Syntéza Nps –

- chemické metody přípravy II

Brno, PS 2012

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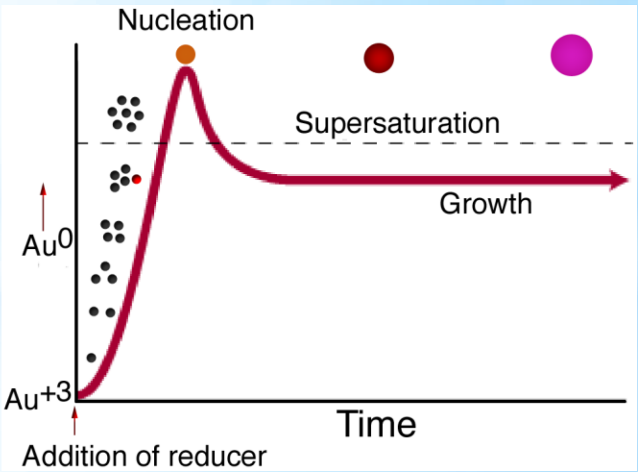
Ofice: UKB A12/M231

Ústav chemie: http://ustavchemie.sci.muni.cz/



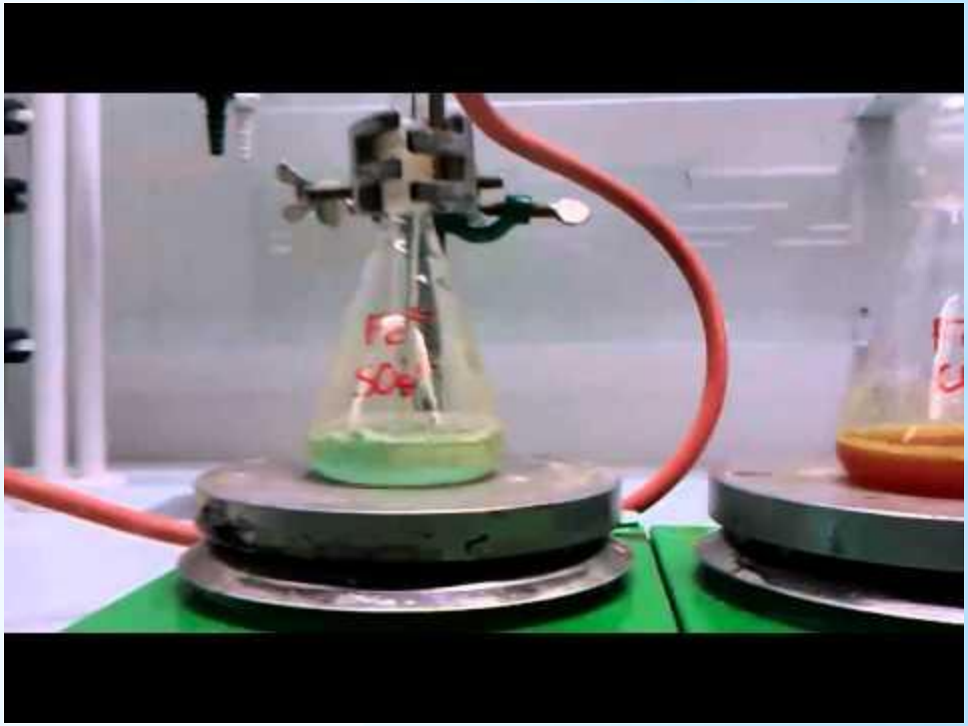
Au-nano

Coprecipitation

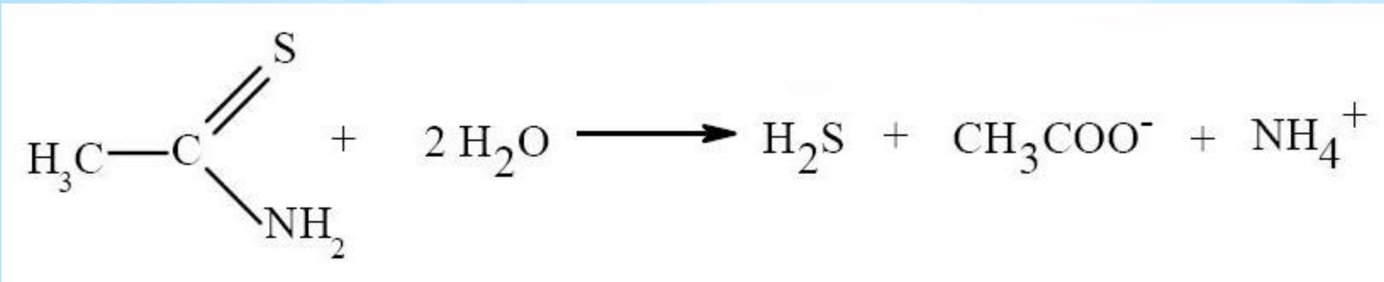
- Sol-gel Processing
- Microemulsions
- Hydrothermal/Solvothermal Synthesis
- Microwave Synthesis
- Sonochemical Synthesis
- Template Synthesis
- Biomimetic Synthesis

Precipitační syntézy NPs

Analogie srážecích reakcí
Problémy: nekontrolovaná velikost, krystaly,…
Používá se zřídka

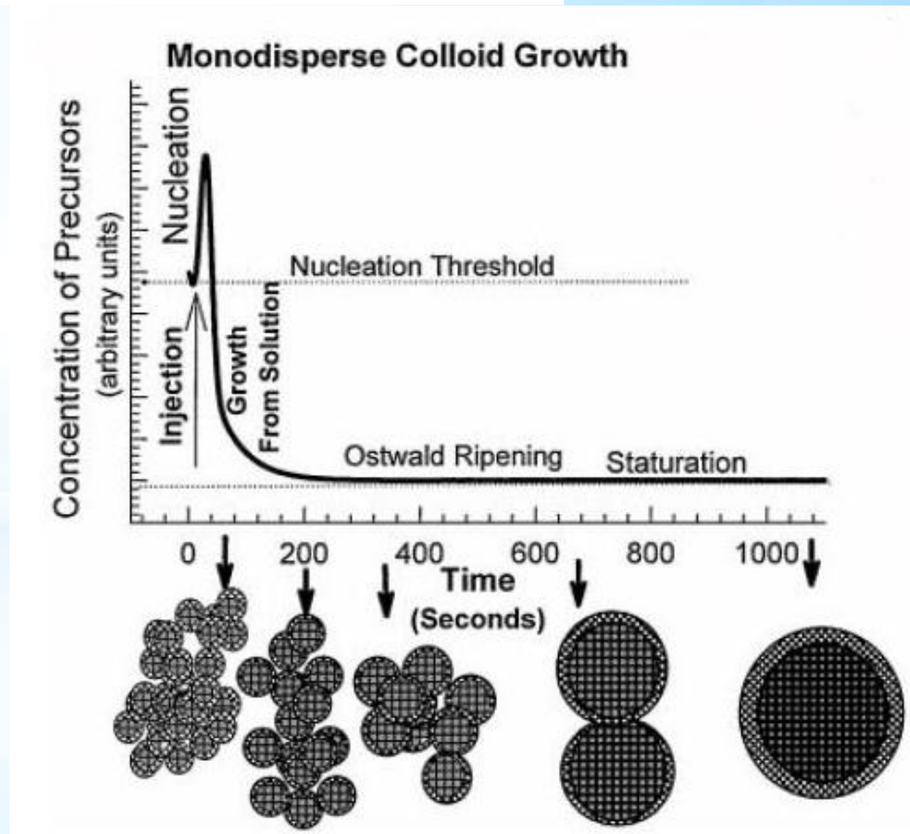


Example: Precipitation of ZnS nanoparticles from a solution containing thioacetamide and zinc acetate



Thioacetamide is used as a sulfide source.

$Zn^{2+} + S^{2-} \rightarrow ZnS$

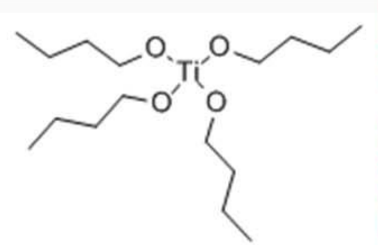


Murray C.B. et al., *Annu. Rev. Mater. Sci.* 2000, *30*, 545.

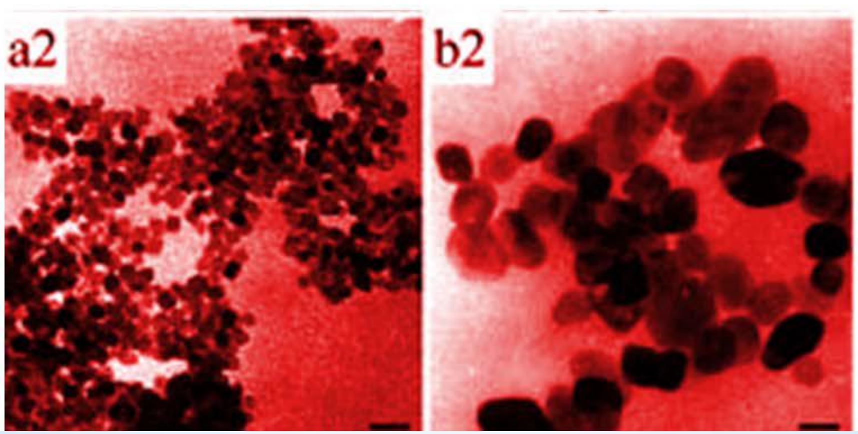
Solvotermální syntéza

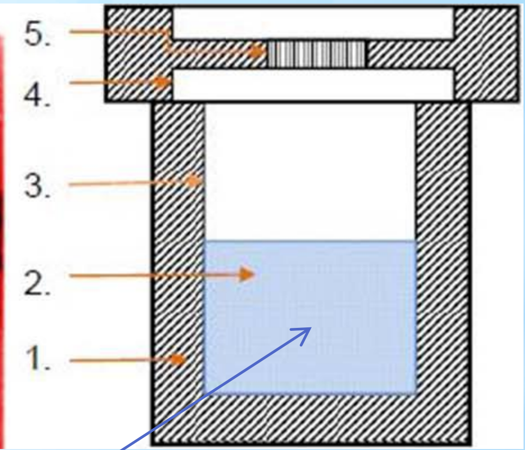
Precursory se rozpustí v horkém rozpouštědle (např. n-butyl alcohol) v autoklávu.
Nevodná rozpouštědla zabezpečují menĕ drastické a selekticnější reakční prostředí. Je-li rozpouštědlem voda pak se proces nazývá hydrotermální syntéza.

