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Magnetic Properties of Nanoparticles Surface-Modified with Oleic Acid

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Oleic-acid-modified magnetite nanoparticles were synthesised by coprecipitation and characterised using structural, spectroscopic, and magnetic methods. X-ray diffraction and transmission electron microscopy confirmed magnetite cores with an average size of approximately 11.5 nm, while Fourier transform infrared spectroscopy demonstrated the chemisorption of oleic acid. Mössbauer spectroscopy revealed superparamagnetic relaxation and collective magnetic interactions. Low coercivity and a blocking temperature of about 160 K indicate predominantly superparamagnetic behaviour at room temperature.

topics: magnetic nanoparticles, superparamagnetism, X-ray diffraction (XRD), Mössbauer spectroscopy

1. Introduction

Magnetite nanoparticles (Fe_3O_4) are widely investigated because their high magnetisation and biocompatibility support applications in biomedicine, catalysis, and magnetic separation. Below the single-domain size limit, thermal fluctuations can induce superparamagnetic behaviour, characterised by field-induced magnetisation and negligible remanence and coercivity. However, their large surface-to-volume ratio promotes oxidation, agglomeration, and dipole–dipole interactions, which may modify magnetic relaxation and blocking processes. Surface functionalisation is therefore essential for controlling particle stability and magnetic properties [1].

Oleic acid is a commonly used surfactant for iron oxide nanoparticles. Its carboxylate group binds to surface iron ions, while the hydrocarbon chain forms a steric barrier that limits aggregation. The magnetic response of coated particles depends on the core size, phase composition, coating efficiency, and interparticle interactions. Complementary analytical methods are therefore required to establish reliable structure–property relationships [2].

In this work, oleic-acid-modified magnetite nanoparticles were synthesised by coprecipitation and characterised by X-ray diffraction (XRD), transmission electron microscopy (TEM), dynamic light scattering (DLS), and Fourier transform infrared (FTIR) spectroscopy. Their magnetic state was examined by Mössbauer spectroscopy, vibrating-sample magnetometry, and zero-field-cooled and field-cooled (ZFC-FC) measurements, with emphasis on superparamagnetic relaxation, magnetic blocking, and collective interparticle interactions.

2. Experiment

Magnetite nanoparticles were prepared by weighing appropriate amounts of $FeSO_4$ and $Fe_2(SO_4)_3$ in a molar ratio of 1:2 and dissolving them in distilled water. Next, the mixture of aqueous solutions of Fe(II) and Fe(III) ions was added dropwise to a previously prepared ammonium base solution (pH = 11). The process of synthesising magnetic nanoparticles has previously been described in detail in [3]. After the dark precipitate had settled, the temperature was set to 100°C whilst stirring

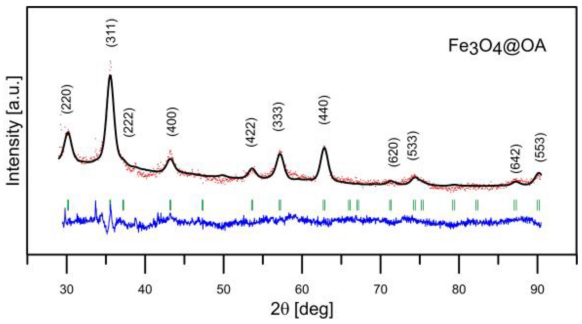

Fig. 1. XRD patterns of oleic acid-modified magnetic nanoparticles; red dots — experimental data, black line — fit, green dashes — Miller indices, blue line — differential spectrum.

continuously. The second stage of the synthesis was then carried out. Then, 3 ml of oleic acid was added dropwise to the nanoparticles. The mixture was stirred for approximately one hour.

