Size Controlled Iron Oxide Nano Octahedra via Sonochemistry and Natural Ageing [1]

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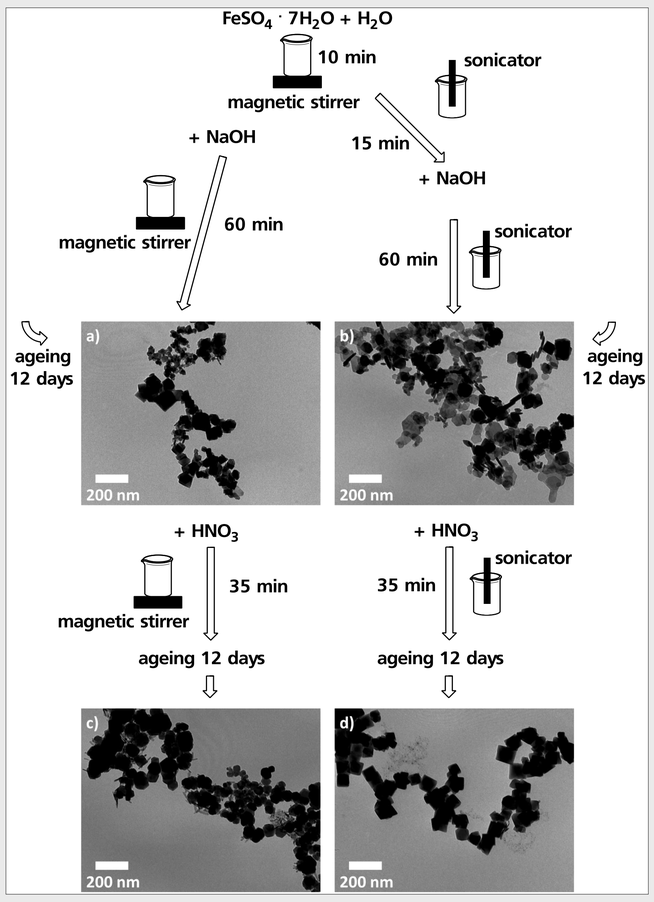
The focus of our work is on the synthesis and characterization of multi-functional biocompatible nanoparticles (NPs) on the basis of iron oxide with selected morphology. Current studies have shown the possibility to use these NPs as a basis for contrast agents which are suitable for T_2-weighted magnetic resonance imaging (MRI) and magnetic particle imaging (MPI). The efficiency of the contrast agents is influenced by the size and morphology of the NPs.

Here, we present a facile way of presetting the shape of iron oxide NPs via ultrasound in combination with nitric acid addition to form octahedra and on top of this controlling the size by simply letting the NPs naturally age.
The characterization of the NPs is done by conventional methods such as transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD) and the magnetic properties of the particles were analyzed with a vibrating sample magnetometer (VSM).

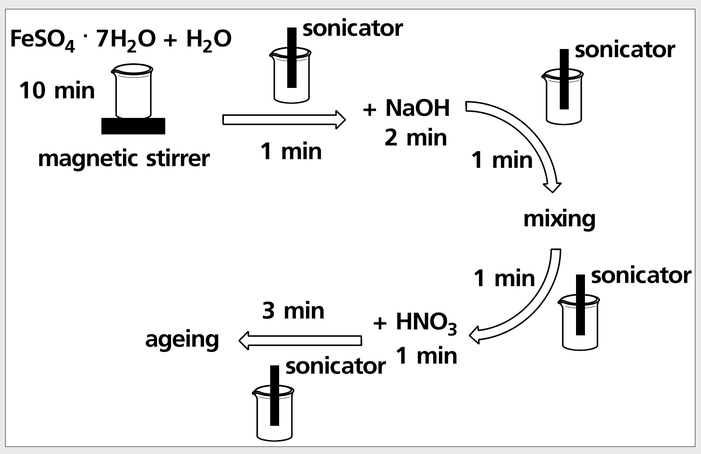
Synthesis

- Comparison of the influence of ultrasound treatment vs. simple stirring on the shape evolution of the NPs.
- Ultrasound treatment alone cannot impose the desired cube look-alike shape of the NPs. Nitric acid addition during the reaction is necessary.
- TEM images a) and b) show the NPs after precipitation with stirring resp. exposure to ultrasound. Images c) and d) show the NPs after addition of nitric acid. The combination of ultrasound and nitric acid treatment yields octahedral NPs (d).



**Reaction schemes showing the influence of ultrasonic treatment on the shape formation of the NPs.
Left-hand side: synthesis via stirring, right-hand side: sonochemical synthesis.**

- In order to render the synthesis process simpler, faster and therefore more feasible for large scale NP production, reaction times were drastically shortened (ten-minute reaction).

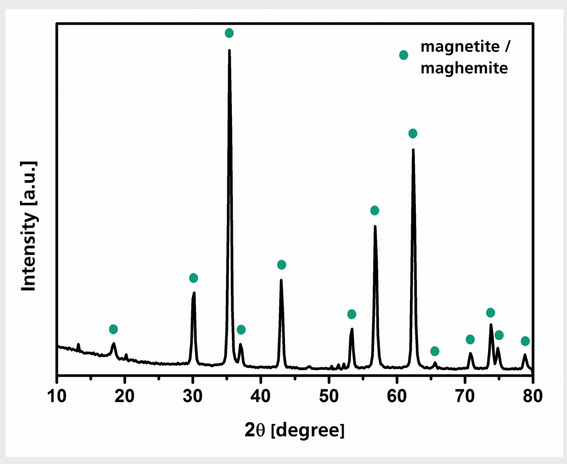


Reaction scheme of a facile and fast process to obtain iron oxide nano octahedra. Subsequent ageing time controls the size of the NPs.

