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Effect of aspect ratio on dielectric, magnetic, percolative and microwave absorption properties of magnetite nanoparticles

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ABSTRACT

Fe_3O_4 nanoparticles with tunable aspect ratio and fixed diameter were synthesized through a hydrothermal process and consequent reduction under hydrogen flow. Static magnetic and microwave electromagnetic properties were measured and it was found that the aspect ratio plays an important role in the microwave dielectric properties, however, static magnetic and microwave permeability were also affected. The real part of the nanorods permittivity was increased 4 times, compared to those of the spherical nanoparticles. The coercivity of the nanorods enhanced because of the higher surface anisotropy and shape anisotropy. A shift of ferromagnetic resonance was observed in their microwave permeability. A significant percolative permittivity behavior was observed in the nanorods especially in their real part of permittivity while such a significant percolative behavior for the spherical nanoparticles was not observed. The nanorods and the spherical nanoparticles produced a reflection loss peak value of about −40 dB at 2 GHz with thicknesses of 4 and 8 mm, respectively. Altogether, with increase in the aspect ratio of the magnetite nanoparticles their microwave attenuation coefficient as their total loss potential increased while their impedance match decreased. This suggests that microwave absorbers with excellent absorption properties can be produced from high aspect ratio nanorods if their impedance matching can be improved.

1. Introduction

Today, electromagnetic (EM) waves especially in microwave frequency range are used extensively in different applications such as wireless communication and radars. So, it has been found that microwave absorbing materials have important role in EM interference shields and radar absorbers. Polymers [1,2], carbon materials [3,4], ferrites [5,6], nonferrite ceramics [7,8], magnetic metals [9,10] and hybrid materials [11,12] have been investigated for their microwave absorbing properties. Different morphologies, complex hierarchical and heterostructured nanoparticles are also considered for their enhanced EM properties. A suitable microwave absorber should be high loss, unreflective for microwaves, lightweight, broadband, low-cost, chemically stable and convenient in terms of applicability. According to the aforementioned practical factors most of complex nanostructures are unsatisfactory although some of them exhibit enhanced EM properties. Moreover, new and more advanced systems are constantly creating new needs. Therefore, as a major challenge for material development, research in this field should be pursued in earnest.

Iron oxides because of their low cost, abundance, nontoxicity, chemical stability, magnetic, catalytic and many interesting properties are one of the most promising materials. They are used in data storage tools [13], catalysts [14], gas sensors [15], electrode materials [16] and electromagnetic wave absorbers [17]. Magnetite as one of the most significant iron oxides is of a great importance. It has half metallic properties, microwave absorption capability, high Curie temperature, and strong spin polarization at ambient temperature. Furthermore, properties of magnetite particles are easily tunable with a change in their shape, dimension and size [18–21].

EM waves are converted to heat through dielectric and magnetic loss mechanisms while entering an absorber. Size, morphology, structural and architectural characteristics of the absorber filler can affect its EM absorption properties. However before an EM wave could be attenuated by an absorber it should be able to enter it with minimum reflection. This ability is provided by the impedance matching of the absorber and air. The ratio of the relative complex permeability ($\mu_r = \mu' - j\mu''$) to the relative complex permittivity ($\varepsilon_r = \varepsilon' - j\varepsilon''$) is considered as characteristic impedance.

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The closer the ratio is to 1, the better the impedance matching [22]. It has been reported that both loss quality and impedance matching can be tailored by controlling the shape, size, composition, porosity, structural and architectural characteristics of the absorber particles. Li and co-workers investigated the EM properties of Fe nanostructures with different morphologies and found that Fe nanowires can be used as a potential microwave absorbing material at quasimicrowave band (L-band) [17]. Jia et al. synthesized Fe_3O_4 nanospheres with different sizes (from ~30 nm to ~100 nm) and characterized their EM properties systematically. Their results showed that the Fe_3O_4 nanospheres with an average size of ~65 nm exhibited the best EM absorption [23]. Wang and co-workers incorporated different amounts of manganese (Mn) into the $BaCoTiFe_{10}O_{19}$ for substituting cobalt (Co). Their results showed the absorption peak shifted to higher frequencies with the substitution [5]. Haung et al. determined the effect of pore morphology and size on the dielectric properties of porous carbons [24]. Guo and co-workers fabricated self-assembled flowerlike α-Fe_2O_3 and γ-Fe_2O_3 with similar size and morphology to study the effect of crystalline structure on EM properties [18]. Liu et al. synthesized a series of $Co_{20}Ni_{80}$ hierarchical structures with different surface morphologies, including flower-, urchin-, ball-, and chain-like morphologies to study the dependency of microwave absorption on architectural characteristics of particles [25].

The electrochemical, magnetic and photocatalytic properties of nanostructures have been mostly considered in iron oxide related literatures. Recently, different hybrid structures of magnetite, such as SiC–Fe_3O_4 hybrid nanowires [26], phthalocyanine copper/magnetite (CuPc/Fe_3O_4) nanohybrids [27], ultrathin Fe_3O_4/carbon nanotube sandwich buckypapers [28], Fe_3O_4/graphene nanosheet (Fe_3O_4/GNS) composites [29], Fe_3O_4@C core–shell nanotubes [30] and MWCNT/Fe_3O_4@ZnO heterotrimers [31], have been widely studied for use in EM absorption applications. However, to the best of our knowledge, systematic researches on the effects of different morphological characteristics on the EM properties of magnetite nanoparticles are not abundant [23,32,33]. The aim of this paper is to find out the effect of aspect ratio on the electromagnetic properties for the hydrothermally synthesized and subsequently reduced magnetite nanoparticles. Nanorods and spherical nanoparticles as typical extremes of aspect ratio were synthesized with a low-cost hydrothermal process with aspect ratio tunability and large-scale production capability in this regard. It is worth noting that it was attempted to synthesize spherical nanoparticles and nanorods with almost similar diameters, so that their aspect ratio variations were only due to their length dimension. The effects of aspect ratio on the complex dielectric and magnetic properties were fully discussed. Furthermore, attenuation and percolation behaviors depending on the aspect ratio variations were studied.

