MORPHOLOGICAL ANALYSIS OF MAGNETIC NANOMATERIALS THROUGH COMPARATIVE METHODS

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Analysis of particles morphology and structure is one of the most important factors for characterizing a material, powder or substance. Several different methods are available in the scientific environment to study material properties such as Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Energy Dispersive Spectroscopy (EDS), Atomic Force Microscopy (AFM). Powder size classifications vary from macroscopic to micro-submicron and ultimately nanometric particle sizes. In this study, a magnetic powder made of magnetite (Fe_3O_4) was synthesized through a co-precipitation method [1,2] and it was analyzed by using XRD, SEM and AFM in order to determine the particle/agglomeration sizes of the powders.

Keywords: AFM; magnetite; nanopowder; SEM; XRD; TEM.

1. Introduction

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are the most used methods for determining particle sizes in both dispersed and agglomerated mediums, with high accuracy and with the possibility of studying the morphology of compound materials [1]. Although

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SEMs display high performances, they present limitations due to their 2D representation of data which leads to the loss of information that can successfully lead to a single particle characterization.

The Atomic Force Microscope (AFM), which relies on a nanometric tip for measuring, can give information on the topography of a sample surface which includes the 3rd dimension Z (height) and it can be used as a complementary analysis for the scanning electron microscope. In the case of the AFM measurement, the tip geometry can influence the results when it comes into contact with various types of particles due to its restriction in measuring beneath the edge of the particle. This leads to an exaggerated width of the resulting image, but the height of the sample is extremely accurate. [2]

X-ray Diffraction (XRD) is used for measuring inter-particle spaces. This leads to the possibility of measuring the crystal structure of a mineral sample [2]. The XRD methods for determining crystallite sizes depend on the diffraction peak broadening and are applicable in the range of 3-100 nm. When particles that go under or beyond the optimal range of determining the crystallite size are analysed, the peak shows either too large broadening or too small respectively [3].

Through High Resolution Transmission Electron Microscopy (HRTEM) it is possible to observe and analyze the atomic arrangement of the sample in order to study the local microstructures (lattice vacancies an defects, screw axes, glide plane) and the atomic arrangement of the nanoparticle surface.[4, 5]

Magnetic nanoparticles have received increased attention due to their broad range of applications such as ultrahigh density magnetic storage [6], ferro fluids [7] and due to their in-vivo / in-vitro biomedical applications [8, 9]. In this study, a magnetic powder made of magnetite (Fe_3O_4) synthesized through a co-precipitation method [10-12]was analyzed separately by using XRD, SEM and AFM in order to determine the particle/agglomeration sizes of the powder.

2. Experimental procedure

Nanopowder synthesis

The synthesis method used to obtain the nanostructured magnetic powders (Fe_3O_4) was the co-precipitation technique from an aqueous solution. This method involves mixing $FeCl_2$ with $FeCl_3$ and then NaOH to adjust the pH to 12. Because of the base environment, the nanoparticles start to precipitate. The powder is then centrifuged and washed to gain a neutral pH and then dried under vacuum in order to protect the particles from oxidizing in contact with the atmosphere [10-12].

Powder characterization

The X-ray diffraction analysis was performed by using a X'PERT PRO MPD (Panalytical) which was equipped with a copper anode which generates Cu

Kα radiation (λ = 1.54065 Å) and by using a 2θ scanning range of 20° to 80°. The crystallite size was determined by using the Scherrer equation.

SEM measurements were done using a Quanta 450 FEG (FEI) scanning electron microscope which has a 1 nm resolution under high vacuum.

For TEM analysis, the powders were dispersed onto a carbon coated copper grid and dried naturally in order to observe the particle morphology. The equipment used for this analysis is a TECNAI F30 G2 high resolution electron microscope with 1Å line resolution equipped with an X-ray dispersive energy (EDS) detector with 133 eV resolution.

AFM was performed by using a MultiView 4000SPM/NSOM (Nanonics Imaging LTD) atomic force microscope equipped with a Cr probe attached to the cantilever for scanning the surface of the sample. The equipment was used in non-contact mode in ambient conditions. The equipment was positioned on air platform and sealed inside a sound/vibration proof room in order to prevent any image distortions from environmental factors. The WSxM 4.0 [13] software was used for data processing and representation of the resulting topographical images.

The purpose of the analysis is to determine particle/crystallite sizes in order to correlate and compare the results from the 3 different equipment used.

