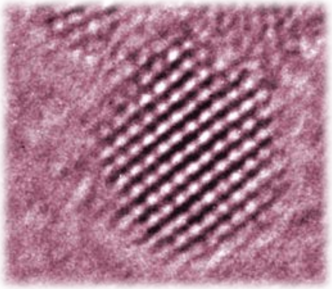

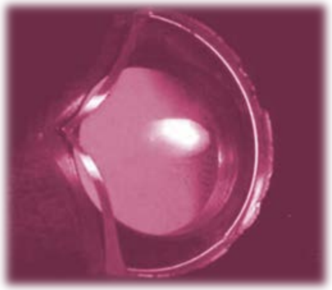

Synthesis of nanoparticles: the role of chemical parameters toward functional materials

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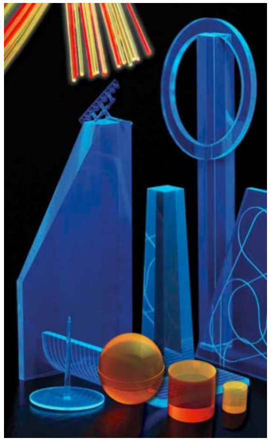
http://www.multimat.mat.ethz.ch

Scintillator materials

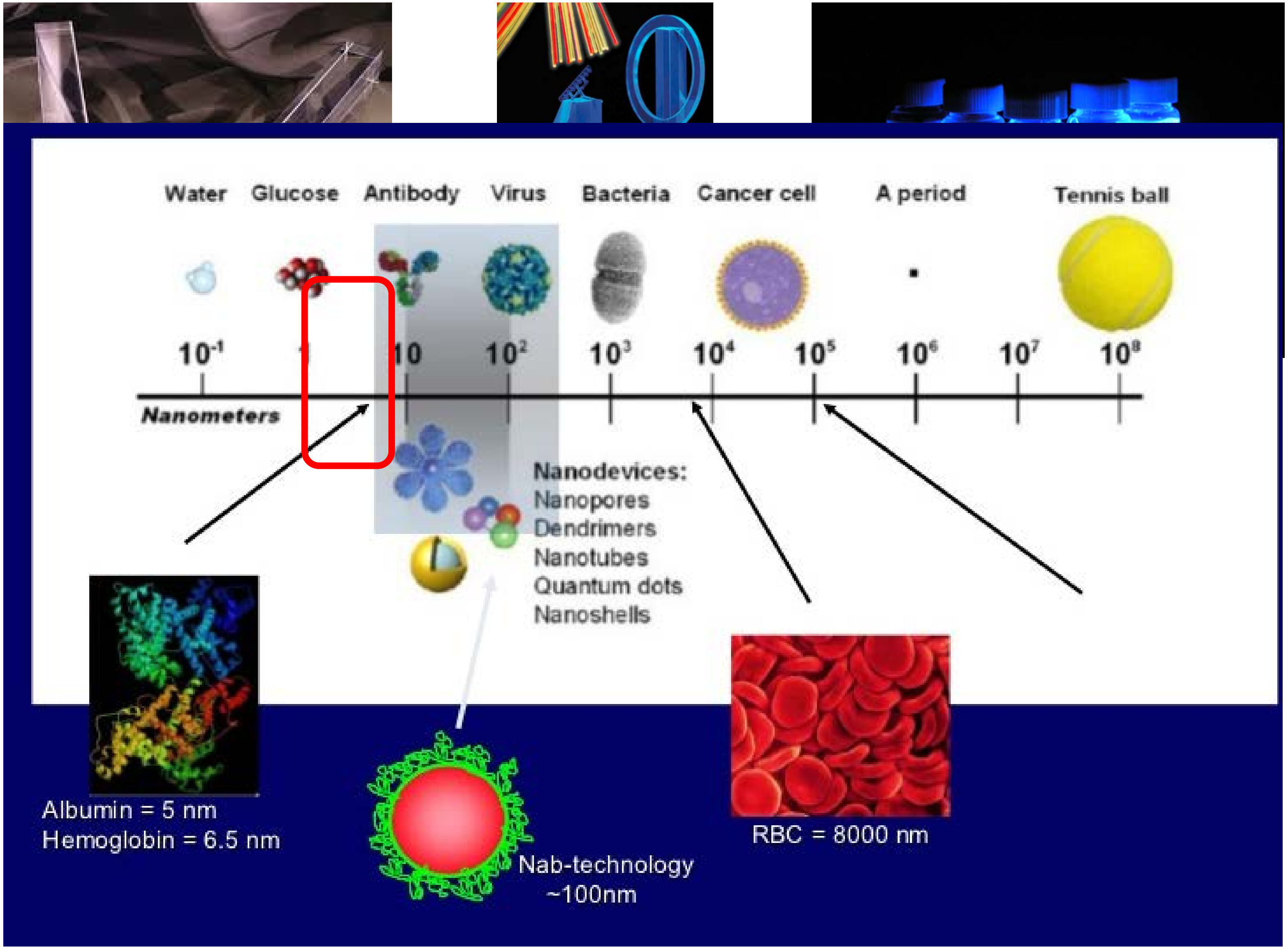
Inorganic
(Single Crystals)



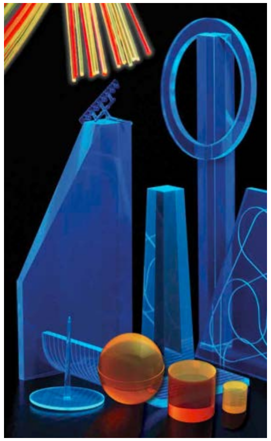
Organic
(Plastic)

Liquid
(Dye solution)

Scintillator materials



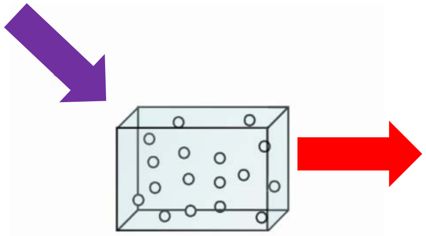
Inorganic
(Single Crystals)



Organic
(Plastic)

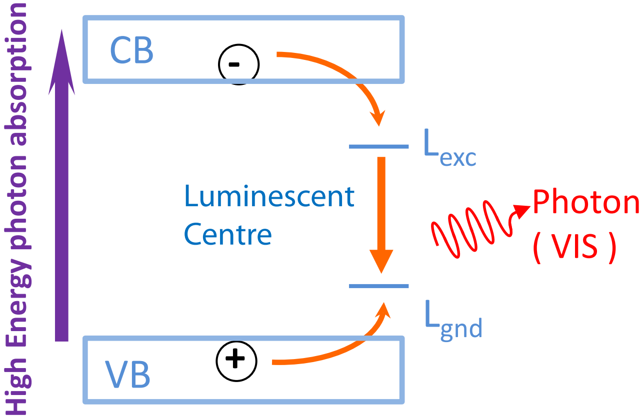
Liquid
(Dye solution)

Transparent in the UV region
EXCITATION



scintillator

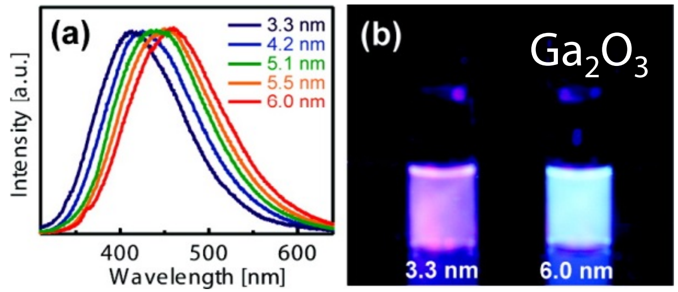
Transparent in the Vis region
EMISSION



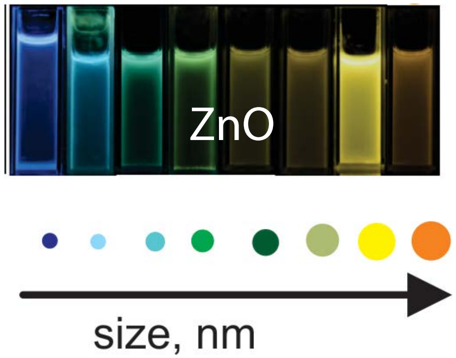
Phosphor nanoparticle

Nanoparticles for optical applications

Unique optical properties depending on particle size: Band-gap modified emitters

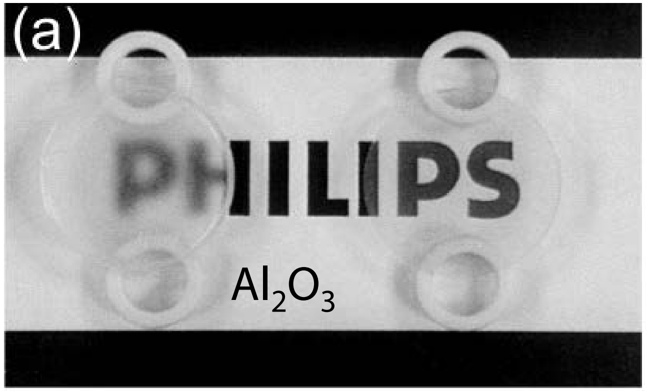


T. Wang *et al. J. Am. Chem. Soc.* **2010**, *132*, 9250

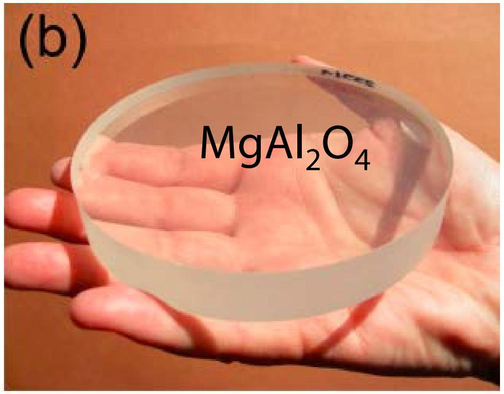


Xu, X. Y. et al *Cryst Eng Comm* **2013**, *15*, 977

Beneficial role of sub-micrometric crystal size for better optical quality of sintered ceramics



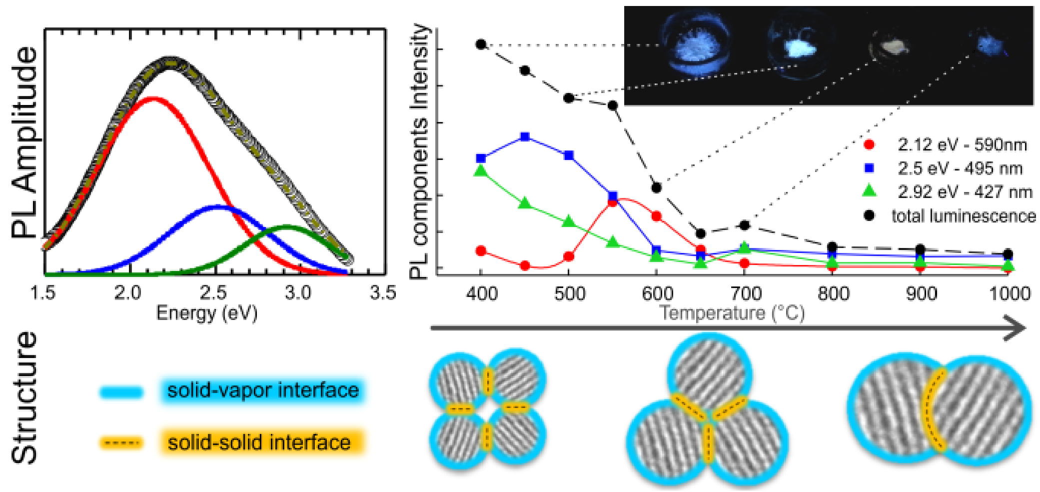
Apetz R. and Van Bruggen M.P.B., *J. Am. Ceram. Soc.* **2003**, *86*, 480



Krell, A. et al. *J. Am. Ceram. Soc.* **2010**, 93, 2656

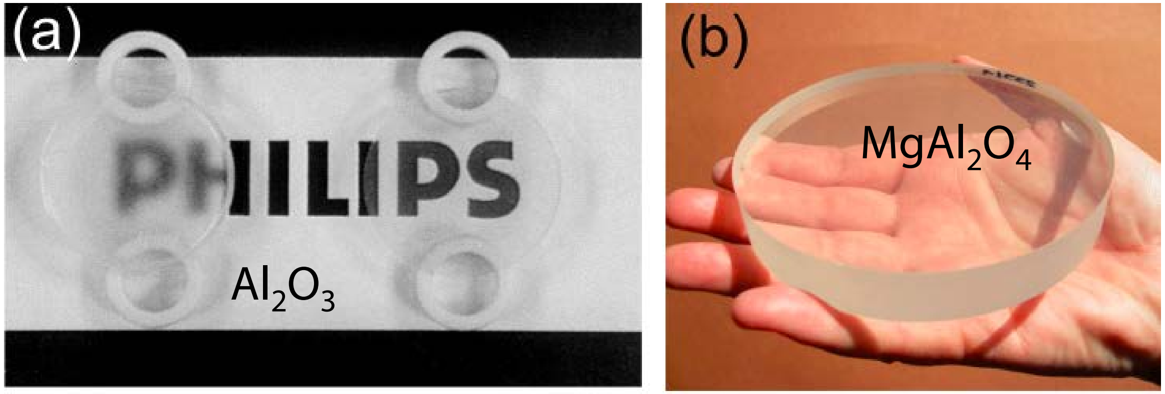
Nanoparticles for optical applications

Engineered luminescence related to defects due to the high interface area in nanosized polycrystals



Villa, I. et al. *Chem. Mater.* **2016**, 28 , 3245–3253

Beneficial role of sub-micrometric crystal size for better optical quality of sintered ceramics



Apetz R. and Van Bruggen M.P.B., *J. Am. Ceram. Soc.* **2003**, *86*, 480

Krell, A. et al. *J. Am. Ceram. Soc.* **2010**, 93, 2656

From nano to macro

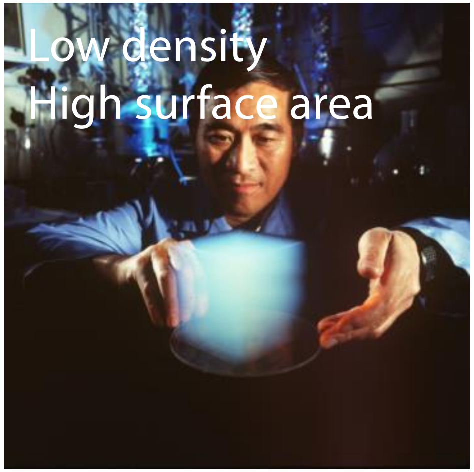
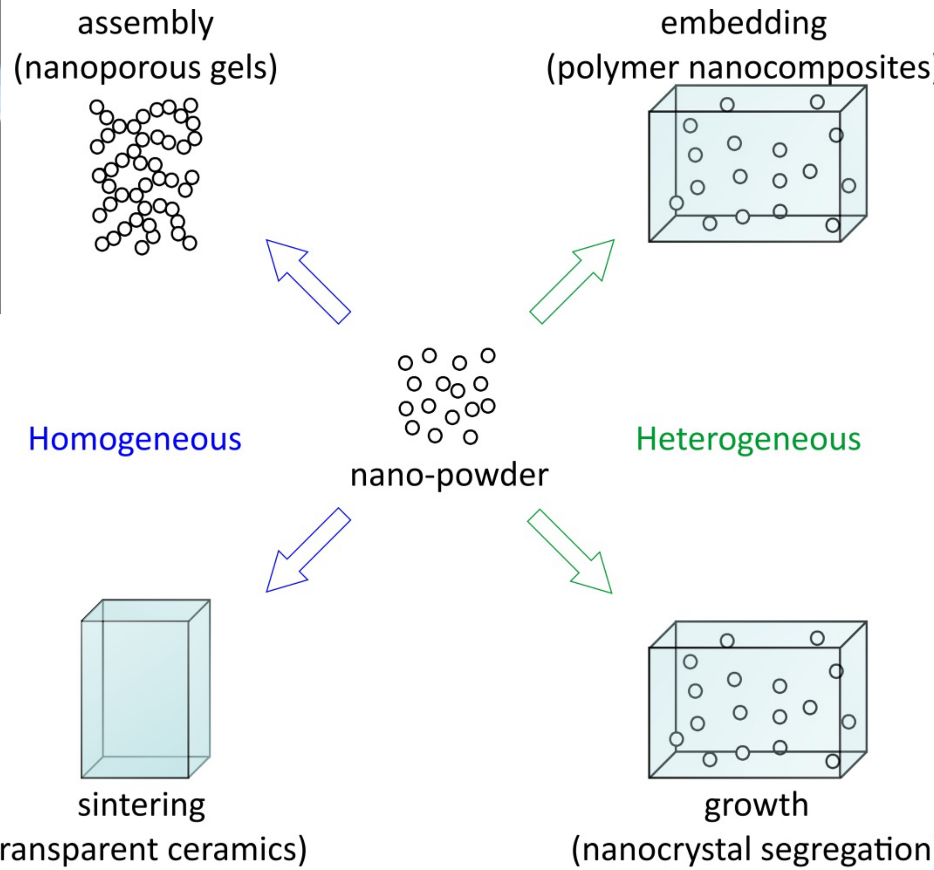
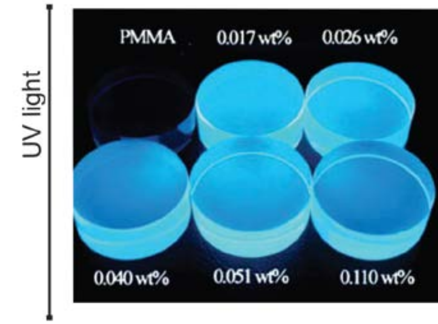


Image: http://stardust.jpl.nasa.gov/highres/aerogel_peter.jpg

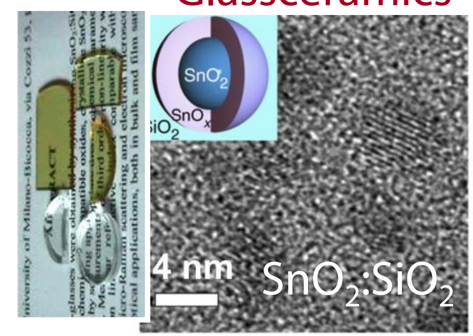


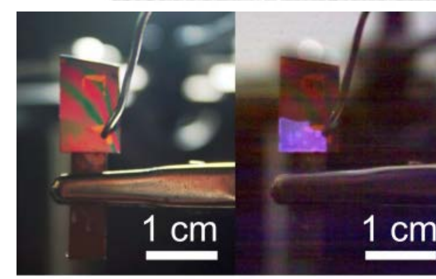
PMMA:ZnO



S. Li *et al*, *Adv. Mater.* **2007**, *19*, 4347

Glassceramics





Nat. Commun. **2012**, *3*, 690

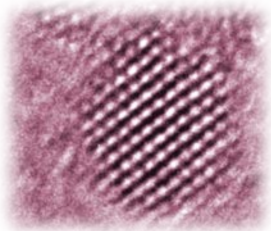
Lu_2O_3:Eu ceramic

Cherepy, N. J. et al.**2010**; SPIE Vol. 7805.