Precursor:
Titanium
n-butoxide



Example: TiO2 Nanocrystallites



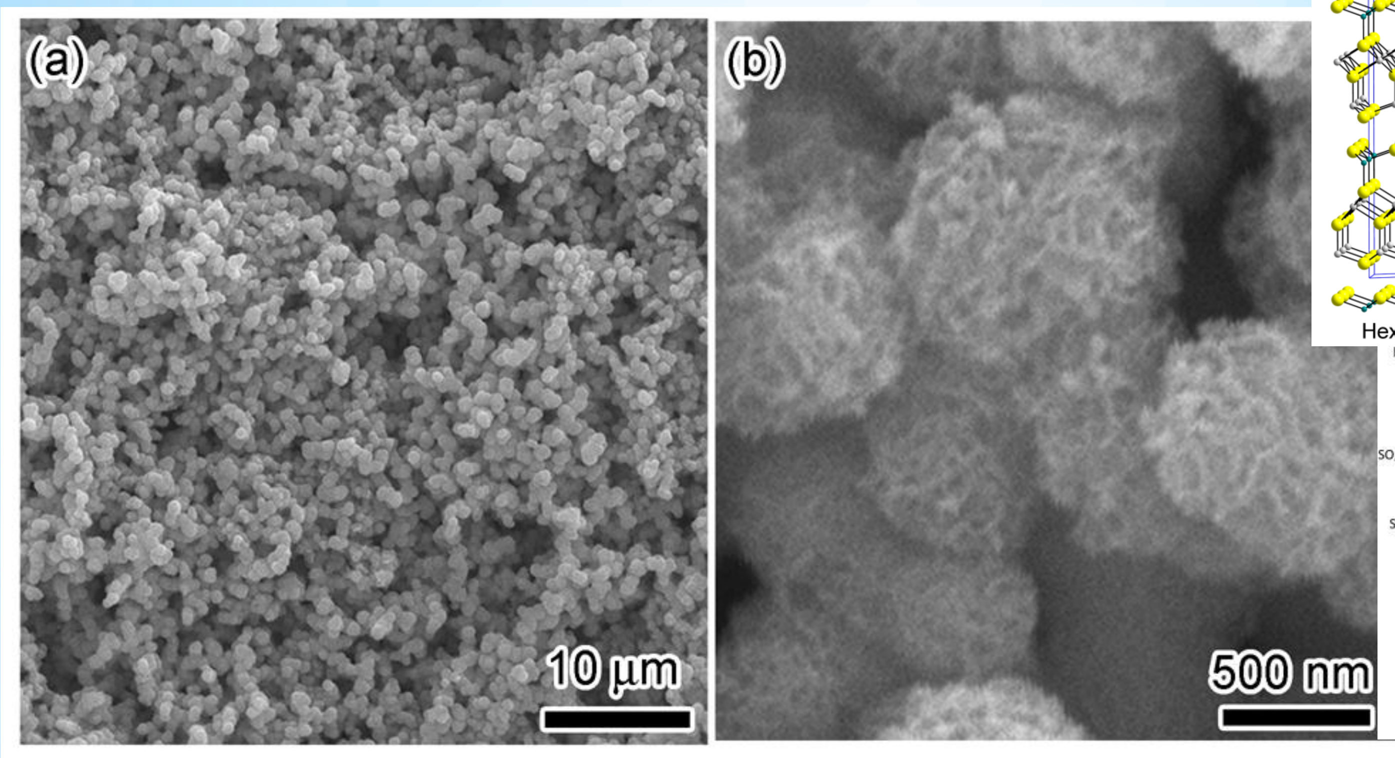


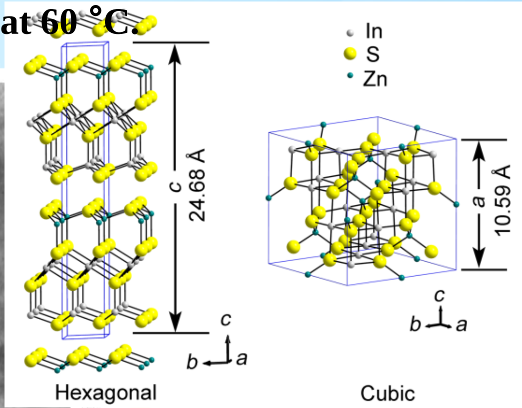
Precursor solution with butyl alcohol

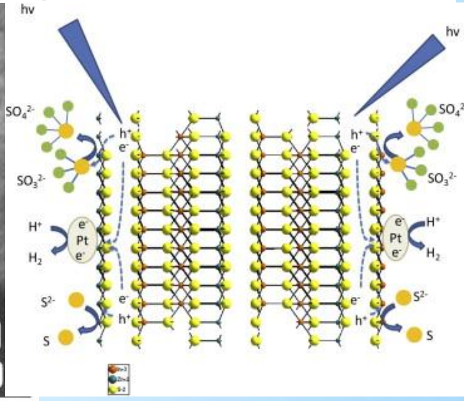
Hlavně pro přípravu oxidů

Příklad: Solvotermální syntéza $ZnIn_2S_4$

$ZnIn_2S_4$ microspheres prepared by an oleylamine-assisted solvothermal method. Procedure, 1 g of oleylamine and 0.03 mmol of $Zn(AC)_2$ were firstly dissolved in 24 mL tetrahydrofuran (THF) at room temperature to obtain a homogenous solution by vigorous magnetic stirring for 0.5 h, and then 0.06 mmol of $InCl_3$ and 0.5 ml of CS_2 were added under magnetic stirred. The mixed solution was then transferred into a 30 mL Teflon-lined autoclave, and kept at 180 °C for 24 h. After the autoclave was cooled to room temperature naturally, a yellow precipitate was obtained, then it was filtered and washed with absolute ethanol and distilled water for several times. Finally $ZnIn_2S_4$ was obtained after drying in vacuum at 60 °C.





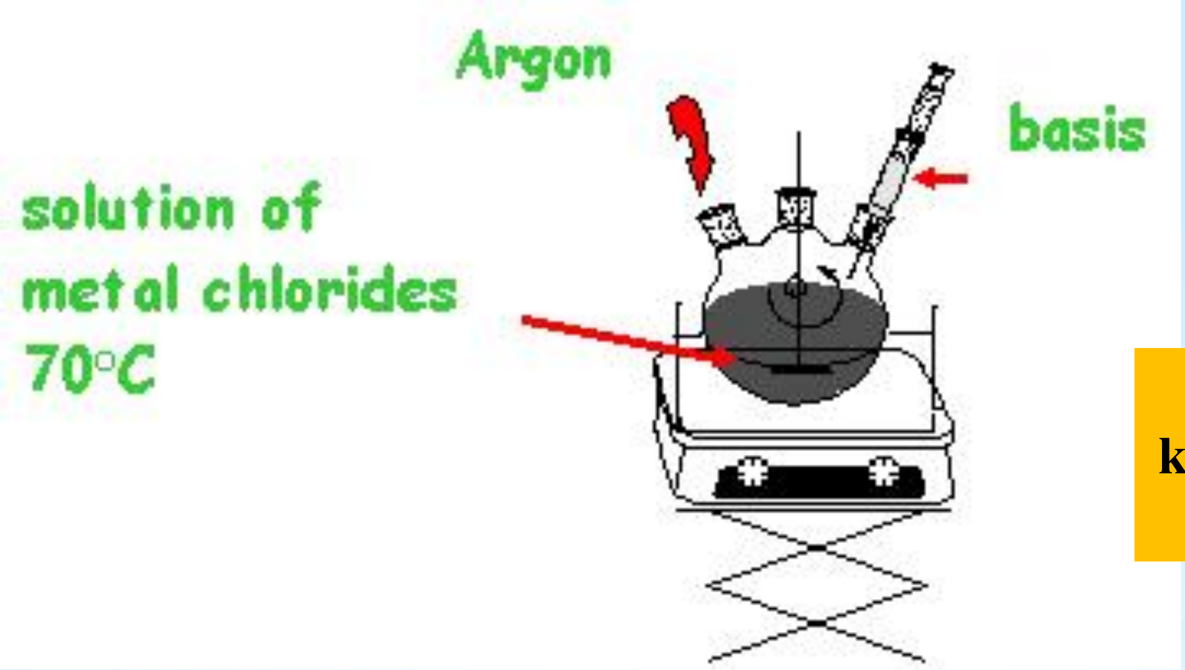


Aplikace fotokatalýza

Yu, J. C. et al. *J. Solid State Chem.* 2005, *178*, 321; *Cryst. Growth Des.* 2007, *7*, 1444

http://www.sciencedirect.com/science/article/pii/S036031991201840X

Hydrotermální syntéza Oxidů

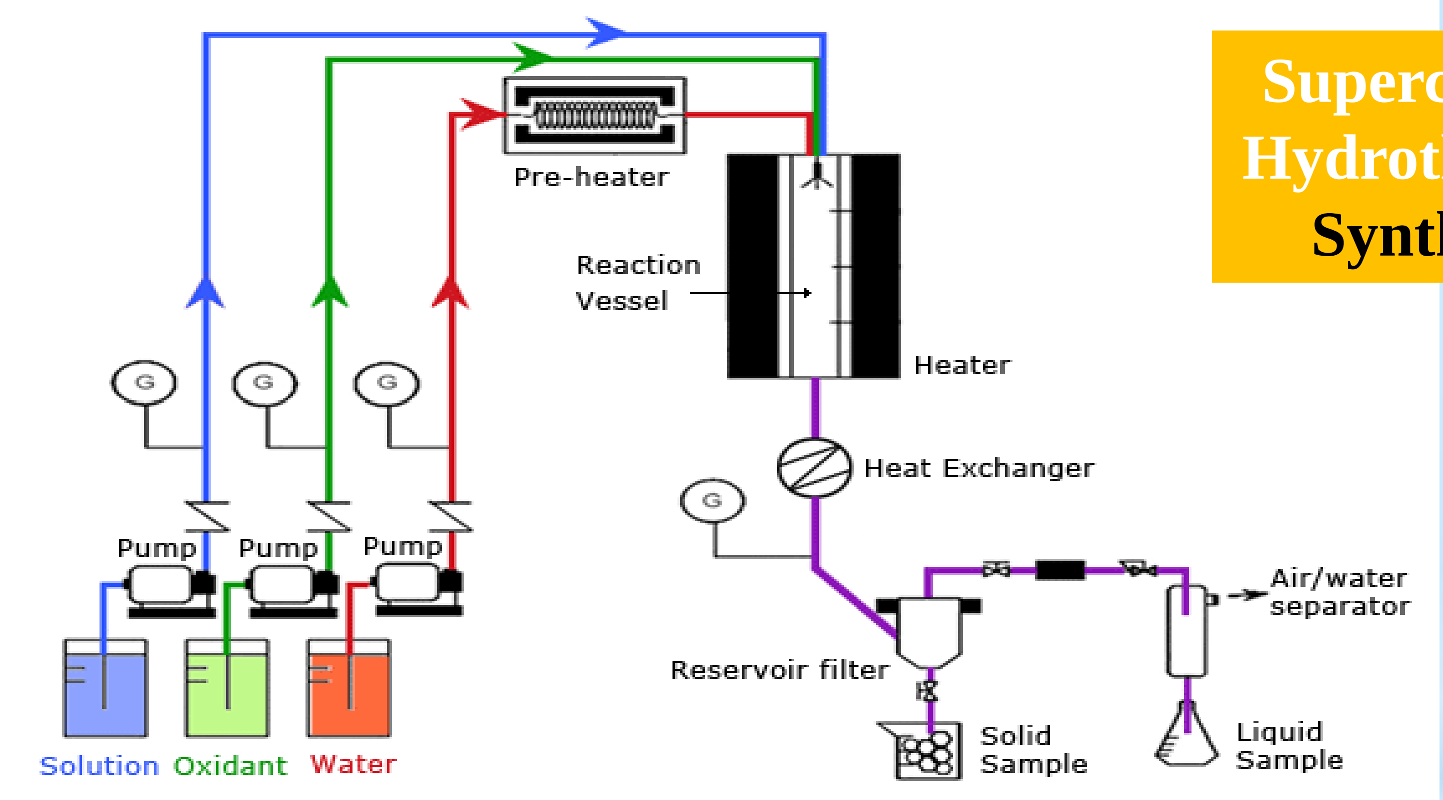


K oxidaci stačí kyslík rozpuštěný ve vodě

Iron oxides ze solí Fe:
Step 1: The pH is increased up to 10-14 by adding ammonium bases, ($N(CH_3)_4$-OH), ($N(C_2H_5)_4$-OH) or ($N(C_3H_7)_4$-OH).
Step 2: The nanoparticles are then submitted to a hydrothermal treatment between 150 and 250°C.