3. Results and discussion

XRD analysis

Through the data obtained by x-ray diffraction it is possible to calculate the crystallite size by using the Scherrer equation:

$$d = {K\lambda}/{(B\cos\theta)} \tag{1}$$

Where: d = crystallite average size; K = shape factor (0.9); λ = x-ray wavelength; B = instrument broadening (FWHM – full width at half maximum); θ = theta, half of the Bragg angle (radians)

The diffractogram for the powder is presented in Fig. 1.

From the pattern we can observe that the width of the peaks is narrow which indicates that the powder particles are nanosized. For the calculation of the crystallite size, 3 main peaks were used corresponding to the hkl values (112); (103) and (400) due to their isolated positions from the other peaks and their high intensity. The FWHM for each of the peaks was extracted by using the Origin software. The calculated crystallite sizes vary between 7 and 30 nm.

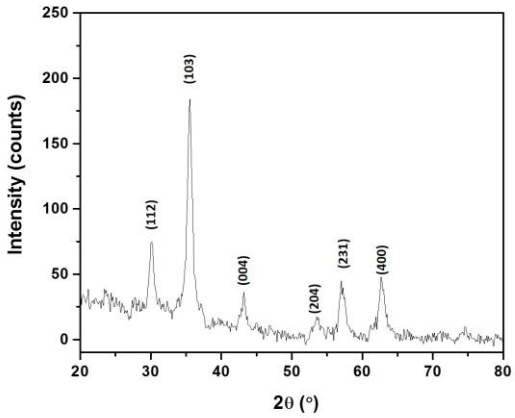

Fig. 1 XRD pattern for synthesized Fe_3O_4 powder.

SEM analysis

The powder was fixed on a carbon tape in order to ensure stability and conductivity of the sample throughout the analysis. Due to the fact that the particles are nanosized and magnetic, the SEM parameters were adjusted to a smaller voltage (5kV) and a smaller spot size (2.0) in order to remove the sliding effect induced by the electron beam. The results can be observed in Fig. 2.

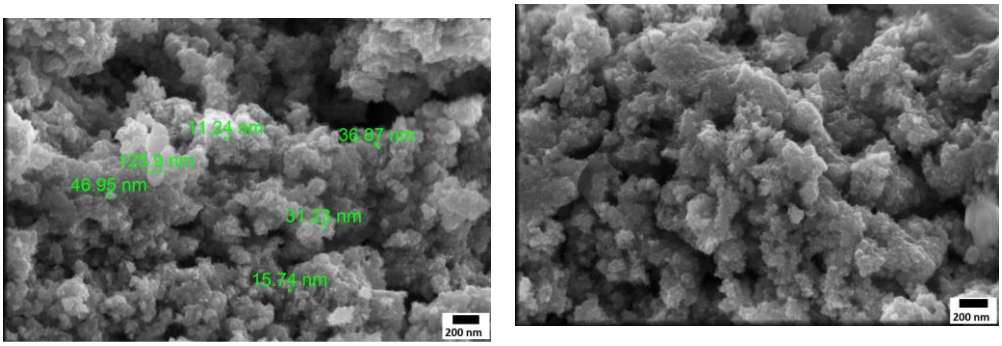

Fig. 2 SEM image of synthesized Fe_3O_4 powder with measurements.

The powder shows high agglomeration of the particles with particle sizes varying from approximately 10 to 40 nm and agglomeration sizes varying from nano to the submicron range.

AFM analysis

The powder preparation for this analysis involved dispersing the particles on a glass surface before AFM observation. The scanning speed used for analyzing the surface was 8 ms/point. The resulting topographic image can be observed in Fig. 3 along with profiles of the various agglomerations observed.