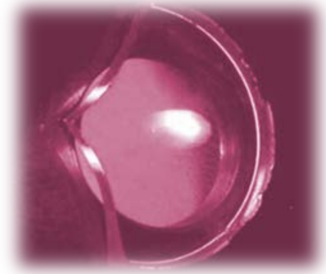
A bottom–up strategy to fabricate optical grade functional materials.

From nano to macro

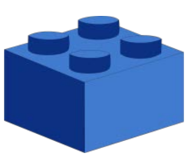
Nanoparticles as building blocks

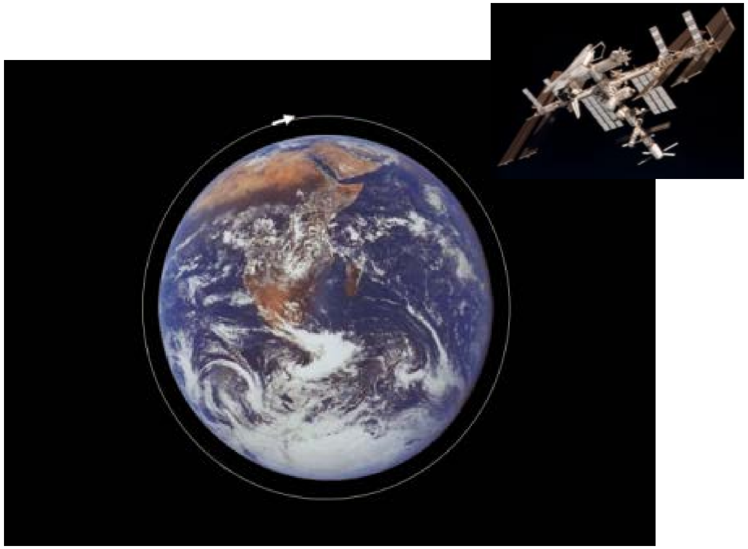


Bridging 7 orders of magnitude in length scale!



nanoscale → **macro**scale





Nanoparticles synthesis: aqueous sol-gel

In words: Conversion of a precursor solution into an inorganic solid (mainly metal oxides) by hydrolysis and condensation reactions.

Precursor solution → „Polymerisation“ → Metal Oxide

1) Hydrolysis
2) Condensation

1) Sol (dispersion of colloidal particles in a liquid)
2) Gel (interconnected, rigid, and porous network enclosing a continuous liquid phase)

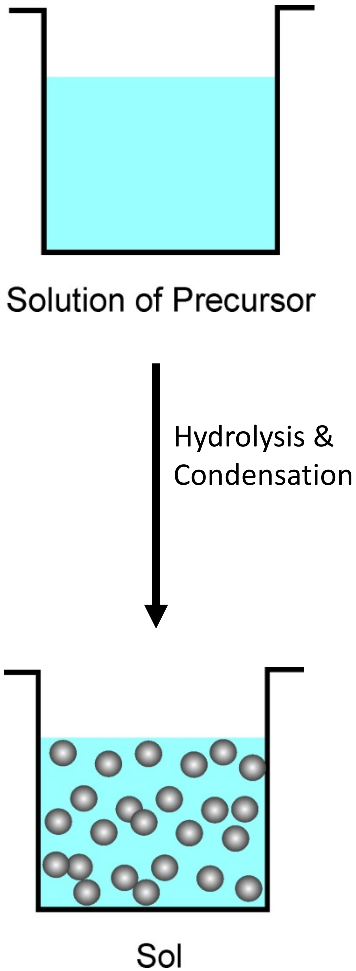
1. Metal Organic Compounds:

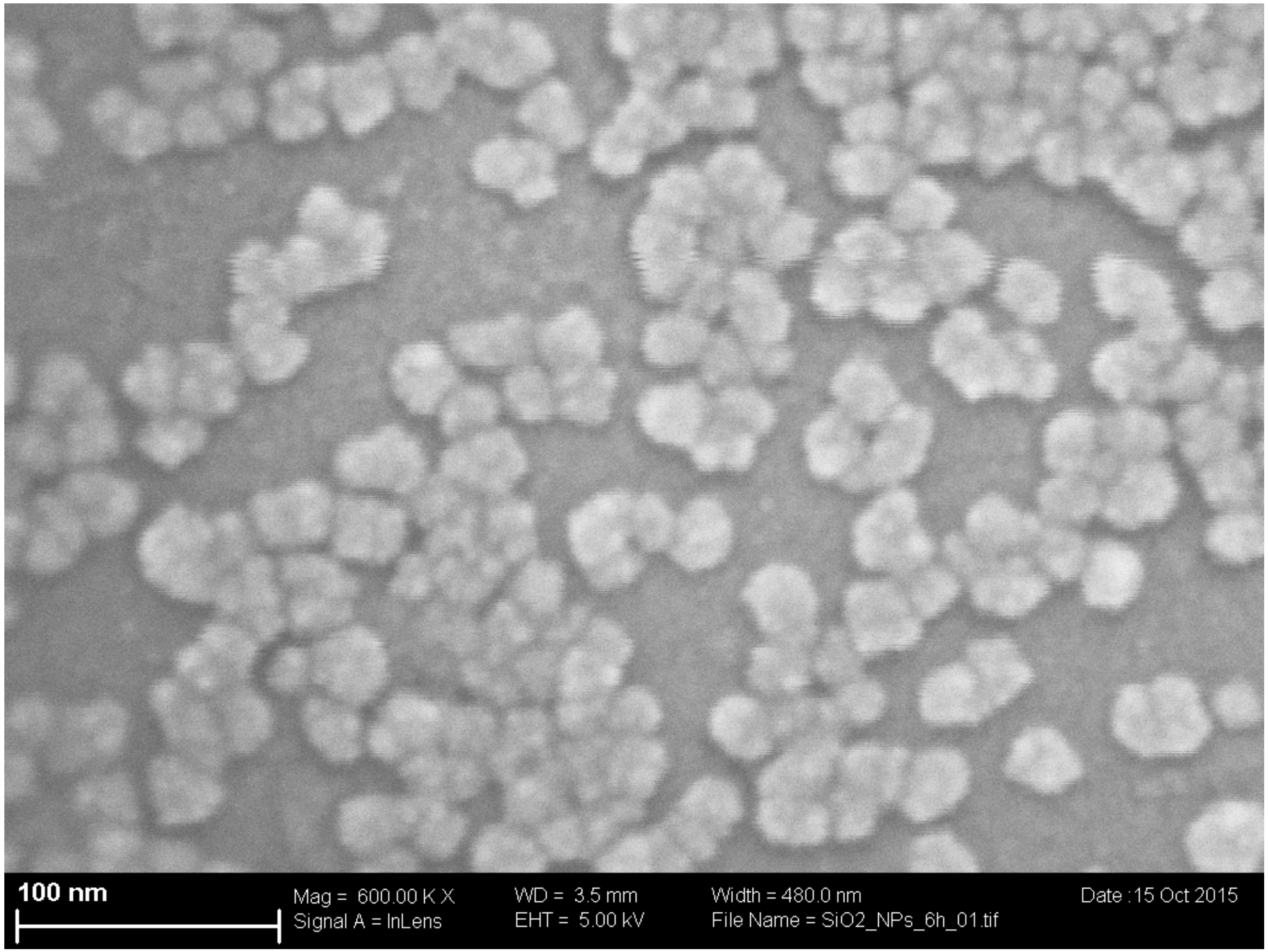
Mainly Metal Alkoxides $M(OR)_n$

2. Metal Salts:

Chlorides MCl_n, Acetates $M(OOCCH_3)_n$, Nitrates $M(NO_3)_n$, Sulfates $M(SO_4)_n$,…

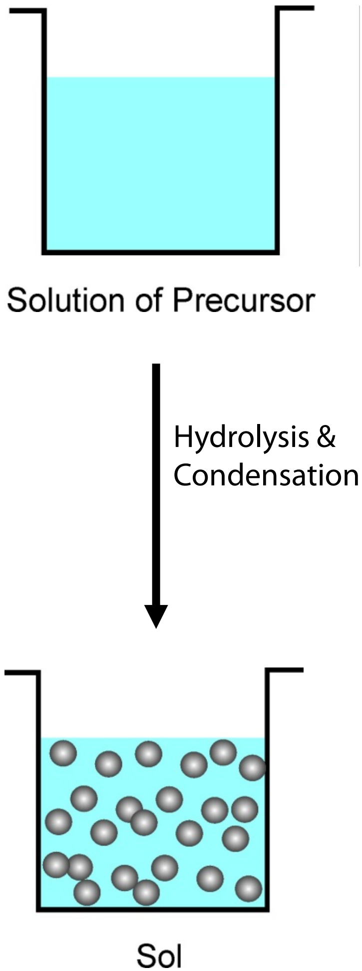
Nanoparticles synthesis: aqueous sol-gel





Stöber synthesis of SiO_2 NPs

Hydrolysis and Condensation



Metal Alkoxides $\xrightarrow{H_2O}$ **Metal Oxide Network**

(dissolved in an organic solvent that is miscible with water)

1) Hydrolysis
2) Condensation

Hydrolysis (Exchange of OR against OH)

$$\equiv M-\boxed{OR} + H_2O \longrightarrow \equiv M-\boxed{OH} + ROH$$

Condensation:

(Elimination of H_2O or ROH)

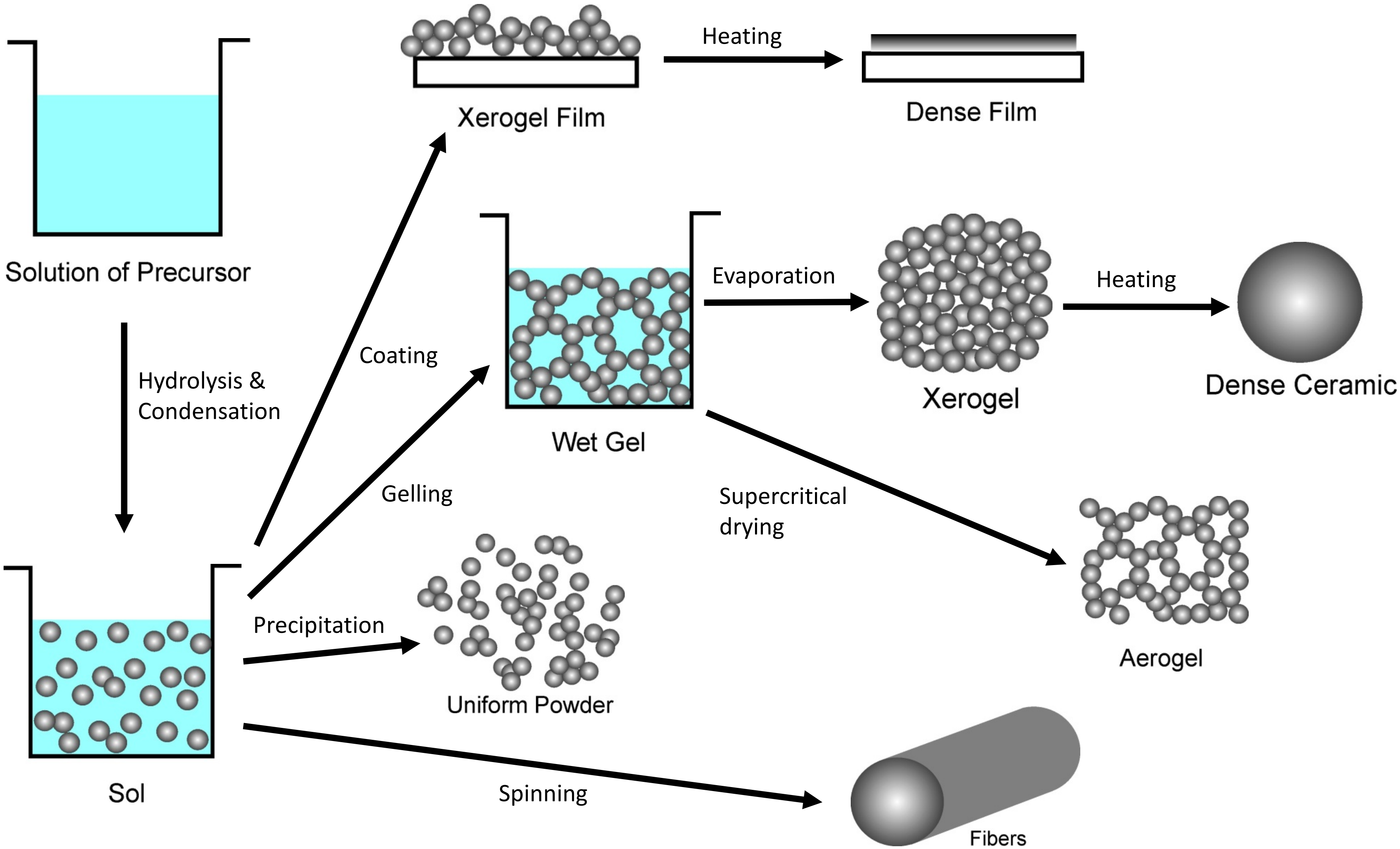
(Formation of M-O-M bond)

$$\equiv M-\boxed{OH + H}O-M\equiv \longrightarrow \equiv M-O-M\equiv + \boxed{H_2O}$$

$$\equiv M-\boxed{OR + H}O-M\equiv \longrightarrow \equiv M-O-M\equiv + \boxed{ROH}$$

Nanoparticles synthesis: aqueous sol gel

The sol-gel process is extremely versatile!



Nonaqueous sol gel

Aqueous:

„Molecular“ Precursor → Metal Oxide Network

Inorganic Polymerization Reactions

1) Hydrolysis
2) Condensation

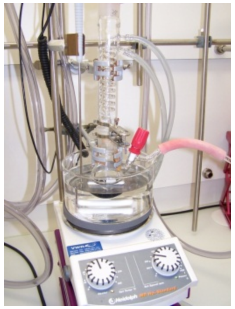
Inorganic salts
Metal alkoxides

The oxygen is supplied by water!

Nonaqueous:

„Molecular“ Precursor + Organic Solvent → Metal Oxide Network

Precursor	Organic Solvent
Metal halides	Alcohols (Benzyl Alcohol,…)
Metal alkoxides	Ketones (Acetophenone,…)
Metal acetylacetonates	Amines (Benzylamine,…)
Metal acetates	„Inert“ Solvents (Toluene,…)
Others (e.g. metal nitrates)	



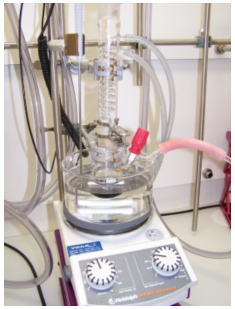
The oxygen is provided by the precursor or the organic solvent!