Hydrothermal Synthesis of Monodisperse Magnetite Nanoparticles. Daou, T. J.; Pourroy, G.; Begin-Colin, S.; Greneche, J. M.; Ulhaq-Bouillet, C.; Legare, P.; Bernhardt, P.; Leuvrey, C.; Rogez, G. Chemistry of Materials (2006), 18(18), 4399-4404.

Kontinuální hydrotermální syntéza Oxidů



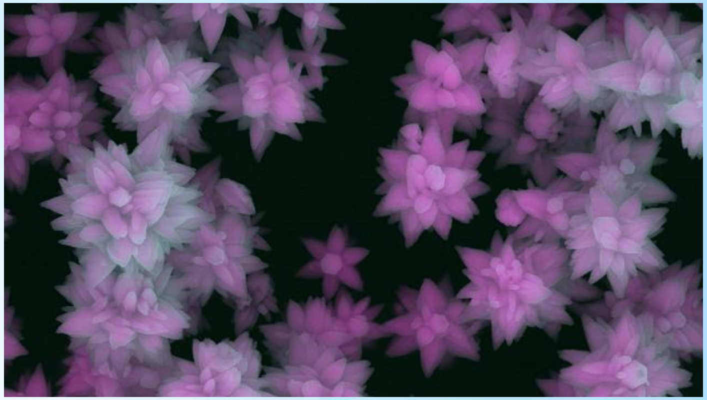
Supercritical Hydrothermal Synthesis

$LiCoO_2$, $LiMnO_2$, CeO_2, CuO, ZnP, TiO_2, $BaFe_{12}O_{19}$, $Ni_xZn_{1-x}Fe_2O_4$

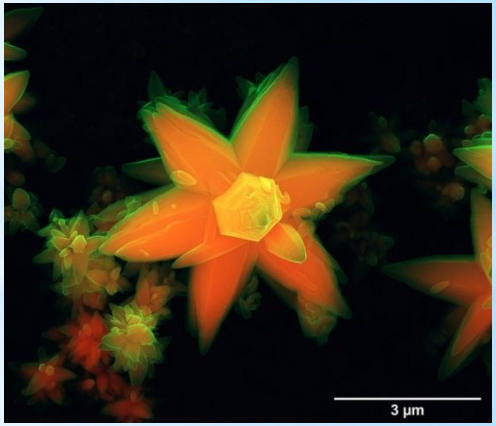
http://www.google.cz/imgres?q=hydrothermal+synthesis+nanoparticle&um=1&hl=cs&sa=N&tbo=d&biw=1344&bih=673&tbm=isch&tbnid=L05Nc5QomOdv8M:&imgrefurl=http://www.suflux.com/EN/prod/supercritical-hydrothermal-synthesis.html&docid=Sa_ZvaupHCgmkM&imgurl=http://www.suflux.com/EN/prod/img/supercritical-hydrothermal-synthesis_img003.gif&w=580&h=400&ei=O5CzULhTjM3hBL25gdAN&zoom=1&iact=hc&vpx=1031&vpy=373&dur=3726&hovh=186&hovw=270&tx=141&ty=98&sig=107486980385906603851&page=3&tbnh=134&tbnw=195&start=52&ndsp=35&ved=1t:429,r:64,s:0,i:281

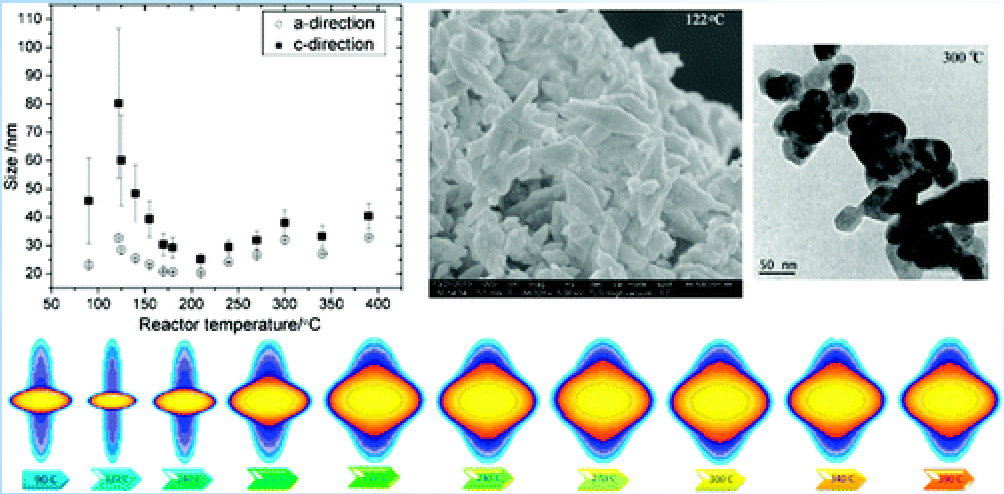
Hydrotermální syntéza ZnO

Formation of ZnO nanoparticles using a fast continuous flow hydrothermal synthesis method. The synthesis conditions have been varied with respect to temperature, pH, and concentration of the $Zn(NO_3)_2{\bullet}4H_2O$ + NaOH aqueous precursor. The different conditions affect the size, morphology, and crystallinity of the produced ZnO nanoparticles…



Zno nanoparticles obtained by hydrothermal synthesis using microwave heating





http://www.faqs.org/patents/app/20110223359

Patent: HYDROTHERMAL SYNTHESIS OF $LiFePO_4$ @ C NANOPARTICLES (Li-články)

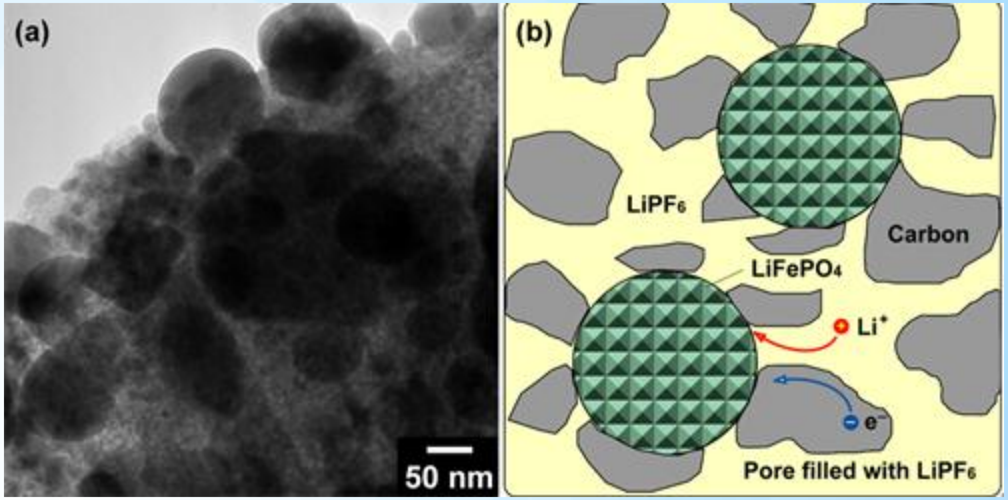
http://www.faqs.org/patents/app/20110223359#ixzz2DL6kwc4r

Claims:

1. A method of forming a film on a substrate, ……………..za použití metody ..za vzniku …filmu lithium containing nanocrystals na substrátu.

2. Prekurzory………… LiH_2PO_4, LiOH, $LiNO_3$, $LiCH_3COO$, LiCl, Li_2SO_4, Li_3PO_4, $Li(C_5H_8O_2)$, and combinations thereof.

3. Rozpouštědla………. : water, diethylene glycol, ethylene glycol, dimethyl sulfoxide (DMSO), polyethylene glycol (PEG), and combinations thereof.



Example 1

http://diit.cz/clanek/lifepo4-akumulatorovy-zazrak-miri-i-do-tuzkovych-baterek

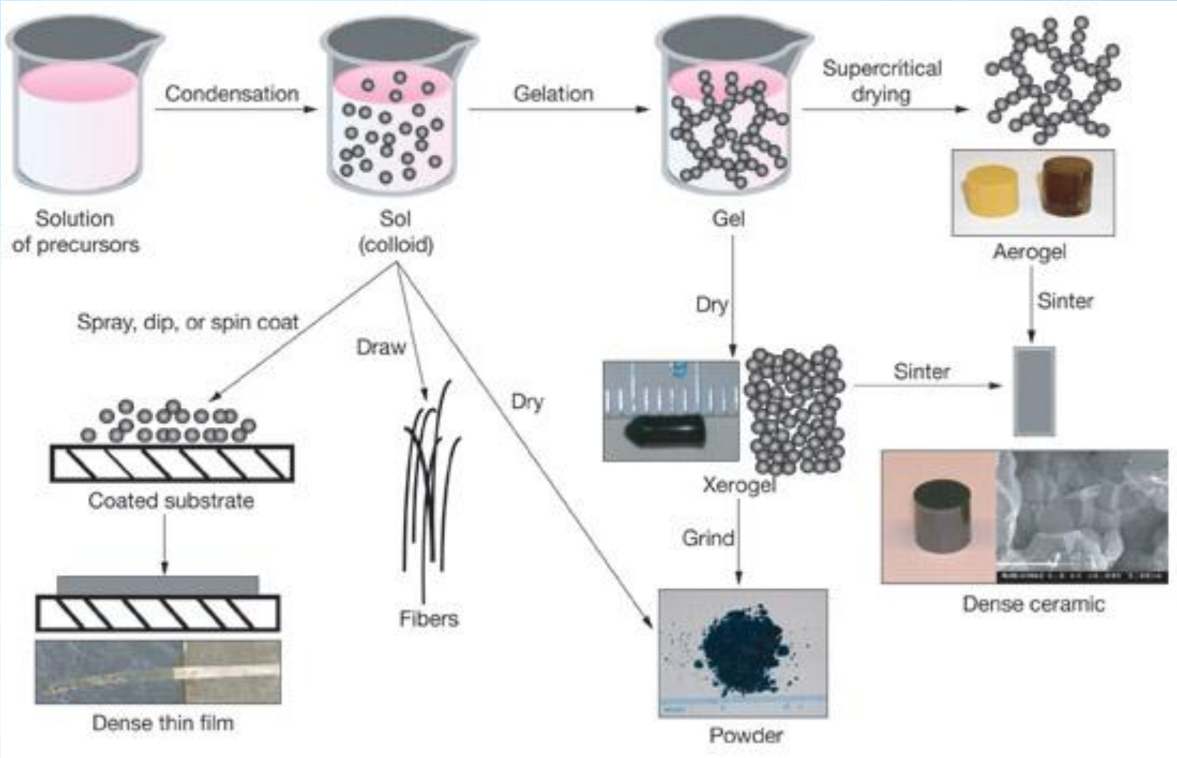
[0053] $LiFePO_4$ nanoparticles were formed via hydrothermal synthesis as follows. A lithium source (LiOH), a phosphate source ($(NH_4)_2HPO_4$), an iron source ($Fe(CH_3COO)_2$), and a carbon source (glucose) were combined to form a deposition mixture. The $LiFePO_4$ may be formed according to the following reaction:

