ULTRAFINE PARTICLES OF IRON(III) OXIDES BY VIEW OF ATOMIC FORCE MICROSCOPE

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INTRODUCTION

The use of atomic force microscopy (AFM) for the characterization of Fe_2O_3 nanopowders is demonstrated with several experimental examples related to the new exhibition of polymorphism in the nano-world. Our experimental experience with AFM analysis of iron oxide particles, advantages and drawbacks of AFM, as well as the influence of sample preparation, artifacts and image deformations on interpretation of AFM data are shown.

From the viewpoint of the basic research

- Iron(III) oxide is a convenient compound for the general study of the polymorphism and magnetic and structural phase transition of nanoparticles.

- **alpha** - hexagonal corundum structure (most frequent polymorphs -hematite)
- **gamma** - cubic spinel structure (maghemite)
- **beta** - cubic bixbyite structure
- **epsilon** - orthorombic structure

From the viewpoint of the applied research

Iron (III) oxide- most commonly used metal oxides with various applications in many environmental and industrial fields:

- production of iron and steel
- geologically and archeologically important earth-samples
- Due to hardness, catalytic activity, surface resistivity and other properties (magnetic, optical, electronic) they are used as abrasives, polishing agents, catalysts, gas sensors, pigments, photoanodes, contrast agents in MRI, etc.

Nanoparticles of Iron(III)oxide exhibit unique features-fundamental importance in industrial application

- development of new electronic and optical devices, information storage, magnetocaloric refrigeration, color imaging, bioprocessing, ferrofluid technology or manufacture of magnetic recording media
- Advantage of using Fe_2O_3 nanoparticles relies on their chemical stability, in contrast to the commonly used ultrasmall particles of pure metals

Methods for synthesis of Fe_2O_3 nanoparticles

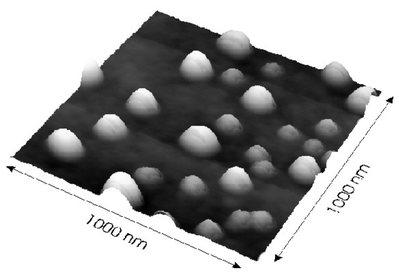
- oxygen-hydrogen flame pyrolysis
- laser pyrolysis
- electrochemical synthesis
- sol-gel method
- vaporization-condensation process in a solar furnace
- micro-emulsion technique
- diod sputter deposition
- thermal decomposition of an aerosol upon a heated substrate
- thermally induced solid-state reaction

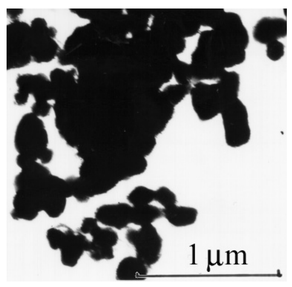
The conventional analysis of the structural, magnetic and electronic properties of Fe_2O_3 nanoparticles:

- XRD
- EPR
- ^{57}Fe Mössbauer spectroscopy
- SQUID magnetization measurement
- Magnetic susceptibility measurement
- EEL spectra
- XAS (X-ray absorption spectroscopy)
- XRD
- DLS
- BET

Comparison of the AFM and TEM images

AFM





TEM

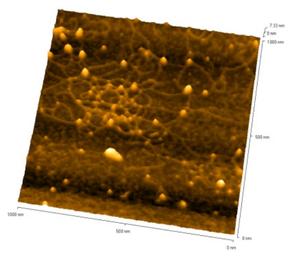
Fe_2O_3 particles prepared by thermal decomposition of ammonium ferrocyanid in air

Position of AFM analysis

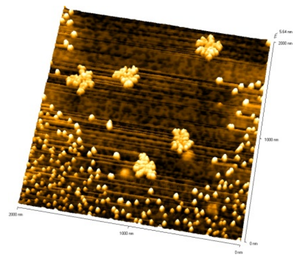
Possition of TEM (or HRTEM) is dominant at the analysis of Fe_2O_3 systems but role of AFM increases step by step

- 3D images allow to examine the real particle morphology including the vertical dimension
- possibility of the determination of some surface characteristic (mean surface rougness, surface fractal dimension...)
- advantages AFM are limited by lower lateral resolution due to tip convolution at ultrasmall particles (less than 10 nm)

Effects related with the sample drying



Water chains among particles



2D clusters

AFM analysis of Fe_2O_3 nanoparticles - instrumentation, sample analysis

AFM Explorer (ThermoMicroscopes-Veeco, USA), Si-tip, non-contact mode (resonant frequencies 180-240 kHz) tip radius less than 10 nm. Measurements were realized in the ranges from 2000x2000 nm to 100x100 nm with resolution 300x300 pixels.
Synthetically prepared mica (Structure Probe, Grade V-4, USA) -chosen as a ground.

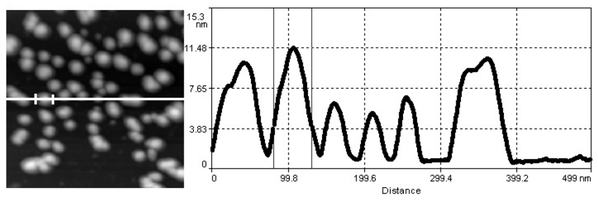
- Dispersion of iron oxide powder in water using of ultrasonification (140 W for 3min)
- Dispersed Fe_2O_3 particles are spread on preheated mica and put into drying oven. Optimal condition of drying (50 °C, 10-15 min.)
- Too long drying time and/or temperature result in significant decrease of the stability of AFM measurement (bad fixation of Fe_2O_3 particles on mica)
- Short drying time is manifested by large clustering of particles to one another and/or by the existence of the water joints among particles that create chains an netted structure. Dryig at higher temperatures (more than 80 °C, less than 5 min.) leads to 2D clusters (see left figers).
- Optimal density of particles seems to be about 0.8 mg/ml H_2O.