Nonaqueous sol-gel

Nonaqueous:

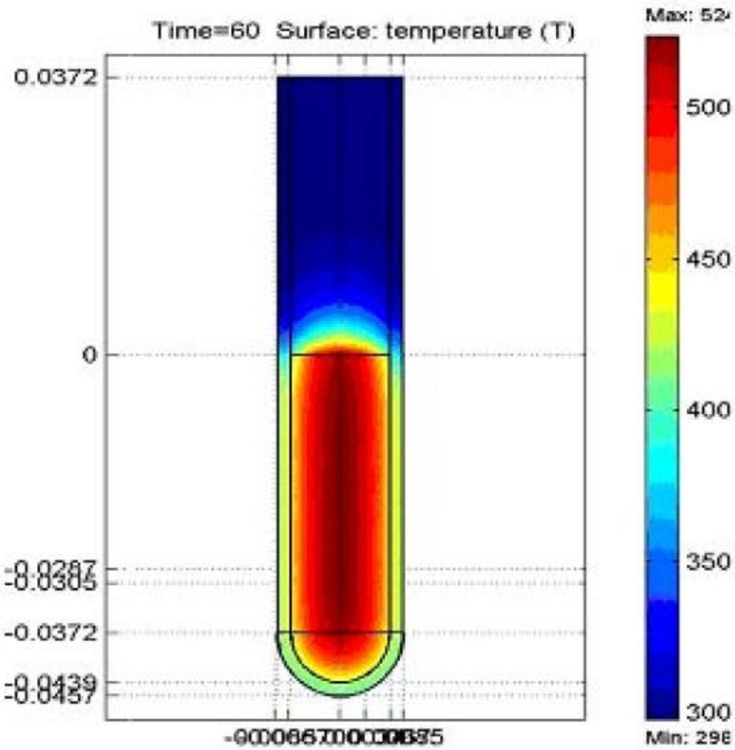
„Molecular“ Precursor + Organic Solvent ⟶ Metal Oxide Network

Metal halides	**Alcohols (Benzyl Alcohol,…)**
Metal alkoxides	**Ketones (Acetophenone,…)**
Metal acetylacetonates	**Amines (Benzylamine,…)**
Metal acetates	**„Inert“ Solvents (Toluene,…)**
Others (e.g. metal nitrates)	

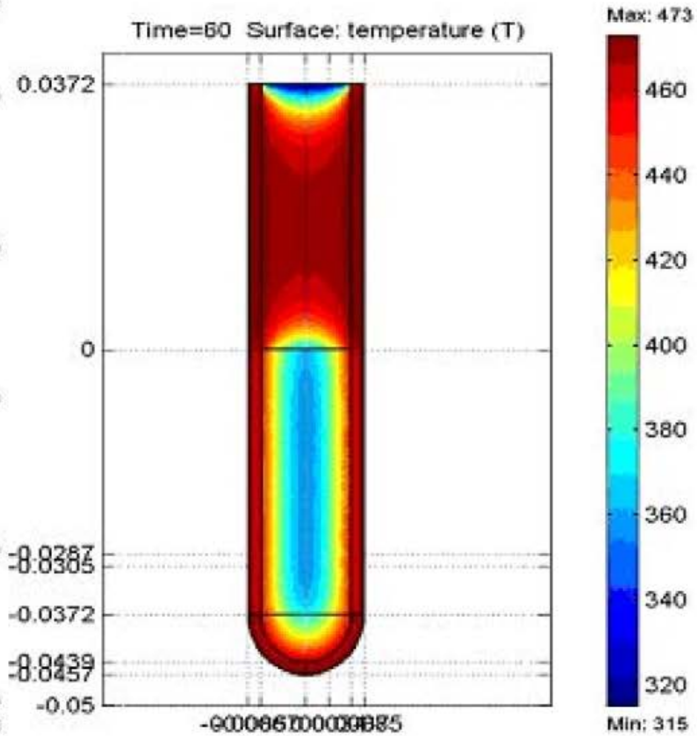


The oxygen is provided by the precursor or the organic solvent!

Microwave vs. Conventional Thermal Heating



Microwave Heating

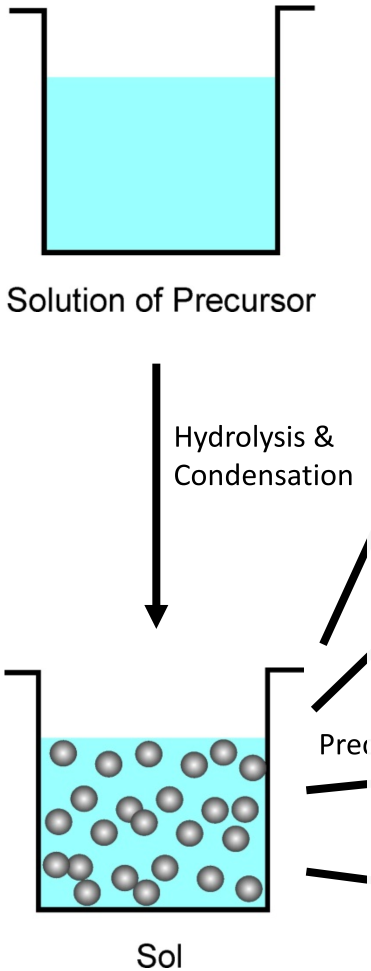


Conventional Heating

- Volumetric heating
- Contactless heating
- Specific heating

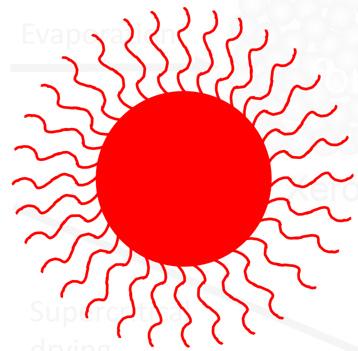
http://www.biotage.com/DynPage.aspx?id=22052

Aqueous vs Nonaqueous Sol-Gel Process



Same versatility due to the formation of nanoparticles.

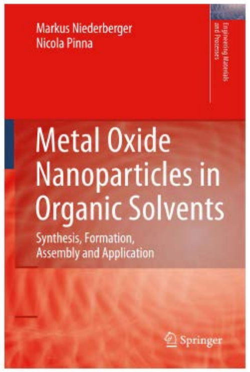
Different reactions:



Richer chemistry

Literature

Books



2009. XIII, 217 p. 65 illus. (Engineering Materials and Processes) Hardcover

M. Niederberger, N. Pinna
Metal Oxide Nanoparticles in Organic Solvents: Synthesis, Formation, Assembly, and Application
Engineering Materials and Processes Series
Springer Verlag, London: **2009**

R. Deshmukh, M. Niederberger
Non-hydrolytic Sol-Gel Routes
In: The Sol-Gel Handbook
Edited by D. Levy and M. Zayat
Wiley-VCH, Weinheim: **2015**

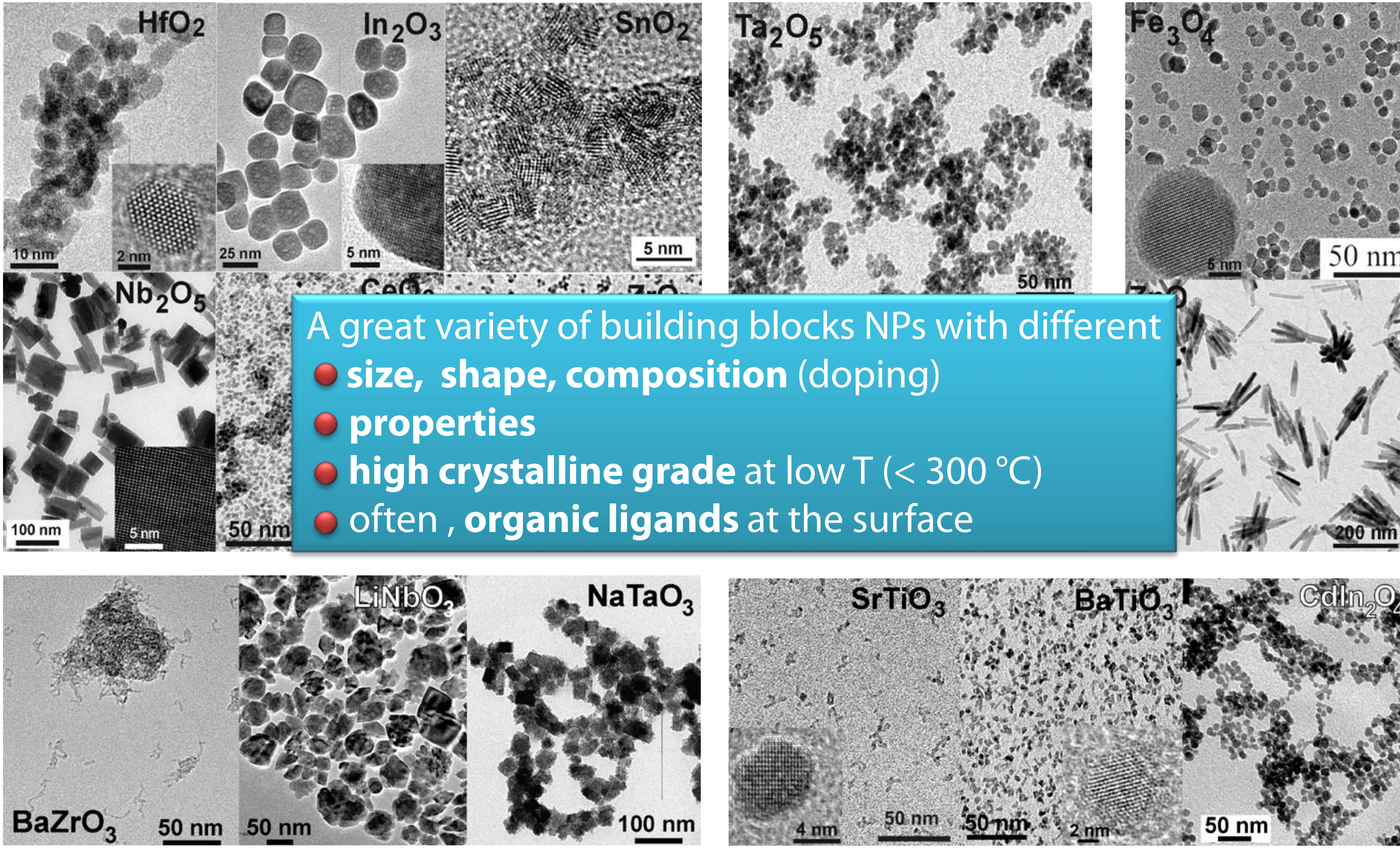
Reviews

P.D. Debecker, P.H. Mutin
Non-hydrolytic sol-gel routes to heterogeneous catalysts
Chem. Soc. Rev. 2012, 41, 3624

P.H. Mutin, A. Vioux
Nonhydrolytic Processing of Oxide-Based Materials: Simple Routes to Control Homogeneity, Morphology, and Nanostructure
Chem. Mater. **2009**, *21*, 582

N. Pinna, M. Niederberger
Surfactant-Free Nonaqueous Synthesis of Metal Oxide Nanostructures
Angew. Chem. Int. Ed. **2008**, *47*, 5292

Nonaqueous sol-gel



A great variety of building blocks NPs with different

- **size, shape, composition** (doping)
- **properties**
- **high crystalline grade** at low T (< 300 °C)
- often , **organic ligands** at the surface

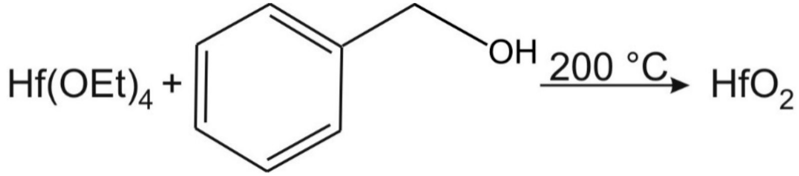
Angew. Chem. Int. Ed. **2008**, *47*, 5292

Doping HfO_2 via nonaqueous sol-gel

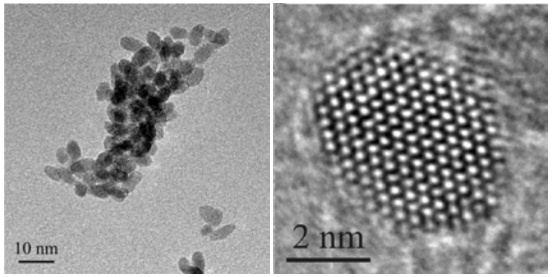
Heavy metal oxide with optical transparency and high density

Requirement for scintillation	Desired property	HfO_2
Transparency	Wide bandgap	**BG > 4.5 eV**
Luminescence centers	Good host for RE	**Trivalent Lanthanides: Eu^{3+}**
Stability	Strong chemical bonds	**T_f = 2758 °C, high inertness**
High stopping power	High Z_{eff} High density	**Z_{Hf} = 72** **d_{HfO2} = 9.68 g cm^{-3}**

Metal Alkoxides and Benzyl Alcohol:



Chem. Eur. J. **2006**, *12*, 7282

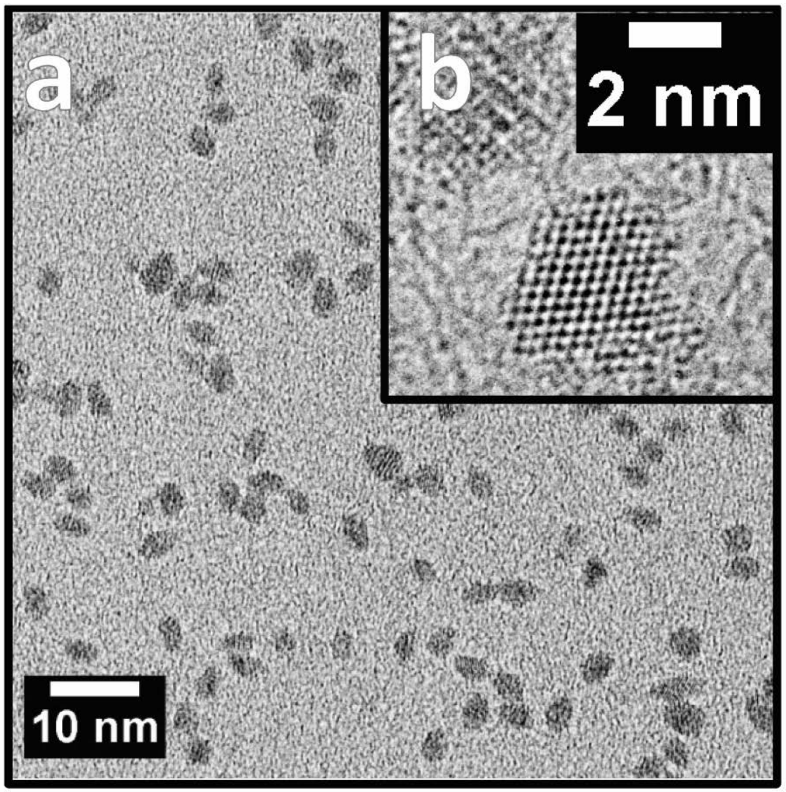


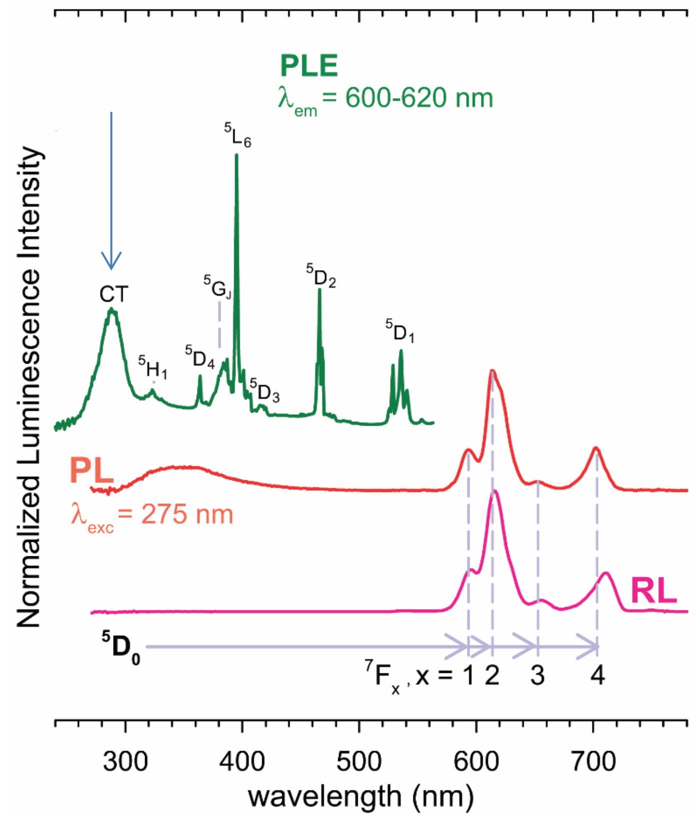
Good candidate for scintillator applications

Luminescent $HfO_2:Eu^{3+}$ nanoparticles

monoclinic

$Hf_{0.97}Eu_{0.03}O_2$ nanophosphor

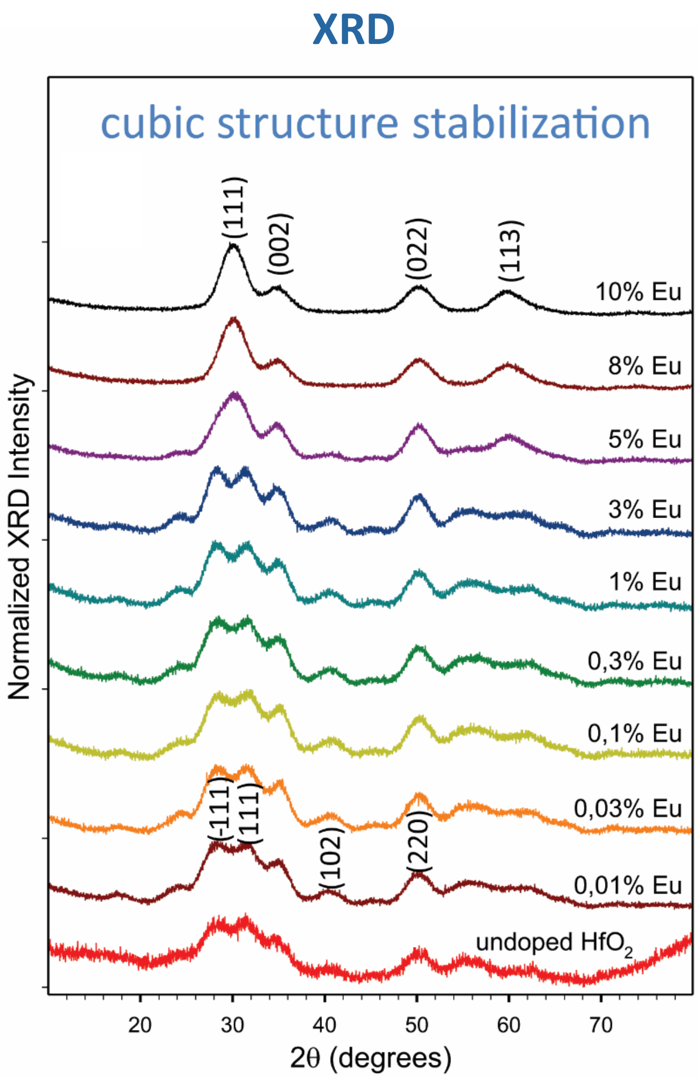


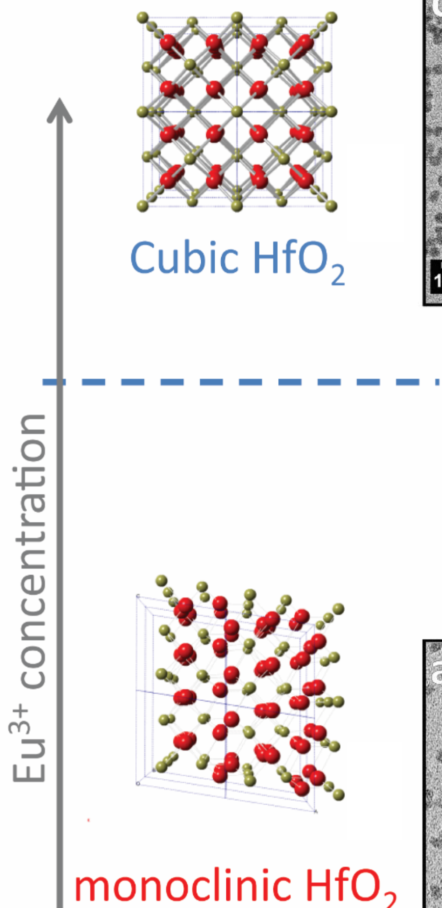


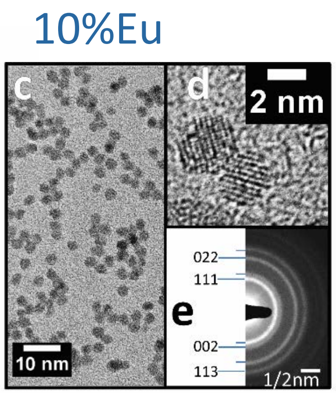
Eu^{3+} ions incorporated in the crystalline lattice

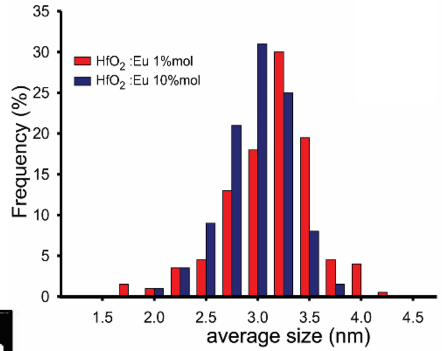
enabling luminescence stimulated either by X-rays or UV illumination.