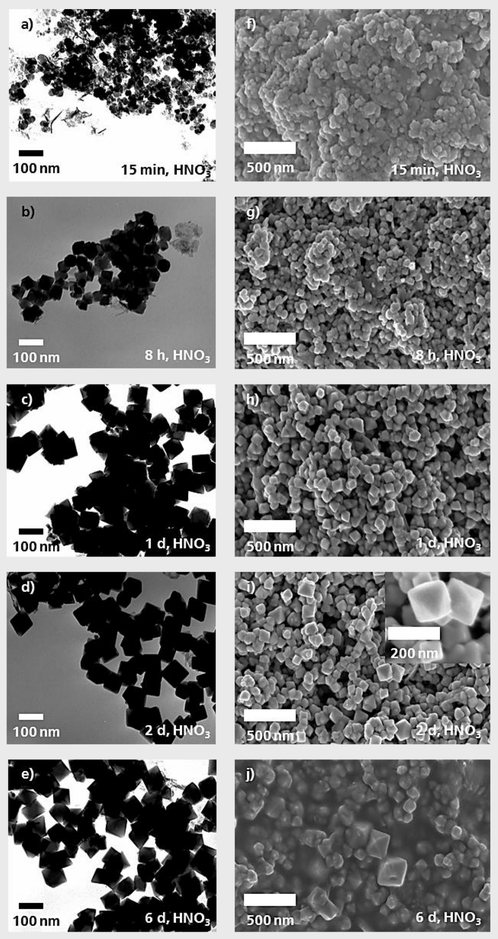
Average particle sizes of samples, aged either 15 min, 8 h, 1 d, 2 d or 6 d. Samples were either washed with deionized water or with nitric acid solution (HNO_3).

sample	average particle size [nm]	
ageing time	washed with H_2O	washed with HNO_3
15 min	59±15	59±11
8 h	93±15	82±14
1 d	113±18	110±20
2 d	113±34	122±26
6 d	126±41	129±56

Structural Properties



Exemplary X-ray diffractogram of 6d aged NPs washed with deionized water. The peaks indicating the crystallinity of the NPs can either be assigned to magnetite (Fe_3O_4) or maghemite (γ-Fe_2O_3).

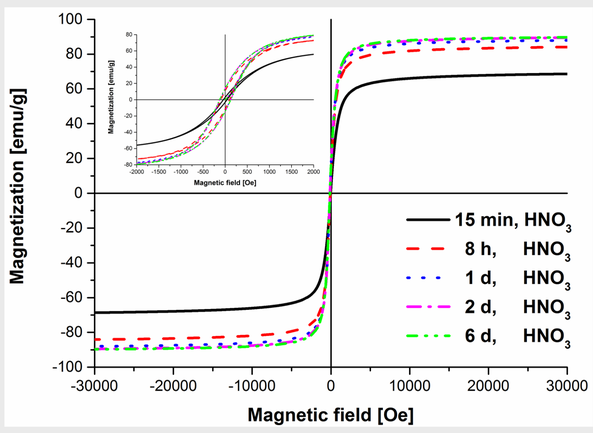


Left column TEM images (a-e) of the NPs obtained after different ageing times. Right column SEM images (f-j) of the same samples. All samples were washed with nitric acid (HNO_3) to stop any further reaction or particle growth. The octahedral shape is emphasized in the inset in image i).

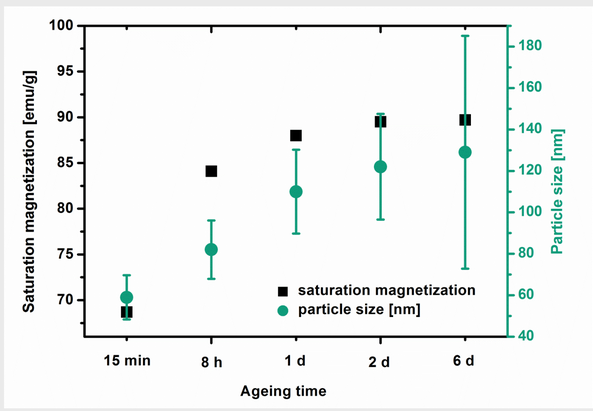
Magnetic Properties

- Magnetization curves of the NPs (aged for different times) measured with a vibrating sample magnetometer (VSM).
- The saturation magnetization increases with ageing time, i.e., with particle size.

Magnetization curves of iron oxide NPs after ageing times of 15 min, 8 h, 1 d, 2 d and 6 d. All samples possess a hysteretic magnetic behavior; saturation magnetizations increase with increasing ageing times.



- Correlation of ageing time with the size and magnetic properties of the NPs.
- Steady increase of particle size with ageing time. Polydispersity increases due to Ostwald ripening.
- Saturation magnetization also increases with ageing time: not linear, but rather follows a saturation curve.



Relation between particle sizes and saturation magnetizations of the NPs with ageing time of 15 min, 8 h, 1 d, 2 d and 6 d.

Summary

- Facile and inexpensive synthesis of multifunctional iron oxide nano octahedra.
- Characterization of structural properties and analysis of the magnetic properties via VSM.

Outlook

- Attachment of biomolecules such as antibodies.
- Investigations of these NPs to be used as contrast agents for MRI and MPI.

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Reference:
[1] K. Mandel, C. Kolb, M. Straßer, S. Dembski, G. Sextl, Size controlled iron oxide nano octahedra obtained via sonochemistry and natural ageing, Colloids and Surfaces A: Physicochemical and Engineering Aspects, *accepted*.

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