$$LiOH+(NH_4)_2HPO_4+Fe(CH_3COO)_2LiFePO_4+2CH.sub- .3COOH\uparrow$$

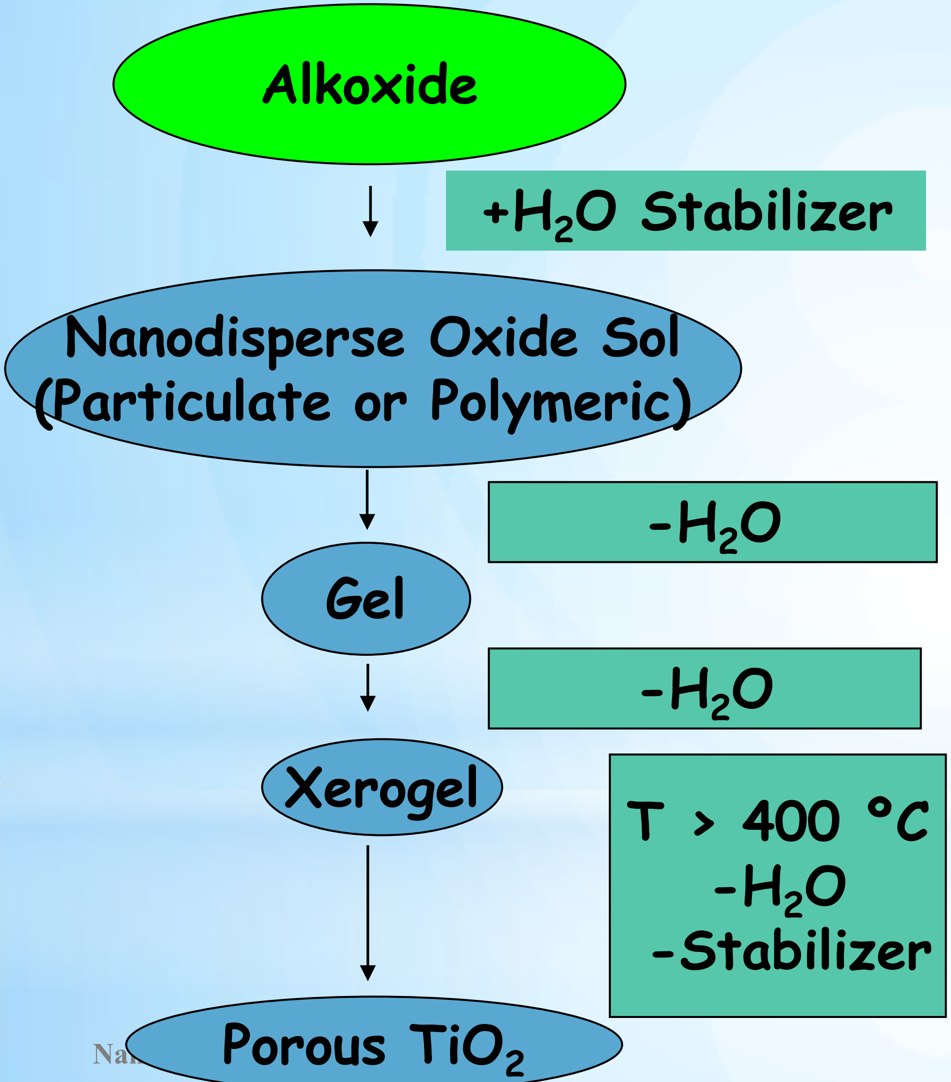
[0054] The deposition mixture was exposed to ultrasonic energy at an energy level of 250 kHz. The deposition mixture was exposed to microwave irradiation for 15 minutes at 230° C. to form carbon coated $LiFePO_4$ via a hydrothermal carbonization reaction. The carbon coated $LiFePO_4$ was subsequently exposed to ultrasonic energy at an energy level of 300 kHz to reduce agglomeration. The carbon coated $LiFePO_4$ was deposited on an aluminum substrate via a thermal spray process at 700° C. to form a $LiFePO_4$/C nanocomposite film comprising lithium containing nanocrystals.

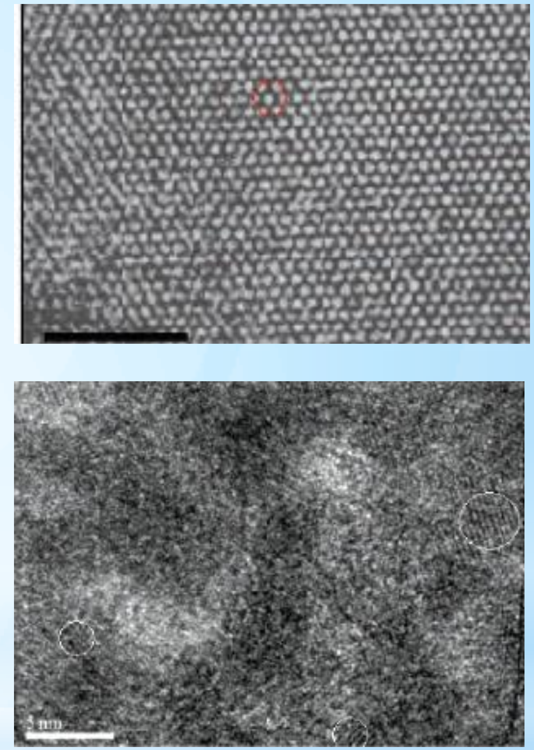
Sol-gel syntéza

• Formation of stable sol solution
• Gelation via a polycondensation or polyesterification reaction
• Gel aging into a solid mass. causes contraction of the gel network, also
(i) phase transformations and
(ii) Ostwald ripening.
• Drying of the gel to remove liquid phases.
Can lead to fundamental changes in the structure of the gel.
• Dehydration at temperatures as high as 8000 oC, used to remove M-OH groups for
stabilizing the gel, i.e., to protect it from rehydration.
• Densification and decomposition of the gels at high temperatures (T > 8000 oC), i.e., to collapse the pores in the gel network and to drive out remaining organic
contaminants



Example: TiO_2 nanoparticle-mediated mesoporous film by sol-gel processing

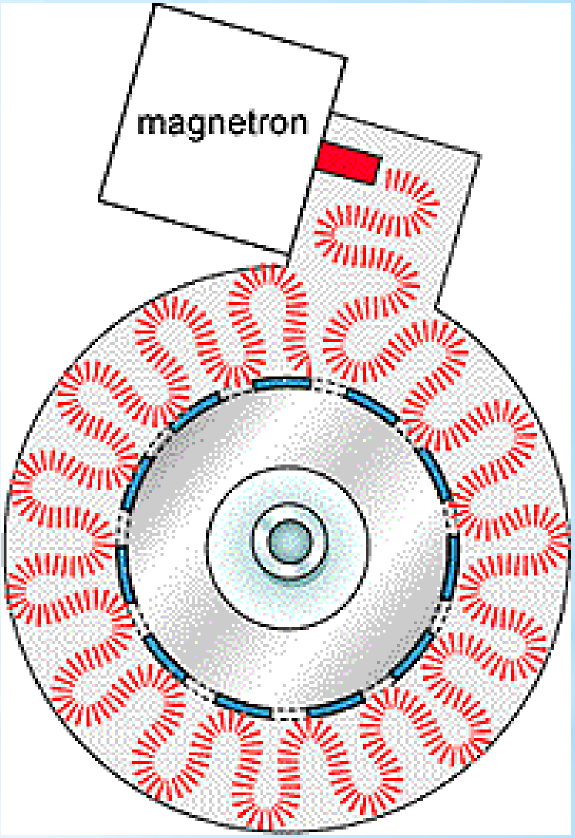




TiO_2 nanoparticle-mediated mesoporous film (Yu, J. C. et al. *Chem. Mater*. 2004, 16, 1523.)

Syntéza za pomoci mikrovlnného ohřevuol-gel syntéza

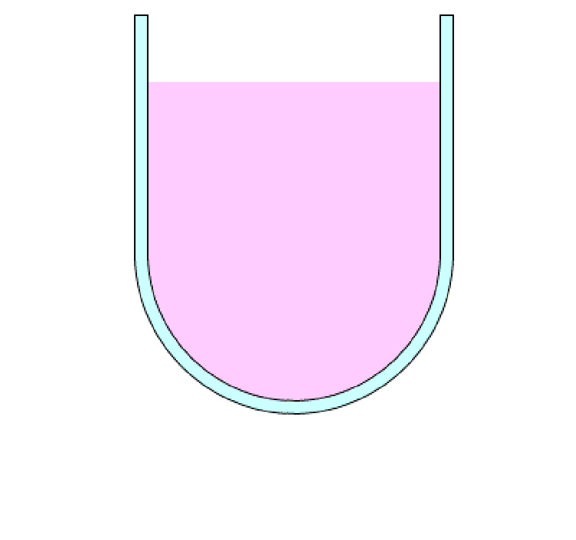
Microwaves are a form of electromagnetic energy with frequencies in the range of 300 MHz to 300 GHz. The commonly used frequency is 2.45G Hz.

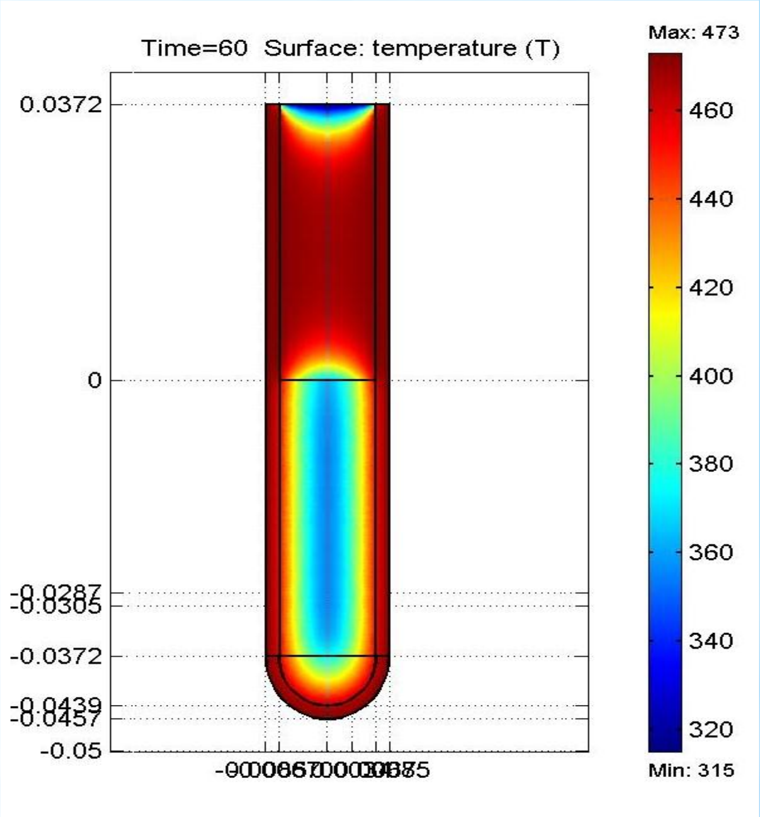


Interactions between materials and microwaves are based on two specific mechanisms: dipole interactions and ionic conduction. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves.