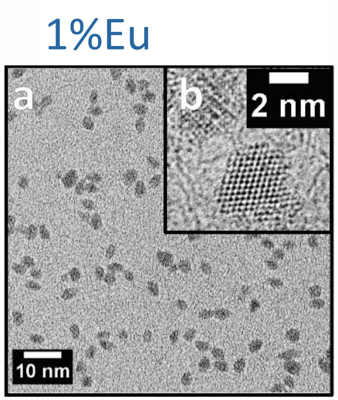
Doping









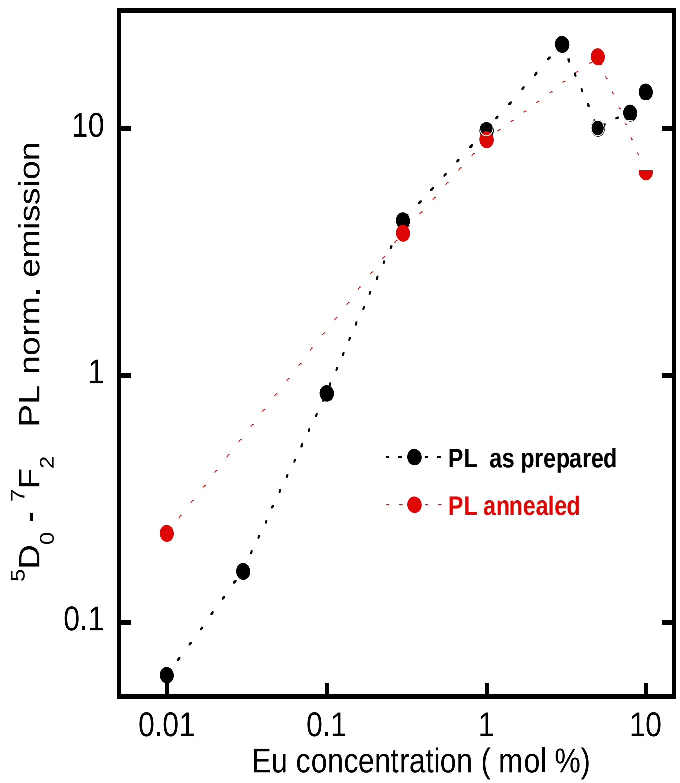


Structural modification.

Singly dispersed ultrasmall nanocrystals.

Lauria A. et al. *ACS Nano* **2013**, **7**[8], 7041

Integrated emission stimulated by 280 nm UvV light

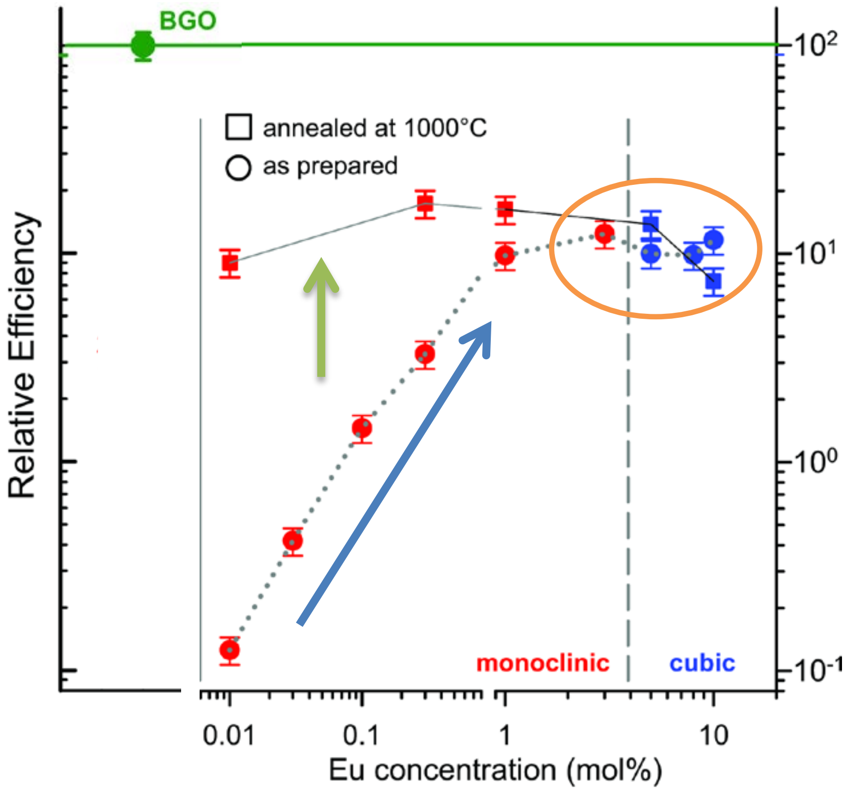


Increase of luminescence with increasing Eu concentration

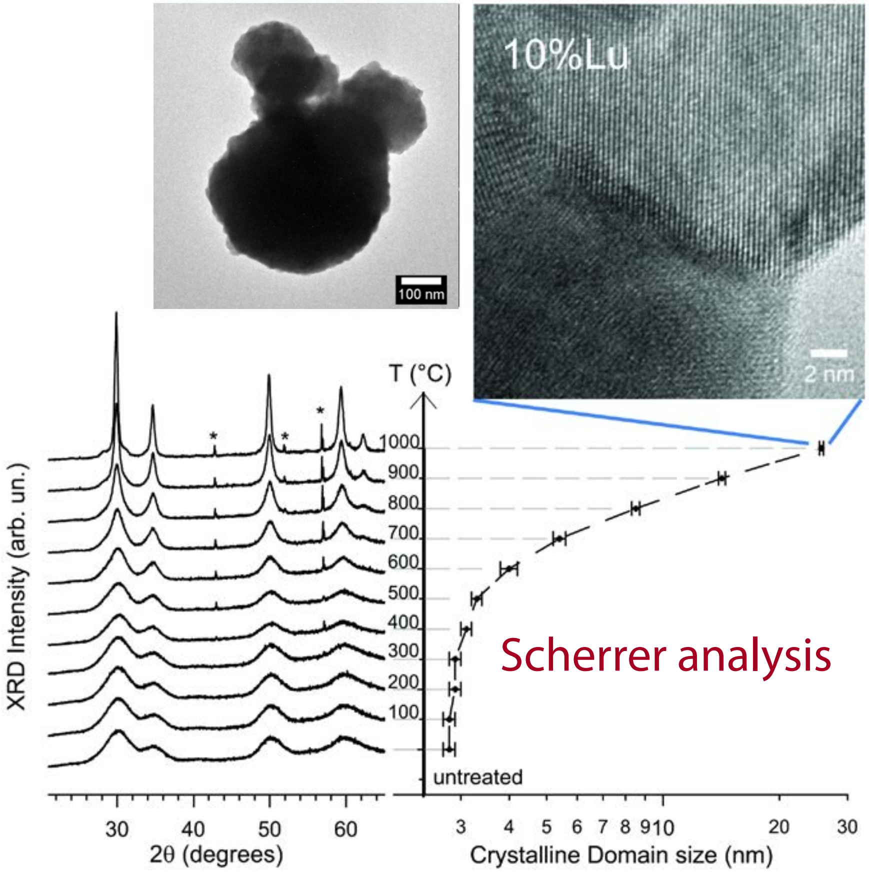
Quenching of luminescence for Eu^{3+} concentration higher than 1 mol%

Doping

Integrated emission stimulated by 20 KeV X-rays



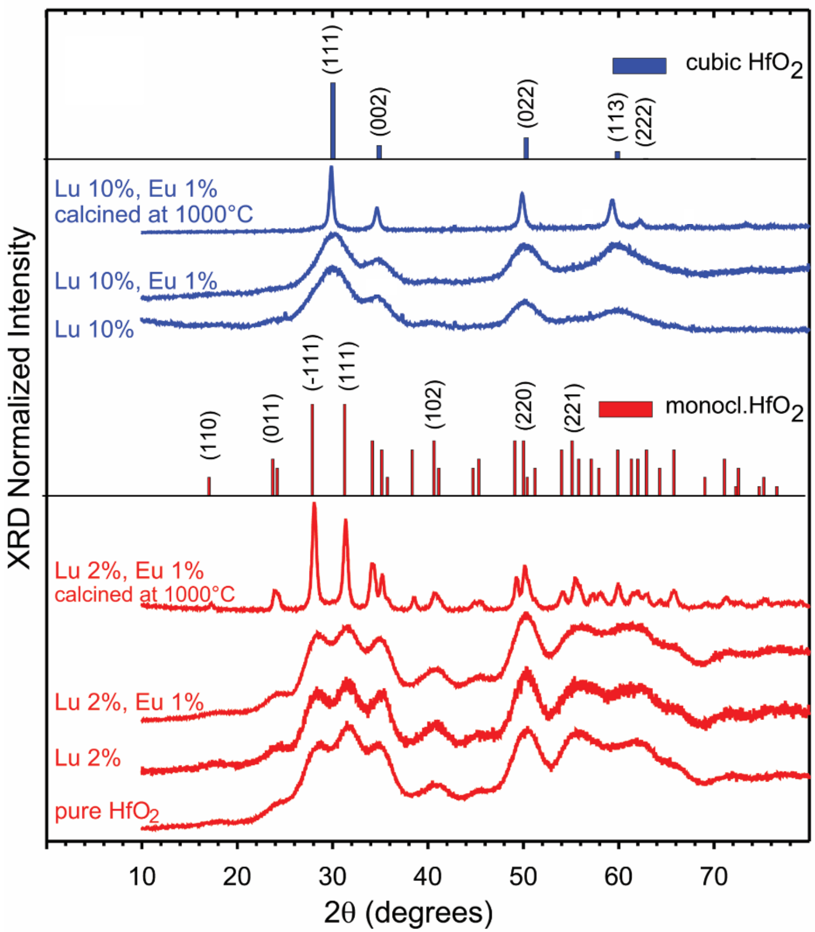
crystal growth

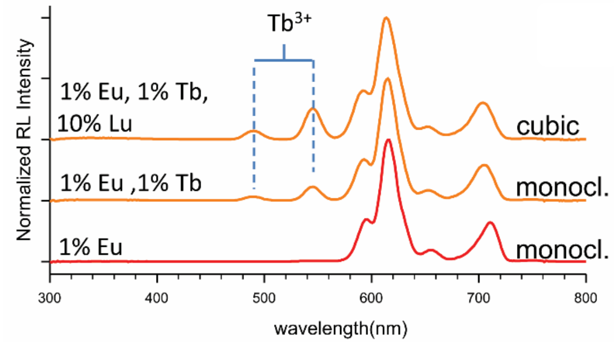


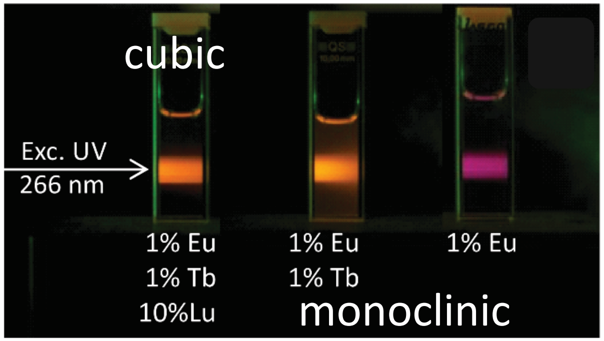
Multifunctional role of RE doping

Lu^{3+} /Eu^{3+} /Tb^{3+} co-doped HfO_2

optically inactive Lu^{3+} (full 4f shell) acting as a structure modifier





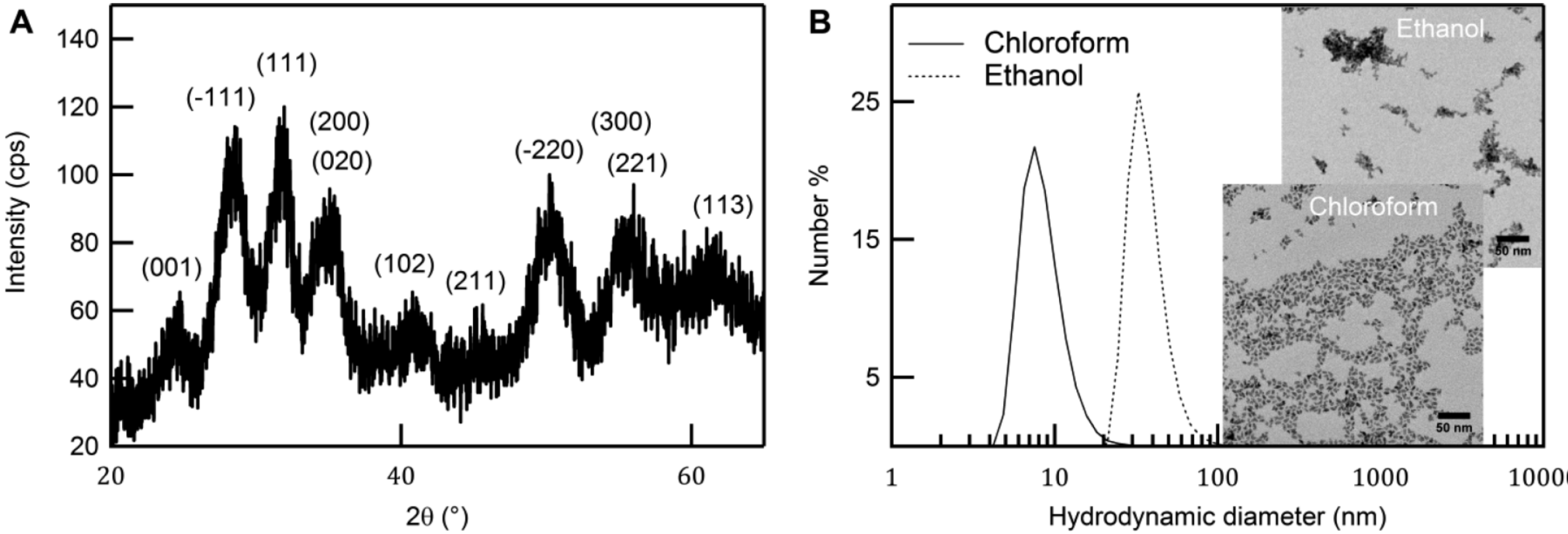


Indipendent control over structure and emission

MW assisted sol-gel chemistry of $HfCl_4$

Surface chemistry

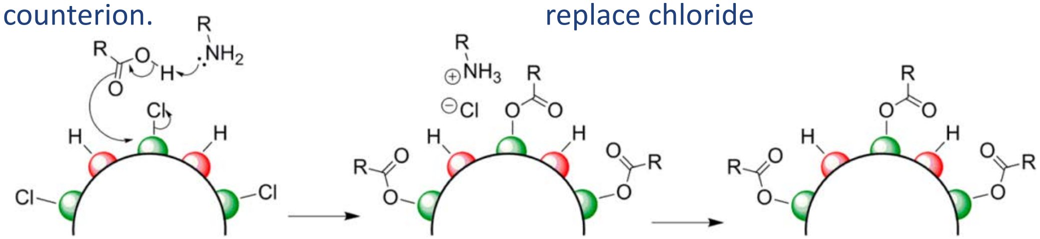
$$HfCl_4 + BnOH \xrightarrow{220\ C\ -\ 3h} HfO_2$$



Surface stabilization is known from literature

As-synthesized nanocrystals are charge-stabilized by protons, with chloride acting as the counterion.

