

# STRUKTURA 2011

Turnov, 20. 6. - 23. 6., 2011

## Lectures - Session I, Monday, June 20

L1

### NANOPARTICLES FOR MULTIPLE IMMUNOLABELING AND NUCLEATION OF POLYMER CRYSTALLIZATION

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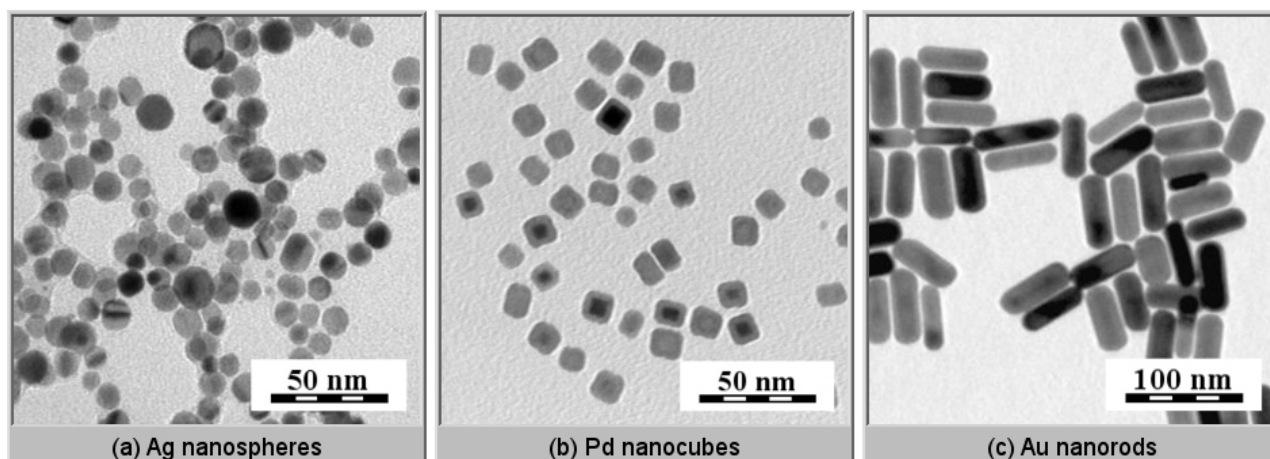
Metallic nanoparticles combine large surface/volume ratio with specific chemical, electronic and optical properties. We describe preparation and characterization of gold, silver and palladium nanoparticles with tunable sizes and/or shapes. It is demonstrated how the nanoparticles are employed in two different fields of research: (a) multiple immunolabeling in biology and (b) nucleation of polypropylene crystallization in polymer science.

In our previous studies, we described numerous nanoparticle syntheses, such as preparation of isometric Au nanoparticles with tunable size within range 4–200 nm [1, 2], isometric Ag nanoparticles [3], isometric Pd nanoparticles with tunable size 3–16 nm [3, 4], isometric core-shell (Ag)Au nanoparticles [5], Pd nanocubes [3] and Au nanorods [6]. The nanoparticles were usually characterized microscopic, spectroscopic and diffraction methods. Transmission electron microscopy (TEM) bright field images of selected metallic nanoparticles are given in Fig. 1.

structure, size, stability, and nucleation effects of the prepared nanoparticles. Selected area electron diffraction

(SAED) and apertureless electron diffraction (ED) verified the structure of synthesized nanoparticles [3]. Quasi-elastic light scattering (QELS) and small-angle X-ray scattering (SAXS) proved the stability of nanoparticle colloidal solutions, which are used during multiple immunolabeling [1–4]. Two-dimensional wide-angle X-ray scattering (2D-WAXS) was employed in quantification of Au-nucleated crystallization of isotactic polypropylene [7–9].

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**Figure 1.** TEM micrographs showing (a) Ag isometric nanoparticles, (b) Pd nanocubes and (c) Au nanorods; the particles were deposited on an electron-transparent carbon film before observation.