The phase composition and structure of the samples were investigated by X-ray diffraction using an Empyrean PANalytical diffractometer with Cu K_α radiation. The scanning range (2θ) extended from 30° to 90°, with a step size of 0.026°. Nanoparticle imaging was performed using a FEI Tecnai G2 X-TWIN transmission electron microscope. All measurements were performed using a lanthanum cathode at a voltage of 200 kV. Samples with a modified and unmodified surface were investigated via FTIR spectroscopy using the attenuated total reflection (FTIR-ATR) technique. The spectra were recorded by means of a Nicolet 6700 (Thermo Scientific) spectrometer equipped with a Smart Orbit ATR accessory (Thermo Scientific) in the range of 400–4000 cm^{-1}. Moreover, the sample was examined with Mössbauer spectroscopy in a wider temperature range. All Mössbauer spectra were recorded in the transmission mode using a constant acceleration POLON spectrometer. Magnetic measurements were performed at room temperature with a vibrating sample magnetometer Quantum Design PPMS-9T/P525 VSM in an external magnetic field up to 13.5 kOe.

3. Results and discussion

To determine the crystallographic structure, the sizes of the magnetic cores, the morphologies of the nanoparticles, and the degree of aggregation, investigations were carried out using several complementary methods. The results of X-ray diffraction studies of oleic acid-modified nanoparticles are shown in Fig. 1. The Miller indices marked on the diffractogram correspond to those characteristic of the magnetite structure. The average size of the nanocrystals in the sample under

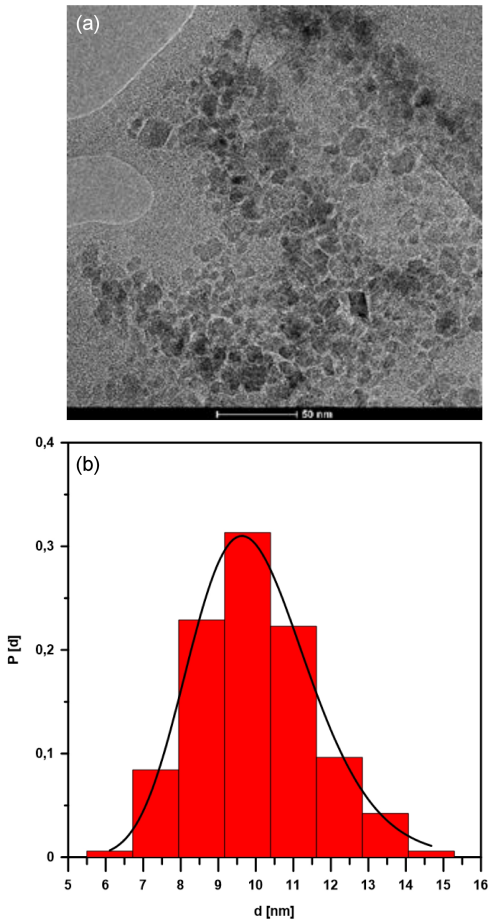

Fig. 2. (a) TEM image of magnetite nanoparticles surface-modified with oleic acid, and (b) a histogram of the nanoparticle size distribution.

investigation is 11.5 ± 0.2 nm. The lattice constants are 8.364 ± 0.001 Å. Comparing the results obtained with the lattice parameters given in the literature [4] — which are 8.397 Å for magnetite and 8.336 Å for maghemite — it can be concluded that the differences are negligible. Given magnetite's susceptibility to oxidation to maghemite, the possibility of the presence of a thin layer of maghemite on the surface of the nanoparticles must be taken into account.

To determine the morphology of the synthesised samples, TEM imaging was carried out, and the results are shown in Fig. 2. The nanoparticles are characterised by an irregular shape but are relatively well separated. Based on a quantitative analysis of the TEM images, the average crystallite sizes in the individual samples were determined, along with their size distributions and standard deviations. The size distributions are presented as histograms.

DLS analyses provide information on the hydrodynamic diameters of nanoparticles and the extent of their agglomeration. In Fig. 3, three peaks in the nanoparticle size distribution can be distinguished.

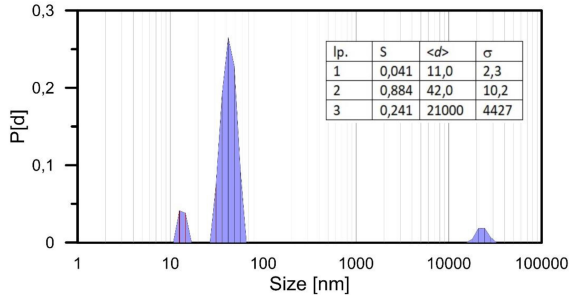

Fig. 3. Distribution of hydrodynamic diameters of nanoparticles determined from DLS measurements for a sample coated with oleic acid. Here, "S" denotes the surface area under the peak, $\langle d \rangle$ denotes the size in nanometres, and σ denotes the standard deviation.