The addition of amines provides the basic environment in which carboxylic acids can dissociate and replace chloride

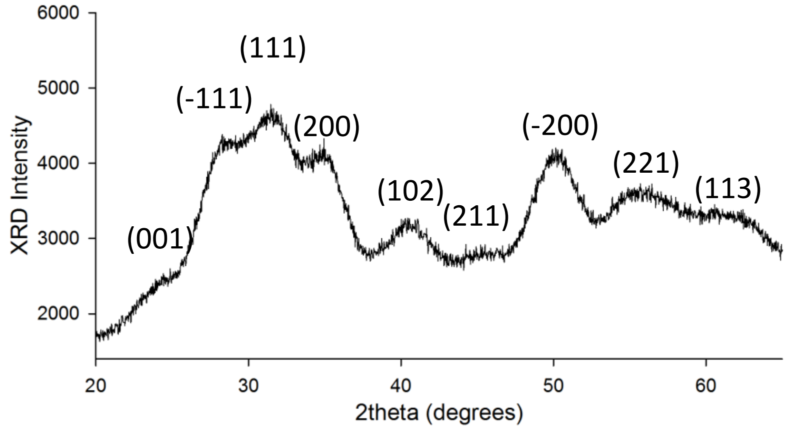


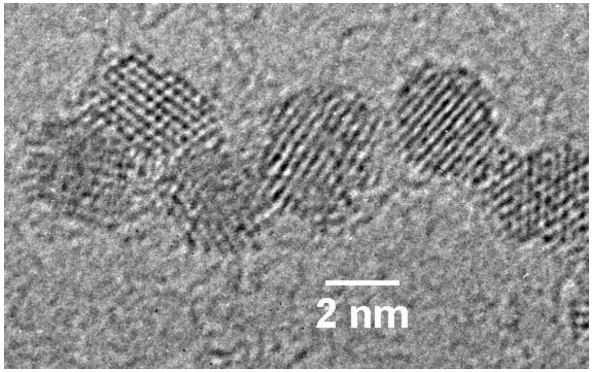
J. Am. Chem. Soc. 2014, 136, 9650–9657

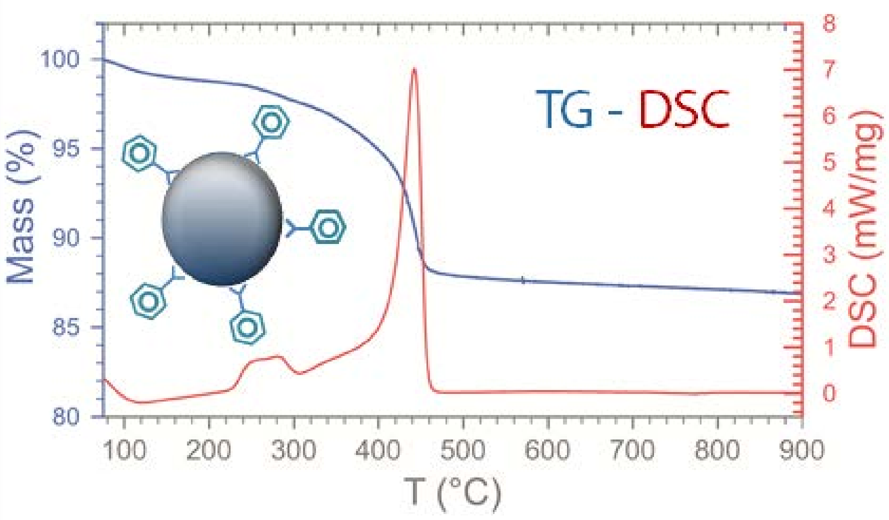
Autoclave sol-gel chemistry of $Hf(t\text{-}BuO)_4$

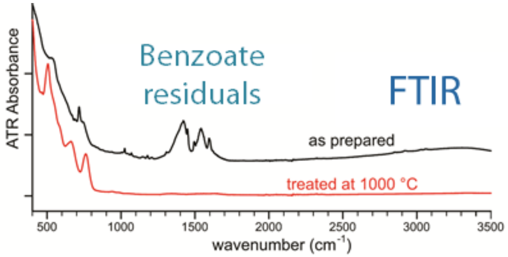
Surface chemistry

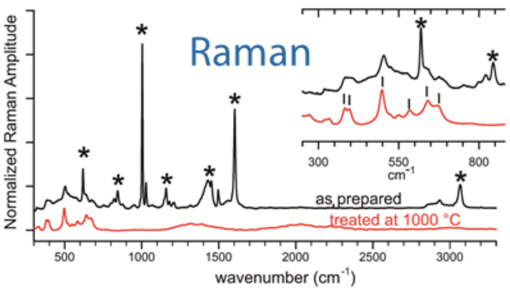
$Hf(t\text{-}BuO)_4 + BnOH \xrightarrow{220\ C\ -\ 3h} HfO_2$





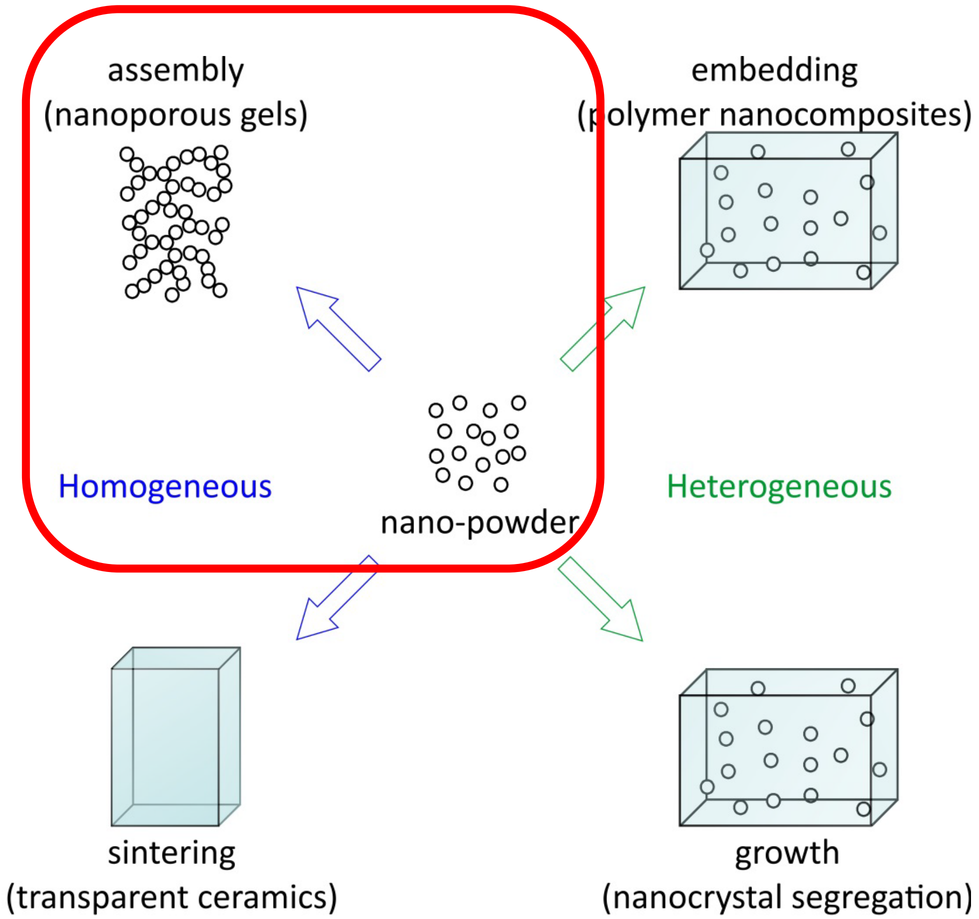


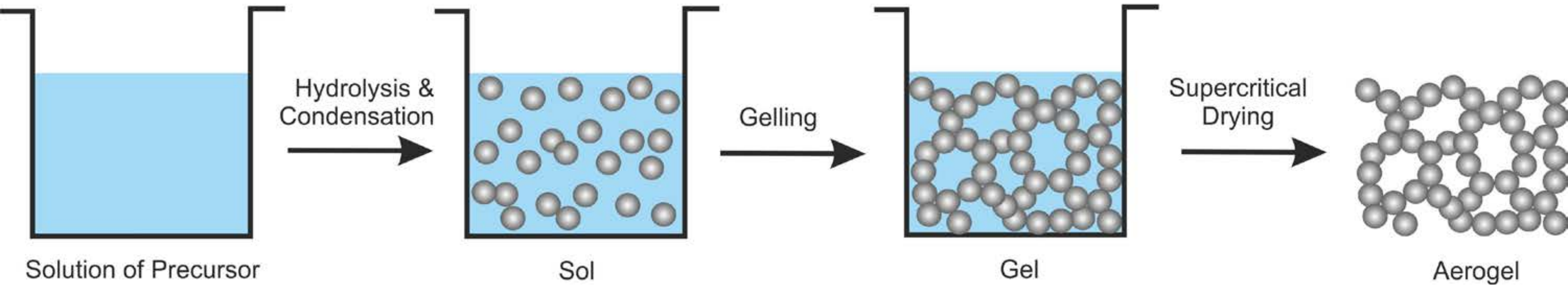




Lauria A. et al. *ACS Nano* **2013**, **7**[8], 7041

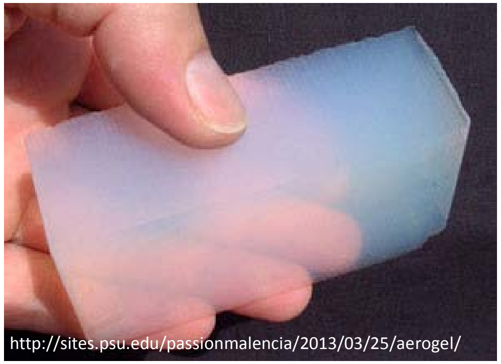
Aerogels

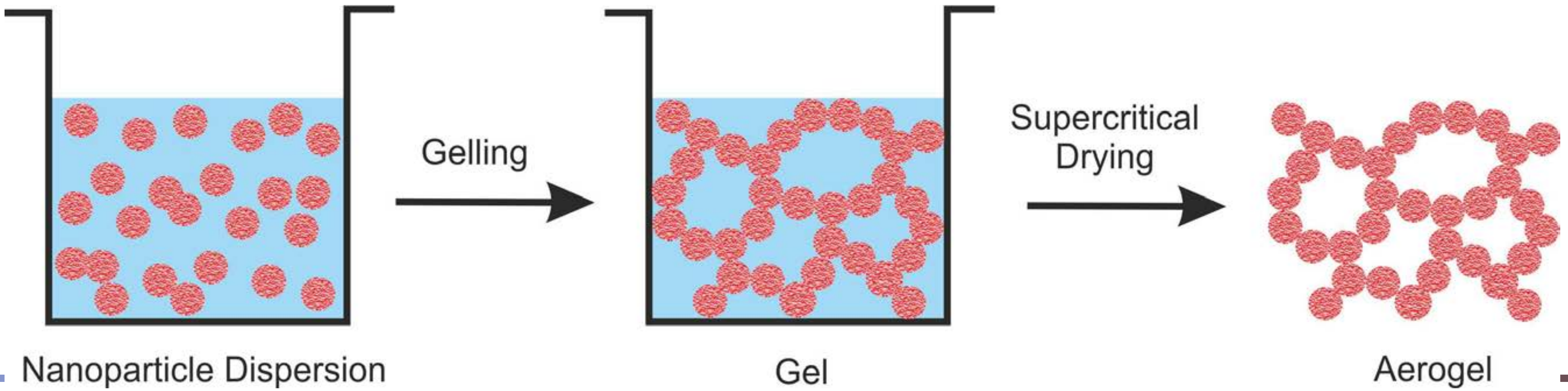

assembly
(nanoporous gels)
embedding
(polymer nanocomposites)
Homogeneous
nano-powder
Heterogeneous
sintering
(transparent ceramics)
growth
(nanocrystal segregation)



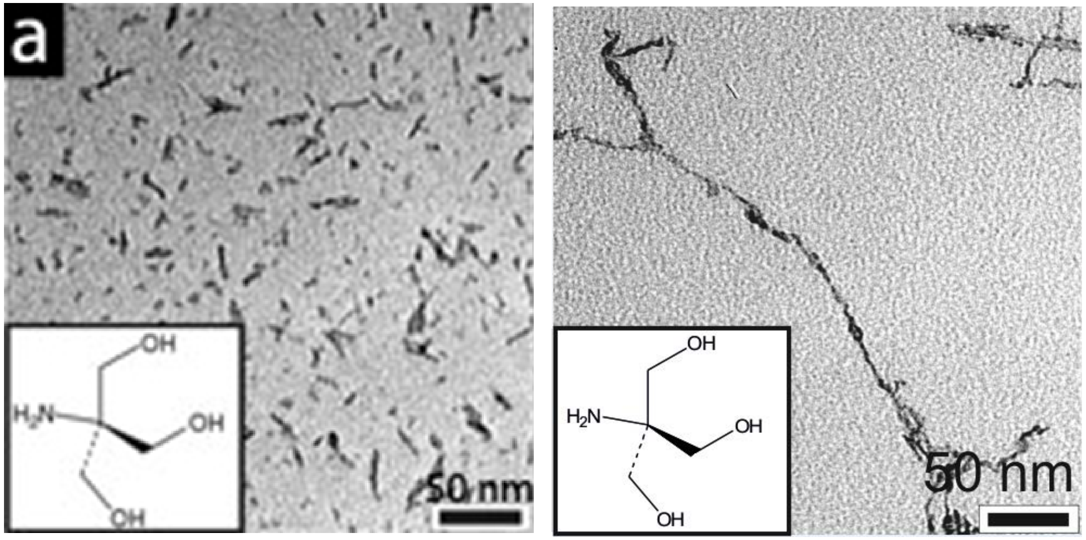
Goals:

- To get a bulk material with nanoscale properties arising from the building blocks
- To have more functions


http://sites.psu.edu/passionmalencia/2013/03/25/aerogel/



Controlled destabilization of 3 nm trizma-functionalized anatase NPs dispersions



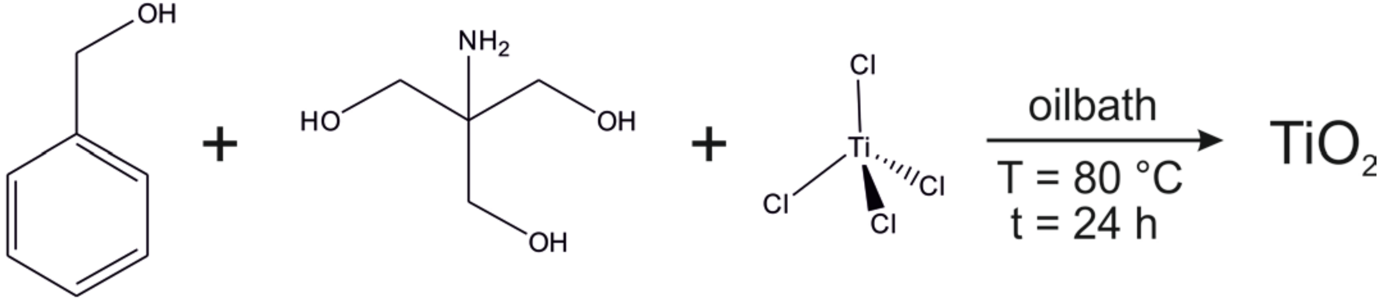
Trizma functionalized anatase NPs[1]
a) before
b) after destabilization

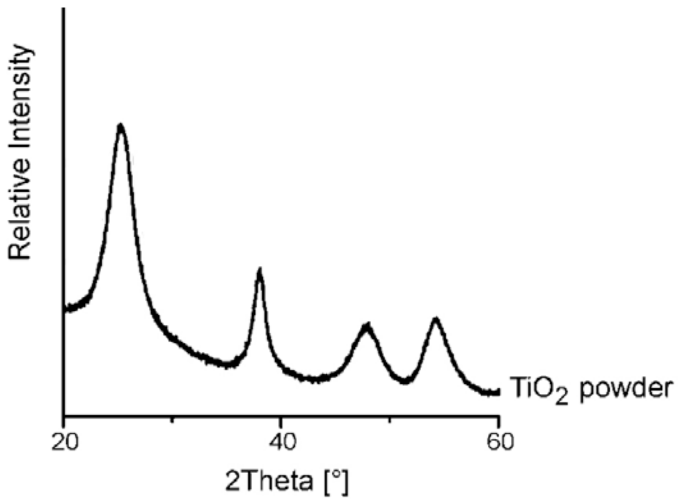
Proposed mechanism for oriented attachment by Polleux et al. in 2005[1]

Theoretical calculations by Grätzel et al. in 1998[2]

[1] Niederberger, M., et al., *Chem. Eur. J.*, **2005**, 11, 3541-3551.
[2] Grätzel, M. et al. *Phys. Rev. Lett.,* **1998**, 81, 14, 2954.

