Magnetization behaviors of Fe₃O₄ nanoparticles studied by frequency-modulated magnetic force microscopy

Xiang Li a,b,*, Zhenhua Li c, Deng Pan a, Zhen Xiang a, Satoru Yoshimura b, Hitoshi Saito b

a School of Materials Science and Engineering, University of Shanghai for Science and Technology, Shanghai 200093, China
b Center for Geo-environment Science, Faculty of Engineering and Resource Science, Akita University, Akita 010-8502, Japan
c Key Laboratory for Magnetism and Magnetic Materials of the Ministry of Education, Lanzhou University, Lanzhou 730000, China

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Fe₃O₄ nanoparticles were synthesized through a sol–gel method. The structure and morphology features of the nanoparticles were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), and high resolution magnetic force microscopy (HR-MFM). The magnetization behaviors of Fe₃O₄ nanoparticles were investigated by using the frequency-modulated magnetic force microscopy (FM-MFM). It was observed that the prepared individual nanoparticles were within 20 nm. The high resolution amplitude and phase images of the nanoparticles were obtained separately by using the FM-MFM technique with an AC magnetic field. The magnetic distribution of the individual nanoparticles (~20 nm) was demonstrated by this technique.

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1. Introduction

Due to its unique magnetic properties, nanostructure iron oxide has aroused much interest lately in the areas of enzyme, protein separations, DNA purifications and cancer therapy such as drug carriers [1,2]. The magnetic nanoparticles (~20 nm) as drug carriers can be targeted to specific cells and delivered only where required [1–4]. Recently, Fe₂O₄ nanoparticles close to superparamagnetism have attracted particularly this interest because of their unique microstructure and magnetic functions [5]. Therefore, study on these magnetic nanoparticles is very important. Magnetic force microscopy (MFM) is an ideal tool to investigate the magnetic behaviors in detail and has high spatial resolution for static magnetic fields from a magnetic sample [6–12]. However, it is difficult for individual magnetic nanoparticles (~20 nm) to be detected, because they are very easy to gather and need enough high resolution to observe especially for the single magnetic nanoparticles (~20 nm), which cause that most of the research on the magnetic nanoparticles are focused on some gathering groups of nanoparticles or the macro-performance. Therefore, it is significant to study magnetic behaviors of individual nanoparticles with high accuracy. Unfortunately, it is difficult for standard MFM to detect individual magnetic nanoparticles with a small diameter in the range of 20 nm and thoroughly distinguish the performance between magnetic nanoparticles and nonmagnetic phase. As a result, standard MFM observation of individual magnetic nanoparticles is rarely reported.

In this report, high resolution magnetic imaging of the individual iron oxide nanoparticles applied in cancer therapy has been carried out using a frequency-modulated magnetic force microscopy (FM-MFM) [13] with a high coercivity FePt tip. A schematic diagram of the FM-MFM system is shown in Fig. 1. Fig. 1 shows the schematic diagram of the FM-MFM system with a soft ferrite core to generate the AC magnetic field applied to the sample. Here, we describe the way of the AC magnetic field applied to the sample and indicate the purpose of the ferrite core used in the FM-MFM system. In the system, the studied soft magnetic Fe₂O₄ sample was put on a soft magnetic ferrite core, which is driven by an AC voltage from a signal generator. The ferrite core can generate a homogeneous alternating magnetic field at the sample surface, which can periodically change the magnetic domain states in the soft magnetic samples, and induce an alternating force between the hard MFM tip and the soft magnetic sample. In the FM-MFM, the AC magnetic domain states of the sample periodically modulate the effective spring constant of the cantilever, causing the frequency modulation (FM) of the cantilever oscillation. The system was based on a conventional JSPM-5400 (JEOL Ltd.) scanning probe microscope. The cantilever is oscillated by a piezoelectric element and the AC field frequency modulates the cantilever resonance. The cantilever deflections are sensed by laser beam deflection. The FM-MFM signal is demodulated using a PLL.
circuit (easyPLL, Nanosurf®). The signal output of PLL is fed into a lock-in amplifier and the AC voltage applied to the magnetic nanoparticles is used as a reference signal. In-phase amplitude signals of the lock-in amplifier are obtained by adding an extra phase so that the out-of-phase signals become zero. In this case, the phase shift arising from the electronics can be compensated. The experiment was done in air atmosphere. The oscillation frequency ($\omega$) of the piezoelectric element was near the resonant frequency of the tip ($\omega_0$). The value of $\omega_0$ was about 256 kHz and the value of $Q$ was about 300. The sample is magnetic iron oxide ($\text{Fe}_3\text{O}_4$) nanoparticles. The nanoparticles were driven by a sinusoidal AC voltage with a zero-to-peak amplitude of 0.008 V and a frequency of 100 Hz. Tapping and lift mode AFM/MFM scans were carried out using a high-coercivity FePt tip (SI-MF40-Hc, Nitto Optical Co., Ltd.). The magnetization direction of the tip is perpendicular to the sample surface. As a result, we can consider that the magnetization direction of the MFM tip will not be changed or moved during measurement and the tip behaves as a monopole type tip.

