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A simple method for quantification of nonstoichiometric magnetite nanoparticles using conventional X-ray diffraction technique

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Contents

1. Materials and Methods

1.1 Synthesis of Fe_3O_4 MNPs

The bare Fe_3O_4 MNPs were prepared by the coprecipitation method, which described in[S1]. Briefly, 7.56 g of $FeCl_3{\cdot}6H_2O$ and 2.78 g of $FeCl_2{\cdot}4H_2O$ were dissolved in 70 mL H_2O, in which was then added to 40 mL of 25% solution of ammonium hydroxide at 50 °C under argon flow/ambient with vigorous stirring. The obtained Fe_3O_4 nanoparticles were washed with ultrapure water five times to remove the synthesis residues then dried at 70 °C under vacuum.

1.2 Synthesis of Fe_3O_4-APTES MNPs

The synthesis of the of silica-coated magnetite nanoparticles was carried out by the well-known Stöber method[S2]. The previously synthesized magnetite nanoparticles were used as cores to be coated with SiO_2. 3-aminopropyltriethoxysilane (APTES, 98% purity, Sigma-Aldrich) was used as NH_2-silica precursor. According[S3], 3.21 g of Fe_3O_4 MNPs was dispersed in 150 mL of ethanol/water (volume ratio, 1:1) solution. Then 13.6 g of APTES was added to the solution under argon atmosphere at 40 °C for 2 h. Molar ratio of APTES to Fe_3O_4 was used as 4:1. The room temperature cooled solution of the formulated Fe_3O_4-APTES MNPs were separated with a Nd-magnet (0.3 T). To avoid the occurrence of nonspecifically bound silane to the particle surfaces, all subsequent silanization reactions were performed in 1/1 mixtures of ethanol/water and extensively washed with water before analysis or further use. Finally, the Fe_3O_4-APTES were vacuum-dried at 70°C during 2 hours.

1.3 Synthesis of Fe_3O_4-HA MNPs

The Fe_3O_4-HA sample was prepared by *in situ* coprecipitation method, which consists of the nucleation and growth of magnetite nanoparticles into HA matrix. The sample of HA was prepared from sodium humate (Powhumus, Germany). The low H/C atomic ratio (0.85[S4]) suggests high content of aromatic structures in the HA preparation. The total acidity of the sample was 5.3 mmol/g of acidic COOH and OH-groups, weight-average molecular weight Mw was 9.9 kD. The MNPs modified with HA (as Fe_3O_4/HA weight ratio 4:1) were prepared by the procedure described in.[S1,S5]

1.4 Simulation of oxidation of MNPs

Oxidation conditions were simulated by mechanical dispersion[S6] of the Fe_3O_4/HA samples in planetary ball mill where the dispersion process takes place between the grinding balls sliding on each other and between the vessel sides and the grinding beads. The Fe_3O_4/HA powder was placed in a wolfram carbide cell with wolfram carbide balls (ball-to-sample mass ratios was 7:1) and dispersed in a high-energy ball mill (SPEX SamplePrep 8000 Mixer/Mill, Metuchen, The Netherlands) at 1425 rpm for 10 min.

1.5 Characterization of the Microstructure of Magnetic NPs (MNPs) by XRD analysis

The phase composition and primary particle size of the samples were determined by X-ray diffraction analysis (XRD) in the Bragg-Brentano geometry using a Philips X-pert diffractometer (Philips Analytical, Eindhoven, The Netherlands, $Cr_{K\alpha 1}$ radiation, λ = 2.28976 Å). The experimental data were smoothed with the well-known algorithm by A. Savitzky and M.J.E. Golay [described in,[S7] corrected by Steinier, Termonia and Deltour in[S8] was used. The measurements were performed at room temperature in the angular range of $10° < 2\Theta < 110°$ with 0.025° resolution and exposure 1 second.

On the one hand, to quantify the oxidation progress, the XRD data were fitted by Pseudo-Voight function for the (440) reflection (interplanar distance d=1.482 Å, 2θ~101.02° at $Cr_{K\alpha}$ radiation) in Origin 2019 Pro. The crystal structure files of the phases were sourced from ICDD (magnetite – *a* = 8.3960 Å [JCPDS-ICDD 19–629] and maghemite – *a* = 8.3515 Å [JCPDS-ICDD 39–1346]).

On the other hand, quantitative analyzes were performed by refinement of the total multiphase spectrum method (the Rietveld method) with a fundamental parameters approach,[S9] using the Math!3 software. Background was handly calculated and a fixed seven-line Kα plus an intensity-refined Kβ emission profile was adopted.

The full width at half maximum (FWHM) was used for particle size determination with the Scherrer equation[S10] using Match! software.