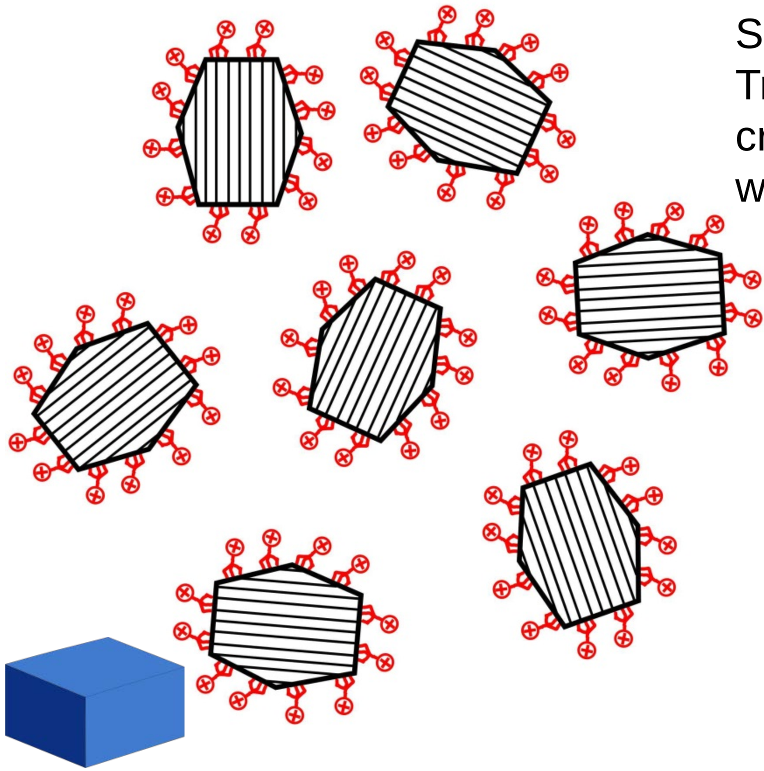
TiO_2 synthesis



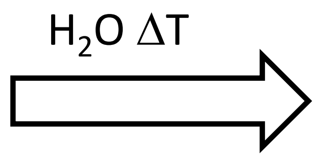


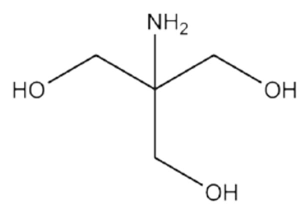
Heiligtag, F. J., et al., *J. Mater. Chem.*, **2011**, 21, 16893-16899.

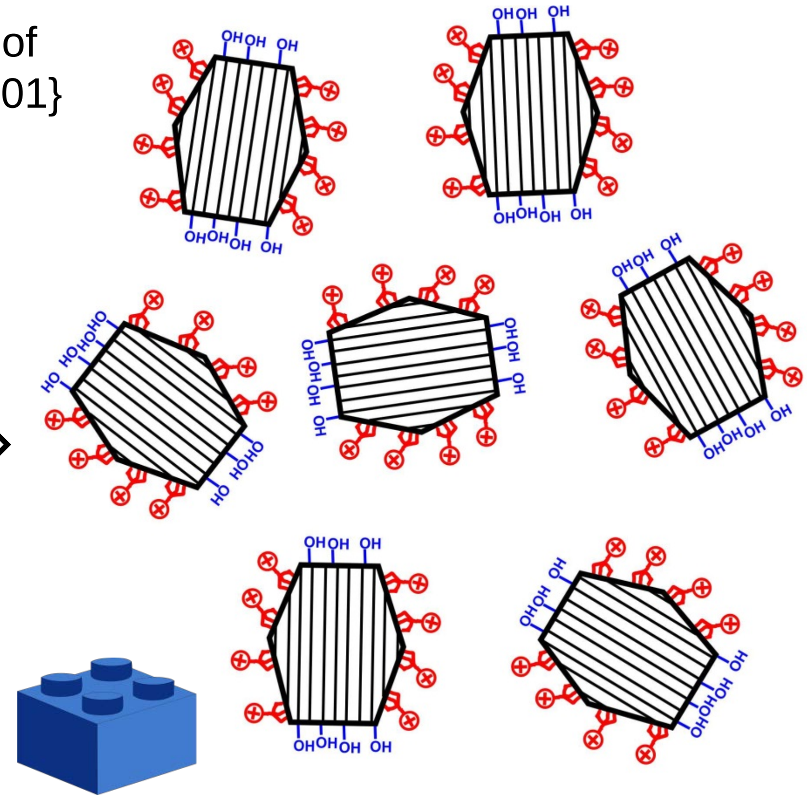
Oriented Attachment along [001] - why?



Selective removal of Trizma from the {001} crystal facets by water







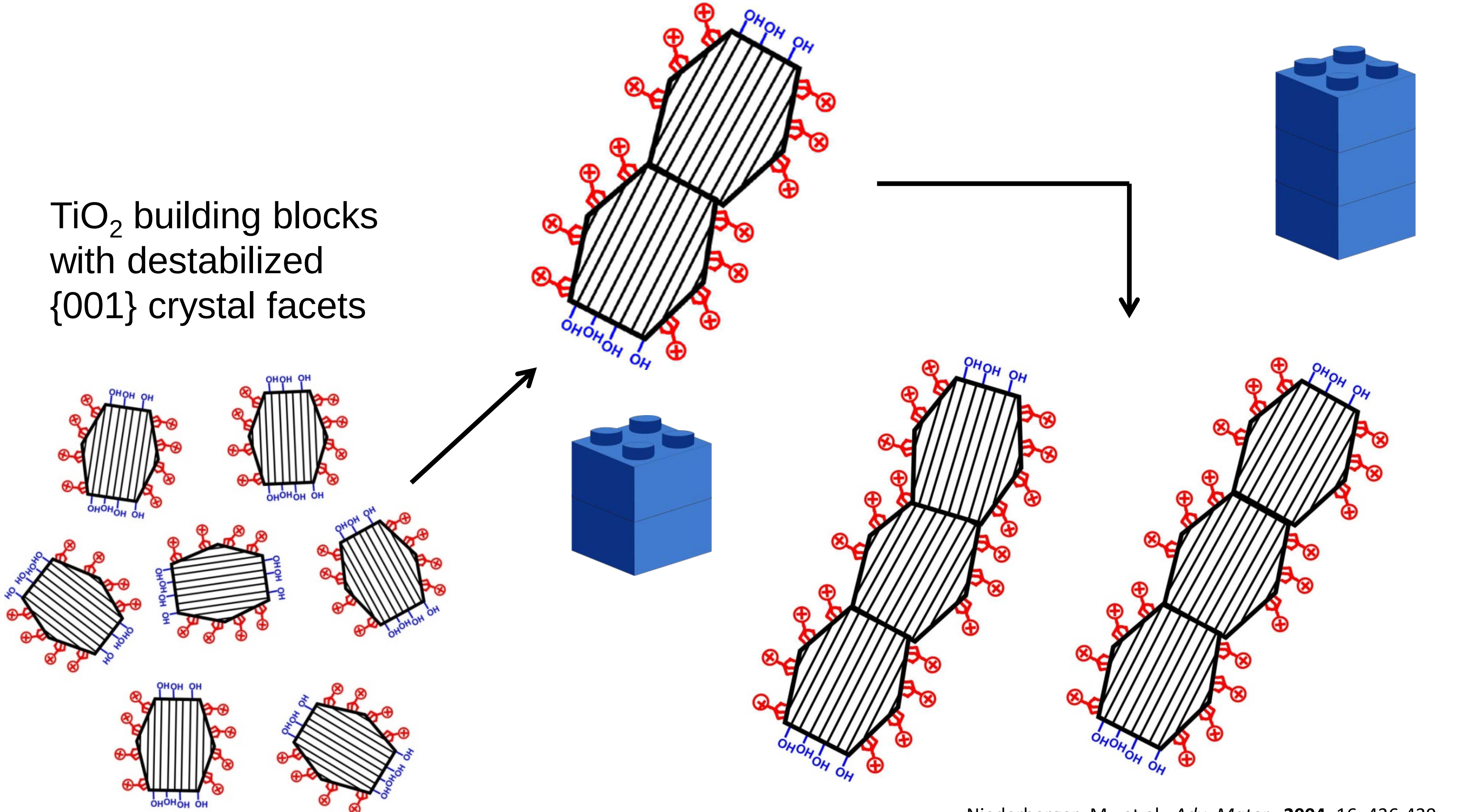
Surface-functionalized TiO_2 building blocks electrostatically stabilized by Trizma

TiO_2 building blocks with destabilized {001} crystal facets

Niederberger, M., et al., *Adv. Mater.*, **2004**, 16, 436-439.
Niederberger, M., et al., *Chem. Eur. J.*, **2005**, 11, 3541-3551.

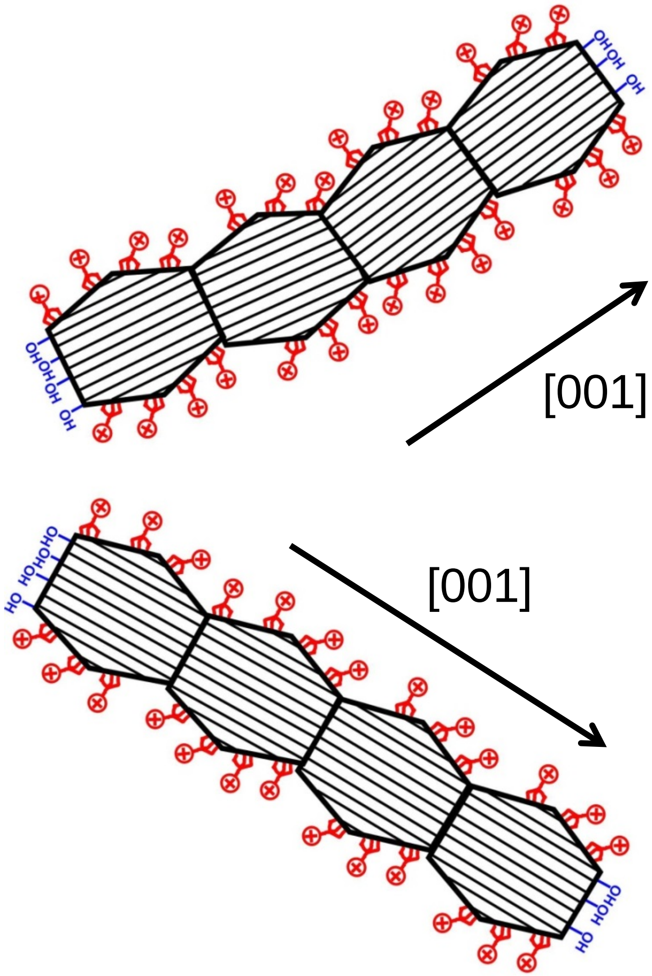
Oriented Attachment along [001] - why?

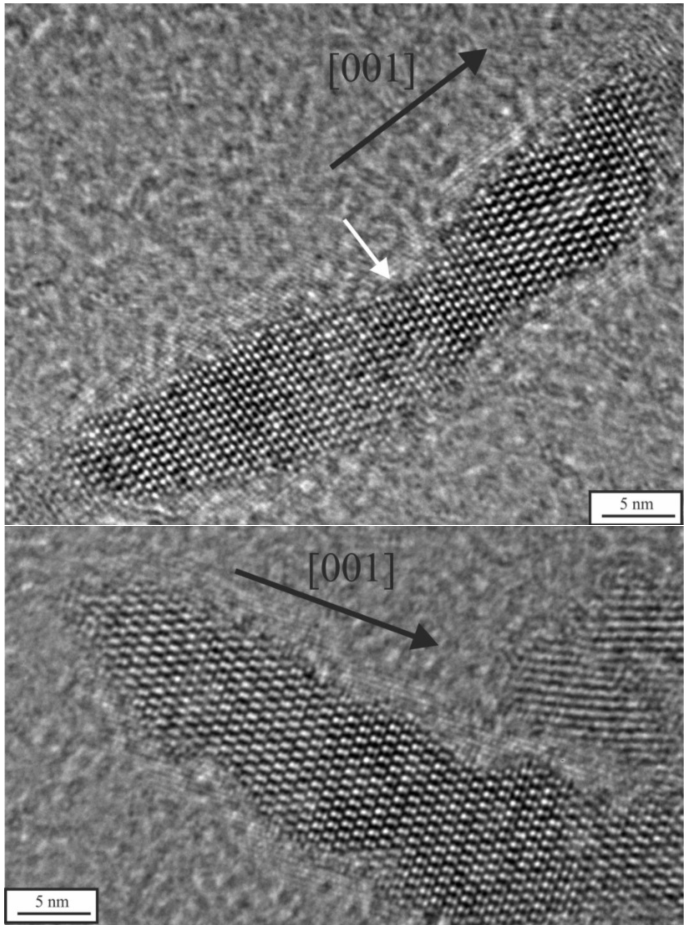
TiO_2 building blocks with destabilized {001} crystal facets



Niederberger, M., et al., *Adv. Mater.*, **2004**, 16, 436-439.
Niederberger, M., et al., *Chem. Eur. J.*, **2005**, 11, 3541-3551.

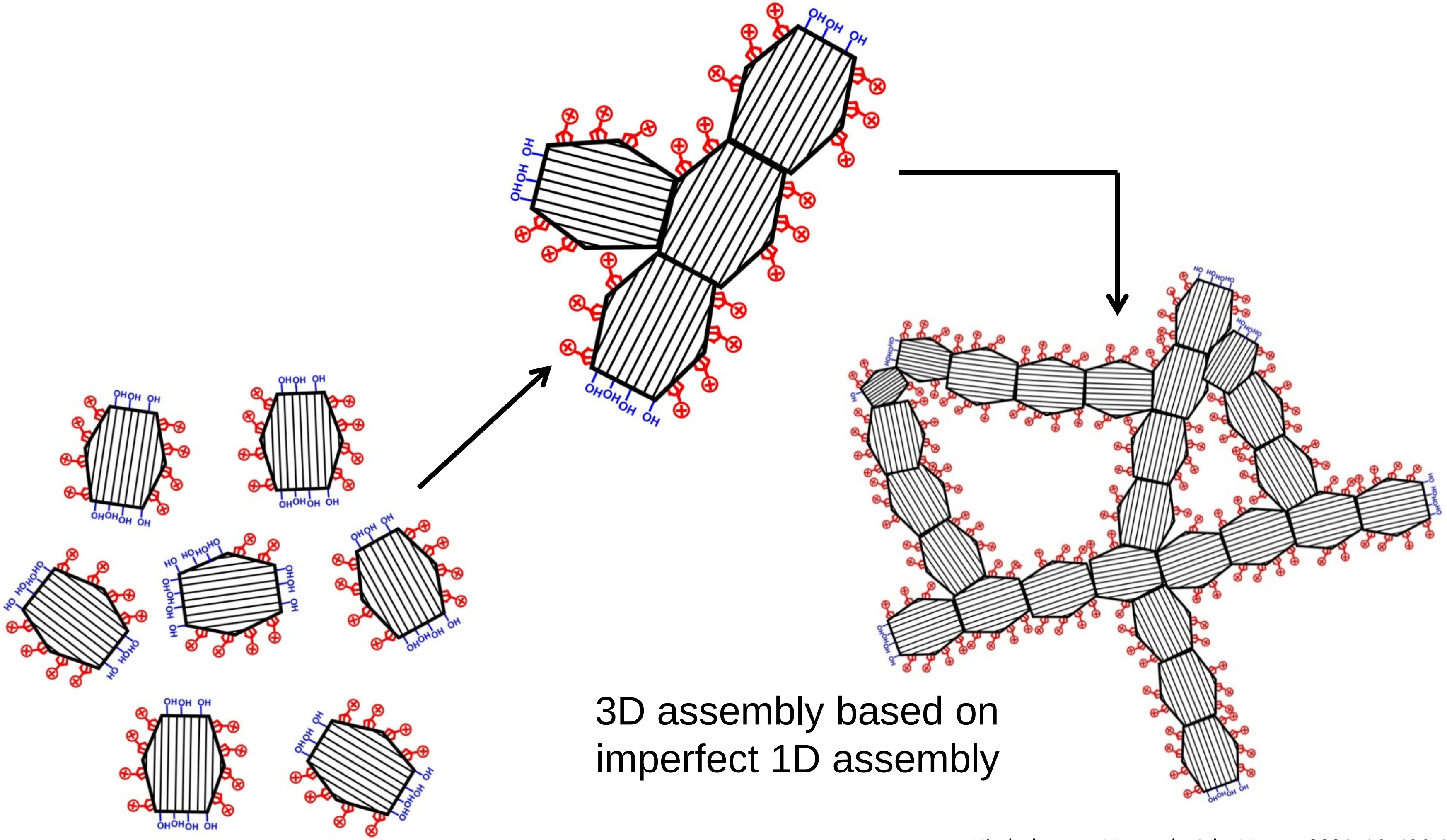
Oriented Attachment along [001] - why?





Niederberger, M., et al., *Adv. Mater.*, **2004**, 16, 436-439.
Niederberger, M., et al., *Chem. Eur. J.*, **2005**, 11, 3541-3551.

Oriented Attachment for 3D assembly

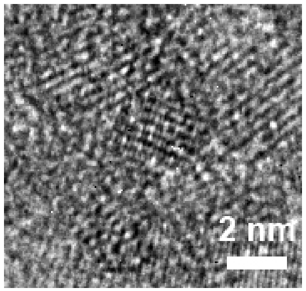


3D assembly based on imperfect 1D assembly

Niederberger, M., et al., *Adv. Mater.*, **2004**, 16, 436-439.
Niederberger, M., et al., *Chem. Eur. J.*, **2005**, 11, 3541-3551.