Therefore, we present the imaging of an AC magnetic field by using the FM-MFM, and investigate the magnetization behaviors of $\text{Fe}_3\text{O}_4$ nanoparticles (\sim 20 nm).

2. Experimental

$\text{Fe}_3\text{O}_4$ powders were obtained by the sol–gel method of nitrates dissolved in distilled water, PEG-20000 as a surfactant. 2 M $\text{NH}_4\text{OH}$ was dropped into the solution until pH 9.0 to form the suspension. The suspension was aged at 90 °C for 3 h, then centrifuged, washed with distilled water and ethanol to reduce agglomeration. The separated solid phase was dried at 90 °C for 7 h, and then the powder obtained was calcined at 550 °C under vacuum for 2 h.

The $\text{Fe}_3\text{O}_4$ powders were deposited on a naturally oxidized Si (110) single crystalline substrates. Firstly, the $\text{Fe}_3\text{O}_4$ powders (0.2 g) were put into a beaker with 15 ml distilled water in a microwave oscillation waterbath for oscillating for 0.5 h. Then, a oxidized Si substrate ultrasonically cleaned with distilled and ion exchanged water was put into the beaker with the $\text{Fe}_3\text{O}_4$ powders for further oscillating for 1 h. Then, the substrate was rapidly taken out from the beaker and finally a deposited film (the oxidized Si substrate with some dispersive $\text{Fe}_3\text{O}_4$ nanoparticles on its surface) was produced. The deposited film was dried at 60 °C for 0.5 h in air. To fully fix the nanoparticles on the substrate and distinguish between magnetic nanoparticles and nonmagnetic nanoparticles, 5 nm height gold particles were sputtered on the substrate. All reagents were purchased from Sigma-Aldrich and used as received.

3. Results and discussion

Fig. 2a shows the XRD pattern of the as-synthesized $\text{Fe}_3\text{O}_4$ powders. The diffraction peaks were indexed to the (111), (220), (311), (400), (422), (511), and (440) planes of $\text{Fe}_3\text{O}_4$ with a fcc spinel structure, which are in good agreement with the data of the JCPSD no. 65–3107. No other peaks for impurities were detected, indicating the high purity of the $\text{Fe}_3\text{O}_4$ powders. The size and morphology of the $\text{Fe}_3\text{O}_4$ powders as-synthesized were analyzed by a TEM image (Fig. 2b). From the image, it can be observed that $\text{Fe}_3\text{O}_4$ powders were of high purity and good uniformity, and the diameters of most $\text{Fe}_3\text{O}_4$ nanoparticles were within 20 nm, with a handful of nanoparticles less than 10 nm and some overlapping. Therefore, the $\text{Fe}_3\text{O}_4$ nanoparticles with a range of sizes on the order of \sim 20 nm were obtained by the sol–gel method.

In order to thoroughly study magnetization behaviors of individual nanoparticles, we analyzed the $\text{Fe}_3\text{O}_4$ nanoparticles, sputtered by the gold particles with 5 nm height, using the FM-MFM. The topographic feature of $\text{Fe}_3\text{O}_4$ sample was shown in Fig. 3a. It can be found that some nanoparticles were not clearly detected, which may be caused by the overlap of two kinds of nanoparticles (magnetic $\text{Fe}_3\text{O}_4$ and nonmagnetic gold particles), and the gold nanoparticles exist on the surface of $\text{Fe}_3\text{O}_4$ nanoparticles. Thus, most nanoparticles seen in the topographic image should be gold nanoparticles and magnetic $\text{Fe}_3\text{O}_4$ nanoparticles.
were difficult to be detected, as topographic imaging mainly probes the surface signals.

