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Full Length Article

Synthesis of core-shell hematite (α-Fe_2O_3) nanoplates: Quantitative analysis of the particle structure and shape, high coercivity and low cytotoxicity

Marin Tadic[a,*], Lazar Kopanja[b,c], Matjaz Panjan[d], Slavko Kralj[d], Jasmina Nikodinovic-Runic[e], Zoran Stojanovic[f]

[a] Condensed Matter Physics Laboratory, Vinca Institute, University of Belgrade, POB 522, 11001 Belgrade, Serbia
[b] Faculty of Mathematics and Computer Science, Alfa BK University, Palmira Toljatija 3, 11070 Belgrade, Serbia
[c] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, PO Box 3503, 11120 Belgrade, Serbia
[d] Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[e] Institute of Molecular Genetics and Genetic Engineering, University of Belgrade, Vojvode Stepe 444a, 11000 Belgrade, Serbia
[f] Institute of Technical Sciences, Serbian Academy of Arts and Sciences, Knez Mihajlova 35/IV, 11000 Belgrade, Serbia

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ABSTRACT

Hematite core-shell nanoparticles with plate-like morphology were synthesized using a one-step hydrothermal synthesis. An XRPD analysis indicates that the sample consist of single-phase α-Fe_2O_3 nanoparticles. SEM and TEM measurements show that the hematite sample is composed of uniform core-shell nanoplates with 10–20 nm thickness, 80–100 nm landscape dimensions (aspect ratio ~5) and 3–4 nm thickness of the surface shells. We used computational methods for the quantitative analysis of the core–shell particle structure and circularity shape descriptor for the quantitative shape analysis of the nanoparticles from TEM micrographs. The calculated results indicated that a percentage of the shell area in the nanoparticle area (share [%]) is significant. The determined values of circularity in the perpendicular and oblique perspective clearly show shape anisotropy of the nanoplates. The magnetic properties revealed the ferromagnetic-like properties at room temperature with high coercivity H_C = 2340 Oe, pointing to the shape and surface effects. These results signify core-shell hematite nanoparticles' for practical applications in magnetic devices. The synthesized hematite plate-like nanoparticles exhibit low cytotoxicity levels on the human lung fibroblasts (MRC5) cell line demonstrating the safe use of these nanoparticles for biomedical applications.

1. Introduction

Nanosized iron oxide polymorphs (α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4, β-Fe_2O_3 and ε-Fe_2O_3) have been the subject of numerous studies in the past ten years due to their unique structural properties, complex magnetic properties and the great diversity of practical applications [1–10]. Key requirements for the safe use of these nanomaterials for practical applications are low toxicity and high stability. The synthesis conditions must be well controlled to obtain fine powders of chosen polymorph with a narrow particle size distribution. Moreover, uniform shapes of the nanoparticles are required in order to achieve specific physical properties convenient for specific applications.

Among iron oxide polymorphs, hematite is the most stable polymorph in the air, highly resistant to corrosion, has low toxicity and cost, and is environmentally friendly. Recent papers describe hematite's wide range of potential applications, such as catalysis, gas sensors, pigments, solar cells, lithium-ion batteries, magnetic and antibacterial materials [11–18]. To modify or improve its physical properties, the focus is on the preparation of the nanosized α-Fe_2O_3. Until now, various synthesis methods have been developed to prepare hematite materials, involving solid-state reactions, sol–gel process, hydrothermal synthesis, solvothermal method, polyol process, mechanical activation, coprecipitation and template method [11,19–28]. The study of the magnetic properties of nanosized hematite particles is of great importance from fundamental and applications points of view. Nanosized hematite is an interesting material for investigation of magnetic properties because it can display antiferromagnetic, weak-ferromagnetic and superparamagnetic properties. The bulk α-Fe_2O_3 compound

* Corresponding author.
E-mail address: marint@vinca.rs (M. Tadic).

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is antiferromagnetic below a Morin temperature (T_M = 263 K), whereas above the T_M, the hematite is weak-ferromagnet with a Neel temperature about 956 K [11]. The Neel and Morin temperatures of the α-Fe_2O_3 nanoparticle are size dependent and both decrease with decreasing particle size. Above the Neel temperature, hematite shows paramagnetic properties. If particles become small enough, the direction of the magnetic moment in a single domain fluctuates due to thermal agitation, leading to superparamagnetic behavior above the blocking temperature T_B, and to the spatial freezing of these moments below T_B [29,30].

Complex magnetic properties of hematite have been recently discussed and a wide range of magnetic properties has been obtained. The influence of the shape of the particles on the coercivity is well known and the increase of the coercivity with increasing aspect ratio has been reported [11,31]. Therefore, the wide range of applications needs specific properties which can be tailored by the distinct size and the shape of α-Fe_2O_3 nanoparticles. Considering the applications of hematite material, various kinds of nanostructures have been prepared, such as nanocrystals, nanowires, nanobelts, nanotubes, nanorods, nanocubes, hollow nanospheres, plate-like particles etc. Jayashainy et al. reported that the coercivity of the α-Fe_2O_3 nanostructures can be influenced by the aspect ratio (AS) of the particles [31]. They suggested that the coercivity value has following trend: nanorods (H_C = 483.29 Oe, AS ∼ 4.46) > nanotubes (H_C = 321.96 Oe, AS ∼ 3) > nanotires (H_C = 277.07 Oe, AS ∼ 1.39). Hence, the coercivity was found to increase with the aspect ratio. Roy et al. reported that the α-Fe_2O_3-Na microcubes rendered enhanced H_C (5.7 kOe) and M_R (0.203 emu g^{-1}) values at room temperature due to the shape and magnetocrystalline anisotropy, as well as increased strain in crystals in the presence of Na^+ ions within the crystal layers [32]. Li et al. also reported that the high aspect ratio enhances the shape anisotropy which in turn induces large magnetic coercivity [33]. Clearly, the shape of nanoparticles is important for improving the physical properties of the hematite. However, an important issue that still needs to be addressed in order to better understand shape-dependent properties is a unique method which can objectively measure the shape of the nanoparticles from the micrographs [34–38].