Aerogels

TiO_2 Assembly



TiO_2 Nanoparticles

H_2O

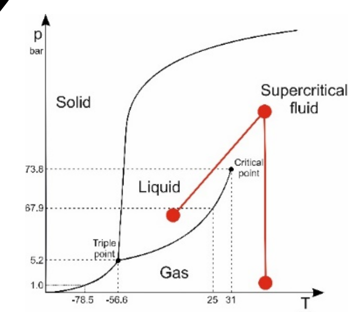
Dispersion

ΔT 30 min

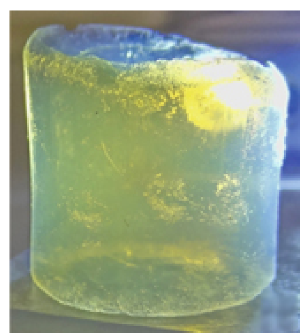
(EtOH)

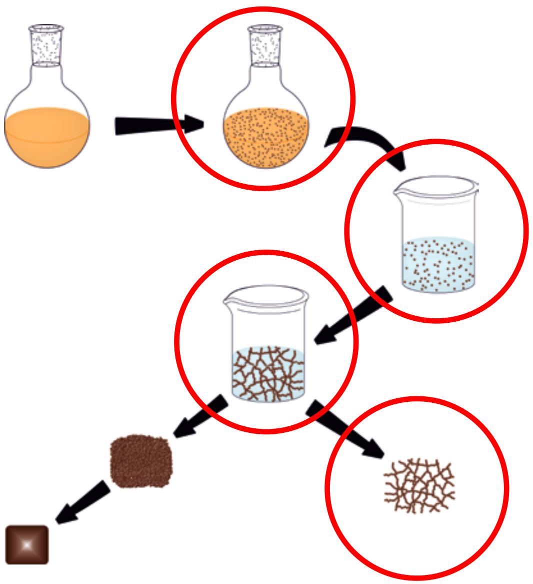
Wet Gel

Supercritical Drying



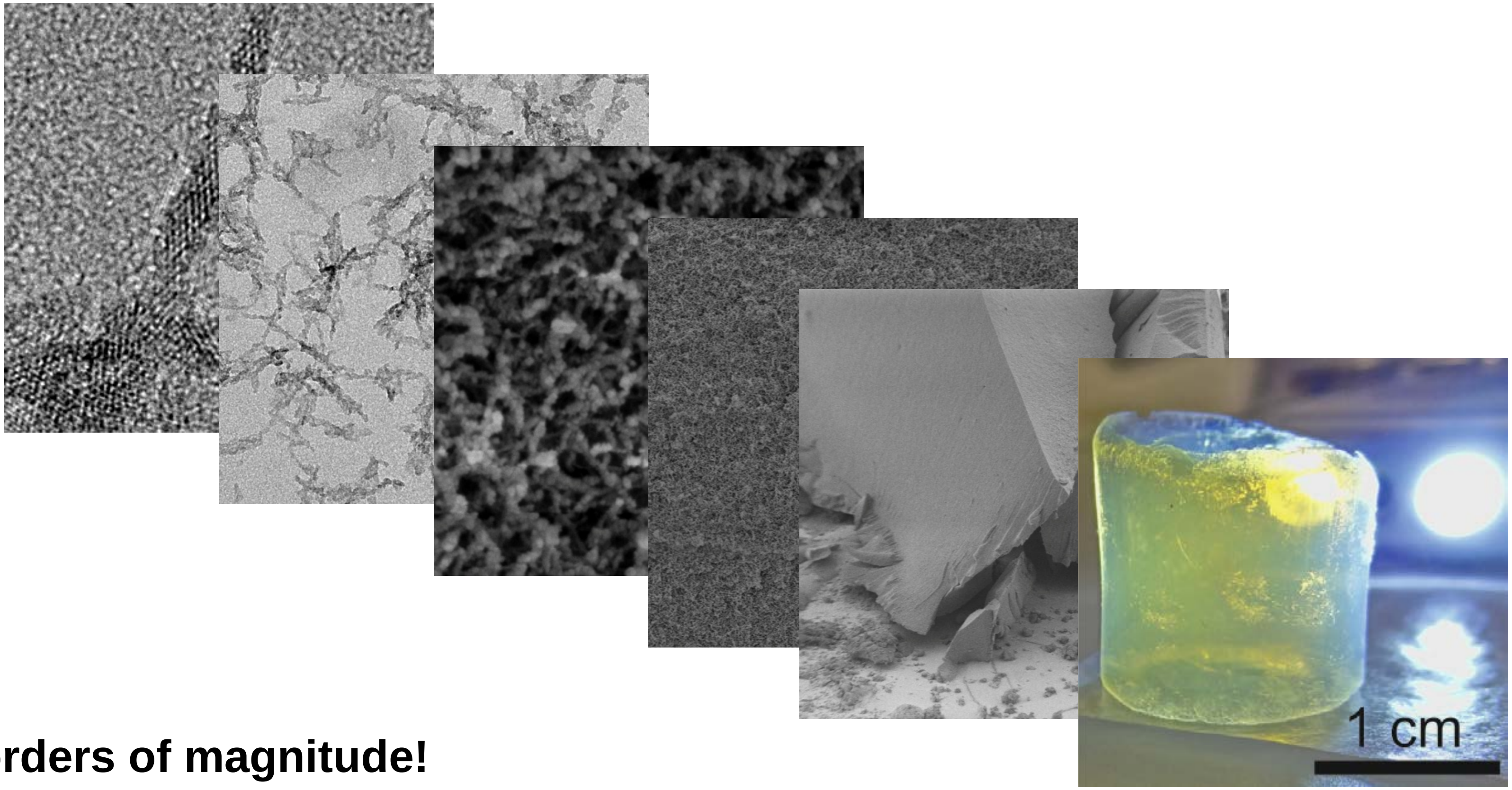
TiO_2 Aerogel



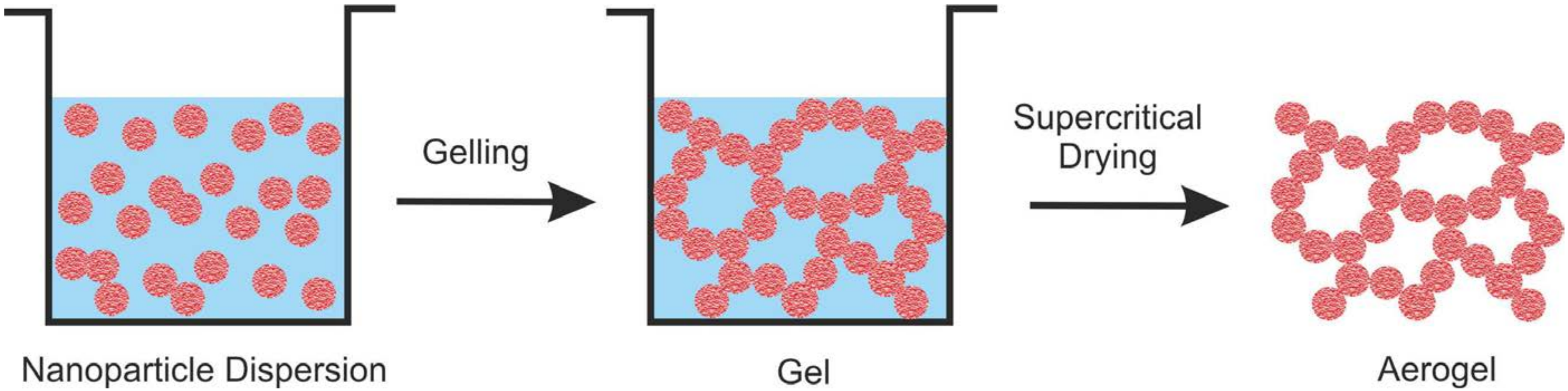


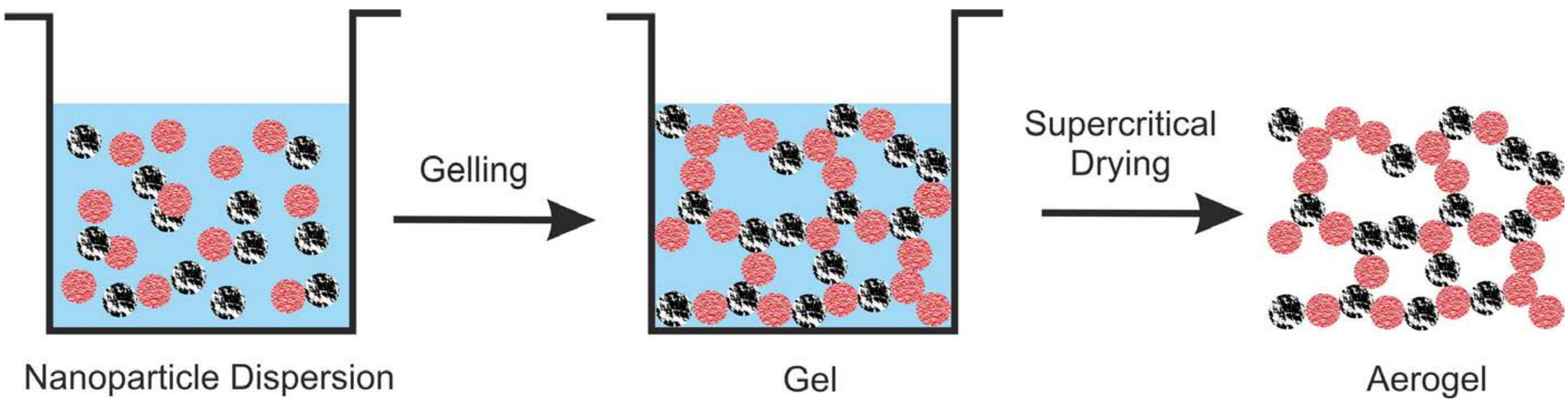
Heiligtag, F. J., et al., *J. Mater. Chem.*, **2011**, 21, 16893-16899.

From Nanoparticles to Aerogel Monoliths



7 orders of magnitude!

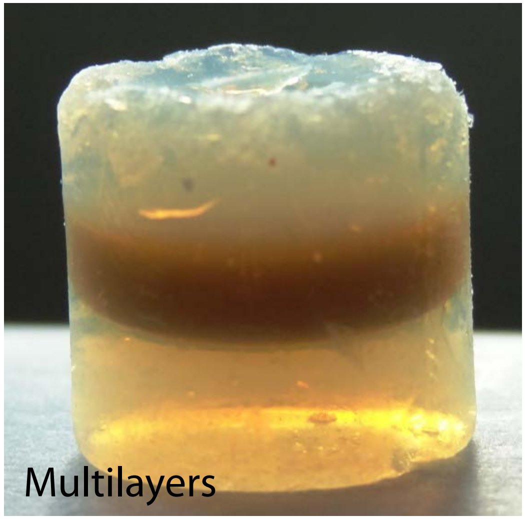

Gelling
Supercritical Drying
Nanoparticle Dispersion
Gel
Aerogel


Gelling
Supercritical Drying
Nanoparticle Dispersion
Gel
Aerogel

Aerogels

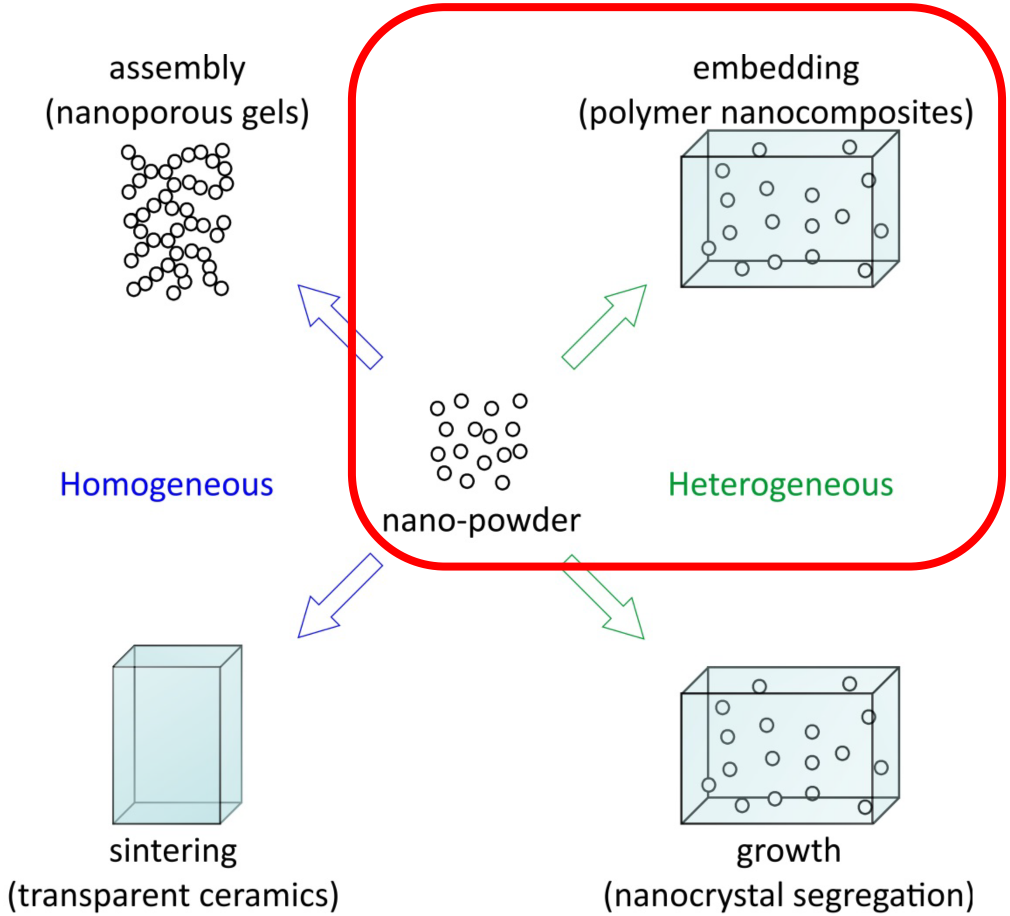
$TiO_2 + Fe_3O_4$

0 mol% 0.25 mol% 0.375 mol% 0.5 mol%



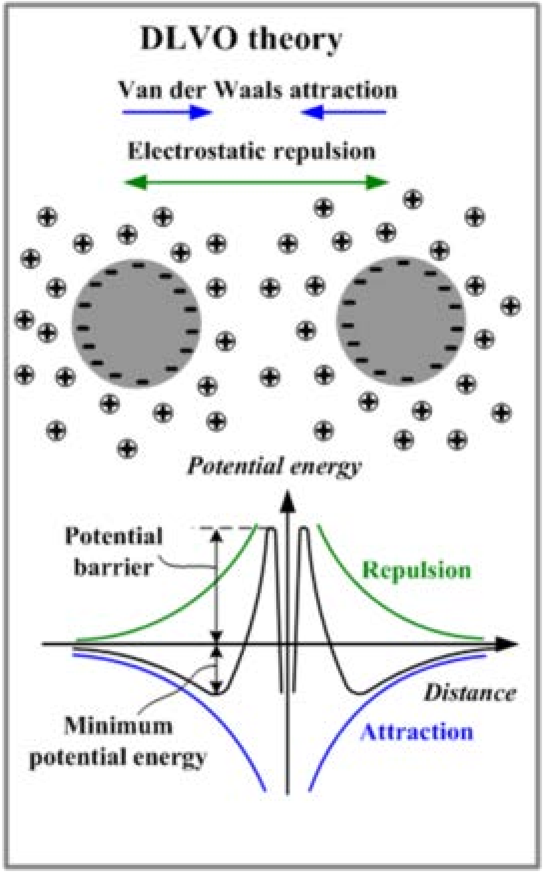
Nanoscale **2014**, *6*, 13213

Composites



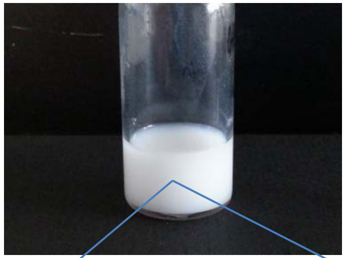
assembly
(nanoporous gels)
embedding
(polymer nanocomposites)
Homogeneous
nano-powder
Heterogeneous
sintering
(transparent ceramics)
growth
(nanocrystal segregation)

Stabilization



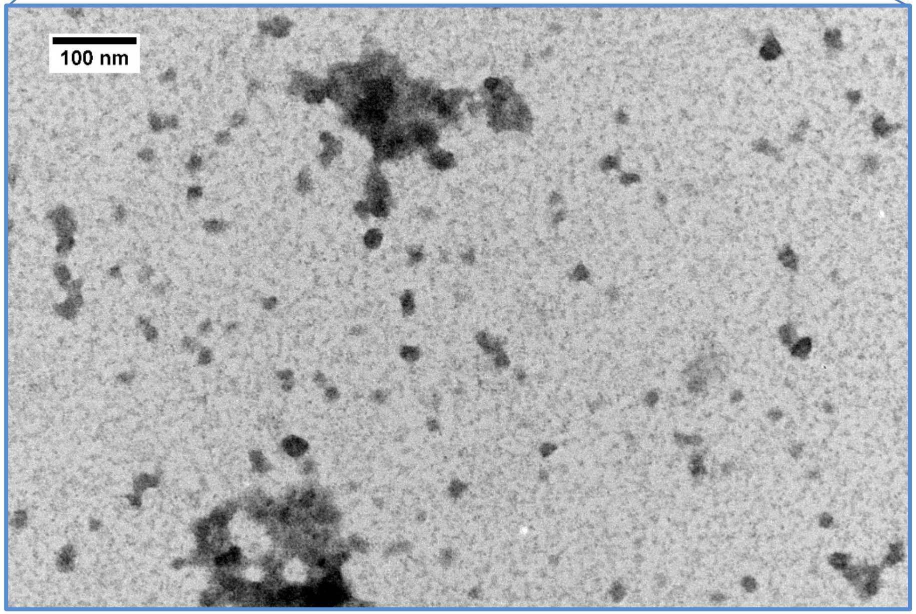
Probability of collision is higher for smaller particles

NP like to agglomerate!