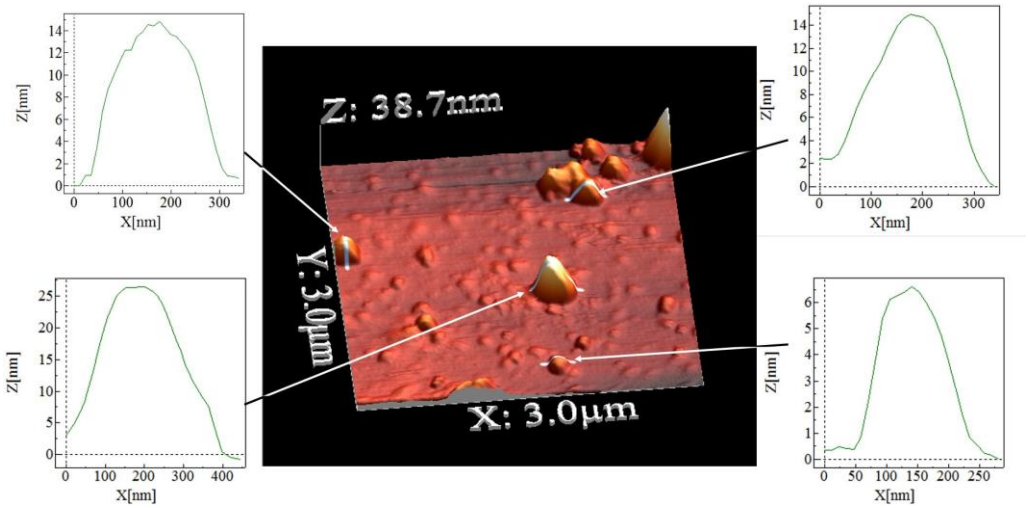

Fig. 3 AFM 3D image of the dispersed powders with height profiles of agglomerations.

Due to its magnetic properties, the powder agglomerates on the surface of the glass. As can be observed through the profiles on the various agglomerations, the width is submicron sized which correlates to the SEM results, while the height of the particles is between 7 and 25 nm.

TEM analysis.

For a more comprehensive analysis of the magnetic powder, the sample synthesized in laboratory conditions was also characterized through TEM analysis. Sample preparation was done through standard operating procedures. The magnetic properties of the powder can also be observed due to the agglomeration of the particles. TEM images of the synthesized powder can be observed in Fig. 4.

TEM analysis also confirms that the powder has an approximate particle size between 10 and 40 nm with a high agglomeration tendency and a d-spacing of 2.55 Å. The SAED analysis displays a specific ring pattern which is associated to nanosized particles. It is also observable that the particles show a sphericle-type shape.

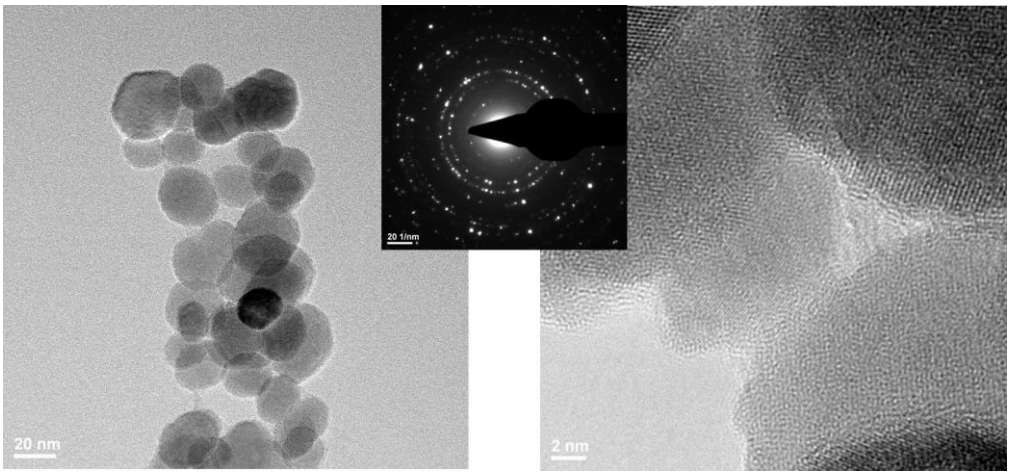

Fig. 4 HRTEM and SAED images of synthesized magnetic powder.

Magnetic nano-powders have become a field of interest for environmental protection throughout the last decade due to the fact that they can adsorb heavy metals and also remove them from waste-waters. Through proper characterization of the morphology of these particles it is possible to determine the limits and capabilities of the powders in the applications that they were synthesized for.

4. Conclusions

By comparing the measurements performed with two different techniques, we can observe that the calculated crystallite sizes of 7-30 nm obtained by XRD has a high accuracy with the values obtained from both SEM and AFM.

Due to the magnetic properties of the powder, the dispersion is not complete and it leads to high agglomeration on the glass surface. The width observed by AFM is also exaggerated due to the tip format because it cannot analyze the edge of the agglomerations properly.

TEM, which is the most comprehensive of the analyses performed, shows that the powders have homogeneous growth across all axes and also confirms that the particle size varies between under 10 nm and around 40 nm.

All of the measurements are complementary, i.e. the XRD reveals basic information on the crystallite size, SEM shows the agglomeration type and also allows for particle measurement in a 2D format. the AFM gives information on the height of the particles and has a 3D representation possibility and TEM gives detailed information on a very high magnification of the synthesized powders. The values lead to the conclusion that the particles show homogeneous growth across all 3-dimensional axes.

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