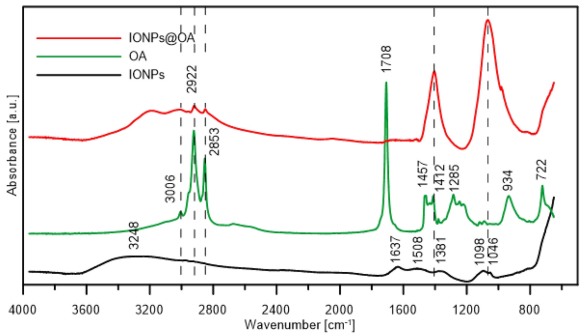

Fig. 4. FT-IR spectrum of magnetite nanoparticles surface-modified with oleic acid.

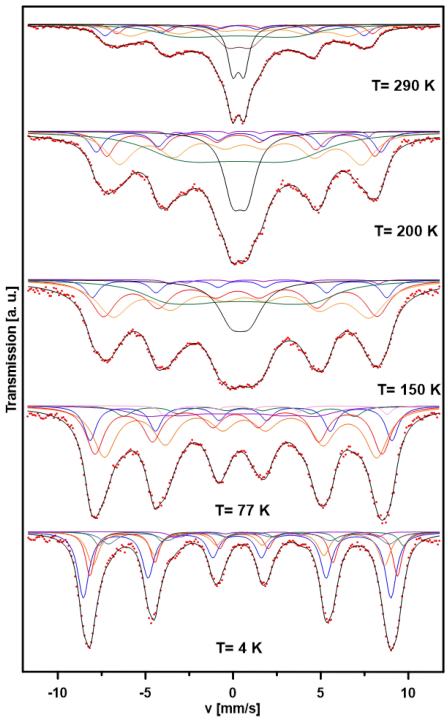

Fig. 5. Mössbauer spectra of magnetite nanoparticles coated with oleic acid, measured at various temperatures.

The first group, visible in the diagram and accounting for less than 10%, consists of individual, size-separated nanoparticles measuring 11 ± 2 nm. These sizes are very similar to the results obtained from XRD and TEM measurements. The largest fraction ($\approx$ 80%) consists of small agglomerates of nanoparticles with sizes of around 40 nm. The proportion of larger agglomerates is only a few per cent.

Figure 4 shows the measurement results for magnetite nanoparticles surface-modified with oleic acid. The black and green solid lines represent the reference spectra of unmodified magnetite nanoparticles (IONPs) and oleic acid (OA), respectively. The red solid line represents magnetite nanoparticles surface-modified with oleic acid.

Following the coating of magnetite nanoparticles with oleic acid, the disappearance of the -COOH absorption band (1708 cm^{-1}) is observed, which is associated with the replacement of hydrogen atoms by heavier iron atoms. In their place, two intense bands appear at 1412 cm^{-1} and 1100 cm^{-1}. It can be assumed that the first — broadened — band arises from the superposition of asymmetric and symmetric stretching vibrations of the OCO- group, which, compared with literature data [5], may have shifted towards lower wave numbers. This would suggest the formation of a complex with a bidentate chelating OCO- group, in which the O–C–O bonds are equivalent and of equal or similar length. In contrast, the band at 1100 cm^{-1} can be attributed to stretching vibrations of a single C–O bond, which further confirms the chemisorption of the surfactant onto Fe_3O_4 nanoparticles with the formation of a carboxylate.

The magnetic properties of the sample were investigated using Mössbauer spectroscopy. The resulting spectra are presented in Fig. 5.