2. Experimental procedures

The precursor of magnetite nanospheres and nanorods were prepared by EDTA-assisted hydrothermal synthesis. Iron nitrate $Fe(NO_3)_3{\cdot}7H_2O$ and EDTA were dissolved in water with a molar ratio of 1:9 (EDTA:FeNit). 2 M NaOH solution was gradually added to the solution and stirred for several minutes until a desired pH was obtained. To obtain nanorods and nanospheres pH was set at 13 and 8 respectively to obtain nanorods and nanospheres. The obtained homogeneous opaque brownish red solution was transferred and sealed in a Teflon lined stainless steel autoclave. The autoclave was heated at 130 °C for 15 h. The obtained product was washed with ethanol and distilled water for 3 times, and finally the samples were dried in an oven at 300 °C. The previous step product was reduced under hydrogen flow (200 ml/min) at 450 °C for 30 min. A schematic design of the production process is shown in Fig. 1. The obtained magnetite nanorods and nanospheres were mixed with paraffin to prepare the standard measurement toroid samples with an outer diameter of 7 mm, and inner diameter of 3 mm, and a thickness of 2 mm. The necessary paraffin was dissolved in toluene and the prepared powder was added to the solution and sonicated for 5 min in an ultrasonic bath. To remove toluene from the composite, the mixture was kept at 80 °C for 10 h. The obtained homogeneous mix was formed in a mold to prepare the desired measurement samples. Paraffin matrix toroid samples for electromagnetic measurements were prepared with 40, 50 and 60 wt.% of each rod-like and spherical nanoparticles. Electromagnetic parameters of the mentioned paraffin matrix toroid samples were measured in frequency range of 1–18 GHz at room temperature by an HP-8722E vector network analyzer (VNA) through the transmission/reflection coaxial airline method. Structural characterizations of the samples were carried out by X-ray diffractometer (XRD Philips X'Pert Pro) with a Cu Kα radiation ($\lambda = 0.154056$ nm). Electron microscopy images were taken on a field-emission scanning electron microscope (Hitachi S-4800 FESEM) at an acceleration voltage of 20.0 kV and a transmission electron microscope (TEM Philips CM200) operated at 200 kV. Electrical conductivity was measured, using four point probe method at room temperature. Magnetic properties were investigated at room temperature using an alternating gradient force magnetometer (VSM/AGFM Meghnatis Daghigh Kavir Co., Iran). The surface area measurements were carried out through a multipoint Brunauer–Emmett–Teller (BET) method, using a surface area analyzer (Autosorb-1, Quantachrome, USA).

3. Results and discussion

3.1. Morphological and structural investigations

Fig. 2 shows SEM images of the spherical and rod-like nanoparticles which are produced from hydrothermal process. As it can be seen, spherical particles have 80–120 nm diameters. The rod-like particles have lengths of about 3–5 μm and their diameters vary in a range of 50–150 nm.

As shown in Fig. 3, XRD pattern of the as prepared nanorods have a goethite phase (pattern a). A phase change to magnetite occurs after reduction in hydrogen gas flow. In Fig. 3, pattern b shows the typical XRD pattern of magnetite spherical nanoparticles and nanorods after hydrogen reduction.

TEM images (Fig. 4) show that magnetite nanoparticles have a porous nature after hydrogen reduction which is caused by eliminating the oxygen atoms from the structure as a result of the hydrogen reduction process. Fig. 4a and b shows rod-like nanoparticles before and after the hydrogen reduction process, respectively. Based on the multipoint nitrogen adsorption/desorption measurements, using Brunauer–Emmett–Teller (BET) method, magnetite porous nanorods and spherical nanoparticles surface areas were 14.41 and 12.31 m^2/g, respectively. The average pore size in both samples was approximately 10 nm.

3.2. Investigation of static magnetic properties

Fig. 5 shows magnetization curves of the magnetite nanorods and nanospheres. Both samples hysteresis loops represent the ferromagnetic behavior in magnetite nanoparticles. The coercivity (H_c), saturation magnetization (M_s), and magnetic remanence (M_r) for the nanospheres are 304 Oe, 85.5 emu/g, and 34.8 emu/g respectively. The mentioned values for the nanorods are 440 Oe, 68.3 emu/g, and 19.8 emu/g, respectively. According to the SBET results spherical nanoparticles have a lower surface area than nanorods. In nanosize particles, surface atoms have a low contribution in the magnetization owing to the disordered magnetic moment structure. Hence, higher M_s value for spherical nanoparticles could be ascribed to their lower surface area compared to that of nanorods. Coercivity (H_c) values for nanorods are higher than those of nanospheres. Nanorods in cross-sectional dimension behave like single domain particles and in longitude direction behave like multidomain particles. However, according to the diameter and the aspect ratio of a rod-like particle it may have single-domain or multidomain behavior. Furthermore, because of the elongated shape of nanorods, the shape anisotropy is added to the magnetocrystalline anisotropy and increases the effective anisotropy and hence the anisotropy field (H_A) increases. H_A could be described as the maximal limit for H_c, therefore an enhancement in H_c can be expected because of an additional shape anisotropy.