Conventional Heating by Conduction

- conductive heat
- heating by convection currents
- slow and energy inefficient process

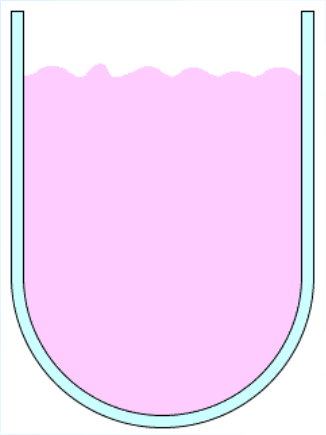


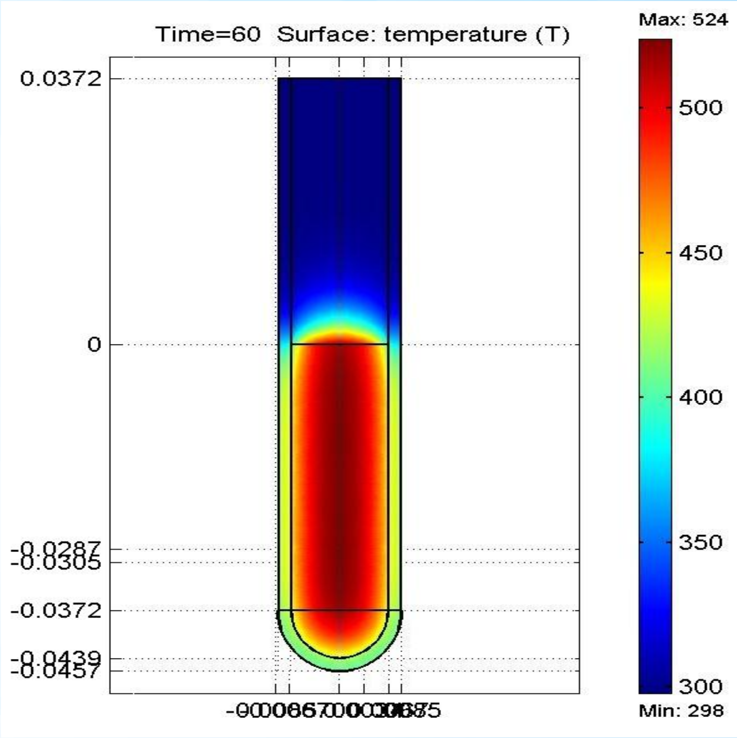


The temperature on the outside surface is in excess of the boiling point of liquid

Heating by Microwave Irradiation

- Solvent/reagent absorbs MW energy
- Vessel wall transparent to MW
- Direct in-core heating
- Instant on-off





inverted temperature gradients !

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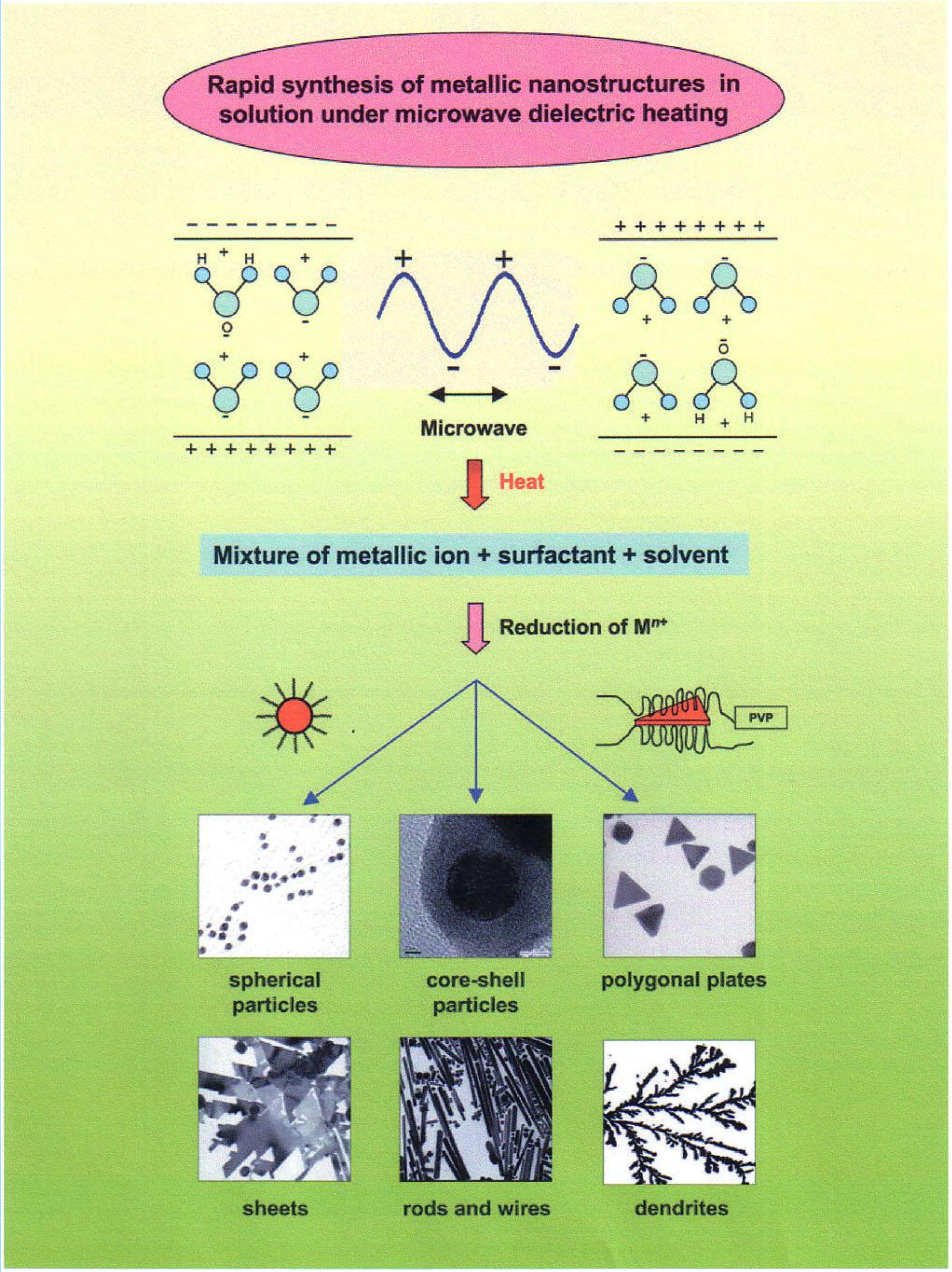
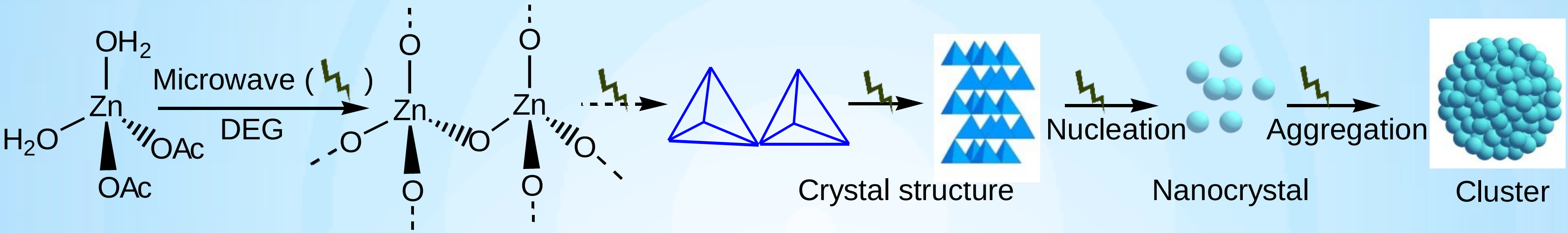


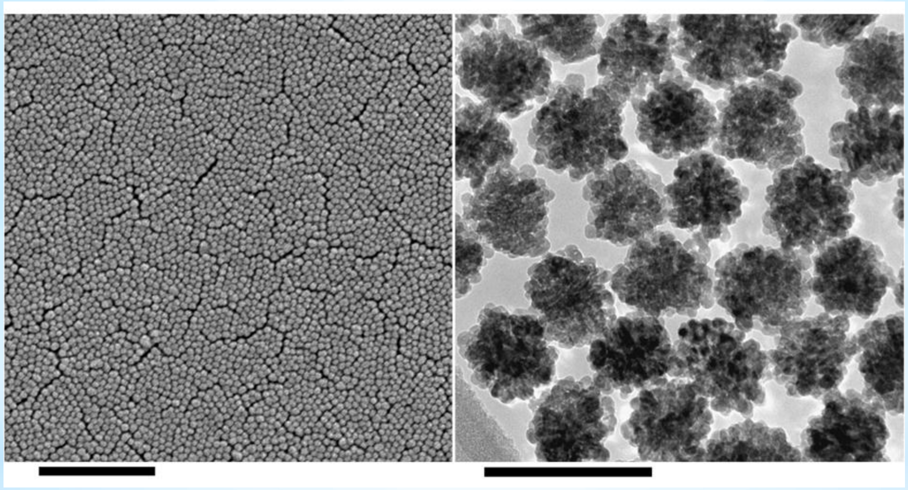
DOI: 10.1002/chem.200400417 Chem. Eur. J. 2005, 11, 440–452

Microwave (MW) rapid heating has received considerable attention as a new promising method for the one-pot synthesis of metallic nanostructures in solutions.

In this concept, advantageous application of this method has been demonstrated by using some typical examples for the preparation of Ag, Au, Pt, and AuPd nanostructures. Not only spherical nanoparticles, but also single crystalline polygonal plates, sheets, rods, wires, tubes, and dendrites were prepared within a few minutes under MW heating. Morphologies and sizes of nanostructures could be controlled by changing various experimental parameters, such as the concentration of metallic salt and surfactant polymer, the chain length of the surfactant polymer, the solvent, and the reaction temperature. In general, nanostructures with smaller sizes, narrower size distributions, and a higher degree of crystallization were obtained under MW heating than those in conventional oil-bath heating

