight vacuum to discharge the water vapor and exhaust gases to vent at the downstream. The sample holder and the connection part were both kept at 100 °C by tape heaters. Thermocouples were inserted near the surface of the atomizer, the surface of the reactor and the sample holder location to monitor and control an axial profile of temperature in experimental time. During this process, the furnace was maintained at the desired pyrolysis temperatures at 700 °C to obtain as-prepared particles with good crystallinity and morphology by spray pyrolysis.

2.3. Coating of MgFe₂O₄ spherical nanoparticles with silica layer

In this step, the obtained as-synthesized MgFe₂O₄ nanoparticles were coated with silica layer by using TEOS as a precursor of silica and HCl as a catalyst according to the sol–gel method. The typical procedure was as follows: A certain amount of as-prepared MgFe₂O₄ nanoparticles were first dispersed in the deionized water and sonicated for 1 h in an ultrasonic cleaning bath for de-agglomeration. After sonication, a solution containing deionized water (10 ml), TEOS (330 μl) and HCl (14.5 μl) which have prepared at 70 °C under continuous magnetic stirring for 12 h was added to the above suspension. Then this stock suspension was sonicated for 24 h to ensure the complete coating. After that, the precipitates were separated from the solution by centrifugation and then re-dispersed in ethanol in order to minimize particle agglomeration for hydrogen bonding. This washing process was repeated three times. Finally, the obtained precipitate was subsequently dried at 80 °C for 5 h in a drier to obtain the core–shell structure of the MgFe₂O₄/SiO₂ nanocomposites. The silica coated MgFe₂O₄ particles thus prepared was preserved for characterization and subsequent uses.

2.4. Characterization of nanoparticles

XRD measurements were performed on a powder sample of synthesized uncoated and silica coated MgFe₂O₄ nanoparticles using X-ray diffractometer (D8 Advance; Bruker Analytik, Germany) with Cu Kα₁ radiation (λ = 1.5418 Å) operated at 40 kV

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