The amplitude and phase images of the sample can be clearly observed in Fig. 3b and c. The scan height was set at 15 nm. The applied AC peak voltage \(V_p\) to the sample is 0.008 V with a frequency of 100 Hz, producing a magnetic field of 3.62 Oe. It can be observed clearly that there are many bright areas in the amplitude image (Fig. 3b). The amplitude signal is always positive. Here, the bright area has the large AC magnetic field, while the dark area has a value near zero for the AC magnetic field. Therefore, the bright areas should be magnetic Fe\(_3\)O\(_4\) nanoparticles, and the dark areas may be nonmagnetic gold particles.

The phase image was measured during the same scan used for the amplitude image, as shown in Fig. 3c. Compared with the amplitude image, the phase one shows that almost all of the magnetic nanoparticles present a characteristic bright–dark dipole contrast (such as particles 1 and 2) and the majority of the dipoles are in the same direction (left bright–right dark like particle 1). It indicates that the Fe\(_3\)O\(_4\) magnetic nanoparticles should be mostly fully magnetized under 3.62 Oe, with most magnetic moments in the same direction. Therefore, it can be estimated that the as prepared Fe\(_3\)O\(_4\) nanoparticles were close to superparamagnetic using the FM-MFM technique instead of conventional magnetic measurement equipments such as the vibrating sample magnetometer and the hysteresis graph analyzer. In addition, the Fe\(_3\)O\(_4\) nanoparticles (in FM-MFM magnetic images Fig. 3b and c) show the shape like thin rods, quite different from the appearance of nanoparticles in the TEM image in Fig. 2b, because the magnetic images of individual magnetic nanoparticles consist of both poles of bright–dark dipoles. So, it is noteworthy that magnetization of the individual magnetic nanoparticles can be observed clearly. The bright area and dark area indicate a phase difference of \(\sim 180^\circ\). It is obvious that the magnetic particles offer a far stronger response than other nonmagnetic nanoparticles, and the magnetic particles remained distinguishable from the background. This result is very helpful to investigate the magnetization behaviors of individual magnetic nanoparticles (\(\sim 20 \text{ nm}\)) clearly.

The fine magnetic domain structures of individual magnetic nanoparticles are clearly shown in Fig. 4. The typical domain structures highlighted by arrows and numbered (1 and 2) in Fig. 3c are replotted, together with the down track FM-MFM signal profiles which are across the center of the selected nanoparticles position (as indicated by the red lines in the images). The results implies that the magnetic nanoparticles are in a single domain (SD) state, respectively. For nanoparticle 1, the left is bright (positive in the phase shift), while the right is dark (negative in the phase shift). It is just opposite to nanoparticle 2. According to the magnetic signal profiles, the magnetic nanoparticles should be of in-plane magnetic domain configurations and the bright area and dark area indicate a phase difference of \(\sim 180^\circ\). The observation of SD suggests that the single nanoparticle size of \(\sim 20 \text{ nm}\) is close to the critical value for the single domain state.

4. Conclusions

In summary, the amplitude and phase images of the individual Fe\(_3\)O\(_4\) magnetic nanoparticles (\(\sim 20 \text{ nm}\)) have been obtained successfully by using the FM-MFM technique. Furthermore, the fine magnetic domain structures and magnetization behaviors of

\[\text{Fig. 3. FM-MFM images of the Fe}_3\text{O}_4 \text{ sample [(a) topography image; (b) amplitude image; (c) phase image].}\]

\[\text{Fig. 4. The down track FM-MFM signal profiles across the center of the selected nanoparticles indicated by the red lines [(a) Nanoparticle 1; (b) nanoparticle 2]. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)}\]
individual magnetic Fe₃O₄ nanoparticles (~20 nm) can be clearly observed. It is very important to definitively investigate individual magnetic nanoparticles with this technique, which is expected to be extremely helpful for present and future application in cancer therapy.

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