Example: Microwave-assisted synthesis of ZnO nanoparticles



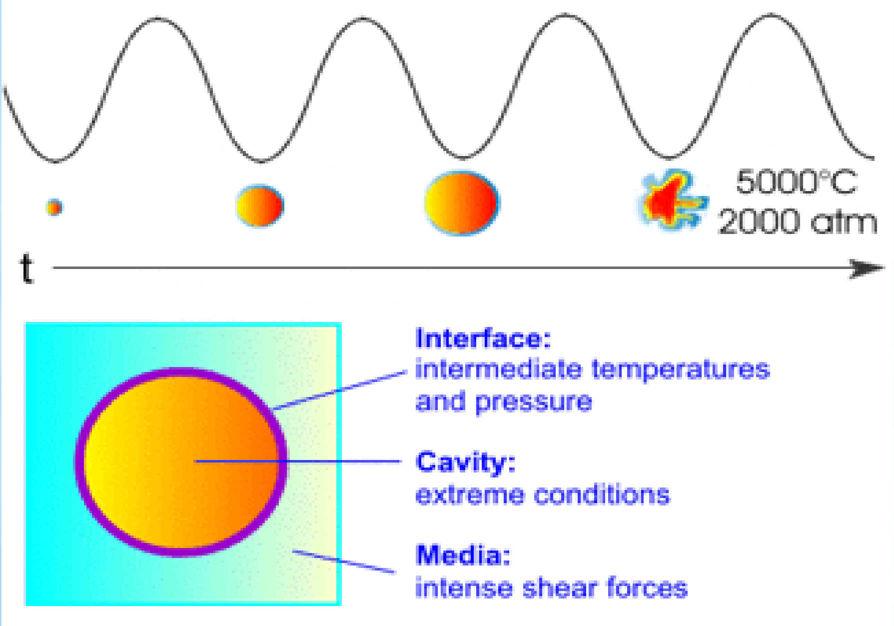


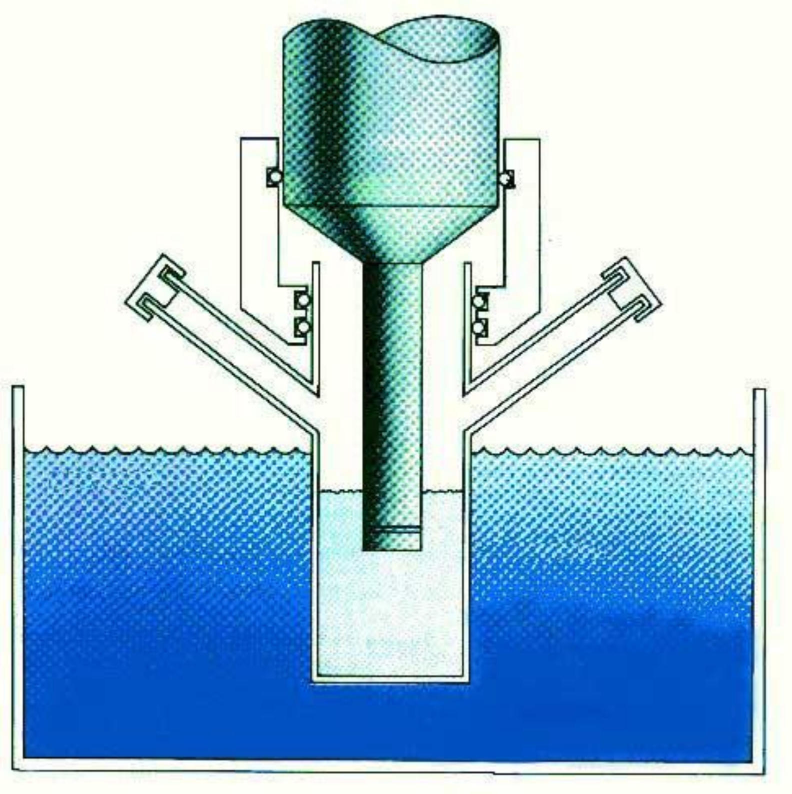
Schematic representation and transmission electron microscope (TEM) images of ZnO-cluster nanoparticles prepared by microwave irradiation

Yu, J. C. et at., *Adv. Mater.* 2008, in press.

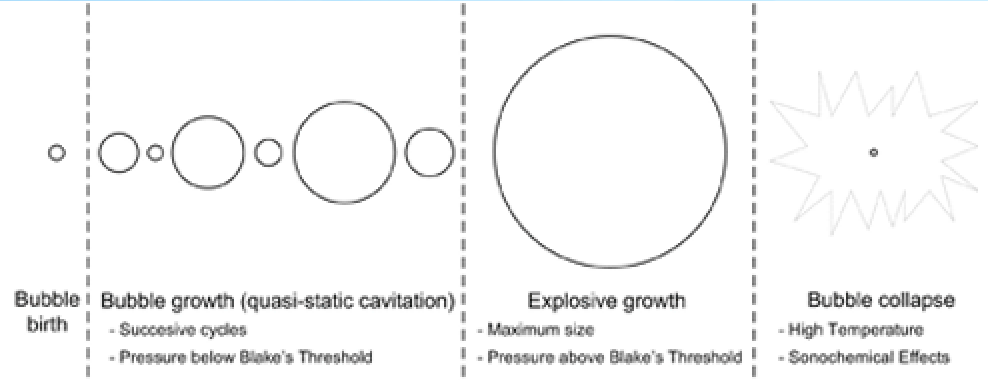
Sonochemická příprava NPs

The use of ultrasound in chemical reactions in solution provides specific activation based on a physical phenomenon: acoustic cavitation. Cavitation is a process in which mechanical activation destroys the attractive forces of molecules in the liquid phase. Applying ultrasound, compression of the liquid is followed by rarefaction (expansion), in which a sudden pressure drop forms small, oscillating bubbles of gaseous substances. These bubbles expand with each cycle of the applied ultrasonic energy until they reach an unstable size; they can then collide and/or violently collapse.

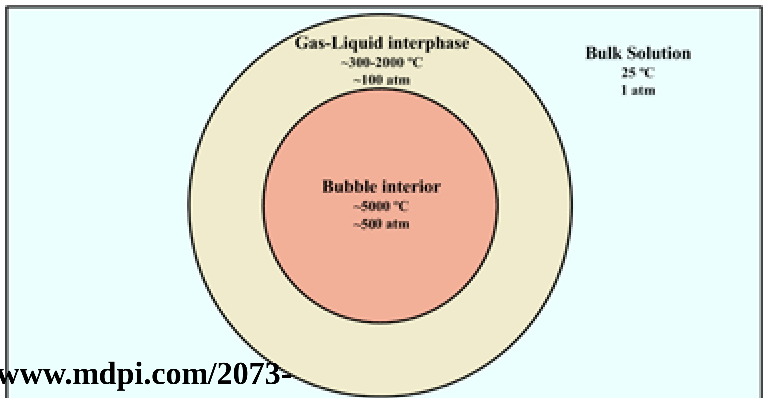




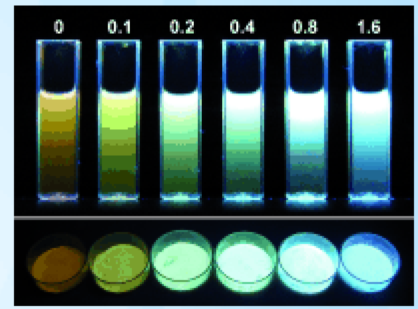
http://www.organic-chemistry.org/topics/sonochemistry.shtm



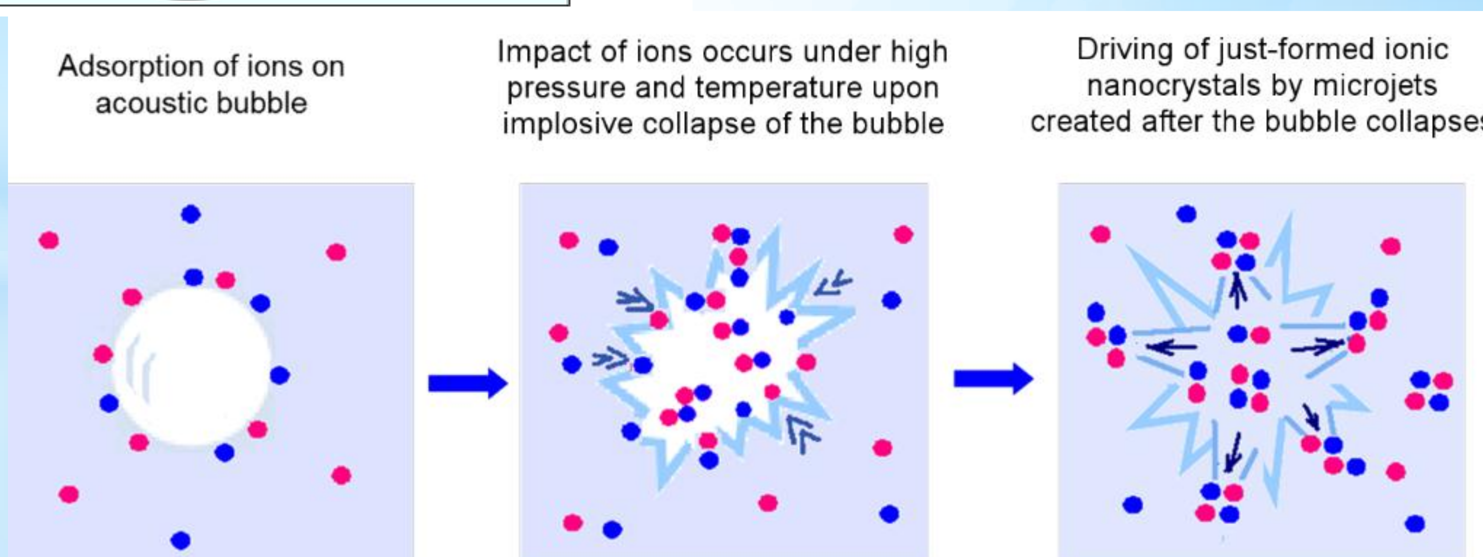
Příprava NPs: Oxidy (ZnO, CuO, …)
Problém: kontaminace materiálem sonifikačního prstu (W, Ti)