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## NANOCRYSTALLINE MATERIALS CONTAINING 3D METALS FOR HYDROGEN STORAGE

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Some composites of Fe, Ti, V, and Zr 3d metals are well known for hydrogen storage ability. We prepared the materials by solid state reaction by mixing and dry milling method. The samples were consequently homogenized by high treatment in various surroundings atmospheres and in the pure vacuum. We were able to prepare intermetallic compounds TiFe, Zr<sub>2</sub>Fe and hydrides ZrH<sub>2</sub>, VH<sub>2</sub>. These

acceptable phases had impurities - Fe, Fe<sub>2</sub>Zr, Ti<sub>2</sub>Fe and oxides (ZrO<sub>2</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O, TiO and Ti<sub>2</sub>O). The dry milling method was used for preparing VFe, Zr<sub>2</sub>Fe and Zr<sub>3</sub>Fe intermetallic compounds.

*extended contribution submitted*

L3

## Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> NANOCOMPOSITE – SHAPE OF THE -Fe<sub>2</sub>O<sub>3</sub> NANOCRYSTALS

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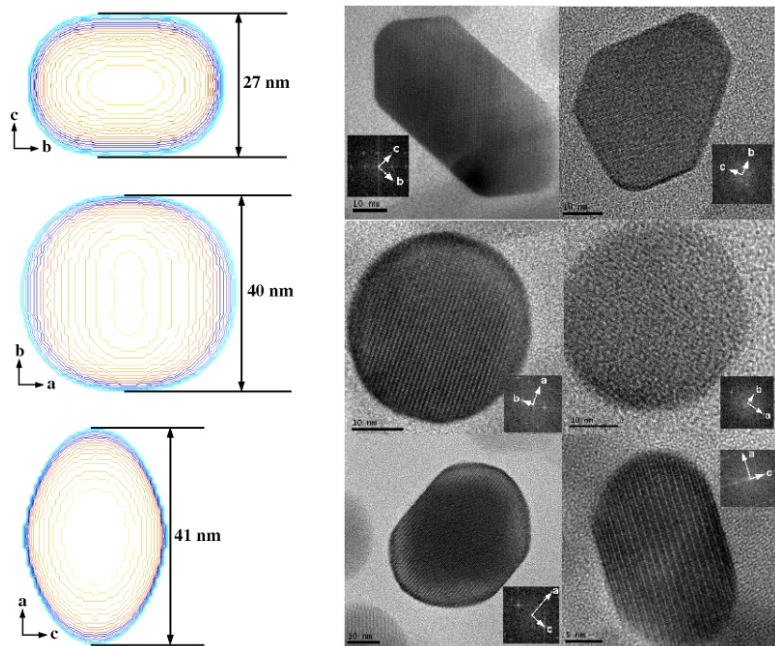
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The first article dealing with the -Fe<sub>2</sub>O<sub>3</sub> was published in 1934 [1]. However, its crystal structure described in the orthorhombic *Pna2*<sub>1</sub> was published in 1998 [2]. The structure of epsilon phase is characterized by the closest packing of the oxygen anions with ABAC stacking. The stacking planes are parallel to (001). The iron cations occupy four different sites. Three of them have octahedral and the last one has tetrahedral coordination polyhedron. The values of the lattice constants are  $a = 5.091 \text{ \AA}$ ,  $b = 8.784 \text{ \AA}$  and  $c = 9.472 \text{ \AA}$ . After a discovery of its giant 2 T room temperature coercivity in 2005 [3] the epsilon phase attracted more attention as these properties predestinates it as a promising

material for magnetic recording and information storage. Moreover, in 2009 Namai et al. used this phase as a high-performance millimeter electromagnetic wave absorber, which opens a possibility of the applications of this material in high-speed wireless communication devices [4].