The spectra collected below the Verwey transition temperature were analysed using a five-component model, whereas the spectra recorded at 150 K and higher temperatures were fitted with four magnetic sextets and a superparamagnetic doublet. Two sextets were assigned to Fe^{3+} ions occupying tetrahedral sites and iron ions with an average valence of $Fe^{2.5+}$ located at octahedral sites in the magnetite crystal lattice. An additional sextet was attributed to iron ions present in the maghemite lattice. The remaining magnetic contribution, characterised by a quasi-continuous distribution of hyperfine magnetic fields, was associated with the superferromagnetic state resulting from collective interactions between the nanoparticles. As is typical for magnetic nanoparticles, the proportion of the superparamagnetic phase increases with temperature; however, the presence of ferromagnetic order at room temperature may indicate strong interparticle interactions.

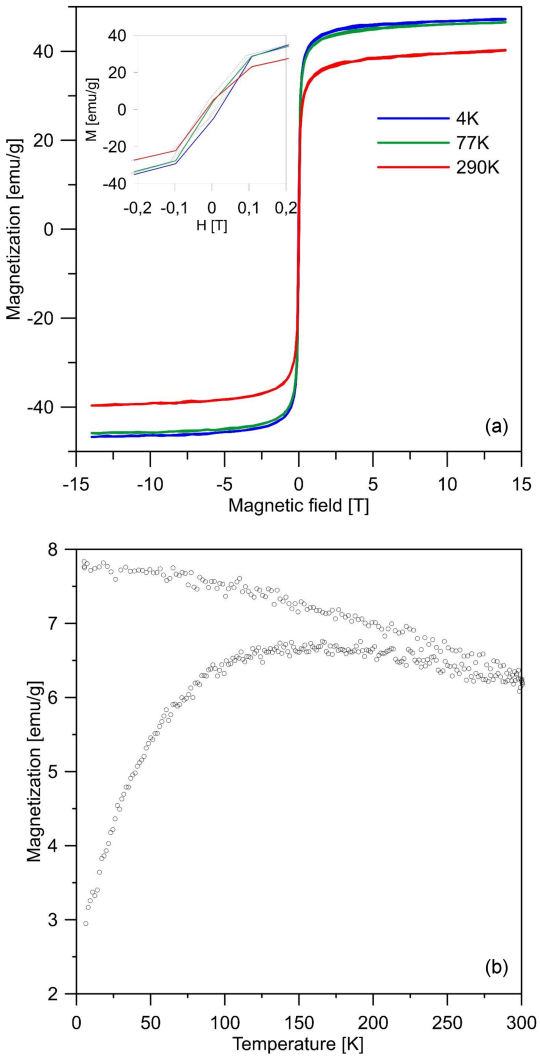

Fig. 6. Hysteresis loops measured at 4, 77, and 290 K for magnetic nanoparticles coated with OA (a). The ZFC–FC magnetisation measured under 100 Oe in the heating cycles (b).

Figure 6a shows the magnetisation as a function of the applied magnetic field at 5, 77, and 290 K. The hysteresis loops exhibit low coercive fields of approximately 14.2, 14.7, and 12.8 Oe, respectively, indicating the magnetically soft character of the nanoparticles and their nearly superparamagnetic behaviour, particularly at room temperature. The corresponding saturation magnetisation values were estimated to be 47.2, 46.4, and 40.2 emu/g, respectively, showing a gradual decrease with increasing temperature.

The ZFC–FC curves (Fig. 6b) exhibit a profile typical of superparamagnetic nanoparticles, where a transition from a magnetically blocked state to a superparamagnetic state occurs as temperature rises. The broad maximum of the ZFC curve, occurring at a temperature of $\approx$ 160 K, corresponds to the average blocking temperature (T_B).

The convergence of the two curves at room temperature suggests that, under these conditions, the majority of magnetite nanoparticles are in the superparamagnetic state, which is consistent with Mössbauer studies.

4. Conclusions

Oleic-acid-modified magnetite nanoparticles were successfully synthesised, with XRD and TEM confirming an average crystallite size of $\simeq$ 11.5 nm, and FTIR demonstrating chemisorption of the surfactant through carboxylate groups. Mössbauer measurements revealed magnetite and maghemite contributions, temperature-dependent superparamagnetic relaxation, and a magnetically ordered component associated with interparticle interactions. The low coercivity, broad ZFC maximum near 160 K, and convergence of the ZFC–FC curves at room temperature indicate that most nanoparticles exhibit superparamagnetic behaviour at 290 K, whereas blocked and collectively interacting states dominate at lower temperatures.

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