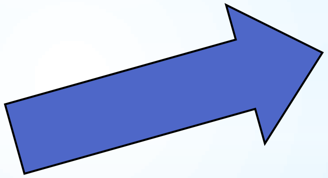
http://www.mdpi.com/2073-4441/2/1/28

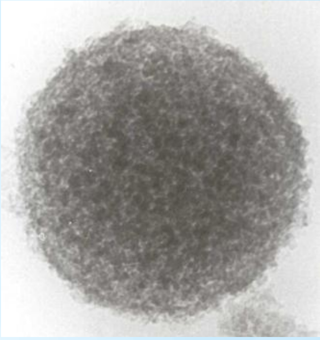


ZnO NPs luminiscent



Examples: sonochemical synthesis of mesoporous TiO_2 particles

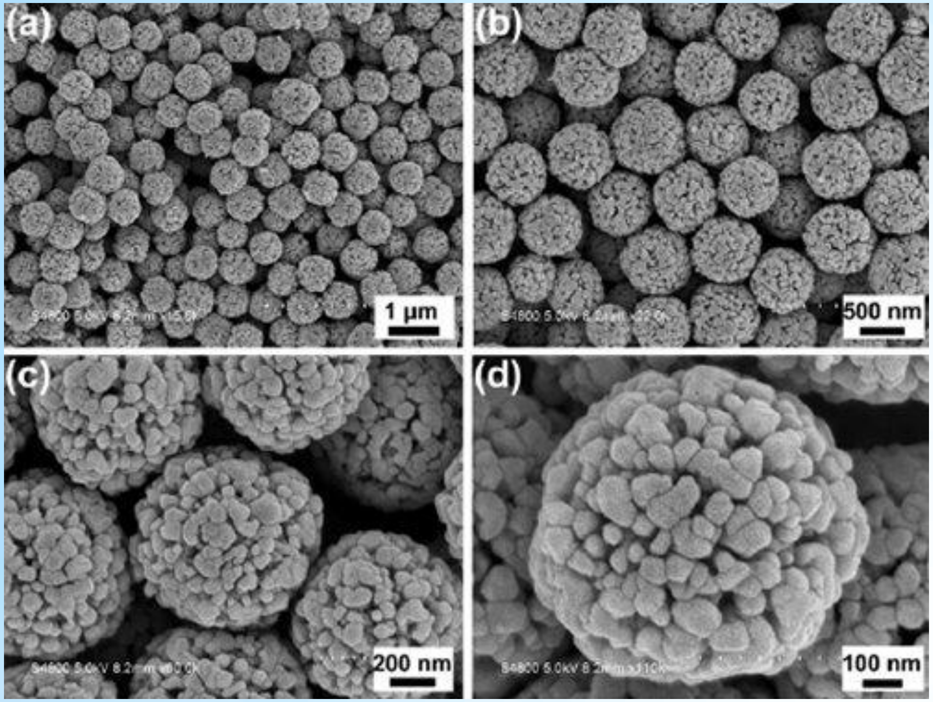




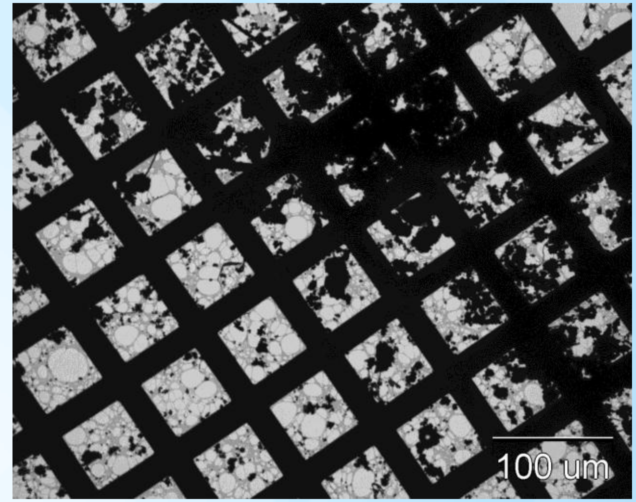
Mesoporous TiO_2

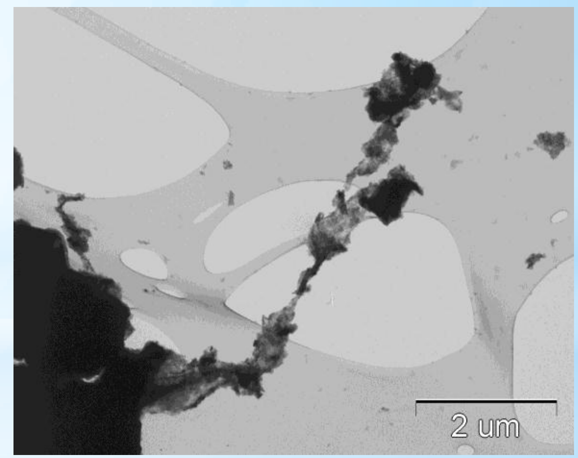
20 kHz sonochemical processor

Příklady NPs připravených sonochemicky



Porézní CuO http://nanotechweb.org/cws/article/lab/37301



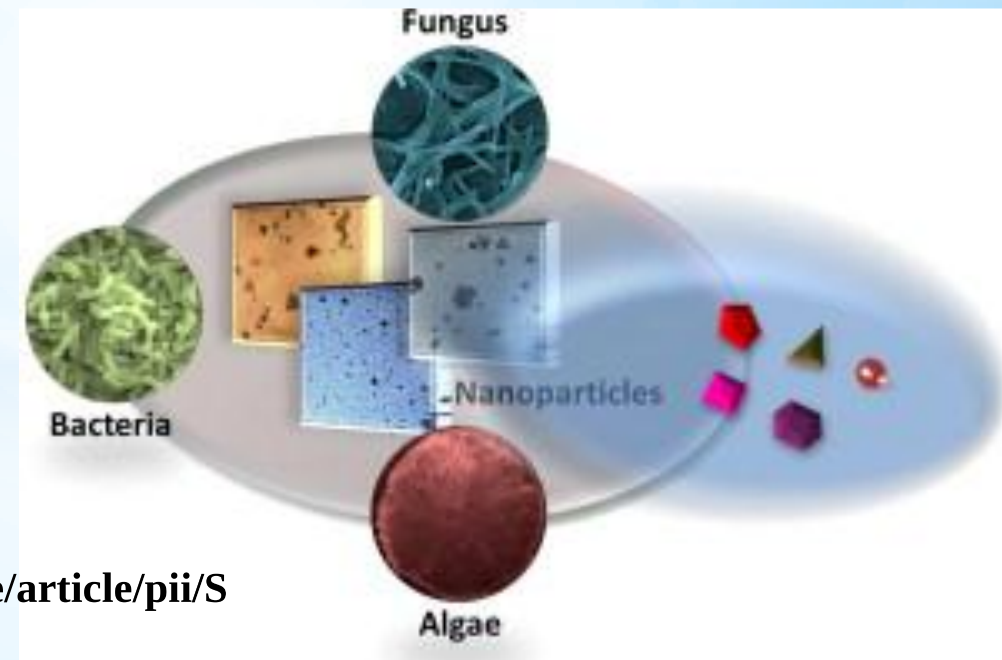


Mikročástice ZnO (kontaminace Ti a W). Syntéza na UCh , L. Pražák)

Biomimetic Synthesis

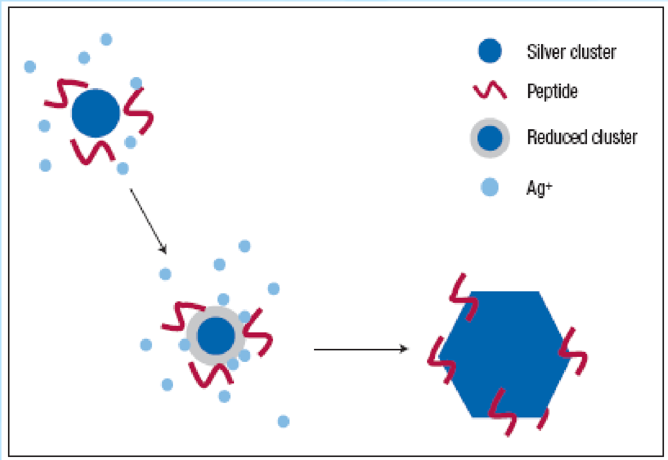
Vytváření nanočástic přirozenými pochody v přírodě

Výhody: Biomimetic or bio-inspired processes generally occur under mild conditions such as room temperature, aqueous environment, and neutral pH, and thus are benign in comparison to traditional chemical reactions. Biologically inspired synthesis, hierarchical structuring, and stimuli-responsive materials chemistry may enable nanostructured materials systems with unprecedented functions .

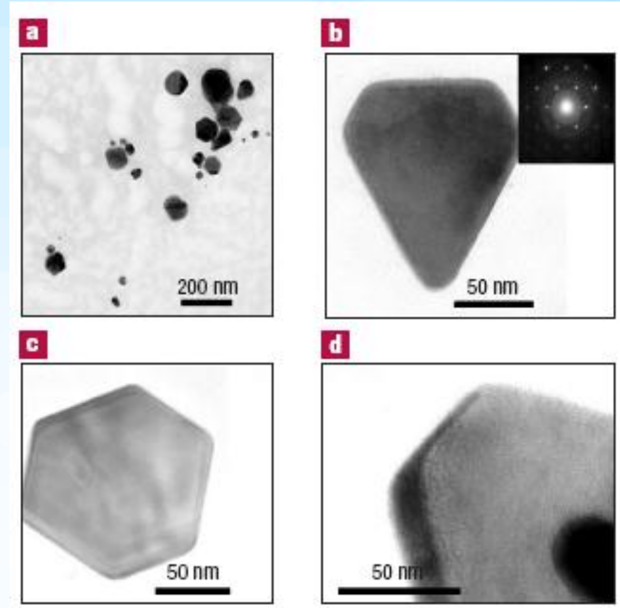


http://www.sciencedirect.com/science/article/pii/S0001868612000954

Examples: biomimetic synthesis

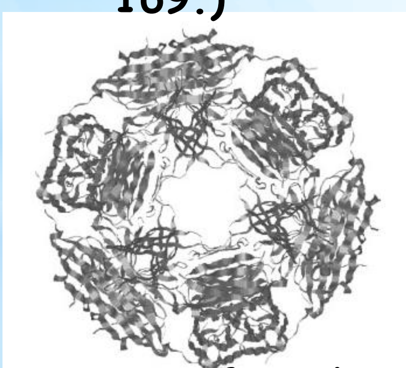


Model for silver crystal formation by silver-binding peptides.

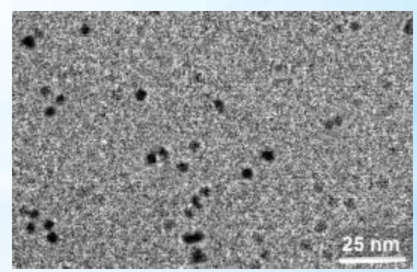


biosynthetic silver nanoparticles.

(Stone M. O. et al. *Nat. Mater.* 2002, *1*, 169.)



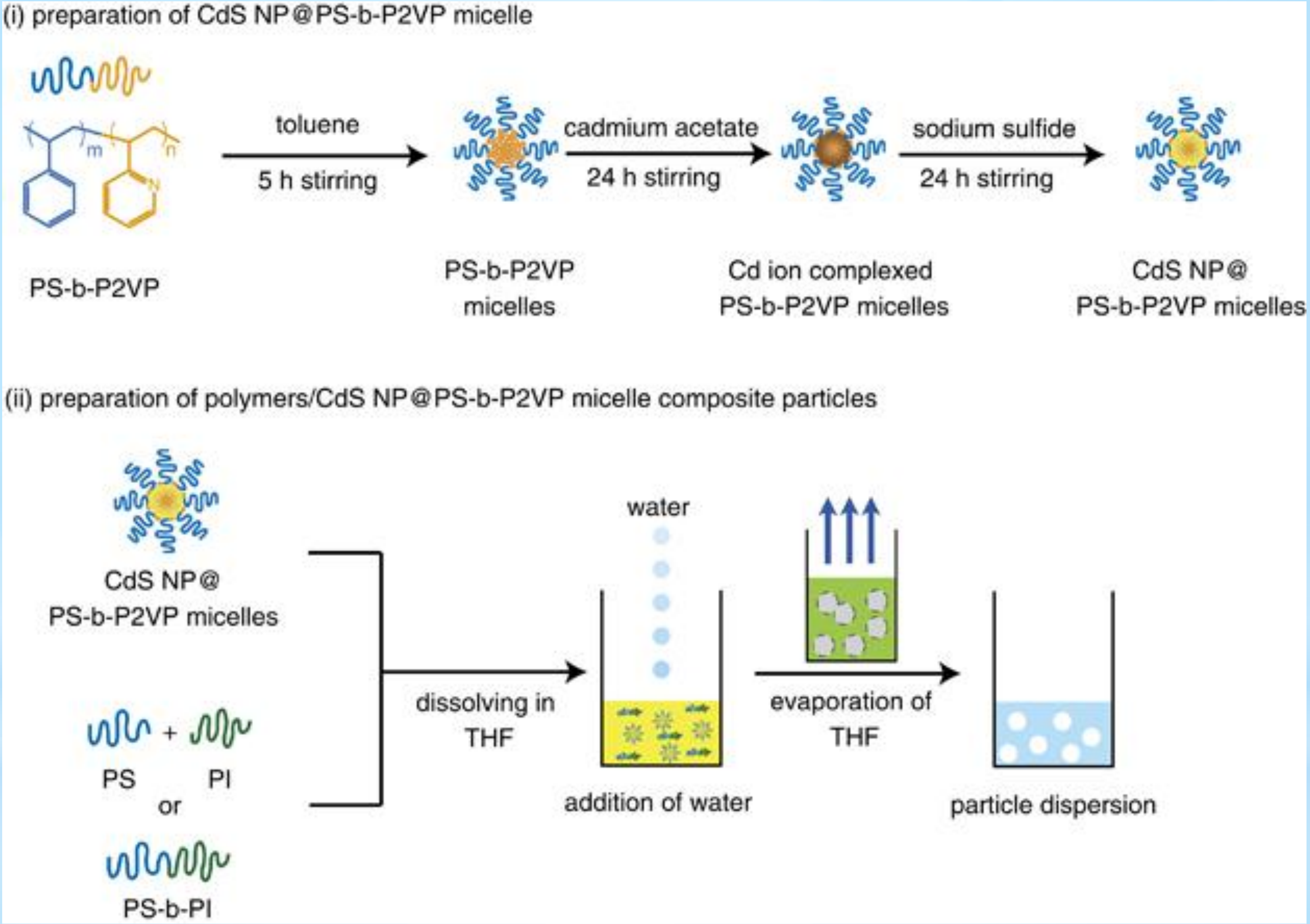
A protein of methanococcus jannaschii MjHsp



Protein-encapsulated CoPt nanoparticles by bio-inspired synthesis

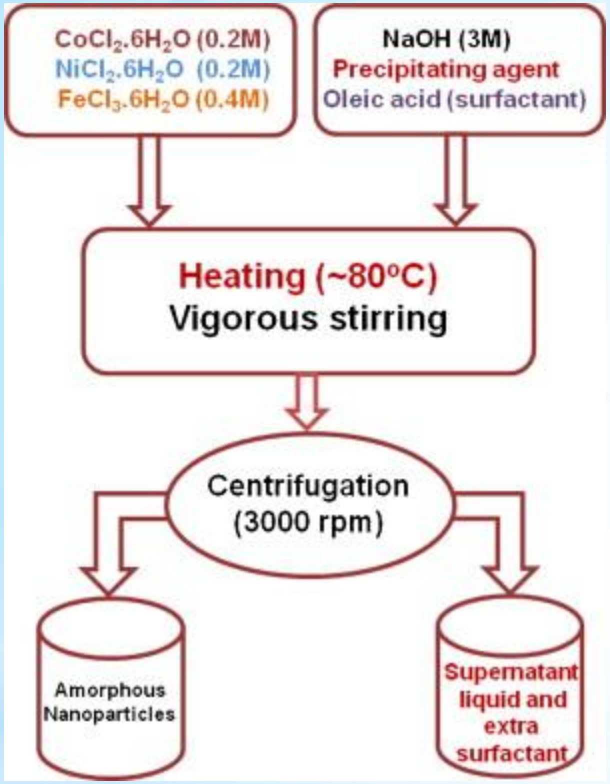
(Stone M. O. et al. *Adv. Funct. Mater.* 2005, *15*, 1489.)