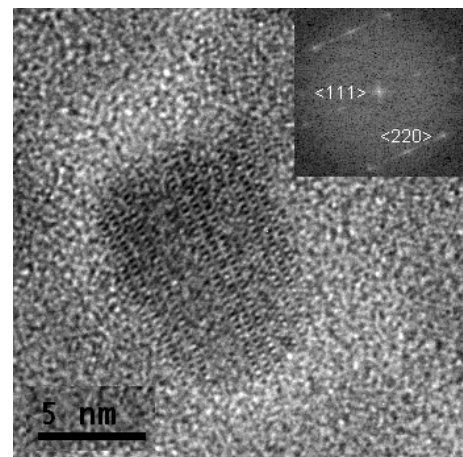
Nanocomposites were prepared by a sol-gel process using complex molecule of ferric cation and organic molecule H<sub>2</sub>L bearing two trimethoxysilyl groups (H<sub>2</sub>L = bis-[3-(trimethoxysilyl)propylamide] of ethylenediaminetetraacetic acid). After hydrolysis and condensation of Si-OMe groups followed by drying, the xerogels obtained



**Figure 1.** Comparison of modeled anisotropic crystal shape (left) with crystals viewed along the corresponding directions in the HR-TEM images (right) of the sample annealed at 1100 °C.

were annealed at final temperatures between 900 and 1100 °C, thus obtaining nanocomposites with 40% weight concentration of iron oxide [5]. The SiO<sub>2</sub> matrix was removed by reacting the nanocomposite with 5 M NaOH at 80 °C for three days. The nanocrystals were then washed several times by distilled water and collected by centrifugation. The transmission electron microscopy (TEM) measurements were conducted using a JEOL JEM-3010, while the X-ray diffraction (XRD) data were collected using a PANalytical X'Pert Pro with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature with the  $2\theta$  range between 10° and 110°. Rietveld analyses were performed by the Fullprof program [6]. As a profile function was used Thompson-Cox-Hastings pseudo-Voigt function. For a modeling of the anisotropic shape of the crystallites were used spherical harmonics.

The epsilon phase is stable only in a restricted size range between approximately 10 to 100 nm. It crystallizes in the Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> system from maghemite and transforms to thermodynamically stable hematite under prolonged heat treatment. The shape of the epsilon phase crystals depends on the size of the crystals. The particles obtained at 1100 °C adopt a disc-like shape flattened in *c* direction with similar diameters in *a* and *b* directions and they are in almost all cases single crystals. The largest crystal faces are (001) and (110) as deduced from the HR-TEM images. These results are in an agreement with XRD data fitting (Figure 1). Table 1 summarizes the volume weighted diameters in the [100], [010] and [001] of the coherently diffracting domains of the epsilon phase. The fastest growth of the crystals in the temperature range between 900 °C and 1100 °C is in the [001] followed by the [100]. The smallest growth is in the [010]. It is important to note that the viscosity of the silica matrix significantly increases at about 1000 °C. Under this temperature the growth of the particles is much slower. To understand this anisotropic growth of

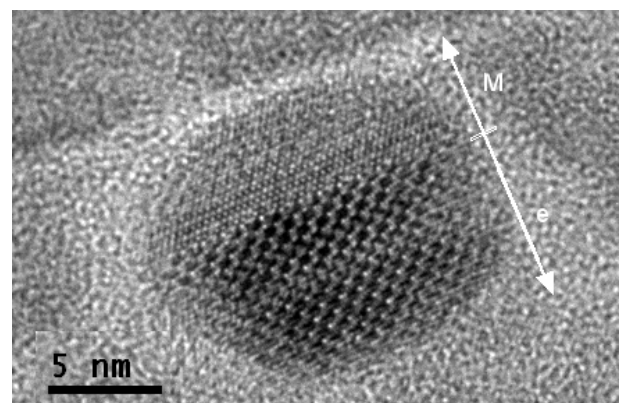


**Figure 2.** HR-TEM image of a maghemite particle observed along *c* direction.

the epsilon crystals it is necessary to understand the basics of the epsilon transformation from maghemite.

Maghemite has a spinel structure, which is described in the cubic space group  $Fd\bar{3}m$ . The stacking of the oxygen anion layers is along  $111$ . The maghemite particles with the size close to 10 nm are flattened in one of the  $111$  directions (Figure 2). Some particles contain domains of both maghemite and epsilon. The contact plane of these phases was found to be  $111_M/[001]$ . Evaluation of the FFTs of the HR-TEM images showed that there is a fixed structural orientation relationship between these two phases ( $110_M$  is parallel to [010] and  $211_M$  is parallel to [100], Figure 3). This orientation relationship is the same as that found by Ding et al. for magnetite and epsilon [7]. Interestingly, the nanowires of magnetite described in this work transformed in the epsilon phase only in case when the nanowires grew along one of the *n* of magnetite (which is the same direction as the  $110$  of maghemite), which could explain why is the largest diameter of the smallest epsilon particles is in the [010].