In this work, we report on the synthesis, magnetic properties, quantitative analysis of the particle structure and particle shape from TEM images as well as cytotoxicity of synthesized core-shell hematite nanoplates.

2. Experimental

All reagents were commercially acquired and used without further purification. The hematite nanoplates samples were synthesized by hydrothermal method. In 75 ml autoclave, we mixed 28.5 ml of ethanol (Sigma Aldrich) and 1.78 g of acetic acid (Sigma Aldrich). Afterwards, we added 0.83 g of $FeCl_3$*$6H_2O$ (Sigma Aldrich). Separately, 1.1872 g of NaOH (Sigma Aldrich) was dissolved in 2.1 ml of distilled water and 2 ml of 96% ethanol. This solution was then added drop by drop under magnetic stirring in the autoclave to neutralize the acetic acid. The autoclave was sealed in digestion bomb and immersed in 180 °C preheated oil bath. After 22 h of treatment, digestion bomb was pulled out of oil and left to cool down for a couple of hours in the air. Liquid phase was then carefully decanted from the autoclave and precipitates were collected. Collected nanoparticles were washed three times with distilled water, one time with ethanol and finally dried in hot air for ten hours.

The crystallinity and crystal phase of the synthesized nanoparticles were examined by X-ray powder diffraction (XRPD, Phillips PW-1710). The size and morphology of the synthesized sample were observed by scanning electron microscopy (SEM, JEOL JSM-7600F) and transmission electron microscopy (TEM, JEOL JEM-2100). Magnetic properties were measured by VSM magnetometer (Lake Shore 7307 VSM).

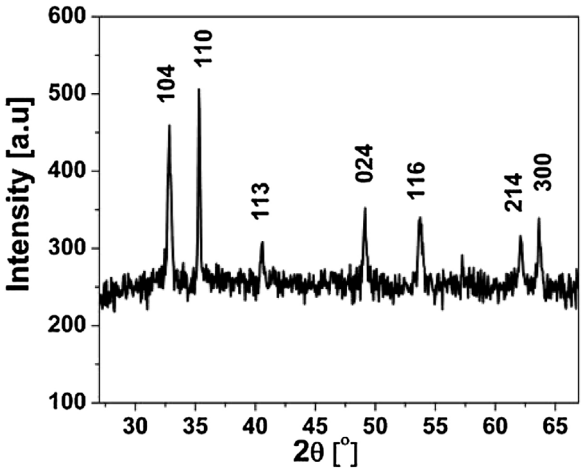

Fig 1. X-ray diffraction pattern of the sample. The Miller indices (hkl) of the peaks are also shown.

The cytotoxicity of the synthesized nanoparticles was assessed on human lung fibroblasts (MRC5) cell line obtained from the ATCC culture collection. The viability of cells was evaluated with 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide reduction assay after 48 h of cell incubation in the media containing test compound at different concentrations [39]. The nanoparticles were re-suspended in the deionized water (50 mg/mL) and used as a solution with the highest concentration tested, 500 μg/mL. Morphological appearance of the treated cells was evaluated using DM IL LED Inverted Microscope (Leica Microsystems, Wetzlar, Germany) under 20× magnification.

3. Results and discussion

Phase identification and structural analysis of the sample have been carried out by X-ray powder diffraction (XRPD). The XRPD pattern of the synthesized sample is shown in Fig. 1. As shown in the figure, the diffraction peaks assigned to α-Fe_2O_3 are strong, which indicate that the particles are well crystallized. No additional peaks have been observed in the XRPD pattern. The morphology of α-Fe_2O_3 nanoparticles has been investigated by SEM microscope. The SEM micrographs (Fig. 2(a) and (b)) of the nanoparticles show that all nanoparticles are of plate-like structure with about 10–20 nm thickness and 80–100 nm landscape length (aspect ratio ∼5). Furthermore, the morphology and the structure of the samples were characterized by transmission electron microscopy (TEM). As it can be seen from lower magnification TEM images (Fig. 3(a)–(d)) the nanoparticles show well defined plate-like shapes. Careful inspection of Fig. 3(c) and (d) reveals that nanoparticles are composed of the core-shell structure with a thin amorphous shell of about 3–4 nm.

The crystal growth of the particle consists of two steps: nucleation and growth. These processes are affected by the interaction of intrinsic crystal structure and the external conditions. The concentration of Fe^{3+} ions during the crystal growth decreases with changes in the external conditions and influences the chemical composition and the crystal structure of the surface region. Therefore, the presence of the surface shell in the nanoplates could be due to the fact that these zones are oxygen-rich, that provoking defects and non-crystalline ordering in the α-Fe_2O_3 nanoplates.