Summary

Sample processing can influence the stability of AFM measurement, the found particle size distribution, the general distributin of particles on mica surface, degree of particle agglomeration and thus the image interpretation. Optimized sample processing allow high-quality images

Image processing, artifacts and measurement interpretation

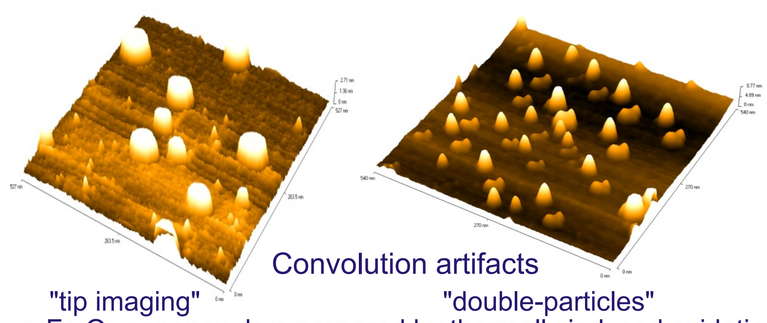
Several artifacts result from the scanning mechanism and the distance between probe and sample during the measurement. The main problem of AFM measurement is the space convolution of a sample with a tip, which distorts the particle shapes and increases their lateral dimensions. The shape distortion is obvious in line cross-sections, were the peak shape doesn´t correspond to the particle profile but manifests the convolution effect, see figer bellow.



The line cross-section of a- Fe_2O_3 particles prepared by thermal of $FeCO_3$

An extreme demonstration of convolution is the so called "tip imaging" which usually occurs during scanning the needl-like objects whose side slope is higher then the slope of the tip and the piramidal or the conical shapes are observed. This artifacts plays an important role also in AFM analysis of Fe_2O_3 particles with the real size less than 10 nm, which appear as the small needles in 3D images (see left figure). →
The other convolution artifacts can be related with the low tip quality. Doubled images oriented in the same manner clearly point at the double end of the tip (see right figure).
The non-symmetric tip convolution may be manifested by elongation of particle in one direction

Effects of "tip imaging" on small particles



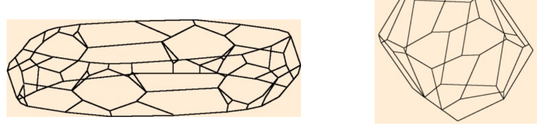
"tip imaging" Convolution artifacts "double-particles"

g- Fe_2O_3 nanopowders prepared by thermally induced oxidation of $FeCO_3$ and $FeSO_4$

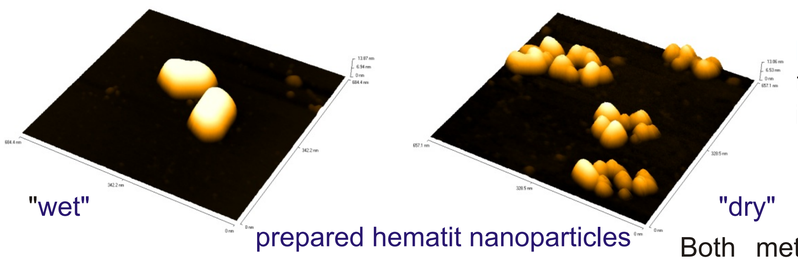
The influence of particle morphology on color quality of α–Fe_2O_3 red pigment synthesized by non-equivalent routes

a- Fe_2O_3 is the oldest-known and the most frequent inorganic pigment, chemically stable,non-toxic, non-bleeding and highly durable with excellent suspenzion properties and very high heat resistance as a superior pigmentary characteristic. It is used in a wide range of application, including paint and coating, rubber and plastic products, textile finishes, building material, and ceramics. Hematit has a rhombohedrally centered hexagonal structure of the corundum type with a close-packed oxygen lattice in which two thirds of the octahedral sites are occupied by Fe^{3+} ions. Its color quality is very sensitive particularly to the particle size, morphology and internal structure (cation substitution, and thus to the rout synthesis)

hexagonal and rhombohedral most frequent habitus



Wet route-reacting a ferrous salt, a reducable aromatic nitrocompound and ammonium hydroxide, operating at a higher temperature, in aqueous medium



"wet" "dry"

prepared hematit nanoparticles

Dry route- solid-sate method based on thermal decomposition of $FeSO_4.7H_2O$ in air

Both methods allow to control the particle size distribution by the choise of the experimental conditions,particularly using the change of the reaction temperature. Mean particle diameters were determined from dynamic light scattering measurements (90 and 92 nm for hematit powder)

The AFM measurements were applied to asses the particle size and morphology and thus to explain the color difference. The hematit nanoparticles with the size of 85-90 nm (after deconvolution) and with the morphology corresponding to very thin hexagonal plates (the ratio of the major lateral dimension to vertical dimension ld/vd 17-25) were observed in AFM images of nanohematite prepared by wet route. Particles of hematite prepared by solid-state metod show the size in range of 80-100 and more symmetric rounded shapes (ld/vd 5-10). Just the different values of vertical dimensions, which are responcible for different color quality, cannot be easily found by using other techniques including TEM