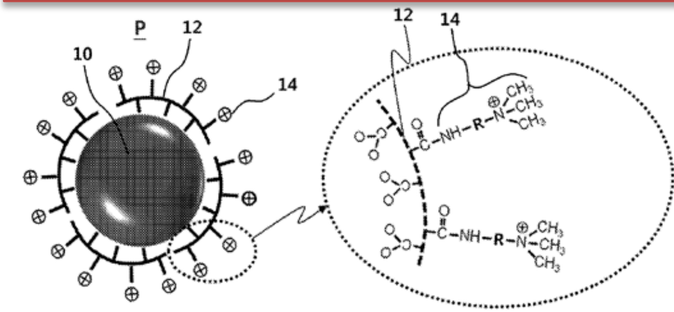


Ethanol suspension

PMMA/NPs

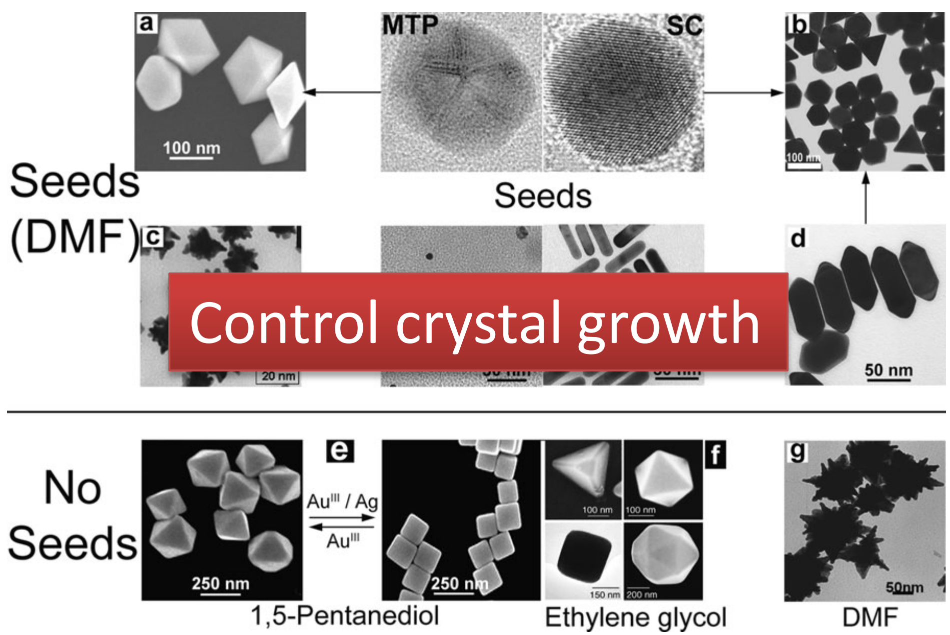


Water stability of SPIONs



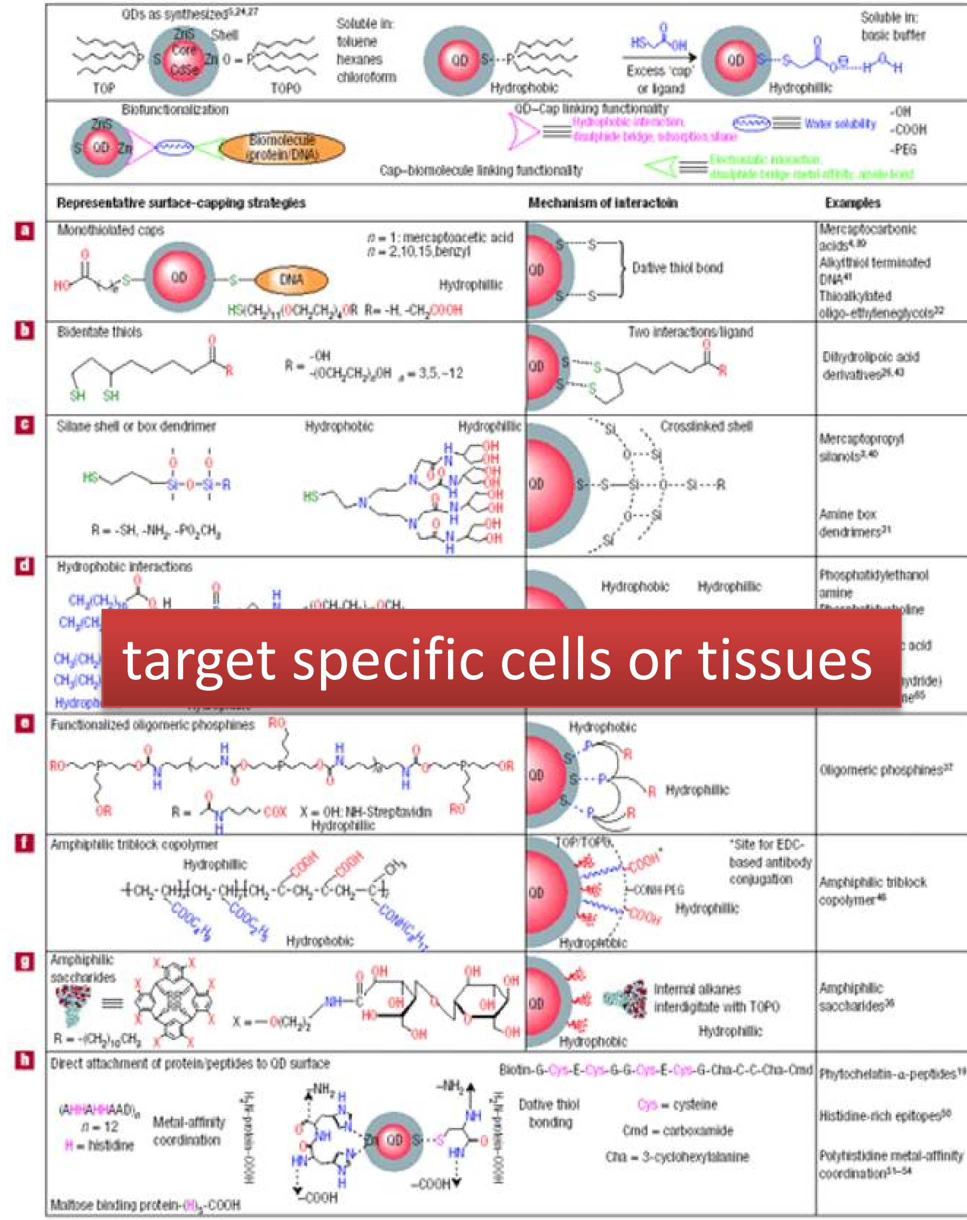
US pat. 20120045399 A1

Control crystal growth



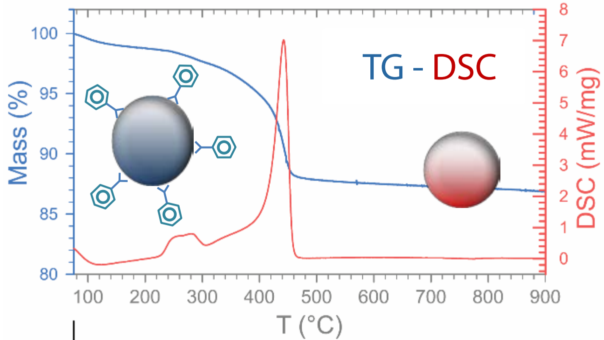
Chem. Soc. Rev., 2008, 37, 1783–1791

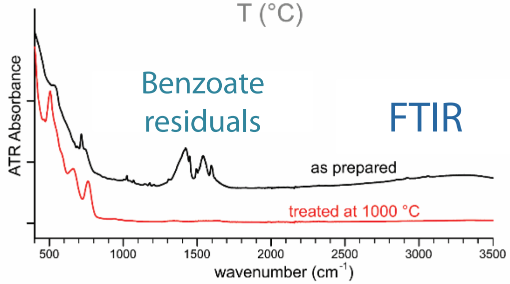
target specific cells or tissues

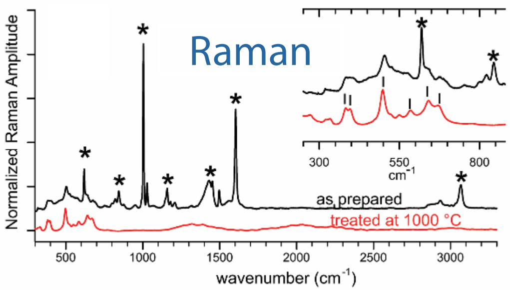


Theranostics 2012; 2(7):681-694. doi:10.7150/thno.3692

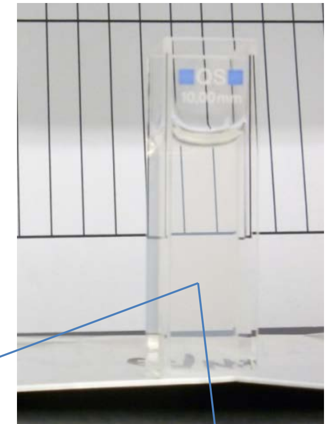
Role of surface chemistry on stabilization of HfO_2 NPs

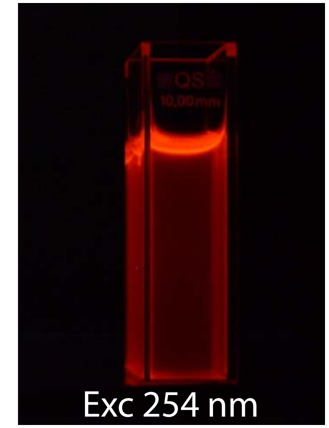


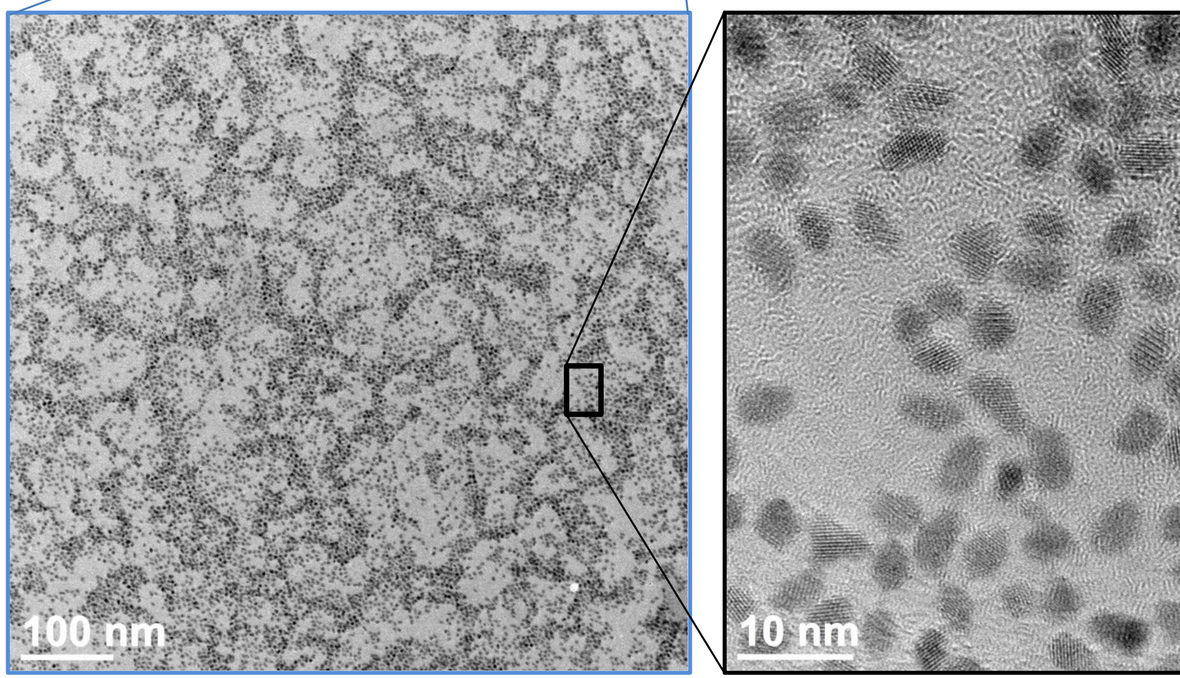




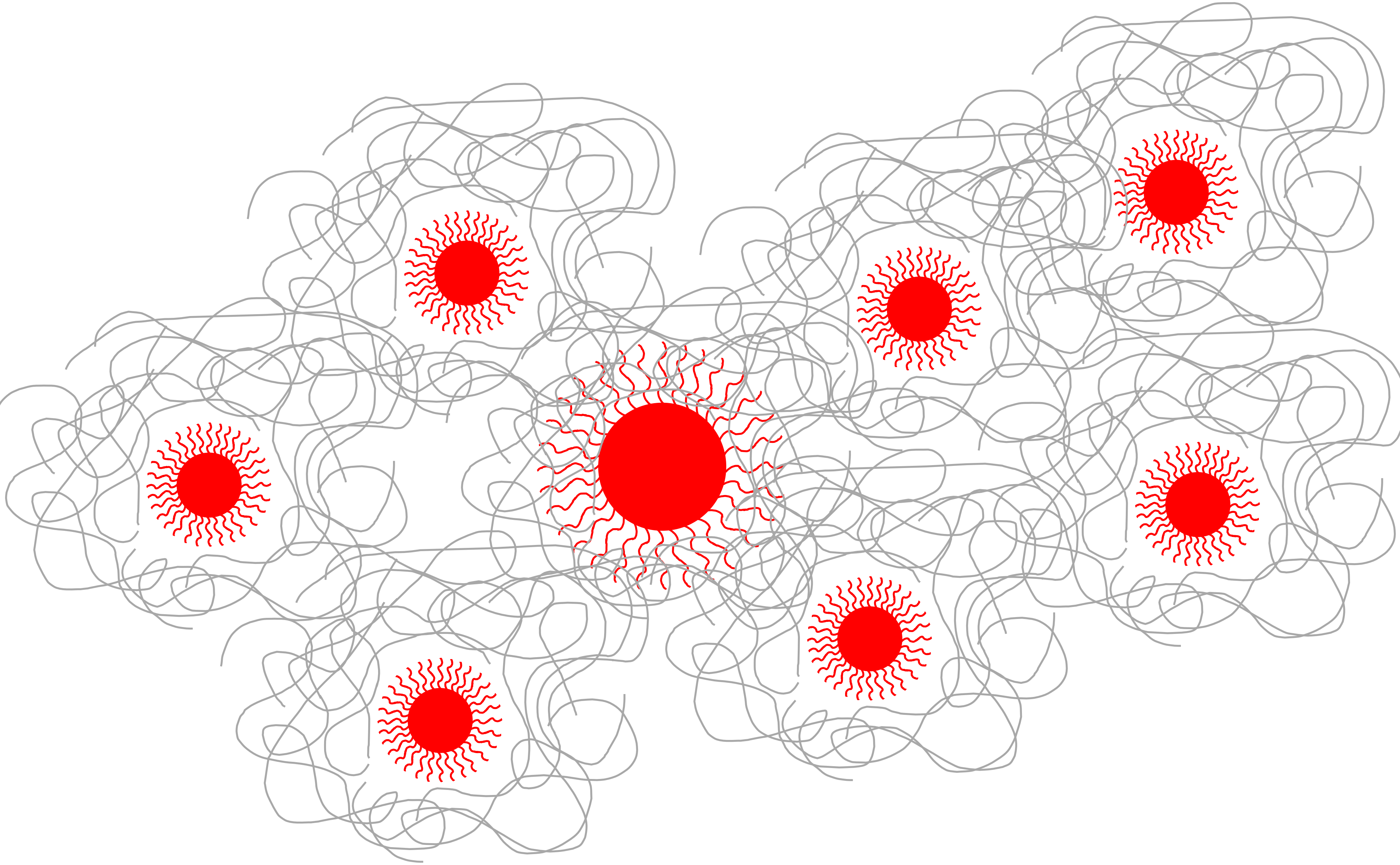
Stable suspensions







Composites



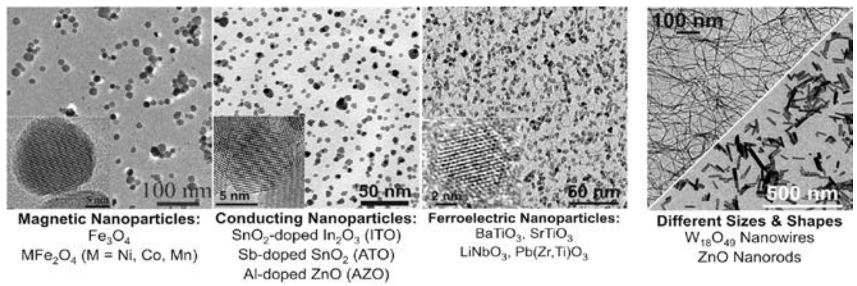
Summary

Chemical synthesis in organic solvents (nonhydrolytic sol-gel chemistry)

Control of composition, size, shape, and surface

Different heating techniques: Oil bath, autoclaves, microwaves

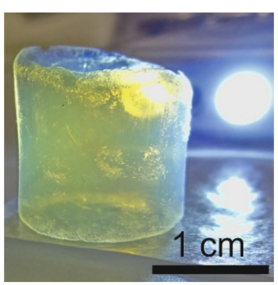
Well-defined nanoparticles as building blocks

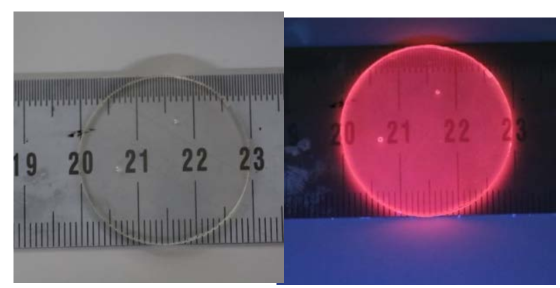


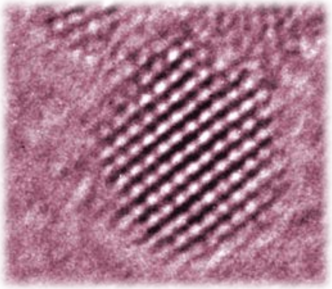
Collective/synergistic properties

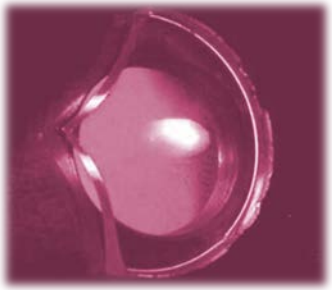
Assembly over several length scales

Macroscopic (multicomponent) materials









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http://www.multimat.mat.ethz.ch