Micelární příprava CdS



http://www.nature.com/pj/journal/v43/n3/fig_tab/pj2010137sc1.html

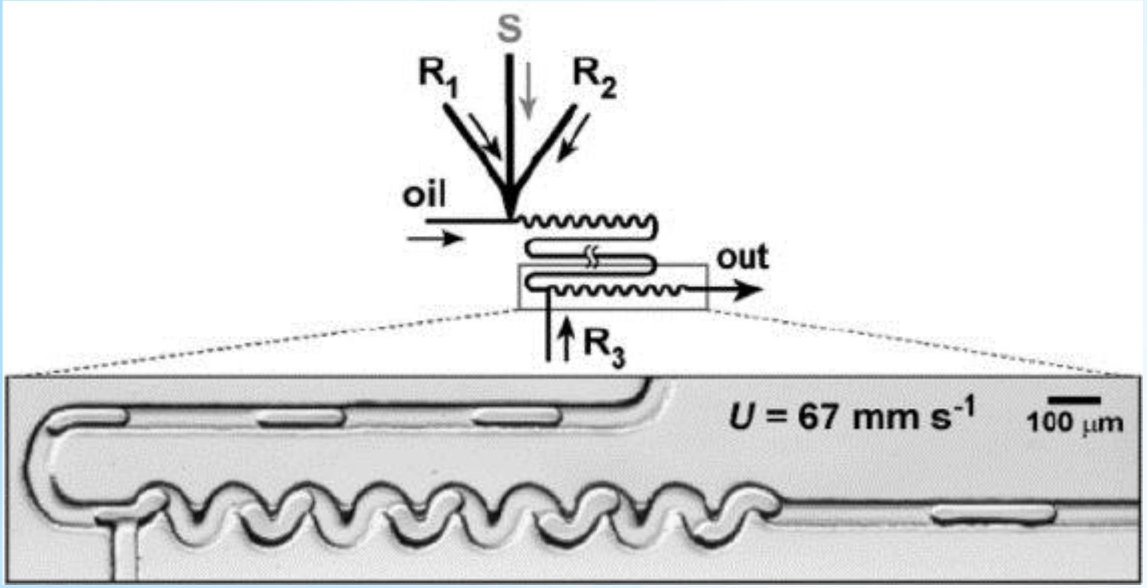
Coprecipitační syntézy NPs

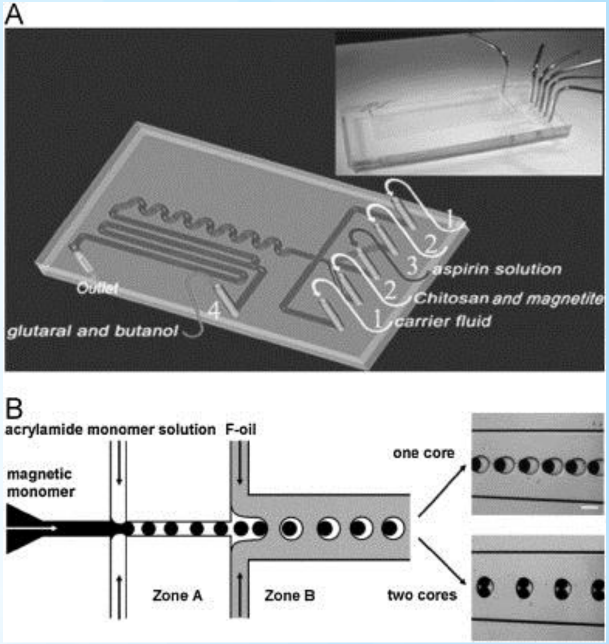


Magnetic nanoparticles of $Ni_{0.5}Co_{0.5}Fe_2O_4$ (size: 18 ± 3 nm)

http://www.sciencedirect.com/science/article/pii/S0254058412001605

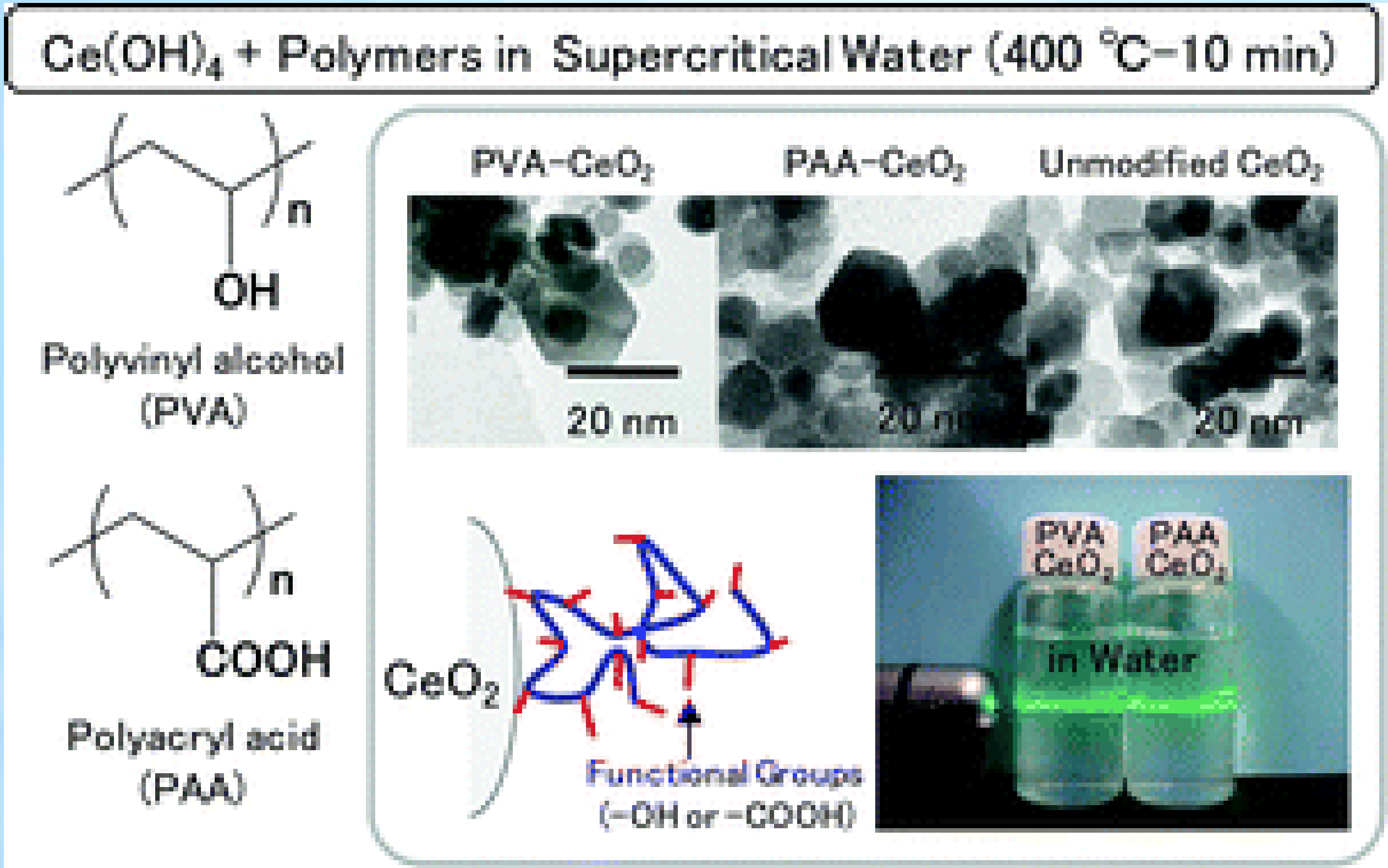
Nanoparticlesynthesis in davkovacích microreactorech





http://www.sciencedirect.com/science/article/pii/S0009250910005142

Příprava NPs za superkrytických podmínek

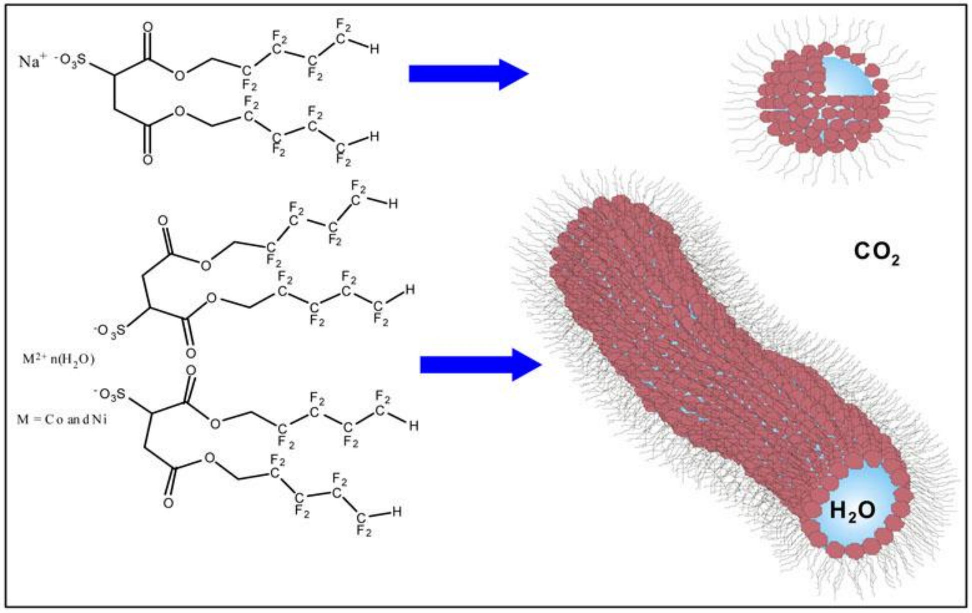


HOT Article: Using supercritical water to make hybrid ceria nanoparticles

http://blogs.rsc.org/ce/2011/01/05/hot-article-using-supercritical-water-to-make-ceria-nanoparticles/

Diskuse

Unconventional Oil and Gas



http://www.netl.doe.gov/newsroom/labnotes/2011/04-2011.html

Volné presentace pro syntézu ke stažení:
http://freedownloadb.com/pdf/nanoparticle-synthesis-methods-ppt
http://ebookbrowse.com/sy/synthesis-of-nanoparticles