2. Results

2.1 Calculation of the lattice parameter

The change of the lattice parameters indicates the formation of nonstoichiometric magnetite $Fe_{3-\delta}O_4$ with Fe^{2+}/Fe^{3+} ratio from 0 for Fe_2O_3 to ½ for Fe_3O_4 due to partial oxidation of Fe^{2+} during drying, functionalization and oxidation. According to the Gorski,[S11] the stoichiometry can easily be converted to the following relationship.

$$X = \frac{Fe^{2+}}{Fe^{3+}} = \frac{1-3\delta}{2+2\delta} \qquad ((S1)$$

2.2 Calculation of the magnetite content

It is known that materials containing nanosized magnetite can be oxidized rather quickly by atmospheric oxygen in air to form magnetite-maghemite solid solutions, which can be described as $Fe_{3-\delta}O_4$.[S12] Such compounds can be represented as a solution of pure substances - magnetite and maghemite and the content of the first component can be expressed through the molar fraction of the first, thus describing the degree (completeness) of the oxidation of the material:

$$x_{Fe_3O_4} = \frac{n_{Fe_3O_4}}{n_{Fe_3O_4} + n_{Fe_2O_3}} \qquad ((S2)$$

where n_m is the amount of substance m (Fe_3O_4 or Fe_2O_3) (mol). From the point of view of the internal structure, the solid solution retains the structure of the initial magnetite with the difference that some of the Fe^{2+} in B-sites are replaced by Fe^{3+} or uncharged vacancies - # in a ratio of 2 to 1: $(Fe^{3+})_A(Fe^{2+}_{1-3\delta}Fe^{3+}_{1+2\delta}\#_\delta)_BO_4$. The nonstoichiometric coefficient δ varies in the range from 0 to 1/3 and is related to the molar content of magnetite in the solution by the expression:

$$\delta = \frac{1 - x_{Fe_3O_4}}{3 + x_{Fe_3O_4}} \qquad ((S3)$$

It is convenient to describe the considered solid solution by the relative content of iron ions with different charges:

$$X = \frac{n_{Fe^{2+}}}{n_{Fe^{3+}}} = \frac{1}{2}x_{Fe_3O_4} = \frac{1-3\delta}{2+2\delta} \qquad ((S4)$$

ranging from 0 to 1/2. Through this parameter X it is possible to express the change in the parameter of the unit cell of the resulting compound:

$$a_{Fe_{3-\delta}O_4} = \mathrm{A} * \mathrm{X} + \mathrm{B}, \qquad ((S5)$$

where $a_{Fe_{3-\delta}O_4}$ (Å) is the unit cell parameter of the $Fe_{3-\delta}O_4$ compound, A and B are the parameters of the linear equation of the straight line passing through the coordinates (0, $a_{Fe_2O_3}$) and (1/2, $a_{Fe_3O_4}$). Thus, the non-stoichiometry coefficient can be calculated from the structural data:

$$\delta = \frac{A - 2(a_{Fe_{3-\delta}O_4} - B)}{3A + 2(a_{Fe_{3-\delta}O_4} - B)} \quad \text{((S6)}$$

However, this approach requires knowledge of the lattice parameter of the material under study, which can be difficult. Therefore, it is urgent to search for a less labor-intensive and time-consuming method for determining the the degree oxidation of a magnetite-maghemite solution. In this work, it is proposed to consider the possibility of solving this problem, relying on data on the position of some predetermined diffraction reflection, assuming that a change in the completeness of the oxidation of the material leads to a change in the unit cell parameter and, consequently, to a regular change in the position of each diffraction reflection in the diffraction spectrum. Indeed, relying on the Wulff–Bragg's condition and the expression for the relationship between the cubic lattice parameter and the interplanar distances, one can show:

$$a = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2sin\Theta} \quad \text{((S7)}$$

where a (Å) - is the unit cell parameter of the $Fe_{3-\delta}O_4$ compound, λ (Å) - radiation source wavelength, hkl - Miller indices, Θ (°) -reflex position. From this expression and (S4), (S5) we get:

$$x_{Fe_3O_4} = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{Asin(\frac{2\Theta}{2})} - \frac{2B}{A} \quad \text{((S8)}$$

From (S8) it follows that the maximum response should be expected when using radiation with the longest possible wavelength. This condition is met by using, for example, a Cr anode. Further, the same effect should be expected for the reflexes with the highest sums (h + k + l). In this case, the corresponding reflexes should have a noticeable intensity for reliable registration. In the case of magnetite and maghemite, this condition is satisfied by reflections with Miller indices (440), having intensities of 40 and 34%, respectively [JCPDS-ICDD 19-629, JCPDS-ICDD 39-1346]. In the case of using a Cr anode, the indicated reflections for magnetite and maghemite [JCPDS-ICDD 19-629, JCPDS-ICDD 39-1346] should theoretically be located at about 100.924 and 101.746 deg. 2Θ. It is easy to show that in the range (100.5, 102.0) deg. 2Θ (and similar angles in this region) the function $\frac{1}{\sin\left(\frac{2\Theta}{2}\right)}$ can be approximated by a linear function of 2Θ:

$$\frac{1}{\sin\left(\frac{2\Theta}{2}\right)} = C * 2\Theta + D \quad \text{((S9)}$$

moreover, since the value of the first derivative of the function in this range is practically equal to -1, the changes and errors in the definition of the function (S9) and its argument - 2Θ will be equal to within the sign. The above arguments show that it is possible to implement a method for monitoring the the degree oxidation of nanomagnetite samples by the position of the (440) reflection on diffraction patterns obtained using Cr radiation according to the linear equation:

$$x_{Fe_3O_4} = \frac{C\lambda\sqrt{h^2 + k^2 + l^2}}{A} * 2\Theta + \frac{D\lambda\sqrt{h^2 + k^2 + l^2} - 2B}{A} \quad \text{((S10)}$$

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