In conclusion the transformation of maghemite to epsilon is probably much faster within a cationic layer than in



**Figure 3.** HR-TEM image of a particle containing both maghemite and epsilon. Arrow points in  $[111]_M$  and  $[001]$ . Perpendicular to this direction is  $110_M/[010]$ .



the direction perpendicular to the atom stacking as evidenced by the different growing rate of the epsilon phase in the  $a$ ,  $b$  and  $c$  directions.

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**Table 1.** Volume weighted diameters on  $\gamma\text{-Fe}_2\text{O}_3$  as a function of the annealing temperature.

Temperature (°C)	[100] (nm)	[010] (nm)	[001] (nm)
900	6(1)	11(1)	3(1)
950	10(1)	10(1)	5(1)
1050	28(2)	24(2)	17(2)
1100	41(3)	40(3)	27(3)

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L4

## VYUŽITÍ VYSOKOTEPLNÍ RTG DIFRAKCE PRO PŘÍPRAVU A CHARAKTERIZACI KOMPOZITNÍCH (NANO)MATERIÁLŮ OBSAHUJÍCÍCH NANOČÁSTICE ELEMENTÁRNÍHO ŽELEZA

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Významná část nanomateriálového výzkumu je v současné době zaměřena na zjištění optimálních podmínek přípravy kompozitních (nano)materiálů s nejrůznějšími fyzikálně-chemickými vlastnostmi, jejich komplexní charakterizaci a testování jejich využitelnosti v nejrůznějších oblastech lidské činnosti. Význam kompozitních (nano)materiálů spočívá zejména v možnosti efektivně kombinovat specifické vlastnosti dvou a více odlišných (nano)materiálů v jednom celku. Výsledný kompozitní (nano)materiál vykazuje vlastnosti, které by nebylo možné získat za použití jednotlivých (nano)materiálů.

Vysokoteplotní RTG prášková difrakce představuje jednu ze stěžejních metod používaných při studiu a laboratorní přípravě kompozitních (nano)materiálů reakcemi v pevné fázi a reakcemi typu pevná fáze - plyn, a to zvláště díky jedinečné možnosti in-situ monitorovat průběhy daných reakcí a zároveň sledovat další kritické parametry kompozitních (nano)materiálů (především střední velikosti koherentních domén a kvantitativní zastoupení jednotlivých fází). V prezentované práci byla použita vysokoteplotní reakční komůrka XRK900 (Anton Paar, GmbH) s pracovním rozsahem teplot RT až 900 °C a tlakem plynů 1 mbar až 10 barů (inertní, oxidační, redukční a nejrůznější reakční plyny a různé relativní vlhkosti

vzduchu) nainstalovaná na práškovém difraktometru X'Pert PRO MPD (PANalytical).

Charakter a využití kompozitních (nano)materiálů obsahujících nanočástice elementárního železa (nanoparticles of zero-valent iron - nZVI) připravovaných v laboratořích Regionálního centra pokročilých technologií a materiálů (PřF UP Olomouc) je v principu dvojitý: nanočástice elementárního železa (<20 nm až ~100 nm) jsou využity jako magnetický nosič pro jinak nemagnetické materiály s výbornými sorpčními vlastnostmi, nebo je v rámci kompozitního (nano)materiálu využito jejich reduktivního účinku, popř. může být využito obou těchto vlastností. Aplikačně jsou velmi důležité kompozitní (nano)materiály typu zeolit-nZVI, jílový minerál-nZVI a uhlík-nZVI. Zabudováním nZVI do silikátové (zeolity, jílové minerály) či uhlíkové matrice vznikne magnetický kompozitní (nano)materiál vhodně aplikovatelný například pro sorpční odstraňování těžkých kovů či organických látek z vodných prostředí s možností jejich následné magnetické separace. V případě kompozitního (nano)materiálu typu uhlík-nZVI se zároveň může uplatňovat i reduktivní účinek nZVI.